



## Reactive nitrogen transport and photochemistry in urban plumes over the North Atlantic Ocean

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[1] Photochemical and transport processes involving reactive nitrogen compounds were studied in plumes of urban pollutants using measurements obtained from the NOAA WP-3 aircraft during the ICARTT study in July and August 2004. Observations close to Boston and New York City were used to characterize urban emissions, and plume transport and transformation processes were studied in aged plumes located up to 1000 km downwind from the east coast of North America. Pollution was observed primarily below 1.5 km altitude in well-defined layers that were decoupled from the marine boundary layer. In aged plumes located over the North Atlantic Ocean, the nitric acid (HNO<sub>3</sub>) mixing ratios were large (up to 50 ppbv), and HNO<sub>3</sub> accounted for the majority of reactive nitrogen. Plume CO and reactive nitrogen enhancement ratios were nearly equivalent in fresh and aged plumes. Efficient transport of HNO<sub>3</sub> explained the observed trace gas ratios and abundances. Without substantial HNO<sub>3</sub> loss, the ratio of HNO<sub>3</sub> to NO<sub>x</sub> was between 13 and 42 in most highly aged plumes and sometimes exceeded calculated photochemical steady state values. Box model calculations that include nighttime reactions that convert NO<sub>x</sub> to HNO<sub>3</sub> reproduce the observations. Photolysis and OH oxidation of over 10 ppbv of HNO<sub>3</sub> that was in the troposphere for days resulted in reformation of hundreds of pptv of NO<sub>x</sub>, which is sufficient to maintain photochemical ozone production. Efficient transport of HNO<sub>3</sub> over the North Atlantic Ocean for days carried both HNO<sub>3</sub> and NO<sub>x</sub> far from their continental sources and increased their photochemical influence.

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### 1. Introduction

[2] Pollutants transported for many hundreds of kilometers can influence the atmosphere and biosphere far beyond the region of emission. When pollutants are transported long distances, photochemical reactions that form secondary products often determine the effects of the anthropogenic emissions upon human health, visibility, climate, and ecosystems. Regional effects include photo-

chemical ozone (O<sub>3</sub>) production in rural areas that is often controlled by the transport of nitrogen oxides from urban areas [Crutzen, 1979; Chameides et al., 1992]. In remote marine environments, nitrogen oxides from continental sources can contribute to photochemical O<sub>3</sub> production that is important to the global atmosphere [e.g., Jacob et al., 1996; Li et al., 2004].

[3] The geographical extent and magnitude of the effects of NO<sub>x</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>) and its oxidation products depend on its lifetime in the atmosphere. NO<sub>x</sub> emitted from vehicle tailpipes, power generation, and other combustion sources contributes to O<sub>3</sub> formation, particle formation, and nitrogen deposition. Over North America, anthropogenic NO<sub>x</sub> is oxidized to nitric acid (HNO<sub>3</sub>), which is subsequently removed from the atmosphere by dry or wet deposition, such that only a small fraction of originally emitted NO<sub>x</sub> reaches the free troposphere [Stohl et al., 2002; Parrish et al., 2004; Li et al., 2004]. Loss of HNO<sub>3</sub> that occurs when pollutants are transported in the shallow marine boundary layer (MBL) [Roberts et al., 1996; Brown et al., 2004; Dibb et al., 2004] or in a well-mixed continental boundary layer [Neuman et al., 2004] results in HNO<sub>3</sub> lifetimes of hours and rapid removal of reactive

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nitrogen from the atmosphere. This efficient removal of reactive nitrogen limits the long-range transport of reactive nitrogen species and their contribution to photochemical  $O_3$  production in the free troposphere.

[4] Studies of anthropogenic  $NO_x$  emitted from coastal areas and transported over oceans have determined e-folding lifetimes for reactive nitrogen to be typically less than 2 days [Stohl *et al.*, 2002; Takegawa *et al.*, 2004]. However, uncertainty remains regarding the fate of  $NO_x$  emissions and their oxidation products on timescales less than 2 days. Stohl *et al.* [2002] noted little loss of reactive nitrogen in the first 2 days of transport, and postulated that the time required for  $NO_x$  to be oxidized could partly explain the apparent conservation of reactive nitrogen in the initial stages of transport. Although Takegawa *et al.* [2004] found similar reactive nitrogen lifetimes for measurements obtained over the Western Pacific Ocean in the winter, they postulated that most reactive nitrogen was removed during the initial stages of transport.

[5] The inefficient transport of  $HNO_3$  to higher altitudes in the free troposphere is markedly different from low-level outflow over water. Strong lifting of air masses normally produces precipitation that removes  $HNO_3$ , whereas  $HNO_3$  can be preserved over long distances in low-level outflow that does not encounter precipitation. For example, high levels of  $NO_x$  oxidation products were observed in thin vertical layers that were usually lower than 1.5 km altitude over the North Atlantic Ocean in August 1993 [Daum *et al.*, 1996]. Over the Gulf of Maine, a strong temperature inversion isolated the air in the MBL from that above [Angevine *et al.*, 1996], such that  $HNO_3$  above the MBL was not in contact with the surface. Transport in cloud-free regions in the lower troposphere over the ocean presents a unique environment for studying chemical transformation processes. Vertical mixing is suppressed by the highly stable stratification, and high concentrations of pollutants can be transported long distances [Spicer *et al.*, 1979; Sillman *et al.*, 1993]. Since the air masses are largely free from additional surface sources of pollutants and are decoupled from surface removal, the interactions between the pollutants can be examined without external influences that often accompany plume transport.

[6]  $HNO_3$  transport pathways are important to ocean plant life, which can be sensitive to the location and magnitude of nitrate deposition to the ocean surface. The additional input of nitrogen from the atmosphere to the ocean provides nutrients that can enhance phytoplankton productivity [Paerl, 1985]. Transported plumes with high concentrations of either gas phase or particulate nitrate that encounter precipitation, which readily removes  $HNO_3$  from the atmosphere and deposits it to the surface, can episodically provide nitrogen to the ocean. This episodic deposition of nitrogen has been shown to enhance marine primary productivity [Owens *et al.*, 1992]. The western Gulf of Maine, where the waters are stratified, is particularly susceptible to nutrient deficiencies [Jordan and Talbot, 2000], whereas coastal regions with enhanced upwelling are often nutrient rich. Hence episodic atmospheric inputs of nitrogen are expected to be important to noncoastal regions of the North Atlantic Ocean.

[7] Transported plumes of urban pollutants were studied here using measurements obtained from the National Oce-

anic and Atmospheric Administration (NOAA) WP-3 aircraft during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) study in July and August 2004. Many of the flights were designed to intercept urban plumes either near the source regions located on the east coast of North America or during transport over the North Atlantic Ocean. The extensive set of fast-response measurements of reactive nitrogen species facilitated a study of the interaction between  $NO_x$  and its oxidation products during plume transport in the lower troposphere.

## 2. Experiment

[8] Trace gases and particles were measured on 16 research flights that were conducted between 9 July and 14 August 2004 when the NOAA WP-3 aircraft was stationed in Portsmouth, NH (43.1°N, 70.8°W), and on 2 transit flights between Florida and Portsmouth. Flights were conducted during both day and night and were up to 8.5 hours in duration. Over the ocean, the aircraft flew between 160 m and 5.2 km altitude, and each flight included altitude profiles to at least 2.7 km altitude. Most level flight legs through urban plumes were conducted at 300–1000 m altitude. Emissions were studied using crosswind transects of plumes close (less than 50 km) to their urban sources, and subsequent transport and transformation processes were studied in plume transects performed up to 1000 km downwind.

[9] Fast-response measurements of trace gases characterized plumes at high spatial resolution. Most measurements were obtained or averaged to once per second, which gives a 100 m horizontal resolution (for the nominal aircraft speed of 100 m s<sup>-1</sup>) and 5 m vertical resolution during altitude profiles (for the typical aircraft ascent and descent rates of 5–6 m s<sup>-1</sup>). Flights were conducted on both clear and cloudy days, but measurements obtained inside clouds are disregarded for this analysis, because the  $HNO_3$  inlet occasionally ingested water droplets that caused brief measurement artifacts. Cloud sampling accounted for less than 2% of the flights examined here.

[10] Gas phase  $HNO_3$  was measured once per second using a chemical ionization mass spectrometer (CIMS) [Neuman *et al.*, 2002] that detected  $HNO_3$  containing cluster ions formed in the selective reaction of  $SiF_5^-$  reagent ions with ambient air. Air was drawn into the instrument at a flow rate of approximately 7.7 slpm through a sideways facing heated Teflon inlet. The residence time in the 50 cm long inlet was less than 120 ms, and the time response of the instrument was 1 s [Neuman *et al.*, 2002]. Particulate nitrate was not detected [Neuman *et al.*, 2003a], but occasionally water droplets were ingested when the aircraft flew through clouds. Standard addition calibrations were performed approximately once per hour by admitting 1.4 ppbv of  $HNO_3$  into the inlet from a permeation source that was pressurized and temperature and flow-controlled. In between flights, the permeation source was removed from the aircraft and was continuously calibrated by UV optical absorption [Neuman *et al.*, 2003b]. The  $HNO_3$  permeation rate from the calibration source averaged 30 ng/min and decreased 2% per week during the 6-week study. The response to the in-flight calibrations varied approximately  $\pm 10\%$  each flight, and

the sensitivity to  $\text{HNO}_3$  detection averaged approximately 1 ion count per second per pptv. The contribution from the instrument background to the signal was measured for 2 min once every 20–40 min, and the background level varied between 100 pptv and 2 ppbv. The highest background levels were caused by the small fraction of  $\text{HNO}_3$  that was slowly released from the instrument's surfaces after large abundances of  $\text{HNO}_3$  had been sampled for extended periods. The measured background levels were subtracted from the total signal. Accuracy was determined from the uncertainties in determining the background levels and instrument sensitivity to be  $\pm(15\% + 50 \text{ pptv})$ . The measurement precision was determined from the  $1 \sigma$  standard deviation on the instrument background to be  $\pm 20 \text{ pptv}$  for 1 s measurements.

[11]  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{NO}$ , and  $\text{NO}_y$  were measured in 4 separate channels of a chemiluminescence detector and were averaged to 1 s.  $\text{NO}_2$  was measured on all but the first two flights of the study, with an uncertainty of  $\pm(8\% + 25 \text{ pptv})$ .  $\text{NO}$  was measured with an uncertainty of  $\pm(5\% + 10 \text{ pptv})$  [Ryerson *et al.*, 2000], and  $\text{O}_3$  was measured with an uncertainty of  $\pm(3\% + 0.1 \text{ ppbv})$ .  $\text{NO}_y$  was measured directly with an uncertainty of  $\pm(10\% + 20 \text{ pptv})$  by catalytic conversion of reactive nitrogen compounds followed by chemiluminescence detection of  $\text{NO}$ .  $\text{NO}_y$  was measured only on the first four flights of the study, whereupon an instrument failure prevented accurate  $\text{NO}_y$  measurement.  $\text{CO}$  was measured once per second using a vacuum UV fluorescence instrument with an uncertainty of 5% and a  $3 \sigma$  detection limit of 1.7 ppbv [Holloway *et al.*, 2000]. Several PAN compounds (PAN, PPN, PiBN, MPAN, APAN, PBzN, PPeN, MoPAN, PnBn) were measured over 100–250 ms intervals once every 2 s using a thermal decomposition chemical ionization mass spectrometer, with an uncertainty of  $\pm 10\%$  and a lower limit of detection of 1 pptv for most compounds [Slusher *et al.*, 2004]. PAN, PPN, and MPAN accounted for the majority (typically 95%) of the PAN-type compounds.  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  were measured by cavity ringdown spectroscopy with an accuracy of  $\pm 25\%$  [Dubé *et al.*, 2006]. The sum of the reactive nitrogen species ( $\Sigma\text{NO}_{yi} = \text{NO} + \text{NO}_2 + \text{HNO}_3 + \text{PANS} + \text{NO}_3 + 2 \times \text{N}_2\text{O}_5$ ) was determined from the individually measured compounds. In the east coast urban plumes sampled during daytime,  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  were usually less than 5 pptv and 1% of  $\Sigma\text{NO}_{yi}$ , and they never exceeded 14 pptv or 2% of  $\Sigma\text{NO}_{yi}$ . In order to achieve the most data coverage,  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  are included in  $\Sigma\text{NO}_{yi}$  only for the 6 flights that occurred at night, when  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  accounted for a nonnegligible fraction of  $\Sigma\text{NO}_{yi}$ . Measurements of actinic flux between 280 and 490 nm were performed both in the upward and downward looking directions at 1 nm resolution using a dual-grating spectrometer/CCD system. Photolysis rates were calculated from the actinic flux measurements using literature values for the absorption cross sections and quantum yields [DeMore *et al.*, 1997].

[12] Uncertainties in the data were assessed by comparing results obtained from different measurement platforms. Several species investigated extensively in this work were also measured on the NASA DC-8 aircraft, which flew alongside the NOAA WP-3 on 3 flights for periods of 46, 39, and 44 min. The  $\text{CO}$  and  $\text{NO}_2$  measurements on the two aircraft agreed within the stated uncertainties, and  $\text{NO}$  levels

were too low to compare quantitatively. Slopes of linear least squares fits between the measurements of PAN on each aircraft agreed within the stated uncertainties, although the intercepts for the fits were outside the stated uncertainties. The  $\text{HNO}_3$  measurements obtained on the two platforms were well correlated and had offsets between 20 and 200 pptv.  $\text{HNO}_3$  levels ranged from 400 to 6000 pptv for over 80% of the comparison periods, during which the combined uncertainties of the NOAA WP-3 and University of New Hampshire Mist Chamber  $\text{HNO}_3$  measurements were between 21 and 25%. The DC-8  $\text{HNO}_3$  measurements were  $\sim 30\%$  lower than those from the WP-3, and this difference was larger than the combined uncertainties of the measurements. The accuracy of the WP-3  $\text{HNO}_3$  data was also examined by comparing  $\text{NO}_y$  and  $\Sigma\text{NO}_{yi}$  measurements aboard the WP-3 on the 2 flights when both  $\text{NO}_2$  and  $\text{NO}_y$  were measured. On these 2 flights, the absolute ratio of  $\text{HNO}_3$  to  $\text{NO}_y$  averaged 0.53. Since  $\text{HNO}_3$  was a majority of  $\text{NO}_y$ , this comparison provided an additional test of  $\text{HNO}_3$  measurement accuracy. A linear least squares fit of  $\Sigma\text{NO}_{yi}$  to  $\text{NO}_y$  had a slope of 1.07 and  $r^2 = 0.99$ , and  $\text{NO}_y$  and  $\Sigma\text{NO}_{yi}$  agreed within their stated uncertainties. The data comparisons indicated that the measurements reported here agreed with those from other platforms to within at least 50%, and often much better.

### 3. Results

#### 3.1. Data Selection and Plume Identification

[13] Concentrated pollution plumes originating from urban areas on the northeastern coast of the United States that were sampled on 13 flights (7 during the day and 6 at night) are used in this analysis. Measurements of pollutants originating from other regions or sources are not analyzed here to guarantee that all the plumes had similar emission characteristics. Two transit flights between New Hampshire and Florida, two flights that targeted clouds, and one flight that focused on intercepting forest fire plumes are not considered. Data obtained during portions of flights inland from the eastern seaboard are also excluded from this study. Urban plumes were identified on level ( $\pm 50 \text{ m}$ ) crosswind transects greater than 5 min ( $\sim 30 \text{ km}$ ) in duration when  $\text{CO}$  was enhanced more than 30 ppbv above the minimum  $\text{CO}$  value measured on each flight leg. Concentrated forest fire plumes, which also had elevated  $\text{CO}$ , were excluded from consideration using the plumes identified by acetonitrile measurements in the work of *de Gouw et al.* [2006]. Power plant plumes, which were strongly enhanced in  $\text{NO}_x$  or  $\text{HNO}_3$ , but had little or no  $\text{CO}$  enhancement, were also excluded by the requirement that  $\text{CO}$  was enhanced. Of the 93 plumes that were identified by the 30 ppbv enhancement in  $\text{CO}$ , 8 forest fire plumes and 1 plume in a cloud were disregarded for further analysis. An additional 8 plumes could not be fully analyzed because of data gaps during a plume transect caused by instrument diagnostics or failures. One additional plume is disregarded because  $\text{HNO}_3$  and  $\text{NO}_x$  were anticorrelated, because the plume was measured over land and consisted of a mixture of fresh and aged pollutants. The remaining 75 plumes are used for the analysis that follows.

[14] Close to emission sources, plumes were spatially compact and clearly identified by large enhancements in

**Table 1.** Number of Fresh and Aged Urban Plumes Used in This Analysis Shown With the Maximum Reactive Nitrogen Concentration for Each Flight Date<sup>a</sup>

Date (2004)	Plumes	Fresh Plumes	Max. $\Sigma\text{NO}_{y_i}$ , ppbv	Aged Plumes	Max. $\Sigma\text{NO}_{y_i}$ , ppbv
11 Jul	5	2	12	0	—
15 Jul	5	0	—	2	23
20 Jul	9	1	56	7	46
21 Jul	10	0	—	10	55
22 Jul	7	0	—	7	22
25 Jul	2	2	35	0	—
31 Jul	4	2	8	0	—
3 Aug	5	0	—	4	55
6 Aug	2	2	16	0	—
7 Aug	5	4	13	0	—
9 Aug	4	1	14	0	—
11 Aug	11	0	—	10	17
14 Aug	6	0	—	5	29
Total	75	14	—	45	—

<sup>a</sup>Fresh plumes are identified by  $\text{NO}_x/\Sigma\text{NO}_{y_i} > 0.8$ , and aged plumes are identified by  $\text{NO}_x/\Sigma\text{NO}_{y_i} < 0.2$ .

CO and NO<sub>x</sub>. Most of the fresh plumes originated from Boston or New York City, but plumes that were hundreds of kilometers from the coast could not always be connected with a single source and sometimes included contributions from a large area encompassing Philadelphia, Baltimore, and other cities in the eastern United States. Nonetheless, these aged plumes clearly originated from the continental United States, as determined from wind direction measurements and simulations of air mass histories using a Lagrangian particle dispersion model [Stohl *et al.*, 1998]. Occasionally, widespread enhancements in CO and HNO<sub>3</sub> that were not likely from a single urban source were observed over the ocean. In these cases, the entire level flight leg with elevated CO and HNO<sub>3</sub> was identified as a single urban plume, although it may have been formed from coalesced plumes from several urban source regions with different emission times. The longest level flight leg across an urban plume was approximately 250 km, whereupon the aircraft performed altitude profiles that usually sampled cleaner air at higher altitudes.

[15] Using these criteria, between 2 and 10 urban plumes located above the northeastern United States or over the North Atlantic Ocean were identified on each of 13 flights (Table 1). Plumes were observed between 130 and 3000 m altitude and had a horizontal extent that ranged from 20 km to 250 km. The 75 urban plumes sampled during the ICARTT period that are studied here are plotted in Figure 1. Plume chemistry is investigated using ordinary one-sided linear least squares regression analysis to determine correlation slopes for pairs of pollutants in each plume. In most cases the correlation coefficients for the fits were high. Urban emissions are studied using concentration ratios determined from linear correlation slopes, rather than absolute ratios of tracers, in order to avoid the influence of the background trace gas mixing ratios.

### 3.2. Plume Location and Ambient Environment

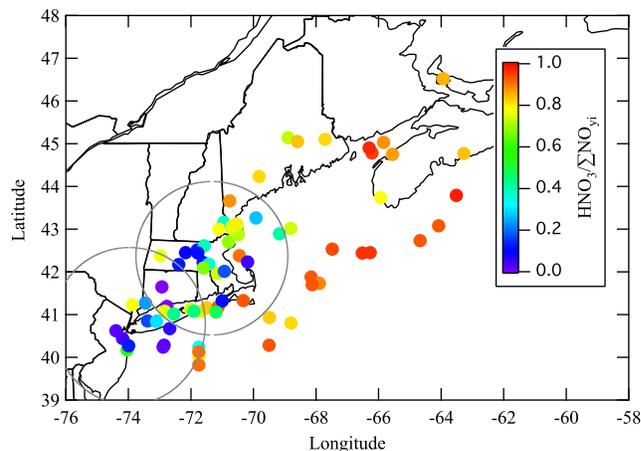
[16] Plumes emitted from the east coast of the United States were frequently transported over the North Atlantic Ocean at low altitudes by predominately southwesterly

flow. Since the aircraft's 160 m lower altitude limit over the ocean was higher than the typical 100 m height of the MBL [Angevine *et al.*, 1996, 2004], plumes that were transported within the MBL were not usually observed here. Because altitude profiles in urban plumes were performed only occasionally, plume vertical structure cannot be characterized completely using the measurements obtained here. Nonetheless, most plumes were observed in layers at altitudes between 160 m and 1.5 km altitude, and plumes rarely extended above 2 km altitude. These concentrated layers of pollutants were often only a few hundred meters in vertical extent.

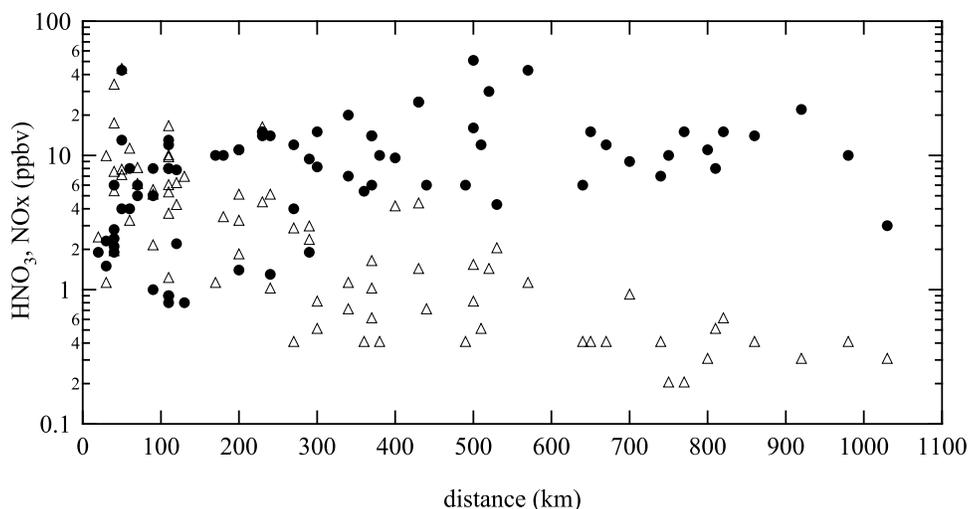
[17] The studied plumes were transported at low altitude, where the ambient temperature in both fresh and aged urban plumes ranged from 11 to 24°C. The temperatures were usually  $20 \pm 2^\circ\text{C}$  during the day and approximately 2°C cooler at night. Since urban plumes were difficult to identify and sample when wind speeds were low and wind direction was variable, most plume studies were conducted when winds were steady and strong. Over land and within the planetary boundary layer, wind speeds were typically  $5 \text{ m s}^{-1}$ . Over the ocean and above the MBL, the wind speeds were usually larger and less variable, with speeds often greater than  $10 \text{ m s}^{-1}$ . Many plumes were sampled hundreds of kilometers downwind of east coast urban areas with transport times of 1 to 2.5 days.

### 3.3. Reactive Nitrogen Partitioning and Abundance

[18] The photochemical environment in the urban plumes is elucidated by examining the reactive nitrogen partitioning. Reactive nitrogen is emitted primarily as NO from mobile and point sources, and these emissions are rapidly oxidized to NO<sub>2</sub> and then more slowly to other reactive nitrogen compounds. The family of reactive nitrogen species ( $\Sigma\text{NO}_{y_i}$ ) represents the originally emitted NO<sub>x</sub> remaining in the atmosphere, and reactive nitrogen partitioning and NO<sub>x</sub> oxidation is quantified using ratios of individual nitrogen compounds to  $\Sigma\text{NO}_{y_i}$ . Ratios are determined from correlation slopes obtained from linear least squares fits of



**Figure 1.** Map of the study region, with 200 km radius circles (gray lines) centered on Boston and New York City. The solid circles indicate the location of urban plumes sampled from the WP-3 aircraft and are colored by  $\text{HNO}_3/\Sigma\text{NO}_{y_i}$ .



**Figure 2.** Maximum values of HNO<sub>3</sub> (solid circles) and NO<sub>x</sub> (open triangles) measured in plumes versus distance from the urban source.

1 s measurements of NO, NO<sub>2</sub>, HNO<sub>3</sub>, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> and 2 s measurements of the PAN compounds with  $\Sigma\text{NO}_{y_i}$  in each urban plume. Since  $\Sigma\text{NO}_{y_i}$  was determined from the individually measured species, and the reactive nitrogen levels in the plumes were usually dominated by either NO<sub>x</sub> (fresh plumes) or HNO<sub>3</sub> (aged plumes), the correlations between NO<sub>x</sub> and  $\Sigma\text{NO}_{y_i}$  in fresh plumes and HNO<sub>3</sub> and  $\Sigma\text{NO}_{y_i}$  in aged plumes was high ( $r^2 > 0.99$ ). Although the PANs, NO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub> never accounted for a majority of  $\Sigma\text{NO}_{y_i}$ , their relationships to  $\Sigma\text{NO}_{y_i}$  were still characterized by high correlations when they accounted for a nonnegligible fraction of  $\Sigma\text{NO}_{y_i}$ . For example, when PANs were  $>10\%$  of  $\Sigma\text{NO}_{y_i}$ , the correlation between PANs and  $\Sigma\text{NO}_{y_i}$  was typically characterized by  $r^2 > 0.80$ . When N<sub>2</sub>O<sub>5</sub> was  $>3\%$  of  $\Sigma\text{NO}_{y_i}$ ,  $r^2$  was greater than 0.75.

[19] In recently emitted plumes that were encountered in close proximity ( $<200$  km) to Boston or New York City, reactive nitrogen was primarily in the form of NO<sub>x</sub>. Fresh plumes are defined here to have  $\text{NO}_x/\Sigma\text{NO}_{y_i} > 0.8$ , where  $\text{NO}_x/\Sigma\text{NO}_{y_i}$  represents the enhancement ratio of NO<sub>x</sub> to  $\Sigma\text{NO}_{y_i}$  determined from the correlation slope of measurements obtained in each urban plume. The urban sources for the fresh plumes were identified from the plume locations and local wind direction. Not all plumes in close proximity to Boston and New York City were fresh, since winds occasionally carried pollutants from other upwind regions into these areas. In fresh urban plumes, the NO<sub>x</sub> abundance ranged from 5 ppbv to 43 ppbv and the  $\Sigma\text{NO}_{y_i}$  abundance was as high as 56 ppbv (Table 1). The NO<sub>x</sub> abundance in air outside of the urban plumes (but at otherwise similar meteorological conditions) was typically  $<200$  pptv. Hence dilution with background air would diminish plume NO<sub>x</sub> concentrations.

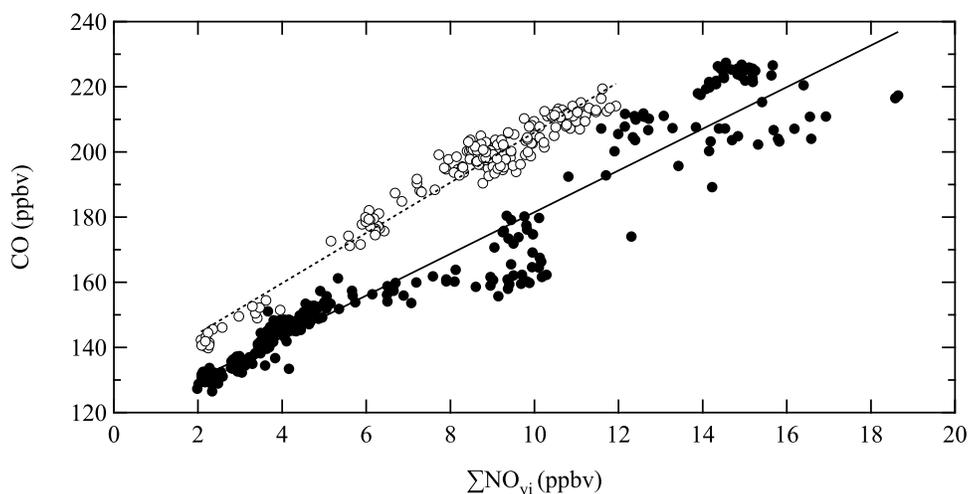
[20] HNO<sub>3</sub> was the most abundant reactive nitrogen species in plumes located over 200 km from Boston and New York City (Figure 1). The  $\Sigma\text{NO}_{y_i}$  abundance in the aged plumes was similar to that in the fresh urban plumes (Table 1), ranging from 6 ppbv up to a maximum of 55 ppbv. The largest HNO<sub>3</sub> concentration was 50 ppbv, and HNO<sub>3</sub> values outside of urban plumes were usually  $<1$  ppbv.

Figure 2 shows the maximum NO<sub>x</sub> and HNO<sub>3</sub> in each plume versus distance from the urban source. The urban source for each plume was identified using wind direction and results from the Lagrangian particle dispersion model. For an average wind speed of  $7 \text{ m s}^{-1}$ , 600 km distance represents one day of transport. HNO<sub>3</sub> concentrations remained high in aged plumes, suggesting that plume dilution and removal of reactive nitrogen were not dominant effects in these plumes that were transported up to 2.5 days.

### 3.4. CO to $\Sigma\text{NO}_{y_i}$ Ratios

[21] The ratio  $\text{CO}/\Sigma\text{NO}_{y_i}$  is used to further examine the effects of plume transport upon reactive nitrogen abundance. The ratio is determined from the enhancements above background of CO and  $\Sigma\text{NO}_{y_i}$  in urban plumes by using the correlation slope between CO and  $\Sigma\text{NO}_{y_i}$  determined from linear least squares fits (Figure 3). CO and  $\Sigma\text{NO}_{y_i}$  were well correlated with  $0.80 < r^2 < 0.98$  in over 80% of the plumes, and always  $r^2 > 0.50$ . Since the lifetime for CO in the troposphere is 1–2 months, CO is approximately conserved in these plumes that are sampled within days from the time of emission. With little dilution and large enhancements above background in both CO and  $\Sigma\text{NO}_{y_i}$ , the  $\text{CO}/\Sigma\text{NO}_{y_i}$  slope is a useful indicator of the extent of reactive nitrogen removal from an air mass. Any loss of reactive nitrogen compounds, either to particles, dry deposition, or wet deposition, would increase  $\text{CO}/\Sigma\text{NO}_{y_i}$ . Studies of urban plumes exported to the free troposphere [e.g., Stohl *et al.*, 2002; Nowak *et al.*, 2004; Takegawa *et al.*, 2004] have shown that CO to  $\Sigma\text{NO}_{y_i}$  ratios increase by over an order of magnitude within several days of emission.

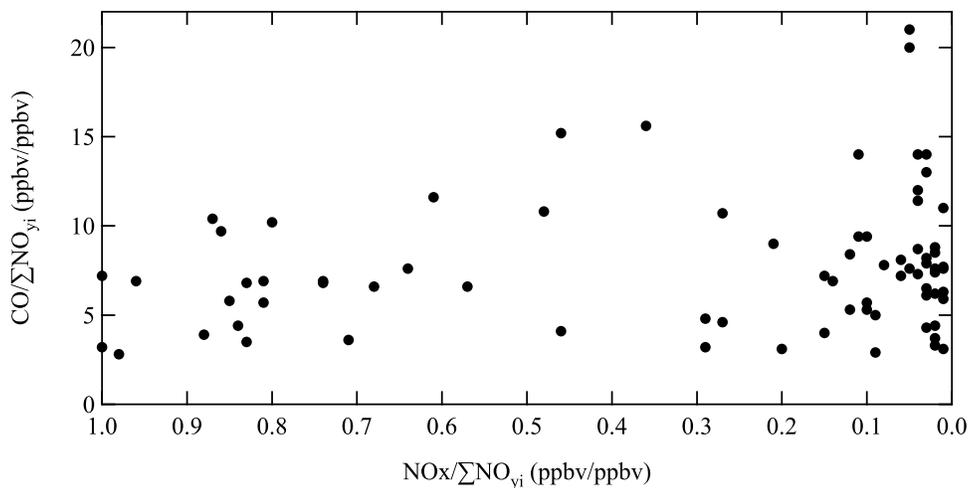
[22]  $\text{CO}/\Sigma\text{NO}_{y_i}$  in aged plumes is also affected by variability in the CO/NO<sub>x</sub> emission ratios. In North American urban areas, the emission ratio has been decreasing in recent years partly because the increased use of catalytic converters on cars has reduced CO emissions [Parrish *et al.*, 2002]. Diesel engines are a minor source of CO, but their NO<sub>x</sub> emissions can be comparable to those from gasoline engines, especially at night and on weekdays [Harley *et al.*, 2001, 2005]. Because the contribution of diesel exhaust



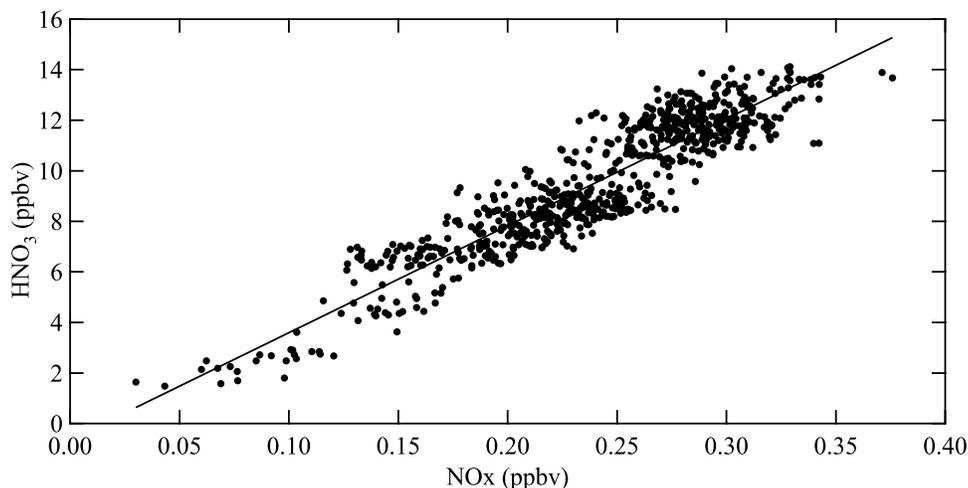
**Figure 3.** Measurements of CO and  $\Sigma\text{NO}_{y_i}$  in fresh (solid circles) and aged (open circles) urban plumes. The fresh plume was sampled 40 km from New York City on 25 July, where  $\text{NO}_x/\Sigma\text{NO}_{y_i} = 0.96$  and  $\text{HNO}_3/\Sigma\text{NO}_{y_i} = 0.04$ .  $\text{CO}/\Sigma\text{NO}_{y_i}$ , determined from the slope of the linear least squares fit (solid line), was 6.4 ppbv/ppbv with  $r^2 = 0.93$ . The open circles were measurements obtained 700 km NE of New York City on 11 August, where  $\text{NO}_x/\Sigma\text{NO}_{y_i} = 0.06$  and  $\text{HNO}_3/\Sigma\text{NO}_{y_i} = 0.82$ . In this aged plume,  $\text{CO}/\Sigma\text{NO}_{y_i} = 7.7$  ppbv/ppbv (dashed line), with  $r^2 = 0.96$ .

relative to automobile exhaust varies with time [Harley *et al.*, 2005], the CO/NO<sub>x</sub> emission ratio also varies with the time of day and day of the week [Harley *et al.*, 2001]. Figure 4 shows the measured CO/ΣNO<sub>y<sub>i</sub></sub> correlation slopes for each urban plume versus NO<sub>x</sub>/ΣNO<sub>y<sub>i</sub></sub>, where NO<sub>x</sub>/ΣNO<sub>y<sub>i</sub></sub> is plotted from 1 to 0 to represent plumes with increasing plume age moving from left to right along the graph's abscissa. The variability in the CO to NO<sub>x</sub> emission ratio is captured in the measurements here. In the 14 fresh plumes with NO<sub>x</sub>/ΣNO<sub>y<sub>i</sub></sub> > 0.8, CO/ΣNO<sub>y<sub>i</sub></sub> was 6.2 ± 2.6, with a median of 6.3 and a range from 3 to 10. This variability in emission ratios limits the precision with which aged and fresh plumes can be compared on the basis of CO/ΣNO<sub>y<sub>i</sub></sub>.

[23] CO to ΣNO<sub>y<sub>i</sub></sub> ratios in aged plumes were often equivalent to those in fresh plumes. In over half the aged plumes that had been oxidized nearly entirely to HNO<sub>3</sub> and transported for several days over the North Atlantic Ocean, CO/ΣNO<sub>y<sub>i</sub></sub> was within the range of emission ratios measured in the fresh plumes (Figure 4). In 45 aged plumes with NO<sub>x</sub>/ΣNO<sub>y<sub>i</sub></sub> < 0.2, CO/ΣNO<sub>y<sub>i</sub></sub> was 8.1 ± 4.0, with a median of 7.6 and a range from 3 to 21. The higher average CO/ΣNO<sub>y<sub>i</sub></sub> in the aged plumes compared to the fresh plumes indicates that reactive nitrogen removal occurred in some plumes. In plumes where most emitted NO<sub>x</sub> had been oxidized to HNO<sub>3</sub> and CO/ΣNO<sub>y<sub>i</sub></sub> was largely unchanged from the time of emission, HNO<sub>3</sub> was transported efficiently



**Figure 4.** CO to  $\Sigma\text{NO}_{y_i}$  correlation slopes in 92 urban plumes, plotted as a function of plume age as represented by the corresponding NO<sub>x</sub> to  $\Sigma\text{NO}_{y_i}$  correlation slope.



**Figure 5.** One-second  $\text{HNO}_3$  and  $\text{NO}_x$  measurements in an urban plume on 21 July, 860 km NE of New York City at 320 m altitude. The  $\text{HNO}_3$  to  $\text{NO}_x$  ratio is determined from the slope of the linear least squares fit to be 42 ppbv/ppbv (solid line) with a square of the correlation coefficient  $r^2 = 0.85$ .

and without detectable loss over the North Atlantic Ocean for hundreds of kilometers.

#### 4. $\text{NO}_x$ Production From $\text{HNO}_3$ Photochemistry

[24] The large abundance of  $\text{HNO}_3$  transported over one day in many urban plumes was important to continued  $\text{O}_3$  and  $\text{NO}_x$  production during transport.  $\text{HNO}_3$  destruction by photolysis or OH oxidation forms  $\text{NO}_x$ , which is then available to promote  $\text{O}_3$  production in more remote regions. Typical  $\text{HNO}_3$  photolysis rates calculated from the aircraft actinic flux measurements during the day were  $7 \times 10^{-7} \text{ s}^{-1}$ . If OH concentrations are assumed to average  $2 \times 10^6 \text{ cm}^{-3}$ , and using the rate constant for the OH +  $\text{HNO}_3$  reaction of  $1.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , the rate of  $\text{HNO}_3$  destruction by OH oxidation would be approximately half as fast. During this study in July and August near  $43^\circ\text{N}$  latitude, the days were approximately 15 hours long. Hence the  $\text{HNO}_3$  lifetime to photolysis and OH oxidation was approximately 18 days. If  $\text{HNO}_3$  were rapidly removed from the atmosphere by dry or wet deposition, then the photochemical lifetime would be inconsequential to reactive nitrogen partitioning or photochemistry. However, with  $\text{HNO}_3$  concentrations elevated to tens of ppbv levels for several days (Figures 1 and 2),  $\text{HNO}_3$  photochemistry results in substantial  $\text{NO}_x$  reformation. For example, in 1 day ( $\sim 5\%$  of the  $\text{HNO}_3$  lifetime), 20 ppbv of  $\text{HNO}_3$  would be expected to produce over 1 ppbv of  $\text{NO}_x$ .

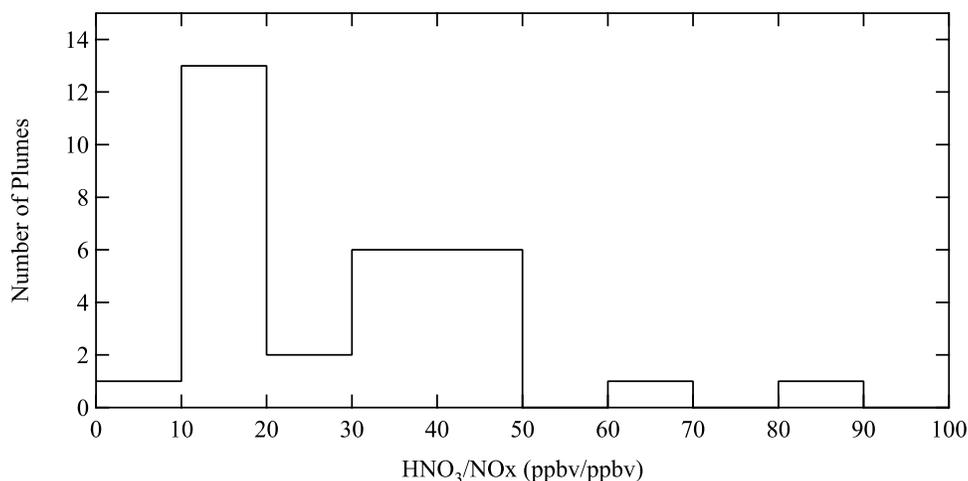
[25] The relationship between  $\text{HNO}_3$  and  $\text{NO}_x$  in urban plumes helps identify the processes controlling the abundance of the reactive nitrogen species.  $\text{HNO}_3$  to  $\text{NO}_x$  enhancement ratios are determined from correlation slopes of linear least squares fits of the 1 s measurements of  $\text{HNO}_3$  to  $\text{NO}_x$  in urban plumes, as shown in Figure 5. The correlation between  $\text{HNO}_3$  and  $\text{NO}_x$  was usually high, with  $r^2 > 0.8$  in over 2/3 of the plumes. In fresh plumes with  $\text{NO}_x/\Sigma\text{NO}_{y_i} > 0.8$ , the median  $r^2$  was 0.44. For aged plumes with  $\text{NO}_x/\Sigma\text{NO}_{y_i} < 0.2$ , the median  $r^2$  was 0.71. Correlation coefficients were lower in fresh plumes because little  $\text{HNO}_3$  had been formed in the plume and most  $\text{HNO}_3$  present was

of different origin than the fresher plume  $\text{NO}_x$ . As  $\text{HNO}_3$  was formed in the plume from  $\text{NO}_x$  oxidation, the correlation between  $\text{HNO}_3$  and  $\text{NO}_x$  increased. If inhomogeneous depositional processes recently removed  $\text{HNO}_3$  from plumes, then the correlation between  $\text{HNO}_3$  and  $\text{NO}_x$  would also be reduced in aged plumes. The observed increase in the correlation coefficients with plume age suggests that  $\text{HNO}_3$  and  $\text{NO}_x$  were linked photochemically and were not strongly affected by recent and sporadic external loss processes or  $\text{NO}_x$  injections. Highly aged plumes with extensive  $\text{NO}_x$  oxidation were identified using the measured CO to  $\text{NO}_x$  ratios. Figure 6 shows a histogram of  $\text{HNO}_3$  to  $\text{NO}_x$  correlation slopes in highly aged plumes, where  $\text{CO}/\text{NO}_x > 100$  so that at least 90% of the  $\text{NO}_x$  was oxidized. Although varying levels of  $\text{NO}_x$  oxidation resulted in a wide distribution of values, the central 2/3 of the  $\text{HNO}_3/\text{NO}_x$  ratios in highly aged plumes ranged from 13 to 42.

[26] The importance of  $\text{HNO}_3$  removal can be assessed by comparing the observations with solutions of rate equations for  $\text{HNO}_3$  and  $\text{NO}_2$ . The steady state solution for the ratio of  $\text{HNO}_3$  to  $\text{NO}_x$  has been commonly used to examine the role of  $\text{HNO}_3$  removal and photochemistry in the troposphere [e.g., Liu *et al.*, 1992]. In the aged urban plumes measured here, PAN was always less abundant than  $\text{HNO}_3$ , since the VOC- $\text{NO}_x$  photochemistry favored  $\text{HNO}_3$  formation relative to PAN. Thus, as a first approximation, only the interconversion between  $\text{HNO}_3$  and  $\text{NO}_2$  is considered. Neglecting all other loss mechanisms for  $\text{HNO}_3$  and  $\text{NO}_2$ , the rate equations are

$$\begin{aligned} \frac{d[\text{HNO}_3]}{dt} &= +k_{\text{OH}+\text{NO}_2} \cdot [\text{OH}] \cdot [\text{NO}_2] - j_{\text{HNO}_3} \cdot [\text{HNO}_3] \\ &\quad - k_{\text{OH}+\text{HNO}_3} \cdot [\text{OH}] \cdot [\text{HNO}_3] \\ \frac{d[\text{NO}_2]}{dt} &= -\frac{d[\text{HNO}_3]}{dt} \end{aligned}$$

where  $j_{\text{HNO}_3}$  is the  $\text{HNO}_3$  photolysis rate measured on the aircraft,  $k_{\text{OH}+\text{HNO}_3}$  is the rate constant for the reactions initiated by OH reaction with  $\text{HNO}_3$  that reform  $\text{NO}_2$ , and



**Figure 6.** A histogram of the number of highly aged urban plumes with CO/NO<sub>x</sub> > 100 as a function of the plume HNO<sub>3</sub> to NO<sub>x</sub> ratio.

$k_{\text{OH}+\text{NO}_2} = 1.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (pressure = 1 atm., temperature = 300 K) is the rate constant for the reaction  $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ . The HNO<sub>3</sub>/NO<sub>2</sub> ratio is obtained from the coupled rate equations. The photochemical steady state solution, which is found by setting  $d[\text{HNO}_3]/dt = 0$  in the first equation, is

$$\frac{[\text{HNO}_3]}{[\text{NO}_2]} = \frac{k_{\text{OH}+\text{NO}_2} \cdot [\text{OH}]}{j_{\text{HNO}_3} + k_{\text{OH}+\text{HNO}_3} \cdot [\text{OH}]}$$

[27] In most aged plumes studied here, the measured O<sub>3</sub> levels were over 90 ppbv and NO<sub>2</sub> and NO were in steady state with NO<sub>2</sub> approximately 5 times larger than NO. HNO<sub>3</sub>/NO<sub>x</sub> is calculated from HNO<sub>3</sub>/NO<sub>2</sub> and the small measured NO to NO<sub>x</sub> fraction. Using diurnally averaged values for OH and  $j_{\text{HNO}_3}$ , the photochemical steady state value for HNO<sub>3</sub>/NO<sub>x</sub> is calculated from the equation above to be 26. Solution of the time-dependent rate equations for HNO<sub>3</sub> and NO<sub>2</sub> show that the steady state value is achieved in several days. While plume age cannot always be determined accurately in the aged plumes that may originate from a combination of sources, uncertainties were reduced in plumes that were sampled over the remote ocean. Urban plumes that were sampled at low altitudes well over 600 km from the coast and away from any recent inputs of pollution were likely over 1 day old, assuming an average wind speed of 7 m s<sup>-1</sup>.

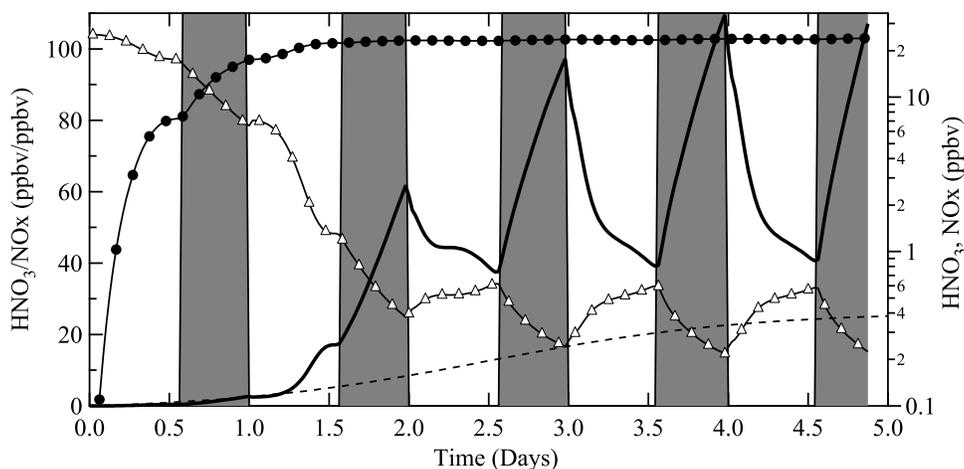
[28] The observed HNO<sub>3</sub>/NO<sub>x</sub> in plumes that were 1–2.5 days old were occasionally different from calculated using the rate equations above (Figure 6). Values of HNO<sub>3</sub>/NO<sub>x</sub> lower than the steady state ratio can be explained by HNO<sub>3</sub> removal during transport or insufficient plume aging to achieve steady state. Values of HNO<sub>3</sub>/NO<sub>x</sub> greater than the calculated steady state value suggest that additional processes may have converted NO<sub>x</sub> to HNO<sub>3</sub>. At night, reactions involving the nitrate radical can produce HNO<sub>3</sub>. N<sub>2</sub>O<sub>5</sub> hydrolysis is the most important HNO<sub>3</sub> formation process, where the N<sub>2</sub>O<sub>5</sub> is formed from reactions of NO<sub>2</sub> with O<sub>3</sub> to form NO<sub>3</sub>, followed by further reactions with NO<sub>2</sub> to form N<sub>2</sub>O<sub>5</sub>. This conversion of NO<sub>x</sub> to HNO<sub>3</sub> influences the reactive nitrogen partitioning in plumes that were transported through the night. At night, photochemis-

try that destroys HNO<sub>3</sub> is inactive, so that nocturnal processing is predicted to increase HNO<sub>3</sub>/NO<sub>x</sub> so that it could exceed the photochemical steady values.

[29] Box model calculations were performed to examine the plausibility that nighttime chemistry affects the observed reactive nitrogen partitioning. The box model was based on the Master Chemical Mechanism (Saunders *et al.* [2003] and <http://mcm.leeds.ac.uk/MCM/>) and uses reactions of 63 VOCs. The model was initiated with typical urban conditions measured in fresh plumes from the WP-3 and run from sunrise for 5 days. The pressure and temperature were set to values typical for the WP-3 flight altitudes in urban plumes. Surface removal of HNO<sub>3</sub> was set to zero in the model to test if the observations were consistent with very slow dry deposition. N<sub>2</sub>O<sub>5</sub> hydrolysis rates were faster than the reaction of NO<sub>2</sub> and O<sub>3</sub> to form NO<sub>3</sub>, which is the rate limiting step for the conversion of NO<sub>x</sub> to HNO<sub>3</sub> at night [Brown *et al.*, 2004]. Figure 7 shows the predicted HNO<sub>3</sub>, NO<sub>x</sub>, and HNO<sub>3</sub>/NO<sub>x</sub> ratio versus time. The inclusion of nighttime chemistry forces the HNO<sub>3</sub>/NO<sub>x</sub> ratio to higher values and at earlier times compared to the simplified rate equations that neglect processing at night. At night, the HNO<sub>3</sub>/NO<sub>x</sub> ratio is predicted to rise sharply when NO<sub>x</sub> is converted to HNO<sub>3</sub> via N<sub>2</sub>O<sub>5</sub> hydrolysis. Since flights were not performed at night over the remote North Atlantic Ocean, the importance of N<sub>2</sub>O<sub>5</sub> hydrolysis to HNO<sub>3</sub> and NO<sub>x</sub> levels in highly aged plumes could only be determined from the measurements during the day. During the day, HNO<sub>3</sub> is destroyed by OH and photolysis, such that NO<sub>x</sub> increases and HNO<sub>3</sub>/NO<sub>x</sub> decreases, and the effects of nighttime chemistry upon HNO<sub>3</sub> formation and NO<sub>x</sub> loss were partially obscured. Despite these limitations, observed HNO<sub>3</sub>/NO<sub>x</sub> ratios greater than the photochemical steady state value can be explained by box model calculations that include nighttime production of HNO<sub>3</sub> from NO<sub>x</sub> in addition to photochemical reactions that interconvert NO<sub>x</sub> and HNO<sub>3</sub>.

## 5. Discussion

[30] The efficient transport of HNO<sub>3</sub> redistributes NO<sub>x</sub> oxidation products far from the source of emission



**Figure 7.**  $\text{HNO}_3/\text{NO}_x$  ratio (solid line),  $\text{HNO}_3$  (solid circles), and  $\text{NO}_x$  (open triangles) predicted using box model calculations that includes daytime and nighttime chemistry. The dashed line neglects nocturnal processing and considers only photochemistry that interconverts  $\text{HNO}_3$  and  $\text{NO}_x$ , and uses 24-hour average values for  $\text{HNO}_3$  photolysis rates and  $\text{OH}$  concentrations. The shaded regions represent night.

(Figure 2). Although the observations here only extend 1000 km from the coast, it is certain that these high  $\text{HNO}_3$  levels in the plumes were eventually reduced, since background  $\text{HNO}_3$  levels are low compared to the plume observations. Since  $\text{HNO}_3$  is highly water soluble, it will be removed from the atmosphere if the plumes encounter precipitation during storm passage or if air masses eventually mix to the MBL.  $\text{HNO}_3$  removal is also expected if these urban plumes were lifted to higher altitudes. Most aged plumes studied here were observed below 1 km altitude and had dew points that were approximately  $5^\circ\text{C}$  lower than the ambient temperature. Thus the air parcels could be lifted another 500 m (using the dry adiabatic lapse rate of  $9.8^\circ\text{C km}^{-1}$ ) before they reached the lifting condensation level where water would start to condense and  $\text{HNO}_3$  would be removed rapidly. If these plumes encounter precipitation, the  $\text{HNO}_3$  levels are expected to be reduced rapidly and the resulting nitrate will be deposited to the remote ocean. Episodic atmospheric inputs of nitrogen to remote oceans may be important biologically, if the waters are not subject to large nitrogen inputs from upwelling or rivers [Jordan and Talbot, 2000]. If  $\text{HNO}_3$  transport is efficient across the entire ocean, nitrogen-containing compounds exported from the United States may deposit in Europe [Holland et al., 2005].

[31] In most environments,  $\text{HNO}_3$  loss or recent  $\text{NO}_x$  injections caused measured  $\text{HNO}_3/\text{NO}_x$  to fall far below the modeled steady state values [e.g., Liu et al., 1992; Jaegle et al., 1998], whereas  $\text{HNO}_3/\text{NO}_x$  measured here was often comparable to the steady state values. Transport in stratified layers over the North Atlantic Ocean is distinct from transport into the upper troposphere or transport in the planetary boundary layer, since depositional loss of  $\text{HNO}_3$  is greatly reduced when the air is neither lifted nor mixed downward. Consequently,  $\text{HNO}_3$  and  $\text{HNO}_3/\text{NO}_x$  are higher in this low-level transport compared to studies in the free troposphere. Furthermore, the high  $\text{HNO}_3/\text{NO}_x$  ratios that were observed and predicted by box model calculations and a steady state approximation indicate that known gas phase chemistry explains the observations and

that heterogeneous processes converting  $\text{HNO}_3$  to  $\text{NO}_x$  need not be hypothesized.

[32] The remote marine atmosphere can be a region of photochemical  $\text{O}_3$  destruction or production, depending upon the  $\text{NO}_x$  levels. Below a few tens of pptv of  $\text{NO}_x$ , photochemical  $\text{O}_3$  destruction dominates in the lower troposphere [Chameides et al., 1992; Jacob et al., 1996], whereas net  $\text{O}_3$  production is expected at higher  $\text{NO}_x$  levels. In aged plumes, enhancements in  $\text{NO}_x$  were typically several hundred pptv, and up to 1.2 ppbv. Observed  $\text{HNO}_3/\text{NO}_x$  ratios were reproduced by a box model that showed photochemical  $\text{NO}_x$  production from  $\text{HNO}_3$ . Hence gas phase  $\text{HNO}_3$  destruction via photolysis and reaction with  $\text{OH}$  enhances the lifetime of  $\text{NO}_x$  in these plumes and maintains  $\text{NO}_x$  at levels high enough to allow for continuing photochemical  $\text{O}_3$  production. Enhanced  $\text{O}_3$  to  $\text{CO}$  relationships have been observed in North American pollution outflow at PICO-NARE, a remote mountaintop site located in the Azores.  $\text{O}_3$  and  $\text{CO}$  were correlated with a slope that was higher than typically observed over or near the continents [Honrath et al., 2004]. Several causes were hypothesized, including continuing  $\text{O}_3$  production in plumes that were transported for days over the ocean. Efficient transport of  $\text{HNO}_3$  above the MBL provides a mechanism for continued  $\text{O}_3$  production that may explain the elevated  $\text{O}_3$  to  $\text{CO}$  relationships observed at a remote marine site.  $\text{NO}_y$  levels in low-level outflow from North America that were sampled at the PICO-NARE station were typically less than 1 ppbv [Val Martin et al., 2005], and much lower than those observed here, reflecting removal of  $\text{HNO}_3$  during the 4–7 day transport period.  $\text{HNO}_3$  removal may have sometimes occurred when air parcels were lofted above the lifting condensation level to the PICO-NARE site at 2.2 km altitude.

[33] The efficient transport of  $\text{HNO}_3$  suggests that  $\text{HNO}_3$  loss to particle formation was negligible, which is consistent with measurements of particle size and composition from the aircraft. Particle size distribution [Brock et al., 2003] and composition [Orsini et al., 2003] measurements aboard the aircraft confirm that the conversion of gas-phase  $\text{HNO}_3$  to

ammonium nitrate was small in the urban plumes. Particle volume and surface area were elevated in aged urban plumes, with surface areas that were typically between 500 and 1000  $\mu\text{m}^2 \text{cm}^{-3}$ . Despite these high particle concentrations,  $\text{HNO}_3$  loss to particles was not evident. Inorganic fine ( $<1 \mu\text{m}$  diameter) particle composition was dominated by ammonium sulfate in the transported plumes, and nitrate abundance was low. In most aged plumes, the nitrate abundance was below 40 pptv ( $0.1 \mu\text{g m}^{-3}$ ), the lower limit of detection for particulate nitrate, and only once was the nitrate greater than 80 pptv ( $0.2 \mu\text{g m}^{-3}$ ) in an aged urban plume. Nitrate values were occasionally elevated in fresh urban plumes, but they were always much less than 1 ppbv and were always a negligible fraction of  $\Sigma\text{NO}_{\text{yi}}$ .

[34] Measurements from surface-based sampling platforms were also consistent with the results presented here. The over flights of the NOAA research vessel *Ronald H. Brown*, which was equipped with measurement capabilities similar to those of the WP-3, showed that the air masses sampled above 160 m by the aircraft were markedly different chemically and meteorologically than those observed at the ocean surface. In the MBL,  $\text{HNO}_3$  mixing ratios and lifetimes are considerably smaller than those aloft. Measurements obtained aboard the *Ronald H. Brown* during the summer of 2002 in the same region determined the  $\text{HNO}_3$  lifetime to be 2.3 hours in the MBL [Brown et al., 2004]. The urban plumes observed from the aircraft were transported in stratified layers above the MBL that were decoupled from the MBL and the ocean surface.

[35] The observed concentrated pollution plumes that were transported efficiently at low levels are consistent with many other studies conducted in this region. High atmospheric stability resulted in limited vertical mixing in air transported over the Gulf of Maine [Angevine et al., 1996]. The transport of pollutants from North America at low levels but above the MBL have been shown to be important to the lower free troposphere over the North Atlantic Ocean [Owen et al., 2006]. Repeated observations of concentrated pollution plumes caused by reduced vertical mixing over water [Spicer et al., 1979; Sillman et al., 1993; Daum et al., 1996; Angevine et al., 1996] suggest that efficient transport of  $\text{HNO}_3$  above the MBL is a common occurrence. The same efficient transport of  $\text{HNO}_3$  observed here may exist over cold land surfaces, where highly stable layers are also formed.

## 6. Conclusions

[36]  $\text{HNO}_3$  was observed in large abundance in urban plumes transported at altitudes between 160 m and 1.5 km over the North Atlantic Ocean in July and August 2004 during the ICARTT study.  $\text{HNO}_3$  accounted for the majority of the reactive nitrogen in nearly all plumes that were over 200 km from New York City or Boston. In many of the plumes that were transported 1–2.5 days,  $\text{CO}/\Sigma\text{NO}_{\text{yi}}$  ratios were comparable to the ratio at the time of emission, indicating that  $\Sigma\text{NO}_{\text{yi}}$  removal was small.

[37] The efficient  $\text{HNO}_3$  transport at low altitudes may partly explain the delayed onset of reactive nitrogen loss in plumes transported over the North Atlantic Ocean from the eastern United States observed by Stohl et al. [2002]. Eventually, the highly soluble  $\text{HNO}_3$  will be lost from the

atmosphere when air masses encounter precipitation or mix to the surface. Studies of long-range transport of pollutants have shown that over 90% of the originally emitted reactive nitrogen is removed from the atmosphere after several days of transport [Stohl et al., 2002; Takegawa et al., 2004; Nowak et al., 2004]. If large concentrations of nitrate eventually deposit to the remote oceans, these regions may be affected since they are likely to be more sensitive to nutrient inputs compared to coastal waters that are often nutrient rich.

[38] The presence of tens of ppbv of  $\text{HNO}_3$  in plumes transported for days is important photochemically, since destruction of  $\text{HNO}_3$  by photolysis and OH reaction reforms  $\text{NO}_x$ . In the troposphere,  $\text{HNO}_3$  is frequently considered to be an irreversible sink for  $\text{NO}_x$ , since the  $\text{HNO}_3$  lifetime to depositional loss is usually much faster than photochemical processes that reform  $\text{NO}_x$ . This assumption is not always valid for stratified low-level outflow over water, where  $\text{HNO}_3$  is transported efficiently in the absence of precipitation or surface loss. The high correlation between  $\text{HNO}_3$  and  $\text{NO}_x$  and the high values of  $\text{HNO}_3/\text{NO}_x$  are consistent with box model calculations that neglect heterogeneous removal of  $\text{HNO}_3$ . In plumes transported up to 1000 km from the coast,  $\text{NO}_x$  levels were hundreds of pptv, which is high enough to maintain photochemical  $\text{O}_3$  production.

[39] **Acknowledgment.** We thank the flight and support crew from the NOAA WP-3 aircraft for their efforts to make these measurements possible.

## References

- Angevine, W. M., M. Trainer, S. A. McKeen, and C. M. Berkowitz (1996), Mesoscale meteorology of the New England coast, Gulf of Maine, and Nova Scotia: Overview, *J. Geophys. Res.*, *101*(D22), 28,893–28,901.
- Angevine, W. M., et al. (2004), Coastal boundary layer influence on pollutant transport in New England, *J. Appl. Meteorol.*, *43*, 1425–1437.
- Brock, C. A., et al. (2003), Particle growth in urban and industrial plumes in Texas, *J. Geophys. Res.*, *108*(D3), 4111, doi:10.1029/2002JD002746.
- Brown, S. S., et al. (2004), Nighttime removal of  $\text{NO}_x$  in the summer marine boundary layer, *Geophys. Res. Lett.*, *31*, L07108, doi:10.1029/2004GL019412.
- Chameides, W. L., et al. (1992), Ozone precursor relationships in the ambient atmosphere, *J. Geophys. Res.*, *97*, 6037–6055.
- Crutzen, P. J. (1979), The role of NO and  $\text{NO}_2$  in the chemistry of the troposphere and stratosphere, *Annu. Rev. Earth Planet. Sci.*, *7*, 443–472.
- Daum, P. H., L. I. Kleinman, L. Newman, W. T. Luke, J. Weinstein-Lloyd, C. M. Berkowitz, and K. M. Busnes (1996), Chemical and physical properties of plumes of anthropogenic pollutants transported over the North Atlantic during the North Atlantic Regional Experiment, *J. Geophys. Res.*, *101*(D22), 29,029–29,042.
- de Gouw, J. A., et al. (2006), Volatile organic compounds composition of merged and aged forest fire plumes from Alaska and western Canada, *J. Geophys. Res.*, *111*, D10303, doi:10.1029/2005JD006175.
- DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina (1997), Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ. 97-4*, NASA Jet Propul. Lab., Pasadena, Calif.
- Dibb, J. E., E. Scheuer, S. I. Whitlow, M. Vozella, E. Williams, and B. M. Lerner (2004), Ship-based nitric acid measurements in the Gulf of Maine during New England Air Quality Study 2002, *J. Geophys. Res.*, *109*, D20303, doi:10.1029/2004JD004843.
- Dubé, W. P., S. S. Brown, H. D. Osthoff, M. R. Nunley, S. J. Ciciora, M. W. Paris, R. J. McLaughlin, and A. R. Ravishankara (2006), Aircraft instrument for simultaneous, in situ measurement of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  via pulsed cavity ring-down spectroscopy, *Rev. Sci. Instrum.*, *77*, 034101, doi:10.1063/1.2176058.
- Harley, R. A., S. A. McKeen, J. Pearson, M. O. Rodgers, and W. A. Lonneman (2001), Analysis of motor vehicle emissions during the Nashville/Middle Tennessee Ozone Study, *J. Geophys. Res.*, *106*, 3559–3567.
- Harley, R. A., L. C. Marr, J. K. Lehner, and S. N. Giddings (2005), Changes in motor vehicle emissions on diurnal to decadal time scales and effects

- on atmospheric composition, *Environ. Sci. Technol.*, *39*(14), 5356–5362, doi:10.1021/ES048172.
- Holland, E. A., B. H. Braswell, J. Sulzmann, and J. F. LaMarque (2005), Nitrogen deposition onto the United States and western Europe: Synthesis of observations and models, *Ecol. Appl.*, *15*(1), 38–57.
- Holloway, J. S., R. O. Jakoubek, D. D. Parrish, C. Gerbig, A. Volz-Thomas, S. Schmitgen, A. Fried, B. Wert, B. Henry, and J. R. Drummond (2000), Airborne intercomparison of vacuum ultraviolet fluorescence and tunable diode laser absorption measurements of tropospheric carbon monoxide, *J. Geophys. Res.*, *105*, 24,251–24,261.
- Honrath, R. E., R. C. Owen, M. Val Martin, J. S. Reid, K. Lapina, P. Fialho, M. P. Dzioebak, J. Kleissl, and D. L. Westphal (2004), Regional and hemispheric impacts of anthropogenic and biomass burning emissions on summertime CO and O<sub>3</sub> in the North Atlantic lower free troposphere, *J. Geophys. Res.*, *109*, D24310, doi:10.1029/2004JD005147.
- Jacob, D. J., et al. (1996), Origin of ozone and NO<sub>x</sub> in the tropical troposphere: A photochemical analysis of aircraft observations over the South Atlantic Basin, *J. Geophys. Res.*, *101*(D19), 24,235–24,250.
- Jaegle, L., D. J. Jacob, Y. Wang, A. J. Weinheimer, B. A. Ridley, T. L. Campos, G. W. Sachse, and D. E. Hagen (1998), Sources and chemistry of NO<sub>x</sub> in the upper troposphere over the United States, *Geophys. Res. Lett.*, *25*, 1705–1708.
- Jordan, C. E., and R. W. Talbot (2000), Direct atmospheric deposition of water-soluble nitrogen to the Gulf of Maine, *Global Biogeochem. Cycles*, *14*, 1315–1329.
- Li, Q., D. J. Jacob, J. W. Munger, R. M. Yantosca, and D. D. Parrish (2004), Export of NO<sub>y</sub> from the North American boundary layer: Reconciling aircraft observations and global model budgets, *J. Geophys. Res.*, *109*, D02313, doi:10.1029/2003JD004086.
- Liu, S. C., et al. (1992), A study of the photochemistry and ozone budget during the Mauna Loa Observatory Photochemistry Experiment, *J. Geophys. Res.*, *97*, 10,463–10,471.
- Neuman, J. A., et al. (2002), Fast-response airborne in situ measurements of HNO<sub>3</sub> during the Texas Air Quality Study, *J. Geophys. Res.*, *107*(D20), 4436, doi:10.1029/2001JD001437.
- Neuman, J. A., et al. (2003a), Variability in ammonium nitrate formation and nitric acid depletion with altitude and location over California, *J. Geophys. Res.*, *108*(D17), 4557, doi:10.1029/2003JD003616.
- Neuman, J. A., T. B. Ryerson, L. G. Huey, R. Jakoubek, J. B. Nowak, C. Simons, and F. C. Fehsenfeld (2003b), Calibration and evaluation of nitric acid and ammonia permeation tubes by UV optical absorption, *Environ. Sci. Technol.*, *37*(13), 2975–2981, doi:10.1021/ES06422L.
- Neuman, J. A., D. D. Parrish, T. B. Ryerson, C. A. Brock, C. Wiedinmyer, G. J. Frost, J. S. Holloway, and F. C. Fehsenfeld (2004), Nitric acid loss rates measured in power plant plumes, *J. Geophys. Res.*, *109*, D23304, doi:10.1029/2004JD005092.
- Nowak, J. B., et al. (2004), Gas-phase chemical characteristics of Asian emission plumes observed during ITCT 2K2 over the eastern North Pacific Ocean, *J. Geophys. Res.*, *109*, D23S19, doi:10.1029/2003JD004488.
- Orsini, D. A., Y. Ma, A. Sullivan, B. Sierau, K. Baumann, and R. J. Weber (2003), Refinements to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water soluble aerosol composition, *Atmos. Environ.*, *37*, 1243–1259.
- Owen, R. C., O. R. Cooper, A. Stohl, and R. E. Honrath (2006), An analysis of the mechanisms of North American pollutant transport to the Central North Atlantic lower free troposphere, *J. Geophys. Res.*, doi:10.1029/2006JD007062, in press.
- Owens, N. J. P., J. N. Galloway, and R. A. Duce (1992), Episodic atmospheric nitrogen deposition to oligotrophic oceans, *Nature*, *357*, 397–399.
- Paerl, H. W. (1985), Enhancement of marine primary production by nitrogen-enriched acid rain, *Nature*, *315*, 747–749.
- Parrish, D. D., M. Trainer, D. Hereid, E. J. Williams, K. J. Olszyna, R. A. Harley, J. F. Meagher, and F. C. Fehsenfeld (2002), Decadal change in carbon monoxide to nitrogen oxide ratio in U.S. vehicular emissions, *J. Geophys. Res.*, *107*(D12), 4140, doi:10.1029/2001JD000720.
- Parrish, D. D., et al. (2004), Fraction and composition of NO<sub>y</sub> transported in air masses lofted from the North American continental boundary layer, *J. Geophys. Res.*, *109*, D09302, doi:10.1029/2003JD004226.
- Roberts, J. M., et al. (1996), Episodic removal of NO<sub>y</sub> species from the marine boundary layer over the North Atlantic, *J. Geophys. Res.*, *101*, 28,947–28,960.
- Ryerson, T. B., E. J. Williams, and F. C. Fehsenfeld (2000), An efficient photolysis system for fast-response NO<sub>2</sub> measurements, *J. Geophys. Res.*, *105*, 26,447–26,461.
- Saunders, S. M., M. E. Jenkin, R. G. Derwent, and M. J. Pilling (2003), Protocol for the development of the Master Chemical Mechanism, MCM v3 (part A): Tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, *3*, 161–180.
- Sillman, S., P. J. Samson, and J. M. Masters (1993), Ozone production in urban plumes transported over water: Photochemical model and case studies in the northeastern and midwestern United States, *J. Geophys. Res.*, *98*, 12,687–12,699.
- Slusher, D. L., L. G. Huey, D. J. Tanner, F. M. Flocke, and J. M. Roberts (2004), A thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacetyl nitrates and dinitrogen pentoxide, *J. Geophys. Res.*, *109*, D19315, doi:10.1029/2004JD004670.
- Spicer, C. W., D. W. Joseph, P. R. Stickels, and G. F. Ward (1979), Ozone sources and transport in the northeastern United States, *Environ. Sci. Technol.*, *13*, 975–985.
- Stohl, A., M. Hittenberger, and G. Wotawa (1998), Validation of the Lagrangian particle dispersion model FLEXPART against large scale tracer experiment data, *Atmos. Environ.*, *32*, 4245–4264.
- Stohl, A., M. Trainer, T. B. Ryerson, J. S. Holloway, and D. D. Parrish (2002), Export of NO<sub>y</sub> from the North American boundary layer during 1996 and 1997 North Atlantic Regional Experiments, *J. Geophys. Res.*, *107*(D11), 4131, doi:10.1029/2001JD000519.
- Takegawa, N., et al. (2004), Removal of NO<sub>x</sub> and NO<sub>y</sub> in Asian outflow plumes: Aircraft measurements over the western Pacific in January 2002, *J. Geophys. Res.*, *109*, D23S04, doi:10.1029/2004JD004866.
- Val Martin, M., R. Honrath, R. C. Owen, J. Kleissl, and K. Lapina (2005), Transport of nitrogen oxides from anthropogenic emissions and boreal forest fires to the central North Atlantic lower free troposphere: Measurements at the PICO-NARE station during the ICARTT study, *Geophys. Res. Abstr.*, *7*, 05759.

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