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Composition and distribution of aerosols over the North Atlantic during the Subsonic Assessment Ozone and Nitrogen Oxide Experiment (SONEX)

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Abstract. We report the mixing ratios of aerosol-associated soluble ions (focusing on SO_4^{2-} and NO_3^-) and HNO_3 over the North Atlantic during NASA's Subsonic Assessment Ozone and Nitrogen Oxide Experiment (SONEX). The SONEX campaign was designed to quantify the impacts of jet emissions in the North Atlantic Flight Corridor (NAFC) by sampling both directly within and far removed from the organized track system. Beryllium-7 activities were also measured to assess the magnitude of stratospheric influence in the SONEX study region. Mixing ratios of aerosol-associated SO_4^{2-} and NO_3^- above 8 km during SONEX were lower than recent measurements over the central United States during the Subsonic Aircraft Contrail and Cloud Effects Special Study (SUCCESS) and the same as those over the remote South Pacific during the Pacific Exploratory Mission-Tropics (PEM-Tropics), suggesting that aircraft emissions cannot yet be a major source of these ions. Furthermore, mean SO_4^{2-} mixing ratios at high altitudes were 65% higher in regions away from the NAFC than they were directly in the track system just a few hours after peak traffic. Nitric acid mixing ratios at the highest DC-8 sampling altitudes were elevated during SONEX compared to PEM-Tropics, but there was no clear signal of enhancement by jet exhaust. Strong correlations with ^7Be indicate that a large fraction of HNO_3 and aerosol-associated SO_4^{2-} measured at high altitudes during SONEX were derived from a stratospheric source.

1. Introduction

Rapid growth in the volume of commercial air traffic has raised concerns that jet exhaust deposited into the upper troposphere and lower stratosphere may significantly modify the composition of, and chemical cycling in, these regions of the atmosphere on global scales. Global and photochemical modeling studies have suggested that these emissions may perturb the O_3 budget [e.g., *Kasibhatla, 1993; Flato and Hov, 1996; Jaegle et al., 1999*], while models of the near-field effects of jet exhaust plumes predict the production of large amounts of HNO_3 and H_2SO_4 (among other perturbations) [e.g., *Anderson et al., 1996; Karcher et al., 1996, 1998; Danilin et al., 1997*].

There does not yet seem to be consensus among the various models regarding the effect of jet emissions on global ozone, nor is there adequate experimental data to document any clear impact. In the case of H_2SO_4 production in very young plumes a growing body of field measurements of volatile ultrafine particles directly in individual plumes appears to demonstrate that there is significant production [e.g., *Hagen et al., 1996; Petzold et al., 1997; Anderson et al., 1999*]. These inferential methods of detecting newly formed sulfate aerosols have been strengthened by recent direct quantification of particulate H_2SO_4 in young exhaust plumes [*Curtius et al., 1998*]. In all of these near-field investigations the detected particles have been very small (<15 nm), hence do not represent much mass. It has not yet been demonstrated that the H_2SO_4 formed in jet exhaust plumes makes a significant impact on the SO_4^{2-} burden in the upper troposphere and lower stratosphere.

We were unable to detect any enhancement of aerosol-associated SO_4^{2-} in young plumes via bulk aerosol sampling during the Subsonic Aircraft Contrail and Cloud Effects Special Study (SUCCESS) campaign [*Dibb et al., 1998*], a finding that was corroborated by *Curtius et al.* [1998], insofar as they could only detect enhancements of H_2SO_4 in plumes a few seconds old before dilution masked the signal.

The NASA Atmospheric Effects of Aviation Project (AEAP), Subsonic Assessment Ozone and Nitrogen Oxide Experiment (SONEX) airborne sampling campaign was designed to quantify any impacts of jet exhaust on regional and larger scales. Sampling was conducted within and around the North Atlantic Flight Corridor, where about 700 commercial jets travel in an organized track system each day. This paper presents observations of aerosol-associated soluble ions and gaseous HNO_3 , complemented by measurements of the stratospheric tracer ^7Be , obtained from the NASA DC-8 during SONEX.

2. Methods

2.1. Sampling

Aerosol samples were collected on 12 flights over the North Atlantic Ocean and on two transit flights between NASA Ames and Bangor, Maine, as part of the AEAP Subsonic Assessment (SASS) SONEX campaign in October–November, 1997 (Figure 1). Given the objectives of quantifying impacts from jet traffic in the North Atlantic Flight Corridor (NAFC), most sampling was conducted at and near cruise altitudes of commercial jets in the upper troposphere or lower stratosphere. We employed the same dual-inlet aerosol sampling system that was used on the Global Tropospheric Experiment (GTE) PEM–West and PEM–Tropics missions [*Dibb*

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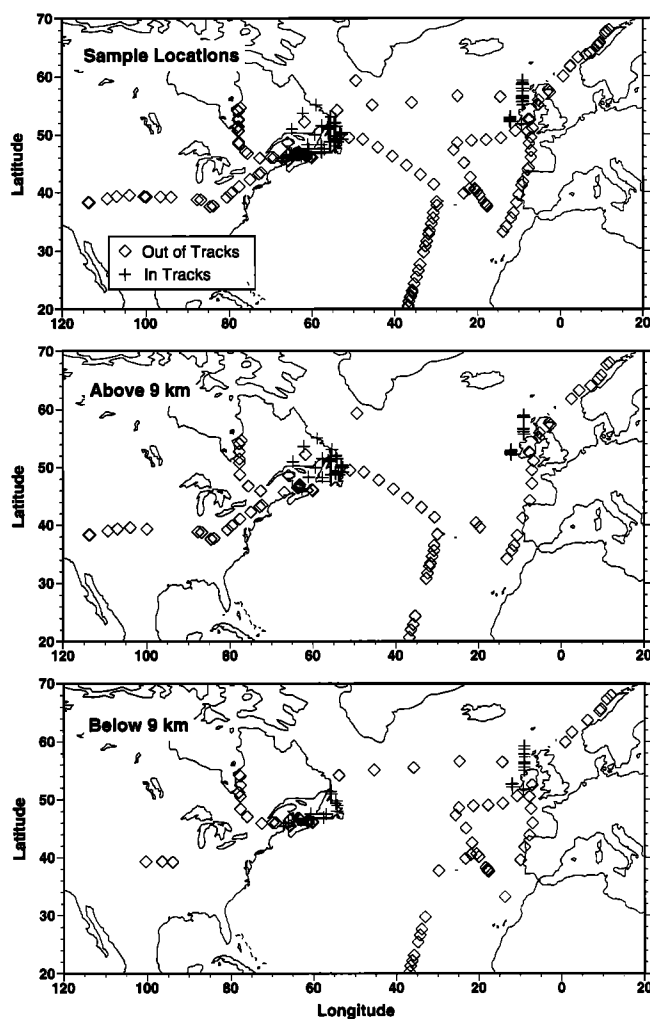


Figure 1. Latitude and longitude coordinates of the DC-8 at the midpoint of each aerosol exposure interval. Note the clusters of samples targeting the NAFC just west of Shannon, Ireland, and near Newfoundland.

et al., 1996, 1997, 1999]. One of the inlets was used to expose 2 μm pore size teflon (Gelman Zeflur) filters for the determination of the mixing ratios of soluble ionic species. The other inlet was used with glass fiber filters (Whatman GF/A) that were analyzed for the activities of the natural radionuclide tracers ^7Be and ^{210}Pb . The integration intervals of both systems were identical, so that the mixing ratios of the ionic species and the radionuclides were determined in the same air masses. Aerosol collection was restricted to flight legs at constant altitude. Exposure times were usually in the 15–20 min range, resulting in collection of a total of 224 paired samples.

In order to address the main SONEX objective, five of the DC-8 flights included repeated crossings of the NAFC shortly after the times of peak traffic. Two of these flights were conducted near Shannon, Ireland (flights 5 and 7), while the other three occurred in the vicinity of Newfoundland (last half of flight 11 (the Terceira to Bangor transit), and flights 12 and 14). We consider all samples collected during passages through the region defined by the organized track system on the dates of these five flights to be "In Tracks," hence potentially impacted by the NAFC extended line source of jet emissions. This definition includes flight legs below the lowest altitude used by commercial traffic. The In Tracks data

set consists of 74 samples. All other samples are considered to be "Out of Tracks" (150 total). Examination of Figure 1 shows that quite a few of the Out of Tracks samples were in close geographic proximity to others collected In Tracks. This reflects the fact that the organized track system moves from day to day in response to upper level winds. It should be pointed out that it is likely that some or all of the Out of Track samples were impacted by jet emissions to some extent since the upper troposphere upwind over North America is heavily influenced by emissions from the thousands of daily flights within the United States and Canada [Thompson *et al.*, 1999]. Our data analysis will search for strong enhancements directly in the flight corridor relative to background air which is not necessarily expected to be pristine.

2.2 Analysis

Our analytical techniques were essentially unchanged from those used on recent GTE campaigns [Dibb *et al.*, 1996, 1997, 1999]. However, we have slightly modified our handling of aerosol filters between exposure and analysis. On all GTE missions through PEM–West B our protocol involved placing exposed filters, still in the cassette, immediately into clean room bags and heat sealing them. Samples were then placed in a cooler with eutectic packs at -20°C for storage until extraction after the flight. Recognizing that the sealed bags contained a small amount of cabin air which could interact with the particles on the filter, we have begun including a purge of the bags with dry zero air. This procedure consists of sealing the clean bags with a tube delivering the zero air inside. A flow rate of about 2 Lpm sweeps cabin air out of the bag and begins to inflate it. At this point the tube is withdrawn, and the bag is sealed again. Filters are then stored in a cooler. We have used this protocol for the SASS SUCCESS and SONEX campaigns as well as during PEM–Tropics. The primary motivation for this change is to exclude any NH_3 in cabin air from contact with the exposed filters.

Concentrations of Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} in aqueous extracts of the teflon filters were determined by ion chromatography. Extractions and quantitation of the anionic species were conducted in the field within 24 hours of each flight. Aliquots of extracts were preserved with chloroform and returned to our laboratory in New Hampshire for cation determinations; these were completed within 6 weeks of the final flight. It should be noted that the mixing ratios of one or more of the species of interest were often below our detection limit. The detection limits are largely determined by variability in the concentrations of the analytes extracted from blank filters (which were generated at a rate of at least two flight $^{-1}$ by loading a filter into the sampling system, opening all valves to allow airflow for 15 s, and then removing the filter). We subtract the mission specific mean blank (nmol of analyte filter $^{-1}$) from each sample. Therefore the mixing ratios at detection limit vary inversely with the volume of air filtered for each sample. During SONEX the magnitude and variability of the blank for Na^+ , K^+ , and Cl^- were large enough to give us little confidence in the low mixing ratios of these species calculated for upper tropospheric and lower stratospheric samples (Table 1). We will therefore omit these three ions from discussion. The blanks for Ca^{2+} were also high relative to the light loading on most exposed samples. We include summary statistics for Ca^{2+} mixing ratios as an indicator of continental dust influence, while Mg^{2+} is retained as a tracer of sea salt. Neither of these main sources of primary aerosol proved to be significant contributors to the aerosol in the upper tropospheric regions sampled during SONEX. The focus of the discussion in this paper will be on the major ions SO_4^{2-} , NO_3^- , and

Table 1. Variability in Composition of Aqueous Extract of Blank Filters

	Cl ⁻	NO ₃ ⁻	SO ₄ ⁼	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Mean, nmol filter ⁻¹	1.0	2.3	0.8	26.5	7.8	3.3	0.4	2.8
s d.	2.5	1.4	0.5	8.7	4.0	2.1	0.4	1.6
Mixing ratio ^a	18.2	10.0	3.6	63.4	29.0	14.9	2.6	11.6

^aAt least two blanks were generated each flight.

^aThis row reflects the uncertainty in mixing ratio (in parts per trillion by volume (ppt)) for a sample of average air volume (3 l m⁻³) during SONEX, based on the standard deviation of the blank. Note that the uncertainty increases (decreases) for smaller (larger) sample volumes. During the SONEX campaign, 70% of samples had volumes between 2.0 and 4.8 m³.

NH₄⁺ for which blank variability generally had small impact on derived mixing ratios.

Glass fiber filters were express mailed to New Hampshire at intervals through the campaign so that ⁷Be activities could be determined by gamma spectrometry as quickly as possible. However, the large number of relatively small volume samples collected created a backlog; the final filters were not counted until 2 months after the last flight. Our ²¹⁰Pb technique (determination of the activity of the ²¹⁰Po daughter by alpha spectrometry) requires approximately 1 year for in-growth of the daughter before counting [Dibb *et al.*, 1996]. At the time of writing these analyses were in progress, with samples from the first 12 flights (approximately 2/3 of the total) completed. As a result, the ²¹⁰Pb distribution will be presented in a subsequent paper.

3. Results

Aerosol SO₄⁼ (p-SO₄⁼) was quantified in all SONEX samples save one collected Out of Tracks above 10 km (Table 2). Beryllium-7 was also above our detection limits most of the time (85 and 87% of samples In Tracks and Out of Tracks, respectively). We were only able to quantify p-NO₃⁻ and p-NH₄⁺ in about half of all samples, with a higher fraction above detection limits for p-NO₃⁻ In Tracks (57%) than Out of Tracks (47%), while the reverse was true for p-NH₄⁺ (50% In Tracks versus 61% Out of Tracks). Mixing ratios of p-Mg²⁺ and p-Ca²⁺ were below detection limits in more than 74% of the samples in both subsets.

There were few striking differences between In Tracks and Out of Tracks mean or median mixing ratios (Table 2). Elevated ⁷Be activities at high-altitude Out of Tracks reflect stronger stratospheric influence encountered at high latitudes northeast of Shannon and when crossing a strong jet stream on flights south of Shannon (Figure 1), rather than depression of the activity in samples within the flight corridor. When mean and median mixing ratios in like altitude bins are compared, all other differences, except one, are comparable to or smaller than the variability within each of the two subsets of data. The single exception is surprising, with mean p-SO₄⁼ mixing ratios above 10 km Out of Tracks exceeding the mean at high-altitude In Tracks by 65% (comparing medians shows a 50% enhancement Out of Tracks) (Table 2). We take this to indicate that any enhancement of p-SO₄⁼ from H₂SO₄ produced in jet exhaust plumes must still be small compared to other sources of p-SO₄⁼ in the upper troposphere above the North Atlantic during the fall. Comparing SONEX data to our measurements during the recent GTE PEM-Tropics and SASS SUCCESS campaigns reinforces this preliminary conclusion (Figure 2). Mean p-SO₄⁼ mixing ratios above 8 km were identical (27 parts per trillion by volume (pptv)) during SONEX and PEM-Tropics; a surprising result considering that PEM-Tropics characterized the remote South Pacific troposphere. During SUCCESS the mean p-SO₄⁼ mixing ratio above 8 km (40 pptv) was nearly 50% higher

than the other two missions. We attributed much of the increase in upper tropospheric p-SO₄⁼ over the central United States during SUCCESS (compared to a mean of 24 pptv measured in the upper troposphere above the North Pacific off California during the same campaign) to convective pumping of polluted boundary layer air [Dibb *et al.*, 1998].

4. Discussion

4.1. Sulfate Aerosol

Given the evidence that jet exhaust was at best a minor source of p-SO₄⁼ even within the flight corridor, we attempt to determine whether the SONEX data provide insight into the dominant sources of p-SO₄⁼ over the North Atlantic during the campaign. Comparison of "quick look" data products produced during the field mission suggested that variations in p-SO₄⁼ were often correlated with variations of HNO₃ and O₃, particularly for samples collected above 7-8 km. Stratospheric injections would be expected to elevate mixing ratios of all three of these species in the upper troposphere, but model predictions that jet exhaust can lead to production of large amounts of HNO₃ as well as perturbations to the balance between O₃ production and loss [Kasibhalla, 1993; Anderson *et al.*, 1996; Karcher *et al.*, 1996; Flato and Hov, 1996; Jaegle *et al.*, 1999] demanded caution before assuming that HNO₃ and O₃ could be considered tracers of stratospheric influence on the upper troposphere during SONEX.

Beryllium-7 is produced throughout the atmosphere, but the maximum production occurs near 15 km [Bhandari *et al.*, 1970]. Processes removing ⁷Be from the troposphere (primarily precipitation scavenging) are much faster than radioactive decay (the primary sink in the stratosphere), thus higher production and weaker removal combine to make ⁷Be activities in the lowermost stratosphere roughly an order of magnitude higher than those in the upper troposphere [Rama, 1963; Bhandari *et al.*, 1966; Dutkiewicz and Husain, 1979, 1985]. More importantly, jet exhaust is definitely not a source of ⁷Be. We therefore consider ⁷Be to be an unambiguous tracer of stratospheric influence on the air masses sampled during SONEX. Correlations of p-SO₄⁼ against ⁷Be above 9 km were quite strong, and have the same slope In Tracks and Out of Tracks (Figure 3a). This is further strong evidence that the jet exhaust source of p-SO₄⁼ must be minimal. We use measured ⁷Be activities and the relationship between p-SO₄⁼ and ⁷Be above 9 km Out of Tracks to estimate the "stratospheric" component of p-SO₄⁼ in all SONEX samples and subtract this from observed p-SO₄⁼. Above 8 km it would appear that essentially all p-SO₄⁼ can be attributed to a stratospheric source (Figure 3b).

4.2. Nitrogen Oxides

We used the same approach to assess the importance of the stratosphere as a source of upper tropospheric nitrogen oxide

Table 2. Comparison of Mixing Ratios of Aerosol Associated Species in Samples Collected Within, and Away From, the North Atlantic Flight Corridor

	NO ₃ ⁻	SO ₄ ⁼	NH ₄ ⁺	Mg ²⁺	Ca ²⁺	⁷ Be
<i>In Flight Corridor</i>						
<8 km (12 samples)						
Mean	16.5	40.9	67.1	5.7	11.2	956
Standard error	9.0	7.8	11.8	3.0	4.7	216
Median	8.9	38.5	72.4	2.8	6.4	847
n ^a	9	12	10	5	6	7
8-10 km (25 samples)						
Mean	17.8	24.2	58.2	3.8	21.9	1071
Standard error	4.7	2.3	10.2	1.7	9.4	294
Median	15.1	22.8	52.9	3.0	9.9	807
n ^a	13	25	17	5	6	21
>10 km (37 samples)						
Mean	18.2	22.	71.8	1.2	8..5	1387
Standard error	4.0	2.0	17.4	0.8	3.2	258
Median	13.8	21.0	91.9	1.2	4.5	1066
n ^a	20	37	10	2	7	35
<i>Outside Flight Corridor</i>						
<8 km (37 samples)						
Mean	10.5	63.1	89.3	1.8	9.4	909
Standard error	2.2	14.3	16.7	0.5	1.8	178
Median	7.0	32.6	60.0	1.5	6.8	629
n ^a	22	37	30	11	17	34
8-10 km (64 samples)						
Mean	9.7	23.3	47.7	2.8	9.3	1230
Standard error	1.8	2.3	8.3	1.0	4.7	208
Median	6.6	17.0	34.3	2.0	4.1	750
n ^a	27	64	31	11	11	53
>10 km (49 samples)						
Mean	13.2	37.5	73.6	2.5	13.3	3714
Standard error	2.4	3.2	8.8	0.8	6.1	533
Median	9.9	31.8	69.5	1.0	7.7	1784
n ^a	24	48	31	13	9	44

Soluble ionic species reported in parts per trillion by volume (pptv), ⁷Be in fCi m⁻³ STP.^aNumber of samples where given analyte was above detection limit.

species during SONEX. Nitric acid mixing ratios at high altitude tended to be higher during SONEX than PEM-Tropics with the reverse observed in the middle troposphere (Figure 4) (HNO₃ was not measured during SUCCESS). The enhancements of HNO₃ between 2 and 8 km during PEM-Tropics were clearly linked to biomass burning plumes [Talbot *et al.*, 1999a], a source not likely to be very important over the North Atlantic during late fall. It should also be noted that the tropical tropopause was usually several kilometers above the highest DC-8 sampling altitude during PEM-Tropics; such was not the case during SONEX. Stratospheric input is thus one possible explanation for the higher HNO₃ mixing ratios observed at high altitudes during SONEX.

A significant contribution of stratospheric HNO₃ is supported by the HNO₃-⁷Be relationships above 9 km (Figure 5). The range (+/- 200 pptv) of "nonstratospheric" HNO₃ in the upper troposphere estimated from the linear fit to the Out of Tracks data indicates that ⁷Be is not a perfect predictor of HNO₃, but the distributions are centered around zero for both the In Track and Out of Track subsets of data (Figure 5b). A stratospheric source appears dominant for SONEX samples with elevated HNO₃, with no evidence for significant enhancements in the NAFC. It is likely that additional non-negligible sources of HNO₃ create the scatter in the HNO₃-⁷Be correlation. We suspect that HNO₃ formed from NO_x produced by

lightning in convective systems (e.g., Pickering *et al.*, unpublished manuscript, 1999) was more important than convective pumping of polluted boundary layer air into the free troposphere, since the latter process should have enhanced p-SO₄⁼ as well, similar to our findings during SUCCESS [Dibb *et al.*, 1998].

Mixing ratios of p-NO₃⁻ in the upper troposphere/lower stratosphere during SONEX were generally lower than those at comparable altitudes during PEM-Tropics and SUCCESS (Figure 6). Enhanced p-NO₃⁻ throughout the mid and upper troposphere over the central United States during SUCCESS presumably reflects mixing of polluted boundary layer air upward, as discussed above in relation to p-SO₄⁼ [Dibb *et al.*, 1998; Talbot *et al.*, 1998]. During PEM-Tropics the troposphere over the South Pacific was extensively impacted by long-range transport of biomass burning emissions, though we noted that the individual plumes generally did not have marked enhancements in the mixing ratios of any aerosol-associated soluble ions [Dibb *et al.*, 1999]. Above 7 km during SONEX the six samples with highest p-NO₃⁻ mixing ratios were all In Tracks (Figure 6), but means and medians suggest only slight enhancement In Tracks compared to Out of Tracks (Table 2). There was no correlation between p-NO₃⁻ and ⁷Be in either subset of data; in fact, the highest p-NO₃⁻ mixing ratios were associated with ⁷Be activities <<1000 fCi m⁻³ (Figure 7). These observations

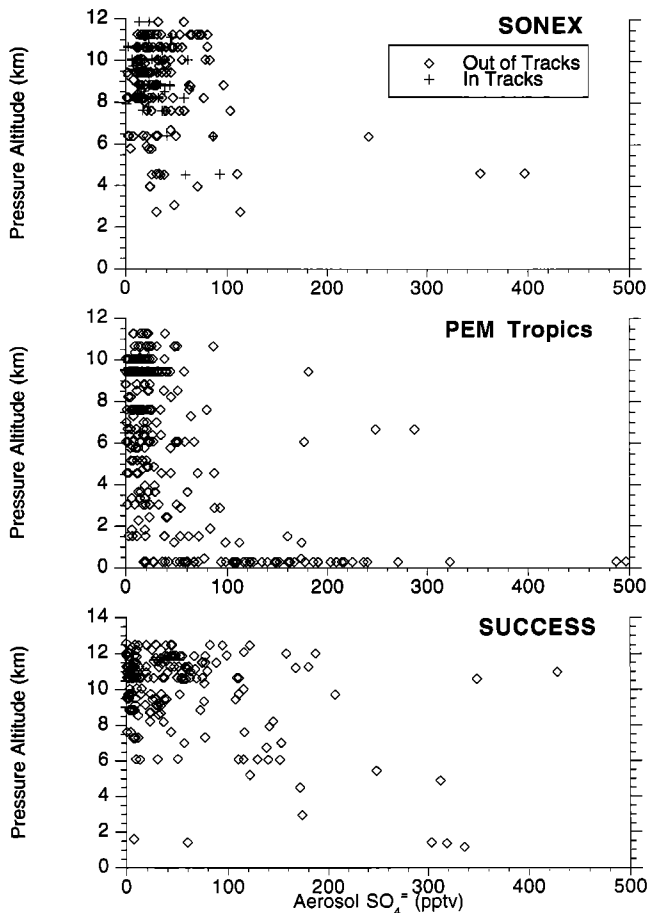


Figure 2. Comparison of p-SO₄⁼ mixing ratios versus altitude during the SONEX, PEM-Tropics, and SUCCESS sampling campaigns.

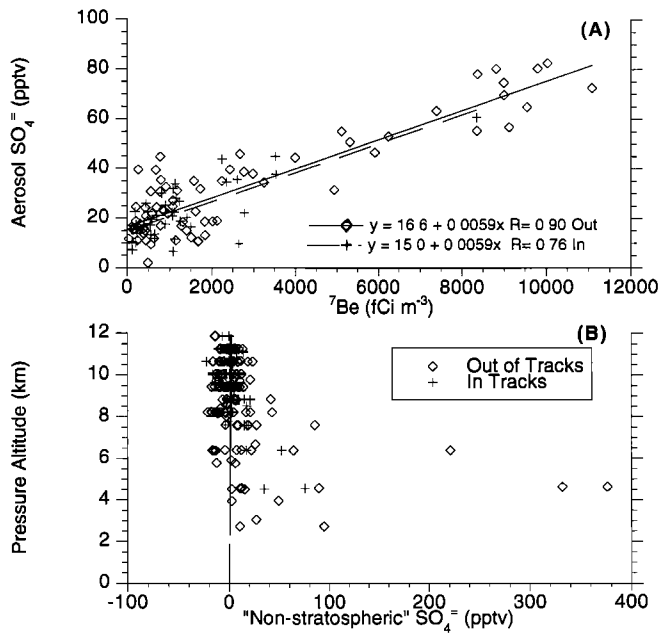


Figure 3. (a) Scatterplot of p-SO₄⁼ against ⁷Be for samples collected above 9 km during SONEX. The lines are least squares fit to the In Tracks and Out of Tracks subsets of data; (b) "Nonstratospheric" SO₄⁼ as a function of altitude. Stratospheric SO₄⁼ was estimated from measured ⁷Be and the least squares fit Out of Tracks shown in Figure 3a.

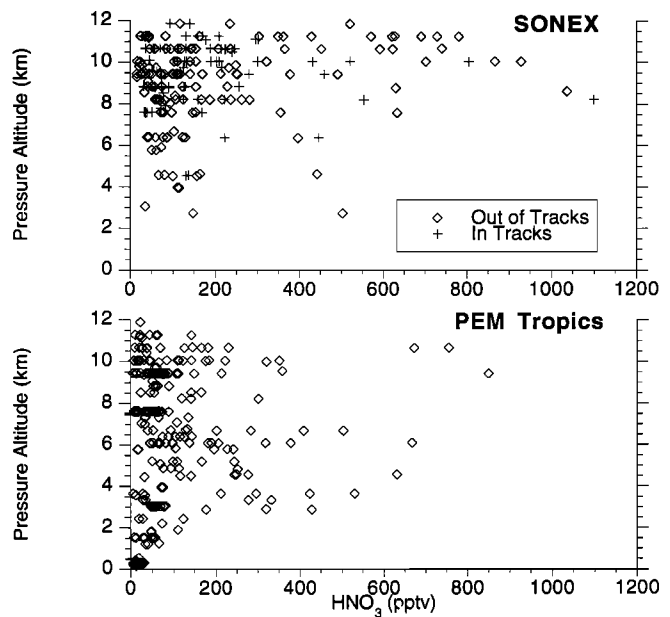


Figure 4. Comparison of HNO₃ mixing ratios versus altitude during the SONEX and PEM-Tropics sampling campaigns.

suggest minimal stratospheric influence on p-NO₃⁻, with occasional, small (several tens of pptv), enhancements possibly attributable to jet exhaust. The low mixing ratios compared to SUCCESS reinforce our belief that surface sources contributed little to upper tropospheric burdens of soluble ions during SONEX.

Total reactive nitrogen oxides (NO_x) were also strongly correlated with ⁷Be above 9 km Out of Tracks. The slope of 0.08 pptv NO_x/fCi m⁻³ ⁷Be (not shown) was quite similar to those found for HNO₃ versus ⁷Be (Figure 5). This is consistent with stratospheric HNO₃ representing the dominant fraction of NO_x in air masses with elevated NO_x Out of Tracks [Talbot et al., 1999b]. In Tracks all samples with high (>1000 ppt) NO_x mixing ratios were associated with relatively low ⁷Be activity (200–2700 fCi m⁻³). These samples were also characterized by NO/NO_x ratios >0.5. Strong enhance-

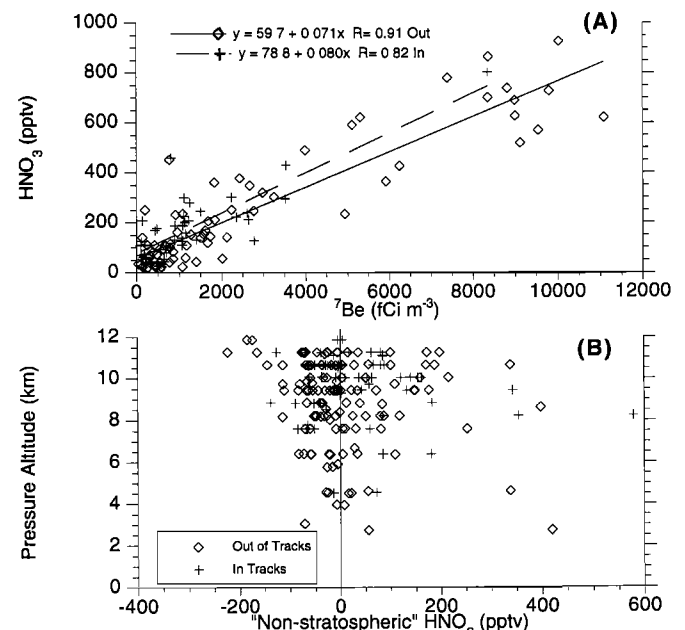


Figure 5. As in Figure 3, but for HNO₃ versus ⁷Be.

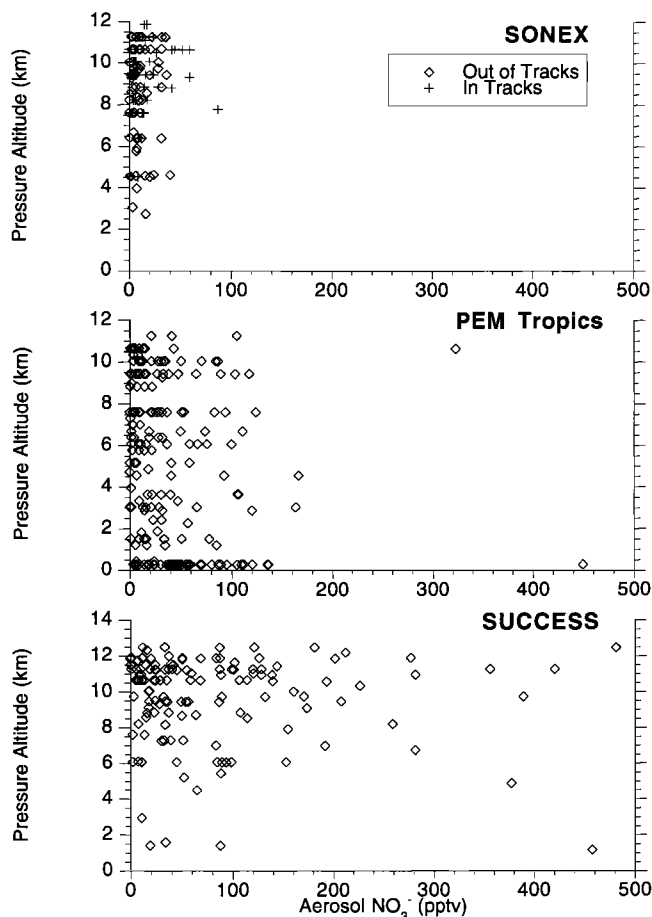


Figure 6. Comparison of p-NO₃⁻ mixing ratios versus altitude during the SONEX, PEM-Tropics, and SUCCESS sampling campaigns.

ments of NO_y In Tracks thus seem to be largely NO_x and can be attributed to emissions from jet aircraft. Our analysis is based on NO and NO_y mixing ratios averaged over the 10-15 min aerosol integration interval; the original high-resolution data set shows that the enhancements we observe In Tracks are due to very large spikes caused by interception of individual, relatively fresh, jet exhaust plumes [Koike *et al.*, this issue; K. Kita *et al.*, unpublished manuscript, 1999]. These authors discuss the high-resolution NO and NO_y data set in detail and conclude that it is not straightforward to identify and quantify enhancements of NO and NO_y within the flight corridor (but not directly influenced by fresh plumes) relative to other upper tropospheric and lower stratospheric air masses sampled during SONEX.

4.3. Distribution of Aerosol-Associated Soluble Ions

Our analysis indicates that any aircraft impacts on the mass of soluble ionic species in the SONEX study region were very subtle, if present at all. The data were separated into four geographic bins, with proximity to the flight corridor disregarded, to search for regional variations in the composition of the aerosol (Table 3). The small number of samples wherein Mg²⁺ and Ca²⁺ could be quantified precludes meaningful analysis. For the four species we were able to quantify in most samples, the substantial variability within each large spatial bin hinders identification of differences between

the bins, as was the case for comparisons in and out of the flight corridor.

Despite these difficulties, the dominant influence of the stratospheric source of p-SO₄⁼ is reflected by parallel enhancements of p-SO₄⁼ and ⁷Be at the highest altitudes in both eastern regions (Table 3). However, it is puzzling that the mean and median mixing ratios of p-NH₄⁺ (considering only those samples where NH₄⁺ was above detection limit) are also elevated in these same bins. Stratospheric p-SO₄⁼ has been shown to be largely H₂SO₄ [Hayes *et al.*, 1980], and the same composition is often assumed for p-SO₄⁼ in the upper troposphere [e.g., Gillette and Blifford, 1971; Huebert and Lazrus, 1980; Whelpdale *et al.*, 1987; Dentner and Crutzen, 1993]. Most of the SONEX aerosol samples collected above 8 km had bulk compositions more acidic than NH₄HSO₄ (Figure 8). If we assume that samples with NH₄⁺ below detection were H₂SO₄, statistical summaries for the four bins suggest that the aerosol is strongly acidic in all regions except the northeast bin (mean (median) values of the NH₄⁺/SO₄⁼ equivalence ratio were 0.63 (0.04), 0.46 (0.09), 0.46 (0.00), and 0.98 (0.65) in the SW, SE, NW, and NE regions, respectively). However, several samples in each region had considerably more NH₄⁺ than would be required to completely neutralize SO₄⁼ (Figure 8), a feature causing the regional means to be so much higher than the medians.

The concentrations of SO₄⁼ and NH₄⁺ in the aqueous extracts of filters with "problematic" NH₄⁺/SO₄⁼ ratios are generally well above detection limits; thus we feel that analytical uncertainties cannot explain the high ratios. Artifact absorption of NH₃ by filters loaded with strongly acidic aerosol [e.g., Hayes *et al.*, 1980] cannot be entirely ruled out, though we see two arguments against this hypothesis. First, our sample handling protocol is designed expressly to limit exposure to air within the aircraft or in the laboratory during collection, extraction, and analysis. The large number of SONEX samples with very low NH₄⁺/SO₄⁼ ratios suggest that our techniques must generally be effective. Second, post-collection neutralization of H₂SO₄ by NH₃ should not drive the equivalence ratio above 1, yet values between 1 and 4 are common in the SONEX data set.

Abundant HNO₃ could react with NH₃ present in excess of H₂SO₄, but this should appear as p-NO₃⁻. Mixing ratios of p-NO₃⁻ in SONEX samples generally account for only a few percent of excess p-NH₄⁺. This hypothesis also fails to address the fundamental issue of how so much NH₃ or p-NH₄⁺ came to be in the upper troposphere or lower stratosphere. Scatterplots of the NH₄⁺/(NO₃⁻ + SO₄⁼) equivalence ratio against ⁷Be show that samples collected above 8 km with large excess NH₄⁺ tend to have more tropospheric character (lower ⁷Be) (Figure 9), but in the eastern regions there are several samples with strong stratospheric influence (⁷Be > 8000 fCi m⁻³) that still have enough NH₄⁺ to neutralize 50-100% of the strong

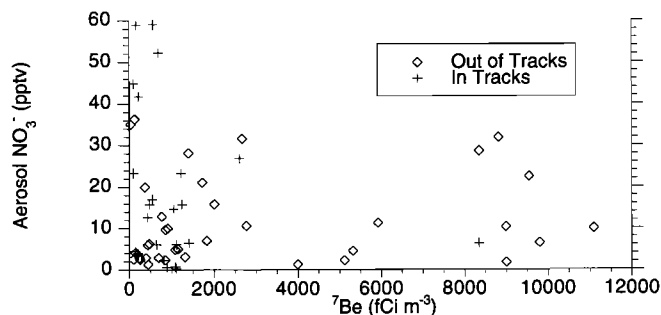


Figure 7. Scatterplot of p-NO₃⁻ against ⁷Be for samples collected above 9 km during SONEX.

Table 3. Statistical Summary of Mixing Ratios of Aerosol Associated Species in Four Geographic Bins Sampled During SONEX

	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	Mg ²⁺	Ca ²⁺	⁷ Be
<i>South of 50°N, West of 50°W</i>						
<8 km (17 samples)						
Mean	20.5	75.8	99.3	4.3	13.4	916
Standard error	7.5	28.0	29.4	2.3	2.9	202
Median	8.9	34.2	61.0	2.8	15.0	692
n ^a	11	17	15	7	10	15
8-10 km (32 samples)						
Mean	9.0	18.9	36.2	1.1	7.2	1011
Standard error	1.8	2.0	8.4	0.5	2.1	174
Median	6.2	16.4	20.6	0.8	8.9	658
n ^a	16	32	17	3	4	29
>10 km (25 samples)						
Mean	11.9	21.3	44.6	2.1	8.6	1470
Standard error	3.8	2.2	9.7	0.8	1.9	295
Median	6.2	18.7	42.1	1.5	8.8	1080
n ^a	14	25	14	6	7	25
<i>South of 50°N, East of 50°W</i>						
<8 km (11 samples)						
Mean	8.0	31.3	42.5	--	10.2	363
Standard error	0.9	9.3	12.8	--	6.7	91
Median	7.3	23.3	31.4	--	4.8	330
n ^a	4	11	6	0	3	9
8-10 km (30 samples)						
Mean	11.3	25.9	52.2	3.5	14.8	1133
Standard error	3.4	4.2	12.9	1.4	10.1	324
Median	8.2	18.2	43.0	3.5	3.8	715
n ^a	12	30	16	6	5	21
>10 km (17 samples)						
Mean	21.4	37.6	74.9	1.1	8.3	4581
Standard error	4.5	5.7	11.9	0.5	3.0	1057
Median	22.5	35.1	70.0	0.6	8.3	2987
n ^a	9	16	8	4	2	13
<i>North of 50°N, West of 50°W</i>						
<8 km (six samples)						
Mean	11.4	92.5	95.4	1.2	9.7	924
Standard error	5.6	32.5	34.0	0.8	4.7	408
Median	11.8	86.1	71.0	0.6	6.3	677
n ^a	5	6	5	3	5	6
8-10 km (10 samples)						
Mean	23.6	26.4	76.6	3.0	25.8	1327
Standard error	12.6	3.9	38.6	--	19.1	871
Median	16.5	23.3	56.1	3.0	7.8	708
n ^a	4	10	3	1	3	7
>10 km (18 samples)						
Mean	14.1	25.7	53.2	0.3	8.5	1777
Standard error	4.6	3.5	26.5	--	5.8	569
Median	9.6	24.0	17.6	0.3	3.7	1083
n ^a	12	18	5	1	4	15
<i>North of 50°N, East of 50°W</i>						
<8 km (15 samples)						
Mean	6.0	42.6	80.6	2.3	4.4	1258
Standard error	1.8	5.8	14.0	0.2	1.4	324
Median	3.5	39.3	76.7	2.4	4.7	693
n ^a	11	15	14	6	6	15
8-10 km (17 samples)						
Mean	15.0	26.5	65.8	3.9	10.7	1486
Standard error	5.0	3.2	11.0	1.7	6.0	442
Median	9.6	26.9	63.1	2.6	5.1	948
n ^a	8	17	12	6	5	17
>10 km (26 samples)						
Mean	16.9	40.0	107.9	4.3	22.7	3423
Standard error	5.6	4.4	13.0	2.2	19.1	699
Median	10.0	34.7	113.5	3.1	4.5	1909
n ^a	9	26	14	4	3	26

Soluble ionic species reported in parts per trillion by volume (pptv), ⁷Be in fCi m⁻³ STP.^aNumber of samples where given analyte was above detection limit.

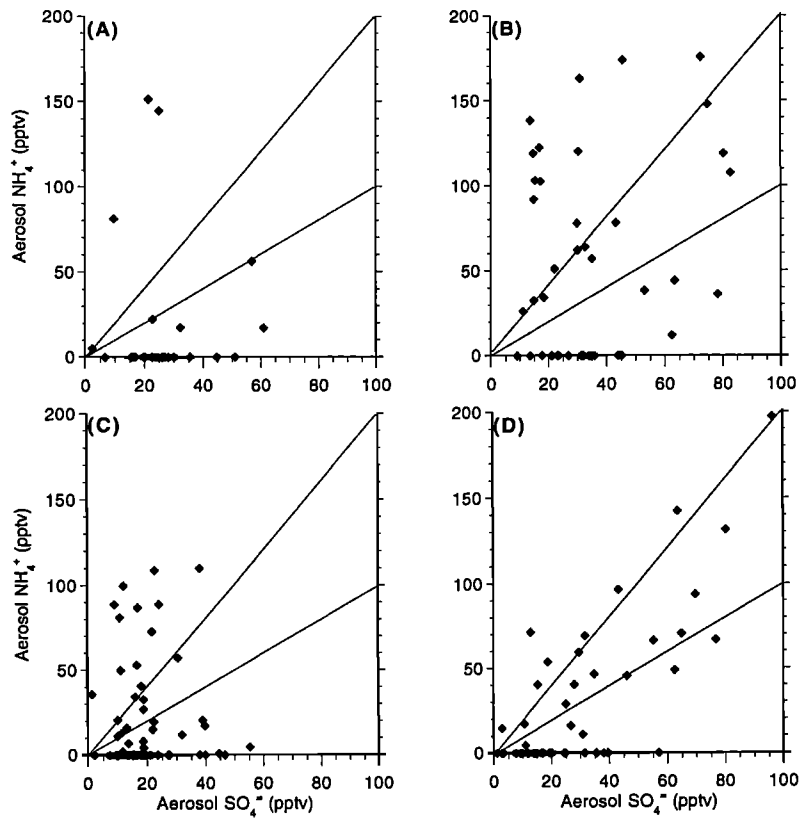


Figure 8. Scatterplots of p-NH_4^+ against p-SO_4^- above 8 km in four geographic regions sampled during SONEX. The lines are the 1:1 and 2:1 molar ratios corresponding to NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$. The regions are (a) north of 50°N , west of 50°W , (b) north of 50°N , east of 50°W , (c) south of 50°N , west of 50°W , and (d) south of 50°N , east of 50°W .

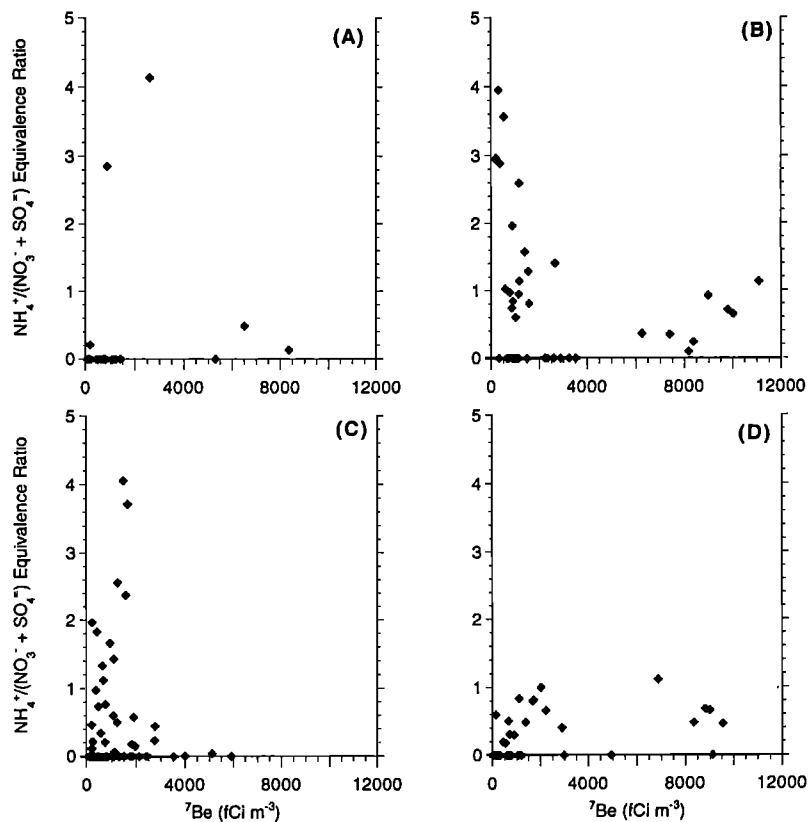


Figure 9. Scatterplots of the $\text{NH}_4^+/(\text{NO}_3^- + \text{SO}_4^-)$ equivalence ratio against ${}^7\text{Be}$ activity above 8 km in the same regions described in Figure 8.

acids. We cannot readily explain these observations, but neither can we find grounds to dismiss them as analytical artifacts. Given that recent modeling of upper tropospheric nitrogen oxide chemistry has shown high sensitivity to the extent to which $p\text{-SO}_4^-$ is neutralized [Schulz *et al.*, 1999], the SONEX results demonstrate the need for much more extensive characterization of the chemical composition of aerosol in the free troposphere.

5. Conclusions

Sampling from the DC-8 during the SONEX campaign found no evidence of significant enhancements of $p\text{-SO}_4^-$ or HNO_3 in the vicinity of the North Atlantic Flight Corridor that could be attributed to emissions from the large volume of commercial jet traffic in this region. Small enhancements of $p\text{-NO}_3^-$ were observed in a few samples within the corridor, but overall there was not a consistent pattern of elevated $p\text{-NO}_3^-$ relative to regions far removed from the corridor.

Correlations with ^7Be indicate that essentially all of the $p\text{-SO}_4^-$, and a large fraction of HNO_3 , above 8 km during SONEX could be accounted for by a stratospheric source. Since we can account for all $p\text{-SO}_4^-$ by stratospheric influence, it appears that vertical pumping of boundary layer air had little impact on the burden of soluble ionic species in the free troposphere during SONEX. This suggests that lightning-derived NO_x is the likely precursor for HNO_3 that did not originate in the stratosphere.

In general, the upper tropospheric aerosol over the North Atlantic was acidic, but we collected a significant number of samples with enough NH_4^+ to fully, and in some cases more than fully, neutralize the strong acids. These results are not completely understood, but indicate the need for additional characterization of aerosol composition in the upper troposphere.

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