FINAL TECHNICAL REPORT

Measurements of Nitric Acid and Aerosol Species Aboard the NASA DC-8 Aircraft During the <u>S</u>ASS <u>O</u>zone and <u>N</u>itrogen Oxide <u>E</u>xperiment (SONEX)

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Summary:

We received funding to provide measurements of the nitric acid (HNO_3) and the chemical composition of aerosols aboard the NASA Ames DC-8 research aircraft during the SONEX mission. These measurements were successfully completed and the final data resides in the Cloud1 computer archive at NASA Ames Research Center.

The interpretation of the data obtained on this mission over the North Atlantic is currently "in press" in special issues of *Geophysical Research Letters* and the *Journal of Geophysical Research*. The papers with the University of New Hampshire as first author constitute this report and summarize the salient features of our data. The paper by Talbot et al. discusses the budget of total reactive nitrogen in the middle and upper troposphere over the North Atlantic Ocean. This topic was an important objective of SONEX, and the budget analysis indicates that the sum of individual species was approximately equal to the measured total reactive nitrogen (NO_y). This is the best budget closure agreement ever achieved in the remote troposphere, and points to the high quality of the individual measurements. The paper by Dibb et al. discusses aerosol chemistry specifically as it related to free tropospheric sulfate related to jet exhaust and stratospheric inputs. Somewhat surprisingly, we found that the stratospheric source appears to dominant the distribution of aerosol sulfate in the free troposphere over the North Atlantic, even in the heavily traveled flight corridors. In addition to these first authored papers, researchers from the University of New Hampshire are co-authors on numerous other companion papers in both special issues.

Reactive Nitrogen Budget During the NASA SONEX Mission

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Abstract

The SASS Ozone and Nitrogen Oxides Experiment (SONEX) over the North Atlantic during October/November 1997 offered an excellent opportunity to examine the budget of total reactive nitrogen (NO_y) in the upper troposphere (8 - 12 km altitude). The median measured NO_y mixing ratio was 425 parts per trillion by volume (pptv). Two different methods were used to measure HNO_3: (1) the mist chamber technique and, (2) chemical ionization mass spectrometry. Two merged data sets using these HNO_3 measurements were used to calculate NO_y by summing the reactive nitrogen species (a combination of measured plus modeled results) and comparing the resultant values to measured NO_y (gold catalytic reduction method). Both comparisons showed good agreement in the two quantities (slope > 0.9 and r^2 > 0.9). Thus, the total reactive nitrogen budget in the upper troposphere over the North Atlantic can be explained in a general manner as a simple mixture of NO_x ($NO + NO_2$), HNO_3, and PAN. Median values of NO_x/NO_y were ≈0.25, HNO_3/NO_y ≈0.35 and PAN/NO_y ≈0.17. Particulate NO_3^- and alkyl nitrates together composed <10% of NO_y, while model estimated HNO_4 averaged 12%.

Introduction

Reactive nitrogen compounds in the Earth's troposphere, primarily believed to be present as NO, NO_2, $HONO$, HNO_3, HNO_4, NO_3, N_2O_5, $CH_3C(O)OONO_2$ (PAN), $RONO_2$ (alkyl nitrates), and particulate NO_3^- [Logan, 1983; Fahey et al., 1985], constitute important controls on O_3, oxidant, and acidity levels on a global scale. The collective sum of these species, commonly referred to as total reactive odd-nitrogen (NO_y) [Fahey et al., 1985], is a quantity useful for general characterization of air parcels in rural and remote atmospheres. Direct measurements of NO_y and its suspected dominant components show good agreement at most continental sites at part per billion by volume (ppbv)

mixing ratios where a simple mixture of NO_x ($NO + NO_2$), HNO_3, and PAN comprise >90% of total NO_y [*Parish et al.*, 1993; *Sandholm et al.*, 1994; *Roberts*, 1995].

At remote locations comparison of direct measurements of NO_y at hundreds of parts per trillion by volume (pptv) and the sum of its components typically show poor agreement by as much as 50% [*Fahey et al.*, 1986; *Ridley et al.*, 1991; *Sandholm et al.*, 1994; *Atlas et al.*, 1992, 1996; *Crosley*, 1996; *Kondo et al.*, 1997a]. In these well processed (i.e., photochemically aged, diluted, and precipitation influenced) air parcels NO_x and HNO_3 should comprise small fractions of total NO_y. In these cases a complex mixture of reactive nitrogen compounds may persist, as evidenced for example by the dominant role of alkyl nitrates in the marine boundary layer NO_y budget over the equatorial Pacific Ocean [*Talbot et al.*, 1999a].

In this paper we present a summary comparison between total NO_y measured directly with a gold catalytic converter [*Fahey et al.*, 1985; *Kondo et al.*, 1997b] and the sum of the individually measured species NO, HNO_3, PAN, PPN, alkyl nitrates, plus modeled NO_2, HONO, HNO_4, N_2O_5, and NO_3 over the North Atlantic during October/November 1997. These data were obtained during the NASA SASS Ozone and Nitrogen Oxides Experiment (SONEX) focused on the North Atlantic flight corridor where ≈700 commercial aircraft traverse it each day at 9 - 12 km altitude between North America and Europe. Air parcels sampled in this region should represent a combination of processed continental and "fresh" aircraft emissions. Thus, a complex mixture of reactive odd-nitrogen compounds might be expected to be prevalent in this tropospheric region. Our findings support this scenario, but indicate that NO_x, HNO_3 and PAN are dominant components of total NO_y.

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Methods

The SONEX mission was conducted from three base stations: Bangor, Maine (USA), Shannon, Ireland, and the Azore Islands. Local flights consisted of four each from Bangor and Shannon, one from the Azores, and transits in between the various locations. All of the data collected on these flights was used in this analysis to constitute a total of 15 science missions ($\approx$ 120 flight hours of data).

The airborne missions were conducted aboard the NASA Ames DC-8 research aircraft which has a flight range of 12 hours at 0.3 - 12.5 km altitude. The majority (>95%) of the data collected during SONEX was obtained at 8 - 12 km altitude, the region impacted directly by trans-Atlantic commercial aircraft routes.

Nitric oxide (NO) and NO_y were sampled through a rear-facing (to help exclude aerosols >1 μm diameter) heated (50°C) PFA teflon tube (6 mm ID) at 1 standard liter per minute (SLPM) flow rate and detected as NO using chemiluminescence [*Kondo et al.*, 1997b]. NO_y was catalytically converted to NO at 50 hPa on the surface of a gold tube heated to 300°C with addition of CO. Data for both measurements were reported at 1 second intervals.

Nitric acid was measured using the mist chamber (MC) technique [*Talbot et al.*, 1997, 1999b] and chemical ionization mass spectrometry (CIMS) [*Miller et al.*, 1999]. The MC instrument utilized a fast flowing (1000-3000 SLPM) fused-silica coated manifold ($\approx$50 mm ID) with the capability to conduct standard additions of HNO_3 down $\approx$95% of the entire length of the inlet. The CIMS instrument used a ram flow inlet ($\approx$830 SLPM) inlet ($\approx$37 mm ID) composed of alodined aluminum and stainless steel pipe. Standard additions of HNO_3 were conducted inside the aircraft testing $\approx$60% of the inlet for passing efficiency.

Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) were measured through a rear-facing inlet (6 mm ID) composed of unheated PFA teflon tubing with a flow rate of 1 SLPM. Calibrations were conducted inside the aircraft testing the passing efficiency of $\approx 40\%$ of the inlet. PAN and PPN were cyrogenically trapped from ambient air and quantified subsequently by electron capture gas chromatography [*Singh and Salas*, 1983].

Alkyl nitrates (methyl nitrate, ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, and 2-butyl nitrate) were sampled through a 6 mm ID stainless steel tube into passivated stainless steel canisters and pressurized to 2750 hPa with a metal bellows pump [*Blake et al.*, 1999]. The canisters were shipped back to the laboratory where the alkly nitrates were cyrogenically trapped and measured using electron capture and mass spectrometry detection coupled with gas chromatography [*Atlas et al.*, 1992; *Blake et al.*, 1999; *Sive*, 1998].

A diel steady-state model [*Jaegle et al.*, this issue] was used to calculate the unmeasured species NO_2, NO_3, N_2O_5, HONO, and HNO_4. The model was constrained with observed NO, CO, H_2O, CH_4, hydrocarbons, pressure, temperature, aerosol surface area, and UV actinic flux.

Database

Although each of the SONEX participating groups reported individual flight data files to the NASA archive (publically available on Cloud1.nasa.ames.gov at NASA Ames Research Center), we used merged data files prepared at Harvard University for the analyses reported in this paper. This provided measurements averaged over the various time intervals and associated model-estimated NO_2, HONO, HNO_4, N_2O_5, and NO_3 for each period [*Jaegle et al.*, 1999]. After various time intervals were tested for the best measurement overlap of reactive nitrogen species, we selected the MC HNO_3 time base (1.5 - 5 minute resolution). This time base provided the maximum number of

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measurement time overlap intervals for both the MC and CIMS HNO_3 data. Particulate-NO_3^- was measured during SONEX with approximately 10 minute time resolution. Since this time resolution was much longer than that of the other reactive nitrogen species, we did not include it in the data analysis. Because the median value of particulate-NO_3^- was 15 pptv during SONEX [*Dibb et al.*, 1999], it represented <5% of the NO_y and its omission for our budget analysis does not significantly influence the conclusions presented here.

Using the MC time-based merged files, we further narrowed the selected data set based on two criteria: (1) a solar zenith angle < 83° and, (2) measurement intervals where NO, HNO_3, PAN, and NO_y were all reported with a time overlap of >50%. This reduced the data points for our analysis from several thousand to n = 700 (MC) and n = 355 for the CIMS measurements. We believe that this final breakdown provides a reasonably consistent set of measurement and model products to evaluate the NO_y budget over the North Atlantic during SONEX.

The NO_y Budget

Compared to most other field campaigns in remote areas, the NO_y budget (i.e., NO_y measured versus the sum of species (NO_y sum) during SONEX was in generally good agreement using either the MC or CIMS HNO_3 data [Figure 1(a) and (b)]. Here the NO_y sum represents the measured species NO, HNO_3, PAN, PPN, methyl nitrate, ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, 2-butyl nitrate, plus modeled NO_2, HONO, HNO_4, N_2O_5, and NO_3. The principal difference in (a) and (b) is the use of MC or CIMS HNO_3 measurements. Plotting the CIMS and MC HNO_3 mixing ratios against each other showed a linear correlation between the two of CIMS-HNO_3 = 0.74 × MC-HNO_3 + 64, with r^2 = 0.75 (not shown).

In both cases the slope of the NO_y budget comparison [Figure 1] was close to 1.0 with r^2 values > 0.90. In particular, it is noteworthy that the agreement extends from NO_y mixing ratios of several ppbv down to 100 pptv or less. The major difference between the two comparisons is in the intercept, 8.4 for the MC and 70 for the CIMS instrument. These values potentially reflect positive bias in the NO_y sum compared to NO_y measured. The majority of the 70 pptv offset in the CIMS data may be attributed to an instrumental background of ≈ 50 pptv which has not been accurately quantified or subtracted from the present CIMS data set [A. Viggiano, personal communication, 1998]. The ≈ 8 pptv offset in the MC HNO_3 is not significantly different than zero based on a 95% confidence limit estimate for these data (i.e., a value well within propagated uncertainties).

In Figure 2 we present the median values of the ratio (NO_y measured/NO_y sum) for each SONEX flight. The colored bars reflect the NO_y budget closure using the MC HNO_3 data merge while the open bars use the CIMS data. Out of a total of 15 flights, the NO_y comparison using the MC data showed 7 ratio values >1 and 8 <1, with the largest variation from 1 being 14%. Such a distribution would be expected from random statistical variation. The CIMS data showed 10 values <1 and 4>1. There appears to be a bias for NO_y sum to be larger on average than NO_y measured, which is probably related to the 50 pptv or so positive offset in the instrument which has yet to be accounted for accurately. On most flights the ratio values using the two data merges were comparable and of the same magnitude, and are within 15% of 1. If we (generously) assign an uncertainty of ±15% to each of the measured reactive nitrogen species, propagation of the combined errors [*Knoll*, 1979] leads to an overall uncertainty near 30%. This is greater than the median differences between NO_y measured and sum using either one of the HNO_3 data sets. Without additionally considering the uncertainties in the modeled reactive nitrogen species, we conclude that

the NO_y measured and sum values are not significantly different on a flight-by-flight basis. Our analysis here considers the SONEX data in a general sense, but there were specific time intervals during individual flights where NO_y measured and sum were different by as much as 50%. Detailed evaluation of these specific time intervals is, however, beyond the scope of this overview paper.

Plotting the median percent difference values (in NO_y measured and sum) versus the measured NO_y mixing ratio showed no correlation ($r^2 < 0.1$, not shown). This indicates that there was no systematic variation in our results as a function of NO_y mixing ratio. The median mixing ratio of NO_y measured during SONEX was 425 pptv, very comparable to that observed during many other airborne campaigns in remote tropospheric regions [Bradshaw et al., 1998]. In is important to note that closure of the NO_y budget during SONEX occurred at mixing ratios of NO_y as small as 70 pptv [Figure 1a]. Within the uncertainties represented in the model and measurements, the NO_y budget agreement suggests that we have a basic understanding of the tropospheric chemistry related to reactive odd-nitrogen compounds. However, the multitude of reactive nitrogen compounds and their potentially variable contribution to the NO_y budget is poorly characterized for any field campaign. In addition, positive interference in measured NO_y by non-reactive nitrogen compounds (e.g., NH_3 and HCN) [Kliner et al., 1997; Bradshaw et al., 1998] is a general concern, but seemingly a small one with regard to the SONEX data [Koike et al., 1999].

Median values of the ratios of NO_x, HNO_3, and PAN to NO_y measured and sum were calculated for each SONEX flight and showed that overall NO_x composed $\approx 25\%$ of NO_y, HNO_3 $\approx 35\%$, and PAN $\approx 17\%$. The alkyl nitrates collectively averaged about 10 pptv, and represented $<5\%$ of NO_y. Although NO_y measured and sum agreed reasonably well, 15-20% of the NO_y could of been present in unmeasured forms, such as HONO, HNO_4, N_2O_5, NO_3, and particulate nitrogen depending

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on solar zenith angle and other chemical parameters. Indeed, the Harvard model calculations predict from 0.1 - 100 pptv of the various unmeasured reactive nitrogen species, with HNO_4 accounting an average of $12 \pm 9\%$ (i.e., 55 ± 30 pptv) of NO_y measured.

In Figure 3(a) and (b) the median value and its ratio to NO_y sum of the various reactive nitrogen species are shown as a function of binned O_3 mixing ratios. These data clearly show that below 80 ppbv O_3 the NO_y budget was dominated by NO_x, with less but still significant contributions of HNO_3 and PAN. At O_3 mixing ratios greater than 80 ppbv stratospheric influence was evident based on concomitant ^7Be concentrations >1000 fCi m^{-3} and CO mixing ratios <50 ppbv [*Dibb et al.*, 1999]. In these air parcels HNO_3 comprised as much as 80% of NO_y sum.

With current measurement and modeling uncertainties (i.e., for many of the parameters an uncertainty can not even be assigned to them) it is not possible to assess the remote tropospheric NO_y budget in a truly rigorous manner. We generally observed good agreement in NO_y measured and sum values over the North Atlantic, but at this time it is not possible to extend this analysis in a more detailed manner.

Acknowledgments:

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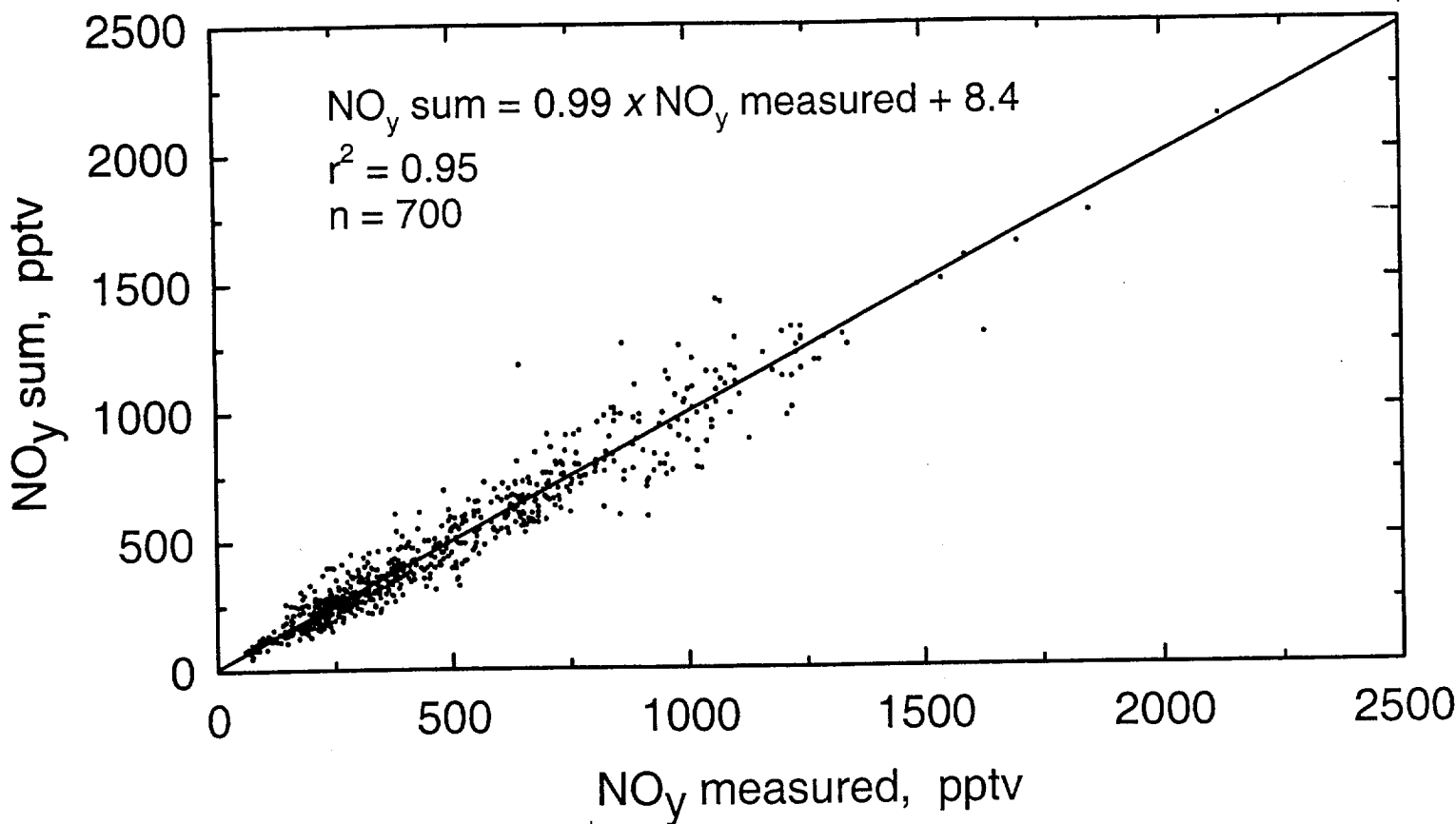
Figure Captions

1.   Linear least squares relationship between measured total reactive nitrogen (NO_y measured) and the sum of measured and modeled reactive nitrogen species (NO_y sum) in the upper troposphere (8 - 12.5 km altitude) over the North Atlantic: (a.) represents the relationship

using the HNO_3 mixing ratio determined with the mist chamber technique, while (b.) utilizes the CIMS values for HNO_3.

2. Comparison of the median values of NO_y measured and sum determined with the MC and CIMS HNO_3 measurements during SONEX science flights 3 - 17. The numbers in a vertical column on the right side of the graph are the median values (pptv) of NO_y measured for each flight. There was no CIMS data for flight 3.

3. (a) Median value of various reactive nitrogen species as a function of binned O_3 mixing ratios. (b) Fractional ratio of reactive nitrogen species shown in (a) to NO_y sum as a function of binned O_3 mixing ratios.

(a.) NO_y budget using mist chamber HNO_3

NO_y sum = 0.99 x NO_y measured + 8.4
r^2 = 0.95
n = 700

NO_y sum, pptv

NO_y measured, pptv

(b.) NO_y budget using CIMS HNO_3

NO_y sum = 0.91 x NO_y measured + 70
r^2 = 0.90
n = 355

NO_y sum, pptv

NO_y measured, pptv

Fig. 1

Fig. 2

(a)

(b)
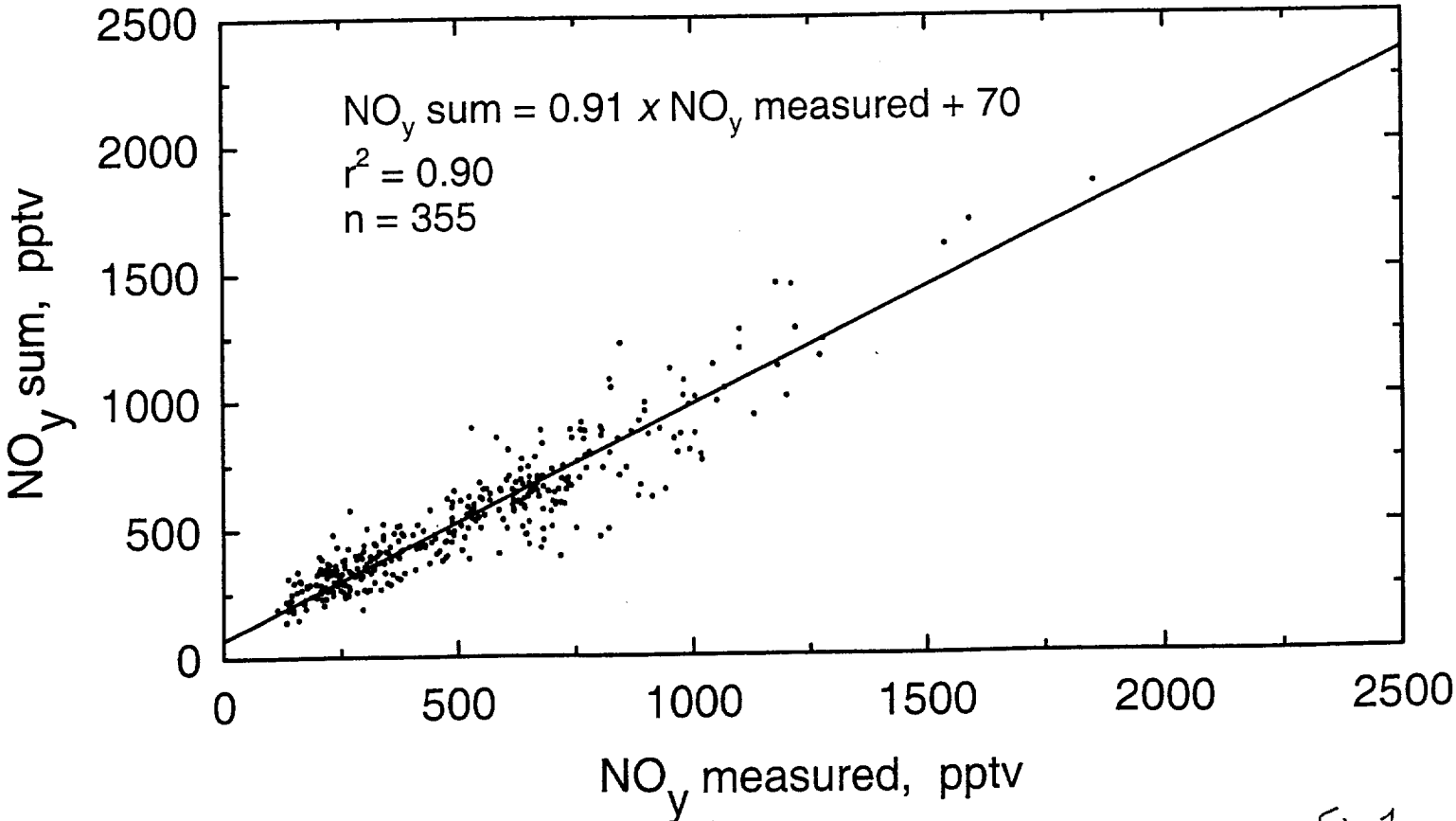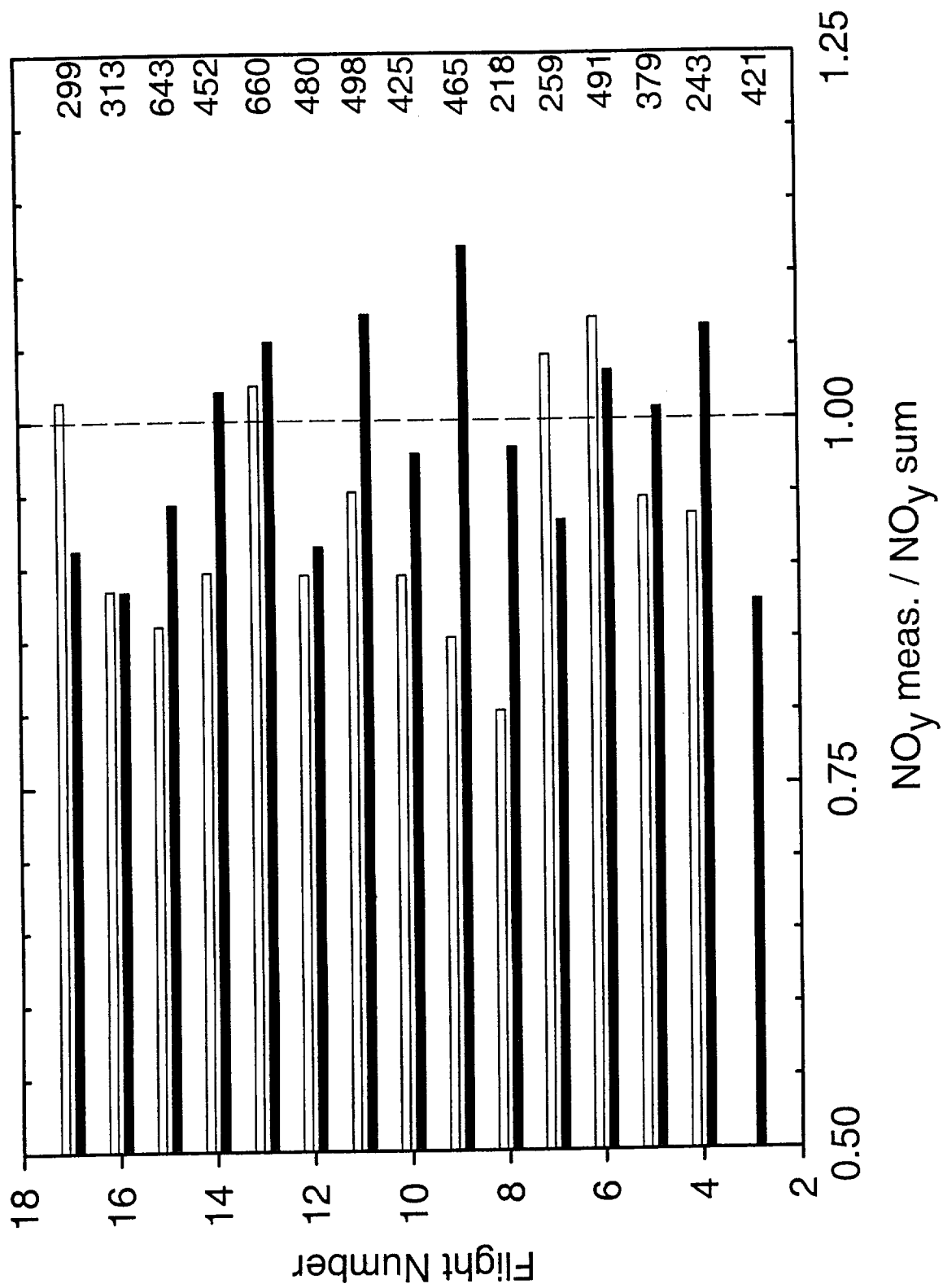
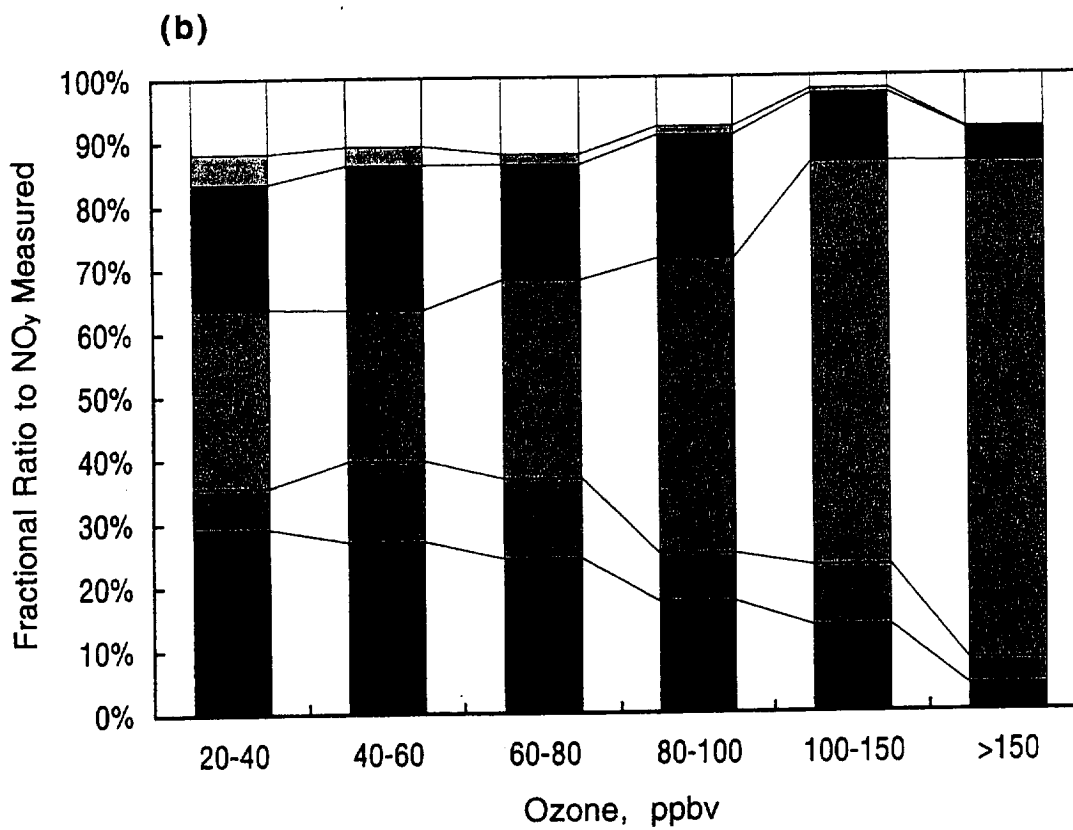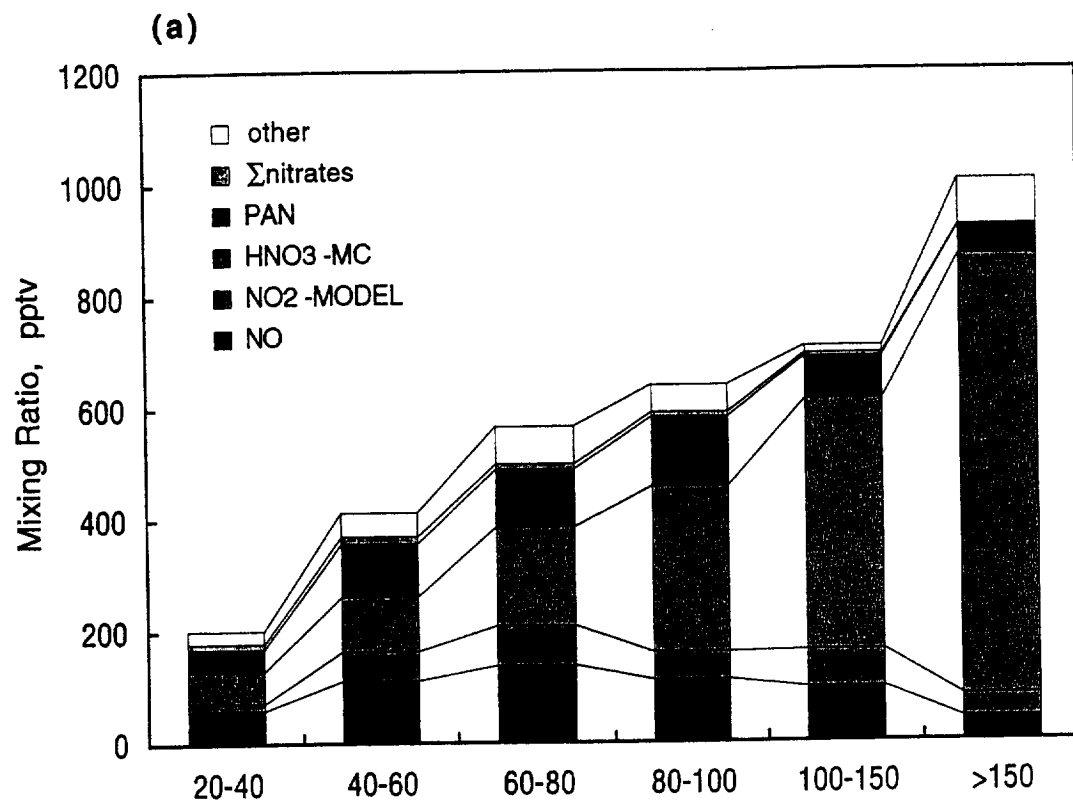

Fig. 3

Composition and Distribution of Aerosols over the North Atlantic during SONEX

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ABSTRACT

We report the mixing ratios of aerosol-associated soluble ions (focusing on $SO_4^=$ 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 $SO_4^=$ and NO_3^- above 8 km during SONEX were lower than recent measurements over the central US during SUCCESS and the same as those over the remote south Pacific during PEM Tropics, suggesting that aircraft emissions can not yet be a major source of these ions. Furthermore, mean $SO_4^=$ 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 [7]Be indicate that a large fraction of HNO_3 and aerosol-associated $SO_4^=$ measured at high altitudes during SONEX were derived from a stratospheric source.

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; *Flatoy 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.*, 1998].

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 $SO_4^=$ burden in the upper troposphere and lower stratosphere. We were unable to detect any enhancement of aerosol-associated $SO_4^=$ in young plumes via bulk aerosol sampling during the 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, 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.

METHODS

Sampling

Aerosol samples were collected on 12 flights over the north Atlantic ocean and on 2 transit flights between NASA Ames and Bangor, Maine, as part of the AEAP 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 GTE PEM West and PEM Tropics missions [*Dibb et al.*, 1996, 1997, 1999]. One of the inlets was used to expose 2 μm pore size teflon (Gelman Zefluor) 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 minute 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 5 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 1000s 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.

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^-, $SO_4^=$, 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 2 flight[-1] by loading a filter into the sampling system, opening all valves to allow air flow for 15 seconds, 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 $SO_4^=$, NO_3^- and NH_4^+ 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 [7]Be 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 ^{210}Pb technique (determination of the activity of the [210]Po 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 ^{210}Pb distribution will be presented in a subsequent paper.

RESULTS

Aerosol $SO_4^=$ (p-$SO_4^=$) 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-NO_3^- and p-NH_4^+ in about half of all samples, with a higher fraction above detection limits for p-NO_3^- In Tracks (57%) than Out of Tracks (47%), while the reverse was true for p-NH_4^+ (50% In Tracks versus 61% Out of Tracks). Mixing ratios of p-Mg^{2+} and p-Ca^{2+} 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 ^{7}Be 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-$SO_4^=$ mixing ratios above 10 km Out of Tracks exeeding 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-$SO_4^=$ from H_2SO_4 produced in jet exhaust plumes must still be small compared to other sources of p-$SO_4^=$ 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-$SO_4^=$ mixing ratios above 8 km were identical (27 pptv) during SONEX and PEM Tropics;

a surprising result considering that PEM Tropics characterized the remote south Pacific troposphere. During SUCCESS the mean p-$SO_4^=$ 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-$SO_4^=$ over the central US 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].

DISCUSSION

Sulfate Aerosol

Given the evidence that jet exhaust was at best a minor source of p-$SO_4^=$ even within the flight corridor, we attempt to determine whether the SONEX data provide insight into the dominant sources of p-$SO_4^=$ over the north Atlantic during the campaign. Comparison of "quick look" data products produced during the field mission suggested that variations in p-$SO_4^=$ were often correlated with variations of HNO_3 and O_3, 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 HNO_3 as well as perturbations to the balance between O_3 production and loss [*Kasibhatla*, 1993; *Anderson et al.*, 1996; *Karcher et al.*, 1996; *Flatoy and Hov*, 1996; *Jaegle et al.*, 1999] demanded caution before assuming that HNO_3 and O_3 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 [7]Be 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 [7]Be activities in the lower-most stratosphere roughly an order of magnitude higher than those in the upper troposphere [*Rama*, 1963; *Bhandari et al.*, 1966; *Dutkiewicz and Husain*, 1979,

stratospheric source appears dominant for SONEX samples with elevated HNO_3, with no evidence for significant enhancements in the NAFC. It is likely that additional non-negligible sources of HNO_3 create the scatter in the HNO_3-^7Be correlation. We suspect that HNO_3 formed from NO_x produced by lightning in convective systems [e.g., *Pickering et al.*, this issue] was more important than convective pumping of polluted boundary layer air into the free troposphere, since the latter process should have enhanced p-$SO_4^=$ as well, similar to our findings during SUCCESS [*Dibb et al.*, 1998].

Mixing ratios of p-NO_3^- 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-NO_3^- throughout the mid- and upper-troposphere over the central US during SUCCESS presumably reflects mixing of polluted boundary layer air upward, as discussed above in relation to p-$SO_4^=$ [*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-NO_3^- 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-NO_3^- and ^7Be in either subset of data, in fact the highest p-NO_3^- mixing ratios were associated with ^7Be activities $<<$ 1000 fCi m-3 (Figure 7). These observations suggest minimal stratospheric influence on p-NO_3^-, with occasional, small (several 10s 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_y) were also strongly correlated with ^7Be above 9 km Out of Tracks. The slope of 0.08 pptv NO_y/fCi m-3 ^7Be (not shown) was quite similar to those found for HNO_3 vs. ^7Be (Figure 5). This is consistent with stratospheric HNO_3

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-$SO_4^=$ 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-$SO_4^=$ must be minimal. We use measured ^7Be activities and the relationship between p-$SO_4^=$ and ^7Be above 9 km Out of Tracks to estimate the "stratospheric" component of p-$SO_4^=$ in all SONEX samples and subtract this from observed p-$SO_4^=$. Above 8 km it would appear that essentially all p-$SO_4^=$ can be attributed to a stratospheric source (Figure 3b).

Nitrogen Oxides

We used the same approach to assess the importance of the stratosphere as a source of upper tropospheric nitrogen oxide 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) (HNO_3 was not measured during SUCCESS). The enhancements of HNO_3 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 km 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 HNO_3 mixing ratios observed at high altitudes during SONEX.

A significant contribution of stratospheric HNO_3 is supported by the HNO_3-^7Be relationships above 9 km (Figure 5). The range (+/- 200 pptv) of "non-stratospheric" HNO_3 in the upper troposphere estimated from the linear fit to the Out of Tracks data indicates that ^7Be is not a perfect predictor of HNO_3, but the distributions are centered around zero for both the In Track and Out of Track subsets of data (Figure 5b). A

representing the dominant fraction of NO_y in air masses with elevated NO_y Out of Tracks [*Talbot et al.*, 1999b]. In Tracks all samples with high (> 1000 ppt) NO_y mixing ratios were associated with relatively low ^7Be activity (200-2700 fCi m^{-3}). These samples were also characterized by NO/NO_y ratios > 0.5. Strong enhancements 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 minute 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 [*Kita et al.*, this issue; *Koike et al.*, this issue]. 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.

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 Mg^{2+} and Ca^{2+} 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-$SO_4^=$ is reflected by parallel enhancements of p-$SO_4^=$ 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-NH_4^+ (considering only those samples where NH_4^+ was above detection limit)

are also elevated in these same bins. Stratospheric p-$SO_4^=$ has been shown to be largely H_2SO_4 [*Hayes et al.*, 1980] and the same composition is often assumed for p-$SO_4^=$ 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 NH_4HSO_4 (Figure 8). If we assume that samples with NH_4^+ below detection were H_2SO_4, statistical summaries for the 4 bins suggest that the aerosol is strongly acidic in all regions except the north east bin (mean (median) values of the $NH_4^+/SO_4^=$ 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 NH_4^+ than would be required to completely neutralize $SO_4^=$ (Figure 8), a feature causing the regional means to be so much higher than the medians.

The concentrations of $SO_4^=$ and NH_4^+ in the aqueous extracts of filters with "problematic" $NH_4^+/SO_4^=$ ratios are generally well above detection limits, thus we feel that analytical uncertainties can not explain the high ratios. Artifact absorption of NH_3 by filters loaded with strongly acidic aerosol [e.g., *Hayes et al.*, 1980] can not 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 $NH_4^+/SO_4^=$ ratios suggest that our techniques must generally be effective. Secondly, post-collection neutralization of H_2SO_4 by NH_3 should not drive the equivalence ratio above 1, yet values between 1 and 4 are common in the SONEX data set.

Abundant HNO_3 could react with NH_3 present in excess of H_2SO_4, but this should appear as p-NO_3^-. Mixing ratios of p-NO_3^- in SONEX samples generally account for only a few percent of excess p-NH_4^+. This hypothesis also fails to address the fundamental issue of how so much NH_3 or p-NH_4^+ came to be in the upper troposphere or lower stratosphere. Scatter plots of the $NH_4^+/(NO_3^- + SO_4^=)$ equivalence ratio against [7]Be show

that samples collected above 8 km with large excess NH_4^+ 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 NH_4^+ to neutralize 50-100% of the strong acids. We can not 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-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.

CONCLUSIONS

Sampling from the DC-8 during the SONEX campaign found no evidence of significant enhancements of p-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-NO$_3^-$ were observed in a few samples within the corridor, but overall there was not a consistent pattern of elevated p-NO$_3^-$ relative to regions far removed from the corridor.

Correlations with ^7Be indicate that essentially all of the p-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-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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Table 1. Variability in composition of aqueous extract of blank filters. At least two blanks were generated each flight.

	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
Std. Dev.	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

a This row reflects the uncertainty in mixing ratio (in parts per trillion by volume (ppt)) for a sample of average air volume (3.1 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 m^{-3}.

Table 2. Comparison of mixing ratios of aerosol associated species in samples collected within, and away from, the North Atlantic Flight Corridor. Soluble ionic species reported in parts per trillion by volume (pptv), ^7Be in fCi SCM^{-1}.

	NO_3^-	$SO_4^=$	NH_4^+	Mg^{2+}	Ca^{2+}	^7Be
In Flight Corridor						
< 8 km (12 samples)						
mean	16.5	40.9	67.1	5.7	11.2	956
std. err.	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
std. err.	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	22.6	71.8	1.2	8.5	1387
std. err.	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
Outside Flight Corridor						
<8km (37 samples)						
mean	10.5	63.1	89.3	1.8	9.4	909
std. err.	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
std. err.	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
std. err.	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

a number of samples where given analyte was above detection limit

Table 3. Statistical summary of mixing ratios of aerosol associated species in four geographic bins sampled during SONEX. Soluble ionic species reported in pptv, ^7Be in fCi SCM^{-1}.

	NO_3^-	$SO_4^=$	NH_4^+	Mg^{2+}	Ca^{2+}	^7Be
South of 50 N, West of 50 W						
< 8 km (17 samples)						
mean	20.5	75.8	99.3	4.3	13.4	916
std. err.	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
std. err.	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
std. err.	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
South of 50 N, East of 50 W						
< 8 km (11 samples)						
mean	8.0	31.3	42.5	--	10.2	363
std. err.	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
std. err.	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
std. err.	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

Table 3. (continued)

	NO_3^-	$SO_4^=$	NH_4^+	Mg^{2+}	Ca^{2+}	^7Be
North of 50 N, West of 50 W						
< 8 km (6 samples)						
mean	11.4	92.5	95.4	1.2	9.7	924
std. err.	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
std. err.	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
std. err.	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
North of 50 N, East of 50 W						
< 8 km (15 samples)						
mean	6.0	42.6	80.6	2.3	4.4	1258
std. err.	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
std. err.	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
std. err.	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

[a] number of samples where given analyte was above detection limit

FIGURE CAPTIONS

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

Figure 2. Comparison of p-$SO_4^=$ mixing ratios versus altitude during the SONEX, PEM Tropics and SUCCESS sampling campaigns.

Figure 3. A) Scatter plot of p-$SO_4^=$ 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) "Non-stratospheric" $SO_4^=$ as a function of altitude. Stratospheric $SO_4^=$ was estimated from measured ^7Be and the least squares fit Out of Tracks shown in A.

Figure 4. Comparison of HNO_3 mixing ratios versus altitude during the SONEX and PEM Tropics sampling campaigns.

Figure 5. As in Figure 3 but for HNO_3 versus ^7Be.

Figure 6. Comparison of p-NO_3^- mixing ratios versus altitude during the SONEX, PEM Tropics and SUCCESS sampling campaigns.

Figure 7. Scatter plot of p-NO_3^- against ^7Be for samples collected above 9 km during SONEX.

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 $(NH_4)_2SO_4$. 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 D0 south of 50 N, east of 50 W.

Figure 9. Scatterplots of the $NH_4^+/(NO_3^- + SO_4^=)$ equivalence ratio against ^7Be activity above 8 km in the same regions described in Figure 8.

(A)

$y = 16.6 + 0.0059x$ R= 0.90 Out
$y = 15.0 + 0.0059x$ R= 0.76 In

Aerosol $SO_4^=$ (pptv)

^7Be (fCi m^{-3})

(B)

◇ Out of Tracks
+ In Tracks

Pressure Altitude (km)

"Non-stratospheric" $SO_4^=$ (pptv)

SONEX

PEM Tropics

Out of Tracks
In Tracks

Pressure Altitude (km)

HNO$_3$ (pptv)

L_i

(A)

$y = 59.7 + 0.071x$ R= 0.91 Out
$y = 78.8 + 0.080x$ R= 0.82 In

HNO$_3$ (pptv)

^{7}Be (fCi m^{-3})

(B)

Pressure Altitude (km)

◇ Out of Tracks
+ In Tracks

"Non-stratospheric" HNO$_3$ (pptv)

SONEX

Out of Tracks ◇
In Tracks +

PEM Tropics

SUCCESS

Aerosol NO_3^- (pptv)