Sensitivity of the NO$_x$ budget over the United States to anthropogenic and lightning NO$_x$ in summer


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[1] We examine the implications of new estimates of the anthropogenic and lightning nitrogen oxide (NO$_x$) source for the budget of oxidized nitrogen (NO$_y$) over the United States in summer using a 3-D global chemical transport model (Model of Ozone and Related Tracers-4). As a result of the Environmental Protection Agency (EPA) State Implementation call, power plant NO$_x$ emissions over the eastern United States decreased significantly, as reflected by a 23% decrease in summer surface emissions from the 1999 U.S. EPA National Emissions Inventory to our 2004 inventory. We increase the model lightning NO$_x$ source over northern midlatitude continents (by a factor of 10) and the fraction emitted into the free troposphere (FT, from 80% to 98%) to better match the recent observation-based estimates. While these NO$_x$ source updates improve the simulation of NO$_x$ and O$_3$ compared to the Intercontinental Chemical Transport Experiment—North America aircraft observations, a bias in the partitioning between nitric acid (HNO$_3$) and peroxyacetyl nitrate (PAN) remains especially above 8 km, suggesting gaps in the current understanding of upper tropospheric processes. We estimate a model NO$_x$ export efficiency of 4%–14% to the North Atlantic in the FT, within the range of previous plume-based estimates (3%–20%) and lower than the 30% exported directly from the continental boundary layer. Lightning NO$_x$ contributes 24%–43% of the FT NO$_x$ export from the U.S. to the North Atlantic and 28%–34% to the NO$_x$ wet deposition over the United States, with the ranges reflecting different assumptions. Increasing lightning NO$_x$ decreases the fractional contribution of PAN to total NO$_x$ export, increases the O$_3$ production in the northern extratropical FT by 33%, and decreases the regional mean ozone production efficiency per unit NO$_x$ (OPE) by 30%. If models underestimate the lightning NO$_x$ source, they would overestimate the background OPE in the FT and the fractional contribution of PAN to NO$_x$ export. Therefore, a model underestimate of lightning NO$_x$ would likely lead to an overestimate of the downwind O$_3$ production due to anthropogenic NO$_x$ export. Better constraints on the lightning NO$_x$ source are required to more confidently assess the impacts of anthropogenic emissions and their changes on air quality over downwind regions.


1. Introduction

[2] Nitrogen oxides (NO$_x$ = NO + NO$_2$) play a key role in atmospheric chemistry [e.g., Seinfeld and Pandis, 2006]. In the troposphere, NO$_x$ contributes to the formation of ozone (O$_3$) and affects the oxidizing capacity of the atmosphere. NO$_x$ is mainly released as NO from combustion, lightning, and soil emissions and then is quickly converted to NO$_2$. It can further be oxidized to peroxyacetyl nitrate (PAN), nitric acid (HNO$_3$), and other minor oxidation products. NO$_x$ and its oxidation products are collectively known as oxidized nitrogen (NO$_y$). Longer-lived NO$_y$, especially PAN and to a lesser extent HNO$_3$, have the potential to act as reservoirs for NO$_x$ and contribute to O$_3$ production on a global scale following export from the NO$_x$ source region [e.g., Maxim et al., 1996; Liang et al., 1998; Horowitz and Jacob, 1999; Li et al., 2002, 2004; Parrish et al., 2004; Hudman et al., 2004; Penkett et al., 2004; Auvray and Bey, 2005]. Deposition of NO$_x$ compounds, mostly in the form of highly soluble HNO$_3$, provides an important source of nutrients for marine, freshwater and terrestrial ecosystems, influencing their productivity and thereby affecting the global carbon cycle [Galloway et al., 2004; Prentice et al., 2001; Vitousek et al., 1997]. Understanding the budget of NO$_y$ is thus necessary to assess the environmental impacts of NO$_x$ sources.
ences in NOx. Within the North American troposphere, significant differences therein. Modeled distribution of NOx, O3, and OH concentrations are largely sensitive to the parameterized lightning NOx production [e.g., Stockwell et al., 1999; Allen and Pickering, 2002; Zhang et al., 2003; Labrador et al., 2004; Hudman et al., 2007; Zhao et al., 2009]. Recent studies have aimed to improve our understanding of lightning NOx sources. For example, by simulating several midlatitude and subtropical thunderstorms during four field projects, Ott et al. [2007, 2010] recommend a mean NOx production of approximately 500 moles per flash for both intracloud and cloud-to-ground flashes. Ott et al. [2010], Kaynak et al. [2008], and Pickering et al. [2006] suggest that a larger percentage of the total lightning NOx source is located in the free troposphere (FT) than proposed in an earlier work [Pickering et al., 1998].

[5] The NASA Intercontinental Chemical Transport Experiment-North America (INTEX-NA) [Singh et al., 2006] was part of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) field campaign over North America during July–August 2004. Within the North American troposphere, significant differences in NOx partitioning between observations and models as well as among models suggest a need for additional studies with models incorporating new constraints on NOx sources and chemistry provided by the INTEX-NA campaign [Singh et al., 2007]. For example, Hudman et al. [2007] found that the INTEX-NA observations are consistent with a 22% decrease in fossil fuel NOx from 1999 in the U.S. National Emission Inventory and that increasing lightning NOx in the GEOS-Chem model by a factor of 4 over Northern Hemisphere midlatitude continents improved the match between simulated NOx species and observations. Hudman et al. [2009] derive a higher observed dO3/dCO ratio of 0.47 from the North American outflow during summer 2004 than that reported by studies in early 1990s, reflecting a decrease in the NOx/CO emission ratio as well as an increase in the ozone production efficiency per unit NOx. They also found North American NOx emissions during summer 2004 enhanced the hemispheric tropospheric ozone burden by 12.4%, with comparable contributions from fossil fuel and lightning (5%–6%). Kaynak et al. [2008] reported a small impact from lightning NOx on maximum 8 h O3 in surface air over the United States (less than 2 ppb in 71% of cases) in summer 2004.

[6] Here we extend these studies by comparing the impacts of changing anthropogenic and lightning sources on the U.S. NOx budget (with a focus on export and deposition), as well as the implications for O3 production and O3 air quality. We use a global 3-D model, Model of Ozone and Related Tracers (MOZART-4) [Horowitz et al., 2003, 2007; Emmons et al., 2010]. The description and evaluation of our simulations are provided in sections 2 and 3. In section 4, we present (1) the tropospheric NOx budget of the United States during the summer of 2004, (2) the sensitivity of the NOx budget to the reported anthropogenic NOx emission changes and to the new constraints on lightning NOx, and (3) an estimate of the export efficiency of U.S. surface NOx emissions to the North Atlantic. The implications of changing NOx emissions on O3 production and O3 air quality are discussed in section 5. Conclusions are given in section 6.

2. Model Description

2.1. The MOZART4 Model

[7] The Model of Ozone and Related Tracers (MOZART) version 4 is updated from MOZART-2 [Horowitz et al., 2003], as described by Emmons et al. [2010]. The particular configuration used in our study (model resolution, meteorology, isoprene chemistry) has been modified from that described by Emmons et al. [2010] and is the same as that used by Horowitz et al. [2007]. Briefly, the model resolution for this simulation is 1.9° latitude by 1.9° longitude, with 64 vertical levels. The driving meteorological fields are from the Global Forecast System and updated every 3 h [Horowitz et al., 2007]. The influx of O3 from the stratosphere is prescribed by the SYNOZ (SYNthetic OZone) technique (500 Tg yr⁻¹) [McLinden et al., 2000]. Convective mass fluxes are diagnosed by the model, using the shallow and midlevel convective transport formulation of Hack [1994] and deep convection scheme of Zhang and McFarlane [1995]. Vertical diffusion within the boundary layer is based on the parameterization of Holtslag and Boville [1993]. Wet deposition is taken from the formulation described in the study by Brasseur et al. [1998]. The monthly mean dry deposition velocities are from Horowitz et al. [2003] except for O3 (taken from Bey et al. [2001]) and PAN (taken from a separate MOZART-4 simulation in which it was calculated interactively to reflect the updates described by Emmons et al. [2010]). Global anthropogenic, biomass burning, and natural emissions are based on the POET (a project studying Precursors (CO, NOx, CH4 and NMVOC) of Ozone and their Effect on the Troposphere) emission inventory for 1997 [Olivier et al., 2003; http://www.aero.jussieu.fr/projet/ACCENT/POET.php], except for biogenic emissions of isoprene and monoterpene, which are calculated interactively using Model of Emissions of Gases and Aerosols from Nature (v.0) [Guenther et al., 2006]. Over North America, we use the daily biomass burning emissions from Turquety et al. [2007] (including CO, NO, SO2, NH3, carbonaceous aerosols, and nonmethane volatile organic compounds) for our simulation of the INTEX-NA field campaign during summer 2004. Anthropogenic emissions
over North America are modified from their POET values as described in section 2.2.

2.2. Anthropogenic Emissions Over the United States

The U.S. surface anthropogenic emissions are from the EPA National Emission Inventory (NEI99, version 3, http://www.epa.gov/ttn/chief/net/1999inventory.html, represented as NO$_x$99). To simulate the reported anthropogenic NO$_x$ reductions, we replace the NEI99 anthropogenic NO$_x$ emissions over the United States (including part of southern Canada and Mexico) with a new inventory for summer 2004 (applied for June, July, and August in 2004, denoted as NO$_x$04). The 2004 anthropogenic NO$_x$ emission inventory was prepared as part of Visibility Improvement State and Tribal Association of the Southeast (VISTAS) [MACTEC, 2005]. It is projected from the VISTAS 2002 U.S. emissions inventory using growth factors from the Economic Growth Analysis System Version 4.0 and is integrated with the actual power plant NO$_x$ emissions obtained from the continuous emissions monitoring data set.

Figure 1 shows the spatial distribution of the differences in surface NO$_x$ emissions from the 1999–2004 inventories (due to anthropogenic emission changes). Besides the expected NO$_x$ reductions in the northeastern United States and the Ohio River Valley [Environmental Protection Agency (EPA), 2005] due to regulations on NO$_x$ emissions under the NO$_x$ SIP call, we also see NO$_x$ reductions in southern California, which may reflect regulations on automobile NO$_x$ emissions there [Frost et al., 2008] or an overestimate of NO$_x$ emissions in the late 1990s (mostly from motor vehicles) [Kim et al., 2009]. After updating the NO$_x$ emission inventory from 1999 to 2004, the total July surface NO$_x$ emissions (including 0.1 Tg N from soil emissions) in the continental United States decreases from 0.68 Tg N in 1999 to 0.52 Tg N in 2004, consistent with the sum of soil and fuel emissions constrained by the INTEX-NA observations in the study by Hudman et al. [2009].

2.3. Lightning NO$_x$ Parameterization

In the MOZART-4 model, lightning flash frequency and the resulting NO$_x$ source are parameterized using the scheme of Price et al. [1997], with the flash frequency determined by the maximum cloud top height, and the cloud-to-ground (CG) to intracloud (IC) flash ratio determined as in the study by Price and Rind [1993]. The NO$_x$ production estimated by this parameterization is around 110 and 1100 moles N per IC and CG flash, respectively. Using the original parameterization, the resulting model lightning NO$_x$ source is 0.027 Tg N during July 1 to August 15 over the United States, much lower than the 0.27 Tg N estimate constrained by the INTEX-NA observations in the study by Hudman et al. [2007]. Our model-simulated CG lightning frequency is also biased low compared to that observed by the National Lightning Detection Network (NLDN) in 2004.

Figure 2. (a) The NLDN observed cloud-to-ground (CG) flash frequency (flashes km$^{-2}$month$^{-1}$), (b) the MOZART-4-simulated CG flash frequency (flashes km$^{-2}$ month$^{-1}$), and (c) the lightning NO$_x$ source (g N m$^{-2}$ month$^{-1}$) after adjusting by a factor of 10 to better match the observational constraints over the contiguous United States (24$^\circ$N–48$^\circ$N, 67.5$^\circ$W–127.5$^\circ$W) during July 2004.
Table 1. U.S. NO, Emissions for July 2004 in the MOZART-4 Simulations

<table>
<thead>
<tr>
<th>NO, Emissions (Gg N)</th>
<th>NO,99LowLght</th>
<th>NO,99HighLght</th>
<th>NO,04HighLght</th>
<th>NO,04LowLght</th>
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<td>420</td>
<td>420</td>
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<td>100</td>
</tr>
<tr>
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<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Biomass burning and aircraft Lightning</td>
<td>18</td>
<td>180</td>
<td>180</td>
<td>18</td>
</tr>
</tbody>
</table>

*See section 2.3 for details.*
surface ozone over the eastern United States of 10–15 ppbv and an underestimate over the western United States by about 8 ppbv. The bias in the eastern United States also exists in other simulations with previous versions of MOZART [Lin et al., 2008; Murazaki and Hess, 2006] and occurs systematically in the multimodel estimates of surface O₃ for the year 2001 of the Task Force on Hemispheric Transport of Air Pollution [Fiore et al., 2009; Reidmiller et al., 2009]. Horowitz et al. [2007] compare MOZART simulations and observations from the ICARTT field campaign over the eastern United States during summer 2004 and find simulated concentrations of trace species (including O₃) generally match observations to within 30% in the U.S. boundary layer (below 2 km), except for NOₓ (overestimated by ~30%) and PAN (overestimated by a factor of ~2).

3.2. MOZART-4 Simulations of the INTEX-NA Campaign in Summer 2004

In this section we compare our suite of MOZART-4 sensitivity experiments (Table 1) with observations made on board the NASA DC-8 aircraft during the INTEX-NA campaign [Singh et al., 2006]. The wide spatial coverage of this aircraft is suitable for comparison with our global model. Our evaluation focuses on NOₓ (NO, PAN, and HNO₃) and other related species (O₃ and OH). We also compare the simulated nitrate wet deposition during summer 2004 with that monitored by the National Atmospheric Deposition Program [NADP, 2010].

3.2.1. Boundary Layer Distributions

Here we focus on the NOₓ 99HighLght and NOₓ 04HighLght simulations (Table 1). Comparisons of selected species below 2 km in the eastern United States are presented in Figure 4. In general, we find that updating the anthropogenic NOₓ emissions from 1999 emission inventory to 2004 has little influence on the spatial correlation with observed NOₓ, O₃, and OH (r > 0.5, except for HNO₃, r = 0.3), but it improves the model biases (represented as the absolute/relative differences between the model value averaged across all sampled grid cells and the observed mean value) except for HNO₃ (Figure 4). The mean NOₓ bias decreases from 153 ppt (30%) in NOₓ 99HighLght to 15 ppt (3%) in the NOₓ 04HighLght simulation and the O₃ bias decreases from 6 ppb (12%) to 2 ppb (4%). The apparent degradation of the spatial correlation for NOₓ when switching from the 1999 to 2004 emission inventory is due to one model grid cell (covering Ohio and Pennsylvania), where the NOₓ 04HighLght simulation underestimates observations by more than NOₓ 99HighLght simulation (excluding that point yields equivalent correlations for the simulations versus observations, r = 0.58). PAN is overestimated (by ~350 ppt in NOₓ 99HighLght and ~250 ppt in NOₓ 04HighLght). This persist when we update all the VOC emissions in addition to NOₓ from the 1999 to the 2004 inventory. The model underestimates HNO₃ (mean bias of ~37 ppt in NOₓ 99HighLght and ~379 pptv in NOₓ 04HighLght). The underestimate of HNO₃ and overestimate of PAN will likely cause an overestimate of NOₓ export from the model boundary layer (BL).

3.2.2. Vertical Distributions

Figure 5 shows the mean profiles of different species within the eastern United States for all the model simulations. In general, the factor of 10 increase in lightning NOₓ improves simulated NOₓ, O₃, and HNO₃ in the free troposphere: the upper tropospheric NOₓ underestimate decreases from 750 to 540 ppt, comparable to the results from Hudman et al. [2007]; the O₃ discrepancy decreases to within 10 ppb; the HNO₃ discrepancy decreases to within 40 ppt above 6 km. The modeled OH and PAN worsen as compared to the observations. OH in the upper troposphere is underestimated by the LowLght simulations by around 50%; the lightning adjustment, while improving the OH prediction above 10 km, leads to an overestimate of OH in the midtroposphere with a maximum bias of 60%. PAN is overestimated by around 70 ppt in the midtroposphere and less than 30 ppt in the upper troposphere in the NOₓ 04HighLght and NOₓ 99HighLght simulations (mean biases are both less than 20%). The different sign and location of maximum biases for NOₓ, PAN, and HNO₃ suggest that a further modification of the lightning NOₓ profile will not help improve the prediction of all these species; therefore, there must be other causes of these biases. As a check on the total NOₓ simulation, we add HNO₃, PAN, and NOₓ (the major NOₓ species) from both model and observations and find that they agree better than the individual species do. For example, between 4 and 8 km, the sum of the major NOₓ species agrees with observations to within 10% after the lightning adjustment.

Hudman et al. [2007] also found problems in HNO₃ and PAN, especially in the mid-upper troposphere, but their PAN was underestimated by ~30% in the upper troposphere, while their HNO₃ was twice the observed value; simply adjusting lightning will not fix that HNO₃ and PAN partitioning bias either. Henderson et al. [2009] noted an NOₓ partitioning problem as compared to observations when they applied several chemical mechanisms (CB05, RACM2, SAPRC07, and GEOS-Chem) in a box model. The NOₓ partitioning bias reflects that some processes important for NOₓ partitioning in the upper troposphere are missing in the model, e.g., overestimates of radical sources and subsequent chemical cycling [Henderson et al., 2009]. A recommendation from their study (already adopted in MOZART-4 [Emmons et al., 2010]) is to use the Blitz et al. [2004] estimate for the acetone quantum yield, which reduces the acetone photolysis and decreases PAN and HOₓ (= OH + HO₂) in the upper troposphere throughout the Northern Hemisphere [Arnold et al., 2005]. Uncertainties in isoprene chemistry are also known to affect PAN formation [e.g., Emmerson and Evans, 2009; Paulot et al., 2009; Pfister et al., 2008b]. We use a 4% yield of isoprene nitrate production from the reaction of isoprene hydroxyperoxy radicals with NOₓ, which best captures the boundary layer concentrations of organic nitrates and their correlation with ozone observed in the INTEX-NA field campaign; however, many uncertainties remain [Horowitz et al., 2007]. The excess PAN relative to HNO₃ in the midtroposphere in our model is likely to lead to an overestimate of the potential influence of U.S. NOₓ emissions on O₃ production and NOₓ deposition in downwind regions.

3.2.3. Wet Deposition of Inorganic Nitrate

We compare the total summer time inorganic nitrate (including nitric acid and aerosol nitrate) wet deposition from the NOₓ 99LowLght, NOₓ 04LowLght, and NOₓ 04HighLght simulations with observations from NADP [2010] (Figure 6) during June–August 2004. The NOₓ 99LowLght simulation is well correlated with observations (r = 0.72). There is a sig-
Figure 4. Modeled versus observed concentrations of selected species below 2 km in the eastern United States during INTEX-NA period from the NO\textsubscript{x}99HighLght simulation (red) and from the NO\textsubscript{x}04HighLght simulation (blue). Model results are sampled every minute along the NASA DC-8 flight tracks in the eastern United States, and then both observations (1 min average) and model results are averaged onto the model grid. Observations shown from NASA DC-8 are (a) NO\textsubscript{x} (calculated as NO (Principal Investigator (PI), W. Brune) [Ren et al., 2008] + NO\textsubscript{2}, PI, R. Cohen) [Thornton et al., 2000], (b) O\textsubscript{3} (PI, M. Avery, NASA LaRC) [Avery et. al, 2001], (c) PAN [Singh et al., 2007], (d) HNO\textsubscript{3} (PI, R. Talbot, University of New Hampshire) [Talbot et al., 2000], and (e) OH [Ren et al., 2008]; the organic correlation slopes of the NO\textsubscript{x}99HighLght and NO\textsubscript{x}04HighLght model simulations are shown as red and blue lines, respectively; the black line indicates a line with a 1:1 slope; here and after, to account for the recent corrections to ATHOS absolute calibration [Ren et al., 2008], the observed OH was scaled up by a factor of 1.64 for comparison with our model. Bias is defined as the relative/absolute difference between mean model result across all sampled grid cells and that of the observation.
significant overestimate of the nitrate wet deposition over northeastern California, the Midwest and the northeast corridor, associated with the overestimate of NOx emissions over these regions. When we update from the 1999–2004 anthropogenic NOx emission, these overestimates are reduced in general (+15% to −5%), especially over the northeast corridor. The modeled correlation also increases to 0.75. Further scaling of the lightning NOx by a factor of 10 does not affect the correlation but leads to a better match with observations over the midwest. However, the uniform scaling causes excessive wet deposition along the east coast. The overestimate of the mean nitrate wet deposition (+30%) compared to the NADP observations in our NOx04HighLght simulation indicates that the lightning NOx source (180 Gg in July)

Figure 5. Mean vertical profiles of NOx (a), O3 (b), PAN (c), HNO3 (d), OH (e), and (f) the major NOx species (NOx, PAN, and HNO3) during the INTEX-NA campaign in July–August 2004. Observations from the DC-8 aircraft (black) are compared with the NOx99LowLght (purple), NOx04LowLght (green), NOx99HighLght (red), and NOx04HighLght (blue) simulations. Horizontal bars show the standard deviations of each data set within each 2 km layer. Simulated concentrations are sampled every minute along all the flight tracks for comparison with the observations. Both observation and models are then averaged within each horizontal model grid in 2 km altitude bins, and finally, these gridded data are averaged (weighted by area) in each layer to get regional mean profiles.
is probably too high. Rather, the discrepancies likely reflect a problem with the flash frequency distribution as seen in Figure 2.

4. Sensitivity of the NO\textsubscript{y} Budget on Anthropogenic and Lightning NO\textsubscript{x} Emissions

4.1. Budget of NO\textsubscript{y} Over the United States

[20] In this section we discuss the chemical processing, deposition, and export of the U.S. NO\textsubscript{x} emissions in July, focusing on the NO\textsubscript{x}04HighLght simulation. We define the contiguous U.S. boundary layer (BL) as the region extending horizontally from 24°N–48°N and 67.5°W–127.5°W, from the surface to about 800 hPa (around 2 km). We also define the contiguous U.S. total column (TC) to refer to the same horizontal region but vertically extending to about 200 hPa. Hereafter, we refer to these lateral boundaries (up to 200 hPa) as “walls”; for example, the lateral boundary at 67.5°W, 24°N–48°N, from the surface to 200 hPa is referred to as the “east wall.”

[21] The TC and BL NO\textsubscript{y} budgets are summarized in Table 2. Around 70% of the total emitted nitrogen is deposited, and the remaining 30% of the emitted nitrogen is exported from the continental boundary layer laterally and vertically. This estimate for export efficiency of emitted nitrogen (30%) is at the high end of the 20%–30% summer ratio in previous Eulerian budget studies [Levy and Moxim, 1987; Horowitz et al., 1998; Liang et al., 1998; Li et al., 2004; Parrish et al., 2004; Pierce et al., 2007]. Raising the BL top from 800 to 730 hPa, to be comparable to these studies, we still find a high value (27%), possibly due to the model overestimate of BL PAN. Eulerian budget estimates are usually higher than those estimated using the NO\textsubscript{y}–CO relationships sampled in the outflow plumes downwind of the United States [e.g., Hudman et al., 2007; Parrish et al., 2004; Li et al., 2004; Stohl et al., 2002]. However, this difference does not necessarily mean the budget estimate is inconsistent with the observations [Li et al., 2004; Parrish et al., 2004] as discussed in section 4.4.

[22] Most of the NO\textsubscript{x} exported from the BL is transported vertically to the free troposphere (about 90%). NO\textsubscript{2} and HNO\textsubscript{3} are the most abundant NO\textsubscript{x} species in the BL (HNO\textsubscript{3} accounts for more than 30%, whereas NO\textsubscript{2} accounts for more than 25% of the BL NO\textsubscript{x} burden) since PAN is ther-
nally unstable in the BL. NO₂ and HNO₃ are also the most abundant components of NOₓ exported from the U.S. BL (each accounts for more than 30%, with PANs contributing over 10%).

[23] Lightning NOₓ accounts for almost 30% of the total U.S. July NOₓ source in the model, similar to that estimated from NLDN [Kaynak et al., 2008]. Around 80% of all emitted NOₓ in the U.S. TC over the United States is deposited and about 20% is exported (Table 2), consistent with the estimate by Sanderson et al. [2008]. Eastward export through the east wall of the United States dominates the export from the TC (116 versus 19 and 17 Gg N exported through the north and south walls, respectively; there is a 29 Gg N inflow through the west wall in July). PANs (PAN + MPAN) contribute 50% and NOₓ contributes 17% to the NOₓ species composing the eastward flux.

[24] Figure 7 shows the NOₓ flux through the east wall of the United States. Outflow dominates the transport here except south of 30°N, where weak inflow into the United States exist. This pattern reflects the dominance of the Bermuda High during July. Because of the location of North American jet stream, a maximum eastward outflow is located between 200 and 400 hPa, centered at around 45°N. Vertical profiles of the relative contribution of major components of NOₓ to this eastward flux in the NOₓ,04HighLght simulation are shown in Figure 8. Near the surface, HNO₃ is by far the largest component of exported NOₓ with a maximum contribution of more than 40%. Wet deposition decreases the HNO₃ contribution with altitude from the surface to 600 hPa, and then its contribution remains almost constant at 30% up to 300 hPa. PANs contribute most to the exported NOₓ above the boundary layer with a maximum contribution of more than 60% located at around 500 hPa, reflecting their longer lifetime at the colder temperatures in the free troposphere (FT). Above 500 hPa, the relative contribution of PANs decreases as that of NOₓ increases.

4.2. Effects of Recent Anthropic NOₓ Emission Reductions on the U.S. NOₓ Budget and Export to the North Atlantic

[25] We determine the effects of the NOₓ emission reductions in response to the SIP call on the budget of NOₓ by comparing the NOₓ,99HighLght and the NOₓ,04HighLght simulations (Table 2). From NOₓ,99HighLght to NOₓ,04HighLght, BL NOₓ emissions decrease by 23%. As a result, the NOₓ burden within the BL decreases by 19% (Table 2, from 19 to 15 Gg N). Meanwhile, the net export of reactive nitrogen from the BL decreases by 20%, while the total deposition from the BL decreases by 24% (Table 2). This nonlinearity between NOₓ emission changes is associated with changes in NOₓ partitioning [Liang et al., 1998]. As surface NOₓ emissions decrease, PAN increases from 22% to 24% while HNO₃ decreases from 36% to 32% of the NOₓ burden. A smaller contribution from HNO₃ (which is efficiently removed by dry and wet deposition) implies a longer NOₓ lifetime (+5% in the BL) and hence a relative increase in the NOₓ burden and export, resulting in a less-than-linear reduction of these two terms. For the same reason, the deposition of NOₓ decreases more than linearly. Similar results occur for the TC over the United States (Table 2). Decreasing the U.S. anthropogenic NOₓ emissions thus lowers the NOₓ burden, NOₓ deposition, and NOₓ export from the United States in summer but decreases NOₓ deposition more efficiently than the NOₓ burden and export.

[26] Decreasing anthropogenic NOₓ emissions also reduces the eastward export through the east wall of the United States (Figure 7b), with the largest reduction near the surface around 42°N and at 300 hPa at around 45°N. The corresponding NOₓ concentration changes along the east wall of the United States (not shown) have a similar pattern. Surface emissions thus have a strong potential to affect not only surface export but also the free tropospheric eastward export north of 40°N, consistent with the dominant export mechanism that is associated with frontal passages at this latitude [e.g., Fang et al., 2009; Owen et al., 2006; Li et al., 2005; Cooper et al., 2001, 2002; Merrill and Moody, 1996].

4.3. Impact of Lightning NOₓ on the U.S. Export to the North Atlantic and Deposition

[27] By comparing the NOₓ,04LowLght and NOₓ,04HighLght simulations, we found that due to the lightning adjustment, the NOₓ source to the FT over the United States (includes inflow through the west wall, BL ventilation, and emissions within the FT) increases by 77%, while the total deposition (only the wet deposition since dry deposition only occurs in the model lowest level) increases by 99% and the export (includes northward, southward, and eastward export) increases by 53%. The less-than-linear variation of NOₓ export and more-than-linear response of NOₓ deposition to the source change reflect the partitioning change (the contribution of HNO₃ increases and that of PANs

### Table 2. July Budget of NOₓ Species in the U.S. (24°–48°N, 127.5°–67.5°W) Boundary Layer (Surface to 800 hPa) and the Total Column (Surface to 200 hPa) (unit: Gg N) in the NOₓ,04HighLght Simulation

<table>
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<th>Simulations</th>
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<td></td>
<td>23/42</td>
<td>3/55</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td></td>
<td>5/12</td>
<td>101</td>
<td>126/302</td>
<td>64/42</td>
<td>4/29</td>
</tr>
<tr>
<td></td>
<td>Others²</td>
<td></td>
<td>2/5</td>
<td>47</td>
<td>8/37</td>
<td>−10/18</td>
<td>1/12</td>
</tr>
<tr>
<td>NOₓ,99HighLght</td>
<td>NOₓ</td>
<td>694/880</td>
<td>19/49</td>
<td>308</td>
<td>177/406</td>
<td>205/151</td>
<td>10/121</td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>531/560</td>
<td>15/34</td>
<td>231</td>
<td>127/230</td>
<td>169/90</td>
<td>10/84</td>
</tr>
</tbody>
</table>

*Values shown in each cell represent BL/TC values.

1Emissions include surface, aircraft, biomass burning, and lightning sources.

2Export across the east wall (along 67.5°W longitude line, extending from 24 to 48°N, from surface to 200 hPa); this term is included in net export.

3Other species include oxidized products from NOₓ other than HNO₃ and PANs, mainly isoprene nitrates.

4There are <4% imbalances between the emissions and the sum of deposition and net export within the BL and the TC.
decreases), consistent with our findings from the anthropogenic emission sensitivity experiment in section 5 (note the opposite sign of the emission perturbations).

[29] The lightning adjustment results in a different pattern of the eastward NO$_y$ flux change (Figure 7c) from that associated with anthropogenic emissions (Figure 7b), with one maximum located around 400 hPa, centered at 42°N. The PAN contribution changes up to 10% in the FT in the lightning perturbation case, whereas it is only about −2% in the anthropogenic emission perturbation case (Figure 8) even though the NO$_x$ emission perturbations within the total column are similar in both experiments. If the adjusted lightning were correct, this partitioning change implies the LowLght simulations would likely overestimate the relative contribution of PAN to the total exported NO$_y$ while underestimating the absolute export of NO$_y$ produced by lightning. Using the NO$_x$ partitioning simulated by the LowLght models would, in this case, overestimate the impact of the U.S. anthropogenic NO$_x$ emission reductions on global and downwind O$_3$ air quality even with good constraints on U.S. anthropogenic NO$_x$ emissions.

[29] Here we estimate the contributions from lightning NO$_x$ sources to the total FT eastward export, the largest export pathway for NO$_y$. For this estimate, we use the NO$_x$04HighLght and NO$_x$04LowLght simulations in which lightning NO$_x$ changes by an order of magnitude. The export change is not linear to the emission change, as the export through the east wall increases from 74 to 106 Gg N (Table 3, +43%) in July after the lightning adjustment (which increases the total FT source by 77%, Table 3). We assume that this change is only due to the lightning NO$_x$ increase over the U.S. plus the increase in the inflow through the west wall (from 24 to 30 Gg N, reflecting the lightning NO$_x$ increase imposed over all the northern hemisphere midlatitude continents). We bracket our estimate of the lightning contribution to the U.S. FT eastward fluxes using the following two limits: (A) the NO$_y$ entering through the west wall blows directly across the region and

Figure 7. Latitudinal pressure section of NO$_y$ fluxes (unit: 10$^{-14}$ moles N s$^{-1}$ cm$^{-2}$) through a wall at 67.5°W, between 24°N and 48°N during July 2004: (top) in the NO$_x$04HighLght simulation, (middle) changes due to the anthropogenic emission reduction (NO$_x$04HighLght minus NO$_x$99HighLght), and (bottom) due to lightning adjustment (NO$_x$04HighLght minus NO$_x$04LowLght); positive values indicate eastward flux changes, whereas negative values indicate westward flux changes.

Figure 8. Relative contribution of the major NO$_y$ components to the total NO$_y$ flux through the east wall (67.5°W, from 24°N–48°N) of the United States in the NO$_x$04LowLght (green), the NO$_x$99HighLght (blue), and the NO$_x$04HighLght (red) simulations.
Table 3. July Budget of NOx Species in the U.S. (24°N–48°N, 127.5°W–67.5°W) Free Troposphere (800–200 hPa)*

<table>
<thead>
<tr>
<th>Experiments</th>
<th>NOx04LowLght</th>
<th>NOx04HighLght</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT Source</td>
<td>203</td>
<td>360</td>
</tr>
<tr>
<td>Burden</td>
<td>19</td>
<td>29</td>
</tr>
<tr>
<td>Deposition</td>
<td>103</td>
<td>205</td>
</tr>
<tr>
<td>Net export</td>
<td>95</td>
<td>145</td>
</tr>
<tr>
<td>Eastward export</td>
<td>74</td>
<td>106</td>
</tr>
</tbody>
</table>

*Unit: Gg N, see section 4.3 for details.

is exported through the east wall and (B) the NOx from the west wall is all deposited within the United States. As shown in Table 4, the increase in lightning NOx in the FT thus contributes from 26 (scenario A) to 32 GgN (scenario B) to the total July NOx eastward export in the NOx04HighLght simulation. The original lightning NOx source over the United States provides 14 Gg N during July. Applying the previous upper and lower bound assumptions of 0%–100% deposition of lightning NOx in this simulation yields a range of 0–14 Gg N contribution from the original lightning to the July eastward export. Combining this range with the estimated range of the enhanced export from the increased lightning yields an estimate for the total lightning contribution of 26–46 Gg N or 24%–43% of the total U.S. NOx export to the North Atlantic in the FT.

With similar assumptions, we estimate the contribution from lightning to wet deposition over the United States. Combining the lightning NOx in the NOx04LowLght simulation (0–14 GgN) with the increase in FT wet deposition from the NOx04LowLght to the NOx04HighLght simulation (96–102 Gg N), we estimate that lightning NOx accounts for 96–116 GgN (47%–57%) of total wet deposition from the FT. Since the lightning source within the BL is only around 2% of the total BL NOx emissions, we assume that its contribution to wet deposition in the BL (134 GgN) is negligible and estimate the lightning NOx contribution to the total U.S. NOx wet deposition to be 28%–34%. Over remote regions, the lightning NOx contribution to total wet deposition may be much higher. Changes in lightning activity may thus be detectable from measurements of nitrate deposition, particularly if subjected to nitrogen isotope analysis.

4.4. Export Efficiency of U.S. Surface NOx Emissions to the North Atlantic

[31] Since the export of NOx to the North Atlantic in the FT is the component affecting O3 production over downwind regions, we modify the traditional Eulerian budget analysis (section 4.1) to isolate this component. Specifically, we calculate the NOx export efficiency (f): f = NOxFT eastward export/NOx emissions, where NOx emissions are surface emissions and the NOxFT eastward export is the NOx flux through the east wall that comes from surface ventilation. Table 4 shows the contributions of different components to the total July FT NOx eastward export in the NOx04HighLght simulation. The eastward export in the FT originating from the surface NOx emissions is estimated to be 22–74 GgN (out of the total surface emissions of 520 Gg N in July), yielding a 4%–14% range for the FT export efficiency to the North Atlantic, with the range resulting from various assumptions (see section 4.3 and Table 4).

[32] As expected, this result is lower than our estimate using the traditional Eulerian budget method of export out of the continental BL (see section 4.1) and other previous Eulerian budget estimates [e.g., Levy and Maxim, 1987; Liang et al., 1998; Horowitz et al., 1998; Li et al., 2004; Parrish et al., 2004; Pierce et al., 2007] since it excludes NOx that deposits within the U.S. FT.

[33] Another method to derive the export efficiency of NOx emissions (hereafter, referred to as the “plume-based method”) uses CO as an inert tracer and estimates the export efficiency using the NOx–CO relationship sampled in the outflow plumes downwind. Parrish et al. [2004] analyzed the difference between the traditional Eulerian budget estimate and the plume-based estimate and attributed it to losses in NOx occurring between export from the continental BL and arrival at the point sampled. Applying this plume-based method, Hudman et al. [2007] reported an NOx export efficiency of 14% ± 8% from GEOS-Chem model and of 16% ± 10% from the ICARTT observations between 2.5 and 6.6 km. Our modified Eulerian budget estimate (4%–14%) falls into the range of this and other plume-based estimates [3%–20%, e.g., Stohl et al., 2002; Parrish et al., 2004; Li et al., 2004; Hudman et al., 2007].

Table 4. Contribution From Different Components to the Total Free Troposphere U.S. NOx Export to the North Atlantic in the NOx04HighLght Simulation During July 2004 (unit: Gg N)

<table>
<thead>
<tr>
<th>Assumptions</th>
<th>FT NOx</th>
<th>Eastward Export</th>
<th>Inflow From the West Wall</th>
<th>Lightning Increase</th>
<th>Original Lightning</th>
<th>Biomass Burning and Aircraft Source</th>
<th>Derived lofted Surface Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>106</td>
<td>29</td>
<td>26</td>
<td>0–14</td>
<td>0–15</td>
<td>22–51</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>106</td>
<td>0</td>
<td>32</td>
<td>0–14</td>
<td>0–15</td>
<td>45–74</td>
<td></td>
</tr>
</tbody>
</table>

*Assumptions: (A) NOx entering through the west wall blows directly across the region and is exported eastward through the east wall; (B) NOx from the west wall is all deposited within the United States.

*Defined as the eastward NOx export flux through the east boundary of the United States (24°N–48°N, 67.5°W) from the NOx04HighLght simulation.

*Calculated as the difference between the NOx04HighLght and NOx04LowLght simulations, see section 4.3.

*See calculations in section 4.3.

*Original lightning in the NOx04LowLght simulation, see section 4.3.

*This term is derived by assuming a 0%–100% contribution from these emission sectors.

*This term is derived as the FT NOx eastward export, other components (inflow from the west wall, local lightning increase, original lightning, biomass burning, and aircraft source).
[34] The accuracy of the plume-based export efficiency estimate depends on many factors, such as the treatment of the background CO [Li et al., 2004] and the altitude of the plumes sampled. Our approach provides an average view of the NO\textsubscript{x} export efficiency in the FT to the North Atlantic.

[35] Results from the anthropogenic sensitivity experiment (section 4.2), in which 157 Gg increases of anthropogenic emissions causes a 5 Gg N increase in the FT eastward export (Table 2), suggest that the anthropogenic NO\textsubscript{x} export efficiency from the increased anthropogenic emission is 3%. However, this estimate is unlikely to represent the “real” anthropogenic export efficiency due to the nonlinearity discussed in section 4.2. Indeed, our analysis above indicates that the export efficiency of the total anthropogenic emissions is greater than 3%. To avoid the impact of nonlinearity induced by emission perturbations from sensitivity studies on the export efficiency calculation, a possible solution is to tag anthropogenic NO\textsubscript{x} within the United States [Horowitz and Jacob, 1999] and thereby quantify its contribution to the eastward NO\textsubscript{x} export.

5. Implications for \textit{O}_3 Production

5.1. \textit{O}_3 Production in the U.S. BL and In the Northern Hemispheric FT

[36] We examine the implications for \textit{O}_3 production from the changes in anthropogenic and lightning NO\textsubscript{x} sources. Our simulations indicate that the 23% decrease in surface NO\textsubscript{x} emission from the 1999–2004 inventory decreases the gross \textit{O}_3 production in the United States BL by 10%, from 17.0 to 15.3 Gmol d\textsuperscript{-1}. The less-than-linear decrease reflects an increase in ozone production efficiency (OPE, from 19.1 to 23.9, calculated as regional mean gross \textit{O}_3 production divided by regional mean NO\textsubscript{x} loss rate), similar to findings from previous studies [Liu et al., 1987; Lin et al., 1988; Jacob et al., 1993; Thompson et al., 1994; Horowitz et al., 1998]. The OPE over the northeastern United States increases by around 20%, higher than the 9% estimate from Hudman et al. [2009], due to a larger NO\textsubscript{x} emission change in our experiment within this region (24%) relative to their work (15%). The direct \textit{O}_3 export out of the U.S. BL decreases by 0.55 Gmol d\textsuperscript{-1} (by 28% of the \textit{O}_3 direct export), around 32% of the decrease in the gross \textit{O}_3 production (1.7 Gmol d\textsuperscript{-1}) within the U.S. BL. This ratio is comparable to that found by Li et al. [2004] when the North American NO\textsubscript{x} anthropogenic emissions were turned off. The decrease in FT \textit{O}_3 production over the United States, due to decreased NO\textsubscript{x} export from the BL, is 0.4 G mol d\textsuperscript{-1}, 73% of the direct \textit{O}_3 export reduction in the U.S. BL from the change in anthropogenic NO\textsubscript{x} emissions.

[37] The enhanced lightning NO\textsubscript{x} increases gross \textit{O}_3 production in the FT over the United States by 49% (from 10.6 to 15.5 G mol d\textsuperscript{-1}). Meanwhile, the OPE is reduced by 46% (from 56.3 to 30.2). A previous study showed a mean FT OPE of 61 over the United States [Liang et al., 1998], similar to our NO\textsubscript{x}0.04LowLght simulation. The gross \textit{O}_3 production in the FT north of 30°N is 55.4 G mol d\textsuperscript{-1} in the NO\textsubscript{x}0.04LowLght simulation, also consistent with the estimate of Wang et al. [1998] (51 Gmol d\textsuperscript{-1} annually). After increasing the lightning NO\textsubscript{x} source in the NO\textsubscript{x}0.04HighLght simulation, the gross \textit{O}_3 production within this region is enhanced to 73.7 G mol d\textsuperscript{-1} (+33%) with the mean OPE reduced from 56 to 39 (~30%). A model with a lightning NO\textsubscript{x} source biased low will overestimate the background OPE along with the relative contribution of PAN to NO\textsubscript{x} export, both of which may lead to an overestimate of the contribution from anthropogenic NO\textsubscript{x} emissions to \textit{O}_3 in downwind regions even if the anthropogenic emissions are well represented. As an illustration, we examine the 500 hPa \textit{O}_3 concentration response over southern Europe to the same anthropogenic emission change over the United States under the original lightning case (\textit{O}_3 (NO\textsubscript{x}99LowLght) - \textit{O}_3 (NO\textsubscript{x}99HighLght)) and under the increased lightning case (\textit{O}_3 (NO\textsubscript{x}99HighLght) - \textit{O}_3 (NO\textsubscript{x}0.04HighLght)). We find that the \textit{O}_3 response in the original lightning (LowLght) case is about 30% higher than that in the increased lightning (HighLght) case. Further efforts are needed to better quantify the lightning NO\textsubscript{x} source to obtain a more reliable evaluation of the impact of anthropogenic NO\textsubscript{x} emissions on global-scale \textit{O}_3 production.

5.2. Surface \textit{O}_3 Over the Contiguous United States

[38] The anthropogenic NO\textsubscript{x} emission reductions from 1999 to 2004 improve \textit{O}_3 air quality, especially in the eastern United States and California (Figure 9). July MDA8 \textit{O}_3 decreases by 9–12 ppbv in these two regions where total \textit{O}_3 is above 70 ppbv. The maximum decrease in MDA8 \textit{O}_3 over the eastern United States occurs to the south of the maximum NO\textsubscript{x} emission change (over Kentucky, Tennessee, and Missouri, Figure 1), consistent with the results of Hudman et al. [2009] and Kim et al. [2006]. Within the northeastern and mid-west United States, the monthly mean MDA8 \textit{O}_3 decreases by around 5–7 ppbv (comparable to 4–6 ppbv from Hudman et al. [2009] and 7 ppbv from Kim et al. [2006]). Over Los Angeles, MDA8 \textit{O}_3 increases despite the decrease of NO\textsubscript{x} emissions, likely reflecting the NO\textsubscript{x}–saturated regime for \textit{O}_3 production there. This trend from 1999 to 2004 is consistent with the trend reported by EPA (www.epa.gov/airtrends/weather/region09.pdf), where \textit{O}_3 is shown to increase over Los Angeles, despite the decrease over most California. Decreases of the monthly mean 24 h average surface \textit{O}_3 concentrations show a similar pattern to MDA8 \textit{O}_3, except the maximum change is lower (6 ppbv). Stronger sensitivity of the MDA8 \textit{O}_3 reflects the rapid photochemical production fueled by local precursor emissions as compared to the complex nighttime processes that affect the 24 h average surface \textit{O}_3 [Russell et al., 1986].

[39] Surface \textit{O}_3 concentrations are weakly affected by the adjustment to the northern hemispheric lightning NO\textsubscript{x} source. The monthly mean MDA8 \textit{O}_3 concentration increases by up to 3.5 ppbv, with the largest increase occurring to the northeast of Florida and to the east of California. We scaled the lightning NO\textsubscript{x} source by a factor of 10 in the NH midlatitudinal continents, and we also reduced the fraction of lightning NO\textsubscript{x} in the surface layer from 20% to 2% (see section 2). These adjustments compensate in the boundary layer. Hence, the surface \textit{O}_3 change is mostly due to the lightning NO\textsubscript{x} change in the FT. The maximum \textit{O}_3 concentration change near Florida is associated with the maximum lightning NO\textsubscript{x} emission change over Florida (Figure 2b). However, the lightning NO\textsubscript{x} change corresponding to the maximum \textit{O}_3 concentration change to the east of California is weak. In this region, subsidence of air dominates, bringing the lightning-influenced air parcels from the free troposphere to the surface, resulting in a decrease of \textit{O}_3.
pogenic emissions). The contribution from lightning NO emissions have decreased since the mid-1990s, especially from 1999 to 2004 in response to the U.S. Environmental Protection Agency (EPA) State Implementation (SIP) call [Kim et al., 2006; Stavrakou et al., 2008; van der A et al., 2008; Frost et al., 2006]. In addition, recent work suggests that lightning NO is higher than previously thought over the midlatitudes of the Northern Hemisphere and that the empirical vertical profile of lightning-produced nitrogen applied in the current generation of CTMs (chemical transport model) needs revision [Ott et al., 2007, 2010; Pickering et al., 2006]. We use the MOZART-4 chemical transport model to examine the budget of NO species in the United States during summer 2004 and investigate its sensitivity to these changes in NO sources.

6. Conclusions

[40] Nitrogen oxides (NOx) and their oxidation products affect the tropospheric O3 budget and the oxidizing power of the atmosphere, as well as ecosystem productivity and thereby the global carbon cycle. U.S. anthropogenic NOx emissions have decreased since the mid-1990s, as well as from 1999 to 2004 in response to the U.S. Environmental Protection Agency (EPA) State Implementation (SIP) call [Kim et al., 2006; Stavrakou et al., 2008; van der A et al., 2008; Frost et al., 2006]. In addition, recent work suggests that lightning NO is higher than previously thought over the midlatitudes of the Northern Hemisphere and that the empirical vertical profile of lightning-produced nitrogen applied in the current generation of CTMs (chemical transport model) needs revision [Ott et al., 2007, 2010; Pickering et al., 2006]. We use the MOZART-4 chemical transport model to examine the budget of NO species in the United States during summer 2004 and investigate its sensitivity to these changes in NO sources.

[41] Our evaluation of the model with observations from INTEX-NA shows that using the 2004 NOx emission inventory versus the 1999 inventory (NEI99) reduces the mean bias of the boundary layer (BL) simulation for most species (including NO3, OH, PAN, and O3) while maintaining the spatial correlations (r > 0.5 for most NOx species). The simulated bias is also smaller than the mean bias in Singh et al. [2007] (bias decreases from 40% to 6% and >100% to 67% for NOx and PAN, respectively). Scaling up the FT NOx lightning emission by a factor of 10 improves the profiles of NOx and O3 relative to observations, but there is still a considerable underestimate (60%) in the upper troposphere for NO3. HNO3 and PAN are not notably improved in our model after the emission adjustments, indicating a bias in chemical partitioning, as found in other models [Singh et al., 2007; Henderson et al., 2009; Yu et al., 2010], possibly reflecting uncertainties in isoprene chemistry [e.g., Emmerson and Evans, 2009; Ito et al., 2009; Pfister et al., 2008b] or the convection related processes that affect the upper troposphere [Bertram et al., 2007]. The simulation using 2004 NOx emissions yields a spatial correlation of 0.75 between modeled nitrate wet deposition and the National Atmospheric Deposition Program (NADP) observations. Increasing the lightning NOx improves nitrate wet deposition prediction over the midwest and inland of southeast United States but worsens over the east coast (Figure 6), likely reflecting a problem in simulated lightning frequency (Figure 2).

[42] We assessed the impact of the anthropogenic and lightning NOx changes on U.S. O3 air quality. Anthropogenic NOx emission reductions lower the monthly mean daily maximum 8 h surface (MDA8) O3 by up to 12 ppb over Kentucky, Tennessee, Missouri, and California and by 5–7 ppb over Northeast Corridor and midwest, consistent with prior studies [Hudman et al., 2009; Kim et al., 2006]. The lightning impact on surface O3 is weaker, especially over the highly polluted regions [Kaynak et al., 2008], in the western United States; this range incorporates several methods for estimating background O3 level [Altshuller and Lefohn, 1996; Lin et al., 2000; Jaffe et al., 2003; Fiore et al., 2002, 2003; Vingarzan, 2004].
although it does raise background O₃ levels by 3 ppbv over the western United States and near Florida and 1 ppbv in other regions.

[45] In our model, most NOₓ emitted in July is removed by wet or dry deposition within the United States (~70% in the boundary layer, BL, and 80% in the total column, TC), with the rest exported. The imposed NOₓ emission changes yield a more-than-linear response of NOₓ deposition and a less-than-linear response of NOₓ export, resulting from the NOₓ partitioning and lifetime changes (e.g., Liang et al., 1998). We estimated the range of lightning NOₓ contribution to the total NOₓ wet deposition over the United States and to the U.S. FT export to the North Atlantic to be 28–34% and 24–43% in the NOₓ04HighLtgh simulation, respectively, with the range reflecting different assumptions (section 4.3 and Table 4).

[46] We further calculate the range of the anthropogenic contribution to the U.S. FT export to the North Atlantic to be 22–74 GgN in July, yielding an estimate for NOₓ export efficiency (the ratio of the anthropogenic export to the North Atlantic between 800 and 200 hPa over total U.S. surface NOₓ emissions) of 4%–14%. The high end of this range is consistent with the plume-based estimates of NOₓ export efficiency during the INTEX-NA campaign (14% ± 8% in the GEOS-Chem model and 16% ± 10% from the INTEX-NA observations between 2.5 km and 6.6 km) [Hudman et al., 2007] and the range of previous plume-based estimates [e.g., Parrish et al., 2004; Li et al., 2004; Stohl et al., 2002].

[47] The adjustment to the lightning NOₓ source increases the fractional contribution of HNO₃ to NOₓ while decreasing that of PAN (Figure 8), suggesting that an underestimate of lightning NOₓ would cause the relative PAN contribution to the total NOₓ export to be overestimated. The Ozone Production Efficiency (OPE) in the FT over the United States and the extratropical Northern Hemisphere decrease from 55 to 30 and from 56 to 39, respectively, when lightning NOₓ is increased. Even if anthropogenic emissions are well represented, an excessive fractional PAN contribution to NOₓ export and northern hemispheric OPE would bias high the estimated impact of the U.S. anthropogenic NOₓ emission reduction on global and downwind O₃ air quality (e.g., at 500 hPa over southern Europe, the response to the same U.S. anthropogenic NOₓ changes are 30% higher in the low versus high lightning cases). Better constraints on the lightning NOₓ source are required to more confidently assess the impacts of anthropogenic emissions and their changes on air quality over downwind regions.

[48] Acknowledgments. The authors would like to thank Rynda Hudman, Robert Pinder, Barron Henderson, Emily Fischer, Kenneth E. Pickering, and Anand Ganadesikan for informative conversations; Rynda Hudman and Songming Fan for insightful reviews, the INTEX-NA campaign team for providing the NASA DC-8 aircraft observational data; and the MOZART-4 development team.

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