Summertime distribution and relations of reactive odd nitrogen species and NO$_x$ in the troposphere over Canada

R. W. Talbot,$^{1}$ J. D. Bradshaw,$^{2}$ S. T. Sandholm,$^2$ H. B. Singh,$^3$ G. W. Sachse,$^4$
J. Collins,$^4$ G. L. Gregory,$^4$ B. Anderson,$^4$ D. Blake,$^5$ J. Barrick,$^4$ E. V. Browell,$^4$
K. I. Klemm,$^{1,6}$ B. L. Lefer,$^1$ O. Klemm,$^{1,6}$ K. Gorzelska,$^{1,7}$ J. Olson,$^2$ D. Herlth,$^3$
and D. O’Hara$^7$

We report here large-scale features of the distribution of NO$_x$, HNO$_3$, PAN, particle NO$_3^-$, and NO$_y$ in the troposphere from 0.15 to 6 km altitude over central Canada. These measurements were conducted in July-August 1990 from the NASA Wallops Electra aircraft as part of the joint United States-Canadian Arctic Boundary Layer Expedition (ABLE) 3B-Northern Wetlands Study. Our findings show that this region is generally NO$_x$ limited, with NO$_x$ mixing ratios typically 20-30 parts per trillion by volume (pptv). We found little direct evidence for anthropogenic enhancement of mixing ratios of reactive odd nitrogen species and NO$_x$ above those in “background” air. Instead, it appears that enhancements in the mixing ratios of these species were primarily due to emissions from several day old or CO-rich-NO$_x$-poor smoldering local biomass-burning fires. NO$_x$ mixing ratios in biomass-burning impacted air masses were usually <50 pptv, but those of HNO$_3$ and PAN were typically 100-300 pptv representing a twofold-threefold enhancement over “background” air. During our study period, inputs of what appeared to be aged tropical air were a major factor influencing the distribution of reactive odd nitrogen in the midtroposphere over northeastern North America. These air masses were quite depleted in NO$_x$ (generally <150 pptv), and a frequent summertime occurrence of such air masses over this region would imply a significant influence on the reactive odd nitrogen budget. Our findings show that the chemical composition of aged air masses over subarctic Canada and those documented in the Arctic during ABLE 3A have strikingly similar chemistries, suggesting large-scale connection between the air masses influencing these regions.

1. Introduction

Reactive odd nitrogen is released into the atmosphere of the northern hemisphere primarily as nitric oxide (NO) and nitrogen dioxide (NO$_2$) from anthropogenic combustion sources and from natural sources such as biomass burning, soil emissions, lightning, and stratosphere-troposphere exchange. Due to the high chemical reactivity of NO$_x$ (NO + NO$_2$ = NO$_x$), it is often converted photochemically to nitric acid ([HNO$_3$] and the reservoir species peroxyacetyl nitrate (PAN)). This conversion takes place in a matter of hours during the summertime [Logan, 1983; Kasting and Singh, 1986]. Atmospheric particles also contain nitrate (p-NO$_3^-$), from sorption of HNO$_3$ to supermicron alkaline particulates [Wolff, 1984] and formation of submicron ammonium nitrate aerosols under certain conditions [Stelson et al., 1979]. Other forms of reservoir reactive odd nitrogen occur in the northern hemisphere’s troposphere, such as peroxypropionyl nitrate (PPN) and various alkyl nitrates (RONO$_2$, R=alkyl), but generally they are found at low concentration [Singh, 1987; Atlas, 1988; Atherton, 1989; Buhr et al., 1990; Ridley et al., 1990a, b].

The reservoir species PAN is a near-source sink for NO$_x$, but its long-range transport and thermal decomposition may ultimately provide a source of NO$_x$ in the remote troposphere [Singh, 1987; Atlas et al., 1992]. Wet and dry deposition of atmospheric nitrate (HNO$_3$ + p-NO$_3^-$) appear to be the principal removal mechanisms for loss of reactive odd nitrogen from the troposphere [Logan, 1983]. Nitric acid is one of the major components of acid precipitation [Galloway and Likens, 1981]. Dry deposition of HNO$_3$ vapor may be an important input of fixed nitrogen to remote area ecosystems [Bakwin et al., 1992; Talbot et al., 1992].

Reactive odd nitrogen species play central roles in tropospheric chemistry. For example, the concentration of NO$_x$ in the troposphere controls photochemical ozone (O$_3$) production or destruction and it also influences hydroxyl radical concentrations (OH) [Levy, 1972; Chameides and Walker, 1973; Crutzen, 1979; Logan et al., 1981]. Ozone and OH are important species as they largely determine the oxidizing capacity of the troposphere.

In this paper we use data for a suite of chemical and physical parameters collected during the NASA Global Tropospheric Experiment/Arctic Boundary Layer Expedition 3B (GTE/ABLE 3B). These data are an important new resource that represents an integrated set of measurements for key tropospheric species in a semiremote region of the northern hemisphere’s atmosphere. Our approach summarizes reactive odd nitrogen chemistry in various air mass characterizations, as observed over the Canadian study areas. We describe the measured distribution of NO, NO$_x$,
HNO₃, PAN, p-NO₃⁻, and total reactive odd nitrogen (NOy = NO + NO₂ + NO₃ + N₂O₅ + HONO + HNO₃ + PAN + higher alkyperoxy nitrates such as PPN + RONO₂ + p-NO₃⁻) in the low- to mid-troposphere over the Hudson Bay lowlands (northern Ontario) and the Schefferville region (northern Quebec and Labrador) of Canada. Then within specific air masses, we examine relationships between reactive odd nitrogen species and correlations with O₃ and CO. We were particularly interested in studying tropospheric chemistry over this region of North America since it is influenced intermittently by natural and anthropogenic emissions. Thus we examined reactive odd nitrogen chemistry in the unique variety of air mass compositions over central Canada that represent the mixing of "background" Arctic air with air influenced by natural and anthropogenic emissions from North America.

2. EXPERIMENT

Detailed aircraft flight scenarios and the overall scientific rationale for GTE/ABLE 3B are described elsewhere [Harriss et al., this issue (a)]. Briefly, the airborne measurements reported here were conducted aboard the NASA Wallops Flight Facility L-188 Electra aircraft. Science missions 2-9 were conducted over the Hudson Bay lowlands in northern Ontario, whereas missions 11-19 were based over northern Quebec and Labrador. Our analysis of reactive odd nitrogen chemistry over Canada draws upon data collected during these 16 core science missions (no reactive odd nitrogen data were collected on mission 12 due to an aircraft power failure). A synopsis of meteorological conditions during ABLE 3B is described in a companion paper [Shipham et al., this issue].

The instrumentation used to measure the reactive odd nitrogen species of interest has been flown on several previous GTE/ABLE missions, so only a succinct summary is given below. The chemiluminescence O₃ and tunable diode laser absorption CO and CH₄ systems are described in detail elsewhere [Gregory et al., 1983; Sachse et al., 1987].

Nitric oxide, NO, and NO₂ were measured simultaneously with the Georgia Tech two-photon/laser-induced fluorescence (TP/LIF) instrument [Braddock et al., 1985; Sandholm et al., 1990]. This spectroscopically selective NO technique simultaneously determined NO, NO₂ produced from the photolysis of NO₃, and NO produced from the reduction of NO₂ compounds using a 300°C calcium fluoride cell with 0.3% CO as a reducing agent. A 1-kW photolytic converter was operated with a photolysis passband of 350 nm < λ < 410 nm, a photolytic yield ranging from 30 to 60% and sample residence times ranging from 2 to 4.5 s. A porcelain-glass coated inlet was used to sample ambient air in an orientation perpendicular to the airstream. These NO₂ measurements were reported using integration times of 90 and 180 s. Accuracy of the instrument calibration is estimated to be ±16% for NO and ±18% for NO₂ and NO₃ at the 95% confidence limit. Limits of detection for a 180-s signal integration were about 3 pptv for NO and about 10 pptv for NO₂ with a signal-to-noise ratio of 2:1. The typical measurement precision for NO₃ (at 95% confidence limit) was circa ±10% at 500 pptv increasing to circa ±20% at 200 pptv [Sandholm et al., 1992; Sandholm et al., this issue].

The NASA Ames PAN instrument provided measurements of this species using electron capture gas chromatography detection from a cryogenically enriched sample of ambient air [Singh and Salas, 1983; Gregory et al., 1990]. The system used an aft facing Teflon inlet with the instrument operated at constant pressure (1050 mbar) isolated from aircraft cabin pressure fluctuations. The sampling time of PAN was typically 90 s followed by an 8-min analysis time. In-flight calibration was accomplished using PAN synthesized in liquid n-tridecane [Gaffney et al., 1984]. The PAN measurements have an estimated accuracy of about ±20% and a precision of ±10%. Given the above conditions, the limit of detection for PAN was about 5 pptv.

Nitric acid and p-NO₃⁻ measurements were performed with the University of New Hampshire (UNH) mist chamber instrument and shrouded atmospheric aerosol sampling systems respectively [Talbot et al., 1990, 1992; R. W. Talbot et al., Improvements in aerosol inlet performance in airborne applications, submitted to Journal of Geophysical Research, 1993]. A recent intercalibration of the mist chamber HNO₃ instrument with the NOAA nylon filter method and the NCAR "Lind" instrument (i.e., a diffusion scrubber) showed agreement within ±25% in the 100-1000 pptv range [E. L. Atlas et al., An intercomparison of three HNO₃ measurement techniques, unpublished data, 1990]. In ABLE 3B the HNO₃ system employed a 40-mm ID inlet with a porcelain-glass coating. The Georgia Tech and UNH sampling systems used identical inlet compositions to ensure uniformity in passing HNO₃ through both instruments. Laboratory testing of a porcelain-coated inlet showed that in the 100-300 pptv range, HNO₃ was passed through the entire ~1.5-m length with 100±3% efficiency. The inlet was mounted perpendicular to the fuselage. This was done to minimize collection of aerosols, especially supermicron particles typically enriched in nitrate. Sampling times were usually 15 min for HNO₃, with a corresponding limit of detection of 10 pptv. The overall uncertainty is estimated to be ±20% for mixing ratios ≥100 pptv increasing to ±30% for mixing ratios near the limit of detection.

The atmospheric aerosol system and an assessment of its performance is described elsewhere [R. W. Talbot et al., Improvements in aerosol inlet performance in airborne applications, submitted to Journal of Geophysical Research, 1993]. The sampling system employed a curved-leading edge 8-mm nozzle housed inside a 150-mm ID shroud. The passing efficiency for submicron particles is believed to be virtually 100%. For supermicron particles the passing efficiency is unknown, but comparison of this inlet with one using a sharp-leading edge nozzle not housed in a shroud showed that p-NO₃ mixing ratios were an average of 150% higher with the current UNH system than those obtained with the other system. Potential sampling problems may still exist for p-NO₃, but it is believed that the relative concentration trends between various air masses are substantially correct. Simultaneous sampling for p-NO₃ with two identical UNH systems indicates the precision was about ±18% [Talbot et al., 1992].

3. RESULTS

3.1. AIR MASS CATEGORIES

The GTE/ABLE 3A data for the North American Arctic and subarctic showed that CO was a good overall indicator of
Air mass chemical compositions over northern Ontario were divided into two categories, "background" (CO 95-105 parts per billion by volume (ppbv)) and biomass-burning impacted (CO 110-120 ppbv). Air mass types over northern Quebec/Labrador were defined as tropical (CO 60-79 ppbv), mixed (CO 80-94 ppbv), "background" (CO 95-105 ppbv), and biomass-burning impacted (CO 110-120 ppbv). A final air mass type with no geographic reference was defined as upper tropospheric/lower stratospheric influenced (CO 105 ppbv and dew point -25ø to -47øC). Each air mass category was comprised of its own discrete data set. The tropical and mixed air mass types were not observed over the Ontario region. The classification "background" air is consistent with findings from GTE/ABLE 3A where CO mixing ratios of 95-105 ppbv were present in Arctic "background" air masses [Harriss et al., 1992]. Mixing ratios of 106-109 ppbv were observed for CO, but data associated with this range in CO were not used in this analysis. At 110 ppbv of CO it was clear that combustion contamination had affected these mixing ratios of CO. For the upper tropospheric/lower stratospheric air mass category, data were included from 0.15 km altitude air mass divisions are subjective, but there was no other alternative except to entirely ignore the boundary layer. We believe our divisions are substantially correct, but caution should be exercised in the interpretation of the <1-km reactive odd nitrogen data. We admit that the <1-km altitude air mass divisions are subjective, but there was no other alternative except to entirely ignore the boundary layer data. We believe our divisions are substantially correct, but caution should be exercised in the interpretation of the <1-km reactive odd nitrogen data. Of the other air mass categories, only the mixed air masses were observed at <1 km altitude. Data collected at <1 km altitude was only incorporated into the mixed grouping when there was simultaneous CO measurements. The data used in this paper represent about 80% of the measurement time intervals during the ABLE 3B flight series.

The "tropical" category appears to represent aged marine air with CO mixing ratios ranging from 60 to 79 ppbv [Anderson et al., this issue]. The overall chemistry of this air mass, especially the hydrocarbon distribution, suggests a low-latitude source, most likely over the Pacific Ocean. Isentropic back-trajectory analysis also supports a tropical origin for this air mass, possibly related to outflow from Typhoon Steve [Shipham et al., this issue].

Over Quebec/Labrador air masses with CO mixing ratios of 80-94 ppbv were frequently encountered. A combination of air mass types appear to have been "mixed" to produce these mixing ratios of CO. For the upper tropospheric/lower stratospheric air mass category, data were included from time periods where CO ≤105 ppbv and the dew point temperature was between -25ø and -47øC. Restriction of CO to ≤105 ppbv removed the obvious cases of fresh biomass-burning influence. The remotely sensed O3 and aerosol distributions were used to help identify intrusions of upper tropospheric/lower stratospheric air [Browell et al., this issue].

The highest mixing ratios of CO appeared to be associated with emissions from biomass-burning. It is important to note that the fires observed within the study area were a combination of peat and forest combustion yielding significant smoke. The few minutes of data that were obtained directly in a biomass-burning plume, close to its source during mission 9, was removed from the northern Ontario biomass-burning group so that the mixing ratios reported in Table 1 better represent "average" conditions.

Mixing ratios for the species of interest in our analysis of the ABLE 3B data were merged into the appropriate air mass categories, defined above, for examination of the large-scale distribution of reactive odd nitrogen associated with the gradient in CO mixing ratio. The majority of the CO data collected below 1 km altitude was obtained in fast response mode (10 Hz). This facilitated flux calculation objectives but resulted in insufficient data for our analysis of the reactive odd nitrogen distribution. Fortunately, slow response (~1 Hz) CO data were available for ascents and descents within the boundary layer and at the very start and end of the low-level (0.15 km altitude) flight legs. These data were used together with the associated mixing ratios of other species, primarily NO, NO2, C2Cl4, selected fluorocarbons (F-12, F-13, F-113), and the hydrocarbons ethene, ethyne, ethane, and propane, to assess the "cleanliness" of the boundary layer air. The air mass distinction was usually quite obvious, since the air masses at 0.15 km altitude were either impacted by biomass-burning or represented "background" air. In fresh biomass-burning emissions, ethene was elevated by an order of magnitude, or more, whereas ethyne, ethane, and propane were enhanced twofold [Blake et al., this issue]. We admit that the <1-km altitude air mass divisions are subjective, but there was no other alternative except to entirely ignore the boundary layer data. We believe our divisions are substantially correct, but caution should be exercised in the interpretation of the <1-km reactive odd nitrogen data. Of the other air mass categories, only the mixed air masses were observed at <1 km altitude. Data collected at <1 km altitude was only incorporated into the mixed grouping when there was simultaneous CO measurements. The data used in this paper represent about 80% of the measurement time intervals during the ABLE 3B flight series.

To summarize reactive odd nitrogen chemistry in various air masses over central Canada, the highest resolution measurements were used for individual species: 90-s intervals for NO, NO2, and NO3; 90-s intervals every 8 min for PAN; 15-min intervals for HNO3; and 20- to 30-min intervals for p-NOy. For consistency with NO and NOe mixing ratios, 90-s averaged values were generated for O3, CH4, and various physical parameters (e.g., altitude, static air, and dew point temperatures) by averaging their highest resolution values over the same time intervals as the NO and NOe measurements. Consequently, mixing ratio statistics reported here for O3 and CH4 may be slightly different than those in companion papers due to our use of 90-s averaged values as individual measurement points for these species. It should be noted that the air mass chemical compositions presented in this paper are not appropriate for assessing the degree of balance in the reactive odd nitrogen budget. A companion paper discusses these aspects of reactive odd nitrogen chemistry over central Canada [Sandholm et al., this issue].

3.2. Occurrence of Air Mass Types Over the Study Region

This section provides a qualitative time series scenario of the occurrence of air mass types sampled over central Canada during ABLE 3B. During the study period we observed more diversity in air mass types over Quebec/Labrador than over
ranging from 60 to nearly 400 ppbv. Missions 11 and 13 believed to have their origins in the upper troposphere/lower stratosphere and, subsequently, subsided to our highest flight altitudes. What appears to have been tropical marine air were sampled which had a variety of CO mixing ratios strongly influenced the chemistry in the 2- to 6-km altitude region on mission 14. Pockets of this characteristically “clean” tropical air were sampled again on missions 15, 16, and 17. However, the overall characteristics of air masses sampled on missions 15-19 were associated with CO mixing ratios of 80-94 (mixed) and 95-105 (background) ppbv. As in the Ontario region, pockets of dry air, presumably originating from aloft (>6 km altitude), were frequently sampled in the 3- to 6-km altitude range during missions 15-19 and again on the return transit flights (to Wallops on missions 20 and 22).

The possibility that fresh industrial contamination was intermixed with the biomass-burning emissions cannot be excluded. The hydrocarbon data indicate no obvious enrichment in C$_2$H$_4$ or fluorocarbons in the biomass-burning plumes [Blake et al., this issue; Sandholm et al., this issue; Wofsy et al., this issue]. For the range of CO and NO$_y$ mixing ratios observed over Canada, there were few cases of clear enhancement in C$_2$H$_4$ and fluorocarbon mixing ratios above those found in “background” air [Sandholm et al., this issue]. In general, mixing ratios of C$_2$H$_4$ over Canada were similar to those in “background” air sampled over Alaska during ABLE 3A [Sandholm et al., 1992]. Isolated cases showed somewhat enhanced toluene and benzene levels, suggestive of potential industrial influence. However, these species appear to have been released or produced from combustion of biomass at high latitudes [Blake et al., this issue]. Our analysis avoids the few incidents of direct industrial contamination observed on missions 10 and 16, where the southerly flow of air into Canada from the United

### Table 1. Selected Chemical Characteristics of Tropospheric Air Masses Over Northern Ontario, Canada, During July 1990

| Species | <1 km | 1-3 km | 3-6 km |
|---------|-------|--------|--------|
| NO      | 7.4   | 8.6    | 6.3    |
| NO$_2$  | 20.7  | 21.2   | 22.4   |
| NO$_3$  | 52.7  | 53.6   | 52.5   |
| PAN     | 26.7  | 26.7   | 26.7   |
| NO   | 11.7  | 11.7   | 11.7   |
| NO$_2$ | 4.7   | 4.7    | 4.7    |
| HNO$_3$| 164.4 | 273.7  | 542.1  |
| CO     | 31.3  | 42.9   | 53.7   |
| CH$_4$ | 1778  | 1761   | 1756   |
|  | | | |
| NO | 13.6  | 11.7   | 6.5    |
| NO$_2$ | 51.5  | 46.2   | 12.0   |
| NO$_3$ | 49.3  | 46.2   | 13.0   |
| HNO$_3$ | 185.8 | 203.2  | 154.0  |
| PAN | 56.8  | 247.1  | 528.2  |
| NO | 21.1  | 12.4   | 89.8   |
| NO$_2$ | 395.0 | 394.3  | 998.0  |
| HNO$_3$ | 35.3  | 247.1  | 528.2  |
| CO | 127.1 | 134.2  | 145.2  |
| CH$_4$ | 1786  | 1777   | 1755   |

Reactive nitrogen species mixing ratios are given in parts per trillion by volume (pptv); all other species are in parts per billion by volume (ppbv). s.d., standard deviation.
States clearly contained industrial contaminants [Blake et al., this issue; Wofsy et al., this issue]. It appears that biomass-burning emissions were the dominant direct source of reactive odd nitrogen to the Canadian study areas during the ABLE 3B program. Based on the C$_2$Cl$_4$ and fluorocarbon data, the magnitude of industrial inputs intermixed with biomass-burning emissions would seem to be no greater under conditions of elevated CO and NO than it was in "background" air [Sandholm et al., this issue]. We find little direct evidence over the Canadian study regions for a major impact of industrial inputs enhancing the mixing ratios of reactive odd nitrogen species above their mean values in "background" air.

3.3. Reactive Odd-Nitrogen Distribution Over a Gradient in CO Mixing Ratios

Tables 1-4 summarize mixing ratio statistics for reactive odd nitrogen species, NO$_y$, O$_3$, CO, and CH$_4$ in the air mass.
TABLE 4. Selected Chemical Characteristics of Upper Tropospheric/Lower Stratospheric Influenced Air Masses at 3-6 km Altitude Over Canada During July/August 1990

| Species | Mean s.d. | Median | Range | N |
|---------|-----------|--------|-------|---|
| NO      | 15 7.8 14 | 3.0-63 | 380   |
| NO₂     | 38 17 39  | 10-111 | 400   |
| NO₃     | 52 23 51  | 18-146 | 364   |
| HNO₃    | 39 28 32  | 10-126 | 45    |
| PAN     | 291 98 297| 34-535 | 106   |
| NO₃⁻    | 7.8 3.1 6.7| <2.0-13 | 19   |
| NO      | 760 564 569| 173-3670 | 380   |
| O₃      | 63 15 64  | 30-103 | 499   |
| CO      | 89 11 91  | 69-105 | 395   |
| CH₄     | 1726 151 1739 | 1718-1760 | 394 |

Reactive nitrogen species mixing ratios are given in pptv; all other species are in ppbv.

categories defined in section 3.1. These statistical data are presented for three altitude bands, <1 km, 1-3 km, and 3-6 km. The altitude brackets were chosen by examining both in situ and remotely sensed vertical distribution data for O₃ and aerosol number density [Anderson et al., this issue; Browell et al., this issue; Gregory et al., this issue]. This examination revealed that below 1 km there were generally smaller O₃ mixing ratios and larger aerosol burdens than above this altitude. A second similar transition was commonly apparent at about 3 km altitude. The tropical and upper tropospheric/lower stratospheric air masses were only intercepted at certain altitudes, as indicated in Tables 2 and 4. Due to the paucity of data, p-NO₃⁻ was only divided into two altitude bands: the boundary layer (<1 km) and free troposphere (>3 km). A detailed presentation of the p-NO₃⁻ data and discussion of the atmospheric aerosol chemistry is given in a companion paper [Gorzelska et al., this issue].

To facilitate comparison of the mixing ratios for various species in the suite of air masses described here, the median values are plotted in Figures 1 and 2. The salient features for each reactive odd nitrogen species and NO₃⁻ are discussed below.

NO. Median NO mixing ratios were consistently below 10 pptv in air masses not influenced by biomass-burning emissions or intrusions of upper tropospheric/lower stratospheric air. Nitric oxide mixing ratios were very similar (6-8 pptv) in "background" air masses over both Canadian study areas. Below 3 km altitude, median NO mixing ratios were the smallest (~5 pptv) in the Quebec/Labrador mixed and tropical air masses. In air impacted by biomass-burning, NO mixing ratios throughout the 0.15- to 6-km column over Ontario were enhanced about twofold over those in "background" air. Over the Quebec/Labrador region, NO enhancement was not observed in air masses impacted by biomass-burning. Nitric oxide mixing ratios in air masses characterized as influenced by the composition of the upper troposphere/lower stratosphere were about twofold larger (median=14 pptv) than in "background" air (medians 6-8 pptv).

NO₃⁻. "Background" air exhibited a remarkably constant NO mixing ratio of about 30 pptv. In the mixed and tropical air masses over Quebec/Labrador, NO mixing ratios were virtually identical to those in "background" air. Air masses over Ontario impacted by biomass-burning emissions exhibited a nearly twofold enhancement in NO₃⁻ mixing ratios (~56 pptv) below 3 km altitude compared to values in "background" air. Over the Quebec/Labrador region, NO₃⁻ enhancement was not observed in air masses impacted by biomass-burning.
air (30 pptv). There was no corresponding enhancement of NO₂ mixing ratios in the 3- to 6-km altitude range. For the Quebec/Labrador region, air masses impacted by emissions from biomass-burning exhibited a 1.5 fold enhancement in NO₂ mixing ratios (43 pptv) in the 3- to 6-km altitude range compared to those in “background” air (30 pptv). Such enhancement of NO₂ was not observed at altitudes below 3 km. Upper tropospheric/lower stratospheric air masses exhibited NO₂ mixing ratios of around 50 pptv in the 3- to 6-km altitude range.

HNO₃. Mixing ratios of HNO₃ in “background” air were quite variable over both Canadian study areas but generally were <100 pptv. The smallest mixing ratios of HNO₃ (<30 pptv) were often observed in the 3- to 6-km altitude range. Nitric acid mixing ratio values were characteristically small (<100 pptv) in the tropical, mixed, and upper tropospheric/lower stratospheric air masses. An exception to this trend was observed in the 1- to 3-km altitude range in the mixed air masses over Quebec/Labrador where HNO₃ mixing ratios were about 100 pptv. In this same region the other reactive odd nitrogen species, including PAN, were also found to have quite small mixing ratios. Over both study regions, biomass-burning emissions appeared to have caused a twofold enhancement of HNO₃ mixing ratios at all altitudes compared to values in “background” air. A nearly threefold enhancement was also observed in biomass-burning impacted air over Ontario in the 1- to 3-km altitude range, where the median mixing ratio of HNO₃ was about 225 pptv compared to a median value of 83 pptv in “background” air. The median HNO₃ mixing ratio in upper tropospheric/lower stratospherically influenced air was 32 pptv, which was identical to that in “background” air over Ontario (29 pptv at 3-6 km) but twofold larger than “background” air values found over Quebec/Labrador (16 pptv).

PAN. The vertical distribution of PAN generally had its familiar increase in mixing ratio with increasing altitude. Like HNO₃, PAN mixing ratios were variable, even in “background” air. In the boundary layer over Ontario, PAN mixing ratios (median = 27 pptv) were about twofold smaller in “background” air than those in similar air masses over Quebec/Labrador (median = 65 pptv). In the 3- to 6-km altitude range, PAN mixing ratios were increased fivefold to sixfold over boundary layer air values. Over Ontario, PAN mixing ratio values within this altitude range in “background” air were about half (median = 162 pptv) of those observed over Quebec/Labrador (median = 321 pptv). The tropical air masses over Quebec/Labrador exhibited the smallest mixing ratios of PAN at 3- to 6-km altitudes (median = 128 pptv). PAN mixing ratios measured coincident with the smallest values of CO in the tropical air were only 30-40 pptv (at 3 km altitude). Such small values of PAN are typical of tropical Pacific air [Ridley et al., 1990a, b; Singh et al., 1990]. Air masses over Ontario influenced by biomass-burning emissions showed a factor of 2-3 enhancement in PAN mixing ratios at all altitudes compared to those in “background” air. In contrast, the only perceivable influence of biomass-burning on PAN mixing ratios over Quebec/Labrador was a twofold increase above the “background” air values (median of 72 versus 140 pptv) in the 1- to 3-km altitude range. The PAN mixing ratios in air masses influenced by the composition of upper tropospheric/lower stratospheric air (median = 297 pptv) were nearly twofold larger than values in “background” air over Ontario (median = 162 pptv) but were similar to values in “background” air over Quebec/Labrador (median = 321 pptv).
The chemical composition of the mixed air over Quebec/Labrador suggests that it may have originated from the
mixing of "background" and tropical air masses. The mixed air masses were quite depleted in HNO₃ and concomitantly NO at low altitudes (Table 3). This suggests possible removal of HNO₃ by precipitating frontal systems moving through the Quebec/Labrador region at this time [Shipham et al., this issue]. It seems likely that cloud processing of the mixed air masses was responsible for the very small NO, mixing ratios (below 50 pptv) observed in these air masses at altitudes below 3 km. Interestingly, the NO mixing ratios in the mixed air masses were not significantly different than those in the other air mass types sampled in this study. This may be indicative of PAN thermal decomposition constantly replenishing NO, as this mechanism appears to provide an important source of NO in the summer Arctic troposphere [Jacob et al., 1992; Singh et al., 1992].

Air masses corresponding to the "mixed" category were not observed in the troposphere over Ontario. We did encounter CO mixing ratios of 80-94 ppbv, but these were only in association with pockets of dry air that are believed to have originated from the upper troposphere/lower stratosphere. There may be a connection between the occurrence of air masses in the Arctic and subarctic with CO mixing ratios of 80-90 ppbv and the mixed air masses identified over Quebec/Labrador. During ABLE 3A, air masses with CO mixing ratios in this range were encountered on flights out of Point Barrow and Bethel, Alaska [Harriss et al., 1992; Sandholm et al., 1992]. A detailed examination of these large-scale connections seems warranted, but this is beyond the scope of this paper. Recent measurements have documented long-range transport of intact haze layers in the summertime Arctic troposphere over North America and Greenland [Brock et al., 1989; Browell et al., 1992]. Our analysis in this paper suggests that specific chemical characteristics are also preserved in some air masses traversing the Arctic and subarctic regions of North America.

During the ABLE 3B study period the occurrence of mixed and tropical air masses over Quebec/Labrador profoundly affected the regional distribution of reactive odd nitrogen. The midtroposphere over eastern Canada received constant westerly flow of aged Pacific and polar air during ABLE 3B [Shipham et al., this issue]. How persistent the injection of tropical air into this regime is remains uncertain. A high frequency of occurrence of this phenomenon would imply a major influence on the atmospheric reactive odd

Fig. 3. Concentrations of CH₄, O₃, NO₂, and NO in various air mass categories over Quebec/Labrador defined by various CO mixing ratio brackets (see text) over the gradient 50-150 ppbv. Symbols are defined as follows: solid square, tropical; plus, mixed; open square, background; asterisk, biomass burning; hour glass, upper tropospheric/lower stratospheric.
4.3. Relationships Between Species

Facets of the data analysis presented in this section used a data set where mixing ratios of the various reactive odd nitrogen species and NOx were averaged over the time span of the HNO3 measurements. This data set was used to examine NOx budget shortfalls [Sandholm et al., this issue] and relationships of PAN and HNO3 with NOx in this paper.

PAN/NOx. Values of the ratio PAN/NOx as a function of air mass category and altitude are given in Table 5. Below 1 km in altitude the ratio typically had a value of less than 2 in all air mass types. The lowest values (< 1) occurred over Quebec/Labrador. The vertical distribution of PAN/NOx is driven largely by the steep gradient in PAN mixing ratios. In the 3- to 6-km altitude range, PAN/NOx values were 6-10, except in the Quebec/Labrador tropical air mass where it was about 3. Indeed, low values of PAN/NOx are typical of the atmosphere over the Pacific Ocean, especially in warm boundary layer air where the ratio usually has values < 1 [Ridley et al., 1990a, b; Singh et al., 1990]. It is interesting to note that values of the ratio PAN/NOx in air masses impacted by biomass-burning over Ontario had essentially the same values as those in "background" air (Figure 4a). This was also the case over the Quebec/Labrador region, even though the ratio values were about a factor of 2 larger than those over Ontario. This geographic difference in ratio values was caused by the twofold larger mixing ratios of PAN at low altitudes over Quebec/Labrador compared to Ontario (Tables 1 and 3). On the average the boundary layer air temperatures were about 10°C warmer over Ontario (~22°C) than Quebec/Labrador (~12°C). This difference in air temperature, combined together with PAN's thermal stability, may explain the observed regional PAN distributions.

The small NOx mixing ratios suggest that we routinely sampled air masses that were aged a few days or had primarily smoldering combustion inputs. It appears that in these air masses the PAN mixing ratio, and thus the value of the ratio PAN/NOx, was controlled mainly by PAN's thermal stability [e.g., Wunderli and Gehrig, 1991]. In the range of tropospheric temperatures measured over Canada, a change of a few degrees could shift the PAN half-life by twofold [Singh et al., 1986]. Only in the 3- to 6-km altitude range, where PAN is much more thermally stable were very high values of the ratio PAN/NOx (15-30) observed. As in the high-latitude atmosphere over Alaska [Sandholm et al., 1992], the ABLE 3B study region over central Canada was dominated by the occurrence of NOx-limited aged air masses. In the boundary layer, release of peroxyacetyl (PA) radicals from PAN decomposition and subsequent PA-related chemistry under such NOx-limited conditions might influence photochemical processes [Ridley et al., 1990a, b] and also lead to formation of oxygenated hydrocarbons [Calvert and Madronich, 1987].

At higher altitudes where PAN's thermal decomposition is much slower than in warm boundary layer air, the value of the PAN/NOx ratio was more variable. Here source/sink processes in various air mass types may have produced a suite of PAN mixing ratios that are better preserved than those in the boundary layer. The wide range of PAN/NOx ratio values in various air mass categories over the Quebec/Labrador region illustrates this point (Figure 4b). Even in "background" air the PAN/NOx ratio exhibited fivefold variability. The upper tropospheric/lower stratospheric air masses also showed a wide range of values, indicating variable influence on PAN/NOx ratio values in the 3- to 6-km altitude range over central Canada.

In general, the PAN/NOx ratio values observed over central Canada were significantly greater, especially in the free troposphere, than those values reported for the atmosphere over the western United States and eastern Pacific Ocean [Singh et al., 1985; Ridley et al., 1990a, b]. The high values were not unexpected, however, based on the PAN/NOx ratios observed at high latitudes during CTE/ABLE 3A. PAN/NOx ratios in the high-latitude free troposphere were commonly 10-15 [Singh et al., 1992], compared to midtropospheric values of 5-6 in maritime air masses and 2-4 in continental air over the western United States and eastern Pacific Ocean [Ridley et al., 1990a, b].

Although in the boundary layer, PAN/NOx ratios in "background" air were very similar over both Canadian study areas, free tropospheric ratio values were significantly larger (p<0.05) over Ontario (median = 9.6) than those over the Quebec/Labrador region (median = 6.7). Isentropic trajectories show that during the ABLE 3B experiment the Ontario region received substantially more direct inputs of high-latitude air masses than did the Quebec/Labrador area [Shipham et al., this issue]. The frequent occurrence of air masses over Ontario with "background" Arctic air CO mixing

| Air Mass                      | <1 km | >3-6 km |
|------------------------------|-------|---------|
|                              | Mean  | s.d.    | Median | Range     | N | Mean  | s.d.    | Median | Range     | N |
| Ontario background           | 2.1   | 0.60    | 2.0    | 1.2-3.7  | 13 | 9.3   | 2.9     | 9.6    | 5.2-15    | 24 |
| Quebec/Labrador background   | 1.6   | 0.67    | 1.6    | 0.49-3.0 | 21 | 6.4   | 2.0     | 6.7    | 1.3-9.6   | 13 |
| Quebec/Labrador mixed        | 1.0   | 0.44    | 1.0    | 0.39-2.4 | 23 | 6.4   | 3.3     | 6.4    | 1.1-12    | 14 |
| Quebec/Labrador tropical     | —     | —       | —      | —       | —  | 3.2   | 1.1     | 2.9    | 1.6-5.0   | 9  |
| Upper tropospheric/          | —     | —       | —      | —       | —  | —     | —       | —      | —        | —  |
| Lower stratospheric          | —     | —       | —      | —       | —  | —     | —       | —      | —        | —  |
| Ontario, BB                  | 1.5   | 1.5     | 1.4    | 0.18-2.9 | 29 | 10.4  | 5.9     | 8.4    | 2.3-29    | 28 |
| Quebec/Labrador, BB          | 1.9   | 0.72    | 1.9    | 0.38-3.0 | 14 | 7.9   | 2.8     | 7.0    | 3.4-15    | 22 |

BB means biomass burning. s.d., standard deviation.
ratios supports the trajectory analysis. "Background" air was observed on every aircraft mission over Ontario, except 8 and 9, where biomass-burning inputs apparently dominated the chemical signature. The relatively large mixing ratios of PAN observed in these high-latitude NO_x-limited "background" air masses [Singh et al., 1992] should have elevated PAN/NO_x ratios over Ontario. Air masses originating from remote lower-latitude regions typically exhibit much lower PAN/NO_x ratios [Singh et al., 1986; Ridley et al., 1990a, b]. Thus "background" air over the Quebec/Labrador region may reflect more influence of middle- and low-latitude aged air inputs than such air masses over Ontario.

HNO_3/NO_x. Tropospheric chemical models predict that in continental regions the HNO_3/NO_x ratio should have a value in the range of 1 to 5, with the lowest values occurring near the surface due to wet and dry deposition of HNO_3 and the presence of NO sources [Fishman and Crutzen, 1977; Logan et al., 1981; Thompson and Cicerone, 1982]. However, ground-based measurements of this ratio at Niwot Ridge, Colorado, seldom exceeded 1 and it was usually between 0.1 and 0.4 [Parish et al., 1986; Fahey et al., 1986]. Over the western United States and eastern Pacific Ocean, reported values of HNO_3/NO_x seem to agree with previous model predictions [Huebert et al., 1990]. Our data for the troposphere over central Canada agree with these same model results at low altitude but showed deviation from model expectations in the midtroposphere.

Values of the ratio HNO_3/NO_x are shown in Figure 5 as a function of altitude. The ratio shows a trend of decreasing values with increasing altitude over the Ontario region (Figure 5a). Contrasting this are the ratio values over Quebec/Labrador that exhibited no altitudinal dependence. Boundary layer values were a factor of 2 larger over Ontario compared to those over Quebec/Labrador, but the ratios over these two regions were similar in free tropospheric air. The boundary layer values of around 1 in the Quebec/Labrador region coincide with model predictions. High-altitude air over Alaska exhibited HNO_3/NO_x values of 2-4 without a perceivable trend with altitude [Sandholm et al., 1992]. Thus the values of HNO_3/NO_x (and HNO_3 mixing ratios) in "background" boundary layer air over Ontario may show influence from inputs of polar air.

Precipitation-modified air masses were encountered more frequently over Quebec/Labrador than over Ontario [Shipham

Fig. 4. Vertical distribution of the ratio PAN/NO_x in selected air mass categories. (a) Ontario: open square, "background"; diamond, biomass burning. (b) Quebec/Labrador: open square, "background"; diamond, mixed; solid square, tropical; triangle, upper tropospheric/lower stratospheric.

Fig. 5. Vertical distribution of the ratio HNO_3/NO_x. (a) "background": solid triangle, Ontario; open square, Quebec/Labrador. (b) biomass burning: solid diamond, Ontario; open diamond, Quebec/Labrador. (c) Quebec/Labrador: plus, mixed; solid square, tropical; open diamond, biomass burning; open triangle, upper tropospheric/lower stratospheric.
Talbot et al., this issue]. Mixing ratios of HNO₃ were larger in "background" air over Quebec/Labrador compared to those over Ontario (Tables 1 and 3), possibly reflecting the somewhat fresher biomass-burning emissions encountered in the Ontario region. However, very small HNO₃ mixing ratios and HNO₃/NO ratios were also observed in "background" air over Quebec/Labrador that we believe was modified by precipitation. The net effect was an occurrence of both high and low values for HNO₃/NO, presumably due to biomass-burning inputs and precipitation scavenging of HNO₃.

The observed values of HNO₃/NO in the free troposphere that are less than 1 do not agree with model predictions which put the value of this ratio closer to 6 [e.g., Thompson and Cicerone, 1982]. However, these models assumed a precipitation removal frequency for HNO₃ that is probably much too low for summertime conditions in boreal and subarctic regions. With respect to "background" air in the 3- to 6-km altitude range over Alaska, "background" air over central Canada at 3-6 km had smaller HNO₃ (~40%) but larger NO (~70%) mixing ratios [Sandholm et al., 1992; Talbot et al., 1992]. These shifts in relative abundance translate to a twofold decrease in the HNO₃/NO ratio over central Canada compared to Alaska. Again, the increase in NO going from the Alaska to Canada could be attributed to thermal decomposition of PAN producing NO more effectively, coupled with a higher precipitation scavenging rate of HNO₃ over Canada. The data support the hypothesis that the transport of high-latitude air to central Canada poses a significant influence on tropospheric chemistry there.

With the exception of the "background" air over Ontario the distribution of HNO₃/NO in all other air mass categories considered here showed no altitude dependency (Figures 5b and 5c). The ratio statistics are summarized in Table 6. Air masses characterized as influenced by upper tropospheric/lower stratospheric air exhibited quite low values of HNO₃/NO. Subsidence of these high-altitude air masses to lower altitudes should result in reduced HNO₃/NO ratios in the midtroposphere. The low value of the ratio in upper tropospheric/lower stratospheric air masses was driven primarily by increased NO mixing ratios.

### Table 6. HNO₃/NO Ratio as a Function of Air Mass Categories

| Air Mass                  | Mean | s.d. | Median | Range  | N  |
|--------------------------|------|------|--------|--------|----|
| Ontario background       | 1.6  | 1.2  | 1.5    | 0.33-4.7 | 37 |
| Quebec/Labrador background | 1.0  | 0.64 | 0.93   | 0.13-2.5 | 37 |
| Quebec/Labrador mixed    | 1.7  | 1.3  | 0.80   | 0.20-4.7 | 38 |
| Quebec/Labrador tropical | 1.2  | 0.80 | 1.1    | 0.21-3.3 | 12 |
| Upper tropospheric/lower stratospheric | 0.77 | 0.46 | 0.65   | 0.20-1.8 | 46 |
| Ontario, biomass burning | 2.9  | 2.8  | 1.9    | 0.48-14 | 63 |
| Quebec/Labrador, biomass burning | 2.7  | 2.0  | 2.4    | 0.24-7.9 | 40 |

The largest values of the ratio HNO₃/NO were found in biomass-burning impacted air masses. With reference to "background" air there were marginal increases in HNO₃/NO ratios in air masses influenced by biomass-burning emissions over Ontario compared to an overall two- and-a-half-fold enhancement over Quebec/Labrador. It appears that the mixed air masses over Quebec/Labrador may have a biomass-burning component in some instances (Figure 5c) to account for HNO₃/NO values greater than about 2.5 (Figure 5c).

NO/O₃. The ratio of NO/O₃ (ppbv/ppbv) was used to examine the relative abundance of NO with respect to O₃ (Figure 6). In aged air masses this ratio should shift to lower values as the NO reservoir is lost to HNO₃ and subsequent wet and dry deposition of atmospheric nitrate. As previously stated, NO and O₃ were correlated in the sense that their mixing ratios increased with increasing altitude. Over Alaska the value of the ratio NO/O₃ exhibited no dependence on altitude, with a median value of about 0.009 in "background" Arctic air. The Quebec/Labrador "background" air data showed this same vertical distribution, exhibiting a value (0.007) similar to that over Alaska. The lack of an altitudinal trend in the ratio indicates that the "background" air was well mixed. The NO and O₃ mixing ratios reported for the midtroposphere over the eastern Pacific Ocean [see Hübeler et al., 1992; Ridley, 1991, for summary] indicate that the NO/O₃ ratio there typically has a value around 0.007. This value is similar to what we observed over Alaska and Canada.

The NO/O₃ ratio over Ontario showed low values in the boundary layer (median = 0.005) undergoing gradual increase to around 0.010 (median value) in the 3- to 6-km altitude range. Boundary layer air over Quebec/Labrador showed substantial variability of NO/O₃ exhibiting a range of values from 0.003 to 0.016, in contrast to the tight distribution around 0.005 over Ontario. Significantly higher O₃ mixing ratios were observed in the boundary layer over Ontario compared to those over Quebec/Labrador, while those of NO were about equal (Tables 1 and 3). Thus the incidence of higher values of NO/O₃ over Quebec/Labrador seems to be caused primarily by the smaller O₃ mixing ratios there. Over Ontario the median mixing ratios of O₃ below 3 km altitude were essentially identical to those observed over Alaska during ABLE 3A [Gregory et al., 1992]. In the 3- to 6-km altitude range, O₃ mixing ratios were significantly smaller over Ontario compared to Alaska, presumably due to a stronger stratospheric influence in the latter region [Browell et al., this issue].

Over both study areas there appears to be ≤20% enhancement in O₃ concentration associated with biomass-burning emissions (Tables 1 and 3). The large values in the ratio NO/O₃ (Figure 6) seem to result primarily from NO₂ enhancement associated with biomass-burning emissions. Over Quebec/Labrador this influence was most pronounced at altitudes of 3-6 km. The NO/O₃ ratios over Ontario showed apparent influence from biomass-burning emissions over the entire altitude range sampled (Figure 6c). This same effect was only apparent in the 3- to 6-km altitude range over Quebec/Labrador (Figure 6d). The upper limit value of the ratio NO/O₃ was about 0.05 over both Canadian study regions. Even though boreal fires seem to be NO₂ poor, they still appear to cause significant enhancement of...
NO\textsubscript{x} mixing ratios over those in "background" air. There appears to be rapid photochemical conversion of NO\textsubscript{y} to other NO\textsubscript{x} species in boreal fire plumes [Jacob et al., 1992; Wofsy et al., 1992]. At lower altitudes, much of the NO\textsubscript{y} was in the form of HNO\textsubscript{3}, whereas above 3-km altitude the PAN component dominated NO\textsubscript{y}.

Anthropogenically influenced air masses a few hundred kilometers from point sources typically show NO\textsubscript{y}/O\textsubscript{3} values near 0.1-0.2 [Trainer et al., 1991]. A main difference between such air masses possibly advected northward from the United States and boreal fire emissions would seem to lie in the production of photochemical O\textsubscript{3}. Urban plumes usually have NO\textsubscript{x}-rich hydrocarbon mixtures which promote photochemical O\textsubscript{3} production [Liu et al., 1987; Chameides et al., 1988; Trainer et al., 1991]. However, boreal fire impacted air masses over Alaska and Canada exhibited relatively small O\textsubscript{3} mixing ratios [Browell et al., 1992; Gregory et al., 1992; Anderson et al., this issue; Browell et al., this issue].

In air masses influenced by the composition of the upper troposphere/lower stratosphere, NO\textsubscript{y}/O\textsubscript{3} ratios (Figure 7a) varied by nearly an order of magnitude (i.e., 0.005 to 0.05) around a median value of 0.012. Air subsiding from aloft into the 3- to 6-km altitude range appears to be much more rich in NO\textsubscript{y} than O\textsubscript{3}. Besides containing elevated NO\textsubscript{y}, the chemical form of the NO\textsubscript{y} enhancement in subsiding air is unknown [Sandholm et al., this issue]. However, biomass-burning and subsidence of upper tropospheric/lower stratospheric air appear to be the principal sources of NO\textsubscript{y} to the midtroposphere over central Canada and cause enhancements of NO\textsubscript{y}/O\textsubscript{3} values over those observed in "background" air over these regions. Just the opposite effect resulted from the tropical air masses which exhibited NO\textsubscript{y}/O\textsubscript{3} ratios <0.01 over Quebec/Labrador (Figure 7b). The small NO\textsubscript{y}/O\textsubscript{3} ratio values in this air mass are indicative of well-aged air. In the 3- to 6-km altitude range the ratio had a median value of 0.004 in the tropical air mass compared to 0.007 in "background" air. The NO\textsubscript{y}/O\textsubscript{3} ratios were indistinguishable in the mixed and "background" air masses at altitudes above 3 km. Below 3 km in altitude the mixed air mass showed NO\textsubscript{y}/O\textsubscript{3} ratios tightly bound around the median value of 0.004 (Figure 7c). The decreased ratio values at low altitudes most likely reflect removal of HNO\textsubscript{3} by precipitation, as discussed earlier in Section 4.2. The mixed and tropical air mass over

![Fig. 6. Vertical distribution of the ratio NO\textsubscript{y}/O\textsubscript{3} in selected air mass categories: (a) Ontario "background"; (b) Quebec/Labrador "background"; (c) Ontario biomass burning; (d) Quebec/Labrador biomass burning.](image-url)
Quebec/Labrador were quite depleted of NO (and O₃), and their occurrence decreased the ratio NO/O₃ at various altitudes. Both of these air masses had chemical signatures consistent with the characteristics expected of aged air that was cloud processed. Our data analysis revealed the relatively high abundance of NO relative to O₃ in the pockets of dry air over central Canada, presumably originating from the upper troposphere/lower stratosphere. If a strong stratospheric influence was present in this air, low values of NOy/O₃ would be expected [McElroy and Salawitch, 1989]. Recent extensive measurements of NOy/O₃ in the upper troposphere and lower stratosphere (5- to 21-ktm altitude) exemplify these expected low ratio values and show its remarkable consistency of 0.0015-0.002 in the tropics and 0.0025-0.004 elsewhere [Murphy et al., 1993]. Elevated HNO₃ mixing ratios should also be found in stratospherically influenced air masses [Russell et al., 1988], unless it is rapidly removed by heterogeneous processes.

The NO and O₃ mixing ratios and thus NOy/O₃ in dry pockets of air over Canada were similar to what was observed in biomass-burning impacted air masses in the 3- to 6-km altitude range (Tables 1 and 3, Figures 6 and 7). However, the NOx mixing ratios were somewhat larger, while those of HNO₃, p-NO₃, and PAN were significantly smaller in these dry pockets of air compared to those in biomass-burning impacted air masses at 3- to 6-km altitudes. The relatively small CO and CH₄ mixing ratios in the dry pockets of air are inconsistent with the idea that with biomass-burning and possibly industrial emissions influenced their chemical composition. In addition, mixing ratios of C₂Cl₄ and selected fluorocarbons and hydrocarbons in the upper tropospheric/lower stratospheric air masses were similar to those observed in the "background" and tropical air masses over Canada (Table 7).

The fact that the median mixing ratios of selected hydrocarbons, C₂Cl₄, and F-12 (Table 7) were essentially the same in the upper tropospheric/lower stratospheric and "background" air masses suggests that these dry air masses were not significantly influenced by stratospheric air. Furthermore, this same comparison may indicate that "background" air has similar chemical composition in the entire tropospheric column over subarctic regions of North America.

On virtually every flight over the Ontario and Quebec/Labrador regions the UV differential absorption lidar (DIAL) zenith data depicted regions of small O₃ mixing ratios in the 7- to 10-km altitude range, with values down to 20 ppbv. This phenomenon was also observed during the transit flights back to Wallops Island, Virginia. Over eastern North America a large number of these low O₃ air masses appeared to be associated with tropical air masses characterized by uniformly small O₃ mixing ratios and low aerosol concentrations (Plate 1). This seemingly tropical air appears to have originated from low latitudes over the Pacific Ocean in association with Typhoon Steve and possibly the Atlantic Ocean as outflow from Hurricane Bertha may have impacted the midtroposphere over eastern North America.

Air masses depleted in O₃ appeared to have both small (Plate 2) and large (Plate 3) aerosol loadings associated with them. The regions of low O₃ over Ontario did not appear to be nearly as extensive in size as the ones observed over Quebec/Labrador [Browell et al., this issue]. Plate 2 illustrates the typical size of the low O₃ regions that were observed over Ontario. This plate illustrates an apparent stratospheric fold penetrating a tropospheric region exhibiting small O₃ mixing ratios. Frequently, we also observed
The first 180 data points were obtained over Ontario, while a very diverse set of chemical and dynamical conditions influenced mixing ratios and enhanced aerosol loadings (Plate 4). Allhaps a more satisfying explanation for the composition of NOx and NO enhancements relative to CO. However, per-described in a companion paper [Sandholm et al., this issue]. The time series of NO mixing ratios in this dry air shows large variability over Ontario but not over Quebec/Labrador. Ozone, on the other hand, shows periodic fluctuations in its mixing ratio from 40 to 100 ppbv across the entire suite of NOx mixing ratios. It may be that the NOx mixing ratios over Quebec/Labrador were consistently diluted in the upper troposphere by intrusion of NOx-depleted tropical air. Subsiding air over this region may have reflected inputs of stratospheric O3 mixed into an upper tropospheric region with low NOx (and CO, CH4, and O3).

We still need to address the confounding situation in the upper tropospheric/lower stratospheric air masses over Canada. This situation may reflect convective outflow of lower-altitude air. Regions of cloud outflows into the upper troposphere were noted on numerous occasions [Browell et al., this issue]. This cloud pumping could have transported boundary layer aerosol particles, including those derived from biomass-burning emissions and associated trace gases (e.g., NOx), to higher altitudes. Note that in the far right portion of Plate 3 there is a region with relatively large O3 mixing ratios but low aerosol concentrations. This region of enhanced O3 may have been photochemically derived. If so, it is in direct contrast to the lack of significant photochemical O3 production in biomass-burning plumes at lower altitudes. We also observed other tropospheric regions with relatively large O3 mixing ratios and enhanced aerosol loadings (Plate 4). All of the specific cases discussed above collectively point to a very diverse set of chemical and dynamical conditions influencing the composition of the upper troposphere. Qualitatively, we illustrate this by plotting coincident mixing ratios of NOx and O3 in the air masses characterized as subsiding from the upper tropospheric/lower stratospheric (Figure 8). The first 180 data points were obtained over Ontario, while the rest were observed independently over Quebec/Labrador. The time series of NOx mixing ratios in this dry air shows large variability over Ontario but not over Quebec/Labrador.

Ozone, on the other hand, shows periodic fluctuations in its mixing ratio from 40 to 100 ppbv across the entire suite of NOx mixing ratios. It may be that the NOx mixing ratios over Quebec/Labrador were consistently diluted in the upper troposphere by intrusion of NOx-depleted tropical air. Subsiding air over this region may have reflected inputs of stratospheric O3 mixed into an upper tropospheric region with low NOx (and CO, CH4, and O3).

We still need to address the confounding situation in the upper tropospheric/lower stratospheric air masses where relatively small mixing ratios of almost all species discussed in this paper are needed in combination with apparent NOx and NOy sources. It appears that other sources of NOx and NOy in the middle to upper troposphere, such as lightning and high-efficiency turbine jet aircraft [Ehhalt et al., 1992], are required to explain our observations. We believe that we have sampled the latter on several occasions, seeing large NOx and NOy enhancements relative to CO. However, perhaps a more satisfying explanation for the composition of the upper tropospheric/lower stratospheric air masses is described in a companion paper [Sandholm et al., this issue].

TABLE 7. Median Mixing Ratios (pptv) of Selected Organic Compounds in Various Air Mass Types Over Canada.

| Air Mass            | C2H4 | C2H6 | C3H8 | C2Cl4 | F-12 |
|---------------------|------|------|------|-------|------|
| Upper troposphere/  |      |      |      |       |      |
| lower stratosphere   | 697  | 88   | 72   | 12    | 492  |
| Ontario background   | 815  | 73   | 88   | 13    | 500  |
| Quebec/Labrador      |      |      |      |       |      |
| background           | 705  | 83   | 90   | 11    | 496  |
| Tropical             | 508  | 25   | 46   | 8.5   | 495  |

The proposed mechanism involves direct photolysis of HNO3 yielding NO2 (and thus NOx). If this NO2 was converted to labile reactive odd nitrogen compounds more rapidly than competing reformation of HNO3, an air mass in the upper troposphere could possibly age losing much more O3 than NOx. Thermally stable HO2NO3 was hypothesized by Sandholm et al. [this issue] to be a dominant component of upper tropospheric NOx over the Canadian study regions. In addition, HNO3 photolysis and HO2NO3 thermal decomposition could lead to enhanced production of PAN and other organic-nitrogen containing compounds, especially in the midtroposphere where hydrocarbon precursors might be more abundant than at higher altitudes. To better clarify the source(s) of reactive odd nitrogen in the pockets of dry air over eastern North America, it would seem desirable to sample this same region again using an aircraft with a much higher altitude ceiling than the NASA Electra.

4.4. Comparison of Arctic Boundary Layer Expedition (ABLE) 3A and 3B Air Mass Compositions

The chemical composition of the upper tropospheric/lower stratospheric air masses over Canada is strikingly similar to what was observed at 3- to 6-km altitudes in the high Arctic during ABLE 3A (Tables 4 and 8). As previously pointed out, the "background" air over Ontario exhibited chemical characteristics suggestive of a high-latitude source (Table 1). During the ABLE 3B program the dominant flow of air in the 3- to 6-km altitude range over the Canadian study region was from the west, with three- to five-day back-trajectory analysis indicating the upper Northwest Territories and Alaska as probable origins [Shipham et al., this issue]. During the July-August 1988 ABLE 3A program a number of air masses were encountered over Alaska that could be envisioned to extend this general flow pattern farther westward. Table 8 gives values for selected chemical variables observed in these air masses during ABLE 3A for which three- to five-day back-trajectory analysis indicates air mass origins of a similar but more westward origin than the NASA Electra.
Plate 1. UV differential absorption lidar (DIAL) representation of the aerosol and O\textsubscript{3} vertical distributions (6- to 11-km altitudes) over eastern North America during mission 19, August 13, 1990.
Plate 2. UV DIAL representation of the aerosol and $O_3$ vertical distributions (5- to 10-km altitudes) over Ontario during mission 2, July 9, 1990.
Plate 3. UV DIAL representation of the aerosol and $O_3$ vertical distributions (5- to 10-km altitudes) over Ontario during mission 3, July 11, 1990.
Plate 4. UV DIAL representation of the aerosol and O₃ vertical distributions (7- to 12-km altitudes) over northern Quebec/Labrador during mission 11, August 1, 1990.
TABLE 8. Selected Chemical Characteristics of Air Masses at 3-6 km Altitude Over Alaska During July-August 1988

| Species | Mean | s.d. | Median | Range | N  | Mean | s.d. | Median | Range | N |
|---------|------|------|--------|-------|----|------|------|--------|-------|----|
| NO      | 10   | 5    | 10     | 3-22  | 71 | 8    | 5    | 7      | 4-15  | 37 |
| NO₂     | 14   | 7    | 11     | 7-36  | 42 | 15   | 5    | 15     | 8-25  | 16 |
| NO₃     | 26   | 10   | 23     | 13-58 | 42 | 20   | 5    | 20     | 14-32 | 16 |
| PAN     | 240  | 105  | 243    | 65-446| 41 | 240  | 65   | 220    | 91-324| 18 |
| NOy     | 550  | 140  | 450    | 178-2688| 75 | 560  | 150  | 450    | 178-2688| 75 |
| O₃      | 75   | 5    | 75     | 50-283| 102| 75   | 5    | 75     | 50-283| 102|
| CO      | 95   | 5    | 95     | 63-106| 74 | 100  | 5    | 100    | 63-106| 74 |
| CH₄     | 1725 | 10   | 1725   | 1658-1745| 83 | 1725 | 10   | 1725   | 1658-1745| 83 |

| Species | Mean | s.d. | Median | Range | N  | Mean | s.d. | Median | Range | N |
|---------|------|------|--------|-------|----|------|------|--------|-------|----|
| NO      | 5    | 5    | 5      | 4-20  | 34 | 5    | 5    | 5      | 4-20  | 34 |
| NO₂     | 15   | 5    | 12     | 9-25  | 19 | 15   | 5    | 12     | 9-25  | 19 |
| NO₃     | 20   | 10   | 20     | 13-38 | 19 | 30   | 10   | 31     | 18-48 | 26 |
| PAN     | 100  | 50   | 75     | 31-200| 31 | 300  | 175  | 315    | 44-703| 26 |
| NOy     | 600  | 530  | 450    | 178-2688| 34 | 450  | 250  | 375    | 185-2688| 34 |
| O₃      | 50   | 10   | 50     | 36-76 | 75 | 80   | 15   | 80     | 48-100| 36 |
| CO      | 95   | 5    | 95     | 81-114| 64 | 130  | 15   | 125    | 97-159| 48 |
| CH₄     | 1722 | 10   | 1723   | 1703-1739| 64 | 1745 | 10   | 1745   | 1697-1760| 48 |

Reactive nitrogen species mixing ratios are given in pptv; all other species are in ppbv.

5. CONCLUSIONS

We have described the distribution of reactive odd nitrogen in the troposphere over central Canada. Various air mass categories were defined by bracketing specific CO mixing ratios over a gradient from 60 to several hundred parts per billion by volume (ppbv). Over Ontario we observed only air masses classified as "background" (CO, 95-105 ppbv) or biomass-burning impacted (CO>105 ppbv). Pockets of dry air were frequently encountered in the 3-6 km altitude range, presumably due to subsidence of upper tropospheric/lower stratospheric air.

During our observational period the atmospheric structure was more complex over Quebec/Labrador than what was observed over Ontario. The intrusion of tropical air (CO, 60-79 ppbv) at altitudes of 2-6 km over Quebec/Labrador had a major influence on the chemistry there. Additional marine air may have been injected into the midtroposphere over North America due to the passage of Hurricane Bertha off the east coast of Canada/United States in early August. Besides "background" and biomass-burning impacted air masses, a mixed air mass was identified over Quebec/Labrador with CO mixing ratios of 80-94 ppbv. Frequent incursions of upper tropospheric/lower stratospheric air also influenced this region.

"Background" air in the Ontario area had chemical characteristics very similar to what was observed in the high-latitude atmosphere over Alaska during ABLE 3A. This did not seem to be the case over Quebec/Labrador. The ABLE 3B meteorological analysis supports this contention, indicating frequent intrusion of continental polar air over Ontario and a predominance of westerly flow with long fetches over the Northwest Territories and Alaska influencing the Quebec/
Laborador area. We find little direct evidence over central Canada for enhancement of mixing ratios of reactive odd nitrogen species and NO_{x} above those in "background" air by anthropogenic emissions. Generally, this region appears to be dominated by NO_{x}-limited aged air masses. Even when the chemistry was apparently driven primarily by biomass-burning impacts, NO_{x} concentrations were typically <50 ppv. Biomass-burning emissions influencing the Canadian study regions appear to be several days old or from CO-rich NO_{x}-poor smoldering local fires. Within the boundary layer NO_{x} appears to be efficiently converted to HNO_{3}, but in the free troposphere, NO_{x} seems to be controlled by the large PAN reservoir which may be derived, to some extent, from biomass-burning emissions.

Our analysis focused on synthesizing the ABLE 3B reactive odd nitrogen data set in a systematic manner to provide a referable baseline for subsequent interpretation of the measurements. Indeed, for this region of the troposphere over North America it appears that CO mixing ratio provides one reasonable basis for formulating air mass categories. This approach was chosen specifically to facilitate examination of the large-scale processes influencing the distribution of reactive odd nitrogen species and NO_{x}. Our analysis has uncovered several seemingly unexplained important features that appear to significantly influence the large-scale tropospheric chemistry over northeastern North America. These features are posed below in the following form of questions:

1. Why is the NO_{x} abundance so high compared to O_{3} in the "upper tropospheric/lower stratospheric" air masses?
2. Are intrusions of NO_{x}-depleted tropical air in the midtroposphere over eastern North America important to the budget of reactive odd nitrogen in this region during summertime?
3. What is the nature of the apparent large-scale connections which seem to promote remarkable consistency in the chemical composition of the North American troposphere from about 52°N latitude to the high Arctic?

These questions are important and their answers should be addressed in future modeling and research aircraft activities.

Acknowledgments. We appreciate the support provided by the staff of the NASA Wallops Flight Facility and the crew of the Electra research aircraft during ABLE 3B. The excellent facilities made available to us and the thoughtful help of the staff of Canador College, North Bay, Ontario, are gratefully appreciated and acknowledged by the UNH group. We appreciate the contributions of Diana Wright and Joann Ward in the preparation of this manuscript. This research was supported by the NASA Global Tropospheric Chemistry program.

6. References

Anderson, B. E., G. L. Gregory, J. D. W. Barrick, J. E. Collins, G. W. Sachse, M. C. Shippam, and C. H. Hudgins, Summertime tropospheric ozone distributions over central and eastern Canada, J. Geophys. Res., this issue.

Atherton, C. S., Organic nitrates in remote marine environments: Evidence for long range transport, Geophys. Res. Lett., 11, 1289-1292, 1989.

Atlas, E., Evidence for C_{2} alkyl nitrates in rural and remote atmospheres, Nature, 331, 426-428, 1988.

Atlas, E. L., B. A. Ridley, G. Hubler, J. G. Walega, M. A. Carroll, D. D. Montzka, B. J. Huebert, R. B. Norton, F. E. Grahek, and S. Schaufler, Partitioning and budget of NO_{x} species during the Mauna Loa Observatory Photochemistry Experiment, J. Geophys. Res., 97, 10,449-10,462, 1992.

Bakwin, P. S., S. C. Wofsy, S. M. Fan, and D. R. Fitzjarrald, Measurements of NO_{x} and NO concentrations and fluxes over Arctic tundra, J. Geophys. Res., 97, 15,455-15,557, 1992.

Blake, D. R., T. W. Smith, Jr., T. -Y. Chen, W. J. Whipple, and F. S. Rowland, Effects of biomass-burning on summertime nonmethane hydrocarbon concentrations in the Canadian wetlands, J. Geophys. Res., this issue.

Bradshaw, J. D., M. O. Rogers, S. T. Sandholm, S. Kesheng, and D. D. Davis, A two-photon laser-induced fluorescence field instrument for ground-based and airborne measurements of atmospheric NO_{x}, J. Geophys. Res., 90, 12,861-12,873, 1985.

Brock, C. A., L. F. Radke, J. H. Lyons, and P. V. Hobbs, Arctic hazes in summer over Greenland and the North American Arctic. I: Incidence and origins, J. Atmos. Chem., 9, 129-148, 1989.

Browell, E. V., C. F. Butler, S. A. Kooi, M. A. Fenn, R. C. Harriss, and G. L. Gregory, Large-scale variability of ozone and aerosols in the summertime Arctic and subarctic troposphere, J. Geophys. Res., 97, 16,433-16,450, 1992.

Browell, E. V., M. A. Fenn, C. F. Butler, W. B. Grant, R. C. Harriss, and M. C. Shippam, Ozone and aerosol distributions in the summertime troposphere over Canada, J. Geophys. Res., this issue.

Buhr, M. P., D. D. Parrish, R. B. Norton, F. C. Fehsenfeld, and R. E. Sievers, Contribution of organic nitrates to the total reactive nitrogen budget at a rural eastern U.S. site, J. Geophys. Res., 95, 9809-9816, 1990.

Calvert, J. G., and S. Madronich, Theoretical study of the initial products of the atmospheric oxidation of hydrocarbons, J. Geophys. Res., 92, 2211-2220, 1987.

Chameides, W. L., and J. C. G. Walker, A photochemical theory of tropospheric ozone, J. Geophys. Res., 78, 8751-8760, 1973.

Chameides, W. L., R. W. Lindsay, J. Richardson, and C. S. Kiang, The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study, Science, 241, 1473-1475, 1988.

Crutzen, P. J., The role of NO and NO_{x} in the chemistry of the troposphere and stratosphere, Annu. Rev. Earth Planet. Sci., 7, 443-472, 1979.

Crutzen, P. J., and M. O. Andreae, Biomass-burning in the Tropics: Impact on atmospheric chemistry and biogeochemical cycles, Science, 250, 1669-1678, 1990.

Ehhalt, D. H., F. Rohrer, and A. Wahner, Sources and distribution of NO_{x} in the upper troposphere at northern midlatitudes, J. Geophys. Res., 97, 3725-3738, 1992.

Fahey, D. W., G. Hubler, D. D. Parrish, E. J. Williams, R. B. Norton, B. A. Ridley, H. B. Singh, S. C. Liu, and F. C. Fehsenfeld, Reactive nitrogen species in the troposphere: Measurements of NO, NO_{x}, HNO_{3}, particulate nitrate, peroxyacetyl nitrate (PAN), O_{3}, and total reactive odd oxygen (NO_{x}) at Niwot Ridge, Colorado, J. Geophys. Res., 91, 9781-9793, 1986.
Fishman, J., and P. J. Crutzen, A numerical study of tropospheric photochemistry using a one-dimensional model, *J. Geophys. Res.,* 82, 5897-5906, 1977.

Gaffney, J. S., R. Fajer, and G. L. Senum, An improved procedure for high purity gaseous peroxyacetyl nitrate production: Use of heavy lipid solvents, *Atmos. Environ.,* 18, 215-218, 1984.

Galloway, J. N., and G. E. Likens, Acid precipitation: The importance of nitric acid, *Atmos. Environ.,* 15, 1081-1085, 1981.

Gorzelska, K., R. W. Talbot, K. Klemm, B. Lefer, O. Klemm, G. L. Gregory, and B. Anderson, Chemical composition of the atmospheric aerosol in the troposphere over the Hudson Bay lowlands and Quebec-Labrador regions of Canada, *J. Geophys. Res.,* this issue.

Gregory, G. L., C. H. Hudgins, and R. A. Edahl, Laboratory evaluation of an airborne ozone instrument which compensates for altitude/sensitivity effects, *Environ. Sci. Technol.,* 17, 100-103, 1983.

Gregory, G. L., J. M. Hoell, Jr., B. A. Ridley, H. B. Singh, B. Grendrud, L. J. Salas, and J. Shetter, An intercomparison of airborne PAN measurements, *J. Geophys. Res.,* 95, 10,077-10,087, 1990.

Gregory, G. L., B. E. Anderson, L. S. Warren, E. V. Browell, D. R. Bagwell, and C. H. Hudgins, Tropospheric ozone and aerosol observations: The Alaskan Arctic, *J. Geophys. Res.,* 97, 16,451-16,471, 1992.

Gregory, G. L., B. E. Anderson, J. D. Barrick, C. H. Hudgins, D. R. Bagwell, and D. R. Blake, Analysis of tropospheric aerosol number density for aerosols of 0.2- to 3-μm diameter: Central and northeastern Canada, *J. Geophys. Res.,* this issue.

Harriss, R. C., G. W. Sachse, G. F. Hill, L. Wade, K. E. Bartlett, J. E. Collins, L. F. Steels, and P. C. Novelli, Carbon monoxide and methane in the North American Arctic and subarctic troposphere: July-August 1988, *J. Geophys. Res.,* 97, 16,589-16,599, 1992.

Harriss, R. C., S. C. Wofsy, J. M. Hoell, Jr., R. J. Bendura, J. W. Drewry, R. J. McNea, D. Pierce, V. Rabine, and R. L. Snell, The Arctic Boundary Layer Expedition (ABLE) 3B: July-August 1990, *J. Geophys. Res.,* this issue (a).

Harriss, R. C., G. W. Sachse, J. E. Collins, L. O. Wade, K. B. Bartlett, R. W. Talbot, E. V. Browell, L. A. Barrie, G. F. Hill, and L. G. Burney, Carbon monoxide and methane over Canada: July-August 1990, *J. Geophys. Res.,* this issue (b).

Hübner, G., et al., Total reactive oxidized nitrogen (NO₃) in the remote Pacific troposphere and its correlation with O₃ and CO: MLOPEX 1988, *J. Geophys. Res.,* 97, 10,427-10,447, 1992.

Huebert, B. J., et al., Measurements of the nitric acid to NO ratio in the troposphere, *J. Geophys. Res.,* 95, 10,193-10,198, 1990.

Jacob, D. J., et al., Summertime photochemistry of the troposphere at high northern latitudes, *J. Geophys. Res.,* 97, 16,421-16,431, 1992.

Kasting, J. F., and H. B. Singh, Nonmethane hydrocarbons in the troposphere: Impact on odd hydrogen and odd nitrogen chemistry, *J. Geophys. Res.,* 91, 13,239-13,256, 1986.

Levy, H., II, Photochemistry of the lower troposphere, *Planet. Space Sci.,* 20, 919-935, 1972.

Liu, S. C., M. Trainer, F. C. Fe hsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hubler, and P. C. Murphy, Ozone production in the rural troposphere and implications for regional and global ozone distributions, *J. Geophys. Res.,* 92, 4191-4207, 1987.

Logan, J. A., Nitrogen oxides in the troposphere: Global and regional budgets, *J. Geophys. Res.,* 88, 10,785-10,807, 1983.

Logan, J. A., M. J. Prather, S. C. Wofsey, and M. B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res.,* 86, 7210-7254, 1981.

McElroy, M. B., and R. J. Salawitch, Changing composition of the global stratosphere, *Science,* 243, 763-770, 1989.

Murphy, D. M., D. W. Fahey, M. H. Proffitt, S. C. Liu, K. R. Chan, C. S. Eubank, S. R. Kawa, and K. K. Kelly, Reactive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res.,* 98, 8751-8773, 1993.

Parrish, D. D., R. B. Norton, M. J. Bollinger, S. C. Liu, P. C. Murphy, D. L. Albritton, F. C. Fe hsenfeld, and B. J. Huebert, Measurements of HNO₃ and NO₂-particulates at a rural site in the Colorado mountains, *J. Geophys. Res.,* 91, 5379-5393, 1986.

Ridley, B. A., Recent measurements of oxidized nitrogen compounds in the troposphere, *Atmos. Environ.,* 25, 1905-1926, 1991.

Ridley, et al., The behavior of some organic nitrates at Boulder and Niwot Ridge, *Colorado, J. Geophys. Res.,* 95, 13,949-13,961, 1990a.

Ridley, B. A., et al., Ratios of peroxyacetyl nitrate to active nitrogen observed during aircraft flights over the eastern Pacific Ocean and continental United States, *J. Geophys. Res.,* 95, 10,179-10,192, 1990b.

Russell, J. M., III, C. B. Farmer, C. P. Rinsland, R. Zander, L. Froidevaux, G. C. Toon, B. Gao, J. Shaw, and M. Gunson, Measurements of odd nitrogen compounds in the stratosphere by the ATMS experiment on Spacelab 3, *J. Geophys. Res.,* 93, 1718-1736, 1988.

Sachse, G. W., G. F. Hill, L. O. Wade, and M. G. Perry, Fast response, high-precision carbon monoxide sensor using a tunable diode laser absorption technique, *J. Geophys. Res.,* 92, 2071-2081, 1987.

Sandholm, S. T., J. D. Bradshaw, K. S. Dorris, M. O. Rogers, and D. D. Davis, An airborne compatible photofragmentation two-photon laser-induced fluorescence instrument for measuring background tropospheric NO, NO₂, and NO₃, *J. Geophys. Res.,* 95, 10,155-10,161, 1990.

Sandholm, S. T., et al., Arctic tropospheric observations related to NO₂ distributions and partitioning: ABLE 3A, *J. Geophys. Res.,* 97, 16,481-16,509, 1992.

Sandholm, S. T., et al., Summertime partitioning and budget of NO compounds in the troposphere over Alaska and Canada, *J. Geophys. Res.,* this issue.

Shipham, M. C., A. S. Bachmeier, D. R. Cahoon, Jr., G. L. Gregory, B. E. Anderson, and E. V. Browell, Meteorological interpretation of the Arctic Boundary Layer Expedition (ABLE) 3B flight series, *J. Geophys. Res.,* this issue.

Singh, H. B., Reactive nitrogen in the troposphere, *Environ. Sci. Technol.,* 21, 320-327, 1987.
Singh, H. B., and L. J. Salas, Methodology for the analyses of peroxyacetyl nitrate (PAN) in the unpolluted atmosphere, *Atmos. Environ.*, 17, 1507-1516, 1983.

Singh, et al., Relationship between peroxyacetyl nitrate and nitrogen oxides in the clean troposphere, *Nature*, 318, 347-349, 1985.

Singh, H. B., L. J. Salas, W. Viezee, Global distribution of peroxyacetyl nitrate, *Nature*, 321, 588-591, 1986.

Singh, et al., Peroxyacetyl nitrate measurements during CITE 2: Atmospheric distribution and precursor relationships, *J. Geophys. Res.*, 95, 10,163-10,178, 1990.

Singh, H. B., D. Herlth, K. Zahnle, D. O’Hara, J. D. Bradshaw, S. T. Sandholm, R. Talbot, P. J. Crutzen, and M. Kanakidou, Relationship of PAN to active and total odd nitrogen at northern high latitudes: Possible influence of reservoir species on NOx and O3, *J. Geophys. Res.*, 97, 16,523-16,530, 1992.

Stelson, A. W., S. K. Friedlander, and J. H. Seinfeld, A note on the equilibrium relationship between ammonia and nitric acid and particulate ammonium nitrate, *Atmos. Environ.*, 13, 369-371, 1979.

Talbot, R. W., A. S. Vijgen, and R. C. Harriss, Measuring tropospheric HNO3: Problems and prospects for nylon filter and mist chamber techniques, *J. Geophys. Res.*, 95, 7553-7561, 1990.

Talbot, R. W., A. S. Vijgen, and R. C. Harriss, Soluble species in the summer Arctic troposphere: Acidic gases, aerosols, and precipitation, *J. Geophys. Res.*, 97, 16,531-16,543, 1992.

Thompson, A. M., and R. J. Cicerone, Clouds and wet removal as causes of variability in the trace gas composition of the marine troposphere, *J. Geophys. Res.*, 87, 8811-8826, 1982.

Trainer, M., et al., Observations and modeling of the reactive nitrogen photochemistry at a rural site, *J. Geophys. Res.*, 96, 3045-3063, 1991.

Wofsy, S. C., et al., Atmospheric chemistry in the Arctic and subarctic: Influence of natural fires, industrial emissions, and stratospheric inputs, *J. Geophys. Res.*, 97, 16,731-16,746, 1992.

Wofsy, S. C., S. -M. Fan, D. R. Blake, J. D. Bradshaw, S. T. Sandholm, H. B. Singh, G. W. Sachse, and R. C. Harriss, Factors influencing atmospheric composition over subarctic North America during summer, *J. Geophys. Res.*, this issue.

Wolff, G. T., On the nature of nitrate in coarse continental aerosols, *Atmos. Environ.*, 18, 977-981, 1984.

Wunderli, S., and R. Gehrig, Influence of temperature on formation and stability of surface PAN and ozone: A 2-year field study in Switzerland, *Atmos. Environ.*, 25, 1599-1608, 1991.

---

B. Anderson, J. Barrick, E. V. Browell, J. Collins, G. L. Gregory, and G. W. Sachse, NASA Langley Research Center, Hampton, VA 23665.

D. Blake, Department of Chemistry, University of California-Irvine, Irvine, CA 92717.

J. D. Bradshaw, J. Olson, and S. T. Sandholm, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332.

K. Gorzelska, Now at Central Institute for Labor Protection, Warsaw, Poland.

D. Herlth, D. O’Hara, and H. B. Singh, NASA Ames Research Center, Moffett Field, CA 94035.

K. I. Klemm and O. Klemm, Now at Fraunhofer-Institut für Atmosphärische Umweltforschung, Garmish-Partenkirchen, Germany.

B. L. Lefer and R. W. Talbot, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824.

(Received August 12, 1992; revised June 25, 1993; accepted June 29, 1993.)