

1 **Surface and lightning sources of nitrogen oxides in the United States:**
2 **magnitudes, chemical evolution, and outflow**

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39 **Running Title:** NO_y sources, evolution, and export

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41 **Key Words:** reactive nitrogen, pollution, lightning
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43 **Index Terms:** 0322 Atmospheric Composition and Structure: Constituent Sources and Sinks, 0345
44 Pollution: urban and regional (0305 , 0478 , 4251), 0368 Troposphere: constituent transport and
45 chemistry, 3324 Lightning, 9350 North America
46
47
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49 **Submitted to the Journal of Geophysical Research – Atmospheres, August 10, 2006**
50

Abstract

We use observations from the ICARTT study over eastern North America during summer 2004, interpreted with a global 3-D model of tropospheric chemistry (GEOS-Chem) to test current understanding of the regional reactive nitrogen (NO_y) budget, including nitrogen oxide radicals ($\text{NO}_x = \text{NO} + \text{NO}_2$) and their principal reservoirs (PAN, HNO_3). We evaluate the model representation of NO_y sources, chemical evolution, and outflow. We find boundary layer NO_x data confirm a 50% decrease in power plant and industry NO_x emissions over eastern United States between 1999 and 2004 due to the NO_x SIP Call. Observed 8-12 km NO_x concentrations were 0.55 ± 0.36 ppbv, larger than in previous United States aircraft campaigns (ELCHEM, SUCCESS, SONEX). We show lightning was the dominant source of this NO_x and had ~ 10 ppbv impact on upper tropospheric ozone. Simulating upper tropospheric NO_x requires a factor of 4 increase in NO_x yield (to 500 mol/flash). However, a major uncertainty relating NO_x quantitatively to lightning is OH; OH concentrations were a factor of 2 lower than can be explained from current photochemical models. A Lagrangian analysis of the fraction of North American NO_x emissions vented to the free troposphere (f) using NO_y -CO correlations shows observed $f=16\pm 10\%$ and modeled $f=14\pm 8\%$, consistent with previous studies. Export from 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 United States contribution to tropospheric ozone through NO_x and PAN export.

1 1. **Introduction**

2 Quantifying the sources and fate of nitrogen oxides ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$) over northern mid-
3 latitudes continents is critical for assessing anthropogenic influence on global tropospheric ozone
4 [*Pickering et al.*, 1992; *Jacob et al.*, 1993; *Thompson et al.*, 1994; *Li et al.*, 2004]. The
5 International Consortium on Atmospheric Transport and Transformation (ICARTT) study [*Singh*
6 *et al.*, 2006a; *Fehsenfeld et al.*, 2006], which took place in July – August 2004 over the eastern
7 United States and the North Atlantic, provides an opportunity for this purpose. We present here a
8 global 3-D model analysis of ICARTT observations for NO_x , its chemical reservoirs, and related
9 species to quantify continental NO_x sources from combustion and lightning, determine the
10 chemical fate of NO_x in the United States boundary layer and in North American outflow, and
11 examine the implications for ozone.

12 Ozone production in the troposphere is principally limited by the supply of NO_x [*Chameides*,
13 1992]. Fossil fuel combustion accounts for over half of the global NO_x source [*Intergovernmental*
14 *Panel on Climate Change (IPCC)*, 2001]. The United States has been actively reducing its
15 summertime NO_x emissions since 1998 to decrease ozone smog. The Environmental Protection
16 Agency (EPA) NO_x State Implementation Plan (SIP) Call mandated that 22 eastern states and the
17 District of Columbia revise their SIPs to meet state-specific total NO_x emissions reductions by
18 2003 (Phase 1) and further reduction by 2007 (Phase 2). By 2003, all 22 states had reduced NO_x
19 point source emissions to their Phase 1 levels. *Frost et al.*, [2006] determined that as a result
20 emission rates of power plant NO_x have decreased approximately 50% between 1999 and 2003.
21 NO_x levels in the U.S. will likely continue to drop. In March 2005, the EPA issued the Clean Air
22 Interstate Rule, which will, when fully implemented, permanently reduce NO_x emissions to 60%
23 of 2003 levels in 25 eastern states, and the District of Columbia. The ICARTT observations offer
24 an opportunity to check on these emission reductions.

25 Oxidation of NO_x to HNO_3 , peroxyacetylnitrate (PAN), and other minor products takes place
26 on the order of hours, so that rapid ozone production is confined to the continental boundary layer

1 (CBL), seemingly limiting its affect on global ozone. However, the dependence of ozone
2 production on NO_x is highly nonlinear; the ozone production efficiency per unit NO_x consumed
3 (OPE) increases rapidly as the NO_x concentration decreases [*Liu et al.*, 1987]. This means that a
4 small fraction of emitted NO_x exported to the free troposphere by frontal lifting, deep convection,
5 or boundary layer venting could lead to significant ozone production in the free troposphere over
6 the continent or just downwind [*Jacob et al.*, 1993; *Thompson et al.*, 1994]. Similarly, PAN
7 (which is thermally unstable and not water-soluble) can be vented from the boundary layer and
8 transported on a global scale at cold temperatures, eventually decomposing to release NO_x as air
9 masses subside. The resulting NO_x produces ozone with high efficiency because background NO_x
10 concentrations are low. Quantifying the sources, chemical evolution, and export of anthropogenic
11 NO_x (and PAN) is thus critical to understanding the North American contribution to the global
12 ozone budget. This contribution is important from the perspective of ozone as a greenhouse gas
13 [*Mickley et al.*, 2004] and for intercontinental transport of ozone pollution [*Jacob et al.*, 1999;
14 *Holloway et al.*, 2003].

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

21 Early Eulerian models found that the fraction f of NO_x emitted in the United States that is
22 exported out of the CBL as NO_y (sum of NO_x and its oxidation products) ranges from 25% in
23 summer to 35% in winter [*Horowitz et al.*, 1998; *Liang et al.*, 1998]. Subsequent Lagrangian
24 analyses using NO_y -CO correlations measured from aircraft in free tropospheric outflow (2-6
25 km), over the North Atlantic in September (NARE '97) seemed to contradict these model results,
26 with estimates of f ranging from only 3% [*Stohl et al.*, 2002] to 9 ± 14 % [*Parrish et al.*, 2004].

1 *Li et al.* [2004] reconciled the Eulerian and Lagrangian approaches by pointing out that the early
2 Eulerian models had insufficient HNO₃ scavenging, while the Lagrangian models underestimated
3 background CO. They derived a consistent value $f = 17\text{-}20\%$ by both approaches for the
4 NARE'97 period. The ICARTT study offers far more geographical coverage and chemical
5 information in the boundary layer and the free troposphere than previous studies, enabling better
6 constraints on the estimates of anthropogenic export and associated NO_y speciation, as well as the
7 underlying source and chemical factors.

8 **2. The ICARTT Study**

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

15 The NOAA NEAQS- ITCT 2004 campaign [*Fehsenfeld et al.*, 2006] took place July 3 –
16 August 15, 2004 over the NW Atlantic and the NE United States out of Portsmouth, New
17 Hampshire (Figure 1). It used a WP-3D aircraft (ceiling ~6 km). The NASA INTEX-A campaign
18 [*Singh et al.*, 2006a] took place June 29 – August 14 over the central and eastern United States,
19 and the North Atlantic, from bases at Edwards (California), St. Louis (Missouri), and Portsmouth
20 (New Hampshire) (Figure 1). It used a DC-8 aircraft (ceiling ~12 km). We make use here of 1-
21 minute average measurements of ozone, CO, CH₂O (NCAR measurement used for DC-8), HNO₄,
22 H₂O₂, NO (Pennsylvania State U. measurement used for DC-8), NO₂, HNO₃ (U. New Hampshire
23 measurement used for DC-8), PAN, OH, and HO₂ concentrations. As shown in Figure 1, the WP-
24 3D remained close to New England throughout the mission, focusing on emissions verification
25 and chemical transformation of major urban pollution plumes

1 Ventilation of the eastern United States in summer is primarily driven by cyclones
2 tracking eastward typically every 5 days in the 45° - 55°N band [Li *et al.*, 2005]. During ICARTT
3 a persistent trough along the east coast led to cyclones extending further south [Fuelberg *et al.*,
4 2006]. This paucity of stagnant surface high pressure led to a record low number of air quality
5 violations in the eastern United States for summer 2004 [Thompson *et al.*, 2006]. Another
6 mechanism for CBL venting, particularly in the south, is by deep convection from surface
7 heating; this mechanism is often associated with lightning activity. Summer 2004 was a typical
8 lightning year as will be discussed in Section 6.

9 3. Model Description

10 We simulate the ICARTT chemical observations with the GEOS-Chem global 3-D model of
11 tropospheric chemistry (version 7.02; <http://www.as.harvard.edu/chemistry/trop/geos/>) driven by
12 assimilated meteorological observations from the Goddard Earth Observing System (GEOS-4) of
13 the NASA Global Modeling and Assimilation Office (GMAO). The model is applied to a global
14 simulation of ozone-NO_x-VOC-aerosol chemistry with 120 species simulated explicitly. A
15 general description of GEOS-Chem is given by Bey *et al.* [2001] and a description of the coupled
16 oxidant-aerosol simulation as used here is given by Park *et al.* [2004]. Emissions in the model are
17 as described by Park *et al.* [2004] unless specified otherwise.

18 Meteorological fields in the GEOS-4 data have a temporal resolution of 6 hours (3 hours
19 for surface variables and mixing depths) and a horizontal resolution of 1° latitude by 1.25°
20 longitude, with 55 vertical sigma levels between the surface and 0.1 hPa (including about 16 in
21 the troposphere and 5 in the boundary layer up to 2 km). For input to GEOS-Chem we degrade
22 here the horizontal resolution to 2° latitude by 2.5° longitude. The ozone flux is specified globally
23 with the Synoz method [McLinden *et al.*, 2000] and distributed according to the GEOS-4
24 meteorological fields, while the NO_y flux is calculated from N₂O oxidation in the model
25 stratosphere [Bey *et al.*, 2001]. Global cross-tropopause fluxes of ozone and NO_y are 495 Tg O₃
26 yr⁻¹ and 2 Tg N yr⁻¹, respectively. The simulations are conducted for July-August 2004 and are

1 initialized with a 18-month spin-up simulation. For comparison with observations, the model was
2 sampled along the aircraft flight tracks and times.

3 A major focus of our work is to use the ICARTT observations to test and improve U.S.
4 NO_x emission estimates. We will show simulations with “original” emissions based on a priori
5 information, and “improved” emissions that reflect the ICARTT constraints and improved
6 understanding. These emissions for the ICARTT period (July 1 – August 15, 2004) are
7 summarized in Table 1. Original fossil and biofuel emissions in the United States are from the
8 EPA 1999 National Emission Inventory (NEI99). They amount to 0.79 Tg N for July 1 –August
9 15 and 6.2 Tg N annually, with distribution shown in Figure 2 (left). Transportation accounts for
10 35%, industry 17%, power generation 26%, and other sources 22% (mostly non-road vehicles).
11 As we will see in section 5, this inventory overestimates observed NO_x concentrations in the U.S.
12 boundary layer, consistent with reduction of NO_x emissions from point sources (power plants,
13 industry) by 50% from 1999 to 2004 driven by the NO_x SIP Call [*Frost et al.*, 2006]. Reduction
14 of the power plant and industry sources results in the improved inventory of Table 1 and Figure 2
15 (right). The ICARTT data also show that CO emissions in the NEI99 inventory are 30% too high,
16 as discussed below, and we make this adjustment in the improved inventory.

17 The global lightning source of NO_x in GEOS-Chem is 4.7 Tg N yr^{-1} from 2.7×10^9
18 flashes, computed with the scheme of *Price and Rind* [1992] that relates number of flashes to
19 convective cloud top heights, and distributed vertically following *Pickering et al.* [1998] (55-
20 75% above 8 km, up to 23% in lowest km). The resulting U.S. emissions for the ICARTT period
21 (original inventory) are 0.067 Tg N for the contiguous United States and coastal waters (130-
22 70°W, 25-50°N), concentrated over the Southwest and along the Gulf of Mexico. As we will see
23 in section 6, successful simulation of the ICARTT upper tropospheric NO_x observations in
24 GEOS-Chem requires a factor of 4 increase in this source along with an upward shift to the July
25 mean tropopause height, and this is included in the improved inventory.

1 Extensive and persistent boreal forest fires took place in Alaska and NW Canada in
2 summer 2004; in contrast, there were no significant fires in Siberia. We use the daily biomass
3 burning inventory of *Turquety et al.* [2006] for North American fires during ICARTT. This
4 inventory was constructed by combining daily area burned reports from government agencies and
5 hot spots detected from space by the MODIS instrument with estimates of fuel loadings and
6 emission factors depending on the type of ecosystem burned. This inventory for CO was
7 evaluated against MOPITT columns as described by *Turquety et al.* [2006]. North American CO
8 and NO_y fire emissions for July 1 –August 15 are 20 Tg CO, 0.3 Tg N. Short-lived VOCs emitted
9 from fires drive fast conversion of NO_x to PAN, slowing down ozone formation [*Jacob et al.*,
10 1992] but this is inadequately represented in the model [*Hudman et al.*, 2006]. In the improved
11 emission inventory we release 80% of the biomass burning NO_x as PAN.

12 A number of previous studies have applied GEOS-Chem to interpret North American
13 chemical observations including surface data for ozone [*Fiore et al.*, 2002, 2003ab; *Li et al.*,
14 2002a] and aerosols [*Park et al.*, 2003, 2004, 2006; *van Donkelaar et al.*, 2006ab], ozonesondes
15 [*Li et al.*, 2002b, 2005], and satellite observations of NO₂ [*Martin et al.*, 2002, 2003],
16 formaldehyde [*Palmer et al.*, 2001, 2003, 2006], and aerosols [*Liu et al.*, 2004, 2005].
17 Applications of GEOS-Chem to interpretation of the ICARTT data, using the same model version
18 as here, are presented by *Turquety et al.* [2006] for biomass burning over North America
19 constrained by MOPITT observations, *Millet et al.* [2005] for formaldehyde, *Liang et al.* [2006]
20 for Asian influence over North America, *Xiao et al.* [2006] for acetylene, *Heald et al.* [2006] for
21 organic aerosols, and *Hudman et al.* [2006] for ozone-CO relationships. Of particular relevance to
22 our work are the previously mentioned GEOS-Chem study by *Li et al.*, [2004], which
23 successfully reproduced observed export of NO_y from North America during the NARE'97
24 campaign, and the study by *Martin et al.*, [2006], which applied GEOS-Chem to space-based
25 observations of NO₂ columns from SCIAMACHY as a test of NO_x emission during ICARTT.

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1 4. Hydrogen oxide radicals and reservoir species

2 Figure 3 shows simulated and observed mean vertical distributions of OH, HO₂, H₂O₂, CH₂O,
3 and HNO₄ for the ensemble of INTEX-A flights. In this comparison we have excluded fresh
4 pollution plumes, biomass burning plumes, and stratospheric air as diagnosed by NO_x/NO_y > 0.4
5 mol mol⁻¹ or NO₂ > 4 ppbv and altitude < 3 km (the latter criterion being used when all NO_y
6 components were not available from the INTEX-A data); HCN > 500 pptv or CH₃CN > 225 pptv;
7 and ozone/CO > 1.25 mol mol⁻¹ respectively. OH increases with altitude from 0.15 pptv at the
8 surface to 0.43 pptv at 11 km, while HO₂ decreases from 19 pptv at the surface to 5 pptv at 11 km
9 reflecting the positive relationship of OH/HO₂ ratio with NO [Jaeglé *et al.*, 2000]. H₂O₂
10 concentrations gradually decrease from 2.6 pptv at the surface to 0.15 pptv at 11km, reflecting the
11 decrease in water vapor [Heikes *et al.*, 1992]. CH₂O similarly decreases with altitude. HNO₄, an
12 important HO_x reservoir in the upper troposphere [Jaeglé *et al.*, 2000], has an 8-9 km peak of 62
13 pptv.

14 OH and HO₂ in the original simulation match observations in the lowest 1 km, but are too
15 high above by 60% and 30% respectively. Increasing the lightning NO_x source in the improved
16 simulation decreases HO₂ while increasing OH. Above 8km, this corrects the HO₂ overestimate
17 but worsens the OH overestimate. Similar HO_x simulation biases are found in a box model
18 constrained with local ICARTT observations [Olson *et al.*, 2006b; Ren *et al.*, 2006]. H₂O₂ is well
19 simulated in the free troposphere, but is overestimated below 3 km by ~30% due to the H₂O₂
20 source from HO₂ uptake by aerosols [Martin *et al.*, 2003]. The CH₂O simulation, discussed
21 in detail by Millet *et al.*, [2006], matches observations closely. HNO₄ is well matched in the
22 original simulation but is overestimated by 30% when the lightning source is increased.

23 The HO_x simulation bias shown in Figure 3 has important implications for the interpretation
24 of the NO_x data, and similarity between the GEOS-Chem and box model biases [Olson *et al.*,
25 2006b] indicates that it is not a model-specific problem. Previous simulations of OH and HO₂

1 observations in the upper troposphere at northern mid-latitudes do not show such bias [*Jaeglé et*
2 *al.*, 1997, 2000; *Wennberg et al.*, 1998]. We assume in what follows that the model HO_x is
3 correct, but will return at the end to examine the effects of this assumption.

4 **5. Boundary Layer NO_x over the United States**

5 Figure 4 compares simulated and observed mean vertical distributions of CO, NO_x, PAN,
6 HNO₃, and ozone concentrations for the ensemble of DC-8 and WP-3D flights. Observed CO,
7 NO_x, PAN, and HNO₃ are elevated below 3 km, reflecting anthropogenic sources over the
8 continent. The model with original emissions is too high for all four species. *Parrish*, [2006]
9 using urban ambient measurements of the CO/NO_x ratio along with fuel sales data confirms the
10 magnitude of the NEI99 NO_x on-road transport source and infers a long-term increase for 1985-
11 1999, but finds that CO from on-road transport, which makes up 60% of total CO emissions in
12 the United States, is overestimated in by 50%. Reducing this source in the improved inventory
13 decreases the mean CO bias from 45 ppbv to 20 ppbv in the WP-3D data and from 20 to 10 ppbv
14 for the DC-8 data (Figure 4).

15 Figure 5 shows the spatial distribution of the model NO_x bias in the boundary layer using the
16 NEI99 inventory. The overestimate is mainly over the Midwest and the Gulf Coast, not over the
17 Northeast. *Martin et al.*, [2006], using a combination of ICARTT and satellite (SCIAMACHY)
18 data, find that NO_x emissions along the East Coast, where on-road transport source dominates
19 NO_x emissions, were underestimated using NEI99 during 2004 consistent with *Parrish* [2006].
20 Stationary sources (power plants and industry) are heavily concentrated in Midwest and South
21 (Figure 2). Reducing the U.S. NO_x emissions from stationary sources by 50% from 1999 to 2004
22 to account for the NO_x SIP Call [*Frost et al.*, 2006] removes much of the model boundary layer
23 NO_x bias (Figure 4); the median model-to-observed ratio in the Midwest decreases from 1.9 to
24 1.3.

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26

1 **6. Upper tropospheric NO_x over the United States**

2 NO_x concentrations observed in ICARTT show a decrease from the boundary layer to the free
3 troposphere, but then a sharp rise with altitude above 6 km (Figure 4). Mean concentrations reach
4 0.55 ± 0.36 ppbv at 8-12 km altitude, higher than in the boundary layer. The NO/NO_x molar ratio
5 averages 75% both in the observations and the model (all data are for daytime). Observed PAN
6 shows a broad maximum at 6-10 km. In contrast, HNO₃ is depleted in the free troposphere due to
7 scavenging during uplift. Mean ozone increases with altitude from 50 ppbv near the surface to 75
8 ppbv at 8km.

9 The original model greatly underestimates the upper tropospheric NO_x enhancement; the
10 discrepancy increases with altitude from a factor of 3 at 8 km to a factor of 5 at 11 km. Simulated
11 PAN is too low by ~30% while HNO₃ is well simulated. Ozone is too low by 10 ppbv throughout
12 the free troposphere. As we will see these discrepancies appear to be largely due to an
13 underestimate of the lightning NO_x source over the United States.

14 Measurements of upper tropospheric NO_x from previous aircraft campaigns over the United
15 States indicated much lower concentrations than observed in ICARTT. *Jaeglé et al.*, [1998] report
16 mean NO concentrations from the SUCCESS campaign out of Kansas (April – May 1996) of
17 0.030 ± 0.022 ppbv for 8-10 km and 0.061 ± 0.045 ppbv for 10-12 km. *Ridley et al.*, [1994]
18 report mean NO concentrations of 0.2 ± 0.1 ppbv over New Mexico during during ELCHEM
19 (July – August 1989), even though convection was frequently targeted. SONEX observations in
20 October-November 1997 over Maine and Atlantic Canada indicate mean NO concentrations
21 between 6-12 km of 0.1 ppbv (all data) and 0.23 ppbv (convective outflow) [*Crawford et al.*,
22 2000]. SUCCESS and SONEX were in spring and fall, whereas lightning over the United States
23 peaks in June-August; ELCHEM took place in the southwestern United States whereas maximum
24 lightning is over the Gulf Coast [*Orville and Huffines*, 2001].

1 Figure 6 (left) shows the observed spatial distribution of upper tropospheric NO_x. Values
2 exceeding 1 ppbv extend over much of the Southeast and Midwest. Deep convective injection of
3 boundary layer pollution cannot explain these high values since the NO_x mixing ratio above 8 km
4 is greater than that in the boundary layer (Figure 4). Aircraft emissions cannot provide an
5 explanation either because the geographical distribution does not match, and in any case these
6 emissions are fairly well constrained from atmospheric measurements [Meijer *et al.*, 2000] and
7 represent only a small source of upper tropospheric NO_x (Table 1).

8 Lightning provides the best explanation for the elevated NO_x in the upper troposphere
9 during ICARTT. Figure 7 (left) shows National Lightning Detection Network (NLDN) mean
10 lightning flash rates for July 1- August 15. The NLDN data (>100 sites in the continental United
11 States) were collected by Vaisala (www.vaisala.com) and supplied to us by the Global Hydrology
12 Resource Center at NASA Marshall Space Flight Center. Flash detection efficiencies are ≥90%
13 over the continental United States and degrade rapidly off-shore and beyond U.S. borders
14 (detection goes to zero at ~1000 km). The NLDN network measures only cloud-to-ground
15 lightning flashes, and intracloud flashes are estimated to be about 3 times that amount [Boccippio
16 *et al.*, 2001]. The NLDN lightning activity is heaviest in the Gulf of Mexico region but also has
17 maxima in the Midwest. An additional tongue of lightning activity extends along the southwest
18 U.S. over Arizona and New Mexico. We see substantial coincidence in Figure 6 and 7 between
19 the geographical distribution of lightning and that of upper tropospheric NO_x.

20 2004 was not an anomalous year for lightning over the United States, as shown in Figure
21 8 with total NLDN lightning flash counts for July-August 2000-2005. There is a notable jump in
22 lightning flashes from 2001 to 2002, which reflects an upgrade to detection completed during
23 2002. The comparable years are thus 2003-2005. Simulated lightning counts computed using
24 consistent GEOS-4 meteorology for 2000-2005 also show relatively little interannual variability
25 in total lightning over the contiguous United States, with 2004 being typical. We find in the

1 model that lightning flash rates over the eastern United States in 2004 are everywhere within 20%
2 of the 1995-2005 mean.

3 We can make a gross estimate of lightning emissions over the United States during
4 ICARTT by using NLDN flash rates corrected for an intra-cloud/cloud-to-ground flash ratio of
5 ~ 3 (Figure 7) and a 500 mol NO_x /flash production rate derived from the mean peak NLDN
6 current [Ott *et al.*, 2006]. We deduce an emission of 0.45 Tg N from the NLDN dataset. This is a
7 factor of 7 above the original GEOS-Chem simulation (Table 1). The model captures the
8 maximum in the southern United States but is too low offshore and over the Midwest (Figure 7).
9 We tried to improve this model distribution with alternate lightning parameterizations based on
10 cloud mass flux or convective precipitation [Allen and Pickering, 2002], but the cloud mass flux
11 parameterization did not capture the Gulf maximum while the convective precipitation scheme
12 did not capture the lightning distribution over land.

13 The global lightning source of NO_x in GEOS-Chem is 4.7 Tg N yr^{-1} from 2.7×10^9
14 flashes, corresponding to 125 mol/flash, a factor of 4 below the Ott *et al.*, [2006] estimate,
15 justifying a factor of 4 increase to the GEOS-Chem lightning source over the United States.
16 Figure 6 (right) shows the resulting mean 8-12 km NO_x concentrations, successful over the South,
17 but still showing discrepancies in the Midwest due to model error in the geographical distribution
18 of lightning. On a global scale though, a NO_x yield of 500 mol/flash would appear to lead to an
19 excessive lightning source. The OTD-LIS v1.0 gridded satellite lightning climatology produced
20 by the NASA LIS/OTD Science Team (Principal Investigator, Dr. Hugh J. Christian, NASA /
21 Marshall Space Flight Center), available from the Global Hydrology Resource Center
22 (<http://ghrc.msfc.nasa.gov>), yields 1.5×10^9 flashes yr^{-1} . Combining a NO_x yield of 500 mol/flash
23 with this global estimate would imply a lightning source of 10.5 Tg N/year, which seems too high
24 based on constraints from satellite observations [Boersma *et al.*, 2005; Martin *et al.*, 2006b] and
25 tropical ozonesondes [Martin *et al.*, 2002]. Peak currents, which determine NO_x yield, may be
26 different for tropical vs. mid-latitude storms [K.E. Pickering, pers. comm.].

1 The lifetime of NO_x in the upper troposphere is a major uncertainty in scaling the
2 lightning source to match the ICARTT observations. As shown in section 4, the model OH
3 concentration in the upper troposphere is a factor of 2 higher than observed. A test of NO_x
4 lifetime is to compare the simulated and observed frequency distributions of NO_x concentrations
5 at 8-12 km, as shown in Figure 9. If the model lifetime were too short due to excessive OH, then
6 one might expect the variability in the model to be larger than observed, but Figure 9 shows that
7 this is not the case.

8 The large lightning source inferred from the ICARTT observations has important
9 implications for tropospheric ozone. *Li et al.*, [2005] found that a semi-permanent upper level
10 cyclone above the southern United States in summer allows ozone build-up in the upper
11 troposphere by trapping convectively lifted precursors and lightning NO_x . *Cooper et al.*, [2006]
12 confirmed the resulting ozone maximum by analysis of ozonesonde data during ICARTT. Figure
13 4 shows that the improved simulation with increased lightning largely removes the upper
14 tropospheric ozone bias in the original model. The residual bias appears due to insufficient
15 lightning generation in the Midwest (Figure 7).

16 **7. Chemical evolution and Export of U.S. NO_x emissions**

17 In this section we use the ICARTT data to estimate the export of NO_y from the United States to
18 the free troposphere and the speciation of this NO_y . We define here NO_y in both data sets as NO_y
19 = $\text{NO}_x + \text{HNO}_3 + \text{PAN}$, ignoring minor species such as alkyl nitrates and nitrate aerosol that
20 accounted typically for less than 10% NO_y and for which observations were sparse and only on
21 the DC-8. Figure 10 shows the simulated and observed NO_y speciation below 2km. Here and
22 from now on model results are from the improved simulation with reduced fuel NO_x emissions
23 and increased lightning (Table 1). The mean observed NO_x/NO_y ratio at 0-2 km is 30% in the
24 Northeast/Midwest, reflecting the density of sources, 21% in the South, and 15% offshore. The
25 dominant component of NO_y in all three regions is HNO_3 , averaging 53% in the
26 Northeast/Midwest and 75% offshore. The PAN fraction is highest in the south (20%), which

1 could reflect high isoprene emissions [Horowitz *et al.*, 1998]. The model is remarkably successful
2 at reproducing these fractions and patterns.

3 We can estimate the export fraction f of NO_y from the North American boundary layer,
4 following the approach of Parrish *et al.* [2004], by viewing CO as an inert tracer and comparing
5 the enhancement ratio $\Delta\text{NO}_y/\Delta\text{CO}$ in North American pollution outflow to the anthropogenic
6 molar emission ratio R :

$$7 \quad f = R \cdot \alpha \frac{\Delta\text{NO}_y}{\Delta\text{CO}} \quad (1)$$

8 where $\alpha = 1.2$ is a scaling coefficient to account for boundary layer CO production from
9 oxidation of biogenic VOCs, in particular isoprene [Chin *et al.*, 1994]. Enhancements are
10 calculated relative to background concentrations of 95 ppbv CO [Li *et al.*, 2004] and 100 pptv
11 NO_y [Parrish *et al.*, 2004]. We use $R = 5.9 \text{ mol mol}^{-1}$ from our improved model simulation for the
12 United States east of 100°W . Assuming constant values for these variables is obviously an
13 oversimplification but provides a simple observationally-based diagnostic of export. Li *et al.*
14 [2004] present a detailed analysis of the validity of this approach from a 3-D model perspective.

15 We apply equation (1) to every anthropogenic pollution plume observed between 2.5 and
16 6.6 km as defined by a CO enhancement $\Delta\text{CO} > 30$ ppbv. Plumes above 6 km are ignored due to
17 lightning NO_x interference, and we also exclude biomass burning plumes diagnosed from nitrile
18 data (section 4). Anthropogenic pollution plumes defined in this manner represent 11% of the
19 combined INTEX-A and ITCT2k4 data at 2.5-6.5 km. From these data we find a mean NO_y
20 export efficiency $f = 16 \pm 10\%$ to the free troposphere with mean composition of 13% NO_x , 40%
21 PAN, and 47% HNO_3 . Sampling the model along the ICARTT flight tracks shows a comparable
22 value in both magnitude and variability: $f = 14 \pm 8\%$ with mean composition of 9% NO_x , 42%
23 PAN, and 49% HNO_3 . Previous studies using aircraft data for North American outflow in
24 NARE'97 [Li *et al.*, 2004; Parrish *et al.*, 2004] and Asian outflow in TRACE-P [Koike *et al.*,
25 2003; Miyazaki *et al.*, 2003] similarly found f values in the range 10-20%.

1 Figure 11 shows the vertical distribution of f and the speciation of this exported NO_y . The
2 total number of plumes observed decreases with altitude both in the model and in observations.
3 Highest observed mean and variability in f ($18 \pm 11\%$) is at 2.5-3.5 km, where HNO_3 dominates
4 the NO_y export fraction (54%). The model in that altitude range shows a similar value of f (15 ± 9
5 %) and HNO_3 fraction (55%). *Parrish et al.* [2004] proposed that this shallow venting is due to
6 fair weather cumulus breaking through the afternoon boundary layer. In the model, outflow from
7 such shallow wet convection would experience only limited scavenging of soluble species [*Liu et*
8 *al.*, 2001]. The decrease in export efficiency f with altitude in the model and observations reflects
9 HNO_3 scavenging during lifting. We see from Figure 13 that PAN is the principal component of
10 exported NO_y above 4 km, both in the observations and in the model. This dominance of PAN in
11 free tropospheric continental outflow of NO_y has been previously observed in aircraft campaigns
12 downwind of North America [*Parrish et al.*, 2004] and Asia [*Miyazaki et al.*, 2003].

13 **8. Conclusions**

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

19 ICARTT observations in the continental boundary layer provide top-down verification of the
20 recent decrease in stationary NO_x emissions in the eastern United States mandated by the NO_x
21 SIP Call. Model simulation of NO_x in ICARTT indicates that the latest comprehensive national
22 emission inventory done for 1999 (NEI 99) is too high over the Midwest by almost a factor of 2
23 though not over the Northeast (where mobile sources dominate NO_x emissions). This is consistent
24 with the 50% reduction in stationary sources from 1999 to 2004 inferred from power plant
25 smokestack monitoring [*Frost et al.*, 2006] and amounts to a 22% decrease in U.S. anthropogenic
26 NO_x emissions, to 0.62 Tg N for the July 1-August 15 ICARTT period. GEOS-Chem emissions

1 of anthropogenic NO_x during that same period were 0.98 Tg N for East Asia and 0.53 Tg N for
2 Europe.

3 Observed NO_x concentrations in ICARTT show a sharp rise above 6 km with mean
4 concentrations reaching 0.55 ± 0.36 ppbv at 8-12 km, higher than observed in the U.S. boundary
5 layer and much higher than observed in the upper troposphere on previous U.S. aircraft
6 campaigns (SONEX, SUCCESS, ELCHEM). A close correspondence is observed between the
7 spatial distribution of upper tropospheric NO_x during ICARTT and lightning flash counts
8 observed from the National Lightning Detection Network (NLDN), identifying lightning as the
9 dominant source for the observed NO_x. Using NLDN flash rates scaled by a factor of 4 to account
10 for intra-cloud flashes [Bocippio *et al.*, 2001] and assuming a 500 mol NO_x/flash production
11 rate following Ott *et al.*, [2006], we deduce a lightning NO_x emission of 0.45 Tg N over the
12 United States and adjacent coastal areas. This is a factor of 7 higher than in the standard GEOS-
13 Chem simulation, which uses a yield of 125 mol NO_x/flash for a global lightning NO_x source of
14 4.7 Tg N yr⁻¹. We can reproduce the upper tropospheric NO_x observed over the southern United
15 States in ICARTT by increasing the lightning NO_x yield in the model by a factor of four to the
16 Ott *et al.* [2006] value. This also provides a successful simulation of the observed frequency
17 distribution of upper tropospheric NO_x, and it corrects the 5-10 ppbv low ozone bias in the free
18 troposphere in the model, illustrating the critical importance of lightning on summertime ozone.
19 The factor of four increase is probably not extrapolatable globally as the resulting global lightning
20 source in the model (19 Tg N yr⁻¹) would be too high relative to observational constraints
21 [Boersma *et al.*, 2005; Martin *et al.*, 2006b]. Mid-latitude storms may have more energy per
22 lightning flash than tropical storms.

23 Uncertainty in OH concentrations in the upper troposphere is a major limitation for
24 interpreting quantitatively the observed NO_x concentrations in terms of an implied lightning NO_x
25 source. Simulated upper tropospheric OH concentrations in GEOS-Chem are about a factor of 2
26 higher than observed in ICARTT, and the same bias is found in box photochemical model

1 calculations constrained with the aircraft observations [*Olson et al.*, 2006b; *Ren et al.*, 2006]. As
2 discussed by *Olson et al.* [2006b] and also in *Spivakovsky et al.* [2000], this discrepancy is
3 beyond what one might expect from standard error propagation in a photochemical model, and
4 could point to some fundamental flaw in understanding of upper tropospheric HO_x chemistry that
5 would in turn affect the simulated NO_x lifetime. At the same time, previous aircraft observations
6 at northern mid-latitudes did not show such discrepancies with models [*Jaeglé et al.*, 2000]. A
7 model decrease of OH by a factor of 2 would correspondingly decrease the required increase in
8 the lightning NO_x source.

9 We examined the speciation of NO_y over the United States, in the observations and in the
10 model, to gain insight into the chemical evolution and export of NO_y. The NO_x fraction is largest
11 in the boundary layer over the Northeast, averaging 30%, and reflecting the density of sources.
12 PAN makes a somewhat larger contribution to NO_y in the Southeast than elsewhere, possibly
13 reflecting isoprene emissions. The model reproduces well the observed partitioning of NO_y for all
14 regional and altitudes, implying a good understanding of NO_y chemistry.

15 We estimated the export efficiency f and related speciation of NO_y out of the North American
16 boundary layer with a Lagrangian analysis of NO_y-CO correlations in the free troposphere,
17 following the approach of *Parrish et al.* [2004]. For the ICARTT data at 2.5-6.5 km altitude we
18 found $f = 16 \pm 10\%$ for observations and $14 \pm 8\%$ in the model, consistent with previous studies of
19 North American and Asian outflow [*Li et al.*, 2004; *Parrish et al.*, 2004; *Koike et al.*, 2003;
20 *Miyazaki et al.*, 2003]. The highest export efficiency is in the lower free troposphere but is then
21 mostly HNO₃ venting from shallow convection. We find that PAN is the dominant component of
22 exported NO_y (>50%) in pollution plumes above 3.5 km consistent with previous studies of Asian
23 outflow. The successful simulation of export of North American NO_y offers confidence to current
24 model estimates of North American influence on the global NO_y and ozone budgets [*Li et al.*,
25 2004].

26

- 1 **Acknowledgments.** This work was supported by the NASA Global Tropospheric Chemistry
- 2 Program and the NOAA Office of Global Programs. The authors would like to thank K.E.
- 3 Pickering, J.H. Crawford, J.R. Olson, and G. Chen for many useful discussions.

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1 **Table Captions**

2
3 **Table 1.** Contiguous United States NO_x Emissions for July 1 – August 15, 2004

4
5 **Figure Captions**

6
7 **Figure 1.** Flight tracks for ITCT 2k4 (black) and INTEX-NA (red) aircraft campaigns (July 1-
8 August 15). Shaded areas define regions used in comparisons between model and observations:
9 South (pink), Northeast (light green) and Midwest (orange).

10
11 **Figure 2.** EPA National Emissions Inventory (NEI99 v1) anthropogenic NO_x emissions for July
12 1999 (left). Improved emissions are for July 2004 (right) including a 50% reduction in power
13 plant and industrial emissions. Color scale saturates at 0.50.

14
15 **Figure 3.** Mean vertical profiles of OH, HO₂, H₂O₂, HCHO and HNO₄ as sampled by the
16 INTEX-A DC-8 aircraft on July 1 - August 15, 2004. Model results using the original (red) and
17 improved (green) simulations and compared to observations (black). Horizontal bars are standard
18 deviations on the observations. Here and in subsequent figures, the ICARTT observations have
19 been filtered to remove urban plumes, biomass burning plumes, and stratospheric air as described
20 in text. Model results are sampled along the flight tracks at the time of flights. Modifications to
21 emissions from the original to the improved simulation include a four-fold increase in the
22 lightning source, upward extension of the lightning source to the July mean tropopause height,
23 and a 50% reduction of the NEI99 v1 CO transport and NO_x power plant and industry sources.

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25 **Figure 4.** Same as Figure 3 for CO, NO_x, PAN, HNO₃, and ozone concentrations as sampled the
26 DC-8 (top) and the WP-3 (bottom) aircraft.

27
28 **Figure 5.** Median simulated-to-observed NO_x concentrations in the lowest 2km using the NEI99
29 v1 inventory.

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31 **Figure 6.** ICARTT upper tropospheric NO_x concentrations (8-12 km), observed (left) and
32 simulated (right) averaged over 2° x 2.5° model grid. Modifications to "improved" simulation as
33 described in text, including increasing lightning emissions over the box region in Figure 1 by a
34 factor of four.

35
36 **Figure 7.** Mean lightning flash rates for July 1 - August 15, 2004. Observations of cloud-to-
37 ground lightning from the National Lightning Detection Network, multiplied uniformly by a
38 factor of 4 to account for intracloud lightning, are compared to GEOS-Chem results.

39
40 **Figure 8.** Cloud-to-ground lightning flash counts in July-August 2000-2005 over the United
41 States. National Lightning Detection Network flash counts (grey bars) are compared to modeled
42 flash counts derived using GEOS-4 meteorology for the domain 130-70°W, 25-50° N grey and
43 white bars). Model flash counts are divided uniformly by a factor of 4 to account for intracloud
44 lightning. The jump in NLDN data between 2001 to 2002 reflects an upgrade in detection; thus,
45 comparable years are 2003-2005.

46
47 **Figure 9.** Histogram of DC-8 observed (black line) and improved simulated (grey bars) NO_x
48 between 8-12 km. Emissions used as in the "improved" GEOS-Chem simulation described in
49 text.

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1 **Figure 10.** Mean relative contributions of NO_x , PAN, and HNO_3 , to total NO_y defined as $\text{NO}_y =$
2 $\text{NO}_x + \text{PAN} + \text{HNO}_3$ in the ICARTT data (July 1 - August 15, 2004). Fresh urban, biomass
3 burning, and stratospheric plumes have been excluded as described in the text. Observations from
4 the DC-8 and WP-3D aircraft are compared to model results sampled along the flight tracks.

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6 **Figure 11.** Speciated export efficiency of NO_y (defined as $\text{NO}_y = \text{NO}_x + \text{PAN} + \text{HNO}_3$) from the
7 North American boundary layer during ICARTT, derived from equation (1) as a function of
8 altitude. Observations (left) are compared to model results (right). Parameters used in equation (1)
9 are given in the text and are the same for model and observations.

Table 1. Contiguous United States NO_x Emissions for July 1 – August 15, 2004¹

<u>Source Type</u>	<u>Magnitude (Tg N)</u>
Fuel	0.62 ² (0.79)
Biomass burning ³	0.003 (0.01)
Fertilizer	0.18
Soils	0.11
Aircraft	0.021
Lightning ⁴	0.27 (0.068)
Total	1.2

¹ The “improved” emissions reflect the constraints from the ICARTT observations. Original a priori estimates used in GEOS-Chem are given in parentheses.

² Improved fuel emissions include 0.28 Tg N from transport, 0.17 Tg N from power generation and industry, and 0.17 Tg N from other fuel use including industrial solvents, aircraft takeoff and landing, residential fossil fuel, residential biofuel, and all other anthropogenic sources.

³ North American fires during ICARTT were mainly in Alaska and Canada, each contributing 0.14 Tg N.

⁴ Lightning sources are for the region $-130^{\circ} \leq \text{longitude} \leq -70^{\circ}$ and $25^{\circ}\text{N} \leq \text{latitude} \leq 50^{\circ}\text{N}$.

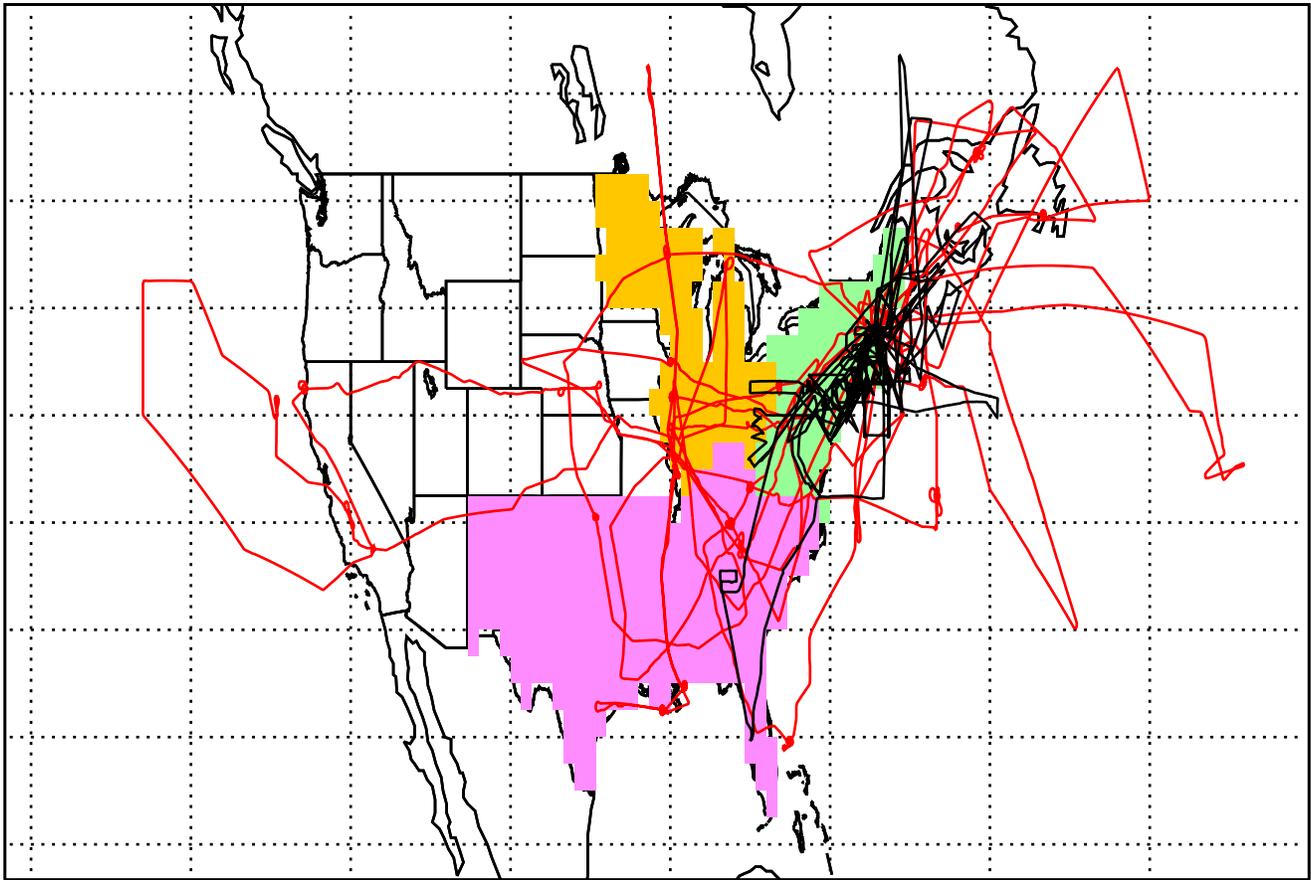


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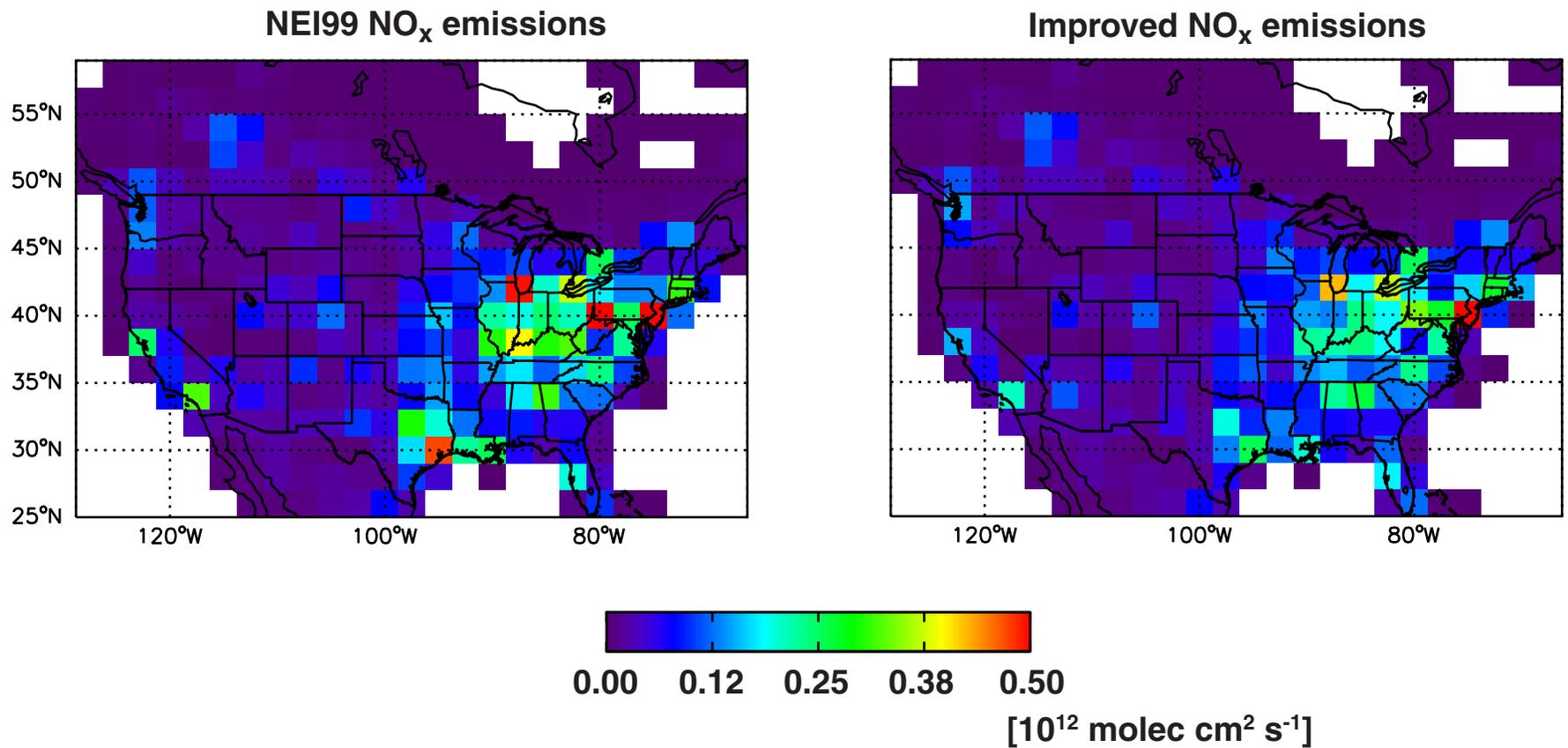


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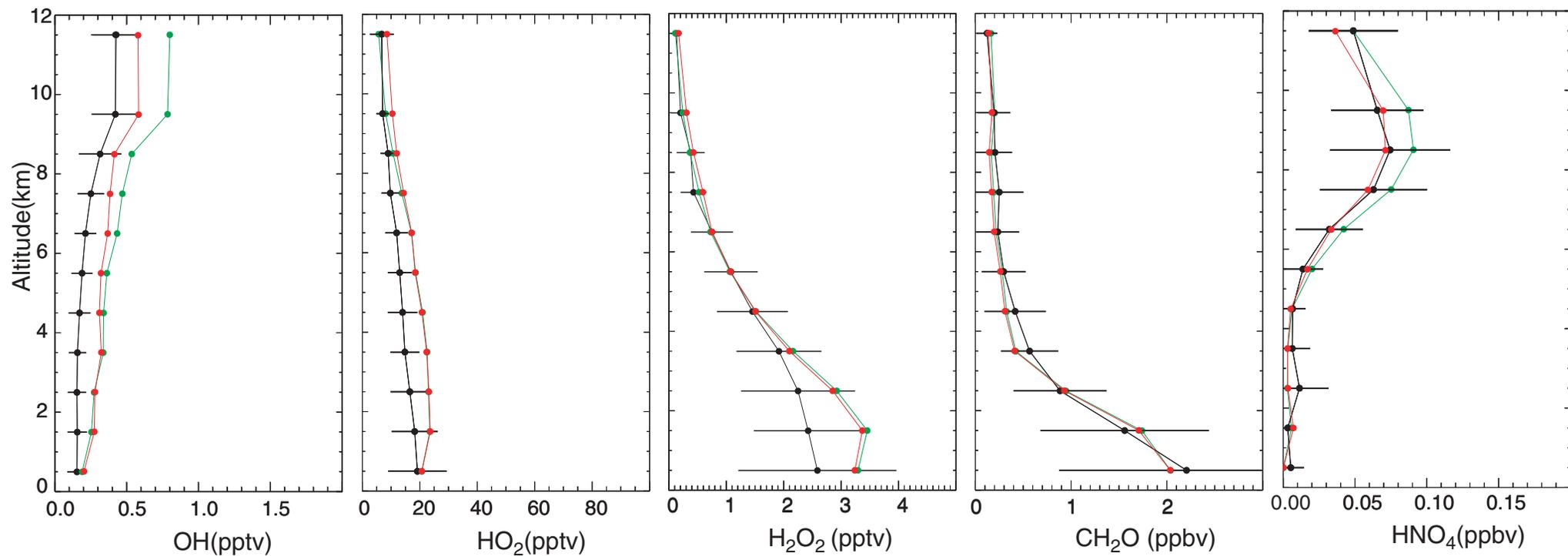


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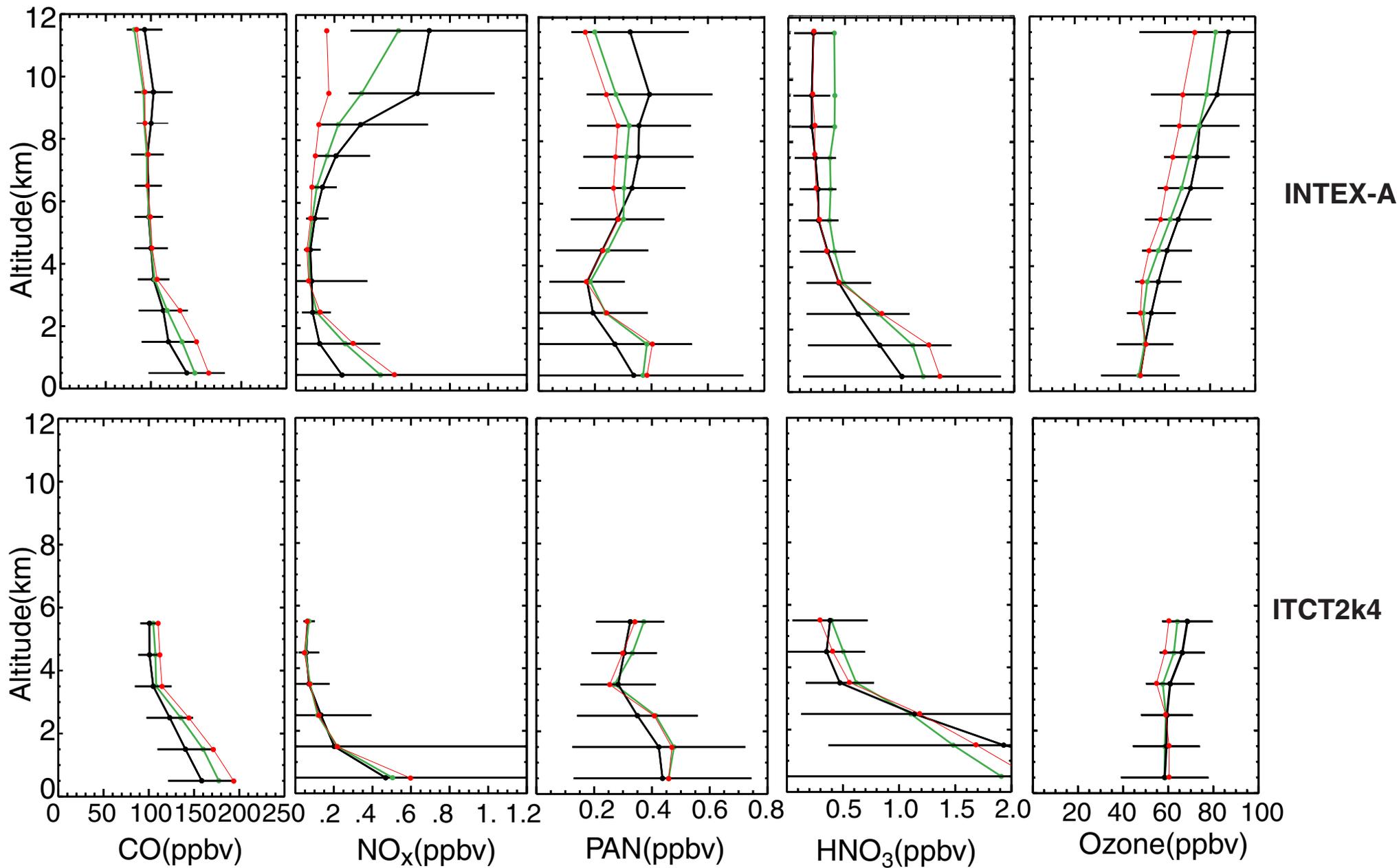


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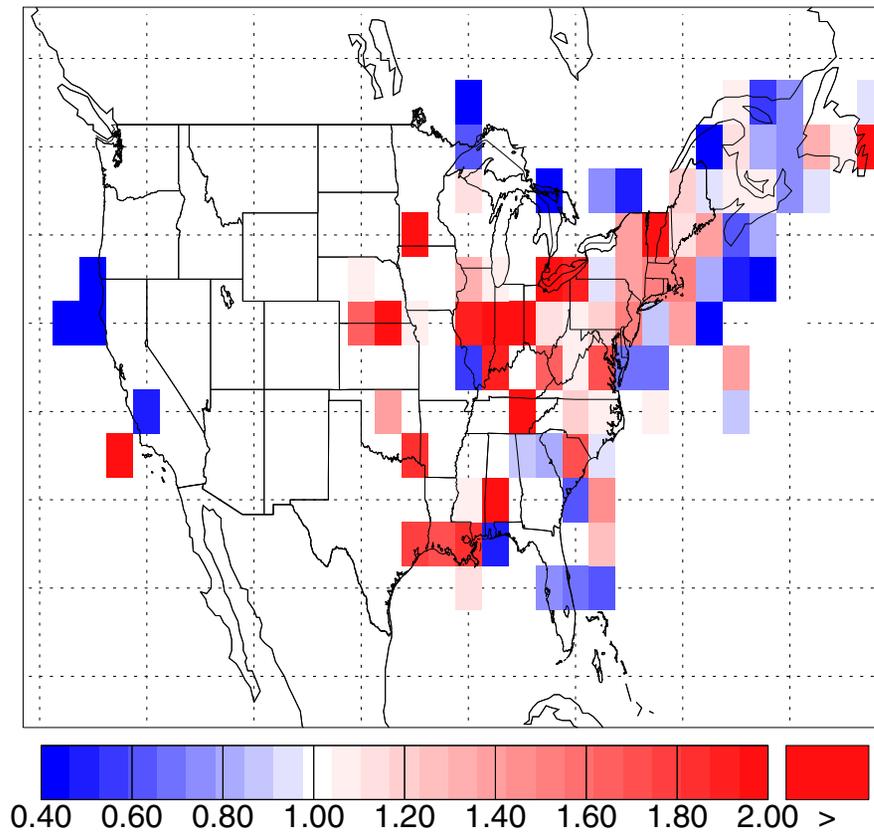


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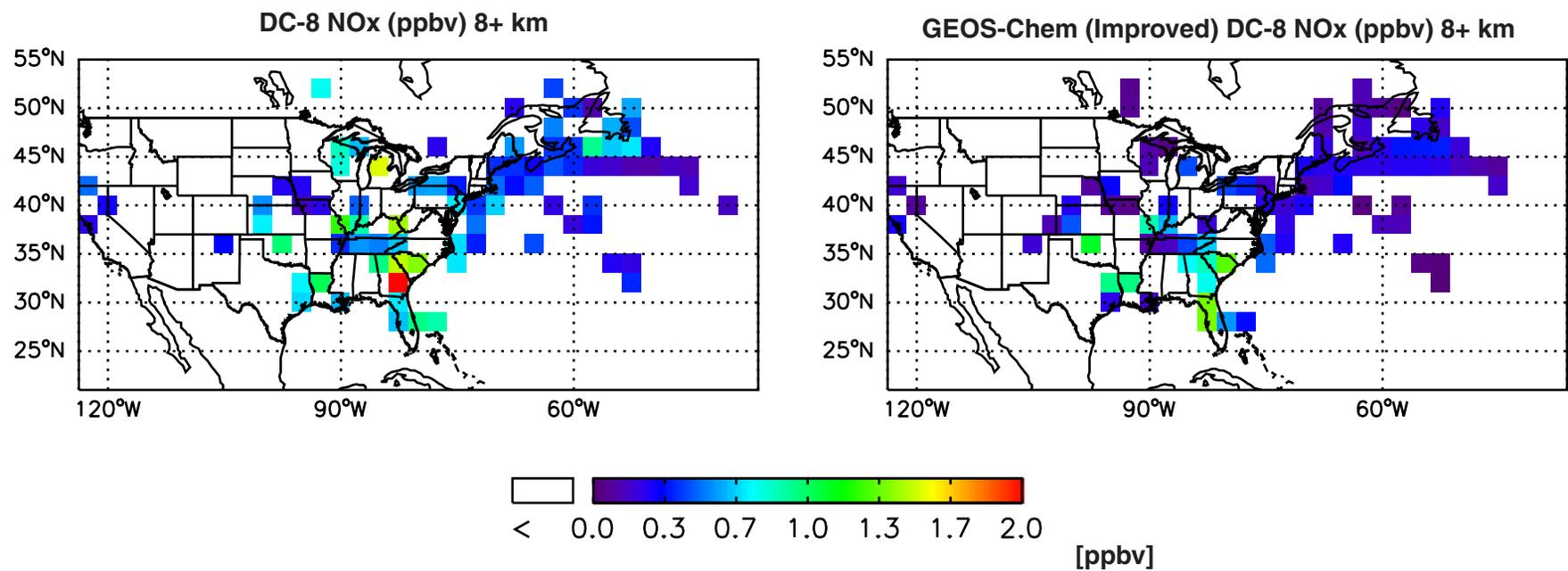


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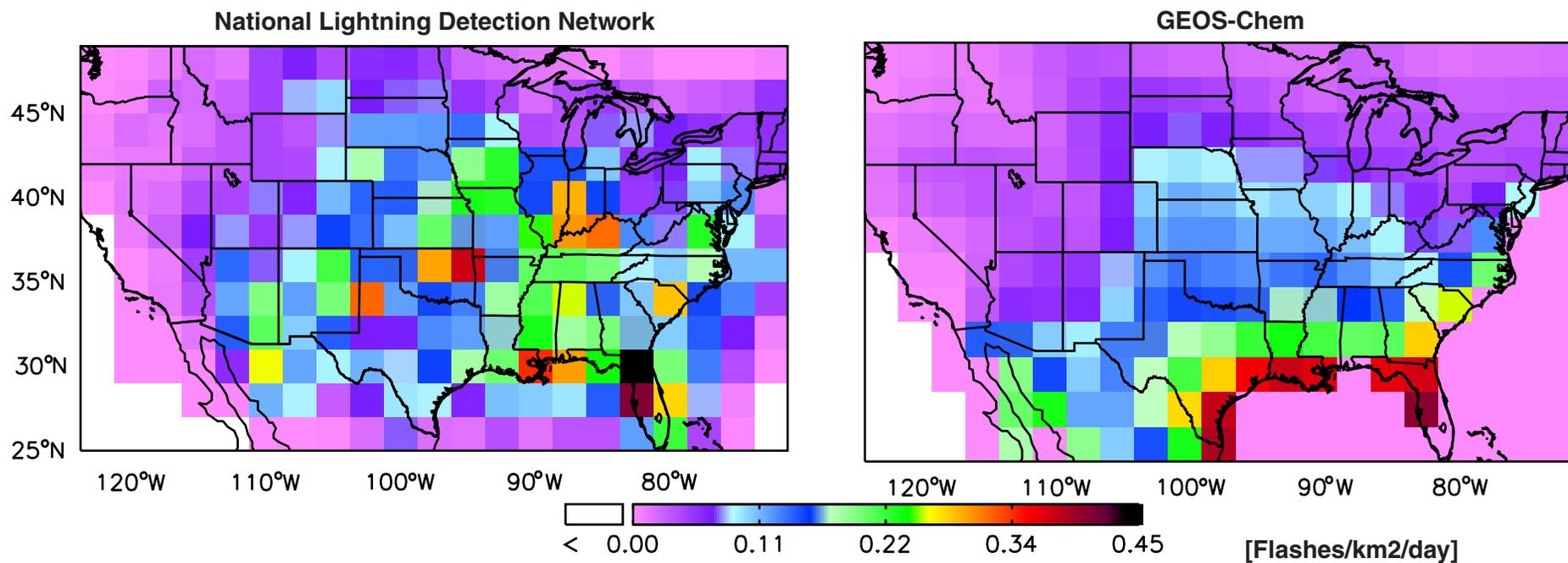


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Cloud-to-Ground Lightning Flashes (July-August)

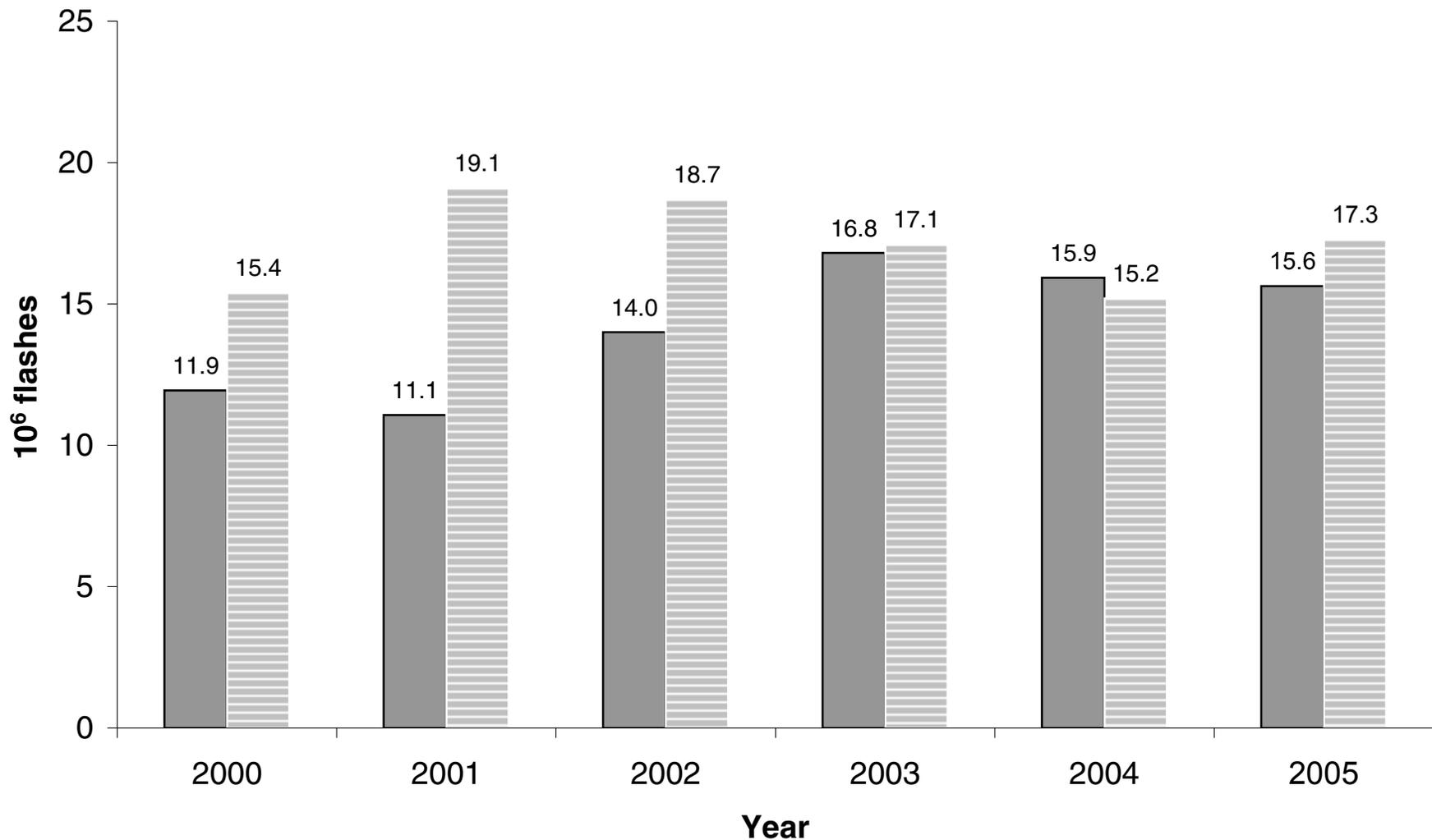


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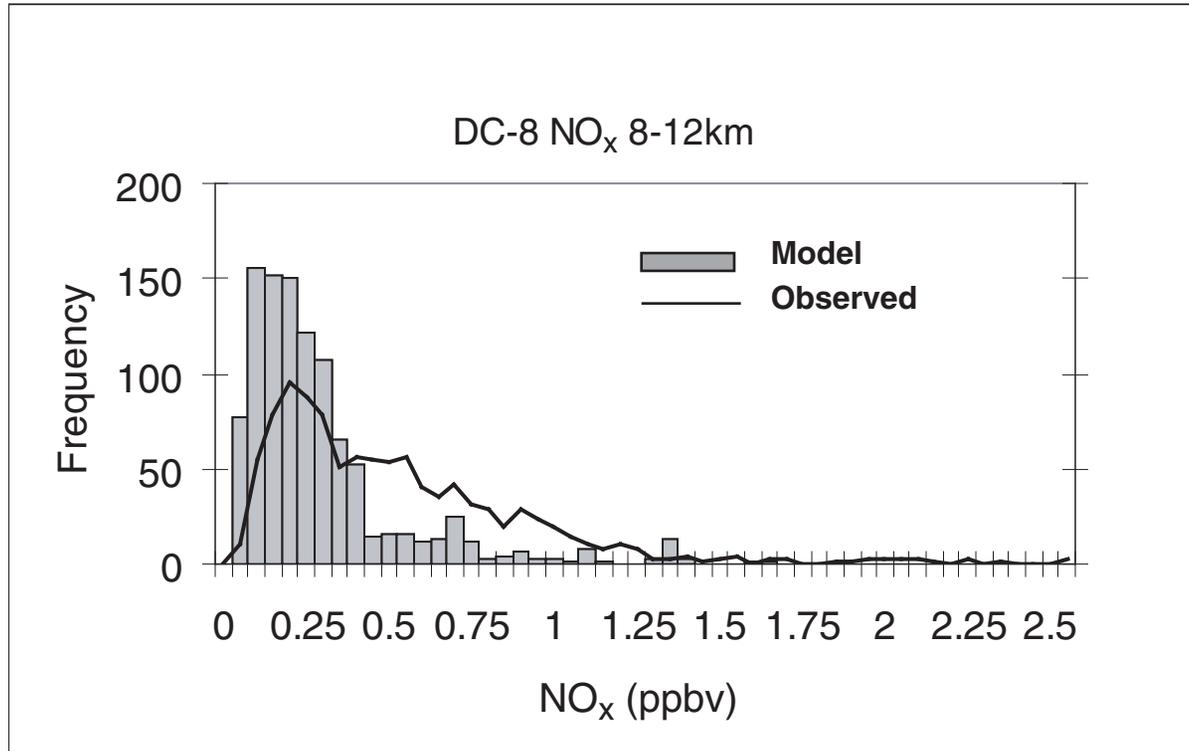


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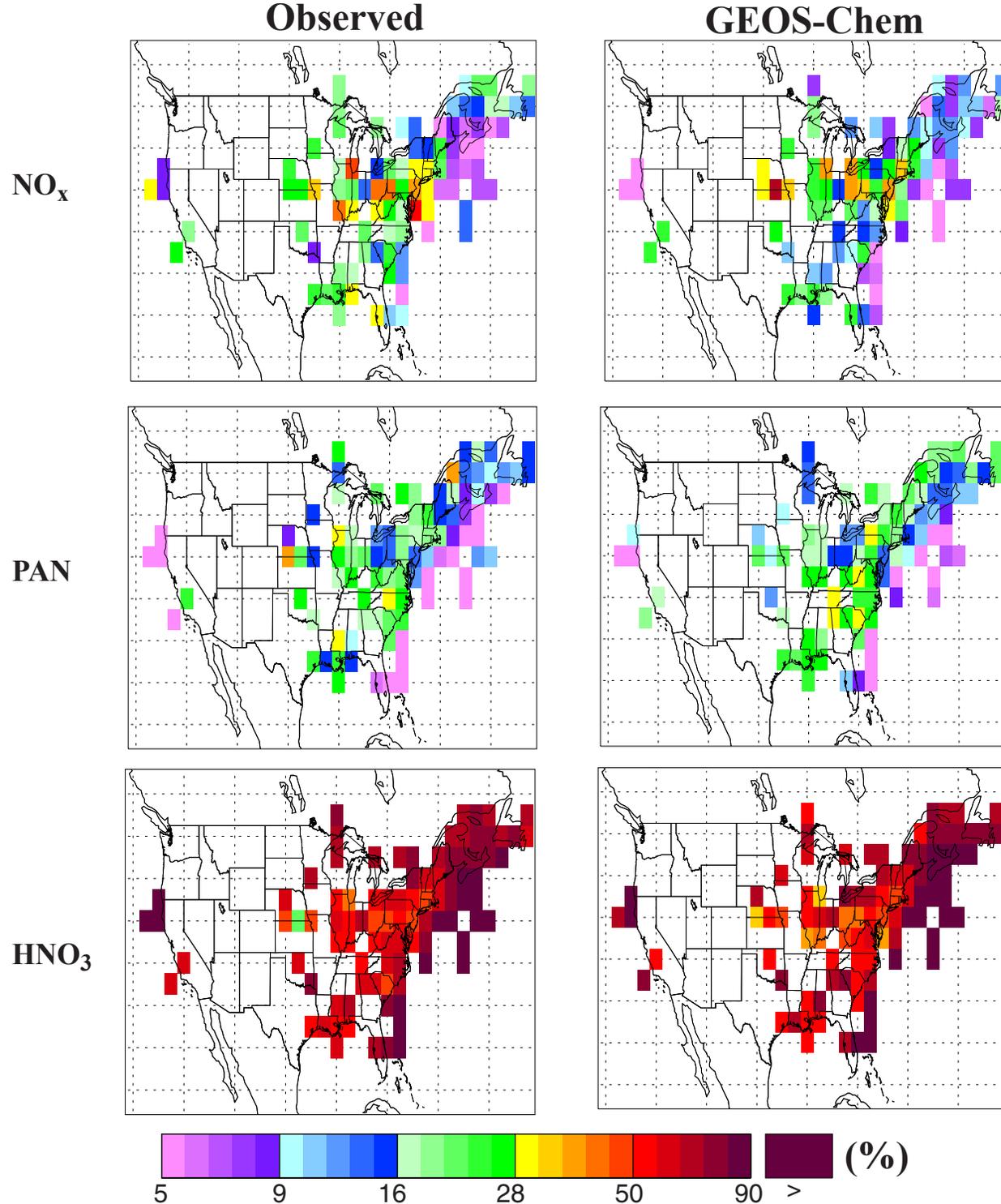


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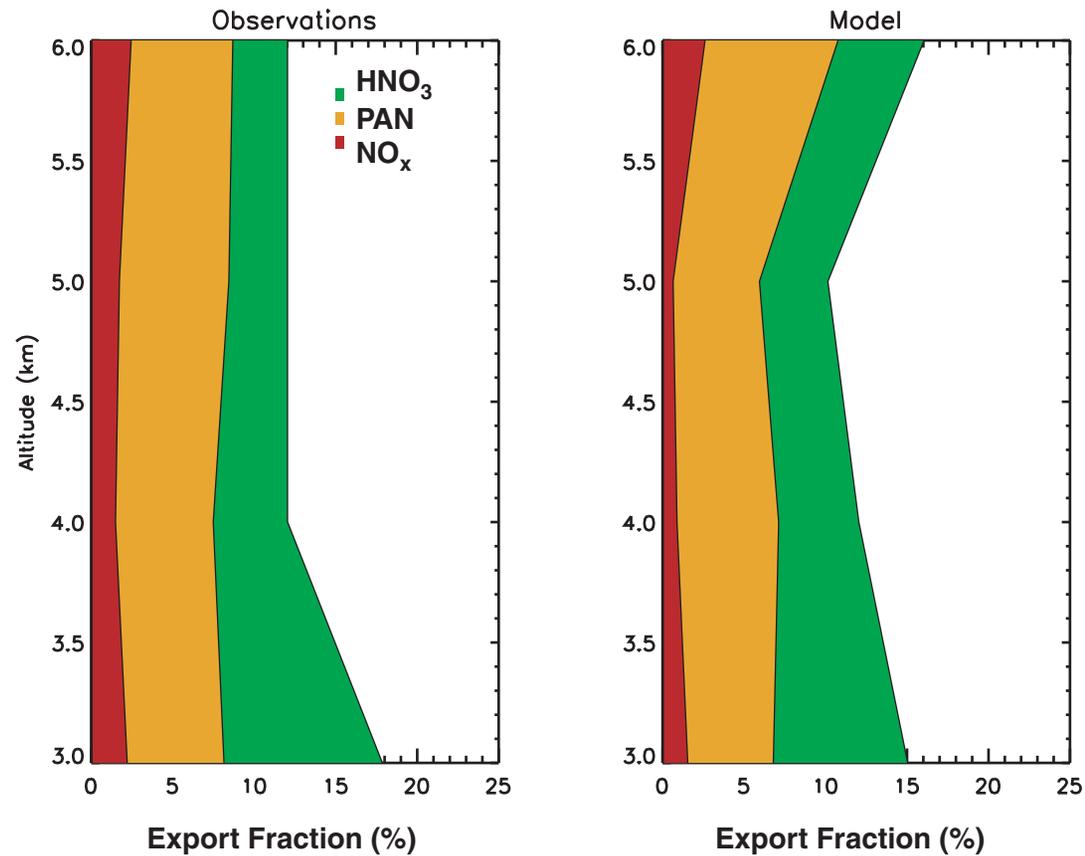


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