Surface and lightning sources of nitrogen oxides over the United States: magnitudes, chemical evolution, and outflow

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Abstract

We use observations from two aircraft during the ICARTT campaign over the eastern United States and North Atlantic during summer 2004, interpreted with a global 3-D model of tropospheric chemistry (GEOS-Chem) to test current understanding of the regional sources, chemical evolution, and export of nitrogen oxides. The boundary layer NO_x data provide top-down verification of a 50% decrease in power plant and industry NO_x emissions over the eastern United States between 1999 and 2004. Observed 8-12 km NO_x concentrations in ICARTT were 0.55 ± 0.36 ppbv, much larger than in previous United States aircraft campaigns (ELCHEM, SUCCESS, SONEX). We show that regional lightning was the dominant source of this NO_x and increased upper tropospheric ozone by 10 ppbv. Simulating the ICARTT upper tropospheric NO_x observations with GEOS-Chem require a factor of 4 increase in the model NO_x yield per flash (to 500 mol/flash). Observed OH concentrations were a factor of 2 lower than can be explained from current photochemical models, and if correct would imply a broader lightning influence in the upper troposphere than presently thought.. An NO_y -CO correlation analysis of the fraction *f* of North American NO_x emissions vented to the free troposphere as NO_y (sum of NO_x and its oxidation products PAN and HNO_3) s shows observed $f = 16 \pm 10\%$ and modeled $f = 14 \pm 8\%$, consistent with previous studies. Export to the lower free troposphere is mostly HNO_3 but at higher altitudes is mostly PAN. The model successfully simulates NO_y export efficiency and speciation, supporting previous model estimates of a large U.S. contribution to tropospheric ozone through NO_x and PAN export.

1. Introduction

Quantifying the sources and fate of nitrogen oxides ($NO_x \equiv NO + NO_2$) over northern mid-latitudes continents is critical for assessing anthropogenic influence on global tropospheric ozone [*Pickering et al*., 1992; *Jacob et al.,* 1993; *Thompson et al.*, 1994; *Li et al.,* 2004]. The International Consortium on Atmospheric Transport and Transformation (ICARTT) aircraft study [*Singh et al.,* 2006a; *Fehsenfeld et al*., 2006], which took place in July – August 2004 over the eastern United States and the North Atlantic, provides an opportunity for this purpose. We present here a global 3-D model analysis of ICARTT observations for NO_x, its chemical reservoirs, and related species including hydrogen oxide (HO_x) radicals to quantify continental NO_x sources from combustion and lightning, determine the chemical fate of NO_x in the United States boundary layer and in North American outflow, and examine the implications for ozone.

Ozone production in the troposphere is principally limited by the supply of NO_x [*Chameides*, 1992]. Fossil fuel combustion accounts for over half of the global NO_x source [*Intergovernmental Panel on Climate Change (IPCC)*, 2001]. The United States has been actively reducing its summertime NO_x emissions since 1998 to decrease ozone smog. The Environmental Protection Agency (EPA) NO_x State Implementation Plan (SIP) Call mandated that 22 eastern states meet state-specific total NO_x emissions reductions by 2003 (Phase 1) and further reduction by 2007 (Phase 2). By 2003, all 22 states had reduced NO_x point source emissions to their Phase 1 levels. *Frost et al.,* [2006] determined from stack sampling that power plant emissions of NO_x decreased 50% between 1999 and 2003. NO_x levels in the U.S. will likely continue to drop. In March 2005, the EPA issued the Clean Air Interstate Rule, which will, when fully implemented, permanently reduce NO_x emissions to 60% of 2003 levels in 25 eastern states. The ICARTT observations offer an opportunity to check on these emission reductions.

Oxidation of NO_x to HNO_3, peroxyacetylnitrate (PAN), and other minor products takes place on the order of hours, so that rapid ozone production is confined to the continental boundary layer (CBL), seemingly limiting its affect on global ozone. However, the dependence of ozone

production on NO_x is highly nonlinear; the ozone production efficiency per unit NO_x consumed (OPE) increases rapidly as the NO_x concentration decreases [*Liu et al.,* 1987]. This means that a small fraction of emitted NO_x exported to the free troposphere by frontal lifting, deep convection, or boundary layer venting could lead to significant ozone production in the free troposphere over the continent or downwind [*Jacob et al., 1993; Thompson et al.*, 1994]. Similarly, PAN (which is thermally unstable and not water-soluble) can be vented from the boundary layer and transported on a global scale at cold temperatures, eventually decomposing to release NO_x as air masses subside. Quantifying the sources, chemical evolution, and export of anthropogenic NO_x (and PAN) is thus critical to understanding the North American contribution to the global ozone budget. This contribution is important from the perspective of ozone as a greenhouse gas [*Mickley et al.*, 2004] and for intercontinental transport of ozone pollution *[Jacob et al*., 1999; *Holloway et al*., 2003].

Early Eulerian models found that the fraction *f* of NO_x emitted in the United States that is exported out of the CBL as NO_y (sum of NO_x and its oxidation products) ranges from 25% in summer to 35% in winter [*Horowitz et al*., 1998; *Liang et al*., 1998]. Subsequent Lagrangian analyses using NO_y-CO correlations measured from aircraft in free tropospheric outflow (2-6 km), over the North Atlantic in September (NARE '97) seemed to contradict these model results, with estimates of *f* ranging from only 3% [*Stohl et al*., 2002] to 9 ± 14 % [*Parrish et al*., 2004]. *Li et al.* [2004] reconciled the Eulerian and Lagrangian approaches by pointing out that the early Eulerian models had insufficient HNO_3 scavenging, while the Lagrangian models underestimated background CO. They derived a consistent value *f* = 17-20% by both approaches for the NARE'97 period. The ICARTT study offers far more geographical coverage and chemical information in the boundary layer and the free troposphere than previous studies, enabling better constraints on the estimates of anthropogenic export and associated NO_y speciation, as well as the underlying source and chemical factors.

In addition to convectively lofted NO_x, a highly uncertain source of NO_x to the upper troposphere is from lightning. Global lightning source estimates range from 1 to 12 Tg yr^{-1} [*Price et al.,* 1997; *Nesbitt et al.*, 2000], with the most recent estimates in the range 1-6 Tg N yr^{-1} [*Boersma et al.,* 2005; *Beirle et al*., 2006; *Martin et al.*, 2006b]. Past studies disagree on the relative importance of lightning versus convective injection in supplying upper tropospheric NO_x [*Jaeglé et al.,* 1998; *Levy et al.,*1999; *Grewe et al*., 1999; *Li et al.*, 2005]. Here we use the ICARTT data to examine the contribution of each.

2. The ICARTT Study

ICARTT took place over eastern North America and the North Atlantic in July-August 2004. A major objective was to quantify North American sources and outflow of pollutants and climatically important species. Two principal components directed at that objective were the NOAA New England Air Quality Study/Intercontinental Transport and Chemical Transformation (NEAQS-ITCT 2004) and the NASA Intercontinental Transport Experiment – North America, Phase A (INTEX-A).

The NOAA NEAQS- ITCT 2004 campaign [*Fehsenfeld et al.*, 2006] took place July 3 – August 15, 2004 over the NW Atlantic and the NE United States out of Portsmouth, New Hampshire (Figure 1). It used a WP-3D aircraft (ceiling ~6 km). The NASA INTEX-A campaign [*Singh et al.,* 2006a] took place June 29 – August 14 over the central and eastern United States, and the North Atlantic, from bases at Edwards (California), St. Louis (Missouri), and Portsmouth (New Hampshire). It used a DC-8 aircraft (ceiling ~12 km) with extensive vertical profiling and boundary layer mapping at 1 kft. (Figure 1) The WP-3D remained close to New England throughout the mission, focusing on emissions verification and chemical transformation of major urban pollution plumes. Detailed descriptions of aircraft payloads and measurement techniques are in *Fehsenfeld et al.*, [2006] and *Singh et al.,* [2006a] for the WP-3D and DC-8 respectively.

We make use here of the following 1-minute average measurements (accuracies given in parentheses for DC-8, WP-3D respectively): ozone (5%,3%); CO (5%,2.5%); CH_2O (10%, DC-

8 NCAR measurement only),; HNO_4(15%, DC-8 only); H_2O_2(20%, DC-8 only); NO (15%, 5%) DC-8 Pennsylvania State U. measurement only); NO_2 (10%,8%); HNO_3 (15%, 15%); PAN(15%,15%), OH(15%, DC-8 only), and HO_2 (15%, DC-8 only). We estimate the concentration of NO_y in free tropospheric export from the DC-8 data as the sum of NO_x, PAN, and HNO_3. Nitrate aerosol, organic nitrates other than PAN, and HNO_4 were also measured aboard the DC-8 [*Cohen et al.*, 2000; *Dibb et al.*, 2003; *Huey et al.*, 2004], but accounted for less than 10% of NO_y in the free troposphere and the data sets were sparse.

Ventilation of the eastern United States in summer is primarily driven by cyclones tracking eastward typically every 5 days in the 45° - 55°N band [*Li et al.*, 2005]. During ICARTT a persistent trough along the east coast led to cyclones extending further south [*Fuelberg et al.,* 2006], and lack of stagnant surface high pressure led to a record low number of air quality violations [*Thompson et al.,* 2006]. *Parrish et al.* [2004] found that outflow from fair weather cumulus rising to 3-4 km provides an additional ventilation mechanism. Yet another mechanism, particularly in the south, is deep convection from surface heating [*Li et al.,* 2005]; this mechanism is often associated with lightning activity.

3. **Model Description**

We simulate the ICARTT observations with the GEOS-Chem global 3-D model of tropospheric chemistry (version 7.02; http://www.as.harvard.edu/chemistry/trop/geos/) driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS-4) of the NASA Global Modeling and Assimilation Office (GMAO). The model is applied to a global simulation of ozone-NO_x-hydrocarbon-aerosol chemistry with 120 species simulated explicitly. A general description of GEOS-Chem is given by *Bey et al*. [2001] and a description of the coupled oxidant-aerosol simulation as used here is given by *Park et al.* [2004]. Partitioning of total nitric acid between the gas and aerosol phases is calculated using the MARS-A thermodynamic equilibrium model [*Binkowski and Roselle*, 2003]. Emissions in the model are as described by *Park et al.* [2004] unless specified otherwise.

Meteorological fields in the GEOS-4 data have a temporal resolution of 6 hours (3 hours for surface variables and mixing depths) and a horizontal resolution of 1° latitude by 1.25° longitude, with 55 vertical sigma levels between the surface and 0.1 hPa (including about 16 in the troposphere and 5 in the boundary layer up to 2 km). For input to GEOS-Chem we degrade here the horizontal resolution to 2° latitude by 2.5° longitude. Mean afternoon boundary layer heights over the eastern United States in the GEOS-4 data for the ICARTT period are 1100 ± 400 m AGL. Tropopause heights are 13.3 ± 2.2 km. The cross-tropopause ozone flux is specified globally with the Synoz method [*McLinden et al.,* 2000] while the NO_y flux is calculated from N_2O oxidation in the model stratosphere [*Bey et al.,* 2001]. Global net cross-tropopause fluxes of ozone and NO_y are 495 Tg O_3 yr^{-1} and 2 Tg N yr^{-1}, respectively. The model wet deposition scheme [Liu et al., 2001] includes contributions from scavenging in convective updrafts, and rainout and washout from convective anvils and large-scale precipitation, and it allows for return to the atmosphere following evaporation. Soluble gases are taken up by liquid water on the basis of their effective Henry's law, by ice on the basis of co-condensation or surface coverage, with species-specific retention efficiencies when droplets freeze, as described by Mari et al., [2000]. The simulations are conducted for July-August 2004 and are initialized with a 18-month spin-up simulation. For comparison with observations, the model is sampled along the aircraft flight tracks and times. The comparisons exclude fresh pollution plumes as diagnosed by NO_x /NO_y > 0.4 mol mol^{-1} or (if NO_y is not available) NO_2 > 4 ppbv and altitude < 3 km; biomass burning plumes as diagnosed by HCN > 500 pptv or CH_3CN > 225 pptv; and stratospheric air as diagnosed by ozone/CO >1.25 mol mol^{-1}. These filters exclude 8%, 22% (fresh pollution plumes); 5%, 8% (biomass burning plumes), and 6%, 0% (stratospheric air) of the overall data set for the DC-8 and WP-3D, respectively.

A major focus of our work is to use the ICARTT observations to test and improve U.S. NO_x emission estimates. We will show simulations with "standard" emissions based on a priori information from the standard version of the GEOS-Chem model, and "improved" emissions that

reflect the ICARTT constraints and improved understanding. These emissions for the ICARTT period (July 1 – August 15, 2004) are summarized in Table 1. Original fossil and biofuel emissions in the United States are from the EPA 1999 National Emission Inventory (NEI99). They amount to 0.79 Tg N for July 1 –August 15 and 6.2 Tg N annually, with distribution shown in Figure 2 (left). Transportation accounts for 35%, industry 17%, power generation 26%, and other sources 22% (mostly non-road vehicles). As we will see in section 5, NO_x concentrations, are overestimated using the 1999 inventory, in the U.S. boundary layer, consistent with reduction of NO_x emissions from power plants by 50% from 1999 to 2004 driven by the NO_x SIP Call [*Frost et al*., 2006]. These reductions are being added to subsequent inventories. Reduction of the power plant and industry sources results in the improved inventory of Table 1 and Figure 2 (right). The ICARTT data also show that CO emissions in the NEI99 inventory are 30% too high, as discussed below, and we make this adjustment in the improved inventory.

The global lightning source of NO_x in GEOS-Chem is computed with the scheme of *Price and Rind* [1992] that relates number of flashes to convective cloud top heights as described in *Wang et al.*, [1998]. We scale the NO_x production to 4.7 Tg N yr^{-1} globally, resulting from 2.7 x 10^9 flashes, and distribute this source vertically following *Pickering et al.* [1998] (55-75% above 8 km, up to 23% in lowest km). The resulting U.S. emissions for the ICARTT period (original inventory) are 0.067 Tg N for the contiguous United States and coastal waters (130-70°W, 25-50°N), concentrated over the Southwest and along the Gulf of Mexico. As we will see in section 6, successful simulation of the ICARTT upper tropospheric NO_x observations in GEOS-Chem requires a factor of 4 increase in this source along with an upward shift to the July mean tropopause height, and this is included in the improved inventory.

Extensive and persistent boreal forest fires took place in Alaska and NW Canada in summer 2004; in contrast, there were no significant fires in Siberia. We use the daily biomass burning inventory of *Turquety et al.* [2006] for North American fires during ICARTT. This inventory was constructed by combining daily area burned reports from government agencies and

hot spots detected from space by the MODIS instrument with estimates of fuel loadings and emission factors depending on the type of ecosystem burned. This inventory for CO was evaluated against MOPITT columns as described by *Turquety et al.* [2006]. North American CO and NO_y fire emissions for July 1 –August 15 are 20 Tg CO, 0.3 Tg N. Short-lived hydrocarbons emitted from fires drive fast conversion of NO_x to PAN, slowing down ozone formation [*Jacob et al.*, 1992] but this is inadequately represented in the model where the fastest-reacting pyrogenic hydrocarbon is propene [*Hudman et al*., 2006]. In the improved emission inventory we release 80% of the biomass burning NO_x as PAN.

4. Hydrogen oxide radicals and reservoir species

Hydrogen oxide radicals ($HO_x \equiv$ OH + peoxy radicals) and their reservoirs (H_2O_2, CH_2O, HNO_4) largely define the photochemical environment for NO_x oxidation and ozone production. Figure 3 shows simulated and observed mean vertical distributions of OH, HO_2, H_2O_2, CH_2O, and HNO_4 for the ensemble of INTEX-A flights. Observed OH increases with altitude from 0.15 pptv at the surface to 0.43 pptv at 11 km, while HO_2 decreases from 19 pptv at the surface to 5 pptv at 11 km reflecting the positive relationship of OH/HO_2 ratio with NO [*Jaeglé et al.*, 2000]. H_2O_2 concentrations gradually decrease from 2.6 pptv at the surface to 0.15 pptv at 11km, reflecting the decrease in water vapor [*Heikes et al.,* 1992]. CH_2O also decreases with altitude, reflecting the boundary layer source from oxidation of isoprene [*Millet et al.,* 2006]. HNO_4, a thermally unstable molecules that is an important HO_x reservoir in the upper troposphere [*Jaeglé et al.,* 2000], has an 8-9 km peak of 62 pptv.

OH and HO_2 in the original simulation match observations in the lowest 1 km, but are too high above by 60% and 30% respectively. Measurement nominal accuracy for both is 15%, well below this bias [*Ren et al*., 2006]. Increasing the lightning NO_x source in the improved simulation decreases HO_2 while increasing OH. This fully corrects the HO_2 overestimate but worsens the OH overestimate above 5 km. Similar HO_x simulation biases are found in a box photochemical model

constrained with local ICARTT observations [*Olson et al.,* 2006b; *Ren et al.,* 2006], and which closely reproduces GEOS-Chem results. The OH bias must reflect either instrument error or a fundamental flaw in current understanding of HO_x photochemistry; see *Olson et al.* [2006b] and *Ren et al.* [2006] for further discussion. In what follows we take the model OH at face value but will also discuss the effect of possible model bias.

The model simulates in general well the concentrations of the HO_x reservoirs H_2O_2, CH_2O, and HNO_4 (Figure 3). H_2O_2 is unbiased in the free troposphere, but is overestimated below 3 km by ~30%; a possible cause is the model conversion of HO_2 to H_2O_2 in aerosols [*Martin et al.,* 2003], which recent measurements find to be much lower than previously estimated [*Thornton and Abbatt,* 2005]. The CH_2O simulation, discussed in detail by *Millet et al.*, [2006], matches observations closely and is largely insensitive to changes in OH (which affect sources and sinks in the same direction). HNO_4 is well matched in the original simulation but is overestimated by 30% when the lightning source is increased.

5. Boundary Layer NO_x over the United States

Figure 4 compares simulated and observed mean vertical distributions of CO, NO_x, PAN, HNO_3, and ozone concentrations for the ensemble of DC-8 and WP-3D flights. Observed CO, NO_x, PAN, and HNO_3 are elevated below 3 km, reflecting anthropogenic sources**.** The model with original emissions is too high for all four species. Reducing the U.S. NO_x emissions from stationary sources by 50% from 1999 to 2004 to account for the NO_x SIP Call [*Frost et al.,* 2006] removes much of the model boundary layer NO_x bias over the Midwest United States. This corresponds to a 20% overall in the anthropogenic NO_x source (Table 1). *Parrish,* [2006], using urban ambient measurements of the CO/NO_x ratio along with fuel sales data, previously found that the on-road vehicular source in the NEI99 inventory is accurate for NO_x but 50% too high for CO. Applying this correction to the on-road vehicular CO source, which represents 60% of total CO emissions in the United States according to NEI99, decreases the mean CO bias from 35

ppbv to 20 ppbv in the WP-3D data and from 25 to 19 ppbv for the DC-8 data (Figure 4). Further source reduction would be needed to match the boundary layer observations for CO.

6. Upper tropospheric NO_x over the United States

NO_x concentrations observed in ICARTT show a decrease from the boundary layer to the free troposphere, but then a sharp rise with altitude above 6 km (Figure 4). Mean concentrations reach 0.55 ± 0.36 ppbv at 8-12 km altitude, higher than in the boundary layer. The NO/NO_x molar ratio averages 75% both in the observations and the model for the 8-12 km region (all data are for daytime). Observed PAN shows a broad maximum at 6-10 km. In contrast, HNO_3 is depleted in the free troposphere due to scavenging during uplift. Mean ozone increases with altitude from 50 ppbv near the surface to 75 ppbv at 8km.

The original model greatly underestimates the upper tropospheric NO_x enhancement; the discrepancy increases with altitude from a factor of 3 at 8 km to a factor of 5 at 11 km. Simulated PAN is too low by ~30% while HNO_3 is well simulated. Ozone is too low by 10 ppbv throughout the free troposphere.

Measurements of upper tropospheric NO_x from previous aircraft campaigns over the United States indicate much lower concentrations than observed in ICARTT. *Jaeglé et al.,* [1998] report mean NO concentrations from the SUCCESS campaign out of Kansas (April – May 1996) of 0.030 ± 0.022 ppbv for 8-10 km and 0.061 ± 0.045 ppbv for 10-12 km. *Ridley et al.,* [1994] report mean NO concentrations of 0.2± 0.1 ppbv over New Mexico during during ELCHEM (July – August 1989), even though convection was frequently targeted. SONEX observations in October-November 1997 over Maine and Atlantic Canada indicate mean NO concentrations between 6-12 km of 0.1 ppbv (all data) and 0.23 ppbv (convective outflow) [*Crawford* et al., 2000]. SUCCESS and SONEX were in spring and fall, whereas lightning over the United States

peaks in June-August; ELCHEM took place in the southwestern United States whereas maximum lightning is over the Gulf Coast [*Orville and Huffines*, 2001].

Figure 5 (left) shows the observed spatial distribution of mean upper tropospheric NO_x concentrations. Values exceeding 1 ppbv extend over much of the Southeast and Midwest. Deep convective injection of boundary layer pollution cannot explain these high values since the NO_x mixing ratio above 8 km is greater than that in the boundary layer (Figure 4). Aircraft emissions cannot provide an explanation either because the geographical distribution does not match the aircraft corridor along the Eastern United States and North Atlantic [*Gauss et al.*, 2006], and in any case these emissions are fairly well constrained from atmospheric measurements [*Meijer et al.,* 2000] and represent only a small source of upper tropospheric NO_x (Table 1). Transport of NO_x from the stratosphere is also well constrained by atmospheric observations and is negligibly small, about 0.2 Tg N yr^{-1} globally [*Murphy et al.,* 1993*; Jacob et al,* 1996]

Lightning provides the best explanation for the elevated NO_x in the upper troposphere during ICARTT. Figure 6 (left) shows National Lighting Detection Network (NLDN) mean lightning flash rates for July 1- August 15. The NLDN data (>100 sites in the continental United States) were collected by Vaisala (www.vaisala.com) and supplied to us by the Global Hydrology Resource Center at NASA Marshall Space Flight Center. The NLDN network measures only cloud-to-ground lightning flashes, and intracloud flashes are estimated to be about 3 times that amount [*Boccippio et al*., 2001].Cloud-to-ground flash detection efficiencies are >90% over the continental United States and degrade rapidly off-shore and beyond U.S. borders. The NLDN lightning activity is heaviest in the Gulf of Mexico region but also has maxima in the Midwest. An additional tongue of lightning activity extends along the southwest U.S. over Arizona and New Mexico. We see substantial coincidence in Figure 5 and 6 between the geographical distribution of lightning and that of upper tropospheric NO_x.

2004 was not an anomalous year for lightning over the United States, as shown in Figure 7 with total NLDN lightning flash counts for July-August 2000-2005. There is a notable jump in

lightning flashes from 2001 to 2002, which reflects an upgrade to detection completed during 2002. The comparable years are thus 2003-2005. GEOS-Chem lightning counts computed using consistent GEOS-4 meteorology for 2000-2005 also show relatively little interannual variability in total lightning over the contiguous United States, with 2004 being typical. We find in the model that lightning flash rates over the eastern United States in 2004 are everywhere within 20% of the 1995-2005 mean.

We can make a rough estimate of lightning emissions over the United States during ICARTT by using NLDN flash rates, which only measure cloud-to-ground, multiplying by 4 to account for intracloud flashes [*Boccipio et al.,,* 2001], and assuming a 500 mol NO_x /flash production rate derived from the mean peak NLDN current [*Ott et al*., 2006]. We deduce an emission of 0.45 Tg N from the NLDN dataset. This is a factor of 7 above the standard GEOS-Chem simulation (Table 1). The model captures the maximum along the Gulf Coast but is too low offshore and over the Midwest (Figure 6). We tried to improve this model distribution with alternate lightning parameterizations based on cloud mass flux or convective precipitation [*Allen and Pickering,* 2002], but the cloud mass flux parameterization did not capture the Gulf maximum while the convective precipitation scheme did not capture the lightning distribution over land.

The global lightning source of NO_x in GEOS-Chem is 4.7 Tg N yr^{-1} from 2.7 x 10^9 flashes, corresponding to 125 mol/flash, a factor of 4 below the *Ott et al.*, [2006] estimate, justifying a factor of 4 increase to the GEOS-Chem lightning source over the United States. Figure 5 (right) shows the resulting mean 8-12 km NO_x concentrations, successful over the South where lightning flashes are correctly simulated, but still showing discrepancies in the Midwest due to model error in the geographical distribution of lightning.

On a global scale though, a NO_x yield of 500 mol/flash would appear to lead to an excessive lightning source. The OTD-LIS v1.0 gridded satellite lightning climatology produced by the NASA LIS/OTD Science Team (Principal Investigator, Dr. Hugh J. Christian, NASA /

Marshall Space Flight Center), available from the Global Hydrology Resource Center (http://ghrc.msfc.nasa.gov), yields 1.5 x 10^9 flashes yr^{-1}. Combining a NO_x yield of 500 mol/flash with this global estimate would imply a lightning source of 10.5 Tg N/year, which seems too high based on constraints from satellite observations [*Boersma et al.,* 2005; *Martin et al.*, 2006b] and tropical ozonesondes [*Martin et al.,* 2002]. While physical mechanisms responsible are not well understood, recent observational evidence suggests that NOx yields per flash are lower in tropical than in mid-latitude storms [*Huntrieser et al.*, 2006].

The lifetime of NO_x in the upper troposphere is a major uncertainty in scaling the lightning source to match the ICARTT observations. As shown in section 4, the model OH concentration in the upper troposphere is a factor of 2 higher than observed. Figure 8 shows simulated and observed frequency distributions of NO_x concentrations at 8-12 km on the 2^ox2.5^o model grid. If the model lifetime were too short due to excessive OH, then one might expect the variability in the model to be larger than observed, but Figure 8 shows that this is not the case, adding some support to the simulated NO_x lifetime.

The large lightning source inferred from the ICARTT observations has important implications for tropospheric ozone. *Li et al.,* [2005] found that a semi-permanent upper level cyclone above the southern United States in summer allows ozone build-up in the upper troposphere by trapping convectively lifted precursors and lightning NO_x. *Cooper et al.,* [2006] confirmed the resulting ozone maximum by analysis of ozonesonde data during ICARTT, and found an associated 11-14 ppbv contribution to ozone from lightning averaged over the eastern United States. Figure 4 shows that the improved simulation with increased lightning largely removes the upper tropospheric ozone bias in the original simulation (reduction in surface anthropogenic NO_x emissions in the improved simulation decreases upper tropospheric ozone by only 1-2 ppbv). The residual bias appears due to insufficient lighting generation in the Midwest (Figure 6). We find in the model that lightning enhances upper tropospheric ozone by ~10 ppbv, consistent with the analysis of *Cooper et al.,* [2006].

7. Chemical evolution and export of U.S. NO_x emissions

In this section we use the ICARTT data to estimate the export of anthropogenic NO_y from the U.S. boundary layer to the free troposphere and the speciation of this NO_y. Figure 9 shows the simulated and observed NO_y speciation below 2km. Here and from now on model results are from the improved simulation with reduced fuel NO_x emissions and increased lightning (Table 1). The mean observed NO_x/NO_y ratio at 0-2 km is 30% in the Northeast/Midwest, reflecting the density of sources, 21% in the South, and 15% offshore. The dominant component of NO_y in all three regions is HNO_3, averaging 53% in the Northeast/Midwest and 75% offshore. PAN is favored in the South, despite high temperatures, likely due to large isoprene emission [*Horowitz et al*., 1998]. The mean PAN/NOx ratio is 1.02 in the Northeast/Midwest and 1.54 in the South. The model is remarkably successful at reproducing these fractions and patterns.

We can estimate the export efficiency f of NO_y from the North American boundary layer, following the approach of *Parrish et al.* [2004], by viewing CO as an inert tracer and comparing the enhancement ratio $\Delta NO_y/\Delta CO$ in North American pollution outflow to the anthropogenic molar emission ratio R of CO to NO_x:

$$f = R \cdot \alpha \frac{\Delta NO_y}{\Delta CO} \qquad (1)$$

where α is a correction factor to account for the CO source from boundary layer oxidation of nonmethane hydrocarbons, particularly biogenic isoprene [*Chin et al.,* 1994]. Derivation of the export efficiency following (1) requires estimates of R, α, and the background NO_y and CO concentrations to which the enhancements Δ are referenced. By adopting constant values for these variables, as discussed by Li et al. [2004], we obtain a simple observationally-based diagnostic of export for testing more elaborate models such as GEOS-Chem. We use here and background concentrations of 95 ppbv CO [*Li et al.,* 2004] and 100 pptv NO_y [*Parrish et al*., 2004], $\alpha = 1.2$ [*Chin et al.*,1994], and $R = 5.9$ mol mol^{-1} from

our improved GEOS-Chem simulation for the United States east of 100°W. *R* varies little by region between the Midwest (5.6), South(5.9), and Northeast(6.1).

We apply equation (1) to every anthropogenic pollution plume observed by the DC-8 and WP-3D between 2.5 and 6.5km as defined by a CO enhancement $\Delta CO > 30$ ppbv. Plumes above 6 km are ignored due to lightning NO_x interference, and we also exclude biomass burning plumes diagnosed from nitrile data (section 2). Anthropogenic pollution plumes defined in this manner represent 11% of the combined INTEX-A and ITCT2k4 data at 2.5-6.5 km. From these data we find a mean NO_y export efficiency f =16±10% to the free troposphere with mean composition of 13% NO_x, 40% PAN, and 47% HNO_3. Sampling the model along the ICARTT flight tracks shows a comparable value in both magnitude and variability: f =14 ± 8% with mean composition of 9% NO_x, 42% PAN, and 49% HNO_3. Previous studies using aircraft data for North American outflow in NARE'97 [*Li et al.*, 2004; *Parrish et al.*, 2004] and Asian outflow in TRACE-P [*Koike et al.*, 2003; *Miyazaki et al.*, 2003] similarly found f values in the range 10-20%.

Figure 10 shows the vertical distribution of f and the speciation of this exported NO_y. Highest observed mean and variability of f (18 ±11%) is at 2.5-3.5 km, where HNO_3 dominates the NO_y export fraction (54%). The model in that altitude range shows a similar value of f (15 ± 9 %) and HNO_3 fraction (55%). *Parrish et al.* [2004] proposed that this shallow venting is due to fair weather cumulus breaking through the afternoon boundary layer. In the model, outflow from such shallow wet convection would experience only limited scavenging of soluble species [*Liu et al.*, 2001]. In a 2-km deep updraft column 63% of HNO_3 would be scavenged, allowing for some HNO_3 export to the free troposphere, consistent with observations.

The export efficiency f decreases with altitude in the model and observations reflecting HNO_3 scavenging during uplift, except between 5.5-6.5 km in the model, where lightning may begin to affect the calculation. We see from Figure 10 that PAN is the principal component of exported NO_y above 4 km, both in the observations and in the model.

This dominance of PAN in free tropospheric continental outflow of NO_y has been previously observed in aircraft campaigns downwind of North America [*Parrish et al.*, 2004] and Asia [*Miyazaki et al.*, 2003].

8 Conclusions

The ICARTT study in summer 2004 provided extensive observations of reactive nitrogen (NO_y) species over the eastern United States and western North Atlantic, from the surface to 12 km altitude. We have interpreted these observations with a global 3-D model of tropospheric chemistry (GEOS-Chem) to place constraints on the sources, chemical evolution, and export of NO_y from North America.

ICARTT observations in the continental boundary layer provide top-down verification of the recent decrease in stationary NO_x emissions in the eastern United States mandated by the NO_x SIP Call. Model simulation of NO_x in ICARTT indicates that the latest comprehensive national emission inventory done for 1999 (NEI 99) is too high over the Midwest by almost a factor of 2. This is consistent with the 50% reduction in stationary sources from 1999 to 2004 inferred from power plant smokestack monitoring [*Frost et al.*, 2006] and amounts to a 22% decrease in U.S. anthropogenic NO_x emissions, to 0.62 Tg N for the July 1-August 15 ICARTT period. GEOS-Chem emissions of anthropogenic NO_x during that same period were 0.98 Tg N for East Asia and 0.53 Tg N for Europe.

Observed NO_x concentrations in ICARTT show a sharp rise above 6 km with mean concentrations reaching 0.55 ± 0.36 ppbv at 8-12 km, higher than observed in the U.S. boundary layer and much higher than observed in the upper troposphere on previous U.S. aircraft campaigns (SONEX, SUCCESS, ELCHEM). A close correspondence is observed between the spatial distribution of upper tropospheric NO_x during ICARTT and lightning flash counts observed by the National Lightning Detection Network (NLDN), identifying lightning as the dominant source for the observed NO_x. Using NLDN flash rates for July 1- August 15, scaled up by a factor of 4 to account for intra-cloud flashes [*Boccippio et al.*, 2001], and assuming a 500

mol NO_x /flash production rate following *Ott et al*., [2006], we deduce a lightning NO_x emission of 0.45 Tg N over the United States and adjacent coastal areas. This is a factor of 7 higher than in the standard GEOS-Chem simulation, which uses a yield of 125 mol NO_x/flash for a global lightning NO_x source of 4.7 Tg N yr^{-1}. We can reproduce the upper tropospheric NO_x observed over the southern United States in ICARTT by increasing the lightning NO_x yield in the model by a factor of four to the *Ott et al.* [2006] value.

This also provides a successful simulation of the observed frequency distribution of upper tropospheric NO_x , and corrects a 5-10 ppbv low bias in the simulation of ozone in the free troposphere in the model. The factor of four increase is probably not extrapolatable globally as the resulting global lightning source in the model (19 Tg N yr^{-1}) would be too high relative to observational constraints [*Boersma et al.,* 2005; *Martin et al.,* 2006b]. Recent observations suggest that mid-latitude storms have higher NOx yields than tropical storms [*Huntrieser et al.*, 2006].

Uncertainty in OH concentrations in the upper troposphere is a significant limitation for interpreting quantitatively the observed NO_x concentrations in terms of an implied lightning NO_x source. Simulated upper tropospheric OH concentrations in GEOS-Chem are about a factor of 2 higher than observed in ICARTT, and the same bias is found in box photochemical model calculations constrained with the aircraft observations [*Olson et al.,* 2006b; *Ren et al.*, 2006]. As discussed by *Olson et al.* [2006b] and also in *Spivakovsky et al.* [2000], this discrepancy is beyond what one might expect from standard error propagation in a photochemical model, and points either to instrument error or to some fundamental flaw in understanding of upper tropospheric HO_x chemistry that would in turn affect the simulated NO_x lifetime. A model decrease of OH by a factor of 2 would correspondingly decrease the required increase in the lightning NO_x source.

We examined the speciation of NO_y over the United States, in the observations and in the model, to gain insight into the chemical evolution and export of NO_y. The NO_x fraction is largest

in the boundary layer over the Northeast, averaging 30%, and reflecting the density of sources. PAN makes a somewhat larger contribution to NO_y in the Southeast than elsewhere, possibly reflecting isoprene emissions. The model reproduces well the observed partitioning of NO_y for all regional and altitudes, implying a good understanding of NO_y chemistry.

We estimated the export efficiency *f* and related speciation of NO_y out of the North American boundary layer with a Lagrangian analysis of NO_y -CO correlations in the free troposphere, following the approach of *Parrish et al.* [2004]. For the ICARTT data at 2.5-6.5 km altitude we find $f = 16\pm10\%$ in the observations and $14\pm8\%$ in the model, consistent with previous studies of North American and Asian outflow [*Li et al.,* 2004; *Parrish et al.,* 2004; *Koike et al.,* 2003; *Miyazaki et al.,* 2003]. The highest export efficiency is in the lower free troposphere but is then mostly HNO_3 venting from shallow convection. We find that PAN is the dominant component of exported NO_y (>50%) in pollution plumes above 3.5 km, consistent with previous studies of Asian outflow. The successful simulation of export of North American NO_y offers confidence in current model estimates of North American influence on the global NO_y and ozone budgets [*Li et al.*, 2004] with implications for intercontinental pollution [*Li et al*., 2002]..

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Table Caption

Table 1. Contiguous United States NO_x Emissions for July 1 – August 15, 2004

Figure Captions

Figure 1. Flight tracks for ITCT 2k4 (right) and INTEX-NA (left) aircraft campaigns (July 1- August 15) shaded by altitude. Shaded areas define regions (left) used in comparisons between model and observations: South (mid-grey), Northeast (light grey) and Midwest (dark grey).

Figure 2. Mean July-August anthropogenic NO_x emissions in the United States. 1999 values from the EPA National Emissions Inventory (NEI99 v1) are compared to 2004 values including a 50% reduction in point source emissions. Emissions from Canada and Mexico are from GEIA scaled to 1998 following *Bey et al.,* [2001]. Colorscale saturates at 5 x 10^{12} molecules/cm^{-2} s^{-1}

Figure 3. Mean vertical profiles of OH, HO_2, H_2O_2, HCHO and HNO_4 concentrations. Observations from the DC-8 aircraft (thick black) are compared to model results using the original (dashed grey) and improved (thick grey) simulations and compared to observations (black). Horizontal bars are standard deviations on the observations. Here and in subsequent figures, the ICARTT observations have been filtered to remove urban plumes, biomass burning plumes, and stratospheric air as described in text. Model results are sampled along the flight tracks at the time of flights. Modifications to emissions from the original to the improved simulation include a four-fold increase in the lightning source, upward extension of the lightning source to the July mean tropopause height, and a 50% reduction of the NEI99 v1 CO transport and NO_x point source emissions.

Figure 4. Same as Figure 3 for CO, NO_x (median), PAN, HNO_3,and ozone concentrations as sampled by the DC-8 (top) and the WP-3D (bottom) aircraft.

Figure 5. Mean upper tropospheric NO_x concentrations (8-12 km) during ICARTT (July - August 2004). Observations (left) are compared to improved model values (right) over the 2ox2.5o model grid. The improved model has a factor of four increase in the United States lightning emissions relative to the standard GEOS-Chem version.

Figure 6. Mean lightning flash rates for July 1 - August 15, 2004. Observations of cloud-to-ground lightning from the National Lightning Detection Network, multiplied uniformly by a factor of 4 to account for intracloud lightning, are compared to standard GEOS-Chem results.

Figure 7. Cloud-to-ground lightning flash counts in July-August 2000-2005 over the United States. National Lightning Detection Network flash counts (grey bars) are compared to modeled flash counts in GEOS-Chem derived using GEOS-4 meteorology for the domain 130-70°W, 25-50°N (grey and white bars). Model flash counts are divided

uniformly by a factor of 4 to account for intracloud lightning [*Boccipio et al*., 2001]. The jump in NLDN data between 2001 to 2002 reflects an upgrade in detection; thus, comparable years are 2003-2005.

Figure 8. Frequency distribution of concentrations at 8-12 km altitude during ICARTT. Observations (line) are compared to results from the improved model with increased lightning source (grey bars). The frequency distribution is shown as he number of occurances on the 2°x2.5° grid.

Figure 9. Mean relative molar contribution of NO_x, PAN and HNO_3, to total NO_y defined as NO_y=NO_x+PAN+HNO_3 in the ICARTT data (July 1 - August 15, 2004). Urban, biomass burning, and stratospheric plumes have been excluded as described in the text. Observations from the DC-8 and WP-3D aircraft are compared to model results sampled along the flight tracks.

Figure 10. Speciated export efficiency of NOy (defined as NO_y = NO_x + PAN + HNO_3) from the North American boundary layer during ICARTT, derived from equation (1) as a function of altitude. Observations (left) are compared to model results (right).