Seasonal variation of nitrogen oxides in the central North Atlantic lower free troposphere

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¹Dept. of Civil and Environmental Engineering, Michigan Technological University, Houghton, Michigan, USA ²Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA X - 2 VALMARTIN ET AL.: REMOTE NORTH ATLANTIC NITROGEN OXIDES Measurements of NO, NO₂ and NO_u (total reactive nitrogen Abstract. oxides) made at the Pico Mountain station, 38.78°N 28.67°W, 2.3 km asl, from July 2002 to August 2005 are used to characterize the seasonal and diurnal variations and the speciation of nitrogen oxides in the background lower free troposphere (FT) over the central North Atlantic Ocean. These observations reveal a well-defined seasonal cycle of nitrogen oxides ($NO_x = NO + NO_2$) and NO_{y} , with higher mixing ratios during the summertime. Observed NO_{x} and NO_y levels are consistent with long-range transport of emissions, but with significant removal en-route to the measurement site. Larger summertime nitrogen oxides levels are attributed to impacts of boreal wildfire emissions and more efficient export of NO_{y} from eastern North America during this season. Reactive nitrogen over the central North Atlantic lower FT largely exists in the form of PAN and HNO₃ ($\sim 80-90\%$ of NO_u) year-round. A shift in the composition of NO_y from dominance of PAN to dominance of HNO₃ occurred from winter-spring to summer-fall, as a result of changes in temperature and photochemistry over the region. A further comparison of the nitrogen oxides measurements with results from the global chemical transport (GCT) model GEOS-Chem identifies differences between the observations and the model, with simulated nitrogen oxides significantly larger than the observations.

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1. Introduction

Reactive nitrogen species are critical to the chemistry of the atmosphere. Photochemical production of O_3 depends on the concentration of NO_x (NO+NO₂), which in turn, influences the concentration of tropospheric OH. Species that affect OH are important, as reaction of OH provides the dominant path for removal of a variety of atmospheric pollutants [*Crutzen*, 1979; *Logan*, 1983]. In addition, nitric acid, the primary end product of NO_x oxidation, is one of the major components of acid deposition.

Understanding the impact of NO_x on tropospheric O_3 on a global scale is important 7 for several reasons. Ozone is considered the third most important anthropogenic greenhouse gas [IPCC, 2007]. In addition, slightly elevated levels of O_3 , at concentrations q not far above current ambient levels in many regions, pose a serious concern because of 10 their effects on the human respiratory system and ecosystems. In particular, there is an 11 increasing concern regarding intercontinental transport of O₃ pollution since it appears 12 to be changing the composition of the background troposphere [Simmonds et al., 2004; 13 Jaffe et al., 2003] and making it more difficult for countries downwind to achieve their air 14 quality standards [Li et al., 2002; Derwent et al., 2004]. 15

In the Northern Hemisphere, emissions of nitrogen oxides are dominated by anthropogenic sources in urban and industrial regions [Logan, 1983]. In addition, as a result of increased area burned and fire frequency over the boreal region [Kasischke and Turetsky, 2006], emissions from the boreal wildfires have resulted in a significant source of NO_x to the atmosphere during the summer season [Goode et al., 2000; Andreae and Merlet, 2001]. The impact of NO_x emissions from these sources on global O₃ is limited as oxidation of

 NO_x to HNO_3 , peroxyacetyl nitrate (PAN) and other minor compounds occurs in less 22 than one day in the continental boundary layer (BL). However, the dependence of O_3 23 production of NO_x is highly non-linear [Liu et al., 1987]. This means that the number 24 of O_3 molecules produced per molecule of NO_x consumed, known as the O_3 production 25 efficiency, increases as NO_x concentration decreases. As a result, the export of small frac-26 tions of emitted NO_x may lead to significant O_3 production in the remote troposphere 27 [Jacob et al., 1993]. The export of NO_x away from the source regions is facilitated by the 28 export of PAN, a thermally unstable, insoluble species, out of the continental BL, followed 29 by the transport of PAN on a global scale at cold temperatures, and decomposition to 30 NO_x as the airmasses become warmer [Moxim et al., 1996]. It has been suggested that, 31 similar to PAN, the export of HNO_3 followed by photolysis to NO_x can be an important 32 source of NO_x even in the lower troposphere [Neuman et al., 2006]. Thus, quantifying 33 the magnitude of nitrogen oxides and their chemical evolution in the remote troposphere 34 is fundamental to understand the impact of anthropogenic emissions on the global O_3 35 budget. 36

Field measurement campaigns have been conducted in the last two decades to characterize the spatial and temporal distribution of tropospheric NO_x and to determine the resulting effect of NO_x emissions on the O_3 budget. However, data composites of results from many of these campaigns show that the spatial and temporal coverage of remote tropospheric NO_x measurements is still quite sparse and reflects a strong seasonal and regional bias [*Emmons et al.*, 1997; *Bradshaw et al.*, 2000; *Emmons et al.*, 2000; *DiNunno et al.*, 2003]. In addition to measurement campaigns, global chemical transport (GCT) models have been developed to derive the global impact of anthropogenic and boreal wildfire emissions on the O_3 budget. However, it is difficult to assess the uncertainty of the resulting estimates, in particular those related to NO_x sources and photochemical processes. The evaluation of GCT models using nitrogen oxides observations in the free troposphere (FT) has been limited by a lack of data in remote regions [*e.g. Thakur et al.*, 1999; *Lawrence and Crutzen*, 1999].

Recently, satellite-derived data have been used to derive global and regional NO_x bud-51 gets [e.g. Leue et al., 2001; Martin et al., 2004; Jaeglé et al., 2005; Richter et al., 2005] 52 and detect intercontinental transport of nitrogen oxides plumes from boreal wildfires 53 [Spichtinger et al., 2001] and anthropogenic sources [Wenig et al., 2003; Stohl et al., 54 2003]. More recently, satellite data have been used to evaluate GCT models [e.g. Liu55 et al., 2006; Chandra et al., 2004]. However, the limited measurements of nitrogen oxides 56 in the remote lower FT make the evaluation of satellite-derived data difficult [Leve et al., 57 2001; Martin et al., 2004]. 58

The data presented in this paper constitute a multi-year record of NO, NO_x and NO_y 59 in the central North Atlantic lower FT determined at the Pico Mountain station. These 60 data are analyzed with two purposes: to characterize the seasonal and diurnal variation 61 of nitrogen oxides in the background lower FT over the central North Atlantic region 62 and to determine the partitioning of reactive nitrogen over this region. Observations are 63 also compared with simulations from the GCT model GEOS-Chem to assess our current 64 understanding of the fate and transport of nitrogen oxides in the remote North Atlantic 65 troposphere. Additional analyses are presented in a companion paper (Val Martín et 66

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al, Large-scale impacts of anthropogenic pollution and boreal wildfires on the nitrogen oxides levels over the central North Atlantic region, submitted to *J. Geophys. Res.*, 2007, hereinafter referred to as *Val Martín et al*, submitted), in which we use these observations of nitrogen oxides in combination with simultaneous measurements of CO and O₃ to assess the degree to which transport of anthropogenic and boreal wildfire emissions affect nitrogen oxides levels and the resulting implications for the hemispheric NO_x and O₃ budgets.

2. Methodology

⁷⁴ Measurements of NO, NO₂, NO_y were made at the Pico Mountain station from July 20, ⁷⁵ 2002 to August 25, 2005. We present here measurements of nitrogen oxides analyzed in ⁷⁶ combination with measurements of CO also made at the Pico Mountain station. Because ⁷⁷ the Pico Mountain station and measurement details have already been described elsewhere ⁷⁸ [Honrath et al., 2004; Kleissl et al., 2007; Owen et al., 2006; Val Martín et al., 2006], only ⁷⁹ a brief summary of the most relevant experimental aspects is presented here.

2.1. Measurement Site

The Pico Mountain station is located on the summit of Pico mountain (2.2 km asl) in the Azores Islands, Portugal (38.78°N, 28.67°W). During all seasons, the station is well above the regional marine boundary layer, which is typically less than 1 km in height from May to September and less than 1.4 km from October to April [*Kleissl et al.*, 2007]. Upslope flow can bring air from lower altitudes to the station, including occasionally from the marine BL. However, upslope flow affects the Pico Mountain station much less than it does many other mountain observatories. An intensive study of the occurrence

of upslope flow on Pico Mountain indicated that, from May to September, less than 25%87 of the measurement time presented the meteorological conditions required for an airmass 88 from below the marine BL to reach the summit via buoyant uplifting, *i.e.*, weak synoptic 89 winds and strong insolation. From October to April, buoyant upslope flow is unusual, 90 but strong synoptic winds provide the potential for mechanical uplifting. This potential 91 mechanical upslope flow has a strong seasonal cycle, which depends on stronger winds and 92 higher marine BL heights during winter. As a result, the monthly potential frequency of 93 marine BL lofting to the summit is 35–60% from October to April, whereas it is less 94 than 20% from May to September. The actual frequency of BL impacts is smaller than 95 this, however, because Pico Mountain is very steep and narrow, and airflow around the 96 mountain modifies the upslope flow. Impacts of mechanical and buoyant upslope flow 97 on nitrogen oxides, CO and O_3 are small [Kleissl et al., 2007], indicating that the air 98 sampled at the site is usually negligibly influenced by island pollution. or differing mixing 99 ratios in the marine BL below. The results obtained in this study are consistent with this 100 expectation. For example, in periods with potential mechanical and/or buoyant upslope 101 flow mean NO_x was 33 ± 5 pptv (mean ± 2 -standard error of the mean), whereas it was 102 30 ± 1 pptv during non-upslope flow periods. 103

2.2. Measurements

¹⁰⁴ NO, NO₂, and NO_y were determined by an automated NO_{x,y} system, which used estab-¹⁰⁵ lished techniques for high sensitivity detection: NO detection by O₃ chemiluminescence ¹⁰⁶ [*Ridley and Grahek*, 1990], NO₂ by conversion to NO via ultraviolet photodissociation ¹⁰⁷ [*Kley and McFarland*, 1980; *Parrish et al.*, 1990], and NO_y by Au-catalyzed reduction ¹⁰⁸ to NO in the presence of CO [*Bollinger et al.*, 1983; *Fahey et al.*, 1985]. A detailed de¹⁰⁹ scription of the $NO_{x,y}$ system including operation, sensitivities, conversion efficiencies, ¹¹⁰ precision and artifacts can be found in *Val Martín et al.* [2006].

Measurements were recorded as 30-s averages (NO and NO₂) and 20-s averages (NO_u) 111 every 10 min, and further averaged to obtain the 30-min averages used in this work. The 112 instrumental detection limit $(2-\sigma)$ of the 30-min averages was 6.5 to 16 pptv for NO, 13 113 to 17 pptv for NO₂, 14 to 21 pptv for NO_x and 7.5 to 21 pptv for NO_y based on the 114 artifact correction uncertainty and the precision $(2-\sigma)$ of the instrument. Ninety percent 115 of the measurements had detection limits less than 6.5 pptv for NO, 16 pptv for NO₂ 116 and NO_x, and 19 pptv for NO_y. Measurement accuracy is estimated to be 5% (July 20, 117 2002–July 17, 2003), 7% (July 17, 2003–May 1, 2004) and 4% (May 1, 2004–August 27, 118 2005) based on total uncertainty of the sample and calibration mass flow controllers and 119 the NO standard calibration gas mixing ratio. 120

Accuracy of the NO_y measurements depends on the effective conversion of NO_y com-121 pounds and the lack of significant conversion of non-NO_y compounds [Fahey et al., 1985; 122 Kliner et al., 1997; Kondo et al., 1997, in addition to the accurate determination of 123 the resulting NO. Based on regular calibrations and standard addition tests with NO_2 , 124 i-propyl nitrate and HNO₃ in ambient air, the observed NO_u included 80–100% of the 125 actual NO₂ level (typically >97%), with similar values expected for PAN [Fahey et al., 126 1985], 62–100% of the actual HNO₃ level (typically >80%), and 61–100% of the actual 127 i-propyl nitrate (typically >80%). Due to occasional degradation of the NO_y converter, 128 measurements of NO_y were corrected for non-unity NO_y conversion by using the NO_2 129 conversion efficiencies measured at the system. A maximum correction of 20% was ap-130 plied to a few of the measurements made before March 2003 and a maximum correction 131

of 8% was applied to measurements made from mid-July to mid-August 2004. No correc-132 tion was made after mid-August 2004 as the NO_2 conversion efficiency was constant to 133 the expected value of 97–100%. In addition, NO_{y} observations in March–May 2003 and 134 May–June 2004 presented an additional uncertainty of 13% and 5% due to uncertainty in 135 the NO_{y} sensitivity determination. Based on the NO_{y} composition estimated at the Pico 136 Mountain station (section 3.3.1) and the uncertainty of NO determination, the total NO_{u} 137 uncertainty, mainly due to potentially incomplete conversion to NO, was estimated to be 138 at worst $\sim 55\%$, from March to May 2003 (less than 3% of the total dataset). During most 139 periods, total measured uncertainty was $\leq 20\%$ at NO_y levels of 100 pptv and $\leq 15\%$ at 140 NO_{y} levels of 500 pptv. Interference of non- NO_{y} species was not a problem in this study as 141 inferred from the very low conversion efficiencies (always less than 0.5%; typically 0.3%) 142 during regular testing using standard addition of CH₃CN. 143

As discussed by Val Martín et al. [2006], unexpected spikes were sometimes observed in 144 ambient NO_x and NO_y , and were attributed to volcanic emanations. To avoid including 145 these observations in our analysis, we used methods similar to but slightly more stringent 146 than those used previously [Val Martín et al., 2006]. First, we excluded measurements 147 made during calm winds (wind speed below 2 m s⁻¹) and when wind data were not 148 available. Two exceptions were made. The fire-impacted period of September 1–5, 2004, 149 which did not present the typical spikes associated with volcanic emissions [Val Martín 150 et al., 2006] was included, although wind speeds were lower than 2 m s⁻¹. During the 151 periods of October–May and June 2004, wind data were scarce due to ice blockage or 152 malfunctioning of the sensor and observations when wind data were not available were 153 included. However, including these observations did not compromise our results as the 154

nitrogen oxides levels in the limited calm wind periods during these months were not 155 significantly different than those in the overall data. (For example, from October to May, 156 mean NO_x was 26 ± 2 pptv (mean ± 2 -standard error of the mean) in periods with wind 157 speeds below 2 m s⁻¹, whereas it was 28 ± 1 pptv for the overall period.) Second, we 158 excluded observations that exhibited high ambient variability. For this purpose, periods 159 with high ambient variability were defined as those when the standard deviation of the 160 30-s points in a 30-min period (SD) was above 8 pptv for NO or above 20 pptv for 161 NO_2 or NO_x , or the NO_y SD exceeded 20pptv + 0.5($[NO_y] - 50$), where the second term 162 was included to allow for increased ambient variability during periods of high $[NO_{y}]$. 163 Observations made within ± 3 hours of identified high variability observations were also 164 excluded. The wind speed criterion removed about 20% of the measurements from the 165 overall dataset, and the ambient variability screen criterion removed an additional 20% for 166 NO_y and 34% for NO_x . Finally, with the purpose of identifying additional periods with 167 potential influence of volcanic emissions, we excluded observations made during buoyant 168 upslope flow as described by *Kleissl et al.* [2007]. These periods were characterized by 169 low wind speeds, conditions in which volcanic emissions may potentially be detectable. 170 This screening removed an additional 6% and 3% of the NO_y and NO_x measurements, 171 respectively, mostly during the summer. 172

In remote regions without significant biogenic NO_x emissions, nighttime NO values are expected to be zero due to the rapid oxidation of NO by O_3 and the expected absence of local sources [*Ridley et al.*, 1998; *Peterson et al.*, 1998]. This was true for all seasons, with the exception of summer 2004, which presented a nighttime median of 3 pptv. It was not possible to conclusively determine the reason for the generally non-zero nighttime

NO levels during summer 2004. However, the weather at Pico that summer was unusual 178 since it was dominated by high relative humidity (RH) and calm wind periods. This 179 may have resulted in a very small but detectable flux of NO from soil bacteria around 180 the station. These non-zero nighttime NO observations could not be removed by any 181 screening criterion attempted and systematically affected the measurements during this 182 season. These emissions would presumably affect NO during the daytime and NO_x both 183 day and night as well. However, the interference from this source does not appear to 184 significantly affect the results: if we exclude the 2004 NO summertime observations, 185 the diurnal cycle and seasonal variation presented below do not significantly change. For 186 example, summer daytime median NO was 7.9 pptv in 2002–2005, whereas it was 7.7 pptv 187 excluding the summer 2004 dataset. 188

Finally, during some sunny summer periods the temperature of the NO₂ converter system increased to the extent that PAN decomposition could have produced a detectable positive bias in the NO₂ measurements. At the maximum temperature recorded in the NO₂ converter system (39° C), up to about 2–4 pptv NO₂ could have been produced during the ~8 second residence time in the NO₂ converter. This small interference may have contributed to the apparent daytime NO₂ source described below, at least during summer and early fall.

We also analyzed measurements of CO made from July 2002 to August 2005. The CO measurement methods are described in detail elsewhere [*Owen et al.*, 2006; *Honrath et al.*, 2004].

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2.3. GEOS-Chem and FLEXPART Simulations

Simulations of the global chemical transport model GEOS-Chem were conducted for 199 comparison with the observations. GEOS-Chem version 7.01 was driven by 3-hourly as-200 similated meteorological fields from the Goddard Earth Observing System of NASA [Bey 201 et al., 2001]. The spatial resolution of the model was 2° latitude by 2.5° longitude with 202 26 levels between the surface to 0.1 hPa. Global anthropogenic emissions were determined 203 following the procedure described by *Bey et al.* [2001]. Over the continental U.S. and Eu-204 rope, the anthropogenic emissions were based on the U.S. EPA NEI-97 [EPA, 1997] and 205 the European Monitoring and Evaluation Program for European countries [*EMEP*, 1997]. 206 Biomass burning emissions were obtained from Duncan et al. [2003] with monthly mean es-207 timates relocated using Moderate-resolution Imaging Spectroradiometer fire counts. More 208 information on these emissions and additional sources (e.q., lightning, stratospheric injec-209 tion) is presented elsewhere [Bey et al., 2001]. 210

To evaluate the sensitivity of our measurements to stratospheric transport, we used 211 the FLEXPART particle dispersion model version 6.2 [Stohl, 1998; Stohl et al., 2005]. 212 FLEXPART was driven with data from the European Centre for Medium Range Weather 213 Forecasts (ECMWF) [ECMWF, 2005] with a 1°x 1° horizontal resolution, 60 vertical levels 214 and a temporal resolution of three hours, using meteorological analyses at 0000, 0600, 215 1200, and 1800 UTC, and ECMWF 3-hr forecasts at 0300, 0900, 1500 and 2100 UTC. 216 We ran FLEXPART in its forward mode to simulate the transport of a stratospheric 217 O_3 tracer. This was done by releasing particles in the lower stratosphere. Each particle 218 carried a mass of ozone determined by the potential vorticity (PV) at the particles initial 219 location and release time. Particles released where PV was greater than 2.0 pvu were 220

given a specific mass according to $MO_3 = Mair \times PV \times C$, where Mair was the mass of air represented by a particle and $C = 60 \times 10^{-9} \text{pvu}^{-1}$ was the ozone/PV relationship [*Stohl et al.*, 2000]. Particles were then allowed to advect through the stratosphere and into the troposphere according to the winds. At any one time, approximately 4 million particles were present in the model for these stratospheric tracer runs. Particles were carried in the model for 20 days before being removed. This tracer is referred to here as FLEXPART Strat-O₃.

3. Results and Discussion

Figure 1 presents an overview of the nitrogen oxides measurements at the Pico Mountain station from July 2002 to August 2005. All 30-min averages of daytime NO, NO_x and NO_y are shown as time series, and bar plots represent the distribution of the data by season and year.

Significant variability is apparent in the data at all times of the year. A large number of factors contribute to the magnitude and the changes of the nitrogen oxides levels. In this section, three aspects of the data are analyzed: diurnal cycles, seasonal variation and partitioning of NO_y . These aspects are not entirely independent but provide a structure for discussion.

3.1. Diurnal Cycles

²³⁷ Diurnal cycles of nitrogen oxides can be caused by photochemical, transport and emis-²³⁸ sion processes whose strength vary between day and night. Table 1 summarizes the ²³⁹ statistical parameters of the diurnal cycles of NO, $[NO]/[NO_2]$, NO₂ NO_x and NO_y for ²⁴⁰ each season. As an example, Figure 2 displays the diurnal variation for the springtime

measurements of NO, $[NO]/[NO_2]$, NO₂ and NO_y. (Similar variation was present in the 241 other seasons.) For the $[NO]/[NO_2]$ analysis, values that deviated from the mean by more 242 than three times of the standard deviation were removed. This was done because NO_2 243 and NO measurements are related as the calculation of NO₂ includes the NO mixing ratio. 244 Hence, rare outliers in the NO measurements may result in NO₂ outliers, which produces 245 unrealistic [NO]/[NO₂] values that may significantly affect the mean [Yang et al., 2002].

To test for the existence of a consistent diurnal variation, we examined both the median 247 and the mean of the data in the nighttime and daytime subsets. Nighttime values were 248 observations made between 23:00 and 5:00 UTC; daytime values were those made when 249 the solar zenith angle was below 62°. These cutoffs were chosen to allow significant 250 numbers of data points in both subsets while providing daylight and nighttime conditions 251 in all seasons. As expected, Table 1 indicates that robust diurnal cycles exist for NO and 252 $[NO]/[NO_2]$ ratios in all seasons, with median diurnal amplitudes of 5–7 pptv and 0.3– 253 0.4, respectively. The phase of these cycles is consistent with photochemical causes: the 254 maximum occurs around the time of maximum insolation at local solar noon (14:00 UTC 255 for spring; Figure 2), indicating a dominance of production of NO from photolysis of NO_2 , 256 whereas the minimum occurs at nighttime, indicating dominance of NO destruction by 257 reaction with O_3 . 258

Given the observed NO cycle amplitude, a negative amplitude of similar magnitude 259 should be present in the NO_2 cycle as NO_2 is photolyzed to NO during daytime. Figure 2c 260 and Table 1 indicate that a very weak negative diurnal variation or no variation was 261 present for NO₂, with median diurnal amplitudes of -2 to 3 pptv. This small negative or 262 non-existent amplitude suggests the presence of a small source of NO_2 during daytime. As 263

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discussed in section 2, this may be partially the result of interference of PAN decomposition in the photolysis cell during summer and early fall. The absence of a negative or no diurnal variation of NO₂ results in the presence of a diurnal cycle for NO_x from spring to fall, with amplitudes medians of 4 to 8 pptv (Table 1).

Consistent with our expectation that diurnally varying upslope flow does not affect 268 the measurements [Kleissl et al., 2007], Figure 2d and Table 1 show that no significant 269 diurnal variation was present for NO_{y} , with the exception of the summer, which exhibited 270 a negative median amplitude of 36 pptv. This may be due to the strong removal nature of 271 summertime NO_y , which is composed primarily by HNO_3 , as shown below in section 3.3.1. 272 Summertime RH measurements at the Pico Mountain station indicate that the percentage 273 of NO_y observations made in the presence of clouds (RH above 96%, section 3.3.1) was 274 larger during the daytime (24%) than at nighttime (16%), which may result in a stronger 275 wet removal of HNO_3 during the day. 276

Comparisons of the diurnal variation observed at the Pico Mountain station to those 277 observed at other remote marine FT stations are not straightforward. As opposed to the 278 Pico Mountain station, ground-based mountaintop stations (e.g., Mauna Loa Observatory 279 (MLO) over the North Pacific Ocean and Izaña over the eastern Atlantic Ocean) are 280 typically characterized by a diurnal downslope-upslope flow regime [*Ridley et al.*, 1998; 281 Fischer et al., 2004]. However, spring diurnal amplitudes of ~ 8 pptv for NO and ~ 0.4 for 282 NO/NO_2 were observed at MLO during a rare event in which free tropospheric air was 283 sampled all day [*Ridley et al.*, 1998], similar to the spring amplitude observed at the Pico 284 Mountain station for NO $(8 \pm 2 \text{ pptv})$ and for $[\text{NO}]/[\text{NO}_2]$ (0.4 ± 0.2) . 285

3.2. Seasonal Variation

In this section, we first determine the seasonal variation of nitrogen oxides on a monthly basis. Second, we compare the mixing ratios of nitrogen oxides at the Pico Mountain station with observations from previous studies.

²⁸⁹ 3.2.1. Annual Cycle

Figures 3a-c present the annual cycle of nitrogen oxides at the Pico Mountain station. 290 All years are included, and the monthly medians in each year are indicated with numerals 291 to the right of each bar. For NO_{u} , Figure 3c shows the seasonal cycle determined when 292 dry conditions were present (RH below 60%). (Lower NO_y levels were observed when 293 RH was high, due to removal into fog droplets, as discussed further in section 3.3.1.) In 294 Figure 3d, the annual cycle of CO is also shown for comparison. The monthly statistics 295 plotted in Figure 3 are available in Val Martín [2007]. It is clear from Figure 3a-d that 296 there is a large interannual variability in the CO and nitrogen oxides monthly medians 297 within some months. Large variability of CO at hemispheric scales is known to occur, 298 and has mainly been associated with variations in biomass burning emissions [e.q., Novelli 299 et al., 2003; Edwards et al., 2004; Honrath et al., 2004]. Although interannual variability 300 is also apparent for the nitrogen oxides, we find that in some cases this variability may 301 be due to the limited number of observations available and the fact that transport events 302 result in large standard deviations within each month. For example, NO_x in October 2002 303 was significantly higher $(47 \pm 3 \text{ pptv}; \text{mean}\pm 2\text{-standard error of the mean})$ than in 2003 304 $(28 \pm 1 \text{ pptv})$ and 2004 $(31 \pm 3 \text{ pptv})$ because NO_x observations were only available for 305 about 10 days in 2002, which happened to coincide with two North American outflow 306 events. 307

Figure 3d shows a sharp seasonal cycle for CO, with a minimum median of 90 ppbv in 308 July–August and a maximum median of 146 ppbv in March. CO is oxidized by OH, and 309 the annual variation of CO is driven to a large extent by the annual cycle of OH, which 310 is closely related to the water vapor and the solar intensity cycle [Novelli et al., 1992]. 311 In addition to photochemical processes, seasonal variation in synoptic flow patterns, and 312 the associated changes in source regions and transport times to the measurement site 313 can also affect the background levels of CO. Based on a clustering analysis of backward 314 trajectories to the Pico Mountain station [Strane et al., Major source regions to the 315 Pico Mountain station: Transport, chemical observations, and interannual variability, 316 manuscript in preparation, more frequent transport from the Atlantic basin and longer 317 transit times from the North American continent in summer may also explain the lower 318 observed summertime CO. The annual variation of OH concentrations and transport 319 patterns was also noted to modulate the non-methane hydrocarbons (NMHC) sampled at 320 the Pico Mountain station [Helmig et al., Analysis of transport and oxidation chemistry in 321 the North Atlantic region from interpretations of NMHC measurements at Pico Mountain, 322 Azores, submitted to J. Geophys. Res., 2007 (hereinafter referred to as Helmig et al., 323 submitted)]. 324

In contrast to CO, the seasonal variation of nitrogen oxides is more complex. The variation of nitrogen oxides in the troposphere remote from sources of NO_x depends largely on the partitioning of NO_y [Atlas et al., 1992; Ridley et al., 1998], which in turn, is controlled to a larger extent by the rate of loss of the reservoir species and by the recycling of NO_x from these reservoirs. Moreover, since the loss processes differ among compounds, each process may result in a different effect on NO_y. For example, thermal decomposition of PAN regenerates NO₂, which changes the partitioning of NO_y but not the total NO_y, whereas wet and dry deposition of HNO₃ results in a change in total NO_y as nitrogen is removed from the atmosphere.

Figure 3a shows that NO_x observations exhibited a distinct seasonal cycle, with the 334 overall variability at all percentiles larger from July to October than in the other months. 335 However, monthly medians did not reveal a clear pattern. Similar monthly medians 336 were present all year round (17–31 pptv). (To avoid the possible interference from a 337 small daytime bias in NO_2 during some summer periods (section 3.1), we also compared 338 nighttime NO_x medians and found similar results: 16-28 pptv). Because the lifetime of 339 NO_x in the lower FT (on the order of $\leq 1 \text{ day } [Liu \ et \ al., 1987]$) is shorter than the transit 340 time from NO_x source regions to the measurement site, it is clear that in-situ sources 341 of NO_x are required to provide these NO_x levels all year round. This implies that PAN 342 decomposition and potentially photolysis of HNO_3 in the airmasses that reach the Pico 343 Mountain station provide a supply of NO_x to the lower FT in this region, in particular 344 during summer seasons. 345

Due to the rapidly increasing solar insolation and decreasing O_3 concentrations from 346 spring to fall, one may expect a shift of NO_x partition toward NO as photolysis of NO_2 347 increases and the rate of the reaction of NO with O_3 decreases. However, the actual situa-348 tion was somewhat different. Figure 3b shows that daytime NO mixing ratios exhibited a 349 small broad peak from July to September, with medians of 9–12 pptv. The increase in NO 350 during these months is consistent with the increase in solar radiation and generally lower 351 O_3 concentrations observed at the Pico Mountain station (not shown). However, a peak 352 was also present in March, with a median of 11 pptv. Although not fully understood, this 353

³⁵⁴ behavior may be the result of a slower rate of reaction of NO with peroxy radicals, which
³⁵⁵ may be present in low concentrations during this month due to a reduced availability of
³⁵⁶ OH.

As shown in Figure 3c, NO_y observations exhibited a well-defined seasonal cycle, with larger values in June–September (medians 296–338 pptv) than in October–May (medians 125–312 pptv). There are several causes that may be responsible for this behavior.

First, synoptic-scale changes in the lofting mechanisms over the continents may result 360 in seasonal changes in the export of emissions. *Parrish et al.* [2004] proposed that shallow 361 venting of the continental BL to the lower FT, driven by surface heating and associated 362 with fair weather cumulus breaking through the afternoon BL, may provide an important 363 lofting mechanism for anthropogenic emissions over the eastern U.S. This mechanism, 364 which is expected to be most frequent in summer, results in a significant export of nitrogen 365 oxides to the North Atlantic region [e.q. Parrish et al., 2004; Li et al., 2004; Hudman et al., 366 2007], and is likely to contribute to the larger summertime levels of NO_y observed at the 367 Pico Mountain station. This assertion is consistent with further analysis of impacts of 368 North American outflow presented by Val Martín et al., [submitted]. 369

Second, boreal wildfires have been recently recognized to be a significant source of nitrogen oxides to the North Atlantic troposphere [Val Martín et al., 2006; Singh et al., 2007]. NO_y means from July to September —typically the boreal fire season— exceeded the medians by 13–18%, showing extreme excursions from the median in the positive direction. The higher variability of NO_y in these months reflects the high but varying influence of boreal wildfire emissions [Val Martín, submitted]. Thus, summertime wildfire emissions result in higher levels of NO_y.

Finally, variation in the input from stratospheric or upper tropospheric sources could 377 also contribute to changes in nitrogen oxides. NO_x production by lightning varies sea-378 sonally, with the maximum production occurring in the Northern Hemisphere during 379 summer [Nesbitt et al., 2000]. Stratospheric injection is found to be more important dur-380 ing springtime [e.q. Parrish and Fehsenfeld, 2000; Merrill and Moody, 1996], although 381 injections are also frequent in summer [Thompson et al., 2007]. To assess the impact of 382 stratospheric and upper tropospheric transport to the Pico Mountain station, we used 383 FLEXPART Strat-O₃ values from July 2002 to August 2005. This analysis indicated that 384 stratospheric O_3 occasionally impacts the measurement site, but the overall impact is 385 rather small: the average \pm 2-standard deviation of all FLEXPART Strat-O₃ values was 386 7 ± 9 ppbv, without significant variation on a seasonal basis. On an event basis, we did not 387 find any consistent correlation between nitrogen oxides levels and FLEXPART Strat-O₃, 388 *i.e.*, enhancements of NO_y were not correlated with increases in the FLEXPART Strat- O_3 389 values. We thus conclude that stratospheric air did not significantly contribute to the 390 changes in the nitrogen oxides observed at the Pico Mountain station. 391

³⁹² 3.2.2. Comparison to Previous Measurements

Table 2 compares the mixing ratios of nitrogen oxides at the Pico Mountain station with observations from previous aircraft studies in the North Atlantic troposphere and from two ground-based stations, MLO over the North Pacific Ocean and Jungfraujoch (JFJ) station over central Europe. Values are compiled by seasons. The majority of these studies were made during the summer season. Thus, we focus here on summertime observations, unless indicated otherwise.

It is evident that nitrogen oxides levels at the Pico Mountain station (median 322 pptv 399 for NO_u and 29 pptv for NO_x ; Table 2 rows 2 and 13) are lower than those observed at 400 other studies over the western North Atlantic at 0.5–6 km altitudes (652–1000 pptv for 401 NO_y and 40–55 pptv for NO_x ; Table 2 rows 5–8 and 16–19). Lower NO_y and NO_x at the 402 Pico Mountain station indicate that removal of NO_y and rapid oxidation of NO_x in the 403 airmasses may occur as a result of longer transport times over the ocean. In addition, 404 lower NO_y and NO_x levels may also indicate a smaller influence of stratospheric and upper 405 tropospheric transport. NO_x and NO_y typically exhibit a C-shaped profile near source 406 regions, with high concentrations near the surface decreasing through the FT and then 407 rising sharply at altitudes generally above 6 km $[e.q. Singh \ et \ al., 2007]$. This is the result 408 of the combination of atmospheric oxidation with the location of the emissions (BL and 409 upper troposphere) and convection. 410

Nitrogen oxides levels observed at MLO (median 168–374 pptv for NO_y and 25–36 pptv 411 for NO_x ; Table 2 rows 3 and 14) were similar to those observed at the Pico Mountain 412 station (147–322 pptv for NO_y and 21–29 pptv for NO_x) all year round. Similar to the 413 Pico Mountain station, MLO is a remote marine observatory, in which well-aged airmasses 414 are sampled during downslope conditions [*Ridley et al.*, 1998]. Thus, observed levels at 415 MLO also reflect the strong removal of NO_y and rapid oxidation of NO_x in the airmasses 416 during transport. In contrast, larger NO_x and NO_y medians present at the continental 417 JFJ observatory (350–581 pptv for NO_y and 87–133 pptv for NO_x ; Table 2 rows 4 and 418 15) suggest the input of relatively fresh NO_x emissions from the continental BL [Zellweger 419 et al., 2003]. 420

3.3. Average Partitioning of NO_y

DRAFT

To better understand the changes on the nitrogen oxides over the central North Atlantic lower FT, we examined the partitioning of NO_y into its three principal components: NO_x , HNO₃ and PAN.

$_{424}$ 3.3.1. Estimation of NO_y Partitioning

 NO_y partitioning was estimated using the NO_x and NO_y measurements in combination 425 with station measurements of RH, taking advantage of the fact that HNO_3 is removed 426 from the gas phase when clouds are present. Several studies have demonstrated the rapid 427 and efficient scavenging of nitric acid within clouds [e.g. Chameides, 1984; Peterson et al., 428 1998; Garrett et al., 2006]. For example, Chameides [1984] showed that HNO₃ levels de-429 creased by two orders of magnitude in less than 100 seconds after marine cloud formation. 430 Consistent with those studies, NO_y levels at the Pico Mountain station were reduced 431 in the presence of clouds as noted in section 3.2.1. Thus, measurements of NO_{y} levels 432 during in- and out-of-cloud periods can be used to estimate the mixing ratio of cloud-433 scavenged NO_y species, *i.e.*, HNO₃, by assuming that HNO₃ is scavenged into clouds 434 droplets during in-cloud periods [Peterson et al., 1998]. (Even for the smallest observed 435 orographic clouds (~1500 m radius) and typical higher wind speeds (~12 m s⁻¹; 95th 436 percentile of wind speed observations when NO_y was available), there was enough time 437 $(\sim 125 \text{ s})$ for HNO₃ to be scavenged into the cloud droplets before air reached the mea-438 surement site.) For this purpose, we subdivided the observations into periods above 96%439 RH and below 60% RH in order to identify in- and out-of-cloud intervals at the site, 440 respectively. The RH cutoffs were selected so as both subsets contained similar num-441 bers of data points and, at the same time, cloud and cloud-free periods were present at 442 the measurement site. Archived photos of the conditions at the station confirmed cloud 443

and cloud-free periods under those cutoffs. Monthly $[HNO_3^*]$ values were determined by 444 subtracting the monthly averages of NO_{y} observed during "in-cloud" periods from those 445 observed during "out-of-cloud" periods; $[PAN^*]$ was determined by subtracting NO_x from 446 NO_y in simultaneous observations during "in-cloud" periods, and $[NO_x]$ and $[NO_y]$ were 447 determined using direct observations made during "out-of-cloud" periods. (The terms 448 HNO_3^* and PAN^* are used here to indicate estimated, not directly measured values of 449 these species.) Table 3 summarizes the NO_y levels during "in-cloud" and "out-of-cloud" 450 periods, and the derived fraction of reactive nitrogen species on a seasonal basis, *i.e.*, 451 $[HNO_3^*]/[NO_y], [PAN^*]/[NO_y]$ and $[NO_x]/[NO_y]$. Figure 4a shows the monthly variation 452 of the $[HNO_3^*]/[NO_y]$, $[PAN^*]/[NO_y]$ and $[NO_x]/[NO_y]$. 453

A limited number of more direct estimates of HNO_3^* were also made, using alternating 454 measurements of $[NO_y]$ - $[HNO_3]$ and NO_y . Measurements of $[NO_y]$ - $[HNO_3]$ were made in 455 August 2004 and 2005 by removing HNO_3 from NO_y before sampling using a nylon filter 456 attached to the NO_y inlet [e.g. Parrish et al., 1986; Yamamoto et al., 2001]. [HNO₃] was 457 determined by difference from NO_{u} ; [PAN^{*}] was determined as ([NO_u]-[HNO₃]) minus 458 $[NO_x]$. These measurements provide an additional method to test the consistency of 459 our approach. The fraction of reactive nitrogen species estimated directly from these 460 tests (53–62% HNO₃, 23–34% PAN* and 9–16% NO_x) is similar to that deduced for the 461 summer $(71 \pm 9\% \text{ HNO}_3^*, 21 \pm 8\% \text{ PAN}^* \text{ and } 12 \pm 8\% \text{ NO}_x)$. 462

To confirm that the changes in RH used in this analysis were independent of the origin and the chemical history on the airmasses, we inspected the variation of CO in the "incloud" and "out-of-cloud" periods when NO_y measurements were available. As shown in Figure 4b, CO did not exhibit a clear relationship with RH, *i.e.*, monthly CO averages

were variable all year round, independent of "in-cloud" and "out-of-cloud" conditions. However, significant larger monthly CO means for the "out-of-cloud" periods from July to September may indicate a dominance of fire-impacted boreal region outflow, which is characterized by low RH and elevated CO levels [*Val Martín et al.*, 2006]. This influence of boreal emissions during "out-of-cloud" conditions may have resulted in an overestimation of HNO₃ and underestimation of PAN levels during summer, since NO_y is enhanced during boreal wildfire events.

In this analysis, we neglected the possible influence of aerosol and alkyl nitrates. The 474 $NO_{x,y}$ system inlet used at the Pico Mountain station excludes large aerosol particles, but 475 allowed sampling of the ≤ 10 micron aerosol fraction [Hangal and Willeke, 1990; Peterson 476 and Honrath, 1999]. However, sub-micron size aerosol nitrates are not efficiently measured 477 in our system as conversion efficiency for these compounds are low [Miyazaki et al., 2005]. 478 The contribution of alkyl nitrates to NO_y in the remote marine troposphere is very small 479 [Singh et al., 2007; Reeves et al., 2007]. For example, alkyl nitrates accounted for less 480 than 2% of the tropospheric NO_y in the lower FT over the North Atlantic Ocean during 481 the ICARTT study [Singh et al., 2007]. Thus, although the presence of alkyl nitrates may 482 introduce a bias in our estimation of PAN, this bias is expected to be very small. 483

 $_{484}$ 3.3.2. Variation of NO_y Partitioning

From Figure 4a, it is evident that although reactive nitrogen is principally emitted as NO, it largely exists in its secondary reservoir forms in the central North Atlantic lower FT all year round. Low NO_x/NO_y ratios (11–19%; Table 3) are consistent with long-range transport and photochemical processing times to the measurement site. Because of the relatively short lifetime of NO_x compared to NO_y , NO_x/NO_y is expected to decrease with ⁴⁹⁰ increasing airmass age. In the remote lower FT, typical NO_x/NO_y values of 10–17% have ⁴⁹¹ been observed all year round [*Ridley et al.*, 1998; *Atlas et al.*, 1992; *Singh et al.*, 2007], ⁴⁹² consistent with the values observed at the Pico Mountain station.

The shift from dominance of PAN in winter-spring to dominance of HNO₃ in summer-493 fall in Figure 4a is noteworthy. The small contribution of PAN during the summer 494 $(21\pm8\%; \text{ Table 3})$ is attributed to the strong thermal decomposition of PAN to NO_x 495 in the North Atlantic lower FT. Conversely, the large fraction of HNO_3 (71±9%; Ta-496 ble 3) is directly related to the efficient formation of HNO_3 from reaction of NO_x with 497 OH, as conversion of NO_x to HNO_3 is 5 times faster during summer than winter [Logan, 498 1983]. Indirectly, the strong decomposition of PAN during the summer may result in the 499 formation of HNO_3 as NO_x is ultimately converted to HNO_3 . 500

To evaluate the effect of temperature on PAN, we examined the lifetime of PAN with 501 respect to thermal decomposition in the airmasses during transit to the Pico Mountain 502 station. For this purpose, we extracted the average temperature from the HYSPLIT model 503 output [Draxler and Rolph, 2003] for the 10-day backward trajectories arriving at the 504 measurement site. More information on the HYSPLIT backward trajectories is presented 505 elsewhere [Honrath et al., 2004; Val Martín et al., 2006]. We calculated the average 506 temperature in the airmasses from the measurement site to 3 days upwind. This average 507 temperature is the typical temperature that the airmasses encounter before arriving at 508 the Pico Mountain station. We then used those average values to calculate the lifetime of 509 PAN. Figure 4a shows the lifetime of PAN in the airmasses determined from the monthly 510 average upwind temperatures from July 2002 to August 2005. The average lifetime of 511 PAN under those conditions ranged from 5 days in March (average temperature -4.4°C) 512

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to 0.5 days in August (average temperature 8.9°C). Therefore, the dominance of PAN in NO_y in winter–early spring is consistent with the longer lifetime of PAN in the airmasses, whereas the rapid decomposition of PAN in the airmasses during the summer results in the lower PAN fraction observed during that season. Due to the rapid oxidation of NO_x by OH in the summer (≤ 1 day), PAN decomposition may result in the formation of HNO₃ before the airmasses reach the Pico Mountain station.

⁵¹⁹ 3.3.3. Comparison to Previous Observations

⁵²⁰ A comparison of the distribution of NO_y species at the Pico Mountain station to those ⁵²¹ collected over the western North Atlantic Ocean during the NARE and ICARTT aircraft ⁵²² campaigns from spring to fall [*Parrish et al.*, 2004; *Li et al.*, 2004; *Singh et al.*, 2007; ⁵²³ *Hudman et al.*, 2007] allows for some speculation on the behavior of nitrogen oxides ⁵²⁴ across the North Atlantic region. Table 4 compares the fractions of reactive nitrogen ⁵²⁵ species measured during the ICARTT and NARE campaigns with those estimated at the ⁵²⁶ Pico Mountain station.

Our spring-fall estimates of the fraction of NO_x (9–19%), PAN* (21–45%) and HNO₃* 527 (47-71%) are similar to those observed over the western Atlantic Ocean in those other 528 studies (5–13% for NO_x, 21–47% for PAN and 40–72% for HNO₃; range of averages in 529 2–4 km and 2.5–6.5 km altitudes from Table 4). However, as discussed in section 3.2.1, 530 levels of NO_y at the Pico Mountain station are 2–3 times lower than those over the 531 western Atlantic region, indicating the significant removal of HNO₃ during transport to 532 the measurement site. These results suggest that to maintain the observed fractions of 533 NO_x and HNO_3^* at the Pico Mountain station, decomposition of PAN to NO_x and further 534 oxidation of NO_x to HNO_3 must occur in the airmasses. 535

⁵³⁶ 3.3.4. Comparison to GEOS-Chem

Figures 5a-c compares the measurements with results obtained from the global chemical 537 transport model GEOS-Chem for NO_{y} , HNO_{3}^{*} , PAN* and NO_{x} . Additionally, the model-538 data comparison for CO is shown in Figure 5d. GEOS-Chem simulations were available 539 from January to December, 2005, whereas data from the Pico Mountain station in 2005 540 were available only from January to August. To be able to compare a full year cycle, we 541 compared GEOS-Chem simulations to all data in 2002–2005. To avoid potential biases 542 resulting from interannual variability, we also compared GEOS-Chem simulations to the 543 data available in 2005 only. The model-data comparison focuses mainly on the median 544 since this value is less affected by the variability resulting from large episodic events, with 545 the exception of HNO_3^* and PAN^* , which are based on the estimated averages. 546

From Figure 5a, it is apparent that GEOS-Chem reproduces the annual variation of 547 NO_{y} observed at the Pico Mountain station. However, GEOS-Chem tends to overestimate 548 NO_{u} . As shown in Figure 5b, this overestimation is mainly due to an excess of HNO_{3} . 549 For example, during summer, GEOS-Chem produces monthly HNO₃ medians 50–150 pptv 550 greater than the 2005 NO_{y} medians at the Pico Mountain station, and about a factor of 551 two higher than our estimated HNO_3 . This problem is known to occur in multiple GCT 552 models [e.g. Lawrence and Crutzen, 1998; Bey et al., 2001; Singh et al., 2007], and may 553 be related to an overestimation of OH concentrations [Singh et al., 2007], to insufficient 554 scavenging in the model [Bey et al., 2001] or a combination of these and other causes. 555

Because of the scavenging scheme used in GEOS-Chem, it has been suggested that the model allows for significant escape of nitrogen oxides to the lower FT and reasonably accurate simulation of shallow convection from the U.S. BL to the lower FT during summer

[Li et al., 2004; Hudman et al., 2007]. The strong summer peak in the GEOS-Chem NO_y 550 cycle indicates that enhanced summertime export may be partially responsible for the 560 increased summertime NO_y levels over the central North Atlantic lower FT, as suggested 561 above. However, the larger summertime values produced by GEOS-Chem indicate an 562 inability to capture the actual magnitude of NO_y over the North Atlantic lower FT. 563 Figure 5b shows the comparison between simulated PAN levels and observations. The 564 model produces an annual variation of PAN similar to that estimated at the Pico Moun-565 tain station. However, GEOS-Chem tends to underestimate PAN, in particular from July 566 to September, when GEOS-Chem values are a factor of 6–7 times lower than the observa-567 tions. This behavior may be related to an excessive decomposition of PAN in the model 568 resulting from inaccurate temperature parameters and/or location of the airmasses, or 569 underestimation of NO_x and/or NMHC emissions. Finally, a removal efficiency for HNO_3 570 within the clouds present at the Pico Mountain station less than 100% could also con-571 tribute to this model-data difference, since PAN* was calculated by assuming complete 572 removal of HNO_3 in the presence of clouds at the station. Were this the case, it would also 573 reduce the HNO_3 model-data difference during summer, but only by 20%, not changing 574 the conclusion that $[HNO_3]$ exceeds the simulated values. 575

⁵⁷⁶ A comparison of simulated and observed NO_x levels is shown in Figure 5c. Similar to ⁵⁷⁷ our measurements, GEOS-Chem does not simulate a clear seasonal cycle for the median ⁵⁷⁸ NO_x values. GEOS-Chem simulations produce monthly medians (21–35 pptv) similar to ⁵⁷⁹ those observed at the Pico Mountain station (21–30 pptv in 2005 and 16–29 pptv in 2002– ⁵⁸⁰ 2005). However, the model does not capture the very large variability in the NO_x mixing ⁵⁸¹ ratios, particularly that associated with transport of boreal wildfires in summer 2005.

This is not unexpected, since the version of GEOS-Chem used here did not incorporate
 interannual variation in boreal fire activity.

Figure 5d shows observed and modeled CO values. GEOS-Chem CO exhibits a seasonal 584 variation similar to that observed at the Pico Mountain station, but systematically under-585 estimates the CO observations in 2005 by 10 to 25 ppby. This behavior has been noted 586 previously [Bey et al., 2001], and may be related to an excess of OH in the model and/or 587 to the underestimation of the CO emissions. During July–September, this difference is 588 more apparent. GEOS-Chem simulates a sharp decrease of CO through these months, 589 whereas observed CO remain stable. This may be related to the strong impact of boreal 590 wildfire emissions during these months in both 2004 and 2005, which it is not simulated 591 by the fire emission inventory used in this GEOS-Chem simulation. 592

This comparison shows that, although current GCT models have become more sophisticated [*Singh et al.*, 2007], uncertainties in simulating nitrogen oxides in the remote lower FT remain. These uncertainties are clearly related to errors in emission sources and limitations in our understanding of the nitrogen oxides chemistry in the remote troposphere.

4. Summary and Conclusions

⁵⁹⁷ Measurements of nitrogen oxides made at the Pico Mountain station from July 2002 ⁵⁹⁸ to August 2005 were used to estimate the magnitude and seasonal variability of nitrogen ⁵⁹⁹ oxides over the central North Atlantic lower FT and to determine the processes that ⁶⁰⁰ contribute to this variability.

These measurements reveal the presence of a well-defined seasonal cycle of nitrogen oxides in the background central North Atlantic lower FT, with larger mixing ratios during the summertime. We attribute the presence of larger summertime nitrogen oxides levels to X - 30 VALMARTIN ET AL.: REMOTE NORTH ATLANTIC NITROGEN OXIDES

⁶⁰⁴ impacts of boreal wildfire emissions and a more efficient export of NO_y from eastern North ⁶⁰⁵ America during this season. Median NO_x (17–31 pptv) and NO_y (125–338 pptv) observed ⁶⁰⁶ at the Pico Mountain station were lower than those previously observed over the western ⁶⁰⁷ North Atlantic region and more similar to those observed at the remote marine North ⁶⁰⁸ Pacific MLO station. The observed NO_x and NO_y levels were consistent with long-range ⁶⁰⁹ transport of emissions with significant removal upwind of the measurement site.

Observations of NO_x and NO_y and estimates of PAN and HNO₃ indicate that reactive nitrogen over the central North Atlantic lower FT largely exists in the form of HNO₃ and PAN, independent of the season. The shift from dominance of PAN in winter–spring to dominance of HNO₃ in summer–fall is attributed to strong decomposition of PAN to NO_x and efficient formation of HNO₃ from rapid reaction of NO_x with OH during the summer and fall seasons.

Nitric acid contributes 53–71% of NO_y during the summer. Given the significant removal of NO_y during transport, this suggests that the oxidation of NO_x resulting from decomposition of PAN in the airmasses during subsidence, or advection over the ocean with minimal removal, results in a significant source of HNO₃ to the central North Atlantic lower FT. The decomposition of PAN in the airmasses has important implications for O₃ formation, since released NO_x is available to form O₃ before oxidation to HNO₃ during transport to the central North Atlantic lower FT.

A comparison of nitrogen oxides observations with GEOS-Chem simulations indicates that GEOS-Chem reproduces the seasonal variation of nitrogen oxides over the central North Atlantic lower FT. However, it does not capture the magnitude of the cycles. Important differences were found for PAN, a critical species in the global formation of O₃ via dispersal and release of NO_x . This underscores the need for continuing evaluation of the accuracy of simulations of nitrogen oxides chemistry in highly aged pollution plumes.

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(Caption on next page)

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Figure 1. Time series of daytime NO (top), NO_x (middle) and NO_y (bottom) at the Pico Mountain station. Daytime NO are observations when the solar zenith angle was below 62° (see text for explanation). Each data point represents a 30-min average. Bar plots indicate the distribution of the data for each season and year. The medians (red circles) and the means (black squares) are shown along with the central 67% (yellow box) and the central 95% (thin black lines). The number of 30-min average measurements (in black) and the median (in red) included in each distribution are given above the plot for each bar. Distributions with fewer than 20 data points are not shown.



Figure 2. Springtime diurnal cycles of (a) NO, (b) $[NO]/[NO_2]$, (c) NO₂ and (d) NO_y. All 30-min average data are plotted, with the exception of $[NO]/[NO_2]$ (see text for explanation). A few data points outside the plot boundaries are not shown to make the cycle more apparent (25 for NO and NO/NO₂, 8 for NO₂ and 1 for NO_y). Symbols and error bars are the same as in Figure 1.



(Caption on next page)

Seasonal cycle of (a) NO_x , (b) daytime NO, and (c) NO_y in dry conditions Figure 3. (see text for explanation) and (d) CO. Bar plots indicate the distribution of the data for each month, independent of the year of measurement. Symbols and error bars are the same as in Figure 1. Months with fewer than 20 data points are not shown. The median for each month and year are plotted by numerals to the right of the bar plots (2: year 2002, 3: year 2003, 4: year 2004 and 5: year 2005). Medians with fewer than 20 data points are not shown.



(Caption on next page)

Figure 4. Seasonal cycle of a) partitioning of reactive nitrogen (HNO₃*, PAN* and NO_x) and average lifetime of PAN with respect to thermal decomposition in the air arriving at the Pico Mountain station, and b) CO in "in-cloud" (RH> 96%) and "out-of-cloud" (RH< 60%) periods. (See text for explanation.) Symbols represent monthly averages for HNO₃* (green circles), PAN* (blue triangles), NO_x (red diamonds), CO RH> 96% (red squares) and CO RH< 60% (black circles) and average of the monthly means for PAN lifetime (black squares). Error bars indicate the 2-standard error of the mean for CO, NO_x and PAN*, the uncertainty (2- σ) based on propagation of errors for HNO₃* and the minimum and maximum estimated monthly PAN lifetime.

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(Caption on next page)

Figure 5. Comparison of observations a) NO_y in dry conditions (see section 3.2.1 for explanation), b) HNO_3^* and PAN^* , c) NO_x and d) CO to GEOS-Chem simulations. Symbols represent monthly medians in 2002–2005 (blue solid circles) and in 2005 (cyan solid squares) for NO_y , NO_x and CO; monthly medians in 2005 for GEOS-Chem NO_y , NO_x and CO (black open circles); monthly averages in 2002–2005 for HNO_3^* (green solid circles) and PAN* (blue solid triangles) and in 2005 for GEOS-Chem HNO_3 (black open circles) and GEOS-Chem PAN (black open triangles). Error bars indicate the 10th and 90th percentile for observed and simulated NO_y , NO_x and CO, the standard deviation of all estimates of PAN* and GEOS-Chem simulations of HNO_3 and PAN, and the uncertainty $(2-\sigma)$ based on propagation of errors for HNO_3^* .

Table 1.	Statistical parameters of the nitrogen oxides diurnal cycle. Reported average,
standard de	eviation (SD), median and number (N) of the 30-min average observations in
pptv for NO	O, NO ₂ and NO _y .

		Day	$ytime^{a}$		Nig	$httime^{a}$		Ampli	$tude^{b}$
Season	Data	${\rm Mean}{\pm}{\rm SD}$	Median	Ν	${\rm Mean}{\pm}{\rm SD}$	Median	Ν	$\Delta \mathrm{mean}$	$\Delta \mathrm{median}$
Spring ^c	NO	9 ± 8	7	454	1 ± 3	1	889	8 ± 2	7
	$NO:NO_2$	0.4 ± 0.5	0.3	89	0.1 ± 0.4	0.0	277	0.4 ± 0.2	0.3
	NO_2	21 ± 11	21	148	19 ± 11	18	308	2 ± 4	3
	NO_x	29 ± 16	26	124	20 ± 11	18	322	9 ± 6	8
	NO_y	184 ± 123	178	704	184 ± 111	166	905	0 ± 24	12
$\operatorname{Summer}^{\operatorname{c}}$	NO	9 ± 5	8	369	2 ± 4	2	947	6 ± 1	6
	$NO:NO_2$	0.4 ± 0.3	0.3	236	0.1 ± 0.3	0.0	660	0.3 ± 0.1	0.3
	NO_2	25 ± 13	23	296	28 ± 16	25	740	-3 ± 4	-2
	NO_x	37 ± 18	33	323	31 ± 16	26	781	6 ± 5	7
	NO_y	222 ± 180	165	542	247 ± 208	201	1099	-25 ± 40	-36
$\operatorname{Fall}^{\operatorname{c}}$	NO	9 ± 5	8	387	1 ± 3	0	660	8 ± 1	7
	$NO:NO_2$	0.3 ± 0.2	0.3	265	0.0 ± 0.1	0.0	415	0.3 ± 0.1	0.3
	NO_2	28 ± 16	24	297	30 ± 17	26	452	-2 ± 5	-2
	NO_x	36 ± 20	31	294	31 ± 16	26	458	6 ± 6	4
	NO_y	160 ± 102	141	511	163 ± 108	134	738	-4 ± 24	7
Winter ^c	NO	7 ± 6	5	64	0 ± 2	0	562	7 ± 3	5
	$NO:NO_2$	0.4 ± 0.3	0.4	40	0.0 ± 0.2	0.0	447	0.4 ± 0.2	0.4
	NO_2	24 ± 13	24	50	25 ± 16	23	462	-1 ± 8	1
	NO_x	26 ± 14	23	49	24 ± 14	22	441	1 ± 9	0
	NO_y	156 ± 79	145	76	152 ± 88	128	512	4 ± 39	16

^a Daytime are observations when the solar zenith angle was $< 62^{\circ}$; Nighttime are observations made between 23:00–5:00 UTC.

^b Amplitude is expressed as the difference between the means (Δ mean) and the medians (Δ median) of daytime and nighttime. Uncertainty (2- σ) is based on propagation of errors.

^c Seasons are: spring (March, April, May), summer (June, July, August), fall (September, October, November) and winter (December, January, February).

of remote regions	Winter
ree troposphere	Fall
oxides in the lower f	Summer
of nitrogen	Spring
Observation c	apling Altitude
Table 2.	San

))	
	Sampling	Altitude	Sprir	18	Summ	er	Fall		Wint	er		
Year	Location	(km)	$Mean\pm SD$	Median	$\mathrm{Mean}{\pm}\mathrm{SD}$	Median	$Mean\pm SD$	Median	$Mean\pm SD$	Median	Source ^a	
$NO_y ~(pptv)$												
$2002 - 2005^{\rm b}$	C Atl	2.2	257 ± 115	229	358 ± 160	322	228 ± 121	195	165 ± 73	147	[1]	
1991 - 1992	N Pac	3.4	368 ± 109	374	203 ± 99	188	177 ± 70	168	204 ± 82	187	[2]	
1997 - 1999	W Eur	3.6	748 ± 614	581	653 ± 570	529	553 ± 477	422	501 ± 659	350	[3]	
2004	W Atl	2^{-4}			809 ± 610	652					[4]	
1996 - 1997	W Atl	2-4	545 ± 74	550			434 ± 267	377			[5]	
1988 - 1993	W Atl	0.5 - 3			817 ± 104	850			675 ± 248	675	[9]	
		36			969 ± 65	1000			467 ± 76	450	[9]	
1993	C Atl	1			495 ± 214	480					[2]	
1993	E Atl	2.4			390 ± 100	390					[8]	
2000	N Ame	2^{-3}		275 - 450						275 - 300	[6]	
NO_x (pptv)												
2002 - 2005	C Atl	2.2	23 ± 14	21	32 ± 17	29	33 ± 19	28	27 ± 16	24	[1]	
1991 - 1992	N Pac	3.4	39 ± 15	36	29 ± 12	28	26 ± 9	25	32 ± 11	31	[2]	
1997 - 1999	W Eur	3.6	183 ± 289	98	191 ± 482	133	205 ± 355	115	203 ± 454	87	[3]	
2004	W Atl	2-4			64 ± 63	52					[4]	
1996 - 1997	W Atl	2-4	24 ± 20	23			26 ± 22	20			[5]	
1988 - 1993	W Atl	0.5 - 3			73 ± 67	40					[9]	
		3-6			55 ± 21	55				30	[9]	
1993	E Atl	2.4			50 ± 20	50					[8]	
2000	N Ame	2^{-3}		15 - 50				I		28	[6]	
C Atl: C	ot report entral N	ted; N] forth A	Pac: Nor tlantic; H	th Paci 3 Atl: F	fic; N Ar Eastern N	ne: No √orth /	arth Ame Atlantic;	rica; W W Eui	V Atl: W c: Wester	estern] in Eurc	North Appe.	Atlantic;

^a [1]: Pico Mountain: *This work*, [2]: MLO (B. Ridley, NCAR, USA, personal communication, 2007)

et al. [1998]), [8]: IZANA (Fischer et al. [2004]) and [9]: TOPSE (Wang et al. [2003]). Observations 1997], [7]: NARE93 (*Peterson* from $Emmons \ et \ al.$ [1997] are average \pm SD of several field campaigns over western Atlantic Ocean; [3]: JFJ (Zellweger et al. [2003]), [4]: ICARTT (Singh et al. [2007]), [5]: NARE96&97 (David Parrish, NOAA, USA, personal communication, 2007) [6]: Emmons et al. [1997], [7]: NARE93 (Peterson observations at MLO and Izaña are for downslope conditions and at JFJ for undisturbed conditions. Observations from *Peterson et al.* [1998] are average \pm SD of two periods in the FT. ^b NO $_y$ at the Pico Mountain station determined in dry conditions. **Table 3.** Partitioning of NO_y at the Pico Mountain station.

		Out-oi	f-Cloud ^a	In-Cl	oud ^b			
Season	$\mathrm{NO}_{y}^{\mathrm{c}}$	NO_{x}^{c}	$\mathrm{NO}_y^{\mathrm{c}}$	[PAN*] ^c	[HNO ₃ *] ^c [$[HNO_3^*]/[NO_y]^d$	$[PAN^*]/[NO_y]^c$	$[\mathrm{NO}_x]/[\mathrm{NO}_y]^{\mathrm{e}}$
Spring	259 ± 120	23 ± 11	132 ± 101	117 ± 81	127 ± 31	0.49 ± 0.13	0.45 ± 0.12	0.11 ± 0.05
	(451)	(227)	(351)	(114)				
Summer	365 ± 163	37 ± 17	105 ± 110	76 ± 130	260 ± 30	0.71 ± 0.09	0.21 ± 0.08	0.12 ± 0.08
	(841)	(550)	(475)	(295)				
Fall	223 ± 114	38 ± 20	117 ± 67	65 ± 41	101 ± 20	0.47 ± 0.10	0.29 ± 0.04	0.19 ± 0.07
	(721)	(479)	(981)	(408)				
Winter	157 ± 74	28 ± 13	115 ± 70	63 ± 36	42 ± 17	0.27 ± 0.11	0.40 ± 0.06	0.19 ± 0.06
	(557)	(485)	(500)	(277)				
^a Out	-of-Cloud: (observatio	ons of NO _{y} is	and NO _{x I} $H > 070\%$	nade with I	3H< 60%.		
^c Ave	rage±stand	lard devia	tion of the	. 30-min av	verage obse	rvations (in ppt	v) for NO_y , NC_y	\mathbf{x}_x and
$(2-\sigma)$. In	parenthese	sr exptants s, numbei	t of the 30-1	certannues min averag	ior [muU3 ge observati) are based on ons.	propagauon oi	errors
^d Rat: ^e Mea	ios of the m n of ratios.	ieans. Un Uncertaii	certainty is nty is the 2-	based on -standard	propagation error of the	is of errors $(2-\sigma)$ mean.	·	

Table 4. Partitioning of NO_y estimates (%) reported from ICARTT, NARE and Pico

Study	Altitude (km)	Season	$[\mathrm{NO}_x]/[\mathrm{NO}_y]^\mathrm{a}$	$[\mathrm{PAN}]/[\mathrm{NO}_y]^\mathrm{a}$	$[\mathrm{HNO}_3]/[\mathrm{NO}_y]^\mathrm{a}$	Source
Pico Mountain	2.2	Spring	11	45	49	[1]
		Summer	9 - 16	21 - 34	53 - 71	
		Fall	19	29	47	
		Winter	19	40	27	
NARE 96	2-8	Spring	11	42	47	[2]
	2-8		5	35	60	[3]
	$2-4^{\mathrm{b}}$		5			[3]
	$4-6^{\mathrm{b}}$		3			[3]
NARE 97	2-8	Fall	8	34	57	[4]
	2 - 8		6	33	61	[3]
	2 - 4		7	21	72	[3]
	4-6		6	40	54	[3]
ICARTT	2.5 - 6.5	Summer	13	47	40	[5]
	2.5 - 3.5				54	
	3.5 - 6.5		14	53	33	
ICARTT	2 - 8	Summer	8	35	44	[6]
	2 - 4		8	26	60	
	4-6		7	43	43	

Mountain studies.

—, Not reported.

^a NO_y composition reported is: For Pico Mountain, in spring, fall and winter, average percentages (Table 3), and in summer, minimum and maximum average percentages reported in Table 3 and estimated from alternating measurements of $[NO_y]$ - $[HNO_3]$ and NO_y (see text for explanation); For NARE and ICARTT, average percentages reported in North American outflow [*Parrish et al.*, 2004; *Li et al.*, 2004; *Hudman et al.*, 2007], percentages calculated using means reported every 2 km altitude bins [*Singh et al.*, 2007] or average percentages calculated using 10-sec average observations east of 60°W [David Parrish, NOAA, USA, personal communication, 2007]. [1]: *This work*, [2]: *Parrish et al.* [2004], [3]: David Parrish, NOAA, USA, personal communication, 2007 [4]: *Parrish et al.* [2004] and *Li et al.* [2004], [5]: *Hudman et al.* [2007] and [6]: *Singh et al.* [2007].

 $^{\rm b}$ $\,$ Averages with fewer than 25 data points are not shown.