



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 (HNO₃) mixing ratios were large (up to 50 ppbv), and HNO₃ 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 HNO₃ explained the observed trace gas ratios and abundances. Without substantial HNO₃ loss, the ratio of HNO₃ to NO_x 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_x to HNO₃ reproduce the observations. Photolysis and OH oxidation of over 10 ppbv of HNO₃ that was in the troposphere for days resulted in reformation of hundreds of pptv of NO_x, which is sufficient to maintain photochemical ozone production. Efficient transport of HNO₃ over the North Atlantic Ocean for days carried both HNO₃ and NO_x 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 (O₃) 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 O₃ 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_x (NO_x = NO + NO₂) and its oxidation products depend on its lifetime in the atmosphere. NO_x emitted from vehicle tailpipes, power generation, and other combustion sources contributes to O₃ formation, particle formation, and nitrogen deposition. Over North America, anthropogenic NO_x is oxidized to nitric acid (HNO₃), which is subsequently removed from the atmosphere by dry or wet deposition, such that only a small fraction of originally emitted NO_x reaches the free troposphere [Stohl et al., 2002; Parrish et al., 2004; Li et al., 2004]. Loss of HNO₃ 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 HNO₃ 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⁻¹) and 5 m vertical resolution during altitude profiles (for the typical aircraft ascent and descent rates of 5–6 m s⁻¹). 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 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 HNO_3 that was slowly released from the instrument's surfaces after large abundances of 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 1σ standard deviation on the instrument background to be $\pm 20 \text{ pptv}$ for 1 s measurements.

[11] O_3 , NO_2 , NO , and NO_y were measured in 4 separate channels of a chemiluminescence detector and were averaged to 1 s. NO_2 was measured on all but the first two flights of the study, with an uncertainty of $\pm(8\% + 25 \text{ pptv})$. NO was measured with an uncertainty of $\pm(5\% + 10 \text{ pptv})$ [Ryerson *et al.*, 2000], and O_3 was measured with an uncertainty of $\pm(3\% + 0.1 \text{ ppbv})$. 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 NO . NO_y was measured only on the first four flights of the study, whereupon an instrument failure prevented accurate NO_y measurement. CO was measured once per second using a vacuum UV fluorescence instrument with an uncertainty of 5% and a 3σ 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. NO_3 and N_2O_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, NO_3 and N_2O_5 were usually less than 5 pptv and 1% of ΣNO_{yi} , and they never exceeded 14 pptv or 2% of ΣNO_{yi} . In order to achieve the most data coverage, NO_3 and N_2O_5 are included in ΣNO_{yi} only for the 6 flights that occurred at night, when NO_3 and N_2O_5 accounted for a nonnegligible fraction of ΣNO_{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 CO and NO_2 measurements on the two aircraft agreed within the stated uncertainties, and 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 HNO_3 measurements obtained on the two platforms were well correlated and had offsets between 20 and 200 pptv. 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 HNO_3 measurements were between 21 and 25%. The DC-8 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 HNO_3 data was also examined by comparing NO_y and ΣNO_{yi} measurements aboard the WP-3 on the 2 flights when both NO_2 and NO_y were measured. On these 2 flights, the absolute ratio of HNO_3 to NO_y averaged 0.53. Since HNO_3 was a majority of NO_y , this comparison provided an additional test of HNO_3 measurement accuracy. A linear least squares fit of ΣNO_{yi} to NO_y had a slope of 1.07 and $r^2 = 0.99$, and NO_y and ΣNO_{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 CO was enhanced more than 30 ppbv above the minimum CO value measured on each flight leg. Concentrated forest fire plumes, which also had elevated 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 NO_x or HNO_3 , but had little or no CO enhancement, were also excluded by the requirement that CO was enhanced. Of the 93 plumes that were identified by the 30 ppbv enhancement in 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 HNO_3 and 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^a

Date (2004)	Plumes	Fresh Plumes	Max. ΣNO_{y_i} , ppbv	Aged Plumes	Max. ΣNO_{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	—

^aFresh 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_x. 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 HNO₃ 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 HNO₃ 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 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 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 NO₂ and then more slowly to other reactive nitrogen compounds. The family of reactive nitrogen species (ΣNO_{y_i}) represents the originally emitted NO_x remaining in the atmosphere, and reactive nitrogen partitioning and NO_x oxidation is quantified using ratios of individual nitrogen compounds to ΣNO_{y_i} . Ratios are determined from correlation slopes obtained from linear least squares fits of

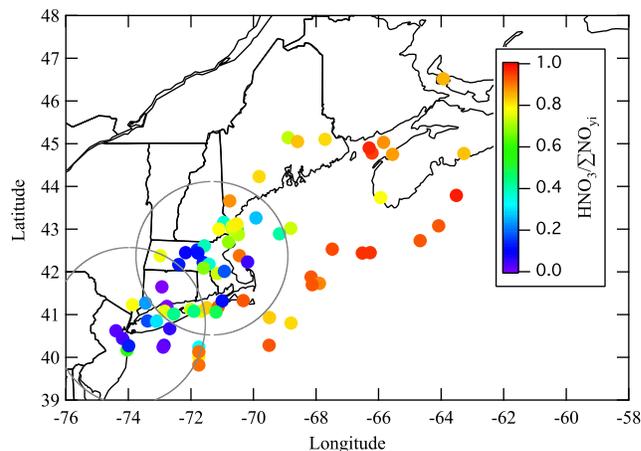


Figure 1. Map of the study region, with 200 km radius circles (gray lines) centered on Boston and New York City. The solid circles indicate the location of urban plumes sampled from the WP-3 aircraft and are colored by $\text{HNO}_3/\Sigma\text{NO}_{y_i}$.

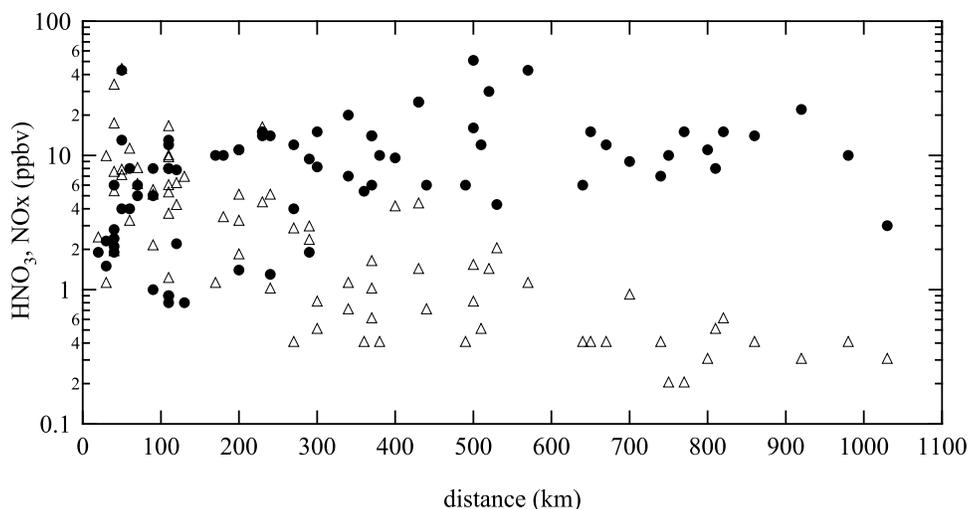


Figure 2. Maximum values of HNO₃ (solid circles) and NO_x (open triangles) measured in plumes versus distance from the urban source.

1 s measurements of NO, NO₂, HNO₃, NO₃ and N₂O₅ and 2 s measurements of the PAN compounds with ΣNO_{y_i} in each urban plume. Since ΣNO_{y_i} was determined from the individually measured species, and the reactive nitrogen levels in the plumes were usually dominated by either NO_x (fresh plumes) or HNO₃ (aged plumes), the correlations between NO_x and ΣNO_{y_i} in fresh plumes and HNO₃ and ΣNO_{y_i} in aged plumes was high ($r^2 > 0.99$). Although the PANs, NO₃, and N₂O₅ never accounted for a majority of ΣNO_{y_i} , their relationships to ΣNO_{y_i} were still characterized by high correlations when they accounted for a nonnegligible fraction of ΣNO_{y_i} . For example, when PANs were $>10\%$ of ΣNO_{y_i} , the correlation between PANs and ΣNO_{y_i} was typically characterized by $r^2 > 0.80$. When N₂O₅ was $>3\%$ of ΣNO_{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_x. 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_x to ΣNO_{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_x abundance ranged from 5 ppbv to 43 ppbv and the ΣNO_{y_i} abundance was as high as 56 ppbv (Table 1). The NO_x 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_x concentrations.

[20] HNO₃ was the most abundant reactive nitrogen species in plumes located over 200 km from Boston and New York City (Figure 1). The ΣNO_{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 HNO₃ concentration was 50 ppbv, and HNO₃ values outside of urban plumes were usually <1 ppbv.

Figure 2 shows the maximum NO_x and HNO₃ 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 m s^{-1} , 600 km distance represents one day of transport. HNO₃ 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 ΣNO_{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 ΣNO_{y_i} in urban plumes by using the correlation slope between CO and ΣNO_{y_i} determined from linear least squares fits (Figure 3). CO and ΣNO_{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 ΣNO_{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 ΣNO_{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_x 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_x 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

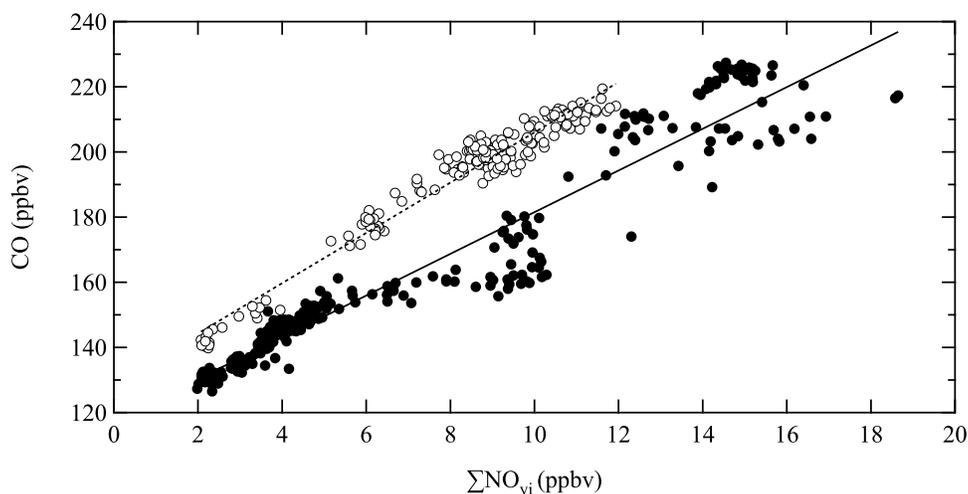


Figure 3. Measurements of CO and ΣNO_{y_i} in fresh (solid circles) and aged (open circles) urban plumes. The fresh plume was sampled 40 km from New York City on 25 July, where $\text{NO}_x/\Sigma\text{NO}_{y_i} = 0.96$ and $\text{HNO}_3/\Sigma\text{NO}_{y_i} = 0.04$. $\text{CO}/\Sigma\text{NO}_{y_i}$, 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_x 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_{y_i} correlation slopes for each urban plume versus NO_x/ΣNO_{y_i}, where NO_x/ΣNO_{y_i} 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_x emission ratio is captured in the measurements here. In the 14 fresh plumes with NO_x/ΣNO_{y_i} > 0.8, CO/ΣNO_{y_i} 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_{y_i}.

[23] CO to ΣNO_{y_i} 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 HNO₃ and transported for several days over the North Atlantic Ocean, CO/ΣNO_{y_i} was within the range of emission ratios measured in the fresh plumes (Figure 4). In 45 aged plumes with NO_x/ΣNO_{y_i} < 0.2, CO/ΣNO_{y_i} was 8.1 ± 4.0, with a median of 7.6 and a range from 3 to 21. The higher average CO/ΣNO_{y_i} in the aged plumes compared to the fresh plumes indicates that reactive nitrogen removal occurred in some plumes. In plumes where most emitted NO_x had been oxidized to HNO₃ and CO/ΣNO_{y_i} was largely unchanged from the time of emission, HNO₃ was transported efficiently

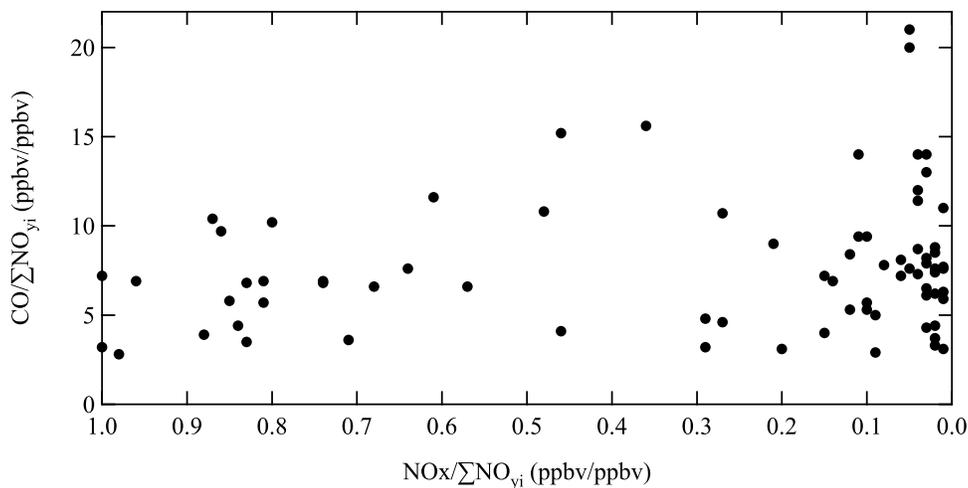


Figure 4. CO to ΣNO_{y_i} correlation slopes in 92 urban plumes, plotted as a function of plume age as represented by the corresponding NO_x to ΣNO_{y_i} correlation slope.

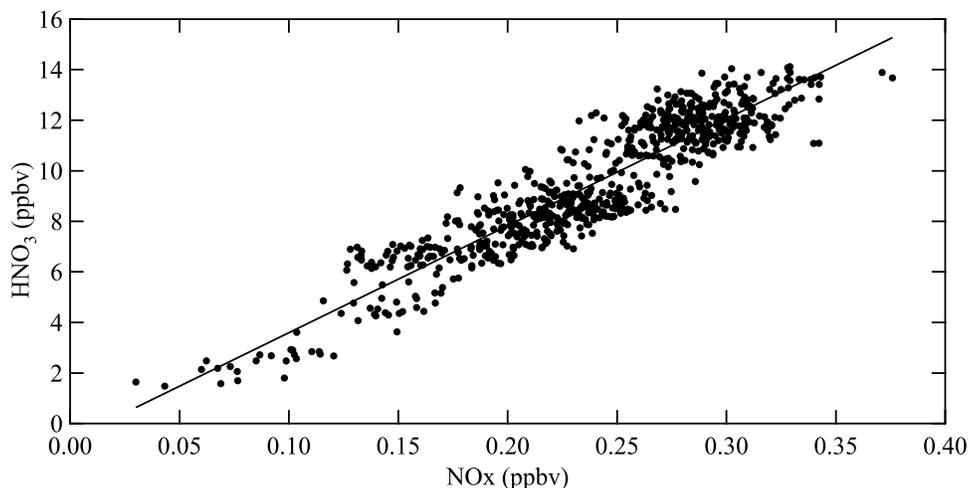


Figure 5. One-second HNO_3 and NO_x measurements in an urban plume on 21 July, 860 km NE of New York City at 320 m altitude. The HNO_3 to NO_x ratio is determined from the slope of the linear least squares fit to be 42 ppbv/ppbv (solid line) with a square of the correlation coefficient $r^2 = 0.85$.

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

4. NO_x Production From HNO_3 Photochemistry

[24] The large abundance of HNO_3 transported over one day in many urban plumes was important to continued O_3 and NO_x production during transport. HNO_3 destruction by photolysis or OH oxidation forms NO_x , which is then available to promote O_3 production in more remote regions. Typical 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 + HNO_3 reaction of $1.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, the rate of HNO_3 destruction by OH oxidation would be approximately half as fast. During this study in July and August near 43°N latitude, the days were approximately 15 hours long. Hence the HNO_3 lifetime to photolysis and OH oxidation was approximately 18 days. If 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 HNO_3 concentrations elevated to tens of ppbv levels for several days (Figures 1 and 2), HNO_3 photochemistry results in substantial NO_x reformation. For example, in 1 day ($\sim 5\%$ of the HNO_3 lifetime), 20 ppbv of HNO_3 would be expected to produce over 1 ppbv of NO_x .

[25] The relationship between HNO_3 and NO_x in urban plumes helps identify the processes controlling the abundance of the reactive nitrogen species. HNO_3 to NO_x enhancement ratios are determined from correlation slopes of linear least squares fits of the 1 s measurements of HNO_3 to NO_x in urban plumes, as shown in Figure 5. The correlation between HNO_3 and 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 HNO_3 had been formed in the plume and most HNO_3 present was

of different origin than the fresher plume NO_x . As HNO_3 was formed in the plume from NO_x oxidation, the correlation between HNO_3 and NO_x increased. If inhomogeneous depositional processes recently removed HNO_3 from plumes, then the correlation between HNO_3 and NO_x would also be reduced in aged plumes. The observed increase in the correlation coefficients with plume age suggests that HNO_3 and NO_x were linked photochemically and were not strongly affected by recent and sporadic external loss processes or NO_x injections. Highly aged plumes with extensive NO_x oxidation were identified using the measured CO to NO_x ratios. Figure 6 shows a histogram of HNO_3 to NO_x correlation slopes in highly aged plumes, where $\text{CO}/\text{NO}_x > 100$ so that at least 90% of the NO_x was oxidized. Although varying levels of NO_x oxidation resulted in a wide distribution of values, the central 2/3 of the HNO_3/NO_x ratios in highly aged plumes ranged from 13 to 42.

[26] The importance of HNO_3 removal can be assessed by comparing the observations with solutions of rate equations for HNO_3 and NO_2 . The steady state solution for the ratio of HNO_3 to NO_x has been commonly used to examine the role of 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 HNO_3 , since the VOC- NO_x photochemistry favored HNO_3 formation relative to PAN. Thus, as a first approximation, only the interconversion between HNO_3 and NO_2 is considered. Neglecting all other loss mechanisms for HNO_3 and 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_{HNO_3} is the 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 HNO_3 that reform NO_2 , and

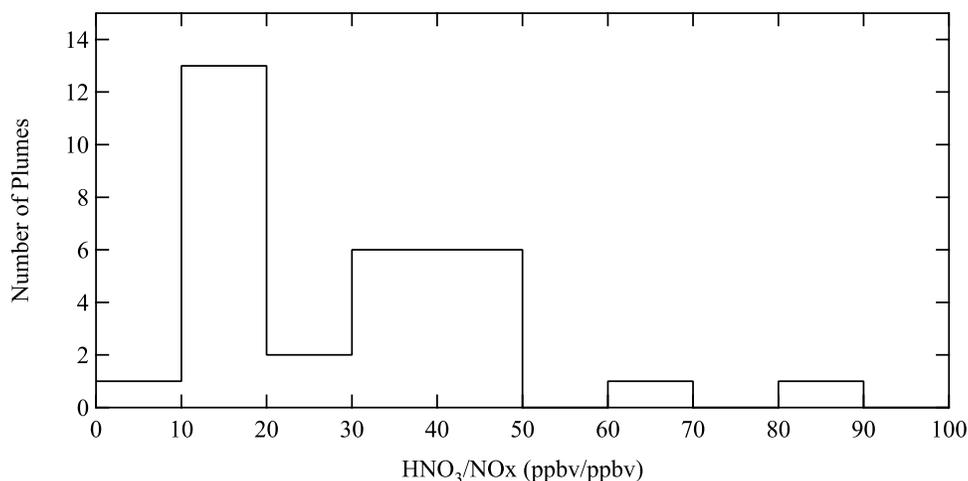


Figure 6. A histogram of the number of highly aged urban plumes with CO/NO_x > 100 as a function of the plume HNO₃ to NO_x ratio.

$k_{\text{OH}+\text{NO}_2} = 1.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (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 HNO₃/NO₂ 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 O₃ levels were over 90 ppbv and NO₂ and NO were in steady state with NO₂ approximately 5 times larger than NO. HNO₃/NO_x is calculated from HNO₃/NO₂ and the small measured NO to NO_x fraction. Using diurnally averaged values for OH and j_{HNO_3} , the photochemical steady state value for HNO₃/NO_x is calculated from the equation above to be 26. Solution of the time-dependent rate equations for HNO₃ and NO₂ 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⁻¹.

[28] The observed HNO₃/NO_x in plumes that were 1–2.5 days old were occasionally different from calculated using the rate equations above (Figure 6). Values of HNO₃/NO_x lower than the steady state ratio can be explained by HNO₃ removal during transport or insufficient plume aging to achieve steady state. Values of HNO₃/NO_x greater than the calculated steady state value suggest that additional processes may have converted NO_x to HNO₃. At night, reactions involving the nitrate radical can produce HNO₃. N₂O₅ hydrolysis is the most important HNO₃ formation process, where the N₂O₅ is formed from reactions of NO₂ with O₃ to form NO₃, followed by further reactions with NO₂ to form N₂O₅. This conversion of NO_x to HNO₃ influences the reactive nitrogen partitioning in plumes that were transported through the night. At night, photochemis-

try that destroys HNO₃ is inactive, so that nocturnal processing is predicted to increase HNO₃/NO_x 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 HNO₃ was set to zero in the model to test if the observations were consistent with very slow dry deposition. N₂O₅ hydrolysis rates were faster than the reaction of NO₂ and O₃ to form NO₃, which is the rate limiting step for the conversion of NO_x to HNO₃ at night [Brown *et al.*, 2004]. Figure 7 shows the predicted HNO₃, NO_x, and HNO₃/NO_x ratio versus time. The inclusion of nighttime chemistry forces the HNO₃/NO_x ratio to higher values and at earlier times compared to the simplified rate equations that neglect processing at night. At night, the HNO₃/NO_x ratio is predicted to rise sharply when NO_x is converted to HNO₃ via N₂O₅ hydrolysis. Since flights were not performed at night over the remote North Atlantic Ocean, the importance of N₂O₅ hydrolysis to HNO₃ and NO_x levels in highly aged plumes could only be determined from the measurements during the day. During the day, HNO₃ is destroyed by OH and photolysis, such that NO_x increases and HNO₃/NO_x decreases, and the effects of nighttime chemistry upon HNO₃ formation and NO_x loss were partially obscured. Despite these limitations, observed HNO₃/NO_x ratios greater than the photochemical steady state value can be explained by box model calculations that include nighttime production of HNO₃ from NO_x in addition to photochemical reactions that interconvert NO_x and HNO₃.

5. Discussion

[30] The efficient transport of HNO₃ redistributes NO_x oxidation products far from the source of emission

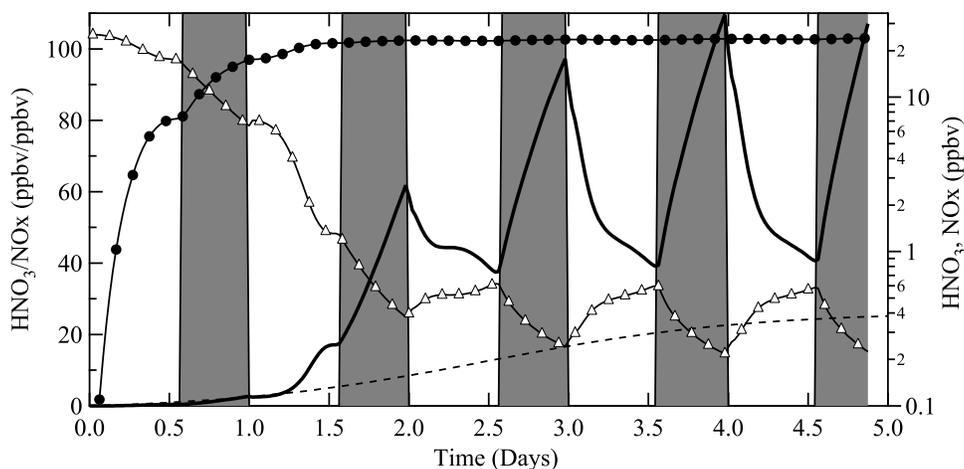


Figure 7. HNO_3/NO_x ratio (solid line), HNO_3 (solid circles), and NO_x (open triangles) predicted using box model calculations that includes daytime and nighttime chemistry. The dashed line neglects nocturnal processing and considers only photochemistry that interconverts HNO_3 and NO_x , and uses 24-hour average values for HNO_3 photolysis rates and 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 HNO_3 levels in the plumes were eventually reduced, since background HNO_3 levels are low compared to the plume observations. Since 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. 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°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 HNO_3 would be removed rapidly. If these plumes encounter precipitation, the 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 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, HNO_3 loss or recent NO_x injections caused measured HNO_3/NO_x to fall far below the modeled steady state values [e.g., Liu et al., 1992; Jaegle et al., 1998], whereas HNO_3/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 HNO_3 is greatly reduced when the air is neither lifted nor mixed downward. Consequently, HNO_3 and HNO_3/NO_x are higher in this low-level transport compared to studies in the free troposphere. Furthermore, the high HNO_3/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 HNO_3 to NO_x need not be hypothesized.

[32] The remote marine atmosphere can be a region of photochemical O_3 destruction or production, depending upon the NO_x levels. Below a few tens of pptv of NO_x , photochemical O_3 destruction dominates in the lower troposphere [Chameides et al., 1992; Jacob et al., 1996], whereas net O_3 production is expected at higher NO_x levels. In aged plumes, enhancements in NO_x were typically several hundred pptv, and up to 1.2 ppbv. Observed HNO_3/NO_x ratios were reproduced by a box model that showed photochemical NO_x production from HNO_3 . Hence gas phase HNO_3 destruction via photolysis and reaction with OH enhances the lifetime of NO_x in these plumes and maintains NO_x at levels high enough to allow for continuing photochemical O_3 production. Enhanced O_3 to CO relationships have been observed in North American pollution outflow at PICO-NARE, a remote mountaintop site located in the Azores. O_3 and 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 O_3 production in plumes that were transported for days over the ocean. Efficient transport of HNO_3 above the MBL provides a mechanism for continued O_3 production that may explain the elevated O_3 to CO relationships observed at a remote marine site. 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 HNO_3 during the 4–7 day transport period. 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 HNO_3 suggests that 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 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, 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, 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 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 HNO_3 above the MBL is a common occurrence. The same efficient transport of HNO_3 observed here may exist over cold land surfaces, where highly stable layers are also formed.

6. Conclusions

[36] 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. 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 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 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 HNO_3 in plumes transported for days is important photochemically, since destruction of HNO_3 by photolysis and OH reaction reforms NO_x . In the troposphere, HNO_3 is frequently considered to be an irreversible sink for NO_x , since the HNO_3 lifetime to depositional loss is usually much faster than photochemical processes that reform NO_x . This assumption is not always valid for stratified low-level outflow over water, where HNO_3 is transported efficiently in the absence of precipitation or surface loss. The high correlation between HNO_3 and NO_x and the high values of HNO_3/NO_x are consistent with box model calculations that neglect heterogeneous removal of HNO_3 . In plumes transported up to 1000 km from the coast, NO_x levels were hundreds of pptv, which is high enough to maintain photochemical O_3 production.

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