Large-scale impacts of anthropogenic pollution and boreal wildfires on the nitrogen oxides over the central North Atlantic region

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Received 7 December 2007; revised 15 April 2008; accepted 19 June 2008; published 6 September 2008.

[1] Transport of North American anthropogenic and boreal wildfire emissions is a large source of nitrogen oxides over the North Atlantic region. To characterize the influence of transport of these emissions on nitrogen oxides levels over the central North Atlantic lower free troposphere (FT) and their further implications for hemispheric O3, we analyze measurements of NOx (NO + NO2), total reactive nitrogen oxides (NOy), CO, and O3 made at the Pico Mountain station (38.47°N 28.40°W, 2.2 km above sea level) in the Azores archipelago from July 2002 to August 2005. Transport of pollution from North America causes significant enhancements of nitrogen oxides year-round. An analysis of the export of United States NOx emissions to the FT based on observed ΔNOx/ΔCO in the anthropogenic plumes indicates that more than 94% of the NOx emitted over the United States is lost within the continent and/or during export out of the United States boundary layer and to the Azores, consistent with previous studies. However, our observations indicate that about 30% of the NOx initially exported out of the United States boundary layer reach the Azores lower FT. NOy was also significantly enhanced in these plumes. Since the lifetime of NOx is shorter than the transport timescale of most events, PAN decomposition and potentially photolysis of HNO3 provide a supply of NOx over the central North Atlantic lower FT. Observed ΔO3/ΔNOx ratios and significant NOx levels remaining in the North American plumes suggest a potential for O3 formation well downwind from North America. Summertime boreal wildfires in North America are responsible for important shifts in the nitrogen oxides distributions toward higher levels, with medians of NOy (117–175 pptv) and NOx (9–30 pptv) greater in boreal wildfire plumes. These findings demonstrate the potential hemispheric scale impact that boreal wildfire and North American anthropogenic events have on background NOx and NOy levels and on the tropospheric O3 budget.


1. Introduction

[2] Understanding the sources and fate of nitrogen oxides over remote regions is important for assessing the influence of export of pollution from the continents on global tropospheric ozone (O3) [Jacob et al., 1993; Hudman et al., 2007]. Tropospheric O3 is formed by photochemical oxidation of CO and hydrocarbons, limited by the availability of NOx (NO + NO2). Over the last century, anthropogenic NOx emissions have resulted in a large global increase of tropospheric O3 [Marenco et al., 1994; Lamarque et al., 2005], with important implications for air quality [Fiore et al., 2002] and the greenhouse effect [Intergovernmental Panel on Climate Change, 2007].

[3] Previous studies, on the basis of North Atlantic Regional Experiment (NARE) and International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) aircraft measurements [e.g., Parrish et al., 2004; Li et al., 2004; Hudman et al., 2007], have estimated that less than 20% of the NOx emitted over the eastern United States is exported to the North Atlantic free troposphere (FT) as NOx (total reactive nitrogen oxides, i.e., the sum of NOx, PAN, HNO3, alkyl nitrates and other minor oxidation products). Further analyses of the composition of NOy indicate that NOx exported out of the North America boundary layer (BL) is mostly HNO3 (~50%), with ~35% as PAN and less than 10% as NOy [e.g., Parrish et al., 2004; Singh et al., 2007]. The large fraction of emitted NOx that is removed from the plumes and the high HNO3/NOx ratio imply that the potential for future O3 production in these plumes in the FT must be limited. However, the dependence of O3 production on NOx is highly nonlinear and the ozone production efficiency per unit NOx consumed increases rapidly as NOx level decreases [Liu et al., 1987].
As a result, the export of a small fraction of emitted NO\textsubscript{x} from the continental boundary layer may lead to important ozone production over the continent or downwind in the remote troposphere [Jacob et al., 1993].

While net photochemical O\textsubscript{3} production typically takes place near the source regions [e.g., Li et al., 2004], observations over the North Atlantic Ocean have indicated that it can also occur during long-range transport events [Reeves et al., 2002; Honrath et al., 2004]. However, the large-scale impacts of long-range transport on the tropospheric O\textsubscript{3} production over the North Atlantic region are uncertain. For example, simulations from two global chemical transport models (CTM) [Auvray et al., 2007] and a photochemical box model constrained by observations [Reeves et al., 2002] indicate that the export of NO\textsubscript{x} emissions from the United States lead to a perturbation of the chemistry over this region through changes in the O\textsubscript{3} production rate. As a consequence, long-range transport events significantly affect O\textsubscript{3} photochemical production over the entire North Atlantic troposphere year-round [Auvray et al., 2007]. However, other studies indicate that the North Atlantic region is in a state of net O\textsubscript{3} destruction all year-round [Kleissl and Levy, 1997] or net O\textsubscript{3} destruction during the summer and net O\textsubscript{3} production during the winter [Tieger et al., 1999].

In addition to anthropogenic emissions, large wildfires over the boreal region can also result in a substantial source of nitrogen oxides to the atmosphere [Goode et al., 2000; Andreae and Merlet, 2001]. Recently, it has been shown that NO\textsubscript{x} emissions from boreal wildfires can be efficiently transported to the North Atlantic region [Val Martin et al., 2006; Singh et al., 2007; Real et al., 2007], resulting in an important impact on the tropospheric O\textsubscript{3} budget [Lapina et al., 2006; Pfister et al., 2006].

In this paper, we study the influence of transport of pollution from North America and boreal wildfires on nitrogen oxides levels in the central North Atlantic lower FT. We analyze measurements of NO, NO\textsubscript{2}, NO\textsubscript{y}, NO\textsubscript{3} and NO\textsubscript{x}, made at the Pico Mountain observatory from late July 2002 to August 2005 with two main purposes: to assess the impacts of long-range transport events from North America on levels of nitrogen oxides on a seasonal basis and their further implications for tropospheric O\textsubscript{3}, and to determine the degree in which boreal wildfire events modulate the summertime NO\textsubscript{y} and NO\textsubscript{x} background levels. These measurements are analyzed in combination with simultaneous measurements of CO and O\textsubscript{3} made also at the Pico Mountain station and simulations from the Lagrangian particle dispersion model FLEXPART [Stohl et al., 2005]. A more detailed analysis of the seasonal variation of nitrogen oxides and the partitioning of reactive nitrogen in the background lower FT over the central North Atlantic region is presented by Val Martin et al. [2008].

2. Pico Mountain Site

The Pico Mountain station is located on the summit caldera of the inactive volcano Pico (altitude 2.2 km) in the Azores Islands, Portugal (38.47°N 28.40°W). The Azores are situated over a region that is frequently impacted by continental emissions. They are often impacted by large-scale transport patterns in the lower FT, which can transport emissions from North America to the Azores in 5 to 7 days [Owen et al., 2006]. Episodically, emissions exported from the eastern United States in warm conveyor belts with the associated convection, followed by subsidence, also reach the Azores [Owen et al., 2006]. In addition, the Azores are affected by outflow from high latitudes, which can carry emissions from boreal wildfires in Canada, Alaska and Siberia and bring them to the Azores 6 to 15 days later [Honrath et al., 2004; Lapina et al., 2006; Val Martin et al., 2006]. The location of the Pico Mountain station also has the advantage of being in the lower FT most of the time [Kleissl et al., 2007] and the influence of island pollution on the air sampled, via upslope flow, is negligible [Kleissl et al., 2007; Val Martin et al., 2008]. Further details of the Pico Mountain station are given by Honrath et al. [2004] and Kleissl et al. [2007].

NO, NO\textsubscript{2}, and NO\textsubscript{y} were sampled by an automated NO\textsubscript{y} system, which used established techniques for high sensitivity detection: NO detection by O\textsubscript{3} chemiluminescence [Ridley and Grahek, 1990], NO\textsubscript{2} by conversion to NO via ultraviolet photodissociation [Kley and McFarland, 1980; Parrish et al., 1990], and NO\textsubscript{y} by Au-catalyzed reduction to NO in the presence of CO [Bollinger et al., 1983; Fahey et al., 1985]. Measurements were recorded as 30-s averages (NO and NO\textsubscript{2}) and 20-s averages (NO\textsubscript{y}) every 10 min, and further averaged to obtain the 30-min averages used in this work. A detailed description of the NO\textsubscript{y} system is presented elsewhere [Val Martin et al., 2006, 2008].

CO was measured by a nondispersive infrared (NDIR) photometer (Thermo Environmental, Inc., Model 48C-TL), modified as described by Parrish et al. [1994] and calibrated daily with a CO calibration gas referenced to the NOAA Global Monitoring Division standard. O\textsubscript{3} was measured with a commercial ultraviolet absorption instrument (Thermo Environmental, Inc., Model 49C). CO and O\textsubscript{3} data were recorded as 1-min averages, and were further averaged to obtain the 30-min averages used here. More details on the CO and O\textsubscript{3} instruments are presented by Honrath et al. [2004] and Owen et al. [2006].

3. FLEXPART Simulations

To investigate the sensitivity of our measurements to upwind emissions, we used the FLEXPART particle dispersion model version 6.2 [Stohl, 1998; Stohl et al., 2005]. FLEXPART was driven with data from the European Centre for Medium Range Weather Forecasts (ECMWF) [European Centre for Medium Range Weather Forecasts, 2005] with a 1° × 1° horizontal resolution, 60 vertical levels and a temporal resolution of 3 h, using meteorological analyses at 0000, 0600, 1200, and 1800 UTC, and ECMWF 3-h forecasts at 0300, 0900, 1500, and 2100 UTC.

We ran FLEXPART in its backward mode to create retroplumes. Retroplumes were initiated every 3 h with 4,000 particles released over a 1-h time interval into a 1° × 1° grid box centered on the Pico Mountain station, over the altitude range of 2000–2500 m above sea level. Particles were followed backward in time for 20 days. To account for differences in air density between the release cell and upwind sources, the residence time of the particles was normalized by the air density in each cell to yield the specific volume weighted residence time (SVWRT).
To evaluate the contribution of anthropogenic emissions, anthropogenic CO tracers at the Pico Mountain station from North American, Asian and European emissions were calculated by multiplying the upwind time-integrated SVWRT in the footprint layer (0–300 m) with emissions, using the approach of Seibert and Frank [2004]. These tracers are referred to as FLEXPART NA-CO, FLEXPART Asia-CO, and FLEXPART Euro-CO in the remainder of this paper. Anthropogenic emissions were based on the EDGAR 3.2 Fast Track 2000 data set [Olivier and Berdowski, 2001].

A fourth CO tracer, from the boreal wildfire emissions in North America (referred to as FLEXPART Fire-CO), was calculated to assess the magnitude of fire impact at the Pico Mountain station. For this purpose, SVWRT in the column 0–7500 m was multiplied with emissions distributed according to air density in the column. Boreal wildfire CO emissions were based on an inventory created by the Boreal Wildland-Fire Emissions Model [Kasischke et al., 2005]. Further details on the boreal wildfire inventory and the FLEXPART Fire-CO are presented elsewhere [Lapina et al., 2008].


To assess the influence of North American anthropogenic emissions over the central North Atlantic lower FT, we compare the enhancements of CO and nitrogen oxides in North American outflow to levels observed in clean air without the influence of recent anthropogenic emissions. The following two sections first describe the identification of North American outflow periods and then present two example episodes.

4.1. Identification of North American Anthropogenic Impact

We identified periods potentially impacted by upwind anthropogenic emissions by selecting those in which the hourly average of CO was at least 15 ppbv higher than the CO background in each season and year, and the average of FLEXPART NA-CO during the event was at least 10 ppbv. For the analysis, we considered as background the 90th percentile of all hourly CO observations for each season and year. This value is typical of clean levels without the influence of emissions at the measurement site and has been identified as background in previous years [Honrath et al., 2004]. Hourly averages of CO were used to smooth the variability of the CO measurements for comparison to the cutoff values. The average of FLEXPART NA-CO values within the periods was used instead of the individual 3-h step values to allow for variability in the timing of the FLEXPART-simulated events. The FLEXPART NA-CO cutoff of 10 ppbv corresponds to approximately the 80th percentile of all model simulated values. Although the choice of these criteria is somewhat arbitrary, the cutoff values were designed to be conservative and ensure that the selected data represent significantly polluted air masses from North America. We tested slightly smaller and larger cutoffs (i.e., 10 ppbv and 20 ppbv above CO background). These criteria changed the length of the anthropogenic-impacted periods selected, but did not change the results presented below.

In addition to outflow strictly from eastern North America, flow patterns passing over North America can also bring air that originated from boreal regions. During these periods, air sampled at the Pico Mountain station may contain a mixture of anthropogenic and boreal wildfire emissions [Honrath et al., 2004; Val Martin et al., 2006]. To exclude the interference of boreal wildfire emissions, we removed those periods in which the corresponding average FLEXPART Fire-CO was above the 0.1th percentile of all simulated values for each season. This resulted in the removal of 35% of the anthropogenic events in summer and early fall. Additionally, transported emissions from North American sources may also be mixed with air containing anthropogenic emissions from Europe and Asia. To limit the events studied to those dominated by North American anthropogenic emissions, we also excluded those periods in which the average FLEXPART Asia-CO or FLEXPART Euro-CO was greater than 50% of the average FLEXPART NA-CO. This screening resulted in the removal of an additional 7% of events.

4.2. Example Episodes

Figure 1 presents two example episodes of transport of anthropogenic pollution from eastern North America to the Pico Mountain station. These two episodes illustrate two different transport mechanisms from North America. Figure 2 shows an example of FLEXPART retroplumes and the source contribution map for each episode. (Additional examples of measurements obtained at the Pico Mountain station during other periods are given by Val Martin et al. [2008, 2006] and Honrath et al. [2004].)

Figure 1a shows the time series of the observations for the episode of 20–24 April 2005. This event was the result of emissions from eastern United States and Canada as described in detail by Honrath et al. [2008]. During 21–24 April air from North America impacted the measurement site. As shown in Figure 2a–2b for the retroplume of 22 April 1800 UTC, air masses spent at least 5 days over North America (numerals 4–9 in Figure 2a) at altitudes lower than 2 km and were transported over the ocean for 3 days (numerals 1–3 in Figure 2a) at 2–4 km altitudes (19–22 April in Figure 2b). Apparently as a consequence of the United States emissions, levels of CO, nitrogen oxides and O3 were substantially enhanced during this period, and nitrogen oxides and O3 were well correlated with CO.

Similarly, levels of CO were also considerably elevated during the 1–3 June 2005 episode, as shown in Figure 1b. This episode was the result of a sudden switch from air masses originating at higher latitudes and altitudes to air masses originating at low altitude over the southeastern United States. This episode, however, exhibited generally small enhancements of nitrogen oxides and O3 and no significant correlation with CO. As shown in Figure 2d–2e for the retroplume of 2 June 1800 UTC, air masses passed over southeastern United States for at least 4 days (numerals 6–9 in Figure 2d) and were transported during 2 days (numerals 4–5 in Figure 2d) within the marine boundary layer (altitudes below 2 km, 28–30 May in Figure 2e) and during 3 days (numerals 1–3 in Figure 2d) at altitudes of about 2 km (30 May through 2 June in Figure 2e), before reaching the measurement site. Strong removal of nitrogen oxides and O3 destruction in the marine BL may have
caused these small enhancements of nitrogen oxides and \( O_3 \). This conclusion is consistent with previous studies, which indicate rapid removal of \( HNO_3 \) within the marine BL [e.g., Peterson and Honrath, 1999; Dibb et al., 2004].

4.3. Comparison of Nitrogen Oxides Levels in Anthropogenic and Nonanthropogenic Outflow

[20] Figure 3 compares the nitrogen oxides mixing ratios observed in periods characterized by anthropogenic emissions with the distribution of nitrogen oxides levels observed in clean periods without the influence of recent anthropogenic emissions, for all seasons. We considered clean periods those in which the overall FLEXPART anthropogenic tracer was lower than the 20th percentile of all simulated values. Statistics of the mixing ratio distributions and the difference between the medians in both distributions are indicated in Figure 3. Additionally, the distribution of all observations is shown for comparison.

[21] Transport of anthropogenic emissions from North America enhanced the nitrogen oxides distribution levels. Average \( NO_y \) mixing ratios during the North American anthropogenic events were above levels observed during clean periods in all seasons (Figure 3a–3d). The difference between the median \( NO_y \) values in the anthropogenic and nonanthropogenic distributions were 22–177 pptv, with significantly higher median values in the anthropogenic distribution, in particular during the summer season. The larger anthropogenic impact during this season is likely the result of a more efficient venting of \( NO_y \) out of the United States BL, as discussed below in section 4.4.

[22] The distributions of \( NO_y \) mixing ratios were also shifted toward higher levels in all seasons, with differences in the median values of 4–11 pptv (Figure 3e–3h). Average \( NO_y \) levels in the anthropogenic events were 30 ± 3 pptv (spring), 33 ± 2 pptv (summer), 41 ± 2 pptv (fall), and 36 ± 2 pptv (winter). These mean values correspond to the 75th percentile of the full distribution each season, with the exception of the summer, which corresponds to the 55th percentile. The presence of high mixing ratios during summer (and early fall) in the nonanthropogenic distributions is the result of impacts of boreal wildfire emissions as discussed below in section 5. If we exclude the observations impacted by boreal wildfires (see section 5), the \( NO_y \) mean in North American outflow corresponds to the 70th percentile of all summertime nonfire impacted observations. Mean levels of daytime NO in these plumes ranged from 8 to 11 pptv, occasionally reaching 20 pptv (not shown). Although these levels may be insufficient for a net \( O_3 \) production [Klonecki and Levy, 1997], they may influence the \( O_3 \) chemical tendency through changes in the \( O_3 \) production rate [Mauzerall et al., 1996].

4.4. Nitrogen Oxides Enhancements in North American Outflow and Estimates of \( NO_y \) Transport Efficiency

[23] Figure 4 (left and middle columns) shows the relationships of \( NO_x \) and \( NO_y \) to CO in the overall data and in
the identified North American outflow periods, on a seasonal basis. To focus primarily on free tropospheric plumes, we excluded from the analysis those events in which the air masses traveled within the marine BL. We considered events in the marine BL those in which FLEXPART retroplumes spent more than 1 day at altitudes below 2 km over the ocean (e.g., Figure 2e). This resulted in a removal of one event during the spring and two events during the summer (not identified as events in Figure 4). It is apparent that transport events from North America occur all year round and that they are responsible for part of the high nitrogen oxides observations during all seasons, consistent with the average difference noted above.

[24] To characterize the amount of NO\textsubscript{x} remaining or released into these plumes during transport, we determined enhancement ratios of NO\textsubscript{y} and NO\textsubscript{x} with respect to CO during each United States outflow period [e.g., Stohl et al., 2002; Parrish et al., 2004]. We first calculated the mean values of $\Delta$CO, $\Delta$NO\textsubscript{y}, and $\Delta$NO\textsubscript{x} in each event and then used those mean values to estimate the ratio relative to CO.
in each anthropogenic event (e.g., ΔNOy/ΔCO). Here Δ indicates the difference between the concentration of the indicated species and the background concentration (e.g., [CO] - [CO]bkgd), with background determined as the 20th percentile of all observations for each species, season and year, as discussed in section 4.1. CO is commonly used as a tracer for NOx emissions because it is emitted by combustion sources along with NOx and has a long lifetime, on the order of one to three months depending on the season [Novelli et al., 1992]. Enhancement ratios are dependent on the background level used [Mauzerall et al., 1998]. In this case, a 10% increase in the background used would produce a 50% increase in ΔNOy/ΔCO and ΔNOx/ΔCO on average.

As discussed by Val Martin et al. [2008], measurements of NOy were affected by the presence of clouds at the measurement site, as HNO3 is rapidly scavenged within clouds [e.g., Chameides, 1984; Peterson et al., 1998; Garrett et al., 2006]. To avoid the possible bias of local removal of HNO3 on the ΔNOy/ΔCO ratios, we excluded from the ΔNOy/ΔCO calculation the NOy observations made when the relative humidity at the measurement site was above 96% [Val Martin et al., 2008]. The resulting seasonally averaged enhancement ratios are presented in Figure 4.

Figure 4 (left column) shows large NOy mixing ratios in all the North American outflow plumes relative to the background levels. However, the ΔNOy/ΔCO ratios were highly variable on an event-to-event basis (2.0 – 17.8 pptv ppbv−1). There are two causes that are likely to contribute to this variation: different NOy to CO emission ratios over the continent, which vary as a function of time and type of fuel by at least a factor of 3 [Neuman et al., 2006], and varying degree of washout processing during transport. On a seasonal basis, the average ΔNOy/ΔCO was larger in summer (11.8 ± 2.1 pptv ppbv−1; Figure 4d) than in winter (4.3 ± 1.4 pptv ppbv−1; Figure 4j), suggesting a more efficient export of NOy from eastern North America during summertime likely as a result of increased shallow venting of the continental BL to the lower FT during this summer season [Parrish et al., 2004; Hudman et al., 2007].

To quantify the fraction (f) of NOx originally emitted that was exported as NOy in North American outflow and transported to the Azores, we compared the ΔNOy/ΔCO observed at the Pico Mountain station to that from United States emissions, using the following approach [Parrish et al., 2004; Hudman et al., 2007]:

$$ f = \frac{\Delta NO_y}{\Delta CO} \times R_{emiss} \times \alpha, $$

where R_{emiss} is the United States CO to NOx emission molar ratio and α is a correction factor accounting for chemical sources and sinks of CO. We included a total correction factor of 0.88 distributed as follow: (1) a correction of 1.2 to account for the increase in the CO export from the United States due to oxidation of NMHCs to CO [Chin et al., 1994] and (2) a correction of 0.73 to account for the 27% decline in the CO mixing ratios during the 5 – 6 day transport time from the United States BL to the Pico Mountain station [Honrath et al., 2004]. We applied this correction factor only to the summertime observations since biogenic hydrocarbon emissions are reduced during the nonsummer seasons and oxidation of CO is not as important in those seasons (≈5 – 10% in 5 – 6 day transport, on the basis of the CO + OH rate constant at 800 hPa [Sander et al., 2003] and
the estimated zonal average OH at 35°N and 800 hPa [Spivakovsky et al., 2000]). For the United States CO to NOx emission ratio, we used the value of 5.9 mol mol⁻¹ for the eastern United States from NEI 99 with modifications described by Hudman et al. [2007], which include a generalized 50% decrease in NOx emissions from power plans reflecting 1999–2004 reductions [Frost et al., 2006], and a 30% decrease in CO emissions reflecting a previous overestimation of transport sector emissions [Parrish, 2006].

[28] The resulting f values (i.e., the NOx efficiency for export and transport) are 3 ± 2% (mean ± 2 standard error of the mean) in spring, 6 ± 1% in summer, 4 ± 2% in fall and 3 ± 1% in winter. The summer season shows an average NOx transport efficiency about two times greater than the other seasons. Although we adjusted the summertime observations, the difference between the summer and non-summer NOx efficiencies for export and transport is not due to this applied correction, as the factor changed the summertime values by only 12%. The Pico Mountain estimated export and transport efficiencies (3–6%) are small but significant relative to previous estimates over the western North Atlantic lower FT (11 ± 6% in spring, 18 ± 11% in summer and 9 ± 5% in fall [Parrish et al., 2004; Li et al., 2004; Hudman et al., 2007]) and the western Pacific free troposphere (10–20% in winter-early spring [Koike et al., 2003; Takegawa et al., 2004]). Consistent with these previous studies, our observation of 3–6% of NOy export and transport efficiency indicates that the majority (94–97%) of NOx emitted over the eastern United States is lost within the continental BL and/or during transport from the United States BL to the FT and on to the central North Atlantic. However, comparison of this range to prior estimates on the basis of near-continent observations (9–18%...
[Parrish et al., 2004; Li et al., 2004; Hudman et al., 2007]) suggests that about 30% of the nitrogen oxides emissions that escape the eastern North America BL reaches the measurement site in the form of NOₓ.

[29] Consistent with the expectation that export of NOₓ may eventually lead to NOₓ released from decomposition of PAN and potentially photolysis of HNO₃, Figure 4 (middle column) shows that NOₓ was also enhanced in the anthropogenic plumes relative to background during all seasons.

[30] Although NOₓ observations in North American outflow were limited in number, enhancements of NOₓ in the North American plumes indicate that North American emissions are an important source of NOₓ to the central North Atlantic lower FT all year-round. The larger mean ∆NOₓ/∆CO ratio during fall suggests that the largest supply of NOₓ to the central North Atlantic lower FT may occur during this season. This effect is probably the result of direct export of NOₓ from North America as some of the fall events were associated with rapid transport from the United States (≤2 days), according to FLEXPART retracemal analysis. In addition, the combination of relatively rapid thermal decomposition of PAN to NOₓ and slower conversion of NOₓ to HNO₃ in the plumes during this season may have also contributed to the NOₓ enhancements [Val Martin et al., 2008]. However, additional measurements to better constrain these enhancement ratios would be useful because the fall values are not significantly greater from those in other seasons.

4.5. Implications for the O₃ Production

[31] We examined the relationship between NOₓ and O₃ on a seasonal basis in Figure 4 (right column) to investigate whether exported nitrogen oxides have the potential to cause O₃ production. Seasonal ∆O₃/∆NOₓ averages are also presented in Figure 4.

[32] The seasonal ∆O₃/∆NOₓ averages indicate an approximately 80-fold, 100-fold, and 60-fold enrichment of O₃ relative to NOₓ (ppbv/ppbv⁻¹) during spring and fall, summer, and winter, respectively. The ∆O₃/∆NOₓ of 100 ppbv ppbv⁻¹ is an order of magnitude higher than that observed in several rural sites in North America during the summer seasons (8.5–10 ppbv ppbv⁻¹ [Trainor et al., 1993; Olczyka et al., 1994]), is on the upper limit of what was encountered in the FT over North America (~38–100 ppbv ppbv⁻¹ [Ridley et al., 1994]) and is moderately larger than those reported over the western North Atlantic region (~10–50 ppbv ppbv⁻¹ [Buhr et al., 1996]). The summer ∆O₃/∆NOₓ observed at the Pico Mountain station is thus consistent with formation of O₃ over the continent and adjacent region, followed by a high NOₓ loss (via HNO₃ wet/dry deposition) and moderate O₃ destruction during transit to the measurement site. The absence of a negative slope implies that O₃ destruction did not dominate O₃ production during the lifetime of these plumes. This result contrasts with prior studies over the North Atlantic region, which concluded that the marine BL and lower FT over the North Atlantic are generally in a state of net O₃ destruction all year-round [e.g., Honrath et al., 2008; Parrish et al., 1998, Reeves et al., 2002]. For example, Parrish et al. [1998] indicated that, upwind of the North Atlantic marine boundary layer during winter, O₃ loss dominates, with a ∆O₃/∆NOₓ ratio of −1.5 to −1 ppbv ppbv⁻¹. The absence of net O₃ destruction in the North American plumes observed at the Pico Mountain station and the significant levels of NOₓ remaining in the plumes imply a potential impact on the regional O₃ budget, even during the winter.

5. Influence of Boreal Wildfires

[33] Transport of North American boreal wildfire emissions substantially impacted the nitrogen oxides measured at the Pico Mountain station during summer 2004 [Val Martin et al., 2006]. On an event-by-event basis, the average levels of nitrogen oxides in boreal wildfire plumes were above levels observed during flow from boreal regions without fire emissions and were well above typical regional summertime background levels [Val Martin et al., 2006]. We expand here this previous work and investigate the degree to which boreal wildfire emissions modulate the nitrogen oxides background in the central North Atlantic lower FT. For this purpose, we analyzed nitrogen oxides observations made from 1 June to 15 September in 2004 and 2005. Similar to summer 2004, summer 2005 boreal wildfire emissions from Canada and Alaska frequently impacted the Pico Mountain station [Lapina et al., 2008]. In summer 2002 and 2003, wildfires emissions from Quebec and Siberia, respectively, impacted the measurement site [Honrath et al., 2004]. However, nitrogen oxides measurements were limited during those summers [Val Martin et al., 2008]. The time frame 1 June through 15 September was selected since it covers the typical active burning season over northern North America [Pfister et al., 2005] and allows for the 1–2 weeks transport time to the measurement site at the end of the season.

[34] We divided the data into two categories: one category representing observations significantly influenced by boreal wildfires (“fire”) and a second category representing observations with minimal or no fire impact (“nonfire”). Fire and nonfire observations were selected on the basis of the intensity of North American boreal wildfires impact simulated by the FLEXPART Fire-CO. The 25th and 75th percentiles of all FLEXPART Fire-CO values for each summer were used for the nonfire and fire cutoffs, respectively. These lower and upper cutoff values were selected to allow both categories to contain a similar number of data points. The cutoff values were different for each year, i.e., 1.4 ppbv and 16.4 ppbv for 2004 and 0.9 ppbv and 5.6 ppbv for 2005, reflecting the different intensity of the boreal wildfires in 2004 and 2005. Figure 5 shows the distribution of NOₓ and NOₓ for the fire and nonfire periods. We also show the distribution for all summer observations. (The distribution of CO is also shown for comparison.) Table 1 summarizes the statistical parameters of each distribution for each summer.

[35] Boreal wildfire emissions affected the summertime distribution of nitrogen oxides at the Pico Mountain station. NOₓ median values in the fire subset were 175 pptv and 117 pptv larger than those in the nonfire subset in 2004 and 2005, respectively. Similarly, the difference in the NOₓ median values were 30 pptv in 2004 and 9 pptv in 2005. As expected, median values for CO were also larger in the fire subset relative to the nonfire subset, with a difference of 40 ppbv in 2004 and 11 ppbv in 2005. A nonparametric
Wilcoxon Sum-rank and a student $t$ test indicated that all distributions and their means were significantly different at the 0.01 level of significance. The larger enhancements observed in 2004 relative to 2005 are due to the higher fire activity over the North American boreal region in 2004 than in 2005: total CO emissions estimated using the Boreal Wildland-Fire Emissions Model were 37 Tg in summer 2004, whereas they were 24 Tg in 2005 [Lapina et al., 2008].

To verify that the difference in the medians was the result of boreal wildfire emissions, we inspected the periods selected in each category. While the nonfire subset contained observations made in a mixture of both nonboreal and boreal air without wildfire emissions, the fire subset included periods when boreal outflow reached the Pico Mountain station during the active burning season [Val Martin et al., 2006]. Although some fraction of the difference between both subsets may be due to the difference in background levels, this effect is rather small compared to the effect of boreal wildfire emissions [Val Martin et al., 2006, Table 1].

Overall, these analyses indicate that boreal wildfires were responsible for a substantial shift in the nitrogen oxides distributions toward higher mixing ratios. Given the long distance from the boreal region to the Pico Mountain station, this implies very large-scale impacts on the background NO$_x$ and NO$_y$ levels in the midlatitude lower FT. These impacts of boreal wildfire emissions on the O$_3$ background over the North Atlantic region consistent with Lapina et al. [2006], the difference between the median values in the nonfire and fire subsets for O$_3$ were 26 ppbv in 2004 and 17 ppbv in 2005 (not shown).

### 6. Summary and Conclusions

Measurements at the Pico Mountain station show that nitrogen oxides levels in the central North Atlantic lower FT are significantly increased when North American anthropogenic emissions are present. The NO$_x$ and NO$_y$ median values during periods when these emissions reached the measurement site were respectively 4–11 pptv and 22–177 pptv larger than those observed during clean periods. $\Delta$NO$_x$/CO enhancement ratios observed in North American outflow indicate that, consistent with previous observations, the majority (94–97%) of NO$_x$ emitted over the United States is removed before or during export out of the United States BL and on to the central North Atlantic. However, these fractions imply that about 30% of the emissions that escape the United States BL are transported as NO$_y$ to the lower FT over the central North Atlantic region. A larger mean $\Delta$NO$_x$/CO values in these plumes indicate that decomposition of PAN to NO$_x$ and potentially photolysis of HNO$_3$ occurring in the air masses during subsidence and/or ad-

### Table 1. Statistics of Summertime NO$_x$, NO$_y$, and CO Distribution

<table>
<thead>
<tr>
<th>Year</th>
<th>NO$_y$ (pptv)</th>
<th>NO$_x$ (pptv)</th>
<th>CO (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Median N</td>
<td>Mean Median N</td>
<td>Mean Median N</td>
</tr>
<tr>
<td>2004</td>
<td>229 169 1529 30</td>
<td>31 27 888 40</td>
<td>94 91 3943</td>
</tr>
<tr>
<td>All</td>
<td>Fire Nonfire</td>
<td>All Fire Nonfire</td>
<td>All Fire Nonfire</td>
</tr>
<tr>
<td>2005</td>
<td>243 234 1006 9</td>
<td>31 28 645 11</td>
<td>97 97 3908</td>
</tr>
<tr>
<td>All</td>
<td>Fire Nonfire</td>
<td>All Fire Nonfire</td>
<td>All Fire Nonfire</td>
</tr>
<tr>
<td>2004</td>
<td>294 288 238 105</td>
<td>36 34 174 105</td>
<td>105 103 863</td>
</tr>
<tr>
<td>2005</td>
<td>228 171 358 94</td>
<td>26 25 202 94</td>
<td>92 1267</td>
</tr>
</tbody>
</table>

$^a$Reported are mean, median, and number (N) of 30-min average observations in pptv for NO$_y$ and NO$_x$ and ppbv for CO.

$^b$$\Delta$Median is the difference between the medians in the fire and the nonfire subsets. (See text for description.)
vection westward to the Azores constitute an important source of NO$_3$ to the central North Atlantic lower FT.

[39] While CTMs indicate that most of the net O$_3$ production occurs near North America [e.g., Li et al., 2004], the observed $\Delta$O$_3$/ANO$_3$ and the significant NO$_y$ levels remaining in the North American plumes suggest that a substantial amount of additional ozone formation occurs in the anthropogenic plumes during transport to the central North Atlantic lower FT.

[40] Boreal wildfire emissions were responsible for important shifts in the nitrogen oxides distributions toward higher levels, when median NO$_x$ and NO$_y$ were respectively 117–175 pptv and 9–30 pptv greater than during periods without the presence of boreal wildfire emissions. Since our observations were made very far downwind from the boreal region, we conclude that aged boreal fire emissions significantly altered the background NO$_x$ and NO$_y$ levels over a large region of the Northern Hemisphere. During the summer, boreal wildfire emissions appear to obscure the impact caused by North American emissions. This highlights the need to understand the impact of boreal wildfires on tropospheric NO$_y$ levels and the resulting implications for O$_3$, even if only to evaluate the influence of anthropogenic emissions on NO$_x$ and O$_3$ budgets during the summer season.

[41] Our analyses show the important hemispheric scale impact that North American outflow and boreal wildfire events have on the background NO$_x$ and NO$_y$ levels and on the tropospheric O$_3$ budget. Recent studies have shown that significant changes in global fossil-fuel NO$_x$ emissions have occurred over the last decades [Richter et al., 2005; Frost et al., 2006] and larger changes are expected in the future. In addition, as a result of climate change, more frequent and severe boreal wildfires are also expected, which may result in an increase in the boreal wildfire emissions [Stocks et al., 1998; Flannigan et al., 2000]. Therefore, the influence of these emissions may grow even larger in the upcoming years.

[42] Acknowledgments. We thank M. Dziobak (Michigan Tech, United States) for helping to maintain the NO$_x$/NO$_y$ system at the Pico Mountain station. P. Fialho (University of the Azores, Portugal) was co-cordinator of the Pico Mountain station during the period of this study and assisted greatly with station operation; he is now station coordinator. In addition, we thank E. Hyer (Marine Meteorology Division at NRL, United States) for supplying the boreal wildfire emission inventory from the Boreal WildLand Fire Emission Model, J. Kleissl (University of California at San Diego, United States) for providing the analysis of upslope flow periods, and D. Henriquez (Institute of Meteorology, Portugal) for providing the ECMWF data used to run the FLEXPART simulations. This work was supported by NOAA, Office of Global Programs grants NA16GP1658, NA06GP25, and NA03AR4310002; the National Science Foundation grants ATM-0215843, ATM-0554586, and INT-0110397; Azores Cooperative Initiative Program USD grant 58-3625-5-127; Azores Regional Secretariat for Science and Technology (project M2.1.1/006/2005, project M2.1.1/001/2008, and project M2.1.1/002/2008); and Program INTERREG IIIIB, Azores, Madeira, and Canaries (project CILMARCOST FEDER-INTERREG IIIIB-05/MAC/2/3/A).