Export of NO$_y$ from the North American boundary layer: Reconciling aircraft observations and global model budgets

Qinbin Li, Daniel J. Jacob, J. William Munger, and Robert M. Yantosca

Division of Engineering and Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA

David D. Parrish

NOAA Aeronomy Laboratory, Boulder, Colorado, USA

[1] Fossil fuel combustion accounts for >50% of the global atmospheric emission of NO$_x$, but this source is concentrated in the polluted continental boundary layer (CBL) and only a small fraction is exported as NO$_y$ (NO$_x$ and its oxidation products) to the global troposphere. Better quantification of this export efficiency is needed because of its implications for global tropospheric ozone. A recent Lagrangian analysis of the NO$_y$-CO correlations observed from the North Atlantic Regional Experiment in September 1997 (NARE'97) aircraft campaign downwind of eastern North America (September 1997) indicated a NO$_y$ export efficiency of <10%, with <10% of the exported NO$_y$ present as NO$_x$. In contrast, previous three-dimensional (3-D) model Eulerian budget analyses for the North American boundary layer indicated NO$_y$ export efficiencies of 25–30%, with 30–35% of the exported NO$_y$ present as NO$_x$. We investigated this apparent discrepancy by simulating the NARE'97 aircraft observations with a global 3-D model of tropospheric chemistry (GEOS-CHEM) and using the model to calculate the NO$_y$ export efficiency both through a Lagrangian analysis of the NO$_y$-CO correlations along the aircraft flight tracks and through an Eulerian budget analysis for the North American boundary layer. The model reproduces the variability and NO$_y$-CO correlations observed in the aircraft data and also at the Harvard Forest surface site in the northeastern United States. We show that the previous Lagrangian analyses of the NO$_y$ export efficiency during NARE'97 were probably biased low because of underestimation of the CO background. Correcting for this bias, we find a NO$_y$ export efficiency of 17 ± 7% in the model and 15 ± 11% in the observations. A similar NO$_y$ export efficiency (20%) in the model is obtained from the Eulerian budget analysis, demonstrating that the Lagrangian and Eulerian approaches are in fact consistent. Export efficiencies of NO$_y$ in previous 3-D model Eulerian budget analyses were probably too high because of insufficient scavenging out of the CBL. Model results indicate that only 6% of the exported NO$_y$ is present as NO$_x$ along the aircraft flight tracks, in agreement with the observations, but that 40% of the NO$_y$ export flux is present as NO$_x$, in agreement with the previous 3-D model analyses. This result reflects the fast oxidation of NO$_x$ between the point of exit from the CBL and the point of sampling by the aircraft. The eventual ozone production in the global troposphere due to exported NO$_x$ and peroxyacetylnitrate (PAN), with equal contributions from each, is comparable in magnitude to the direct export of ozone pollution from the North American boundary layer.   *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; *KEYWORDS:* reactive nitrogen, export efficiency, pollution

1. Introduction

[2] Production of ozone in the troposphere is limited primarily by the availability of nitrogen oxides (NO$_x$ = NO + NO$_2$) [*Chameides et al.*, 1992]. More than half of the global emission of NO$_x$ is from fossil fuel combustion [*Intergovernmental Panel on Climate Change (IPCC)*, 2001], but this source is mainly confined to populated continental regions. This NO$_x$ emitted from fossil fuel combustion (hereafter referred to as anthropogenic NO$_x$) has a lifetime of less than a day against oxidation to HNO$_3$ and peroxyacetylnitrate (PAN). We refer to the sum of NO$_x$, HNO$_3$, PAN, and other minor NO$_x$ oxidation products as total reactive nitrogen (NO$_y$). HNO$_3$ is highly water-soluble and is removed by deposition from the continental boundary layer (CBL) [*Munger et al.*, 1998], but PAN is sparingly soluble and can be therefore exported out of the CBL, eventually decomposing to contribute a major source of NO$_x$ to the remote troposphere [*Moxim et al.*, 1996; *Lamarque et al.*, 1996; *Horowitz and Jacob*, 1999]. The small fraction of anthropogenic NO$_y$ exported from the CBL as NO$_x$ or PAN needs to be better quantified because of its large implications for human influence on global tropospheric ozone [*Jacob et al.*, 1993] and for intercontinental transport of ozone pollution [*Jacob et al.*, 1999; *Li et al.*, 2002a].

[3] Simulations with three-dimensional (3-D) Eulerian models of atmospheric chemistry find that 25–35% of NO$_x$ emitted in the United States is exported out of the CBL as some form of NO$_y$, and that the rest is deposited within the CBL mainly as HNO$_3$ [*Kasibhatla et al.*, 1993; *Horowitz et al.*, 1998; *Liang et al.*, 1998]. The detailed study by *Liang et al.* [1998] indicates little seasonal variation in this export efficiency. It finds more seasonal variation in the composition of the exported NO$_y$; the fraction exported as NO$_x$ varies from 30–35% in summer and fall to 60% in winter.

[4] Aircraft measurements from the North Atlantic Regional Experiment in September 1997 (NARE'97) [*Cooper et al.*, 2001] offer an opportunity to test these model results. Measurements of NO$_y$, NO$_x$, PAN, and carbon monoxide (CO) in North American outflow were made aboard an aircraft based in Newfoundland. By viewing CO as an inert anthropogenic tracer in the outflow, one can use the NO$_y$-CO correlation in the aircraft observations as a measure of the export efficiency of NO$_y$ from a Lagrangian perspective. *Stohl et al.* [2002] thus estimate an export efficiency of 3% from the NARE'97 data above 3 km. A more detailed study of the NO$_y$-CO correlation by D. D. Parrish et al. (Fraction and composition of NO$_y$ transported in air masses lofted from the North American continental boundary layer, submitted to *Journal of Geophysical Research*, 2003) (hereinafter referred to as Parrish et al., submitted manuscript, 2003) using the data from NARE'97 and from four other North American aircraft campaigns estimates an NO$_y$ export efficiency of about 10% in early fall and spring and 20% in summer. These values are much lower than the 3-D model Eulerian budget estimates. The analysis by Parrish et al. (submitted manuscript, 2003) further indicates that NO$_x$ represented only 8% of the NO$_y$ exported to the free troposphere during NARE'97, with PAN contributing 34% and

HNO$_3$ contributing presumably the remainder. This NO$_x$ fraction is considerably lower than the 3-D model estimate of *Liang et al.* [1998].

[5] Similar discrepancies between 3-D model and observation-based estimates of the export efficiency of NO$_y$ have been found for east Asia. A global 3-D model simulation by *Bey et al.* [2001b] indicates that 20–30% of the NO$_x$ emitted in east Asia in spring is exported to the free troposphere as NO$_y$, and that the major component of the exported NO$_y$ is PAN (45%) with NO$_x$ and HNO$_3$ each contributing 25–30%. In contrast, a recent study by *Koike et al.* [2003], using observed NO$_y$-CO correlations in Asian outflow from the TRACE-P aircraft mission in February– April 2001 [*Jacob et al.*, 2003], estimates that only 15% of the NO$_x$ emitted in China is exported to the free troposphere (2–7 km) as NO$_y$. *Koike et al.* [2003] find that PAN was the dominant form of the exported NO$_y$, while only 0.5% remained as NO$_x$ in the free troposphere. A study by *Miyazaki et al.* [2003] using meteorological (back-trajectory) and chemical (tracer correlation) analyses of the TRACE-P observations, estimates similarly that only 10–20% of NO$_x$ emitted from east Asia is exported to the free troposphere.

[6] Such large discrepancies between estimates of the export efficiency of NO$_y$ and of the composition of the exported NO$_y$ have major implications for assessing the effect of anthropogenic NO$_x$ emissions on the global ozone budget. *Liang et al.* [1998] estimated that the eventual ozone production in the free troposphere due to the exported NO$_x$ + PAN is twice as large as the direct export of ozone pollution from the U.S. boundary layer. In contrast, Parrish et al. (submitted manuscript, 2003) argued that anthropogenic production of ozone in the free troposphere must be of little importance because of the small fraction of NO$_y$ exported to the free troposphere as NO$_x$.

[7] We attempt here to understand these apparent discrepancies by using a global 3-D model simulation of the in situ aircraft measurements from NARE'97. We evaluate the model with aircraft and ozonesonde observations from the mission, as well as with surface observations from the eastern United States. By using the model to replicate both the observation-based analysis of the NO$_y$ export efficiency by Parrish et al. (submitted manuscript, 2003) and the CBL NO$_y$ budget analysis of *Liang et al.* [1998], we can shed light on the difference between the two studies. Results have important general implications for the ability of models to describe properly the export of soluble gases and aerosols out of the CBL.

2. The NARE'97 Aircraft Mission

[8] The NARE'97 aircraft mission was conducted from 6 September to 2 October 1997 over the Canadian maritime provinces and the western North Atlantic Ocean [*Cooper et al.*, 2001]. It used a WP-3D aircraft (ceiling 8 km) based out of St John's, Newfoundland. The aircraft flight tracks are shown in Figure 1. A total of 13 flights were conducted, with principal focus on sampling of North American outflow. Daily ozonesondes were launched from Sable Island, Nova Scotia (44°N, 60°W) from 5 September to 5 October.

[9] Ozone was measured aboard the aircraft by a fast-response NO-ozone chemiluminescence instrument [*Ryerson*
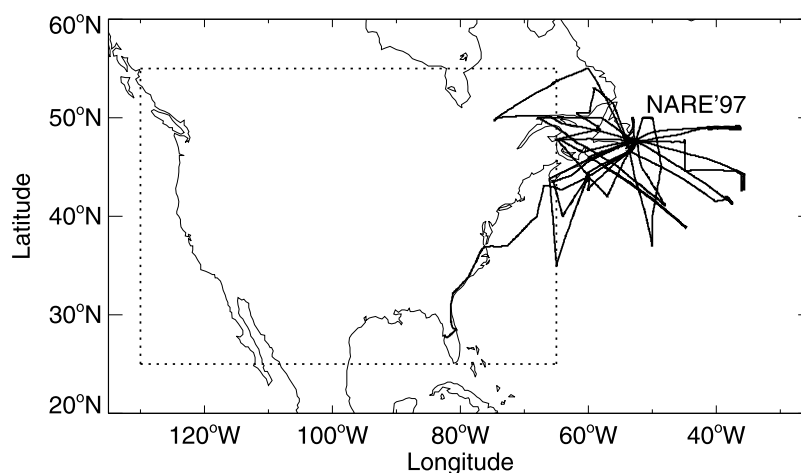
Figure 1. Flight tracks of the NOAA WP-3D aircraft during the North Atlantic Regional Experiment in September 1997 (NARE'97). The rectangle (dashed line) defines the North American domain ($130°-65°$W, $25°-55°$N) used in our budget analysis.

et al., 1998]. CO was measured by vacuum UV fluorescence [*Holloway et al.*, 2000]. NO was detected by ozone-induced chemiluminescence and NO$_x$ was inferred from NO-NO$_2$-O$_3$ photostationary steady state using radiometer data for the NO$_2$ photolysis frequency. Total gas-phase NO$_y$ was measured by Au-tube conversion to NO with added CO followed by ozone chemiluminescence. Measurement accuracy was estimated at 5% for the NO data and +5% to -25% for the NO$_y$ data [*Ryerson et al.*, 1999]. PAN and peroxyacyl nitrate (PPN) were measured at 5 min or shorter intervals by an onboard gas chromatograph with electron capture detection, and the uncertainty in the measurements was estimated to be ±25% at mixing ratios above 50 pptv [*Williams et al.*, 2000]. The original CO, ozone, NO, and NO$_y$ data were reported as 1-s averages; we use here 1-min averages.

[10] *Cooper et al.* [2001, 2002a, 2002b] presented comprehensive analyses of the in situ aircraft observations from the NARE'97. They found that the export of pollution from North America to the free troposphere was largely controlled by midlatitude cyclones and the associated warm conveyor belts (WCBs). They further found that NO$_y$ was efficiently removed from the airstreams that transported polluted boundary layer air to the free troposphere, consistent with the analyses of *Stohl et al.* [2002] and Parrish et al. (submitted manuscript, 2003).

3. Model Description

[11] We use the GEOS-CHEM global 3-D model of tropospheric chemistry driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Data Assimilation Office (DAO). The first description of the model as applied to simulation of tropospheric ozone-NO$_x$-hydrocarbon chemistry was presented by *Bey et al.* [2001a]. We use here GEOS-CHEM version 4.33 (http://www-as.harvard.edu/chemistry/trop/geos), which includes a number of updates as described in particular by *Martin et al.* [2002]. Meteorological fields for 1997 (GEOS-STRAT) are provided at 6-hour frequencies (3-hour frequencies for surface fields and mixing depths) with horizontal resolution of 2° latitude by 2.5° longitude

(degraded here to 4° latitude by 5° longitude) and 26 σ levels in the vertical between the Earth's surface and 0.1 hPa. The boundary layer up to 2 km altitude is resolved with five σ levels. All simulations presented here were conducted for four months (June–September 1997) using standard GEOS-CHEM model output as initial conditions. The first three months were used for initialization and we focus our attention on results for September. Hourly model results were archived and concentrations of CO, ozone, and NO$_y$ species were then sampled along the WP-3D aircraft flight tracks at the time of the flights.

[12] The model includes 80 chemical species and over 300 reactions to describe tropospheric ozone-NO$_x$-hydrocarbon chemistry. Detailed photooxidation schemes are used for major hydrocarbons including isoprene [*Horowitz et al.*, 1998]. The NO$_y$ chemistry is mainly from *DeMore et al.* [1997] and *Horowitz et al.* [1998]. Rate constants for NO$_x$-HNO$_3$ cycling are from *Brown et al.* [1999a, 1999b]. Hydroxy organic nitrates produced by isoprene oxidation appear to decompose quickly to HNO$_3$ on surfaces [*Chen et al.*, 1998], and we assume here that this decomposition is instantaneous. No consideration of phase partitioning between gas-phase HNO$_3$ and aerosol nitrate is included in the model. Reactions of N$_2$O$_5$, NO$_3$, and NO$_2$ in aerosols are included using reaction probabilities from *Jacob* [2000] applied to global 3-D sulfate aerosol fields from *Chin et al.* [1996], as described by *Bey et al.* [2001a].

[13] Dry deposition of oxidants and water soluble species is computed using a resistance-in-series model based on the original formulation of *Wesely* [1989] with a number of modifications [*Wang et al.*, 1998a]. The dry deposition velocities are calculated locally using GEOS data for surface momentum and sensible heat fluxes, temperature, and solar radiation. Wet deposition (applied to HNO$_3$ and H$_2$O$_2$ only) includes scavenging by convective updrafts, anvils, and large-scale precipitation as described by *Liu et al.* [2001].

[14] Global anthropogenic and natural emissions are specified for 1997 following the procedure described by *Bey et al.* [2001a], with updated CO emissions from *Duncan et al.* [2003]. Total anthropogenic emissions of CO and NO$_x$ in the

United States for 1997 are 97 Tg CO yr^{-1} and 6.7 Tg N yr^{-1}, respectively. For comparison, the corresponding values for 1997 are 107 Tg CO yr^{-1} and 6.8 Tg N yr^{-1} in the most recent report available from the U.S. Environmental Protection Agency (EPA) (February 2003, see http://www.epa.gov/ttn/chief/trends/index.html). Transport of ozone from the stratosphere is simulated with the Synoz (synthetic ozone) method of *McLinden et al.* [2000] by imposing a global cross-tropopause flux of 475 Tg O$_3$ yr^{-1}, which provides for a satisfactory simulation of vertical ozone profiles at northern middle and high latitudes [*Bey et al.*, 2001a, 2001b; *Liu et al.*, 2002; *Li et al.*, 2002b]. The cross-tropopause flux of NO$_y$ is 0.65 Tg N yr^{-1}, including 0.17 Tg N yr^{-1} as NO$_x$ and 0.48 Tg N yr^{-1} as HNO$_3$.

[15] A global evaluation of the GEOS-CHEM simulation of tropospheric ozone-NO$_x$-hydrocarbon chemistry using assimilated meteorological data for 1994 (GEOS-1) was presented by *Bey et al.* [2001a]. That simulation underestimated CO concentrations at northern midlatitudes by 10−20 ppbv. *Duncan et al.* [2003] corrected this flaw with additional sources of CO from biogenic methanol and acetone, and updated estimates of nonmethane hydrocarbon (NMHC) emissions from biofuels, fossil fuels, and biomass burning. *Bey et al.* [2001a] found that simulated monthly mean concentrations of NO and PAN at northern midlatitudes were generally within a factor of 2 of aircraft observations with no systematic biases. HNO$_3$ was generally overestimated by a factor of 2−3, possibly because of a combination of insufficient scavenging in the free troposphere and the absence of gas-aerosol partitioning of HNO$_3$ in the model. Overestimate of HNO$_3$ is a frequent problem in global models [*Wang et al.*, 1998b; *Lawrence et al.*, 1999; *Tie et al.*, 2003].

[16] More specific evaluations of the GEOS-CHEM simulation of tropospheric ozone-NO$_x$-hydrocarbon chemistry over North America and in North American outflow have been presented in a number of studies. *Fiore et al.* [2002] showed detailed comparisons with observational statistics for ozone and its precursors in the United States for the summer of 1995. They found that the model reproduces the principal features in the observed distributions of ozone and its precursors. Simulated NO$_x$ and NO$_y$ concentrations were typically within 50% of the observations, with no systematic bias. *Martin et al.* [2002] compared GEOS-CHEM results to tropospheric NO$_2$ columns retrieved from the GOME satellite instrument over the United States; they found strong spatial correlation ($r = 0.78$) and a 18% low bias in the model. *Li et al.* [2002a, 2002b] found strong correlations and no systematic biases in comparisons of model results to time series of observations of surface ozone and CO at coastal and North Atlantic sites.

[17] The focus of model application in this paper is to quantify the export of anthropogenic NO$_y$ from the North American boundary layer and its implications for global ozone production. We define the North American boundary layer as the horizontal domain (130°W−65°W, 25°N−55°N; see Figure 1) extending vertically up to 3 km or 730 hPa. This definition is similar to that used by *Liang et al.* [1998] in their model budget analysis. We will compare results from the standard simulation as described above to those from a sensitivity simulation with no anthropogenic NO$_x$, CO, or NMHC emissions from North America, and diagnose an-

thropogenic NO$_y$ by difference. Although this attribution is not exact because of nonlinearity in NO$_x$ chemistry, the perturbing effect is relatively small [*Lamarque et al.*, 1996]. We also conducted a sensitivity simulation in which only anthropogenic emissions of NO$_x$ from North America were suppressed (CO and NMHC emissions were kept at their values from the standard simulation) and found little difference with the results presented here.

4. Model Evaluation With NARE'97 Data

[18] All comparisons between model and observations in this section use model results sampled along the flight tracks at the time of the flight, and observations averaged over model grid boxes. Figure 2 shows observed and simulated vertical distributions of CO, ozone, NO$_y$, NO, and PAN for the ensemble of NARE'97 flights. Concentrations of CO, NO, and NO$_y$ are elevated in the boundary layer relative to the free troposphere, both in the model and in the observations, reflecting post-frontal continental outflow [*Cooper et al.*, 2001]. Simulated CO concentrations show no bias above 4 km but are 10−20 ppbv higher than observations in the boundary layer. Our previous GEOS-CHEM simulation of surface CO concentrations at Sable Island off the coast of Nova Scotia [*Li et al.*, 2002a] shows that the model reproduces the North American boundary layer outflow with usually no bias except in September 1997 where the outflow events are too large. We thus believe that the overestimate of boundary layer CO during NARE'97 is due to a transport anomaly rather than an overestimate of North American emission sources.

[19] The model reproduces the observed increase of ozone concentration with altitude, which is a well-known feature of observations over the North Atlantic [*Oltmans et al.*, 1996] and reflects efficient production and the long lifetime of ozone in the free troposphere. Boundary layer outflow from North America is not enhanced in ozone in September because of the relatively weak photochemical production and the competing effect of boundary layer sinks from chemistry and deposition [*Parrish et al.*, 1998]. A comparison of simulated and observed ozonesonde vertical profiles at Sable Island during the mission (Figure 3) shows that simulated ozone concentrations agree with observed values to within 5 ppbv through much of the troposphere.

[20] There is no bias in simulated NO concentrations over the range of measurement altitudes, but NO$_y$ and PAN concentrations are overestimated on average by 35% and 50% in the free troposphere, respectively. A scatterplot of simulated versus observed NO$_y$ concentrations in the free troposphere above 2 km (Figure 4) shows that the bias is mainly at low concentrations (background); there appears to be little bias in the simulation of high concentrations (North American outflow). Comparison of model results with observed vertical profiles of PAN and HNO$_3$ from a number of other aircraft missions at northern midlatitudes [*Bey et al.*, 2001a] confirms that the problem is one of background. We find in the model that only 39% of total NO$_y$ in the free troposphere along the NARE'97 flight tracks is of North American anthropogenic origin, consistent with the previous estimated of *Stohl et al.* [2002] and further supporting the view that the model overestimate of NO$_y$ must reflect a background problem. More recent GEOS-CHEM simula-
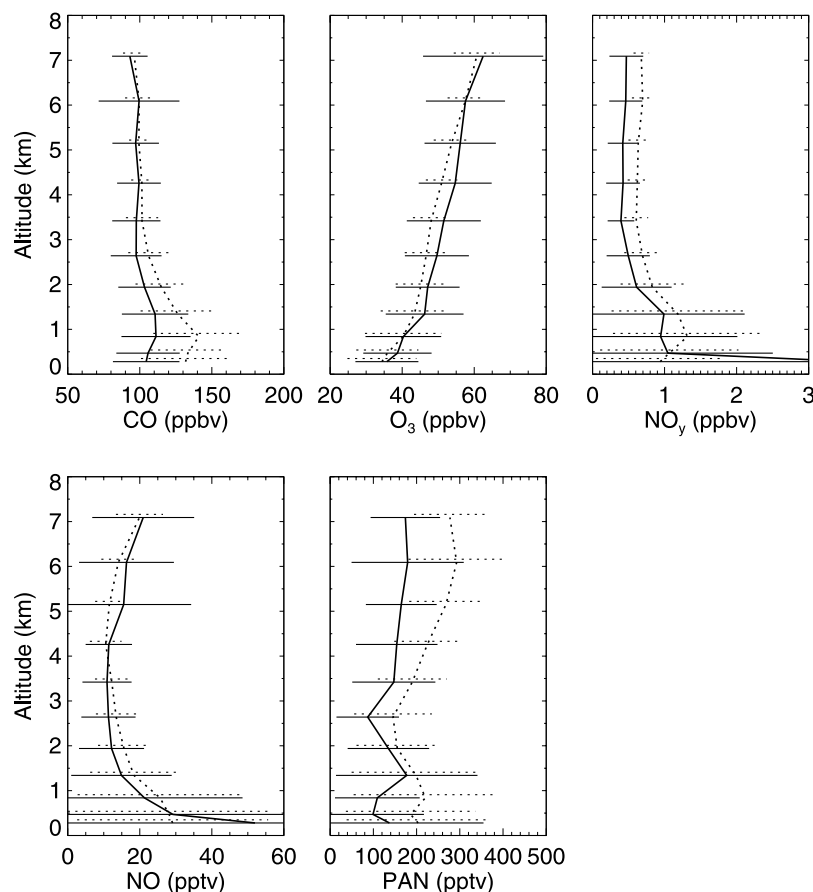
Figure 2. Simulated (dotted line) and observed (solid line) mean vertical profiles of CO, ozone, NO$_y$, NO, and PAN concentrations during NARE'97 (6–29 September 1997). Horizontal bars represent standard deviations. Model results are sampled along the flight tracks at the time of the flights.

tions using GEOS-3 meteorology (available from 1998 on) indicated a much improved simulation of NO$_y$ at northern midlatitude (M. Evans et al., manuscript in preparation, 2003).

5. Export of NO$_y$ From the North American Boundary Layer

5.1. Lagrangian Approach: Mixing Model of Parrish et al. (Submitted Manuscript, 2003)

[21] In the "mixing" model of Parrish et al. (submitted manuscript, 2003), the export efficiency f of NO$_y$ from the North American boundary layer is derived from observations in the North American outflow of the enhancements of CO (ΔCO) and NO$_y$ (ΔNO$_y$) above background:

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

Here R is the anthropogenic emission ratio of NO$_x$ to CO for North America, and α is a scaling coefficient to account for biogenic continental sources of CO, particularly the oxidation of isoprene. Free tropospheric sources of NO$_x$ from lightning and aircraft are mainly in the upper troposphere and would have little impact on the application of equation (1) to the NARE'97 data, which were mainly below 7 km altitude.

[22] Derivation of the export efficiency f from the NARE'97 observations of NO$_y$ and CO concentrations requires assumptions of the background concentrations of NO$_y$ and CO, and of the values of R and α. Table 1 gives the mixing model parameters used by Parrish et al. (submitted manuscript, 2003): 0.1 ppbv for background NO$_y$, 75 ppbv for background CO, $R = 0.176$ mol mol^{-1}, and $\alpha = 1.18$ (the latter from *Chin et al.* [1994]). Figure 5 shows the observed and simulated NO$_y$-CO correlations along the NARE'97 flight tracks. The curves in Figure 5 show relationships corresponding to NO$_y$ export efficiencies of 2%, 5%, 10%, 20%, 50%, and 100% using the Parrish et al. (submitted manuscript, 2003) parameters. Parrish et al. (submitted manuscript, 2003) applied equation (1) to every pair of NO$_y$ and CO concentrations observed in anthropogenic plumes in the free troposphere above 2 km (the top of the boundary layer) during NARE'97. The anthropogenic plumes were defined by ΔCO >30 ppbv. They thus estimated that on average 9 ± 5% of North American anthropogenic NO$_x$ was exported to the free troposphere above 2 km as some form of NO$_y$ (Table 1).

[23] We can estimate similarly the export efficiency of North American anthropogenic NO$_y$ in our model by applying equation (1) to the simulated NO$_y$ and CO concentrations sampled along the NARE'97 flight tracks above 2 km (the top of the boundary layer), with the same values of mixing model parameters (background concentrations of
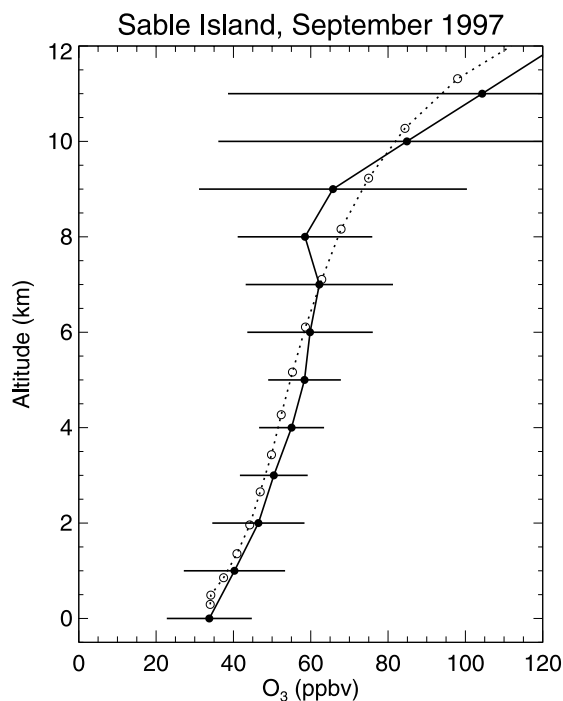
Sable Island, September 1997

Figure 3. Simulated (dashed line) and observed (solid line) mean vertical profile of ozone at Sable Island in September 1997. Horizontal bars represent standard deviations of the observation. A total of 30 ozonesondes were launched during 5 September to 5 October 1997.

NO$_y$ and CO, R, α) as used by Parrish et al. (submitted manuscript, 2003), and the same criteria (ΔCO >30 ppbv) for selection of anthropogenic plumes (26% of the model data). We obtain an average export efficiency of 11.5 ± 3% (Table 1), similar to the Parrish et al. (submitted manuscript, 2003) value.

[24] The above comparison of simulated and observed values of f, using the same values of mixing model parameters for equation (1), tests the similarity in the NO$_y$-CO relationships between model and observations (Figure 5). However, we find that the mixing model parameter values of Parrish et al. (submitted manuscript, 2003) are inconsistent with the model environment, so that the above value of f (at least in the model) should not be viewed as an export efficiency. We obtain the background concentrations of NO$_y$ and CO in the model that are appropriate for application of equation (1) from our sensitivity simulation with no North American anthropogenic emissions. Figure 6 shows correlations along the NARE'97 flight tracks between background concentrations of CO and NO$_y$ from the sensitivity simulation and CO concentrations from the standard simulation, the latter being used as an indicator of North American outflow. We find that the background CO concentration increases in the outflow, reflecting biogenic continental sources of CO in the North American boundary layer in particular from oxidation of isoprene. The background NO$_y$ concentration is lower in the outflow than in free tropospheric air, reflecting the loss of NO$_y$ in the boundary layer by deposition. If we define North American outflow following Parrish et al. (submitted manuscript, 2003) by ΔCO = 30 ppbv above background, then

we find from Figure 6 that appropriate CO and NO$_y$ background concentrations in the model environment for application of equation (1) are 95 ppbv for CO and 0.3 ppbv for NO$_y$. We then also need to use $\alpha = 1$ since the model CO background accounts for biogenic source enhancements in the boundary layer. This biogenic enhancement is about 10 ppbv.

[25] As seen in Figure 6, background CO in the model never drops below 80 ppbv. There is independent evidence that the 75 ppbv value used by Parrish et al. (submitted manuscript, 2003) may be too low, which would cause an underestimate of the NO$_y$ export efficiency. Table 2 shows monthly mean concentrations of CO observed at several northern midlatitude NOAA CMDL sites both upwind and downwind of North American September 1997. These concentrations are filtered on the basis of wind direction such that they represent background conditions [*Novelli et al.*, 2003]. The CO range is 83–96 ppbv. Previous estimates of the background CO concentration at Sable Island (just upstream of the NARE'97 region), taken as the 17th percentile of observed CO concentrations, are 90 ppbv on average for September 1991–1994 [*Parrish et al.*, 1998] and 84 ppbv for September 1997 [*Li et al.*, 2002a].

[26] Observations of the NO$_y$-CO correlation at Harvard Forest (42.5°N, 72.2°W, 340 m altitude), a rural site in central Massachusetts, offer a measure of the CO background typical of the northeastern United States. The features of the Harvard Forest NO$_y$ are discussed by *Munger et al.* [1996]. Figure 7 shows a comparison of simulated (1997) and observed (1994–1996, 2001) daytime (10–16 local time) NO$_y$-CO correlations for September at Harvard Forest. No observations are available for September 1997. NO$_y$ and CO concentrations are strongly correlated, both in the observations and in the model. The observed CO/NO$_y$ slopes are 15–16 mol mol^{-1}, except for 1995, which shows a slope of 11 mol mol^{-1}. The model slope is 16 mol mol^{-1}, consistent with observations. The intercepts of the regres-
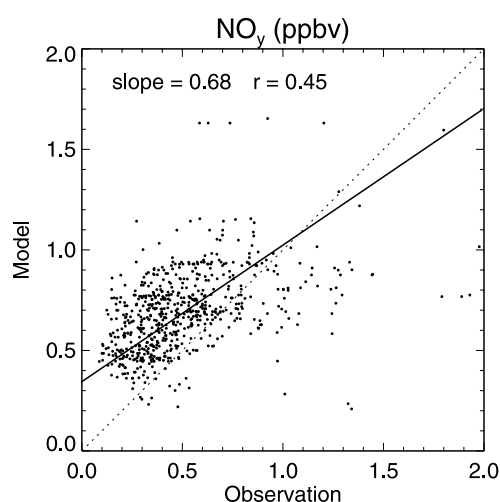
NO$_y$ (ppbv)

Figure 4. Scatterplot of simulated versus observed NO$_y$ concentrations during NARE'97 (6–29 September 1997). Model results are sampled along the flight tracks at the time of the flights, and observations are averaged over the model grid box. The 1:1 and regression lines (reduced major axis method) are also shown.
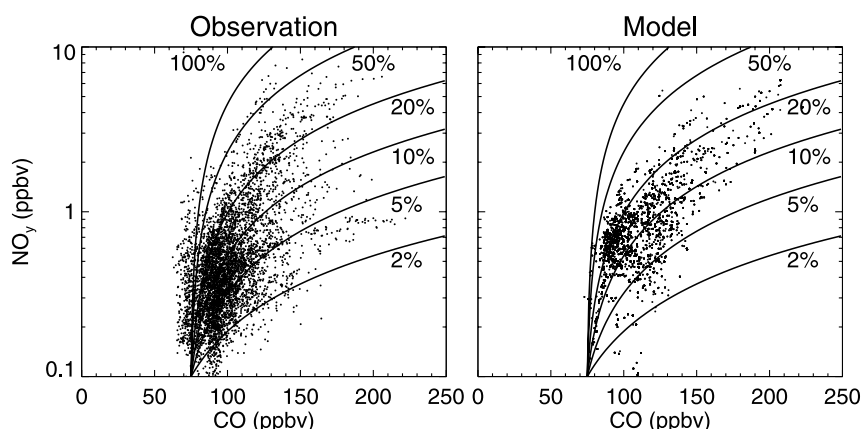
Figure 5. (left) Observed and (right) simulated NO$_y$-CO correlations during NARE'97 (6–29 September 1997). Observations are 1-min averages and include all altitudes. Model results are sampled along the flight tracks at the time of the flights. The curves give the relationships expected from equation (1) for different values of the NO$_y$ export efficiency f (indicated on the plots as percentages) and with values of background CO (75 ppbv), background NO$_y$ (0.1 ppbv), NO$_y$/CO emission ratio (0.176), and α (1) taken from Parrish et al. (submitted manuscript, 2003). See text for details.

sion lines can be taken as representing the background concentrations of CO at that site [*Parrish et al.*, 1991]. The observations thus indicate a CO background of 96–112 ppbv for September 1994–1996 and 76 ppbv for September 2001. Model results indicate a CO background of 105 ppbv for September 1997, comparable to the 1994–1996 values though much higher than the 2001 value.

[27] The anthropogenic emission ratios of NO$_x$/CO in the model are respectively 0.139 and 0.154 mol mol^{-1} for eastern North America (east of 95°W) and all of North America (Figure 1) for September 1997. These values are lower than the 0.176 mol mol^{-1} value used by Parrish et al. (submitted manuscript, 2003) but higher than the 1997 value of 0.128 mol mol^{-1} for the United States estimated by EPA (see section 3). *Stohl et al.* [2002] used $R = 0.16$ mol mol^{-1} in their analysis of the NARE'97 data. We use $R = 0.154$ mol mol^{-1} (taken as the NO$_x$/CO source ratio for North America) in our calculations hereafter. As discussed above, the

the CO background of 95 ppbv determined from our sensitivity simulation includes natural sources of CO, so it is appropriate for us to use $\alpha = 1$ in our application of equation (1). Parrish et al. (submitted manuscript, 2003) used $\alpha = 1.18$ in their analysis. Their value of R (0.176 mol mol^{-1}) divided by $\alpha = 1.18$ gives 0.149 mol mol^{-1}, comparable to the value used here. *Stohl et al.* [2002] used $\alpha = 1$ in their analysis.

[28] With the model results for background concentrations of CO (95 ppbv) and NO$_y$ (0.3 ppbv), together with $R = 0.154$ mol mol^{-1} and $\alpha = 1$, we calculate in the model an average NO$_y$ export efficiency of $f = 17 \pm 7\%$ for North American anthropogenic NO$_y$ during NARE'97 (Table 1). As discussed above, it appears at least that the background CO concentration of 75 ppbv used in the analysis of Parrish et al. (submitted manuscript, 2003) is too low. With a CO background of 95 ppbv that includes the natural boundary layer enhancement, a NO$_y$ background of 0.1 ppbv, $R =$

Table 1. Export Efficiency of NO$_y$ From the North American Boundary Layer (NARE'97 Data)

	Stohl et al. [2002]	Parrish et al. (Submitted Manuscript, 2003)	This Work[a]
Export efficiency[b]	3%	9 ± 5%	11.5 ± 3%[c]
			17 ± 7%[d]
Speciation of exported NO$_y$			
NO$_x$	...	8%	6 ± 4%
PAN	...	34%	36 ± 13%
HNO$_3$	...	57%	52 ± 14%
Mixing model parameters			
Background NO$_y$, ppbv	0.1	0.1	0.3
Background CO, ppbv	70	75	95
R, mol mol^{-1}	0.16	0.176	0.154
α	1	1.18	1

[a]Calculations based on GEOS-CHEM global 3-D model results sampled along the NARE'97 (6–29 September 1997) flight tracks.

[b]Derived from the relationship of NO$_y$ with CO along the NARE'97 aircraft flight tracks, as described in the text. Export efficiencies given by Parrish et al. (submitted manuscript, 2003) and in this work are calculated from equation (1).

[c]Calculated using Parrish et al. (submitted manuscript, 2003) values for the mixing model parameters in equation (1) including background concentrations of CO and NO$_y$ of 75 ppbv and 0.1 ppbv, respectively, $R = 0.176$ mol mol^{-1}, and $\alpha = 1.18$.

[d]Calculated using mixing model parameters for equation (1) consistent with the GEOS-CHEM model environment including background concentrations of CO and NO$_y$ of 95 ppbv and 0.3 ppbv, respectively, $R = 0.154$ mol mol^{-1}, and $\alpha = 1$.
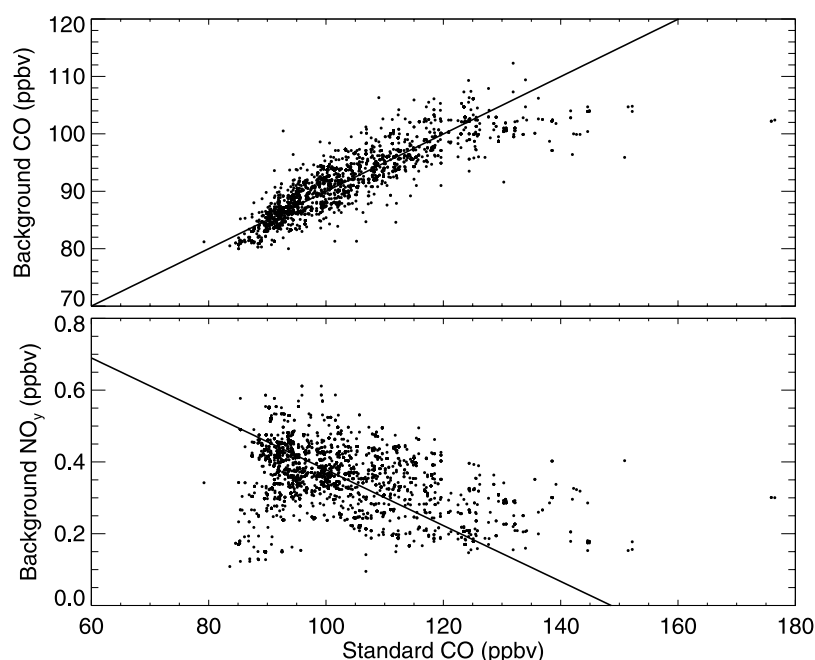
Figure 6. Correlation of background CO and NO$_y$ concentrations with North American outflow in the model sampled along the NARE'97 (6–29 September 1997) flight tracks above 2 km altitude at the time of the flights. The plots show background CO and NO$_y$, as determined from a sensitivity simulation with North American anthropogenic emissions shut off, versus CO in the standard simulation. The regression lines (reduced major axis method) are also shown.

0.154 (our model value), and $\alpha = 1$, they would have obtained $f = 17 \pm 13\%$, same as the model.

[29] The assumption of uniform background concentrations of CO and NO$_y$, in the observations or in the model, is still fairly arbitrary. A different approach for deriving ΔNO$_y$ and ΔCO in the model for application of equation (1) is by sampling along the flight tracks the local difference between the standard simulation and the sensitivity simulation with no anthropogenic North American emissions. Any assumption of a uniform background is then avoided, and ΔNO$_y$ and ΔCO are the true enhancements due to North American anthropogenic emissions in the model environment. In this application, we again set $\alpha = 1$ since the contribution to CO from biogenic emissions is included in the background. We obtain in this manner an average NO$_y$ export efficiency of $f = 17 \pm 6\%$, consistent with the value of $17 \pm 7\%$ obtained

in the above model analysis. Further examination of model results along the NARE'97 flight tracks indicates that NO$_y$ exported from the North American boundary layer is mostly HNO$_3$ (52%), with 36% as PANs and only 6% as NO$_x$, in agreement with the Parrish et al. (submitted manuscript, 2003) observations (Table 1).

5.2. Eulerian Approach: Boundary Layer Budget

[30] Our next step is to compare the NO$_y$ export efficiencies derived in the model from the above Lagrangian perspective along the NARE'97 flight tracks to those

Table 2. Monthly Mean CO Concentrations at Northern Mid-latitude Sites for September 1997[a]

Site Code	Location	Latitude	Longitude	Elevation, m	CO, ppbv
MID	Sand Island, Midway	28.2°N	177.4°W	4	94
SHM	Shemya Island, Alaska	52.7°N	174.1°W	40	94
CBA	Cold Bay, Alaska	55.2°N	162.7°W	25	87
MLO	Mauna Loa, Hawaii	19.5°N	155.6°W	3397	86
CMO	Cape Meares, Oregon	45.5°N	124.0°W	30	96
NWR	Niwot Ridge, Colorado	40.1°N	105.6°W	3475	94
BMW	Tudor Hill, Bermuda	32.3°N	64.9°W	30	85
AZR	Azores, Portugal	38.8°N	27.4°W	40	83
MHD	Mace Head, Ireland	53.3°N	9.9°W	25	87

[a]Data are from the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) network (http://www.cmdl.noaa.gov/info/ftpdata. html). Observations are filtered on the basis of wind direction such that the concentrations represent background conditions [*Novelli et al.*, 2003].
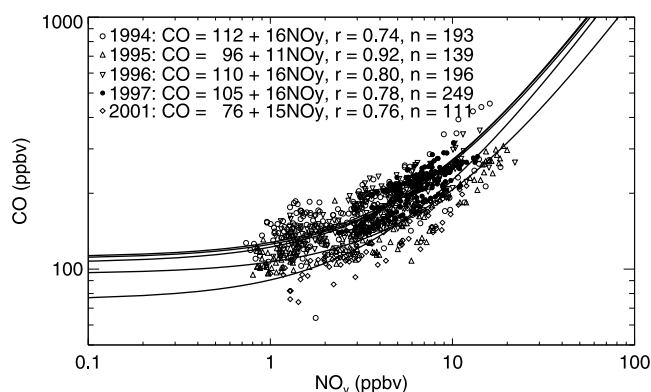

Figure 7. Simulated (1997) and observed (1994–1996, 2001) NO$_y$-CO correlations at Harvard Forest (42.5°N, 72.2°W, 340 m altitude) for September, plotted on a logarithm scale. Data used are daytime only (1000–1600 local time). The regression lines (reduced major axis method) are also shown.

derived from a more standard Eulerian budget calculation for the North American boundary layer, following the approach of *Liang et al.* [1998]. A model budget for anthropogenic NO$_y$ in the North American boundary layer in September 1997 is shown in Table 3. The North American boundary layer is defined as the domain extending horizontally over the domain of Figure 1 and vertically up to 730 hPa (2.6 km). The budget for anthropogenic NO$_y$ is determined by difference between the standard simulation and the sensitivity simulation in which North American anthropogenic emissions are shut off.

[31] We find that the exported anthropogenic NO$_y$ (0.27 Gmol d^{-1}) amounts to 20% of emissions (1.32 Gmol d^{-1}), consistent with the values derived from the Lagrangian model of equation (1) by sampling the model results along the flight tracks. This export efficiency of 20% includes 14% ventilated through the top of the boundary layer (convection, WCBs) and 6% advected through the sides. Previous 3-D model budget analyses for a similar North American domain indicated NO$_y$ export efficiencies of 25–30% (annual) [*Kasibhatla et al.*, 1993], and seasonal values of 25% in summer and 30% in fall [*Liang et al.*, 1998]. Our model values are significantly lower. Concentrations and lifetimes of NO$_y$ species in the North American boundary layer in our model are similar to those of *Liang et al.* [1998] (compare our Table 3 to their Table 3). We attribute their higher NO$_y$ export efficiency to insufficient scavenging of NO$_y$ during export out of the boundary layer. They did not have observations in North American outflow to evaluate that component of their model.

[32] The composition of the exported NO$_y$ in our simulation (40% NO$_x$, 19% PANs, and 37% HNO$_3$) is similar to that of *Liang et al.* [1998] (34% NO$_x$, 26% PANs, and 35% HNO$_3$). The NO$_x$ fraction of the exported NO$_y$ is considerably higher than that along the NARE'97 flight tracks, either in our model or in the observations (Table 1). This reflects in the model the rapid oxidation of NO$_x$ during transport from the point of exit out of the CBL to the point of sampling by the NARE'97 aircraft. Such rapid oxidation of NO$_x$ during transport was also inferred from the TRACE-P observations of the export of NO$_y$ from east Asia in spring [*Miyazaki et al.*, 2003].

5.3. Implications for Ozone

[33] The global enhancement of tropospheric ozone due to North American anthropogenic emissions can be viewed as the sum of three terms: (1) production of ozone in the CBL, (2) near-field production of ozone in the free troposphere from the exported NO$_x$, (3) dispersed production in the global troposphere driven by decomposition of the exported PAN (and to a lesser extent HNO$_3$).

[34] We examine in this section the magnitude of these three terms by difference between our standard simulation and the sensitivity simulation with North American anthropogenic sources shut off. Comparison of the gross ozone (odd oxygen) production rates in the two simulations gives the enhancements in ozone production in the North American boundary layer and in the free troposphere due to North American anthropogenic emissions. We thus find that the ozone production enhancement from North American anthropogenic emissions is 13 Gmol d^{-1} in the North American boundary layer, of which 40% (5 Gmol d^{-1}) is

Table 3. Model Budget of Anthropogenic NO$_y$ in the North American Boundary Layer for September 1997[a]

	NO$_x$	PANs	HNO$_3$	Alkyl Nitrates	Total
Concentration, ppbv	0.27	0.16	0.69	0.03	1.15
Lifetime, days	0.50	0.31	2.0	⋯	⋯
Emission, Gmol d^{-1}	1.32	⋯	⋯	⋯	1.32
Net production, Gmol d^{-1}	−1.11	0.09	1.00	0.02	<0.01
Wet deposition, Gmol d^{-1}	⋯	⋯	0.42	⋯	0.42
Dry deposition, Gmol d^{-1}	0.08	0.04	0.49	<0.01	0.62
Export, Gmol d^{-1}	0.11	0.05	0.10	0.01	0.27
Composition of exported NO$_y$	40%	19%	37%	4%	⋯

[a]The North American boundary layer is defined as the domain extending horizontally over the domain (130°–65°W, 25–55°N) in Figure 1 and vertically up to 730 hPa (about 3 km). The budgets are for NO$_y$ of North American anthropogenic origin, as determined by the difference between the standard simulation and a sensitivity simulation with North American fossil fuel emissions shut off. PANs includes PAN, MPAN (produced by isoprene oxidation), and other peroxyacylnitrates; PAN is by far the most important. Lifetimes are calculated with respect to the sinks from chemical loss and deposition.

exported out of the CBL. This export of pollution ozone is similar to the model estimate of *Liang et al.* [1998] for fall (4 Gmol d^{-1}). The ozone production enhancement outside the North American boundary layer due to North American anthropogenic emissions (i.e., due to exported NO$_y$) is 5.8 Gmol d^{-1}, of which 2.8, 1.3, and 1.7 Gmol d^{-1} are in the free troposphere over North America, in the rest of the global free troposphere, and in the global boundary layer outside North America. In the free troposphere, 70% of the eventual ozone production enhancement takes place in the near-field (i.e., over North America) because of exported NO$_x$. This is illustrated in Figure 8, which shows the ozone production enhancement integrated over the free tropospheric column. We see that the near-field ozone production enhancement has largely been realized by the time that the North American outflow is transported over the NARE'97 domain, consistent with the fast oxidation of NO$_x$ during transport and the low NO$_x$/NO$_y$ ratios observed in NARE'97. Globally, the ozone production enhancement due to exported NO$_x$ (near-field) and to exported PANs (dispersed) in the model are about equal. The eventual ozone production from the exported NO$_y$ is similar to the model estimate of *Liang et al.* [1998] for fall (6 Gmol d^{-1}) and is comparable to the direct export of pollution ozone out of the North American boundary layer.

6. Summary and Conclusions

[35] Recent analyses of the NO$_y$-CO correlation observed during the NARE'97 aircraft campaign downwind of eastern North America in September 1997 have suggested that less than 10% of the NO$_x$ emitted in the North American continental boundary layer (CBL) is exported as NO$_y$ to the free troposphere above 2 km, and that HNO$_3$ is the dominant form of exported NO$_y$ while less than 10% remains as NO$_x$ [*Stohl et al.*, 2002; Parrish et al., submitted manuscript, 2003]. These results apparently contradict previous 3-D model budget analyses that indicate much higher export efficiencies of anthropogenic NO$_y$ from North America (25–30%) [*Kasibhatla et al.*, 1993; *Liang et al.*, 1998] and a much higher fraction of NO$_x$ in the exported NO$_y$ (>30%) [*Liang et al.*, 1998]. Such large differences
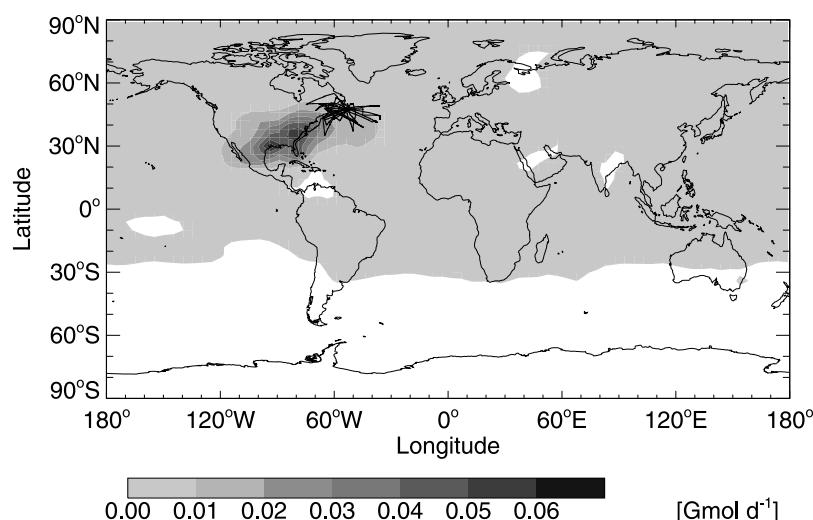
Figure 8. Simulated monthly mean (September 1997) ozone production enhancements due to exported NO$_y$ from the North American boundary layer, integrated over the free tropospheric column. Also shown are the NARE'97 (6–29 September 1997) aircraft flight tracks. See color version of this figure at back of this issue.

need to be understood because of their implications for the ability of models to simulate properly global anthropogenic influences on tropospheric ozone.

[36] We investigated this problem by using the GEOS-CHEM global 3-D model of tropospheric chemistry to simulate the NARE'97 aircraft observations. We diagnosed the export of anthropogenic NO$_y$ species from North America in the model through a Lagrangian analysis of the NO$_y$-CO correlation along the flight tracks (following the previous observation-based analyses) and an Eulerian NO$_y$ budget analysis of the North American boundary layer (following the previous 3-D model analyses).

[37] As a first step in the analysis, we replicated in the model the estimate of the export efficiency of North American anthropogenic NO$_y$ from the NARE'97 data by using the NO$_y$-CO correlations along the NARE'97 flight tracks and applying the mixing model analysis of Parrish et al. (submitted manuscript, 2003) to our model fields. Critical parameters in this mixing model analysis are the CO background, the NO$_y$ background, and the NO$_y$/CO source ratio for North America. Parrish et al. (submitted manuscript, 2003) used background concentrations of 75 ppbv for CO and 0.1 ppbv for NO$_y$, and a NO$_x$/CO molar source ratio $R = 0.176$ mol mol^{-1} corrected by a factor $\alpha = 1.18$ to account for natural CO sources (i.e., an equivalent NO$_x$/CO source ratio of 0.149 mol mol^{-1}). They derived in this manner a NO$_y$ export efficiency of 9 ± 5%. By applying the same values of the mixing model parameters to our simulated NO$_y$-CO correlations along the NARE'97 flight tracks, we obtain an average export efficiency of 11.5 ± 3%, similar to the Parrish et al. (submitted manuscript, 2003) value.

[38] The above result is important as a comparative test of the NO$_y$-CO correlation in the model versus the observations. However, we find that the values of the mixing model parameters assumed by Parrish et al. (submitted manuscript, 2003) are not consistent with our model environment. The actual background concentration of CO in the model is

95 ppbv, as obtained from a sensitivity simulation in which North American anthropogenic emissions are shut off. This background includes a 10 ppbv CO enhancement from North American natural hydrocarbon emissions, principally isoprene. It is consistent with NOAA CMDL observations at northern midlatitude stations in 1997 and with observations at the Harvard Forest Environmental Measurement Site over the past decade. A low bias in the 75 ppbv CO background assumed by Parrish et al. (submitted manuscript, 2003) would result in an underestimate of the NO$_y$ export efficiency in their analysis. At a CO background of 95 ppbv, their observation-derived NO$_y$ export efficiency would be 14.5 ± 11%. The average anthropogenic NO$_x$/CO emission ratio in North America in our model is $R = 0.154$. With this value of R and with background concentrations of 95 ppbv for CO and 0.3 ppbv for NO$_y$, and $\alpha = 1$ (since the CO background includes the contribution from biogenic emissions), we calculate in the model an average NO$_y$ export efficiency of 17 ± 7%. The assumption of a fixed background for CO and NO$_y$ is clearly an over-simplification, and an alternate approach in the model is to define North American anthropogenic NO$_x$ and CO as the local difference between the standard and sensitivity simulation along the NARE'97 flight tracks. We estimate in this manner a NO$_y$ export efficiency of 17 ± 6%, consistent with the above analysis.

[39] North American anthropogenic NO$_y$ along the NARE'97 flight tracks in the model is mostly present as HNO$_3$ (52% on average), with 36% as PAN and only 6% as NO$_x$. This is in agreement with the observations (57% HNO$_3$, 34% PAN, 8% NO$_x$ on average). We find in the model that 39% of the total NO$_y$ in the free troposphere above 3 km along the NARE'97 flight tracks is from North American anthropogenic sources, consistent with the Stohl et al. [2002] estimate of 35%.

[40] Our next step was to conduct an Eulerian budget analysis for anthropogenic NO$_y$ in the North American boundary layer in the model, replicating previous 3-D

model analyses. We obtain in this manner a NO$_y$ export efficiency of 20%, in agreement with the Lagrangian analysis of the model fields along the NARE'97 flight tracks. This value is lower than the 30% value in the previous 3-D model simulation of *Liang et al.* [1998], and we believe that this reflects an underestimate of HNO$_3$ scavenging during export out of the CBL in that simulation. Our Eulerian budget analysis indicates a large contribution of NO$_x$ (40%) to the exported NO$_y$, consistent with *Liang et al.* [1998]. The apparent discrepancy between the high NO$_x$/NO$_y$ ratio in the exported NO$_y$ versus the low NO$_x$/NO$_y$ ratio along the NARE'97 flight tracks can be explained simply by fast oxidation of free tropospheric NO$_x$ between the point of ventilation out of the CBL and the point of sampling by the NARE'97 aircraft.

[41] The contribution of continental NO$_x$ emissions to global production of tropospheric ozone can be viewed as the sum of three processes: (1) production within the CBL followed by export, (2) near-field production in the free troposphere following export of NO$_x$ from the CBL, (3) dispersed production throughout the northern hemisphere following export of NO$_x$ reservoirs, in particular PAN. We estimated and compared the magnitude of these three terms for North American anthropogenic emissions by difference between the standard simulation and the sensitivity simulation with North American anthropogenic emissions shut off. We find that the ozone production enhancement due to North American anthropogenic emissions is 13 Gmol d^{-1} in the CBL, of which 40% (5 Gmol d^{-1}) is exported out of the CBL. The near-field production enhancement of ozone in the free troposphere from the exported NO$_x$ is about 2.8 Gmol d^{-1}, although this value would depend on the definition of the CBL domain. The dispersed ozone production enhancement from exported NO$_x$ reservoirs is about 3.0 Gmol d^{-1}. Production of ozone in the global troposphere from exported NO$_y$ is thus comparable in magnitude to the direct export of pollution ozone out of the North American boundary layer.

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D. J. Jacob, Q. Li, J. W. Munger, and R. M. Yantosca, Department of Earth and Planetary Sciences, Harvard University, 29 Oxford Street, 110G Pierce Hall, Cambridge, MA 02138, USA. (djj@io.harvard.edu; qli@io.harvard.edu; jwm@io.harvard.edu; bmy@io.harvard.edu)

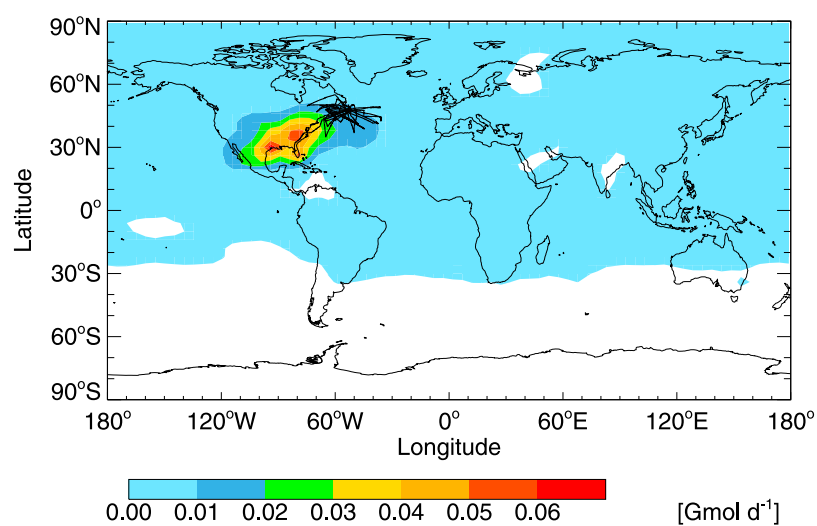D. D. Parrish, NOAA Aeronomy Laboratory, R/E/AL7, 325 Broadway, Boulder, CO 80303, USA. (parrish@al.noaa.gov)

Figure 8. Simulated monthly mean (September 1997) ozone production enhancements due to exported NO$_y$ from the North American boundary layer, integrated over the free tropospheric column. Also shown are the NARE'97 (6–29 September 1997) aircraft flight tracks.