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Journal

Journal of Geophysical Research, 112(D12)

ISSN

0148-0227

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Publication Date

2007

DOI

10.1029/2006jd007664

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Reactive nitrogen distribution and partitioning in the North American troposphere and lowermost stratosphere

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Received 15 June 2006; revised 21 November 2006; accepted 7 December 2006; published 4 April 2007.

[1] A comprehensive group of reactive nitrogen species (NO, NO₂, HNO₃, HO₂NO₂, PANs, alkyl nitrates, and aerosol-NO₃⁻) were measured over North America during July/August 2004 from the NASA DC-8 platform (0.1–12 km). Nitrogen containing tracers of biomass combustion (HCN and CH₃CN) were also measured along with a host of other gaseous (CO, VOC, OVOC, halocarbon) and aerosol tracers. Clean background air as well as air with influences from biogenic emissions, anthropogenic pollution, biomass combustion, convection, lightning, and the stratosphere was sampled over the continental United States, the Atlantic, and the Pacific. The North American upper troposphere (UT) was found to be greatly influenced by both lightning NO_x and surface pollution lofted via convection and contained elevated concentrations of PAN, ozone, hydrocarbons, and NO_x. Observational data suggest that lightning was a far greater contributor to NO_x in the UT than previously believed. PAN provided a dominant reservoir of reactive nitrogen in the UT while nitric acid dominated in the lower troposphere (LT). Peroxynitric acid (HO₂NO₂) was present in sizable concentrations peaking at around 8 km. Aerosol nitrate appeared to be mostly contained in large soil based particles in the LT. Plumes from Alaskan fires contained large amounts of PAN and aerosol nitrate but little enhancement in ozone. A comparison of observed data with simulations from four 3-D models shows significant differences between observations and models as well as among models. We investigate the partitioning and interplay of the reactive nitrogen species within characteristic air masses and further examine their role in ozone formation.

Citation: Singh, H. B., et al. (2007), Reactive nitrogen distribution and partitioning in the North American troposphere and lowermost stratosphere, *J. Geophys. Res.*, 112, D12S04, doi:10.1029/2006JD007664.

1. Introduction

[2] Reactive nitrogen species play a central role in the chemistry of the polluted and unpolluted atmosphere.

They critically determine levels of ozone, acidity, and atmospheric oxidation potential [Crutzen, 1979; Singh et al., 2003a]. When deposited, they act as nutrients in terrestrial and marine ecosystems. The main known constituents of reactive nitrogen in the troposphere are NO, NO₂, peroxyacyl nitrates (PANs; RC(O)OONO₂), nitric acid (HNO₃), peroxynitric acid (HO₂NO₂), alkyl and multifunctional nitrates (RONO₂), and particulate nitrate (NO₃⁻). Other less abundant constituents such as HONO, NO₃, and N₂O₅ play an important role in nighttime chemistry but are quickly decomposed in sunlight [Brown et al., 2006]. Similarly, somewhat long-lived species such as HCN and CH₃CN (lifetime ≈ 6 months) are globally abundant products of biomass combustion [Singh et al., 2003b, and references therein]. In most previous studies it was only possible to measure a subset of these reactive nitrogen species and often the data were limited to the LT. The Intercontinental Chemical Transport Experiment-A (INTEX-A) offered a unique opportunity to investigate the partitioning and distribution of reactive nitrogen species

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from the North American troposphere at a level of detail previously not possible.

[3] INTEX-A was a major field campaign conducted principally over North America and the Atlantic in the summer of 2004 under an international consortium called ICARTT (International Consortium for Atmospheric Research on Transport and Transformation). The ICARTT effort was jointly organized by partners from the United States, Canada, United Kingdom, Germany, and France and its design and implementation was closely coordinated [Fehsenfeld *et al.*, 2006; Singh *et al.*, 2006]. A comprehensive suite of trace gases, aerosols, chemical tracers, and meteorological parameters were measured aboard the NASA DC-8 and its partner aircraft. In this manuscript we mainly use observations from the DC-8 to describe the distribution and partitioning of measured odd nitrogen and its relationship with ozone under polluted and pristine conditions. Observational data are also compared with simulations from multiple models of transport and chemistry to assess our present knowledge of photochemical theory as well as sources and sinks of reactive nitrogen.

2. Measurements

[4] The intensive observational phase of INTEX-A was carried out from 1 July to 15 August 2004 over North America. The NASA DC-8 conducted 18 science flights extending from the mid-Pacific to the mid-Atlantic and covered much of the troposphere (0.2–12 km). The most intensive sampling was done over the eastern United States in collaboration with the NOAA P-3 that operated below 7 km altitude. During this period, the UK BAe146 (ceiling 10 km) and the German Falcon (ceiling 13 km) sampled air downwind of North America over the Atlantic Ocean. A map of the geographical extent covered during INTEX-A/ICARTT and a summary of instrumentation and individual flights is provided in the overview papers by Singh *et al.* [2006] and Fehsenfeld *et al.* [2006]. The meteorological description for the region and for each of the missions is described by Fuelberg *et al.* [2007] who also provided detailed 5–10 day back trajectories along DC-8 flight tracks for the entire mission.

[5] The NASA DC-8 aircraft was equipped with several in situ instruments measuring ozone, reactive nitrogen and hydrogen species, aerosol composition and microphysics, and a variety of chemical tracers. Nitrogen containing constituents measured aboard the NASA DC-8 included NO, NO₂, HNO₃, HO₂NO₂, PAN, PPN, alkyl nitrates, aerosol nitrate, HCN, and CH₃CN. Observations of NO₃ and N₂O₅, measured on the NOAA P-3, were also available for analysis [Brown *et al.*, 2006]. The methods used to measure these species have been previously published and are summarized by Singh *et al.* [2006] and Fehsenfeld *et al.* [2006]. Simply stated, ozone was measured by NO/O₃ chemiluminescence, PANs by electron-capture gas-chromatography (GC), HO₂NO₂ by Chemical Ionization Mass Spectrometry (CIMS), nitric acid by mist chamber/IC analysis, aerosol nitrate by filter collection/IC analysis, hydrocarbons/simple alkyl nitrates by grab sampling and subsequent GC-FID/MS analysis, NO₂ by a Laser-Induced-Fluorescence (LIF), NO by chemiluminescence, and nitriles by GC using a Reduction Gas Detector. The sum of all

peroxyacyl nitrates (Σ PANs) and of alkyl and multifunctional nitrates (Σ ANs) were measured using thermal dissociation (TD) and LIF detection of NO₂ [Day *et al.*, 2002]. Note we define the sum of the simple alkyl nitrates as Σ RONO₂ and refer to measurements of this entire class of species as Σ ANs in this manuscript.

[6] A fast response CIMS instrument on the NOAA P-3 [Flocke *et al.*, 2005] measured PAN and PPN, which were found to be linearly correlated ([PPN] = 0.11 [PAN]; R² = 0.86). We have used this relationship for estimating PPN from PAN when appropriate. We also note that the NO instrument on the DC-8 had limited sensitivity and was only suitable for measuring mixing ratios >100 ppt. NO calculated from NO₂ data (sensitivity \approx 10 ppt) using a steady state box model [Crawford *et al.*, 1999] agreed well with measured values for NO > 100 ppt. To obtain a uniform data set we have defined NO_x as the sum of measured NO₂ and calculated NO.

3. Data Analysis and Models

[7] Merged data files were created to align species measured with varying time resolutions and these files are used in this study. We have also used a variety of chemical and meteorological filters for purposes of air mass characterization. The principal chemical filter for this study was based on CO mixing ratios. When CO data were unavailable, C₂H₆ or C₂H₂ observations, which tended to be linearly correlated with CO, were used to fill data gaps. Although INTEX-A data were principally obtained in the troposphere, stratospheric influences were frequently encountered. Two stratospherically influenced data subsets were created. These included a stringent subset (O₃ > 200 ppb; CO < 60 ppb; and Z > 7 km) used primarily for defining the composition of the lowermost stratosphere (LMS). A somewhat looser definition (O₃ > 120 ppb; H₂O < 100 ppm and Z > 7 km) was employed to remove mixed stratospheric/tropospheric influences from the tropospheric subset. Tropospheric data were further divided into (1) clean background (CO: 60–90 ppb or C₂H₆: 250–600 ppt), (2) polluted air masses (CO: 90–240 ppb or C₂H₆: 600–3000 ppt), and (3) episodic (CO > 240 ppb or C₂H₆ > 3000 ppt). Figures 1a and 1b show the atmospheric distribution of HCN and CO for these subsets. HCN is a unique tracer of biomass combustion [Singh *et al.*, 2003b] while CO is a more generic tracer of all pollution. It is evident from HCN profiles that biomass burning influences were present throughout the troposphere during all periods of pollution. Episodic events contained enhanced signatures of biomass combustion. Furthermore, both HCN and CO profiles provided a reasonable description of what can be expected to be present in the clean background air from historical data in this season [Holloway *et al.*, 2000; Zhao *et al.*, 2002; Edwards *et al.*, 2004]. Multiple tracers were also used to identify specific plumes originating from forest fires, anthropogenic emissions, convection and lightning, and the stratosphere. Data were also segregated geographically to represent Pacific, Atlantic, and continental regions. Total reactive nitrogen (NO_y), was defined as follows:

$$\text{NO}_y = \text{NO} + \text{NO}_2 + \text{HNO}_3 + \text{PAN} + \text{PPN} + \text{HO}_2\text{NO}_2 + \Sigma\text{RONO}_2 + \text{NO}_3^-$$

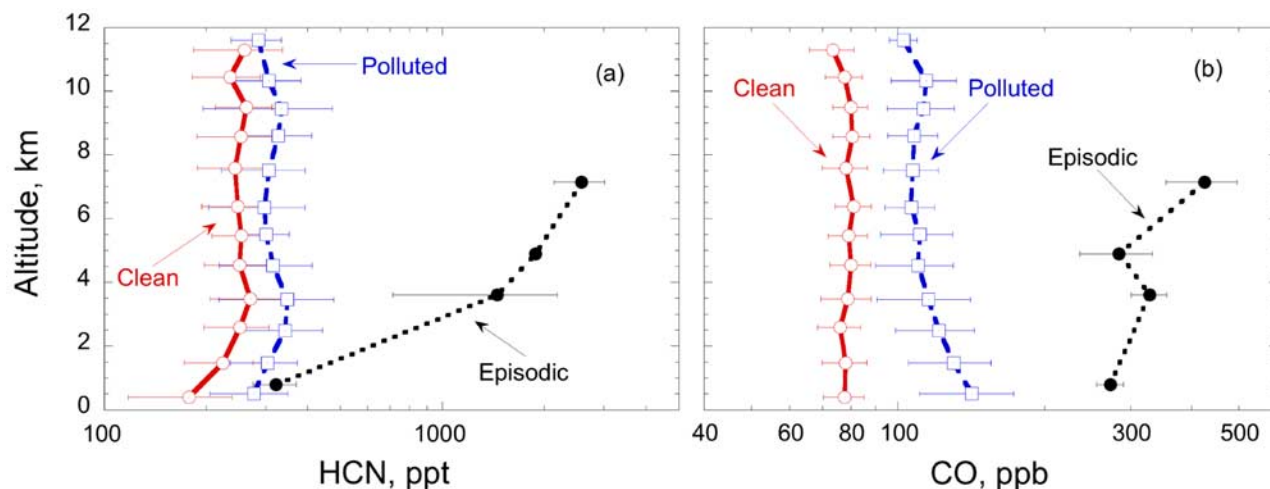


Figure 1. Distribution of two selected tracer species ((a) HCN and (b) CO) under “background,” “polluted,” and “episodic” conditions. See text for more detail.

In several previous studies the extent to which aerosol nitrate was sampled as NO_y has not been accurately identified [Miyazaki *et al.*, 2005]. During INTEX-A, aerosol nitrate was a small fraction of the total NO_y and has been included. N_2O_5 and NO_3 concentrations, as measured on the NOAA P-3, were extremely low and contributed negligibly to NO_y during daytime and minimally ($<0.1\%$ for $Z > 1$ km) at night [Brown *et al.*, 2006]. The above definition of NO_y also omits the complex organic nitrates observed as ΣANs resulting in some bias due to this omission in the boundary layer.

[8] The data collected during INTEX-A were compared with results from three global and one regional chemical transport models (CTMs). The three global CTMs used in this study included GEOS-CHEM [Bey *et al.*, 2001;

Hudman *et al.*, 2007], MOZART [Horowitz *et al.*, 2003; Pfister *et al.*, 2005], and RAQMS [Pierce *et al.*, 2003, 2007]. The global models had a $2^\circ \times 2.5^\circ$ nominal resolution. The regional model STEM had finer resolution and derived its boundary conditions from the MOZART global model [Tang *et al.*, 2004, 2007]. The meteorological and emission fields input into these models were determined independently by each group. The total global NO_x source in these models varied from 40 to 50 Tg N yr^{-1} . However, the distribution of these emissions varied according to the model. For example, global lightning source of NO_x (Tg N yr^{-1}) in RAQMS, GEOS-CHEM, and MOZART was 3, 5, and 9 respectively, prior to adjustment of the lightning NO_x source to match the profiles observed during INTEX-A. More details on these models and their simulation techniques are

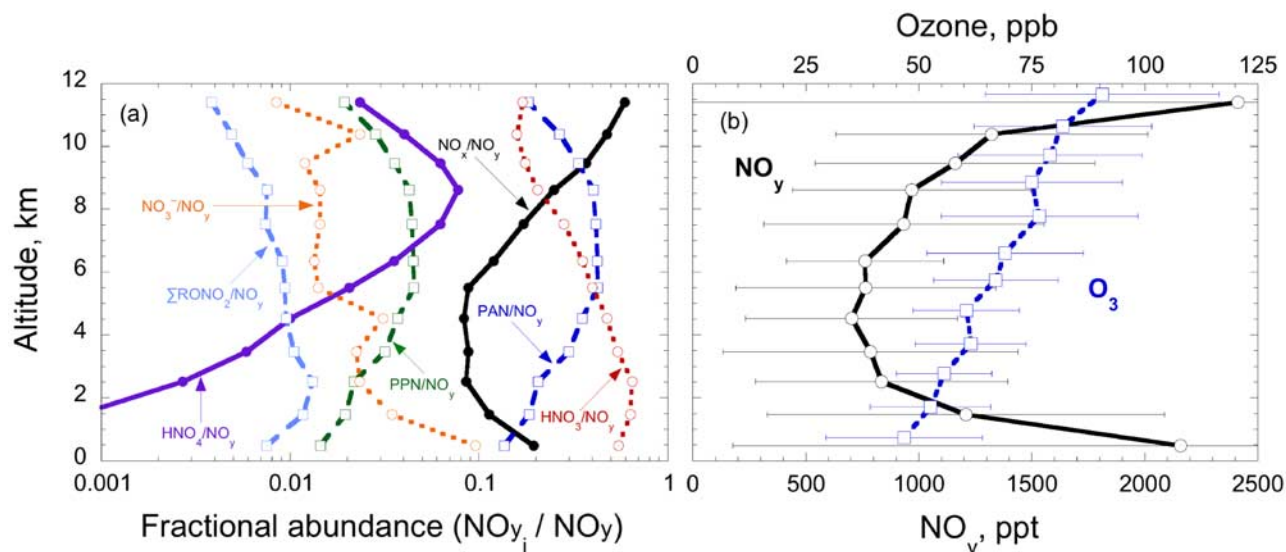


Figure 2. (a) Partitioning of reactive nitrogen in the troposphere and (b) the mean vertical structure of O_3 and NO_y based on INTEX-A observations.

Table 1. Reactive Nitrogen, O₃, and CO Mixing Ratios in the North American Troposphere During INTEX-A

Altitude, km	O ₃ , ppb	CO, ppb	NO _x , ppt	HNO ₃ , ppt	PAN, ppt	PPN, ppt	HO ₂ NO ₂ , ppt	NO ₃ ⁻ , ppt	NO _x , ppt	∑RONO ₂ , ppt	HCN, ppt	CH ₃ CN, ppt
0–2	48.9 ± 16.2 (48.4, 2607) ^a	132.1 ± 37.2 (127.4, 2079)	379 ± 823 (148, 1866)	893 ± 824 (701, 2467)	301 ± 339 (186, 1666)	32 ± 36 (20, 1666)	5 ± 8 (2, 78)	154 ± 183 (101, 1834)	1781 ± 1699 (1374, 1283)	18 ± 13 (15, 1473)	274 ± 76 (267, 1007)	136 ± 35 (132, 1007)
2–4	58.7 ± 11.8 (58.4, 1332)	112.7 ± 35.3 (107.6, 1107)	64 ± 63 (52, 975)	488 ± 358 (404, 1279)	214 ± 245 (158, 1021)	23 ± 26 (17, 1021)	10 ± 23 (2, 615)	110 ± 180 (34, 418)	809 ± 610 (652, 766)	11 ± 7 (9, 899)	337 ± 172 (310, 582)	153 ± 80 (138, 587)
4–6	63.3 ± 13.1 (62.6, 1268)	103.3 ± 26.7 (99.6, 1027)	54 ± 39 (47, 976)	317 ± 234 (269, 1216)	275 ± 228 (217, 981)	29 ± 24 (23, 981)	15 ± 31 (8, 1094)	90 ± 202 (10, 511)	733 ± 523 (613, 737)	9 ± 4 (8, 828)	296 ± 121 (285, 563)	144 ± 69 (136, 570)
6–8	72.4 ± 19.7 (71.3, 1492)	104.7 ± 51.8 (96.9, 1241)	113 ± 85 (92, 1154)	252 ± 185 (210, 1415)	354 ± 253 (298, 1106)	38 ± 27 (32, 1106)	41 ± 34 (73 ± 40)	58 ± 202 (13, 786)	849 ± 511 (755, 856)	9 ± 5 (8, 907)	308 ± 258 (273, 630)	148 ± 97 (137, 667)
8–10	76.6 ± 20.2 (74.3, 1523)	102.3 ± 20.9 (101.3, 1175)	323 ± 288 (240, 1256)	202 ± 186 (146, 1497)	371 ± 217 (339, 1138)	39 ± 23 (36, 1138)	73 ± 40 (66, 1406)	27 ± 45 (11, 909)	1040 ± 570 (931, 923)	10 ± 6 (9, 954)	315 ± 138 (297, 595)	138 ± 40 (133, 720)
10–12	82.7 ± 20.5 (82.2, 942)	96.5 ± 22.8 (93.7, 687)	776 ± 900 (552, 700)	205 ± 153 (159, 901)	338 ± 208 (295, 650)	36 ± 22 (31, 650)	53 ± 30 (49, 868)	34 ± 60 (21, 818)	1430 ± 1052 (1197, 465)	8 ± 6 (7, 586)	274 ± 73 (284, 404)	141 ± 20 (141, 406)
0–12	64.2 ± 20.9 (62.9, 9164)	112.3 ± 37.8 (106.2, 7316)	275 ± 572 (106, 6927)	462 ± 558 (285, 8775)	308 ± 269 (246, 6562)	33 ± 28 (26, 6562)	42 ± 41 (29, 5414)	90 ± 167 (28, 5276)	1152 ± 1099 (829, 5030)	12 ± 9 (9, 5647)	299 ± 153 (285, 3781)	142 ± 63 (136, 3967)

^aMean ± sigma (median, number of points).**Table 2.** Alkyl Nitrate (C₁–C₅) Mixing Ratios in the North American Troposphere During INTEX-A

Altitude, km	CH ₃ ONO ₂ , ppt	C ₂ H ₅ ONO ₂ , ppt	i-C ₃ H ₇ ONO ₂ , ppt	n-C ₃ H ₇ ONO ₂ , ppt	2-C ₄ H ₉ ONO ₂ , ppt	3-C ₄ H ₉ ONO ₂ , ppt	2-C ₅ H ₁₁ ONO ₂ , ppt	∑RONO ₂ , ppt	∑ANs, ^a ppt
0–2	2.3 ± 0.7 (2.1, 1467) ^b	2.3 ± 1.1 (2.0, 1467)	5.4 ± 4.0 (4.4, 1467)	0.7 ± 0.5 (0.6, 1467)	4.6 ± 4.5 (3.5, 1467)	1.4 ± 1.4 (1.1, 1469)	1.8 ± 2.0 (1.3, 1473)	18 ± 13 (15, 1473)	191 ± 204 (147, 1713)
2–7	1.9 ± 0.4 (1.9, 2198)	1.5 ± 0.5 (1.5, 2198)	2.9 ± 1.7 (2.6, 2198)	0.3 ± 0.2 (0.3, 2198)	2.1 ± 2.0 (1.6, 2198)	0.5 ± 0.6 (0.3, 2214)	0.5 ± 0.7 (0.3, 2219)	10 ± 6 (9, 2219)	10 ± 6 (9, 2219)
7–12	2.1 ± 0.5 (2.1, 1890)	1.7 ± 0.7 (1.6, 1890)	3.7 ± 3.0 (2.9, 1890)	0.3 ± 0.2 (0.2, 1900)	1.5 ± 2.1 (0.7, 1894)	0.2 ± 0.5 (0.1, 1936)	0.1 ± 0.3 (0.0, 1950)	10 ± 6 (8, 1950)	10 ± 6 (8, 1950)

^aSum of alkyl nitrates (∑ANs) was measured in the lower troposphere (Z < 4 km) by thermally dissociating these to NO₂ (see text).^bMean ± sigma (median, number of points).

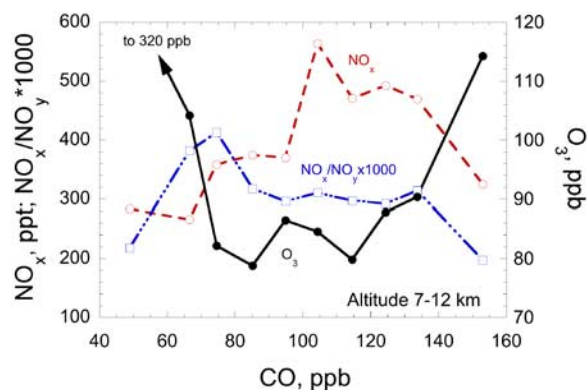


Figure 3. Mean mixing ratios of NO_x and O_3 as a function of CO. The data are binned for 7–12 km altitude and show the transition from the upper troposphere to lowermost stratosphere. Larger NO_x/NO_y ratios indicate more recent NO_x injections.

being published separately [Hudman *et al.*, 2007; Pierce *et al.*, 2007; Tang *et al.*, 2007].

4. Results and Discussion

4.1. Partitioning and Atmospheric Behavior of Reactive Nitrogen

[9] Figures 2a and 2b show the partitioning of reactive nitrogen in the troposphere and the mean vertical structure of O_3 and NO_y based on data collected in INTEX-A. Table 1 provides additional statistical information on the vertical structure of selected reactive nitrogen and tracer species. Table 2 shows the breakdown of individual C_1 – C_5 alkyl nitrates, whose sum is presented in Figure 2a and Table 1, in altitude bins representing lower troposphere (LT; 0–2 km), middle troposphere (MT; 2–7 km) and upper troposphere (UT; 7–12 km). The measured sum of alkyl nitrates ($\sum \text{ANs}$) in the boundary layer was approximately 10 times larger than the sum of individually measured straight chain alkyl nitrates (Table 2), indicating the dominance of more complex organic nitrates. Calculations of the alkyl nitrate production rate following the methods outlined by Rosen *et al.* [2004] and Cleary *et al.* [2005] and using the observed VOC, indicate that isoprene oxidation is by far the largest single source of RONO_2 in the boundary layer. The sum of isoprene nitrate and other alkyl and multifunctional nitrates contribute about 10% to the mean NO_y in the continental boundary layer. Horowitz *et al.* [2007] have used these observations along with a CTM to constrain the chemistry of isoprene nitrate production and loss and the isoprene nitrate deposition rate. They find that relatively slow production rates, fast loss rates, and fast deposition velocities are required to match the data. All of these combine to reduce the concentration of isoprene nitrates relative to options employed in other models.

[10] It is evident from Figure 2a that although reactive nitrogen is principally emitted as NO , throughout much of the troposphere it largely exists in its secondary reservoir forms. The total column of NO_x in the troposphere constituted only about 15% of available NO_y . PAN and HNO_3 together contained around 65% of NO_y , with PAN dominating in the UT and HNO_3 in the LT. A moderate fraction

($\approx 5\%$) of reactive nitrogen in the UT was also due to HO_2NO_2 , which was directly measured for the first time in this mission [Huey *et al.*, 2007]. Gaseous and aerosol nitrates comprised a very small fraction ($< 5\%$) of the tropospheric NO_y reservoir. NO_x was the dominant reactive nitrogen species at altitudes above 9 km (Figure 2a). As stated earlier, higher organic nitrates (e.g., isoprene nitrate) may contribute up to 10% to NO_y in the continental boundary layer. Unlike O_3 , which increased monotonically with altitude (Figure 2b), NO_y showed a C-shaped profile with high concentrations near the surface and in the UT.

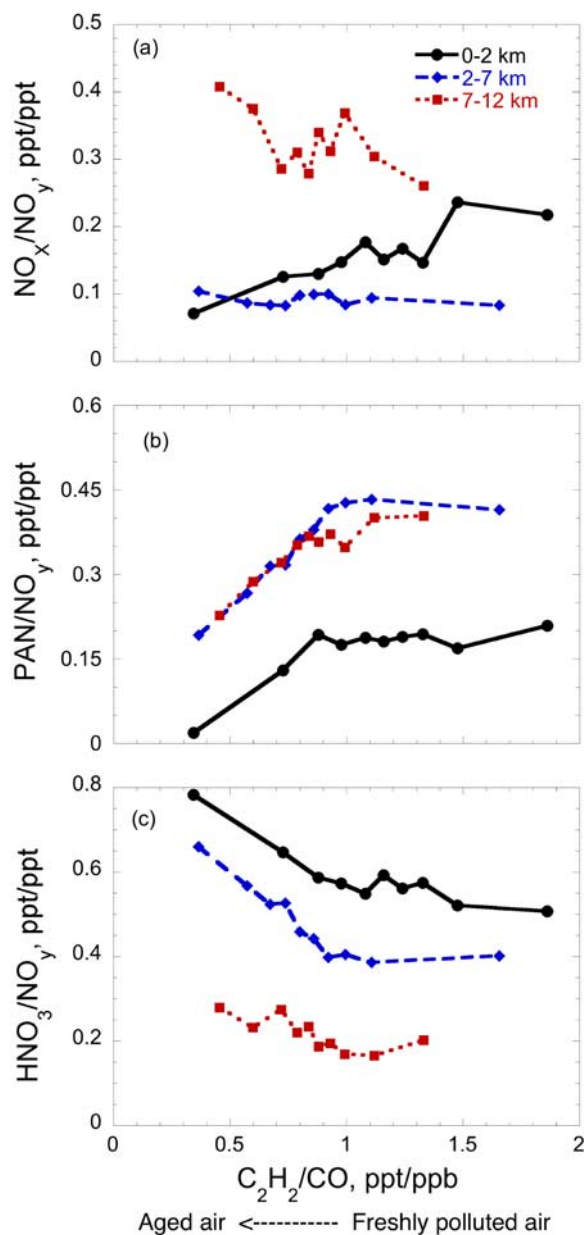


Figure 4. Reactive nitrogen as a function of air mass age in the lower (0–2 km), middle (2–7 km) and upper (7–12 km) troposphere (latitude: 30–50°N, longitude: 260–320°E). Air mass age is defined with reference to time from emission (“chemical clock”). All data were divided into 10 age bins. Each point shown above represents an average of 60–120 observed data points.

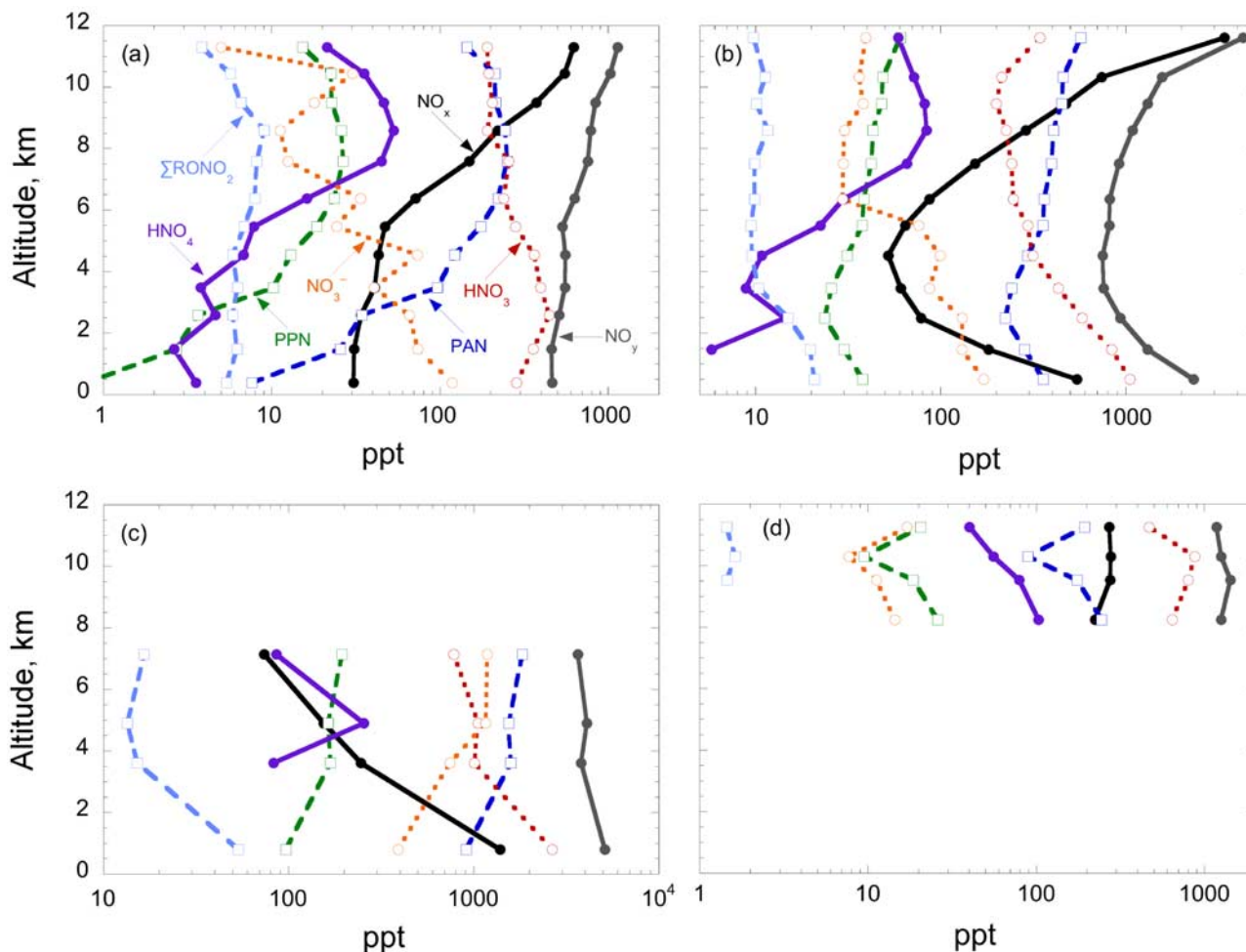


Figure 5. Reactive nitrogen species in the troposphere and lowermost stratosphere. (a) “Background/clean,” (b) “polluted,” (c) “episodic,” and (d) “lowermost stratospheric.” See text for more detail.

[11] Figure 3 shows a plot of NO_x , NO_x/NO_y , and O_3 as a function of CO for the 7–12 km altitude bin. CO is chosen as a convenient tracer that can be used to indicate stratospheric influences (low CO) as well as pollution (high CO). The UT mean NO_x mixing ratios of 300–500 ppt observed during INTEX-A were similar to those previously reported by Brunner *et al.* [2001] from eastern North America and can be considered fairly typical of the summer period. Mean NO_x/NO_y ratios (0.2–0.4) exceeded by a factor of two or more those found in the polluted surface layer and values reported from the midlatitude UT downwind of Asia [Singh *et al.*, 1996; Kondo *et al.*, 1997] and North America [Jaegle *et al.*, 1998; Singh *et al.*, 1999; Koike *et al.*, 2000]. These high NO_x/NO_y ratios provide a direct indication of the relative freshness of UT NO_x sources. NO_x levels in the LMS (mean O_3 -320 ppb) were generally elevated but significantly lower than in the UT. The influence of pollution on UT O_3 was also evident and was generally consistent with the calculated net O_3 production rate of about 5 ppb day^{-1} at these NO_x levels. Aged and polluted air masses indicated by high CO and lower NO_x/NO_y , where photochemistry has occurred over a longer time period, were seen to be associated with large O_3 concentrations.

[12] In many previous studies, the $\text{C}_2\text{H}_2/\text{CO}$ ratio has been used as a “chemical clock” to provide a qualitative measure of air mass age since emission. Figure 4 shows a plot of the fractional reactive nitrogen abundance of key species as a function of this age. Because of the relatively short lifetime of NO_x compared to NO_y , NO_x/NO_y is expected to decrease with increasing air mass age. This was clearly found to be the case in the LT (Figure 4a) where the lifetime of NO_x is short (<0.5 days) and NO_x/NO_y decreased by a factor of 3 with age. In the MT (2–7 km), the NO_x/NO_y ratio was both low (≈ 0.1) and nearly independent of age. We believe that this is indicative of the existence of a steady state between the NO_y reservoir species and NO_x { $\text{PAN} \leftrightarrow \text{NO}_2 + \text{PA}$; $\text{HNO}_3 + h\nu \leftrightarrow \text{NO}_2 + \text{OH}$; $\text{HNO}_3 + \text{OH} \rightarrow \text{NO}_2 + \text{O} + \text{H}_2\text{O}$ }. Model calculations by Jaegle *et al.* [1998] show that a NO_x/NO_y ratio in steady state should be between 0.05 and 0.1 in the troposphere. These low NO_x/NO_y ratios were also seen in extremely aged air masses in the LT.

[13] The UT region (7–12 km) behaved completely differently with high NO_x/NO_y ratios that also increased as a function of age. This is only possible if fresh injections of NO_x are being made in the UT. Benzene (C_6H_6) is a

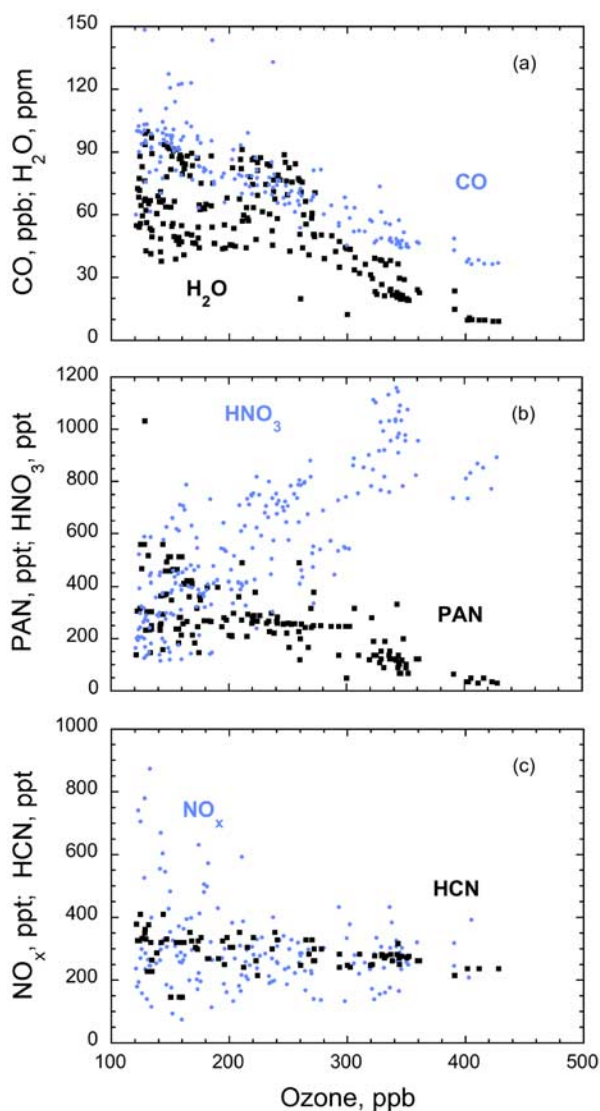


Figure 6. Mixing ratios of key tracer and reactive nitrogen species in the lowermost stratosphere sampled in INTEX-A.

hydrocarbon of surface origin with about a 7-day lifetime, slightly longer than NO_x . $\text{NO}_x/\text{C}_6\text{H}_6$ ratios of about 60 during convective conditions in the UT were significantly higher than the ratios of about 10 observed in the boundary layer even under polluted conditions. This suggests that lofting of surface NO_x by convection could not have contributed more than 20% to the UT NO_x . *Bertram et al.* [2007] analyze the deviation from steady state to show the mean fraction of the UT that is lofted boundary layer air after convection is 17%. Since the mean NO_x in the PBL is on average about half that seen in the UT, this result implies that about 9% of UT NO_x is due to lofted PBL air. Unlike the MT, a steady state with NO_y reservoir species was not achieved in the UT.

[14] During the summer of 2004, wide spread lightning throughout central and eastern North America was observed (M. H. Porter et al., unpublished manuscript, 2006). A gridded (11 km x 11 km) inventory of lightning flashes (cloud-to-ground) over the United States during the entire

INTEX-A period showed 100–250 flashes nearly everywhere east of 110°W with large regions of 500–1600 flash counts. Comparison with previous 6 years suggests that these lightning flash frequencies were slightly above average ($\approx 10\%$) but fairly typical of the summer season. However, lightning sources over North America during INTEX-A required to reproduce the observed UT NO_x were 4–8 times what was assumed in the models (0.4 TgN y^{-1}) [*Martin et al.*, 2006; *Hudman et al.*, 2007; *Cooper et al.*, 2006]. Aircraft emissions add some 0.5 TgN y^{-1} to the UT globally [*Brasseur et al.*, 1998]. We estimate that over North America these emissions ($\approx 0.1 \text{ TgN y}^{-1}$) contribute less than 50 ppt to UT NO_x and made only a small contribution in comparison with lightning effects. As is seen from Figure 3, the lower stratosphere contained much less NO_x than the UT and hence was a minimal contributor. Observations performed over North America in the spring during the SUCCESS campaign showed substantially lower NO_x/NO_y ratios in the UT (≈ 0.15) compared to INTEX-A (≈ 0.3). This is consistent with the seasonal cycle in NO_x reported by *Brunner et al.* [2001] and with the seasonal cycle in lightning.

[15] Unlike NO_x , the response of PAN and HNO_3 to aging was similar at all altitudes (Figure 4). The relative fraction of PAN declined with air mass age, while that of HNO_3 increased. The net increase in HNO_3 with age closely approximated the decrease in PAN. This is consistent with the notion that the PAN reservoir ultimately exerts substantial control on NO_x and subsequently HNO_3 . A separate analysis of PAN chemistry shows PAN is nearly constant once injected into the upper troposphere indicating that most of the aging we observe has occurred in the PBL or MT prior to convection [*Bertram et al.*, 2007].

4.2. Distribution of Reactive Nitrogen

4.2.1. Reactive Gaseous Nitrogen

[16] Figures 5a–5d show the abundance of reactive nitrogen species under “characteristic” conditions in the troposphere and the LMS. Under “clean” or “near background” conditions (Figure 5a), PAN and NO_x were extremely low in the LT where HNO_3 dominated. PAN gradually increased with altitude and in the UT was nearly as abundant as HNO_3 . NO_x mixing ratios increased rapidly above 6 km and became dominant above 8 km. HO_2NO_2 was present in sizable mixing ratios in the UT peaking at about 9 km. HO_2NO_2 , which is highly unstable thermally and easily decomposed at temperatures below 6 km ($\tau < 1$ hours), was present in sizable mixing ratios in the UT peaking at about 8 km. Above 8 km, its loss is slower ($\tau = 6$ –8 hours) mostly determined by reaction with OH and photolysis. The maximum observed at about 8 km coincided with a region of minimum loss. At even higher altitudes the loss rate is nearly constant but production rates are smaller because of reduced HO_2 mixing ratios (X. Ren et al., HOx observation and model comparison during INTEX-NA 2004, unpublished manuscript, 2007, hereinafter referred to as Ren et al., unpublished manuscript, 2007) and air density ($\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2$). In the polluted subset (Figure 5b) nearly all reactive nitrogen concentrations were elevated compared to the background (Figure 5a) and a C-shaped profile with large values in the UT and LT was present for both NO_x and NO_y . A dramatic change

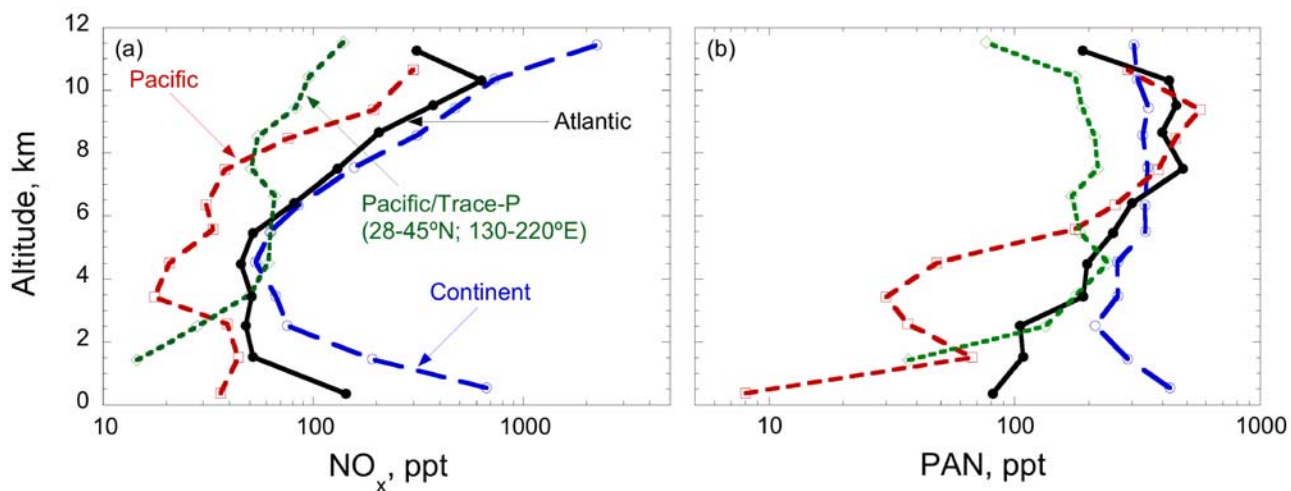


Figure 7. (a) NO_x and (b) PAN over the Pacific, continental North America, and the western Atlantic.

could be seen in PAN, which was now significantly more abundant than HNO_3 at all altitudes above 4 km. HO_2NO_2 still peaked at 9 km but was nearly twice as abundant as under clean conditions largely because of the higher NO_x (as well as HO_x) available under these conditions. Under all conditions, the NO_x levels in the UT were larger than their surface values and could not be attributed to surface pollution alone. Under episodic conditions (Figure 5c), involving extreme levels of pollution, NO_y was extremely high (4–6 ppb) and PAN continued to dominate over HNO_3

at even lower levels. HO_2NO_2 levels of 100–200 ppt, comparable to NO_x , were seen within these plumes at moderately low altitudes. Aerosol nitrate was present at concentrations much larger than NO_x in these air masses. The LMS composition was dramatically different where HNO_3 and NO_x were the dominant species and PAN was rather low (Figure 5d).

[17] Figures 6a–6c show the transition from the troposphere to the LMS ($\text{O}_3 < 440$ ppb) for a select group of species. The NO_x mixing ratios of 200–300 ppt in the LMS

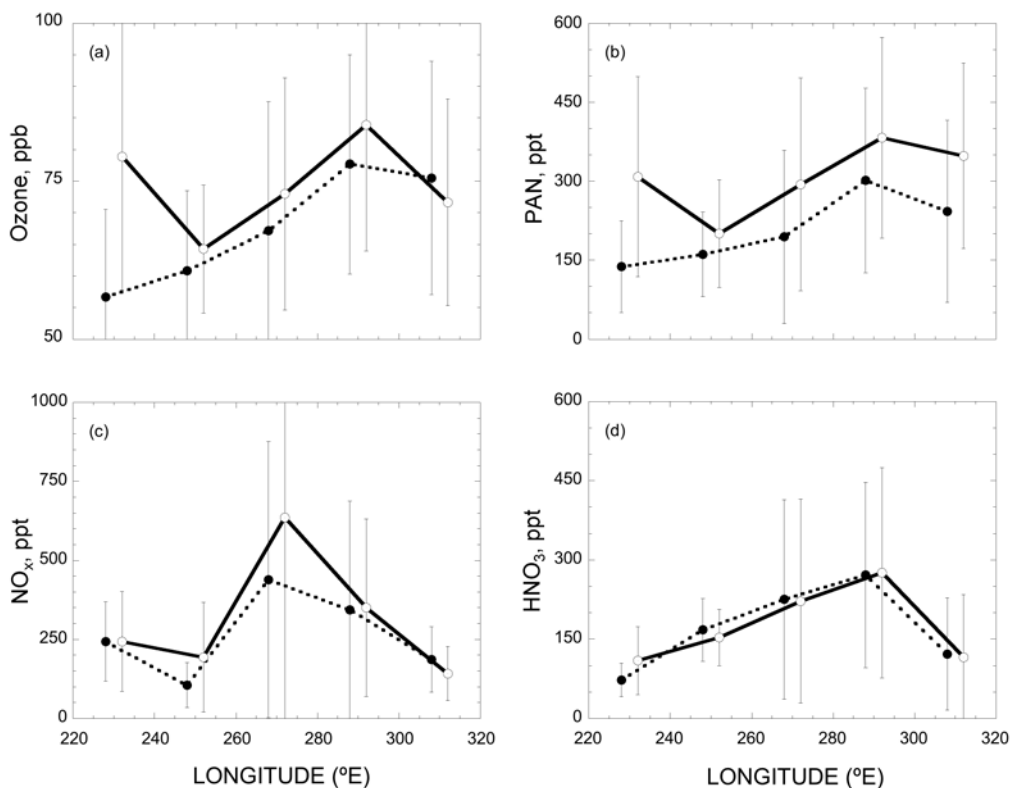


Figure 8. Ozone and reactive nitrogen in the North American upper troposphere (7–12 km; 30–45°N) under “all observed” (solid) and “clean” (dashed) conditions.

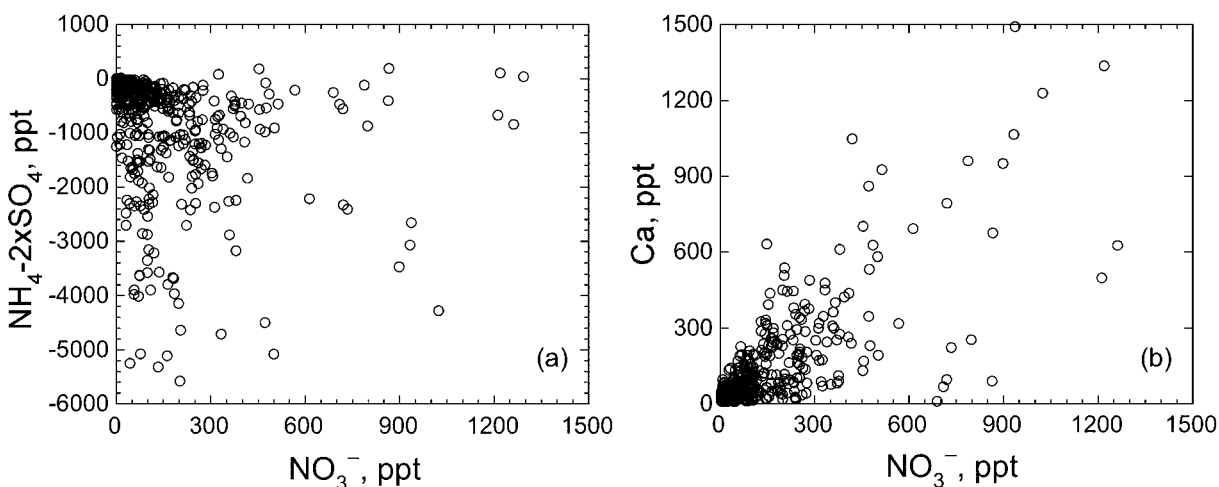


Figure 9. Bulk aerosol nitrate relationship with (a) excess sulfate and (b) calcium ion. All aerosol samples are $<5 \mu\text{m}$ in size.

where steady state with NO_y is likely achieved should be compared with 600–3000 ppt in the UT where convection and lightning are driving the chemistry away from steady state and result in high NO_x (Figures 5a and 5b). Similarly NO_x/NO_y ratio of 0.2 in the LMS can be compared with 0.6 at 12 km. Since NO_x levels in the troposphere continued to

rise to the DC-8 ceiling altitude of 12 km, it is likely that a NO_x maximum above this altitude was present with levels subsequently decreasing toward the tropopause. Such high NO_x maxima coincident with lightning conditions have been observed at subtropical latitudes and over Europe [Huntrieser *et al.*, 2002; Ridley *et al.*, 2004]. In the LMS,

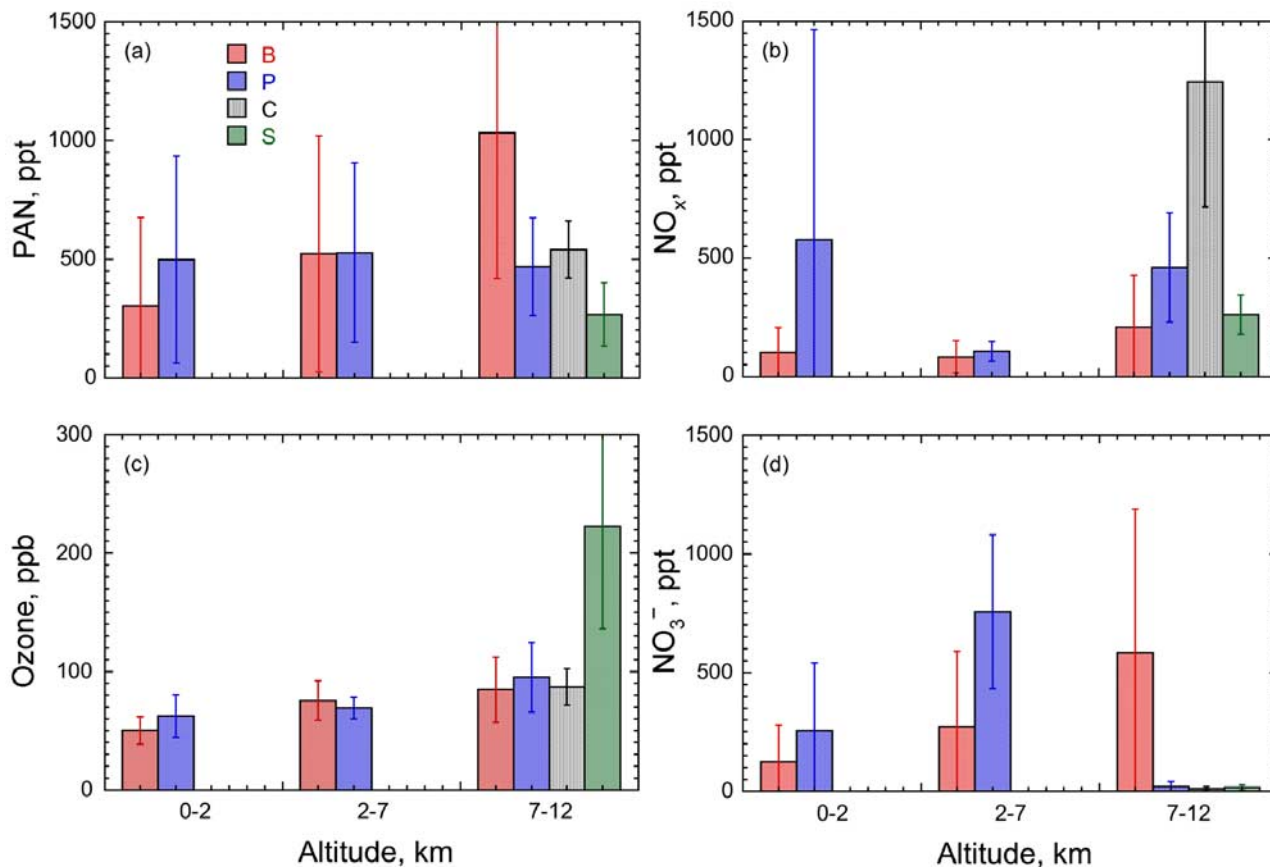


Figure 10. Distribution of selected chemicals in plumes influenced by biomass burning (B), anthropogenic pollution (P), lightning/convection (C), and stratosphere (S). Altitude bins are selected to represent the lower, middle, and upper troposphere.

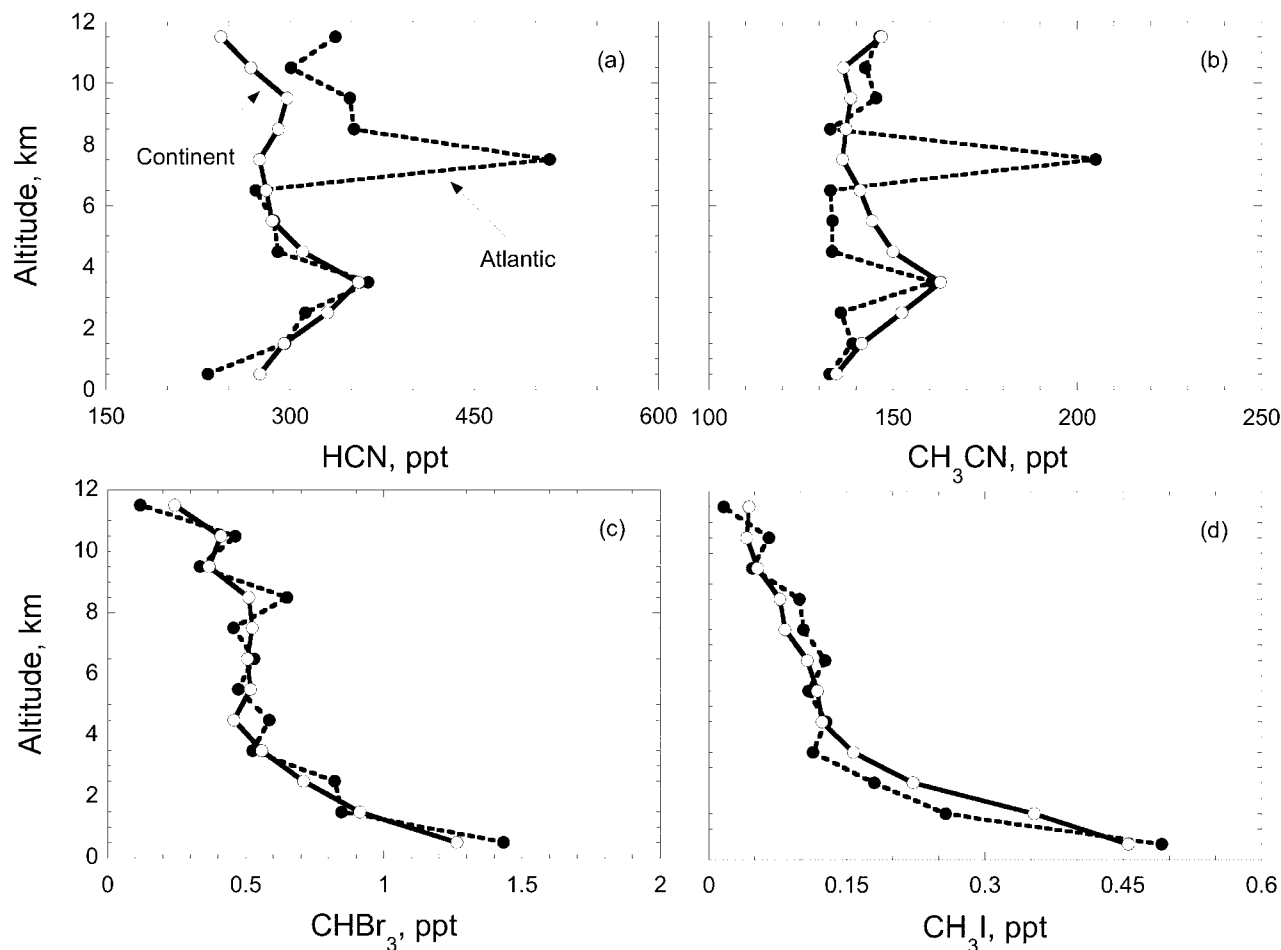


Figure 11. Vertical distribution of nitriles and oceanic sourced tracers.

NO_x and HCN levels remained relatively unchanged while PAN, CO, and H_2O declined and HNO_3 increased. This behavior was similar to what has been previously reported from other locations and seasons [Singh *et al.*, 1997] and the NO_x/HNO_3 ratio is consistent with description of factors affecting HNO_3/NO_x ratios in the lower stratosphere as described by Perkins *et al.* [2001] and Cohen and Murphy [2003].

[18] Figures 7a and 7b show the mean vertical structure of NO_x and PAN from west to east over North America. Since only one flight over the Pacific was conducted during INTEX-A, it is likely biased because of the encounter of Asian pollution in the UT. Therefore we have also included the NO_x and PAN distribution over the Pacific observed during Trace-P in the spring 2001. NO_x levels in the UT increase from west to east. Signatures of continental pollution were similarly seen in the LT for PAN although less so in the UT in part because of the relatively long lifetime of PAN in this region. Figure 8 shows the longitudinal variation in the UT abundance of O_3 and select reactive nitrogen species both under “all observed” and “clean” conditions. Mean O_3 mixing ratios in the UT were enhanced by 10–15 ppb from west to east even under clean conditions with an additional increase of about 5 ppb due to pollution (Figure 8a). This west to increase in UT O_3 was also

observed from the ozonesonde data analyzed by Cooper *et al.* [2006] and is largely attributable to lightning emissions of NO_x . A much larger increase was seen in PAN, an excellent indicator of pollution and photochemical influences (Figure 8b). Lightning and the associated convection had a considerable impact on NO_x over the central US (Figure 8c). The corresponding increase in HNO_3 occurs further East and downwind of the convective source (Figure 8d). In short the North American UT appears to be greatly influenced by lightning and pollution resulting in substantial enhancements in ozone, PAN, and other tracers.

4.2.2. Aerosol Nitrogen

[19] Bulk aerosol ($<5 \mu\text{m}$ size) were filter collected on the DC-8 and their inorganic ion composition determined by methods described by McNaughton *et al.* [2007]. As shown in Table 1, aerosol nitrate (NO_3^-) was present in moderately low concentrations ($<10\%$ of NO_y) mostly in the LT. Aerosol nitrate can be typically formed via reaction of NH_3 and nitric acid ($\text{NH}_3 + \text{HNO}_3 \leftrightarrow \text{NH}_4\text{NO}_3$). Bulk aerosol nitrate was found to be moderately correlated with NH_4^+ ($R^2 = 0.42$) suggesting a chemical form such as NH_4NO_3 . An examination of the NH_4^+ and SO_4^- ion balance (Figure 9a) clearly indicated that throughout this experiment excess sulfate was nearly always present suggesting insufficient ammonia for acid neutralization. This was unlike the

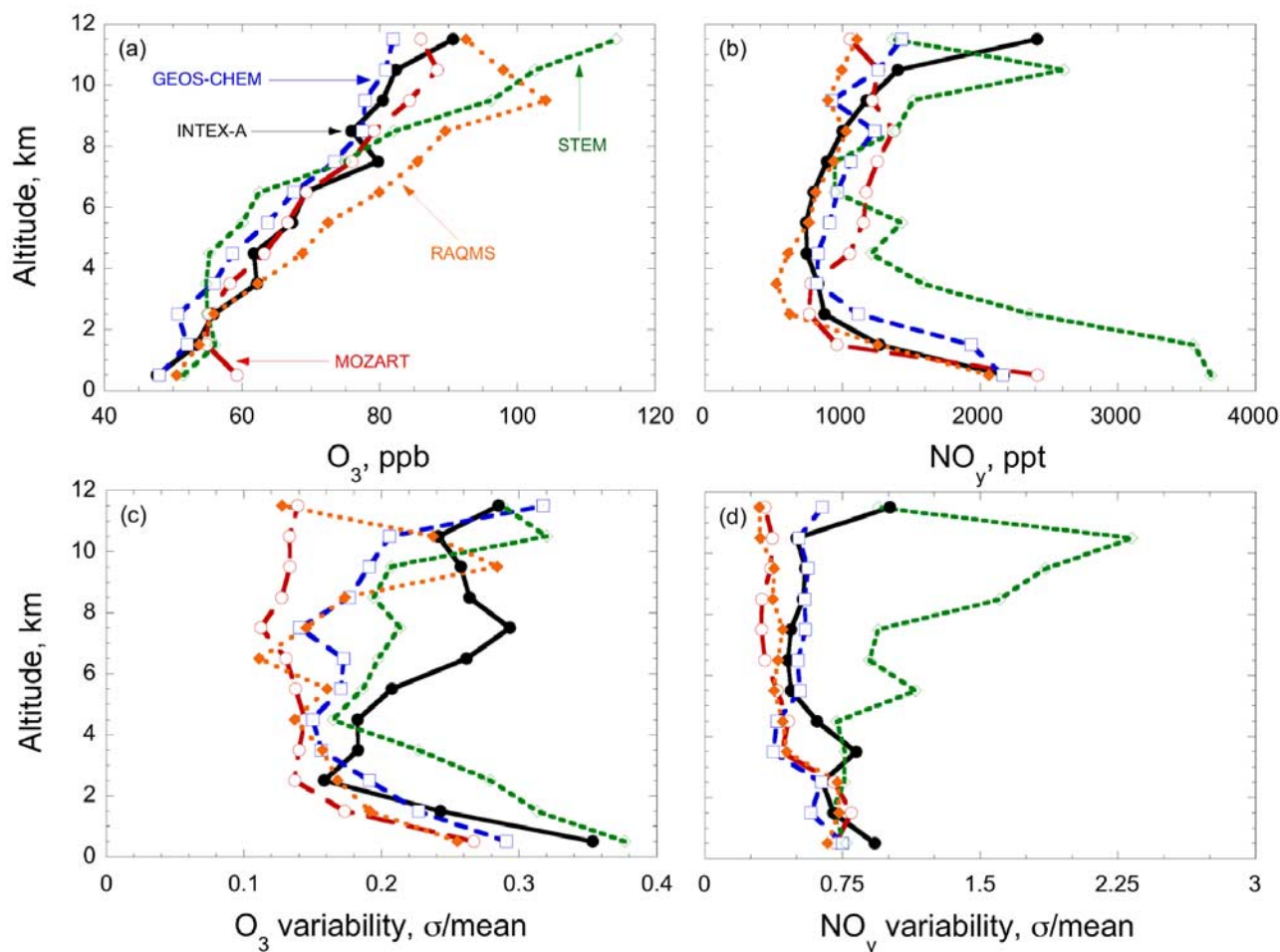


Figure 12. Observed and simulated mixing ratios and variability of O_3 and NO_y over eastern North America ($30\text{--}50^\circ\text{N}$; $260\text{--}320^\circ\text{E}$). (a and b) Mean mixing ratios and (c and d) relative variability.

situation in the Asian pollution outflow where excess ammonium was nearly always present and all SO_4^- had been neutralized [Miyazaki *et al.*, 2005]. Ammonia is preferentially converted to ammonium sulfate as long as SO_4^- is present [Seinfeld and Pandis, 1998], and indeed SO_4^- and NH_4^+ were highly correlated ($R^2 = 0.85$). We conclude that NH_4NO_3 was not the dominant form of the aerosol nitrate observed over North America. Figure 9b further shows that NO_3^- was well correlated with soil elements like calcium. As has been previously noted [Wolff, 1984; Krueger *et al.*, 2004], it appears that the source of this aerosol nitrate is HNO_3 residing on and reacting with soil and crustal particles that are typically of large size (e.g., $2HNO_3(g) + CaCO_3(s) \rightarrow Ca(NO_3)_2(s) + H_2O + CO_2$). This is further supported by the presence of extremely small measured concentrations of submicron NO_3^- , which were independently measured in the LT. Unlike NH_4NO_3 , non-volatile aerosol nitrate salts represents a nearly permanent sink for reactive nitrogen with virtually no chance of return to the gas phase while in the atmosphere before deposition to the land or ocean.

4.2.3. Plumes

[20] Plumes sampled during INTEX-A were segregated into categories representing influences from biomass burn-

ing (BB), anthropogenic pollution (AP), lightning/convection (LC), and the stratosphere (ST). For example, HCN and CH_3CN were highly elevated in BB plumes while high O_3 and low CO and H_2O mixing ratios were characteristic of stratospheric influences. Figure 10 shows the distribution of selected species in these plumes as a function of altitude bins representing LT (0–2 km), MT (2–7 km), and UT (7–12 km). Foremost is the appearance of sizable PAN and relatively low NO_x and O_3 concentrations in BB plumes (Figures 10a–10c). Law *et al.* [2005] explored the development of some of these plumes over the Atlantic and concluded that net O_3 production does eventually occur but is greatly slowed because of the control exerted by PAN on the NO_x reservoir. Another distinct feature was the large NO_x mixing ratios observed in plumes influenced by lightning and convection, which may have frequently coexisted (Figure 10b). Despite the large NO_x values encountered in these LC plumes, O_3 was not significantly elevated (Figure 10c). Using the ratio of NO_x/HNO_3 as an indicator, Bertram *et al.* [2007] show that O_3 is reduced in fresh convection because O_3 mixing ratios are lower in the PBL than in the UT. Ozone is then chemically replenished in the convectively lofted air mass on a timescale of 2–3 days. Both HNO_3 and aerosol nitrate were significantly elevated

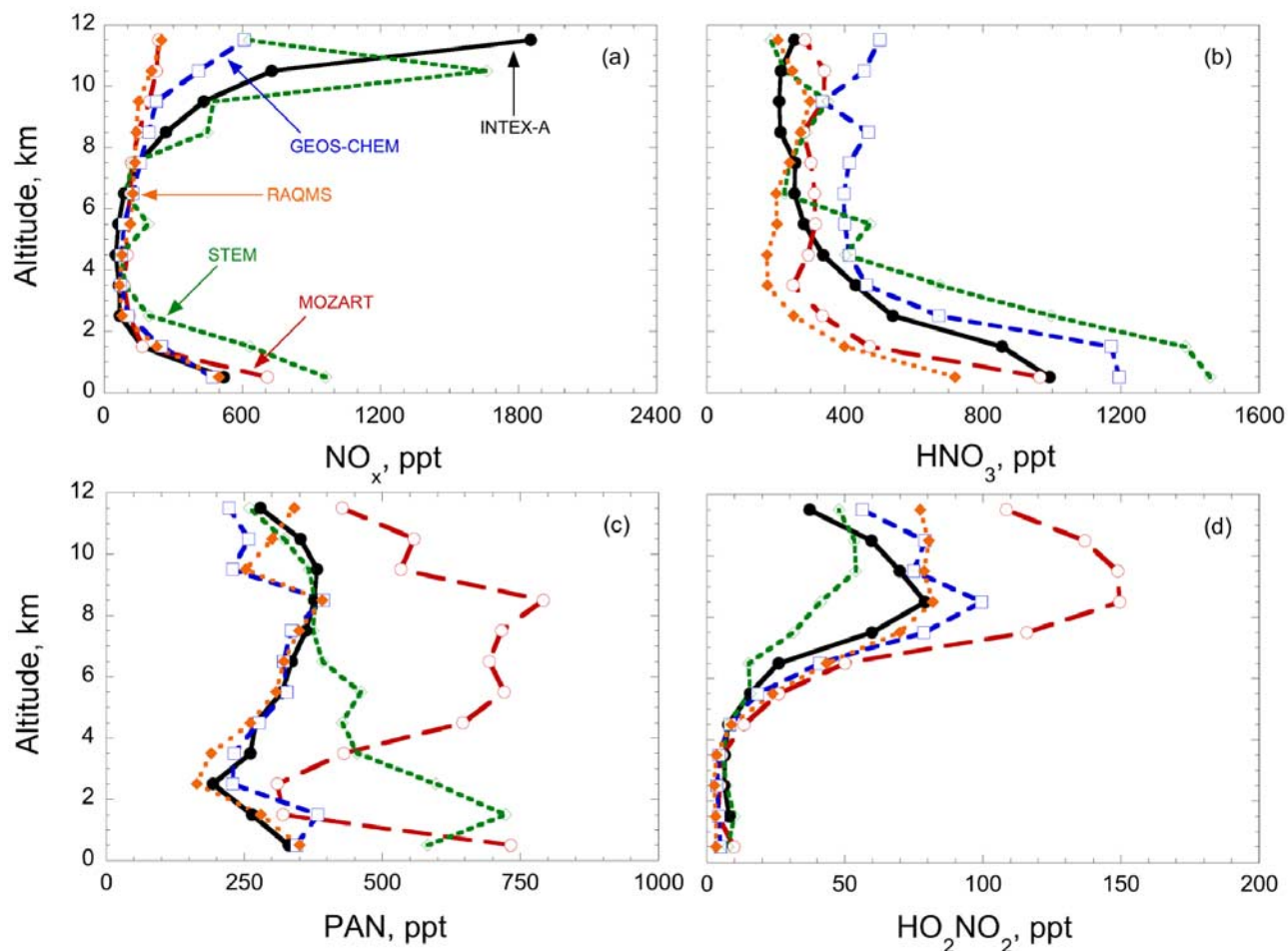


Figure 13. Observed and simulated mixing ratios of selected reactive nitrogen species over eastern North America (30–50°N; 260–320°E).

in plumes influenced by anthropogenic and BB pollution (Figure 10d).

4.2.4. Nitrogen Tracers of Biomass Combustion

[21] HCN and CH₃CN are both excellent tracers of biomass combustion and were linearly correlated ($R^2 = 0.76$) in this data set. Figure 11 shows the vertical structure of HCN and CH₃CN over the Atlantic and continental North America. There is an indication of both an oceanic and soil sink for these species. Although an oceanic sink has been recognized, a soil sink is not known and has not been studied [Singh *et al.*, 2003b]. Figure 11 also shows similar profiles for CHBr₃ and CH₃I, which are both known to have dominant oceanic sources. It is clear from Figure 11 that oceanic influences were widespread in the continental boundary layer. To further explore the potential of soils to act as a sink for nitriles, we used trajectory analysis to compare abundances in air masses that had remained in the boundary layer over land or water for at least 5 days. Overland air masses had mixing ratios of 260 (± 20) ppt and 135 (± 14) ppt for HCN and CH₃CN while overwater air masses had corresponding mixing ratios of 149 (± 33) ppt and 109 (± 18) ppt. In short, air masses in long contact with surface water were far more depleted than those in contact with land surfaces. Despite the appearance of a sink, we conclude that HCN and CH₃CN soil sinks were negligible

or extremely small. This could be due to low contact time between these molecules and soil bacteria allowing rapid rerelease of deposited nitriles. The column of HCN deduced from these measurements is in good agreement with that reported by Zhao *et al.* [2002] from ground-based spectroscopic measurements over Japan.

4.3. Model Simulations

[22] Four models (GEOS-CHEM, RAQMS, MOZART and STEM) reported trace gas concentrations along the DC-8 flight tracks. Figures 12–14 provide a comparison of observations and model simulations over eastern North America (30–50°N; 260–320°E) where most intense aircraft sampling was performed. Figure 12 shows observed and modeled mean mixing ratios of O₃ and NO_y. The four models under consideration deviate from each other and the observations at all altitudes. STEM substantially overestimated O₃ in the UT and NO_y in all of the troposphere. RAQMS calculated extremely low NO_y but overpredicted O₃ possibly because of an unusually large stratospheric input. Models in general tended to predict lesser variability (Figures 12c and 12d) than observations in large part because of their greater spatial averaging.

[23] Figure 13 shows model-data comparison for NO_x, HNO₃, PAN and HO₂NO₂ profiles. Except in the case of

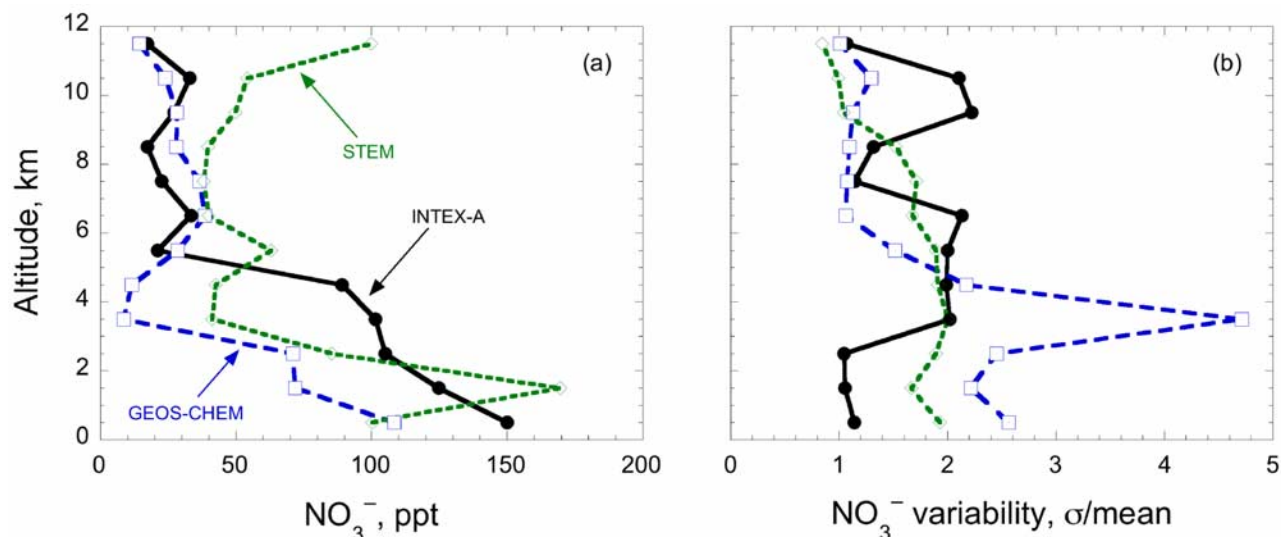


Figure 14. Observed and simulated aerosol nitrate concentrations and variability over eastern North America (30–50°N; 260–320°E). Aerosol size cutoff is 5 μm .

STEM, NO_x was substantially under predicted by all models in the UT. GEOS-CHEM improved its overall prediction by increasing the lightning source over North America by a factor of four [Hudman *et al.*, 2007]. It has recently been suggested that cloud-to-cloud discharges may be a far greater source of NO_x than what has traditionally been believed [Ridley *et al.*, 2005]. An underestimation of the lightning source and uncertainties in its distribution appear to be a common problem in these models. STEM also predicted 50–100% more near surface NO_x and HNO_3 than observed. STEM is using an earlier emissions inventory that does not take into account the substantial emission reductions that have recently been achieved most notably by the U.S. power industry. An intriguing aspect is that in the UT, HNO_3 is typically over estimated while NO_x is underestimated. As has been noted elsewhere (Ren *et al.*, unpublished manuscript, 2007), models are over calculating OH (and HO_2) levels resulting in an over estimation of HNO_3 ($\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$). To simulate HNO_3 correctly a significant revision in the HO_x field would be necessary. Thus the observed NO_x/HNO_3 ratio provides indirect evidence for the accuracy of the OH measurements during INTEX-A. The situation with PAN (and HO_2NO_2) is also confusing with large over estimation by MOZART in the MT and UT and by STEM in the LT. Figure 14 shows the distribution of total aerosol NO_3^- and its simulation by two models. These models are either able to simulate the UT or LT with reasonable accuracy but not both.

[24] While models have become more complex, it is not clear if the overall performance in simulating reactive nitrogen has improved over the last decade [Emmons *et al.*, 1997; Thakur *et al.*, 1999]. Uncertainties are clearly due to errors in sources and meteorology, but probably include mechanistic limitations in our knowledge. In recent years, it has been possible to retrieve NO_2 columns in the troposphere from satellite observations and these have been used to provide extensive data coverage as well as inferences of NO_x emissions [Richter *et al.*, 2005;

Martin *et al.*, 2006]. Retrieval of satellite data requires a priori knowledge of NO_2 structure and the accuracy of retrievals is often dependent on this knowledge. Traditionally, model profiles have been used for this purpose. The NO_2 observations from this study clearly show that the vertical structure of NO_x over continents is highly complex and its extensive characterization is necessary for accurate satellite retrievals.

5. Conclusions

[25] INTEX-A provided a detailed description of the reactive nitrogen, ozone, and tracer field in the North American troposphere. The observations clearly showed that the UT as well as LT is significantly polluted across North America. The UT is also more influenced by far greater lightning NO_x emissions than hitherto believed. NO_x/NO_y ratios are significantly more elevated in the UT than in the LT and support fresh injections of NO_x originating in the free troposphere. PAN appears to be the major carrier of reactive nitrogen in the UT while much of it exists in the HNO_3 reservoir in the LT. Model simulations of reactive nitrogen species cannot be performed accurately because of uncertainties in lightning sources of NO_x as well as in the HO_x field. Further studies employing all of the improvements in model parameterizations identified as important by comparison to the INTEX-A data will be required to evaluate the extent to which we can now accurately represent the distribution and partitioning of tropospheric NO_y during this period or if there are still other unexplained difference between model and observations.

[26] **Acknowledgments.** We thank all ICARTT participants and sponsoring agencies for making this project possible. DC-8 activities were supported by the NASA Tropospheric Chemistry Program. The National Center for Atmospheric Research is sponsored by the National Science Foundation and operated by the University Corporation for Atmospheric Research.

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