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Export of NO_y from the North American boundary layer: Reconciling aircraft observations and global model budgets

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Abstract.

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 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 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 due to underestimate 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 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.

1. Introduction

Production of ozone in the troposphere is limited primarily by the availability of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) [Chameides *et al.*, 1992]. More than half of the global emission of NO_x is from fossil fuel combustion [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 peroxyacetyl nitrate (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, 1993] and for intercontinental transport of ozone pollution [Jacob, 1999; Li *et al.*, 2002a].

Simulations with 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.

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 Parrish *et al.* [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.* [2003] further indi-

cates 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].

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.

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 $\text{NO}_x + \text{PAN}$ is twice as large as the direct export of ozone pollution from the U.S. boundary layer. In contrast, Parrish *et al.* [2003] argued that anthropogenic production of ozone in the free troposphere must be of little importance due to the small fraction of NO_y exported to the free troposphere as NO_x .

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.* [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

The NARE'97 aircraft mission was conducted from September 6 to October 2, 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 September 5 to October 5.

Ozone was measured aboard the aircraft by a fast-response NO-ozone chemiluminescence instrument [Ryerson *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-NO₂-O₃ photostationary steady state using radiometer data for the NO₂ 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 minute 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-second averages; we use here 1-minute averages.

Cooper *et al.* [2001, 2002a, b] 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.* [2003].

3. Model Description

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.

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-HNO₃ cycling are from Brown *et al.* [1999a, b]. Hydroxy organic nitrates produced by isoprene oxidation appear to decompose quickly to HNO₃ on surfaces [Chen *et al.*, 1998], and we assume here that this decomposition is instantaneous. No consideration of phase partitioning between gas-phase HNO₃ and aerosol nitrate is included in the model. Reactions of N₂O₅, NO₃, and NO₂ 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].

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 HNO₃ and H₂O₂ only) includes scavenging by convective updrafts, anvils, and large-scale precipitation as described by Liu *et al.* [2001].

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 TgCOyr⁻¹ and 6.7 TgNyr⁻¹, respectively. For comparison, the corresponding values for 1997 are 107 TgCOyr⁻¹ and 6.8 TgNyr⁻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 O₃ yr⁻¹, which provides for a satisfactory simulation of vertical ozone profiles at northern middle and high latitudes [*Bey et al.*, 2001a, b; *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 HNO₃.

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. HNO₃ was generally overestimated by a factor of 2-3, possibly due to a combination of insufficient scavenging in the free troposphere and the absence of gas-aerosol partitioning of HNO₃ in the model. Overestimate of HNO₃ is a frequent problem in global models [*Wang et al.*, 1998b; *Lawrence et al.*, 1999; *Tie et al.*, 2003].

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 NO₂ 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, b] 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.

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 simu-

lation as described above to those from a sensitivity simulation with no anthropogenic NO_x, CO, or NMHC emissions from North America, and diagnose anthropogenic 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

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.

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.

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 scatter plot of simu-

lated 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 HNO₃ 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 simulations using GEOS-3 meteorology (available from 1998 on) indicated a much improved simulation of NO_y at northern midlatitude [Evans *et al.*, 2003].

5. Export of NO_y from the North American Boundary Layer

5.1. Lagrangian approach: mixing model of Parrish *et al.* [2003]

In the “mixing” model of Parrish *et al.* [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:

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

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.

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.* [2003]: 0.1 ppbv for background NO_y, 75 ppbv for background CO, $R = 0.176 \text{ mol mol}^{-1}$, 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.* [2003] parameters. Parrish *et al.* [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 $\Delta\text{CO} > 30 \text{ ppbv}$. They thus estimated that on average $9 \pm 5\%$ of North American anthropogenic NO_x was exported to the free troposphere above 2 km as some form of NO_y (Table 1).

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 NO_y and CO, R , α) as used by Parrish *et al.* [2003], and the same criteria ($\Delta\text{CO} > 30 \text{ ppbv}$) for selection of anthropogenic plumes (26% of the model data). We obtain an average export efficiency of $11.5 \pm 3\%$ (Table 1), similar to the Parrish *et al.* [2003] value.

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.* [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.* [2003] by $\Delta\text{CO} = 30 \text{ ppbv}$ 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.

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.* [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 America in September 1997. These concentrations are filtered based on 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].

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 in 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 regression 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.

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.* [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 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.* [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.

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

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 Δ NO_y and Δ CO 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 Δ NO_y and Δ CO 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 HNO₃ (52%), with 36% as PANs and only 6% as NO_x, in agreement with the Parrish *et al.* [2003] observations (Table 1).

5.2. Eulerian approach: Boundary layer budget

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 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.

We find that the exported anthropogenic NO_y (0.27 G mol d⁻¹) amounts to 20% of emissions (1.32 G mol 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% ven-

tilated 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.

The composition of the exported NO_y in our simulation (40% NO_x, 19% PANs, and 37% HNO₃) is similar to that of Liang *et al.* [1998] (34% NO_x, 26% PANs, and 35% HNO₃). 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

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 HNO₃).

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 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) due to 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

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 HNO₃ is the dominant form of exported NO_y, while less than 10% remains as NO_x [Stohl *et al.*, 2002; Parrish *et al.*, 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 need to be understood because of their implications for the ability of models to simulate properly global anthropogenic influences on tropospheric ozone.

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).

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.* [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.* [2003] used background concentrations of 75 ppbv for CO and 0.1 ppbv for NO_y, and a NO_x/CO molar source ratio $R = 0.176 \text{ mol mol}^{-1}$ corrected by a factor $\alpha = 1.18$ to account for natural CO sources (i.e., an equivalent NO_x/CO source ratio of $0.149 \text{ mol mol}^{-1}$). They derived in this manner a NO_y export efficiency of $9 \pm 5\%$. 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 $11.5 \pm 3\%$, similar to the Parrish *et al.* [2003] value.

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.* [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.* [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 $14.5 \pm 11\%$. 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 $17 \pm 7\%$. 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 $17 \pm 6\%$, consistent with the above analysis.

North American anthropogenic NO_y along the NARE'97 flight tracks in the model is mostly present as HNO₃ (52% on average), with 36% as PAN and only 6% as NO_x. This is in agreement with the observations (57% HNO₃, 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%.

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 HNO₃ 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.

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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References

- Bey, I., D. J. Jacob, R. M. Yantosca, J. A. Logan, B. D. Field, A. M. Fiore, Q. Li, H. Liu, L. J. Mickley, and M. G. Schultz, Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.*, **106**, 23,073-23,095, 2001a.
- Bey, I., D. J. Jacob, J. A. Logan, and R. M. Yantosca, Asian chemical outflow to the Pacific: Origins, pathways and budgets, *J. Geophys. Res.*, **106**, 23,097-23,113, 2001b.
- Brown, S. S., R. K. Talukdar, and A. R. Ravishankara, Rate constant for the reaction $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ under atmospheric conditions, *Chem. Phys. Lett.*, **299**, 277-284, 1999a.
- Brown, S. S., R. K. Talukdar, and A. R. Ravishankara, Reconsideration of the rate constants for the reaction of hydroxyl radicals with nitric acid vapor, *J. Phys. Chem.*, **103**, 3031-3037, 1999b.
- Chameides, W. L., F. C. Fehsenfeld, M. O. Rodgers, C. Cardelino, J. Martinez, D. D. Parrish, W. Lonneman, D. R. Lawson, R. A. Rasmussen, P. Zimmerman, G. J. Greenberg, P. Middleton, and T. Wang, Ozone precursor relationships in the ambient atmosphere, *J. Geophys. Res.*, **97**, 6037-6055, 1992.
- Chen, X. H., D. Hulbert, and P. B. Shepson, Measurements of the organic nitrate yield from OH reaction with isoprene, *J. Geophys. Res.*, **103**, 25,563-25,568, 1998.
- Chin, M., D. J. Jacob, J. W. Munger, D. D. Parrish, and B. G. Doddridge, Relationship of ozone and carbon monoxide over North America, *J. Geophys. Res.*, **99**, 14,565-14,573, 1994.
- Chin, M., D. J. Jacob, G. M. Gardner, M. S. Foreman-Fowler, P. A. Spiro, and D. L. Savoie, A global three-dimensional model of tropospheric sulfate, *J. Geophys. Res.*, **101**, 18,667-18,690, 1996.
- Cooper, O. R., J. L. Moody, D. D. Parrish, M. Trainer, J. S. Holloway, T. B. Ryerson, G. Hubler, F. C. Fehsenfeld, S. J. Oltmans, and M. J. Evans, Trace gas signatures of the airstreams within North Atlantic cyclones: Case studies from the North Atlantic Regional Experiment (NARE'97) aircraft intensive, *J. Geophys. Res.*, **106**, 5437-5456, 2001.
- Cooper, O. R., J. L. Moody, D. D. Parrish, M. Trainer, J. S. Holloway, G. Hubler, F. C. Fehsenfeld, and A. Stohl, Trace gas composition of midlatitude cyclones over the western North Atlantic Ocean: A seasonal comparison of O₃ and CO, *J. Geophys. Res.*, **107D(7)**, 10.1029/2001JD000902, 2002a.
- Cooper, O. R., J. L. Moody, D. D. Parrish, M. Trainer, J. S. Holloway, T. B. Ryerson, G. Hubler, F. C. Fehsenfeld, S. J. Oltmans, and M. J. Evans, Trace gas composition of midlatitude cyclones over the western North Atlantic Ocean: A conceptual model, *J. Geophys. Res.*, **107D(7)**, 10.1029/2001JD000901, 2002b.
- DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ.*, 97-4, 1997.
- Duncan, B. N., J. A. Logan, A. C. Staudt, R. Yevich, and J. A. Logan, Interannual and seasonal variability of biomass burning emissions constrained by satellite observations, *J. Geophys. Res.*, **108(D2)**, 4100, doi:10.1029/2002JD002378, 2003.
- Evans, M. et al., Understanding the emissions, processing, export and impact of Asian oxides of nitrogen, *J. Geophys. Res.*, manuscript in preparation, 2003.
- Fiore, A. M., D. J. Jacob, I. Bey, R. M. Yantosca, B. D. Field, and J. G. Wilkinson, Background ozone over the United States in summer: Origin and contribution to pollution episodes, *J. Geophys. Res.*, **107(D15)**, doi:10.1029/2001JD000982, 2002.
- Horowitz, L. W., J. Liang, G. M. Gardner, and D. J. Jacob, Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry, *J. Geophys. Res.*, **103**, 13,451-13,76, 1998.
- Horowitz, L. W., and D. J. Jacob, Global impact of fossil fuel combustion on atmospheric NO_x, *J. Geophys. Res.*, **104**, 23,823-23,840, 1999.
- Holloway, J. S., R. O. Jakoubek, D. D. Parrish, C. Gerbig, A. Volz-Thomas, S. Schmitgen, A. Fried, B. Wert, B. Henry, and J. R. Drummond, Airborne intercomparison of vacuum ultraviolet fluorescence and tunable diode laser absorption measurements of tropospheric carbon monoxide, *J. Geophys. Res.*, **105**, 24251-24261, 2000.
- Intergovernmental Panel on Climate Change (IPCC), *Climate Change 2001: The Scientific Basis*, edited by J. T. Houghton et al., p. 944, Cambridge University Press, New York, 2001.
- Jacob, D. J., J. A. Logan, G. M. Gardner, R. M. Yevich, C. M. Spivakovsky, and S. C. Wofsy, Factors regulating ozone over the United States and its export to the global atmosphere, *J. Geophys. Res.*, **98**, 14,817-14,826, 1993.
- Jacob, D. J., J. A. Logan, and P. Murti, Effect of rising Asian emissions on surface ozone in the United States, *Geophys. Res. Lett.*, **26**, 2175-2178, 1999.
- Jacob, D. J., Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ.*, **34**, 2131-2159, 2000.
- Jacob, D. J., J. Crawford, M. M. Kleb, V. S. Connors, R. J. Bendura, J. L. Raper, G. W. Sachse, J. Gille, L. Emmons, and C. L. Heald, The transport and chemical evolu-

- tion over the Pacific (TRACE-P) mission: Design, execution, and first results, *J. Geophys. Res.*, *108*(D20), 9000, doi:10.1029/2002JD003276, 2003.
- Kasibhatla, P. S., H. Levy II, and W. J. Moxim, Global NO_x, HNO₃, PAN, and NO_y distributions from fossil fuel combustion emissions: A model study, *J. Geophys. Res.*, *98*, 7165-7180, 1993.
- Koike, M., Y. Kondo, K. Kita, N. Takegawa, Y. Masui, Y. Miyazaki, M. W. Ko, R. J. Weber, D. C. Thornton, G. W. Sachse, S. A. Vay, D. R. Blake, D. G. Streets, F. Flocke, A. J. Weinheimer, F. L. Eisele, S. T. Sandholm, H. B. Singh, and R. W. Talbot, Impact of anthropogenic reactive nitrogen and sulfur compounds from the East Asia region in spring, *J. Geophys. Res.*, *108*(D20), 8789, doi:10.1029/2002JD003284, 2003.
- Lamarque, J.-F., G. P. Brasseur, P. G. Hess, and J.-F. Müller, Three-dimensional study of the relative contributions of the different nitrogen sources in the troposphere, *J. Geophys. Res.*, *101*, 22,955-22,968, 1996.
- Lawrence, M. G., P. J. Crutzen, P. J. Rasch, B. E. Eaton, and N. M. Mahowald, A model for studies of tropospheric photochemistry: Description, global distributions, and evaluation, *J. Geophys. Res.*, *104*, 26,245-26,277, 1999.
- Li, Q., D. J. Jacob, I. Bey, P. I. Palmer, B. N. Duncan, B. D. Field, R. V. Martin, A. M. Fiore, R. M. Yantosca, D. D. Parrish, P. G. Simmonds, and S. J. Oltmans, Transatlantic transport of pollution and its effects on surface ozone in Europe and North America, *J. Geophys. Res.*, *107*(D13), doi:10.1029/2001JD001422, 2002a.
- Li, Q., D. J. Jacob, T. D. Fairlie, H. Liu, R. M. Yantosca, and R. V. Martin, Stratospheric versus pollution influences on ozone at Bermuda: Reconciling past analyses, *J. Geophys. Res.*, *107*(D22), 4611, doi:10.1029/2002JD002138, 2002b.
- Liang, J. Y., L. W. Horowitz, D. J. Jacob, Y. H. Wang, A. M. Fiore, J. A. Logan, G. M. Gardner, and J. W. Munger, Seasonal budgets of reactive nitrogen species and ozone over the United States, and export fluxes to the global atmosphere, *J. Geophys. Res.*, *103*, 13,435-13,450, 1998.
- Liu, H., D. J. Jacob, I. Bey, and R. M. Yantosca, Constrains from ²¹⁰Pb and ⁷Be on wet deposition and transport in a global three-dimensional chemical tracer model driven by assimilated meteorological fields, *J. Geophys. Res.*, *106*, 12,109-12,128, 2001.
- Liu, H., D. J. Jacob, L. Y. Chan, S. J. Oltmans, I. Bey, R. M. Yantosca, J. M. Harris, B. N. Duncan, and R. V. Martin, Sources of tropospheric ozone along the Asian Pacific Rim: An analysis of ozonesonde observations, *J. Geophys. Res.*, *107*(D21), 4573, doi:10.1029/2001JD002005, 2002.
- Martin, R. V., K. Chance, D. J. Jacob, T. P. Kurosu, R. J. D. Spurr, E. Bucsela, J. F. Gleason, P. I. Palmer, I. Bey, A. M. Fiore, Q. Li, and R. M. Yantosca, An improved retrieval of tropospheric nitrogen dioxide from GOME, *J. Geophys. Res.*, *107*(D18), 4351, doi:10.1029/2001JD001480, 2002.
- McLinden, C. A., S. C. Olsen, B. Hannegan, O. Wild, M. J. Prather, and J. Sundet, Stratospheric ozone in 3-D models: A simple chemistry and the cross-tropopause flux, *J. Geophys. Res.*, *105*, 14,653-14,665, 2000.
- Miyazaki, Y., Y. Kondo, M. Koike, H. E. Fuelberg, C. M. Kiley, K. Kita, N. Takegawa, G. W. Sachse, F. Flocke, A. J. Weinheimer, H. B. Singh, F. L. Eisele, M. Zondlo, R. W. Talbot, S. T. Sandholm, M. A. Avery, and D. R. Blake, Synoptic-scale transport of reactive nitrogen over the western Pacific in Spring, *J. Geophys. Res.*, *108*(D20), 8788, doi:10.1029/2002JD003248, 2003.
- Moxim, W. J., Levy II, P. S. Kasibhatla, Simulated global tropospheric PAN: Its transport and impact on NO_x, *J. Geophys. Res.*, *101*, 12,621-12,638, 1996.
- Munger, J. W., S. C. Wofsy, P. S. Bakwin, S.-M. Fan, M. L. Goulden, B. C. Daube, A. H. Goldstein, K. E. Moore, and D. R. Fitzjarrald, Atmospheric deposition of reactive nitrogen oxides and ozone in a temperate deciduous forest and a sub-arctic taiga woodland, 1. Measurements and mechanisms, *J. Geophys. Res.*, *101*, 12,639-12,657, 1996.
- Munger, J. W., S.-M. Fan, P. S. Bakwin, M. L. Goulden, A. H. Goldstein, A. S. Colman, and S. C. Wofsy, Regional budgets for nitrogen oxides from continental sources: Variations of rates for oxidation and deposition with season and distance from source regions, *J. Geophys. Res.*, *103*, 8355-8368, 1998.
- Novelli, P. C., K. A. Masarie, P. M. Lang, B. D. Hall, R. C. Myers, and J. W. Elkins, Reanalysis of tropospheric CO trends: Effects of the 1997-1998 wildfires, *J. Geophys. Res.*, *108*(D15), 4464, doi:10.1029/2002JD003031, 2003.
- Oltmans, S. J., H. Levy II, J. M. Harris, J. T. Merrill, J. L. Moody, J. A. Lathrop, E. Cuevas, M. Trainer, M. S. O'Neill, J. M. Prospero, H. Vömel, and B. J. Johnson, Summer and spring ozone profiles over the North Atlantic from ozonesonde measurements, *J. Geophys. Res.*, *101*, 29,179-29,200, 1996.
- Parrish, D. D., M. Trainer, M. P. Buher, B. A. Watkins, and F. C. Fehsenfeld, Carbon monoxide concentrations and their relation to concentrations of total reactive oxidized nitrogen at two rural U. S. sites, *J. Geophys. Res.*, *96*, 9309-9320, 1991.
- Parrish, D. D., M. Trainer, J. S. Holloway, J. E. Lee, M. S. Warshawsky, F. C. Fehsenfeld, G. L. Forbes, and J. L.

- Moody, Relationship between ozone and carbon monoxide at surface sites in the North Atlantic region, *J. Geophys. Res.*, *103*, 13,357-13,376, 1998.
- Parrish, D. D., T. B. Ryerson, J. S. Holloway, J. A. Neuman, J. M. Roberts, J. Williams, C. A. Stroud, G. J. Frost, M. Trainer, G. Hubler, F. C. Fehsenfeld, F. Flocke, A. J. Weinheimer, Fraction and composition of NO_y transported in air masses lofted from the North American continental boundary layer, *J. Geophys. Res.*, submitted, 2003.
- Ryerson, T. B., M. P. Buhr, G. J. Frost, P. D. Goldan, J. S. Holloway, G. Hubler, B. T. Jobson, W. C. Kuster, S. A. McKeen, D. D. Parrish, J. M. Roberts, D. T. Sueper, M. Trainer, and J. Williams, Emissions lifetimes and ozone formation in power plant plumes, *J. Geophys. Res.*, *103*, 22,569-22,583, 1998.
- Ryerson, T. B., L. G. Huey, K. Knapp, J. A. Neuman, D. D. Parrish, D. T. Sueper, and F. C. Fehsenfeld, Design and initial characterization of an inlet for gas-phase NO_y measurements from aircraft, *J. Geophys. Res.*, *104*, 5483-5492, 1999.
- Stohl, A., M. Trainer, T. B. Ryerson, J. S. Holloway, and D. D. Parrish, Export of NO_y from the the North American boundary layer during 1996 and 1997 North Atlantic Regional Experiment, *J. Geophys. Res.*, *107*(D11), 10.1029/2001JD000519, 2002.
- Tie, X., L. Emmons, L. Horowitz, G. Brasseur, B. Ridley, E. Atlas, C. Stroud, P. Hess, A. Klonecki, S. Madronich, R. Talbot, and J. Dibb, Effect of sulfate aerosol on tropospheric NO_x and ozone budgets: Model simulations and TOPSE evidence, *J. Geophys. Res.*, *108*(D4), 8364, doi:10.1029/2001JD001508, 2003.
- Wesely, M. L., Parameterization of surface resistance to gaseous dry deposition in regional-scale numerical models, *Atmos. Environ.*, *23*, 1293-1304, 1989.
- Wang, Y., D. J. Jacob, and J. A. Logan, Global simulation of tropospheric O₃-NO_x-hydrocarbon chemistry 1. Model formulation, *J. Geophys. Res.*, *103*, 10,713-10,725, 1998a.
- Wang, Y., D. J. Jacob, and J. A. Logan, Global simulation of tropospheric O₃-NO_x-hydrocarbon chemistry 3. Origin of tropospheric ozone and effects of nonmethane hydrocarbons, *J. Geophys. Res.*, *103*, 10,757-10,767, 1998b.
- Williams, J., J. M. Roberts, S. B. Bertman, C. A. Stroud, F. C. Fehsenfeld, K. Baumann, M. P. Buhr, K. Knapp, P. C. Murphy, M. Nowick, and E. J. Williams, A method for the airborne measurement of PAN, PPN, and MPAN, *J. Geophys. Res.*, *105*, 28,943-28,960, 2000.

Table 1. Export efficiency of NO_y from the North American boundary layer (NARE'97 data)

	<i>Stohl et al.</i> [2002]	<i>Parrish et al.</i> [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
<i>R</i> (mol mol ⁻¹)	0.16	0.176	0.154
α	1	1.18	1

^aCalculations based on GEOS-CHEM global 3-D model results sampled along the NARE'97 (September 6-29, 1997) flight tracks.

^bDerived from the relationship of NO_y with CO along the NARE'97 aircraft flight tracks, as described in the text. Export efficiencies in *Parrish et al.* [2003] and in this work are calculated from equation (1).

^cCalculated using *Parrish et al.* [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 α = 1.18.

^dCalculated 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 α = 1.

Table 2. Monthly mean CO concentrations at northern midlatitude sites for September 1997

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

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

Table 3. Model budget of anthropogenic NO_y in the North American boundary layer for September 1997

	NO_x	PANs	HNO_3	Alkyl nitrates	Total
Concentration (ppbv)	0.27	0.16	0.69	0.03	1.15
Lifetime (d)	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%	...

The North American boundary layer is defined as the domain extending horizontally over the domain (130°W - 65°W , 25°N - 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 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.

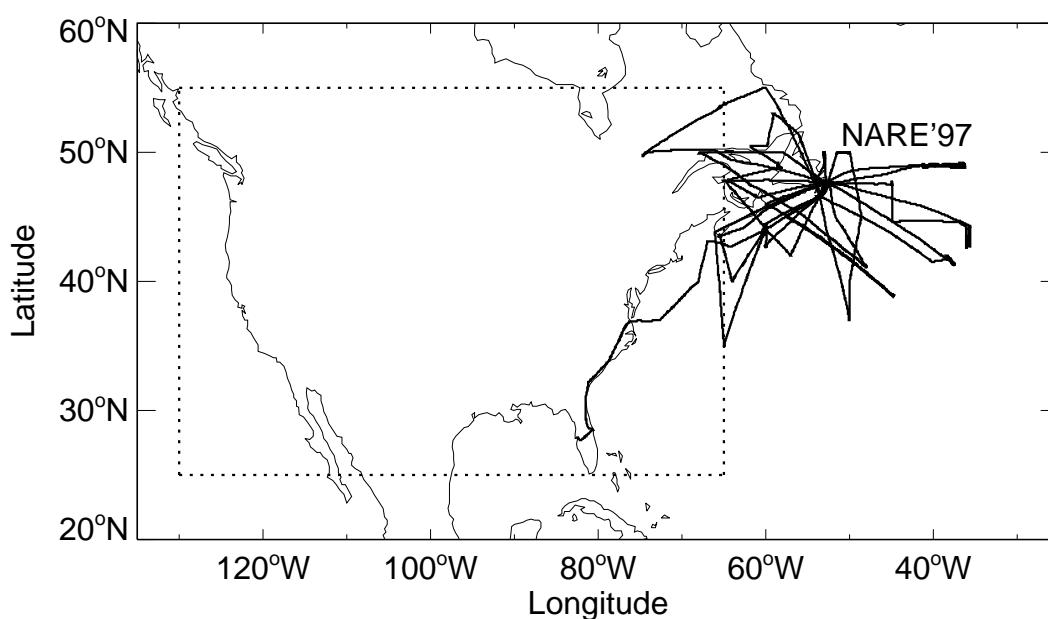


Figure 1. Flight tracks of the NOAA WP-3D aircraft during the North Atlantic Regional Experiment in September 1997 (NARE'97). The rectangle (dashed line) defines the North American domain (130°W - 65°W , 25°N - 55°N) used in our budget analysis.

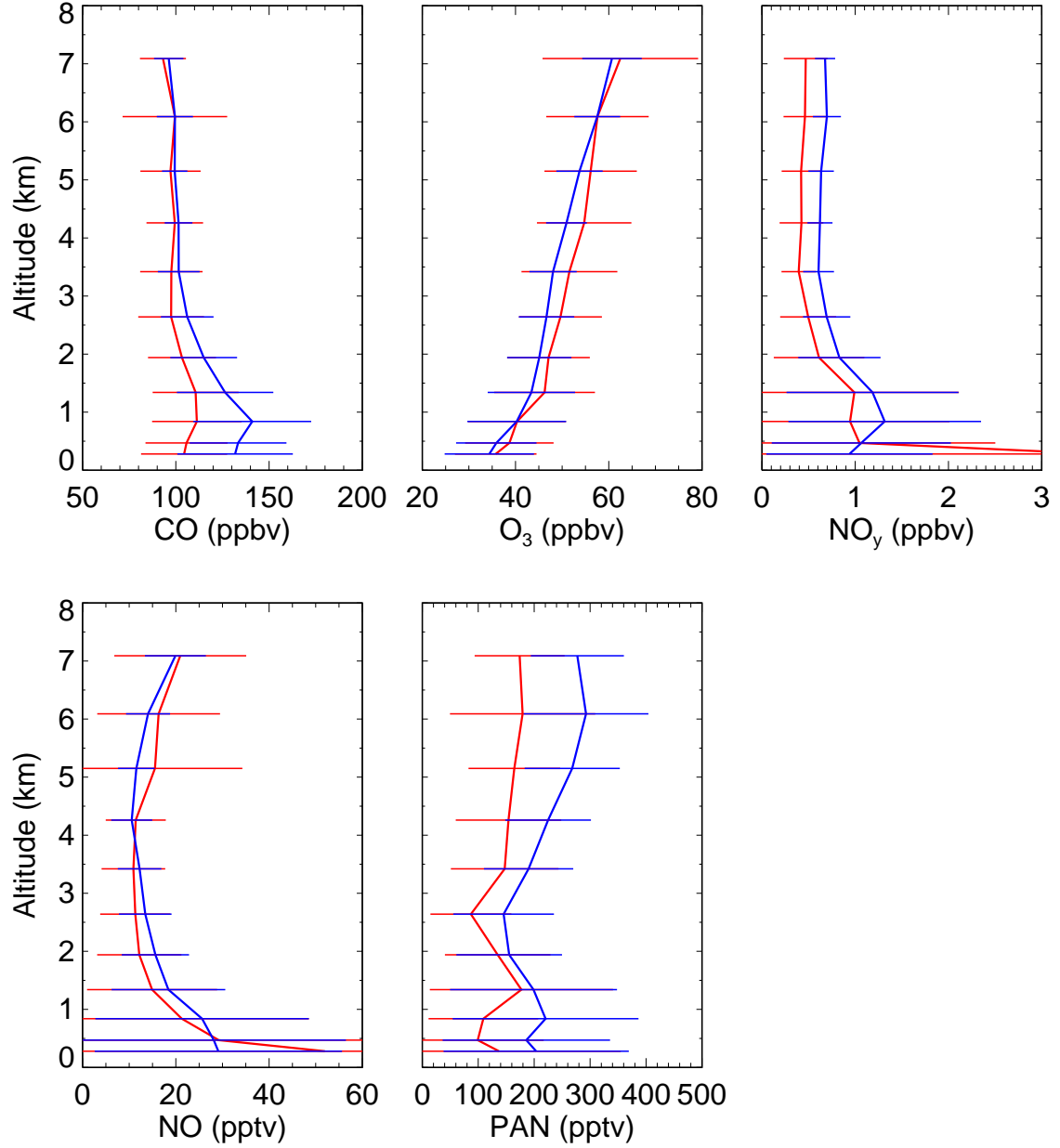


Figure 2. Simulated (blue) and observed (red) mean vertical profiles of CO, ozone, NO_y, NO, and PAN concentrations during NARE'97 (September 6-29, 1997). Horizontal bars represent standard deviations. Model results are sampled along the flight tracks at the time of the flights.

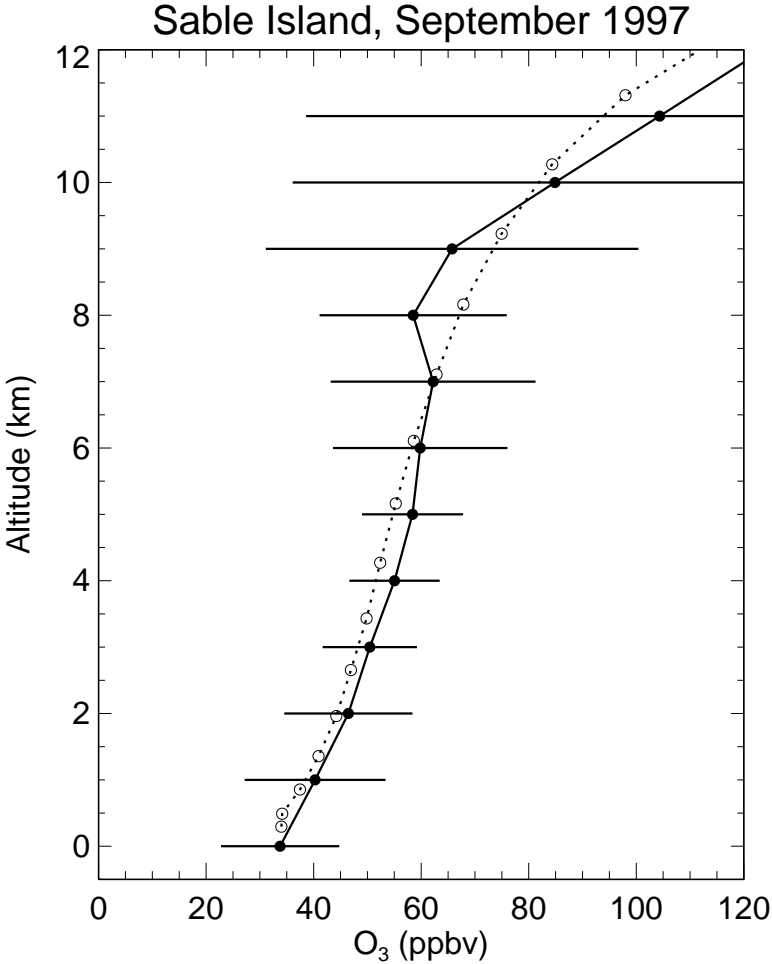


Figure 3. Simulated (dashed line) and observed (solid line) mean vertical profile of ozone at Sable Island in September 1997. Horizontal bars represent standard deviations of the observation. A total of 30 ozone sondes were launched during September 5-October 5, 1997.

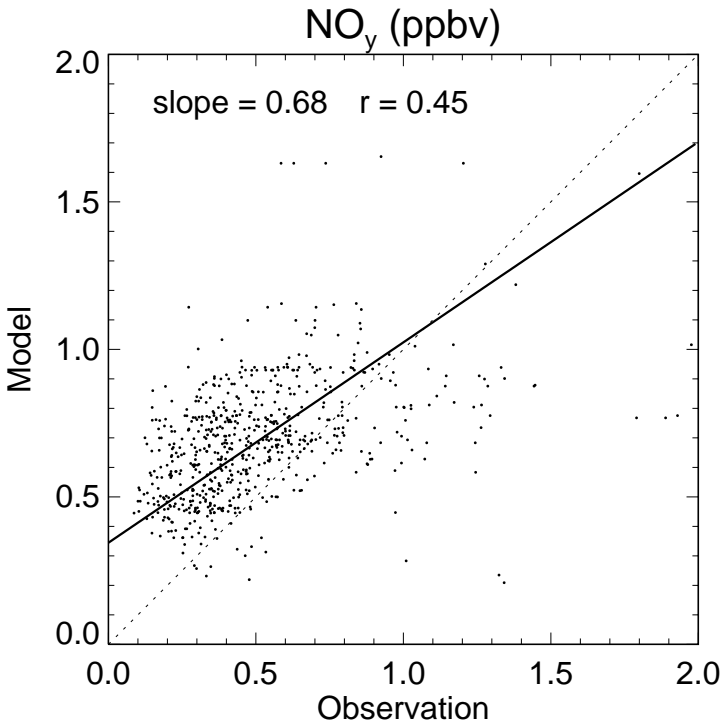


Figure 4. Scatter plot of simulated versus observed NO_y concentrations during NARE'97 (September 6-29, 1997). Model results are sampled along the flight tracks at the time of the flights, and observations are averaged over model grid box. The 1:1 and regression lines (Reduced Major Axis method) are also shown.

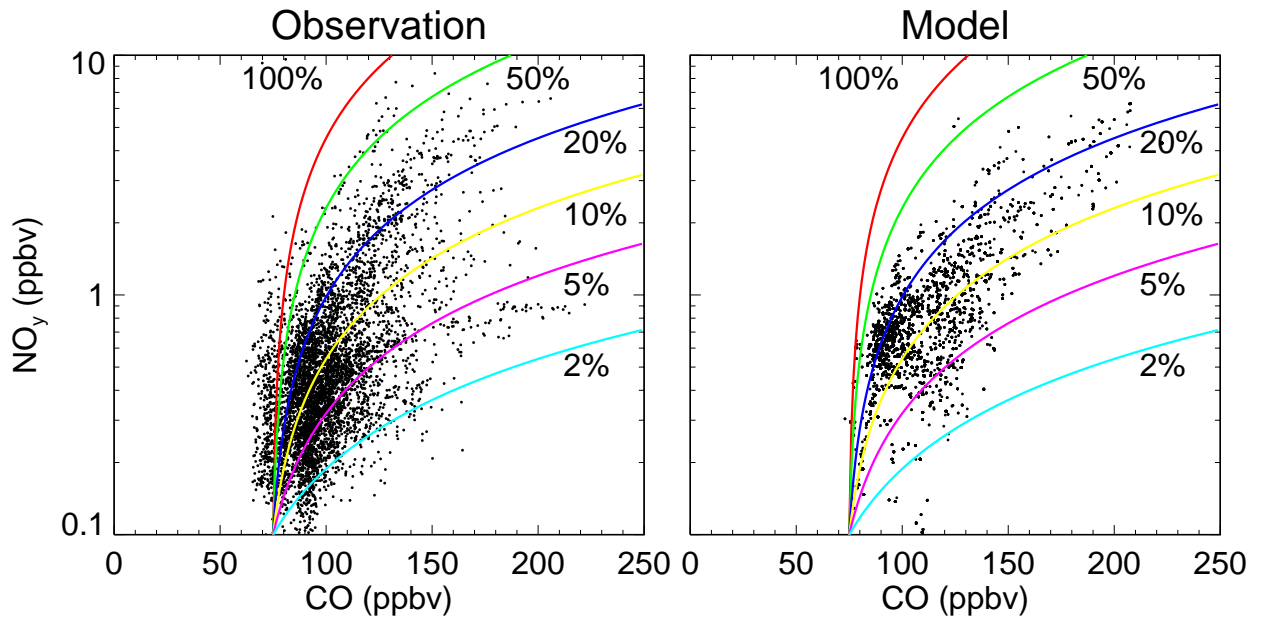


Figure 5. Observed (left panel) and simulated (right panel) NO_y -CO correlations during NARE'97 (September 6-29, 1997). Observations are 1-minute averages and include all altitudes. Model results are sampled along the flight tracks at the time of the flights. The curves give the relationships expected 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.* [2003]. See text for details.

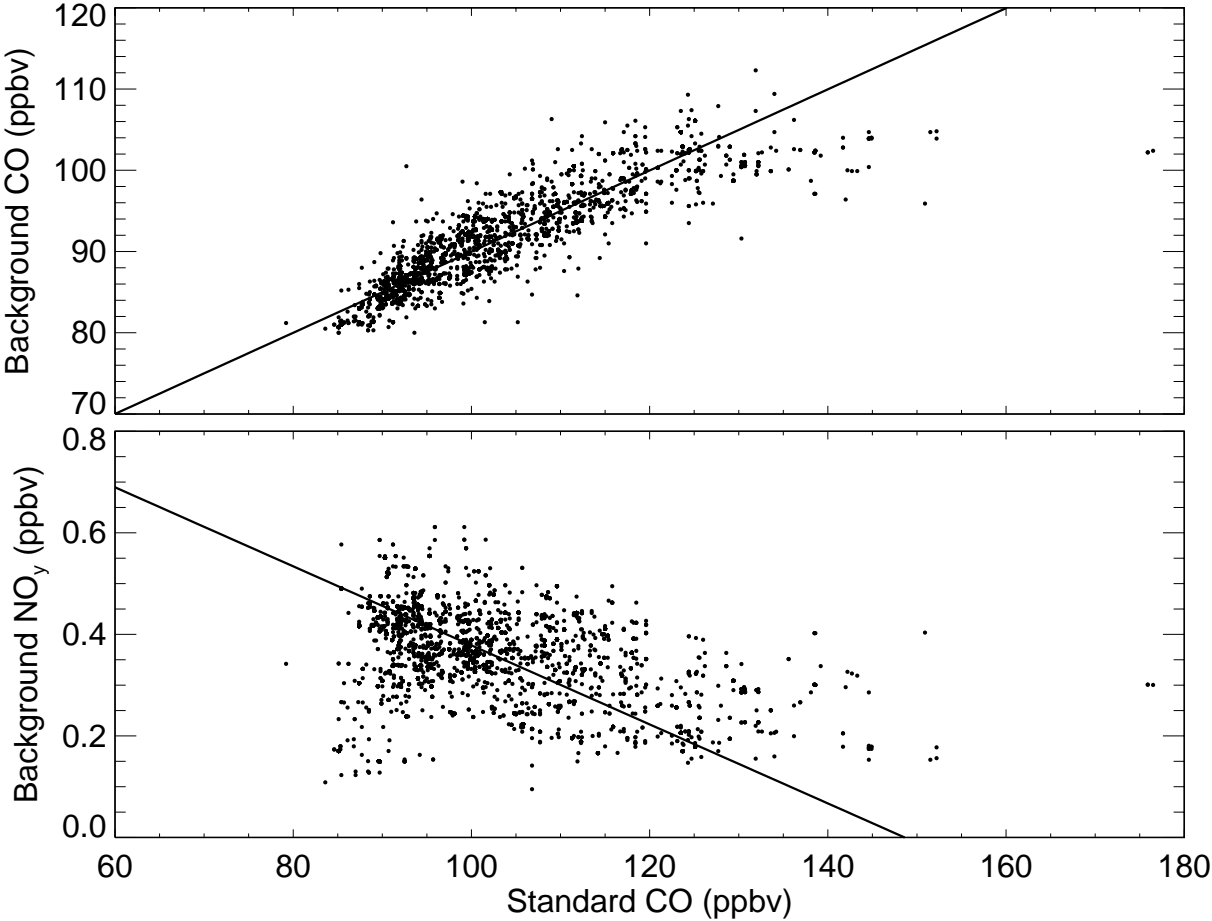


Figure 6. Correlation of background CO and NO_y concentrations with North American outflow in the model sampled along the NARE'97 (September 6-29, 1997) flight tracks above 2 km altitude at the time of the flights. The plots show background CO and NO_y, as determined from a sensitivity simulation with North American anthropogenic emissions shut off, versus CO in the standard simulation. The regression lines (Reduced Major Axis method) are also shown.

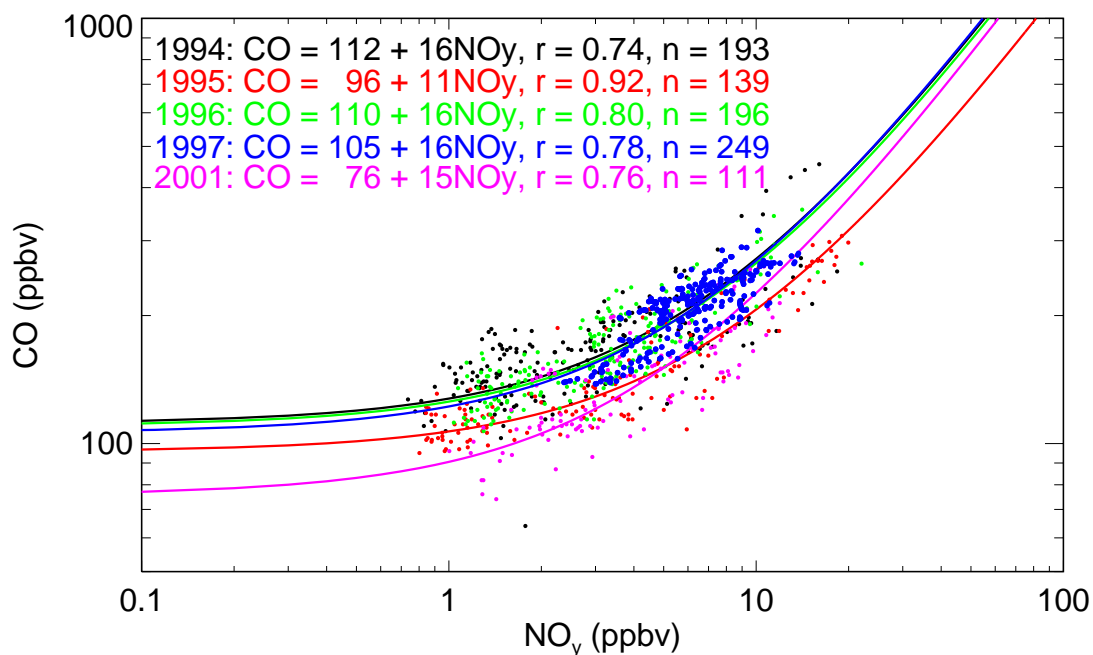


Figure 7. Simulated (1997) and observed (1994-1996, 2001) NO_y -CO correlations at Harvard Forest (42.5°N , 72.2°W , 340 m altitude) for September, plotted on a logarithm scale. Data used are daytime only (10-16 local time). The regression lines (Reduced Major Axis method) are also shown.

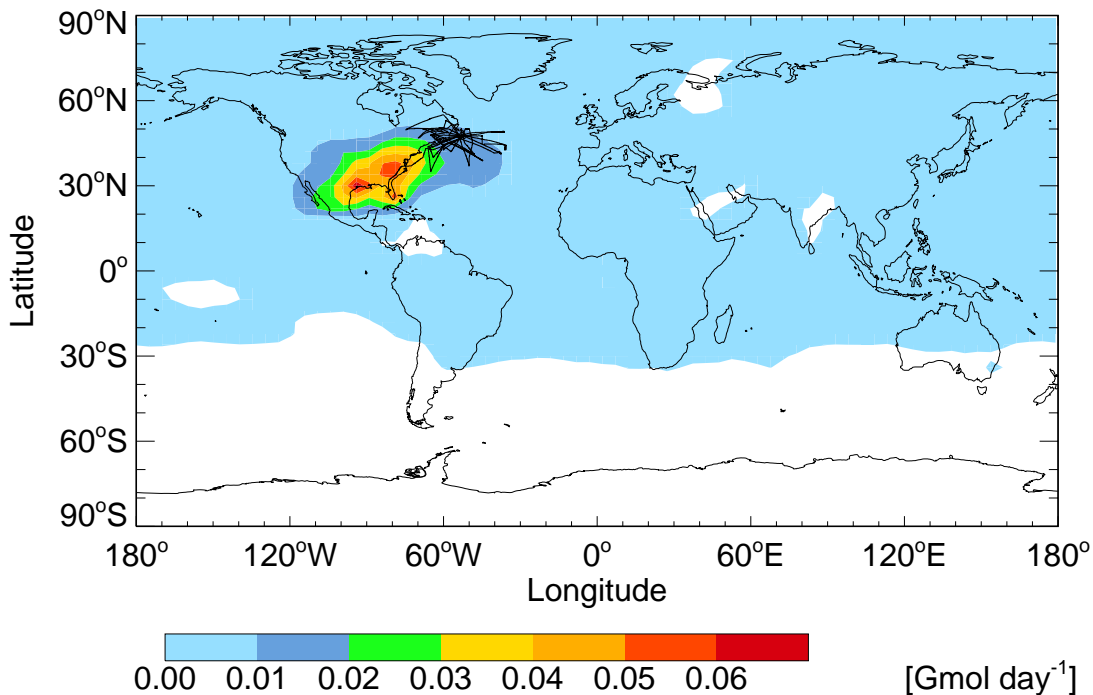


Figure 8. Simulated monthly mean (September 1997) ozone production enhancements due to exported NO_y from the North American boundary layer, integrated over the free tropospheric column. Also shown are the NARE'97 (September 6-29, 1997) aircraft flight tracks.