Reactive nitrogen oxides and ozone above a taiga woodland

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Measurements of reactive nitrogen oxides (NOx and NOy) and ozone (O3) were made in the planetary boundary layer (PBL) above a taiga woodland in northern Quebec, Canada, during June-August, 1990, as part of NASA Arctic Boundary Layer Expedition (ABLE) 3B. Levels of nitrogen oxides and O3 were strongly modulated by the synoptic scale meteorology that brought air from various source regions to the site. Industrial pollution from the Great Lakes region of the U.S. and Canada appears to be a major source for periodic elevation of NOx, NOy and O3. We find that NO/NO2 ratios at this site at midday were approximately 50% those expected from a simple photochemical steady state between NOx and O3, in contrast to our earlier results from the ABLE 3A tundra site. The difference between the taiga and tundra sites is likely due to much larger emissions of biogenic hydrocarbons (particularly isoprene) from the taiga vegetation. Hydrocarbon photooxidation leads to relatively rapid production of peroxy radicals, which convert NO to NO2, at the taiga site. Ratios of NOx to NOy were typically 2-3 times higher in the PBL during ABLE 3B than during ABLE 3A. This is probably the result of high PAN levels and suppressed formation of HNO3 from NO2 due to high levels of biogenic hydrocarbons at the ABLE 3B site.

1. INTRODUCTION

Recent investigations have suggested that the abundance of ozone (O3) is increasing in the troposphere and that the rate of increase is especially rapid at high northern latitudes in summer [Oltmans and Komhyr, 1986; Bojkov, 1988; Ferguson and Rosson, 1992]. Ozone regulates the oxidizing power of the atmosphere and is radiatively active, so that increased ozone levels may have an important influence on atmospheric chemistry and climate. Ozone is also toxic to vegetation, changes in O3 may directly impact the biosphere. Tropospheric O3 levels are regulated primarily by photochemistry, which is sensitively dependent on nitrogen oxide (NOx = NO and NO2) mixing ratios [Liu et al., 1987], surface deposition, and by inputs from the stratosphere.

Industrial processes and biomass burning are probably the largest sources of NOx, with smaller contributions from soil emissions and stratospheric inputs [Logan, 1983]. Photochemistry in the troposphere converts NOx to higher oxides, such as HNO3 and organic nitrates. Many of these species are relatively resistant to further photochemical processing and/or deposition and so may be transported over large distances. The thermal and/or photochemical decomposition of some of the higher oxides, especially peroxycetyl nitrate (PAN) and HNO3, returns NOx to the troposphere.

We report measurements of O3 and nitrogen oxide (NO, NO2, and total NOx) mixing ratios in the planetary boundary layer (PBL) of the atmosphere above and within a taiga woodland canopy, at a location remote from anthropogenic sources. The measurements were made during June-August, 1990, as part of NASA Arctic Boundary Layer Expedition (ABLE) 3B. Observations were made on a 31-m-high tower and from the NASA Electra aircraft. Turbulent fluxes of O3 and total NOx were also measured at the tower and will be reported in a future publication (J. W. Munger et al., manuscript in preparation, 1993, hereinafter referred to as M93).

Section 2 of this paper focuses on the analytical methods and experimental design used at the tower; other papers in this issue discuss methods used on board the aircraft [Talbot et al., this issue; Sandholm et al., this issue]. Section 3 describes the measurements, and section 4 examines the photochemical steady state for NO, NO2 and O3 (section 4.1) and NOx/NOy ratios (section 4.2). Conclusions are summarized in section 5.

2. EXPERIMENT

Overflights of the ABLE 3B ground site by the NASA Electra airplane were made on six days: Julian days 211 (mission 10), 213 (11), 215 (12), 219 (14), 220 (15), and 223 (17). On day 217 the Electra flew in the PBL somewhat to the southeast of Schefferville (mission 13). We will examine observations of NOx and NOy, HNO3, PAN, O3, C2H2 and C2Cl4 obtained in the boundary layer aboard the Electra during these flights. The experimental methods used to obtain these data are given by Talbot et al. [this issue] and Sandholm et al. [this issue], and references therein. The array of NOx species (NO, PAN and HNO3) and other tracers (hydrocarbons, halocarbons, CO) measured aboard the Electra makes the aircraft data set particularly useful for identifying influences on trace gas climatologies, such as industrial pollution and biomass burning [see Wofsy et al., this issue]. We examine aircraft data obtained in the PBL in the region surrounding the Schefferville ground site only; other papers in this issue focus on data obtained above the PBL and over a broader area of...
northeastern Canada and the eastern United States (e.g., Talbot et al., Sandholm et al., Wofsy et al.).

Talbot et al. [this issue] segregate the aircraft data obtained in various altitude intervals with air mass type, on the basis of CO mixing ratios. We take a different approach and average the PBL data for each aircraft mission to determine the dominant influences on the chemical composition of PBL air, during the time period of each flight. We found a high correlation between \( \text{CH}_2\text{O} \) and CO in biomass burning and industrial pollution plumes and therefore focus on measurements of \( \text{CH}_2\text{O} \) as a tracer for burning [see Wofsy et al., this issue]. Mixing ratio data for CO are not available for much of the flight time in the PBL because the CO instrument was operated in a fast response mode for eddy flux measurements.

The tower data provide a nearly continuous record of \( \text{NO}_x \), \( \text{NO}_y \) and \( \text{O}_3 \) mixing ratios for June 27 to August 17 (Julian days 178 to 229), 1990, and include nighttime and periods of inclement weather during which the aircraft did not fly. Further details of the tower measurements are given below.

The tower measurements were carried out in a black spruce taiga woodland 13 km northwest of Schefferville, Province de Quebec, Canada (54° 50' N, 66° 40' W), a town of approximately 3000 inhabitants. No other significant habitations exist within 20 km of the site. The woodland canopy was open with \( \sim 600 \) trees ha\(^{-1}\), and the mean canopy height was 5.6 m. A 31-m-high tower (Rohn 25G) was erected and instrumented for chemical and micrometeorological measurements. Chemical analyzers and data acquisition and control computers were located in a tent about 20 m southeast from the base of the tower. Electrical power was provided by a 12.5-kVA diesel generator located 300 m southeast of the tower.

The experimental design was similar to that described by Bakwin et al. [1992]. Mixing ratios and turbulent fluxes of \( \text{NO}_x \) and \( \text{O}_3 \) were measured at 29 and 31 m height, respectively. Mixing ratios of \( \text{O}_3 \), \( \text{NO} \) and \( \text{NO}_2 \) were measured by sampling through 0.635 cm OD Teflon tubes with inlets fixed at 0.05, 0.85, 2.8, 6.2, 9.5, 18.2, and 30.8 m height on or near the tower. The sampling sequence was from highest to lowest, each location was sampled for 4 min during each profile. The \( \text{NO}_x \) detector was zeroed following sampling from the 0.05-m tube.

Reactive nitrogen oxides (\( \text{NO}_y \)) were converted to NO by gold-catalyzed reaction with \( \text{H}_2 \) at 300°C [Fahey et al., 1986] and quantified using chemiluminescence with \( \text{O}_3 \). The converter consisted of a 90-cm-long, 0.635 cm ID gold-plated (2.5 \( \mu \)m thickness) copper tube and was located at the inlet end of the sampling tube. Calibration gases and \( \text{H}_2 \) were added to the sample air through two 0.16-cm-OID stainless steel tubes that intruded several centimeters into the inlet of the converter tube. The converter design minimized instrument response time to \( \text{NO}_y \) species by minimizing contact of sample air with nonconverting surfaces [Bakwin et al., 1992; M93]. The instrument responded to a pulse input of HNO\(_3\) with a 90% risetime under 2 s.

After passing through the converter, sample air passed through \( \sim 40 \) m of 0.625-cm-OID Teflon tubing to the NO analyzer. Sample flow rate was 900 cm\(^3\) min\(^{-1}\) STP (cm\(^3\) STP). An instrument zero was obtained every 40 min by addition of 50 cm\(^3\) STP of "zero" air containing \( \sim 100 \) ppbv (parts per million by volume) \( \text{O}_3 \) generated using a \( \text{H}_2 \) gas lamp to the sample air just downstream of the converter, so that \( \text{NO} \) was converted to \( \text{NO}_2 \). Calibrations for \( \text{NO} \) were carried out every 3 hours by addition to the sample air at the inlet of the converter of \( \sim 2 \) cm\(^3\) STP of a National Institute for Standards and Technology (NIST) (Gaithersburg, Maryland) traceable standard gas containing 4.42 ppmv \( \text{NO} \) in \( \text{N}_2 \).

Checks on the conversion efficiency for \( \text{NO}_2 \) were performed twice daily. For an efficiency check the NO standard was added to 50 cm\(^3\) STP of "zero" air containing \( \sim 2 \) ppmv \( \text{O}_3 \) in a 4 cm\(^3\) volume just before being introduced into the converter, so that \( \sim 99\% \) of \( \text{NO} \) was converted to \( \text{NO}_2 \). The conversion efficiency remained \( \sim 95\% \) for the full observation period. No measurements of the conversion efficiency for higher \( \text{N} \) oxides were done in the field. In laboratory tests using \( \text{HNO}_3 \) in humidified "zero" air, efficient conversion to \( \text{NO} \) was obtained at sample flow rates up to 5000 cm\(^3\) STP. Also, conversion efficiency for \( \text{NH}_3 \) in humidified air (>20% relative humidity (RH) at 23°C) was found to be negligible in agreement with results from other laboratories (G. Hibbler, personal communication, 1990).

Occasionally local pollution (mainly from the generator) was sampled at the tower. During these periods the variance of the \( \text{NO}_x \) measurements was greatly increased (coefficient of variation > 2 for a 5-min period), so that such intervals were easily identified and were removed from the data set.

A separate detector was used to measure mixing ratios of \( \text{NO} \) and \( \text{NO}_2 \). Nitric oxide was measured by chemiluminescence with \( \text{O}_3 \), and \( \text{NO}_2 \) was measured following photolysis to NO [Bakwin et al., 1992] in a 165 cm\(^3\) quartz cell at a sample airflow rate of 800 cm\(^3\) STP and pressure of 300 torr. The reduced pressure in the photolysis cell minimized the conversion of \( \text{NO} \) to \( \text{NO}_2 \) by ambient \( \text{O}_3 \) [Ridley et al., 1988; Bakwin et al., 1992]. During sampling from each altitude, 2 min were spent in an \( \text{NO} \) mode and 2 min were spent in an \( \text{NO}_2 \) (photolysis) mode.

To zero the \( \text{NO}_x \) detector, a solenoid valve was used to introduce a flow of 50 cm\(^3\) STP "zero" air containing \( \sim 100 \) ppmv of \( \text{O}_3 \) to the sample air just upstream of the quartz cell, with no photolysis, so that \( \text{NO} \) was removed. At night, reaction with ambient \( \text{O}_3 \) is expected to completely remove \( \text{NO} \), providing a check on the zeroing procedure. The mean (standard deviation) nighttime \( \text{NO} \) mixing ratio for 2.8 to 30.8 m was 0.2 (1.1, n=2124) pptv (parts per trillion by volume), with no significant difference between sampling heights (see Figure 3). Nitric oxide mixing ratios at 0.05 m were elevated somewhat due to emission of \( \text{NO} \) from the surface (see below). Previously, we reported an artifact of \( \sim 1.7 \) pptv for our \( \text{NO} \) measurements [Bakwin et al., 1992]. Introduction of a solenoid valve to switch the \( \text{O}_3 \)-laden zeroing air in and out of the sample airstream appears to have eliminated this artifact (<0.5 pptv).

Calibrations for \( \text{NO} \) and \( \text{NO}_2 \) were performed every 3 hours using the methods described by Bakwin et al. [1992]. The NO (compressed gas) and \( \text{NO}_2 \) (permeation tube) calibration standards were compared in the field using gold-catalyzed reaction with \( \text{H}_2 \) to completely convert \( \text{NO}_2 \) to \( \text{NO} \). The NO standard was considered the primary standard in the field and was referenced before and after the field campaign to two NIST standards maintained in our laboratory. No significant change was observed in the working standard between these two comparisons. Estimates of the precision and accuracy of the \( \text{NO} \) and \( \text{NO}_2 \) measurements are given by Bakwin et al. [1992].

An ultraviolet (UV) photometer (Dasibi 1003-AH) was used to determine \( \text{O}_3 \) mixing ratios. The zero level of the photometer was determined frequently by passing the sample air through a screen
impregnated with MnO₂ and was found to be stable to better than ±0.5 ppbv (parts per billion by volume) during the field experiment. To ensure a consistent calibration for ground and aircraft ozone observations, the photometer was compared in the field to a similar instrument calibrated at NASA Langley Research Center. Ozone was also measured continuously at 30.8 m height using a Bendix C₂H₄-chemiluminescence detector that was modified for fast response, and the data were used to compute turbulent fluxes of O₃ (M93).

Solar UV radiation was measured at the tower site using a radiometer identical to those flown on the Electra (Eppley Laboratory, Newport, Rhode Island). The radiometer was mounted on a pole at 6.1 m height, just above the tops of most nearby trees (5-6 m high). The radiometer output was used to compute the photolysis rate for NO₂, J_{NO₂}, following Madronich [1987]:

\[
J_{NO_2} = 1.35E \left[ \frac{1}{(0.56 + 0.03Z) \cos X_o + 0.21 - 0.015Z} + 2A \right]
\] (1)

where E is the radiometer signal (mW cm⁻²), X₀ is the solar zenith angle, A is the albedo for UV radiation, and Z is the station elevation (0.5 km above sea level). The UV albedo was obtained from extrapolation to the surface of the ratio of nadir to zenith looking UV radiometer readings taken aboard the Electra during low-altitude overflights of the ground site (670-1300 m above sea level), giving A=0.03. For X₀ < 70°, equation (1) is expected to yield values for J_{NO₂} accurate to ±20% for both clear and overcast skies [Madronich, 1987; Shetter et al., 1992].

Samples for hydrocarbon and halocarbon analysis were obtained at 10 and 30 m height on the tower on Julian days 220-224. Methods used for sample collection and analysis were similar to those used for aircraft sampling [Blake et al., this issue]. We discuss here results for acetylene (C₂H₂), perchloroethylene (C₂Cl₄), and isoprene.

3. OBSERVATIONS

3.1. Mixing Ratios of NOₓ, NOᵧ, and O₃

Hourly mean mixing ratios of NOₓ, NOᵧ, and O₃ at 30 m above the surface ranged from 15 to >150 pptv, <50 to >1500 pptv, and 5 to 49 ppbv, respectively (Figure 1). The mean and median diurnal cycles for NOₓ, NOᵧ, and O₃ at 30 m height are shown in Figure 2. Maximum NOᵧ and O₃ levels, typically about 270 pptv and 28 ppbv, respectively, were observed near midday, coincident with the maximum rate of vertical mixing. At night, NOₓ and O₃ levels in the surface layer were depressed due to deposition and decoupling from the atmosphere above (M93). Mixing ratios of NOₓ were also somewhat lower at night than in the daytime. The nighttime loss rate for NOₓ (about 1.3 pptv h⁻¹ on average) probably reflects net deposition to the surface (see below) as well as reaction of NOₓ with O₃ to form NO₃, which may be lost by deposition or via further reactions.

Statistics for NOₓ, NOᵧ, and O₃ mixing ratios during midday (1000-1600 eastern standard time (EST)) for Julian days 178 to 229, 1990, are given in Table 1. Probability distributions for NOₓ and NOᵧ were somewhat skewed to a relatively small number of observations with very high mixing ratios; median NOₓ and NOᵧ mixing ratios were lower than the means. The O₃ data were more nearly normally distributed.

Fitzjarrald and Moore [this issue] discuss climatological changes that occurred during the period of our observations. They report a shift in the synoptic regime around Julian day 197, from a cool period of frequent precipitation and westerly to northwesterly flow to a warmer, drier period characterized by southeasterly flow and generally deeper afternoon boundary layers. A return to cooler weather and westerly to northwesterly flow occurred about day 221. These changes in climate are reflected in the NOₓ and NOᵧ mixing ratios (Figure 1); on average, higher daytime levels were observed during the period of generally southwesterly flow than during the cooler periods (Table 1). Ozone levels were not significantly correlated with the climatological changes.

Figure 3 shows the mean vertical distributions (0.05 to 31 m) of NO, NOₓ, NOᵧ, and O₃ at each height for nighttime (2000-0400
was emitted from the surface. The emission rates for NO consistent with the observed gradients are very small, less than $1 \times 10^8$ molecules cm$^{-2}$ s$^{-1}$. During the daytime, emissions of NO from the soil appear to have been about balanced by deposition of NO$_2$ to the plant canopy and ground, resulting in little overall vertical gradient for NO; while at night NO$_2$ deposition slightly exceeded NO emission. The net flux of NO at night ($F_{NO}$) can be estimated as [Bakwin et al., 1992]

$$F_{NO} = F_{O_3} \frac{d[NO]}{dz}$$

At night, $F_{O_3}$ averaged about $5 \times 10^6$ molecules cm$^{-2}$ s$^{-1}$ (M93), the NO and O$_3$ gradients (30.8-0.05 m) were roughly 5 pptv and 15 ppbv, respectively (Figure 3), yielding $F_{NO} = 1.7 \times 10^7$ molecules cm$^{-2}$ s$^{-1}$, or assuming a 100-m-deep nocturnal stable layer, about 0.3 pptv h$^{-1}$, roughly 20% of the observed nighttime loss rate for NO.$_2$.

3.2. Pollution Influences

The time series of NO$_x$, NO$_y$, and O$_3$ (Figure 1) clearly show coherent variations, =1 (e.g., day 195) to 8 (e.g., days 193 to 201) days duration, correlated with surface pressure changes indicating the influence of synoptic scale air mass characteristics. Typically, NO$_x$, NO$_y$, and O$_3$ were enhanced during periods of falling surface pressure, which tended to be associated with air originating from the southwest quadrant, according to 5-day back trajectories for surface air. Mixing ratios were relatively low during periods of rising pressure, most often associated with trajectories from the N hemicircle, indicating Arctic air. Regions to the southwest were apparently significant sources of NO$_x$, NO$_y$, and O$_3$ at the surface.

Mixing ratios of NO$_x$ and NO$_y$ measured at the tower appear to have been somewhat higher than those measured simultaneously aboard the aircraft. Direct comparison is difficult since the aircraft data represent means taken over many kilometers, and because of the small number of data points. The ground site may have been located in a zone of somewhat elevated NOx levels due to natural processes or local anthropogenic pollution. However, the overall agreement of NO$_x$/NO$_y$ ratios between the ground site and the airplane (see below and Figure 7) indicate that local pollution was probably not a significant problem at the ground site.

Table 2 shows mixing ratios of C$_2$H$_2$, CH$_3$Cl, NO$_x$, and O$_3$ on the tower and from the Electra (PBL only) for selected flights. Acetylene is emitted by biomass and fossil fuel burning and has a lifetime of in the troposphere of 2-3 weeks, while CH$_3$Cl is a purely industrial product with a lifetime of 12-14 weeks. Mixing ratios of NO$_x$ and O$_3$ at the ground site were near or below their daytime background values of 247 pptv and 28 ppbv (as defined by medians for days 178-196; see Table 1), respectively, on days 215, 219,
Fig. 3. Mean mixing ratios of NO, NO₂, NOₓ, and O₃ at each sampling height on the tower for daytime (pluses, 1000 to 1600 EST) and nighttime (circles, 2000 to 0400 EST) (Julian days 178-228). Observations lying more than 1.5 times the interquartile distance from the upper and lower quartiles (see Figure 2) have been excluded from the means.

220, 222, 223, and 224, which include the time periods for aircraft missions 12, 14, 15, and 17. These species were significantly above background levels on days 211, 213, and 221, and also C₂Cl₄ mixing ratios exceeded apparent "background" levels of 9.7-12.7 pptv (range of data taken on other days) on days 211 (mission 10) and 221 (no aircraft flight over the ground site). During aircraft mission 10, C₂Cl₄ and C₂H₂ mixing ratios in the PBL over our site reached levels comparable to those observed in the polluted PBL over midlatitude areas during mission 22, indicating that the air sampled was strongly influenced by anthropogenic sources. Elevated mixing ratios of NOₓ, NOₓ, and O₃ were observed at the ground site for about 2.5 days prior to mission 10, indicating that the pollution source was regional, and 5-day back trajectories show that air that reached the site during mission 10 had passed over the Great Lakes region of the United States and Canada (trajectories are presented by Shipham et al. [this issue]), a

| TABLE 2a. Mixing Ratios of C₂H₂, C₂Cl₄, NO₂, O₃, and NOₓ Obtained on the NASA Electra Airplane and on the Schefferville Tower During Overflights by the Electra |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| JDAY, 1990      | FLT   | C₂H₂, pptv | C₂Cl₄, pptv | NO₂, ppbv | O₃, pptv | NOₓ, pptv | NO₂, pptv | NOₓ, pptv |
| 211a            | 10    | 313    | 31.8   | 877    | 52     | 151     | 1429    | 49     | 229    |
| 213             | 11    | 70     | 12.4   | 312    | 43     | 31      | 408     | 40     | 65     |
| 215             | 12    | 115    | 10.8   | nd     | 27     | nd      | 233     | 23     | 49     |
| 217b            | 13    | 106    | 11.4   | 209    | 24     | 33      | nd      | nd     | nd     |
| 219             | 14    | 83     | 10.5   | 133    | 28     | 31      | 267     | 24     | 55     |
| 220             | 15    | 83     | 9.7    | 202    | 20     | 38      | 256     | 21     | 69     |
| 223             | 17    | 70     | 11.9   | 112    | 25     | 31      | 188     | 27     | 39     |
| 227c            | 22    | 337    | 46.6   | 3798   | 68     | 728     |         |        |        |

Here nd denotes no data.

* Schefferville spiral only.

Flight southeast of Schefferville.

Transit flight (midlatitudes).
TABLE 2b. Tower Data for Intervals When Grab Samples Were Taken for Hydrocarbon/Halocarbon Analysis

<table>
<thead>
<tr>
<th>JDAY, C2H2, C2Cl4, NOy, O3, NOx, NOy, NOx, pptv</th>
<th>pptv</th>
<th>pptv</th>
<th>ppbv</th>
<th>pptv</th>
<th>pptv</th>
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<td>10.2</td>
<td>276</td>
<td>21</td>
<td>66</td>
</tr>
<tr>
<td>221</td>
<td>125</td>
<td>16.3</td>
<td>334</td>
<td>38</td>
<td>67</td>
</tr>
<tr>
<td>222</td>
<td>72</td>
<td>11.7</td>
<td>125</td>
<td>24</td>
<td>28</td>
</tr>
<tr>
<td>223</td>
<td>67</td>
<td>12.4</td>
<td>172</td>
<td>27</td>
<td>36</td>
</tr>
<tr>
<td>224</td>
<td>65</td>
<td>12.7</td>
<td>235</td>
<td>29</td>
<td>nd</td>
</tr>
</tbody>
</table>

Table 3 compares the frequency distributions for NO generated from the model for 1430 EST during June-August in the (4° x 5°) grid cell containing the Schefferville tower, with those observed at the tower (1000-1600 EST). We compare the model results and observations for daytime only because at night the observed mixing ratios are somewhat depleted below the shallow inversion by surface deposition and chemistry (see Figure 2). The observed NOx mixing ratios are 10-24 pptv higher than the model for each percentile. Since the only sources for NOx in the model are industrial, these results indicate that "background" NOx levels at the Schefferville site (i.e., air masses that are unaffected by recent NOx inputs) are in the range of 10-24 pptv. This interpretation is supported by our data from the ABLE 3A tundra site [Bakwin et al., 1992], where NOx mixing ratios were typically 12±4 pptv and were apparently little affected by recent emissions. The frequency distribution for NOx in the model agrees well with the observations at the high percentiles, and the model time series (not shown) shows episodes of elevated NOx and O3 of similar magnitude and duration to those observed (Figure 1), indicating that the transport of NOx (or NOx precursors such as PAN) from industrial sources is realistically simulated for this site.

The model predicts large northward transport of NOx and O3 in the PBL at 54°N over eastern Canada during July and negligible transport of NOx and O3 above the PBL. Examination of the model time series for NOx and O3 over the eastern United States and Canada reveals that these species are transported to Schefferville episodically during the approach of low-pressure systems, in harmony with our observations of generally elevated NOx, NOy, and O3 levels during periods of falling pressure. These periods are characterized by subsidence over the study area, which acts to confine industrial pollution within the PBL [Fitzjarrald and Moore, this issue].

4. INFLUENCE OF PHOTOLIEMISTRY ON NOx AND RADICALS

4.1. Photochemical Steady State for NOx and O3

During the daytime, NO, NOy, and O3 are cycled on a timescale of minutes by the reactions

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (3)
\]

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \quad (4)
\]

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (5)
\]

where hv represents photons with wavelengths <420 nm. If isolated from strong sources or sinks for NOx or O3, these reactions may reach a photochemical steady state such that

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}
\]

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

Fig. 4. Value of P = \(J_{\text{NO}}[\text{NO}_2]/k[\text{NO}][\text{O}_3]\), which has been computed from measurements of NO, NOy, O3, temperature (k), and the output of a UV radiometer (\(J_{\text{NO}}\)), plotted against time of day. Hourly means (±1 s.d.) are shown by the dotted curves. Points with P < -1 or P > 13 have been excluded based on examination of the probability distribution function for the data (52 out of 1799 points).
where $k$ is the rate constant for (3) and is a function only of temperature. At steady state, $P$ should exceed unity if reactions other than (3) convert NO to NO$_2$. With $J_{NO}$ computed from the output of the UV radiometer (equation (1)), all of the parameters required to compute $P$ were measured at this site.

The value of $P$, computed for NO$_x$ and O$_3$ measurements taken above the treetops at 6.2, 9.5, 18.2, and 30.8 m, is plotted against time of day in Figure 4. We find that $P$ is not strongly dependent on sun angle during most of the daytime nor on $J_{NO}$ (not shown). During typical midday conditions, $J_{NO} = 0.0055 \text{ s}^{-1}$ and $P = 2.9$ (medians for 1200-1400 EST). These results indicate that reactions of NO with compounds other than O$_3$ play an important role in determining the ratio of NO$_2$ to NO at this site, in agreement with the other measurements in the rural and remote troposphere [Ritter et al., 1979; Kelly et al., 1980; Parrish et al., 1986; Ridley et al., 1992].

Reaction of NO with peroxy radicals (HO$_2$ and RO$_2$, where R represents an organic group) would lead to a value of $P > 1$. The peroxy radical abundance required to produce the observed departure from the simple photochemical steady state of (3)-(5) is given approximately by

$$[\text{HO}_2] + [\text{RO}_2] = [\text{O}_3](P-1) \left( \frac{k'}{k} \right) \label{eq:7}$$

where $k'$ is the rate constant for the reaction of NO with HO$_2$ (note that the rate constants for reaction of NO with HO$_2$, CH$_3$O$_2$, and C$_2$H$_5$O$_2$ are similar [Demore et al., 1990]). The computed peroxy radical mixing ratios are shown in Figure 5. At midday we find that NO$_2$+RO$_2 = 71$ (median, quartiles = 28 and 153) pptv. About half of the variance in the computed peroxy radical mixing ratios is explained by a linear relationship with $J_{NO}$ (Figure 6), and the relationship between HO$_2$+RO$_2$ and $J_{NO}$ is very similar to that reported by Parrish et al. [1986] at Niwot Ridge, Colorado, for summer periods with NO$_x$ mixing ratios between 250 and 1000 pptv. However, NO$_3$ levels at our site are much lower than at Niwot Ridge, rarely exceeding 150 pptv, and we find no significant relationship between peroxy radicals and NO$_3$ at our site. The latter result is in agreement with the observations of Ridley et al. [1992].

4.2. NO$_x$ / NO$_y$ Ratios

Ratios of NO$_x$ to NO$_y$ obtained on the tower and aboard the Electra when flying in the PBL over northeastern Canada show very similar distributions (Figure 7). The ratios are remarkably constant over the range of NO$_x$ mixing ratios sampled and the means (± s.d.) for the tower (0.20±0.10, n=808) and aircraft (0.19±0.09, n=268) are very similar. These low ratios indicate that fresh inputs of NO had not occurred recently relative to the NO$_x$ lifetime (about 1 day). The NO$_x$/NO$_y$ ratios appear to increase somewhat at the lowest NO$_y$ abundances, but this may be due in part to random measurement errors at low NO$_y$ and NO$_x$. Data obtained during ABLE 3A over the tundra of SW Alaska also showed lower NO$_x$/NO$_y$ ratios, 0.08 (±0.02, also apparently uncorrelated with the mixing ratio of NO$_y$ [Bakwin et al., 1992], indicating important differences between processes that control NO$_x$ mixing ratios in these two regions.

5. DISCUSSION

The low mixing ratios of NO$_x$, NO$_y$, and O$_3$ and the low NO$_x$/NO$_y$ ratios observed confirm that this woodland site is indeed remote from direct industrial influence. During periods when "background" (Arctic) air was sampled, NO$_y$ mixing ratios (generally 180-340 pptv) were among the lowest seen at any continental location, and were similar to levels we observed at a tundra site in southwest Alaska during ABLE 3A [Bakwin et al., 1992]. NO$_x$ mixing ratios were also low in "background" (Arctic) air, typically 20-40 pptv, but were 2-3 times higher than at the ABLE 3A tundra site. Background NO$_3$ levels at the taiga site were near the expected crossover point for net production/destruction of O$_3$ by photochemistry.

Elevated mixing ratios of NO$_x$, NO$_y$, and O$_3$ were observed episodically at both the tundra (ABLE 3A [Bakwin et al., 1992]) and
The three-dimensional chemical tracer model (CTM) of Jacob et al. [1993] show that essentially all of the transport of industrial pollution occurs in the PBL.

In the CTM, roughly 5% (0.9 x 10⁹ g N d⁻¹) of the NO₅ emitted by industrial sources in the United States and Canada is transported to the Arctic northward of 60°N during summer. This is approximately equivalent to each of the sources of NO₅ to the Arctic troposphere from biomass burning [Jacob et al., 1992; Wofsy et al., this issue] and from the stratosphere [Jacob et al., 1992]. North American sources supply approximately 35% of the global source of NO₅ from industrial processes, and a large portion of the remainder is emitted at midlatitudes in Europe and Asia. If a similar fraction (5%) of emissions from all industrial sources is exported to or emitted in the Arctic, the total industrial source of NO₅ to the Arctic in summer would be about 2.6 x 10⁹ g N d⁻¹. Examination of statistics for NO₅ emission from industrial sources compiled by Hameed and Dignon [1988] indicates that the 5% estimate may be reasonable for Europe and Asia, where industrial centers reside farther north than in North America.

Measured wet and dry deposition of NO₅ at our site totaled about 35 g N ha⁻¹ month⁻¹ (M93), very similar to deposition rates at the ABLE 3A tundra site at 62°N (36 g N ha⁻¹ month⁻¹ [Bakwin et al., 1992; Talbot et al., 1992]). If we assume that deposition rates measured at these two sites are representative of the world northward of 60°N (3.4 x 10⁹ ha⁻¹) in summer, we would calculate a deposition flux of 4.0 x 10⁸ g N d⁻¹, giving a rough budget for NO₅ for the Arctic troposphere in summer. Sources from industrial pollution (2.6 x 10⁹ g N d⁻¹) would account for about 50% of the total, with the balance from biomass burning (0.9) and the stratospheric input (0.9), approximately balanced by wet and dry deposition (4.0). Mixing ratios of NO₅ observed in the Arctic are much higher in winter than in summer due to increased transport from midlatitudes and reduced loss rates [Honrath and Jaffe, 1992].

Levels of NO₅ in the PBL were low under background conditions (20-40 pptv), leading to slow rates of net photochemical production of O₅, about 0.8 ppbv day⁻¹ (S. M. Fan et al., manuscript in preparation, 1993, hereinafter referred to as F93). Loss of O₅ by deposition to the surface was somewhat larger, about 1.6 ppbv d⁻¹ (M93). Intervals with NO₅ levels in the range 50-150 pptv, persisting for several days, were observed at this site; the elevated NO₅ was contributed at least in part by industrial pollution from the Great Lakes region of the United States and Canada. Biomass fires may also have played a role but cannot be unambiguously distinguished. Periods of elevated NO₅ were associated with elevated O₅ (Figure 1), and the CTM results [Jacob et al., 1993] indicate that the O₅ enhancements could result from enhanced photochemical production (or suppressed loss) within the industrial pollution plumes. Potential O₅ production rates are much greater at this site than at the ABLE 3A tundra site due to higher mixing ratios of large amounts of biogenic hydrocarbons at this site.

NO₅ levels during a 3-week period of generally fair weather and southwesterly flow (Julian days 197-221, Table 1) were on average twice those observed during cooler periods of westerly and northwesterly flow (178-196 and 222-229). Higher NO₅ is expected to lead to greater net production of O₅; however, O₅ levels were not significantly different between these two broad intervals. Southwesterly flow is generally associated with subsidence, with strongly capped PBLs [Fitzjarrald and Moore, this issue], so that the supply of O₅ from aloft may be reduced. Also, since the loss of O₅ by surface deposition is about twice as fast as photochemical production, our result is perhaps not surprising. Further, the periods of strongest southwesterly flow and highest levels of industrial pollution, such as the episodes of days 209-211 and day

![Fig. 7. NOₓ/NOy plotted against NOy for data obtained (a) at the Schefferville tower, and (b) in the planetary boundary layer (PBL) by instruments aboard the NASA Electra airplane. Aircraft data are shown by numbers with 0-7 indicating data from missions 10-17, respectively (excluding mission 16). No data were obtained in the PBL during mission 12 due to equipment failure.](image-url)
results of Trainer et al. [1991] are in harmony with our comparisons.

We find that NO/NO2 ratios observed at the taiga site are not well described by a simple photochemical steady state involving only NO and O3, indicating that other oxidants are important in converting NO to NO2. Peroxy radicals produced from isoprene oxidation are likely the major cause of low NO/NO2 ratios (F93). Oxidation of NO by O3 alone is sufficient to explain NO/NO2 ratios we observed at the tundra site during ABLE 3A [Bakwin, 1989], consistent with estimates of low peroxy radical mixing ratios and production rates from hydrocarbon precursors [Jacob et al., 1992].

Though NOx levels were similar in "background" air at the tundra (ABLE 3A) and taiga (ABLE 3B) sites, NOx/NO2 ratios were 2-3 times higher at the taiga site. Further, PAN/NOx ratios were much higher in the PBL over the taiga site (0.2-0.5 [Sandholm et al., this issue]) than over the tundra site (<0.1 [Sandholm et al., 1992]). These results likely reflect differences in the NOy budgets at these locations. At the tundra site the balance between PAN decomposition and HNO3 formation appears to regulate NOx levels [Jacob et al., 1992]. This balance must also hold for the taiga site, since the essentially all of the NOy measured in the PBL is accounted for by observed species (i.e., NOx, PAN, HNO3, and NOy) [Sandholm et al., this issue]. A major difference between these two sites is the relatively high isoprene emission rates from the taiga vegetation (isoprene emissions from the tundra were essentially zero). Trainer et al. [1991] found that increasing isoprene emissions in their photochemical model of the rural PBL caused a shift of NOx oxidation from HNO3 to organic nitrates, including PAN. The reason for this is threefold: (1) increased isoprene leads to higher rates of peroxy acetyl (PA) radical production during the daytime, suppressing the decomposition of PAN; (2) peroxy radicals from isoprene oxidation convert NO to NO2 leading to an increase in the NO/NO2 ratio and further limiting PAN decomposition; and (3) isoprene and its oxidation products compete directly with NOx for reaction with OH, so that HNO3 formation is reduced as isoprene levels are increased. The results of Trainer et al. [1991] are in harmony with our comparison of the ABLE tundra and taiga sites; the local biota appear to exert a strong influence on NOx/NO and PAN/NOx ratios.

These ideas are being explored further through photochemical modeling of the ABLE 3B data set (F93). Ratios of NOx to NOy measured at a rural site in Pennsylvania during the daytime in summer were about 0.2, though NOx and NOy mixing ratios were much higher than at our taiga site due to the proximity to emissions [Buhr et al., 1990]. At night at the Pennsylvania site, NOx/NOy ratios increased to 0.6-0.8 as NOy emissions continued with reduced rates of conversion to higher oxides [Trainer et al., 1991]. At our site no such nocturnal increase in NOy/NOx was observed. These results indicate that the approach to equilibrium between NOx and NOy is achieved in a few hours under conditions of vigorous photochemical activity and may be maintained for at least several days, even as NOy is depleted by dilution and deposition. At sites where reactive hydrocarbons are not abundant, such as the Mauna Loa Observatory (MLO) [Carroll et al., 1992] and our ABLE 3A tundra site [Bakwin et al., 1992], equilibrium NOx/NOy ratios are somewhat lower, typically around 0.1.

The difference may be explained in part by the by the relative abundance of "missing" NOy species (i.e., [NOy]-([NOx]+[HNO3]+[NO2]+[PAN])). At MLO, about 25% of NOy is "missing" during downslope periods [Atlas et al., 1992], at our ABLE 3A site about half of the observed NOy is "missing" and appears to consist of fairly stable species that are resistant to deposition [Bakwin et al., 1992]. At the Pennsylvania site [Buhr et al., 1990] and our ABLE 3B taiga site [Sandholm et al., this issue], nearly all of NOy is accounted for by measured species. This comparison may indicate that the "missing" NOy species do not play a major role in the budgets of NOy at these sites.

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References


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