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## Summertime distribution and relations of reactive odd nitrogen species and $\text{NO}_y$ in the troposphere over Canada

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We report here large-scale features of the distribution of  $\text{NO}_x$ ,  $\text{HNO}_3$ , PAN, particle  $\text{NO}_3^-$ , and  $\text{NO}_y$  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  $\text{NO}_x$  limited, with  $\text{NO}_x$  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  $\text{NO}_y$  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- $\text{NO}_x$ -poor smoldering local biomass-burning fires.  $\text{NO}_x$  mixing ratios in biomass-burning impacted air masses were usually <50 pptv, but those of  $\text{HNO}_3$  and PAN were typically 100-300 pptv representing a twofold-threelfold 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  $\text{NO}_y$  (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 ( $\text{NO}_2$ ) 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  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2 = \text{NO}_x$ ), it is often converted photochemically to nitric acid ( $\text{HNO}_3$ ) 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 ( $\text{p-NO}_3^-$ ), from sorption of  $\text{HNO}_3$  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 ( $\text{RONO}_2$ , 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  $\text{NO}_x$ , but its long-range transport and thermal decomposition may ultimately provide a source of  $\text{NO}_x$  in the remote troposphere [Singh, 1987; Atlas et al., 1992]. Wet and dry deposition of atmospheric nitrate ( $\text{HNO}_3 + \text{p-NO}_3^-$ ) 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  $\text{HNO}_3$  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  $\text{NO}_x$  in the troposphere controls photochemical ozone ( $\text{O}_3$ ) 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,  $\text{NO}_2$ ,

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$\text{HNO}_3$ , PAN,  $p\text{-NO}_3$ , and total reactive odd nitrogen ( $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_3 + \text{N}_2\text{O}_5 + \text{HONO} + \text{HNO}_3 + \text{PAN} + \text{higher alkylperoxy nitrates such as PPN} + \text{RONO}_2 + p\text{-NO}_3$ ) 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  $\text{O}_3$  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  $\text{O}_3$  and tunable diode laser absorption CO and  $\text{CH}_4$  systems are described in detail elsewhere [Gregory *et al.*, 1983; Sachse *et al.*, 1987].

Nitric oxide,  $\text{NO}_2$ , and  $\text{NO}_y$  were measured simultaneously with the Georgia Tech two-photon/laser-induced fluorescence (TP/LIF) instrument [Bradshaw *et al.*, 1985; Sandholm *et al.*, 1990]. This spectroscopically selective NO technique simultaneously determined NO, NO produced from the photolysis of  $\text{NO}_2$ , and NO produced from the reduction of  $\text{NO}_y$  compounds using a 300°C gold catalytic surface with 0.3% CO as a reducing agent. A 1-kW photolytic converter was operated with a photolysis passband of  $350 \text{ nm} < \lambda < 410 \text{ nm}$ , 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  $\text{N}_x\text{O}_y$  measurements were reported using integration times of 90 and 180 s. Accuracy of the instrument calibration is estimated to be  $\pm 16\%$  for NO and  $\pm 18\%$  for  $\text{NO}_2$  and  $\text{NO}_y$  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  $\text{NO}_2$  with a signal-to-noise ratio of 2:1. The typical measurement precision for  $\text{NO}_y$  (at 95% confidence limit) was circa  $\pm 10\%$  at 500 pptv increasing to circa  $\pm 20\%$  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  $\pm 20\%$  and a precision of  $\pm 10\%$ . Given the above conditions, the limit of detection for PAN was about 5 pptv.

Nitric acid and  $p\text{-NO}_3$  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  $\text{HNO}_3$  instrument with the NOAA nylon filter method and the NCAR "Lind" instrument (i.e., a diffusion scrubber) showed agreement within  $\pm 25\%$  in the 100-1000 pptv range [E. L. Atlas *et al.*, An intercomparison of three  $\text{HNO}_3$  measurement techniques, unpublished data, 1990]. In ABLE 3B the  $\text{HNO}_3$  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  $\text{HNO}_3$  through both instruments. Laboratory testing of a porcelain-coated inlet showed that in the 100-300 pptv range,  $\text{HNO}_3$  was passed through the entire  $\sim 1.5\text{-m}$  length with  $100 \pm 3\%$  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  $\text{HNO}_3$ , with a corresponding limit of detection of 10 pptv. The overall uncertainty is estimated to be  $\pm 20\%$  for mixing ratios  $\geq 100$  pptv increasing to  $\pm 30\%$  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  $p\text{-NO}_3$  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  $p\text{-NO}_3$ , but it is believed that the relative concentration trends between various air masses are substantially correct. Simultaneous sampling for  $p\text{-NO}_3$  with two identical UNH systems indicates the precision was about  $\pm 18\%$  [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 history (see, for example, *Harriss et al.*, 1992). We selected CO to serve as a proxy indicator of air mass composition based on our experience during ABLE 3A, CO's atmospheric chemical lifetime of several months, and CO's passiveness to removal by deposition processes. We use CO mixing ratios here primarily as a relative indicator of combustion inputs to air masses over central Canada. Thus we examined the chemistry of reactive odd nitrogen in air masses exhibiting various degrees of impact from combustion emissions. Hydrocarbon and halocarbon tracer species were used to distinguish biomass-burning from direct industrial inputs [*Wofsy et al.*, this issue].

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  $\pm$ 110 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  $\pm$ 110 ppbv). A final air mass type with no geographic reference was defined as upper tropospheric/lower stratospheric influenced (CO  $\pm$ 105 ppbv and dew point  $-25^{\circ}$  to  $-47^{\circ}\text{C}$ ). 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 the overall chemistry. We chose to omit this small group of data (i.e., CO 106-109 ppbv) from our analysis rather than assign a specific air mass type to it.

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  $\leq$ 105 ppbv and the dew point temperature was between  $-25^{\circ}$  and  $-47^{\circ}\text{C}$ . Restriction of CO to  $\leq$ 105 ppbv removed the obvious cases of fresh biomass-burning influence. The remotely sensed  $\text{O}_3$  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 areas 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 ( $\sim$ 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  $\text{NO}_x$ ,  $\text{NO}_y$ ,  $\text{C}_2\text{Cl}_4$ , 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 to fivefold [*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  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_y$ ; 90-s intervals every 8 min for PAN; 15-min intervals for  $\text{HNO}_3$ ; and 20- to 30-min intervals for  $\text{p-NO}_3$ . For consistency with  $\text{NO}_x$  and  $\text{NO}_y$  mixing ratios, 90-s averaged values were generated for  $\text{O}_3$ ,  $\text{CH}_4$ , 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  $\text{NO}_x$  and  $\text{NO}_y$  measurements. Consequently, mixing ratio statistics reported here for  $\text{O}_3$  and  $\text{CH}_4$  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

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				
	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N
"Background" Air (CO: 95-105 ppbv)															
NO	7.4	3.1	7.0	3.6-30	163	8.6	4.1	6.5	3.7-17	30	6.3	2.8	5.6	2.6-15	112
NO <sub>2</sub>	20	7.6	19	9.5-47	163	21	9.2	18	9.3-42	30	26	10	24	9.1-57	106
NO <sub>x</sub>	21	14	27	14-60	163	24	15	29	14-58	30	22	17	30	13-63	106
HNO <sub>3</sub>	52	36	44	13-129	20	82	20	83	57-106	3	52	43	29	10-134	16
PAN	26	9	27	13-47	35	56	13	54	43-77	4	158	83	162	22-337	28
NO <sub>3</sub> <sup>-</sup>	11	7.9	7.8	<2.0-23	8						2.8	3.2	2.8	<2.0-6.5	3
NO <sub>y</sub>	164	42	165	66-254	163	273	107	263	124-597	30	542	148	522	268-994	112
O <sub>3</sub>	31	3	32	24-37	220	42	9	41	28-64	37	53	7	52	41-72	152
CO	97	3	96	95-100	14	99	4	98	95-105	35	96	5	98	95-105	117
CH <sub>4</sub>	1778	20	1762	1754-1808	14	1761	11	1756	1746-1786	35	1752	13	1756	1728-1779	107
Biomass Burning Impacted (CO>110 ppbv)															
NO	13	6.5	12	4.5-41	152	11	4.9	10	3.9-33	126	11	6.5	11	3.0-50	180
NO <sub>2</sub>	51	25	44	17-122	152	46	20	42	9.9-109	121	30	12	27	8.8-63	176
NO <sub>x</sub>	49	35	59	26-128	152	46	29	53	19-133	121	34	21	39	13-103	176
HNO <sub>3</sub>	185	181	106	33-715	24	203	92	226	31-412	18	154	147	91	28-549	20
PAN	86	58	77	22-297	33	247	138	224	50-725	30	528	267	429	158-1149	39
NO <sub>3</sub> <sup>-</sup>	21	19	12	4.6-58	7						89	80	40	8.6-235	10
NO <sub>y</sub>	395	160	348	190-899	152	594	298	577	185-2300	126	998	570	769	220-2650	180
O <sub>3</sub>	33	7	30	24-51	200	47	8	47	30-60	148	61	10	61	41-86	213
CO	127	20	125	110-168	20	134	21	132	110-222	133	145	38	137	110-256	180
CH <sub>4</sub>	1786	17	1777	1769-1841	20	1771	8	1771	1756-1789	133	1755	9	1756	1726-1772	180

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.

Ontario. The apparent constant mixing of various air mass types over northern Quebec/Labrador provided a convenient gradient in CO mixing ratio for examining the distribution of reactive odd nitrogen.

Missions 2-9 were conducted over northern Ontario/Manitoba during July 1990. During missions 2-5 we sampled largely "background" air intercepting a few biomass-burning plumes on missions 4 and 5. Missions 6-9 were apparently dominated by emissions from biomass-burning in Ontario and long-range transport from fires in western Canada and Alaska [Shipham *et al.*, this issue]. The air masses in the entire 0.15- to 6-km tropospheric column over the study region during missions 6, 8, and 9 were severely affected by biomass-burning emissions. Over Ontario we encountered predominantly either "background" air or air masses apparently influenced predominantly by biomass-burning emissions. Additionally, in the 3- to 6-km altitude range, pockets of dry air (dew point -25° to -47°C) were sampled intermittently on all missions except 6. These dry air masses are believed to have their origins in the upper troposphere/lower stratosphere and, subsequently, subsided to our highest flight altitudes.

Missions 11-19 were centered over northern Quebec/Labrador during August 1990. In this region, air masses were sampled which had a variety of CO mixing ratios ranging from 60 to nearly 400 ppbv. Missions 11 and 13 appeared to be strongly influenced by emissions from biomass burning. What appears to have been tropical marine air 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<sub>2</sub>Cl<sub>4</sub> 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<sub>y</sub> mixing ratios observed over Canada, there were few cases of clear enhancement in C<sub>2</sub>Cl<sub>4</sub> and fluorocarbon mixing ratios above those found in "background" air [Sandholm *et al.*, this issue]. In general, mixing ratios of C<sub>2</sub>Cl<sub>4</sub> 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

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<sub>2</sub>Cl<sub>4</sub> 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<sub>y</sub> 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<sub>y</sub>, O<sub>3</sub>, CO, and CH<sub>4</sub> in the air mass

TABLE 2. Selected Chemical Characteristics of "Tropical Air" at 2-6 km Altitude Over Quebec and Labrador, Canada, During August 1990

Species	CO: 60-79 ppb)				
	Mean	s.d.	Median	Range	N
NO	7.8	5.9	5.0	2.9-44	135
NO <sub>2</sub>	26	10	24	10-61	132
NO <sub>x</sub>	33	14	32	15-105	132
HNO <sub>3</sub>	39	25	33	10-105	12
PAN	121	68	128	34-252	25
NO <sub>3</sub> <sup>-</sup>	2.2	2.6	2.2	<2.0-6.9	5
NO <sub>y</sub>	166	65	135	47-335	135
O <sub>3</sub>	37	8	40	21-51	149
CO	69	6	70	60-80	102
CH <sub>4</sub>	1717	6	1717	1700-1731	102

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

TABLE 3. Selected Chemical Characteristics of Tropospheric Air Masses Over Quebec and Labrador, Canada, During August 1990

Species	<1 km					1-3 km					3-6 km				
	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N
Mixed (CO: 80-94 ppbv)															
NO	5.3	2.7	4.5	3.1-24	116	6.1	4.2	4.4	2.9-23	82	10	5.9	8.8	3.0-30	106
NO <sub>2</sub>	20	12	17	8.3-88	116	22	10	20	9.7-57	82	30	13	30	10-77	104
NO <sub>x</sub>	26	13	22	12-100	116	27	13	25	13-67	82	39	17	40	14-101	104
HNO <sub>3</sub>	22	8	20	11-33	13	99	82	97	13-247	9	63	45	62	11-162	15
PAN	34	11	34	20-54	21	74	54	58	11-194	14	234	87	224	58-479	23
NO <sub>3</sub> <sup>-</sup>	5.8	2.0	5.2	<2.0-8.8	5						4.0	0.1	3.9	3.9-4.0	4
NO <sub>y</sub>	82	31	75	27-222	116	153	160	111	56-919	82	274	128	263	69-825	106
O <sub>3</sub>	22	4	22	14-29	143	33	12	28	20-70	88	51	13	53	21-73	124
CO	86	2	86	82-94	116	90	3	90	82-94	76	89	5	88	80-94	121
CH <sub>4</sub>	1752	5	1751	1726-1761	116	1743	14	1751	1719-1769	76	1739	10	1739	1717-1762	121
"Background" Air (CO: 95-105 ppbv)															
NO	6.2	1.7	6.1	3.5-9.7	72	7.9	3.5	7.0	3.1-18	118	8.6	4.4	7.8	2.8-25	137
NO <sub>2</sub>	24	7	24	13-36	68	24	10	21	7.3-59	118	27	13	23	8.9-75	137
NO <sub>x</sub>	30	9	32	19-43	68	31	11	29	11-72	118	34	16	31	14-84	137
HNO <sub>3</sub>	122	42	113	67-196	6	63	43	51	10-172	14	24	18	16	10-74	18
PAN	68	23	65	47-146	17	109	76	72	11-297	34	317	85	321	104-518	52
NO <sub>3</sub> <sup>-</sup>	6.5	1.0	6.6	4.9-7.8	6						4.5	0.8	4.	<2.0-5.1	5
NO <sub>y</sub>	184	53	181	79-283	72	248	129	215	95-756	118	302	96	313	70-594	137
O <sub>3</sub>	25	7	22	16-41	98	38	12	40	18-67	147	53	14	53	21-88	155
CO	97	1	96	95-99	6	97	3	99	95-105	60	98	2	98	95-105	116
CH <sub>4</sub>	1738	8	1738	1726-1753	6	1718	236	1750	1732-1766	53	1747	5	1746	1732-1766	116
Biomass Burning Influenced (CO>110 ppbv)															
NO	6.5	2.3	6.2	3.6-15	52	7.9	3.8	7.2	3.1-22	97	10	5.8	10	3.0-31	133
NO <sub>2</sub>	26	10	24	11-49	52	27	11	24	12-56	91	37	18	33	11-133	133
NO <sub>x</sub>	26	16	31	15-53	52	26	17	32	19-73	91	40	23	43	19-136	133
HNO <sub>3</sub>	130	82	110	31-270	7	108	72	100	14-271	15	76	51	60	10-206	18
PAN	50	23	45	11-92	14	143	71	140	54-278	20	403	156	396	217-865	29
NO <sub>3</sub> <sup>-</sup>	6.2	0.5	5.9	<2.0-6.6	3						15	6.5	19	7.8-22	6
NO <sub>y</sub>	242	83	258	93-463	52	337	94	336	114-637	97	1057	1103	569	259-6250	133
O <sub>3</sub>	30	9	26	12-45	67	43	10	43	26-66	69	61	11	58	36-90	167
CO	119	10	118	110-136	13	126	13	129	110-143	133	128	35	122	110-355	154
CH <sub>4</sub>	1760	7	1757	1752-1777	13	1759	8	1760	1743-1778	69	1759	14	1754	1735-1825	154

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

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	Dew Point -25 to -47° C; CO < 105 ppbv				
	Mean	s.d.	Median	Range	N
NO	15	7.8	14	3.0-63	380
NO <sub>2</sub>	38	17	39	10-111	400
NO <sub>x</sub>	52	23	51	18-146	364
HNO <sub>3</sub>	39	28	32	10-126	45
PAN	291	98	297	34-535	106
NO <sub>3</sub> <sup>-</sup>	7.8	3.1	6.7	<2.0-13	19
NO <sub>y</sub>	760	564	569	173-3670	380
O <sub>3</sub>	63	15	64	30-103	499
CO	89	11	91	69-105	395
CH <sub>4</sub>	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 O<sub>3</sub> 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 O<sub>3</sub> 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-NO<sub>3</sub> was only divided into two altitude

bands: the boundary layer (<1 km) and free troposphere (>3 km). A detailed presentation of the p-NO<sub>3</sub> 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 NO<sub>y</sub> 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).

**NO<sub>x</sub>.** "Background" air exhibited a remarkably constant NO<sub>x</sub> mixing ratio of about 30 pptv. In the mixed and tropical air masses over Quebec/Labrador, NO<sub>x</sub> 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 NO<sub>x</sub> mixing ratios (~ 56 pptv) below 3 km altitude compared to values in "background"

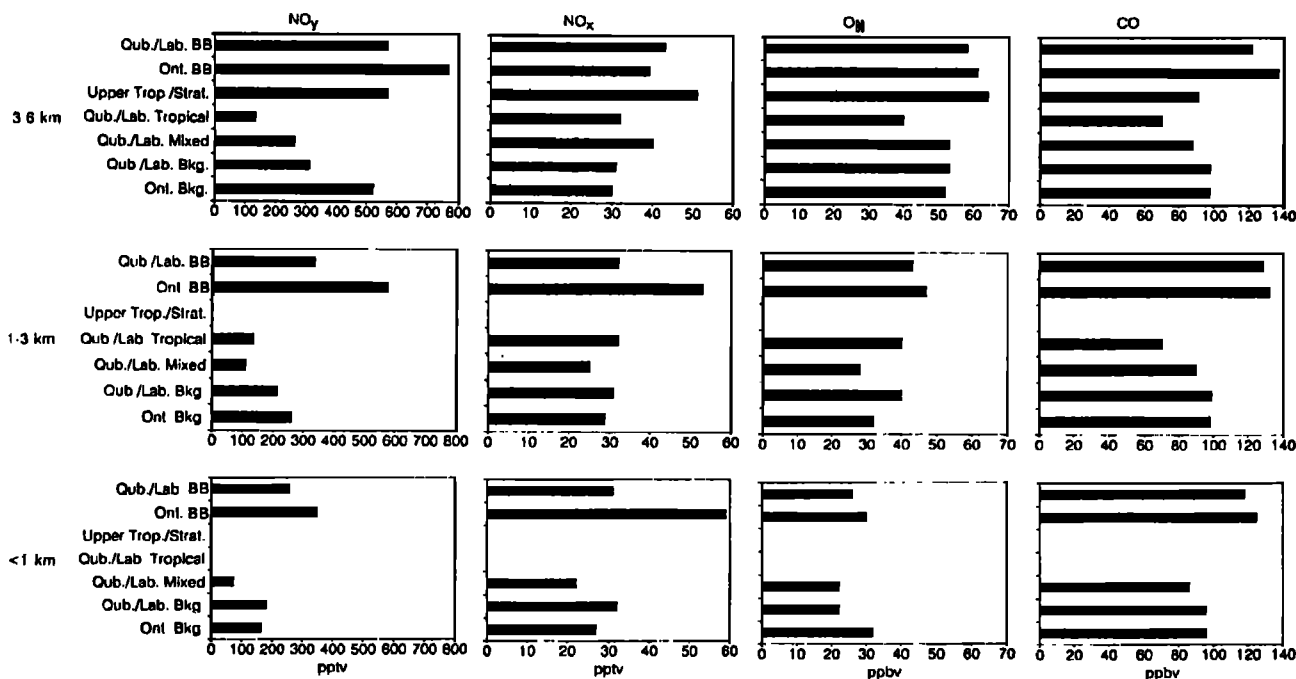


Fig. 1. Vertical distributions of CO, O<sub>3</sub>, NO<sub>x</sub>, and NO<sub>y</sub> over central Canada as represented by the median mixing ratio in each air mass category. BB means biomass burning.

air (30 pptv). There was no corresponding enhancement of NO<sub>x</sub> 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 NO<sub>x</sub> mixing ratios (43 pptv) in the 3- to 6-km altitude range compared to those in "background" air (30 pptv). Such enhancement of NO<sub>x</sub> was not observed at altitudes below 3 km. Upper tropospheric/lower stratospheric air masses exhibited NO<sub>x</sub> mixing ratios of around 50 pptv in the 3- to 6-km altitude range.

**HNO<sub>3</sub>.** Mixing ratios of HNO<sub>3</sub> in "background" air were quite variable over both Canadian study areas but generally were <100 pptv. The smallest mixing ratios of HNO<sub>3</sub> (≤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 HNO<sub>3</sub> 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 HNO<sub>3</sub> 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 HNO<sub>3</sub> was about 225 pptv compared to a median value of 83 pptv in "background" air. The median HNO<sub>3</sub> 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 HNO<sub>3</sub>, 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).

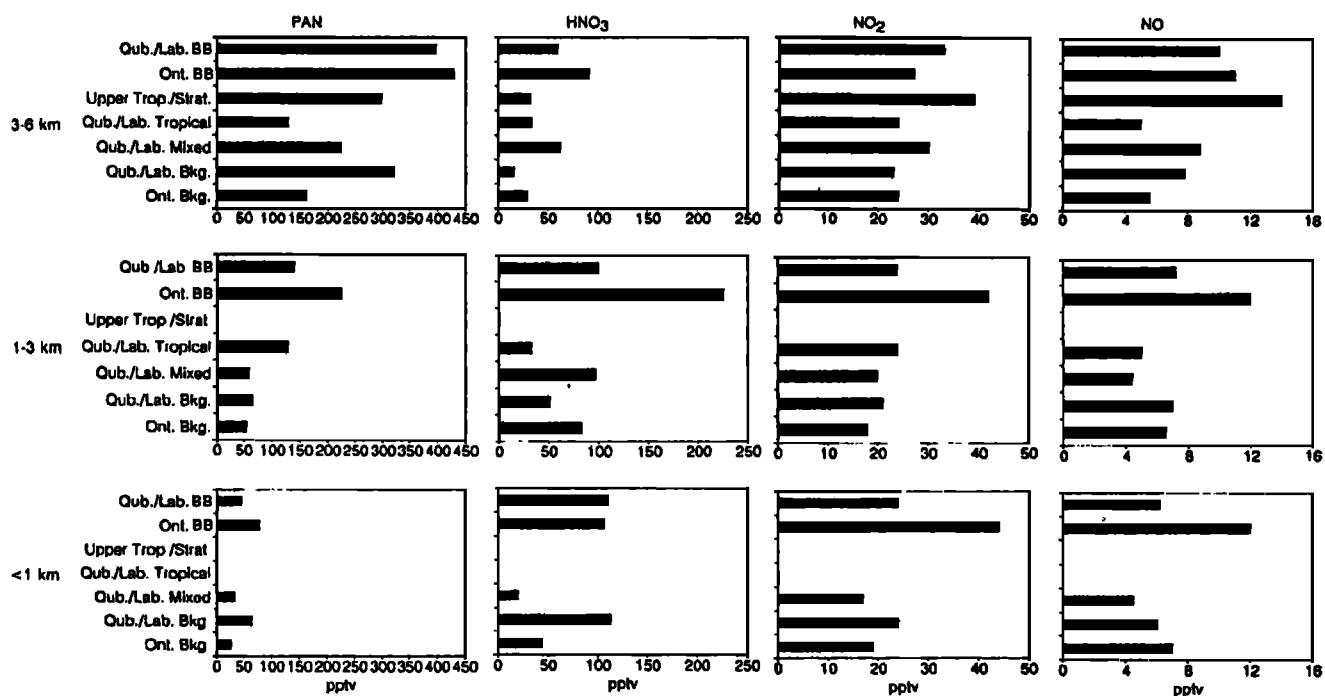


Fig. 2. Vertical distribution of reactive nitrogen species over central Canada as represented by the median mixing ratio in each air mass category.



$p\text{-NO}_3^-$ : Median mixing ratios of  $p\text{-NO}_3^-$  were less than 10 pptv in all air masses except those impacted by biomass-burning emissions. Particle- $\text{NO}_3^-$  mixing ratios were almost always less than coincident vapor phase mixing ratios of  $\text{HNO}_3$ . In air masses influenced by biomass-burning emissions,  $p\text{-NO}_3^-$  mixing ratios were typically twofold larger than those observed in "background" air. In the 3- to 6-km altitude range over Ontario we observed the largest enhancements in  $p\text{-NO}_3^-$ . The increases observed were consistently at least an order of magnitude larger than values in "background" air.

$\text{NO}_y$ : In the boundary layer over both Canadian study areas,  $\text{NO}_y$  mixing ratios were approximately 170 pptv in "background" air masses. Increased altitude in these air masses resulted in  $\text{NO}_y$  mixing ratios that were similar over both study regions (~240 pptv at 1-3 km). However, in the 3- to 6-km altitude range significantly larger values were found over Ontario (median = 522 pptv) than over Quebec/Labrador (median = 321 pptv). The smallest  $\text{NO}_y$  mixing ratios in the boundary layer were associated with the mixed air masses over Quebec/Labrador (median = 75 pptv). At altitudes of 3- to 6-km the tropical air masses exhibited the smallest  $\text{NO}_y$  mixing ratios (median = 135 pptv) of any air mass type. Biomass-burning emissions apparently produced larger enhancements in  $\text{NO}_y$  mixing ratios over central Canada compared to eastern Canada. Below 3 km in altitude,  $\text{NO}_y$  mixing ratios in biomass-burning influenced air over Ontario were enhanced about twofold (medians of 348 and 577 pptv) compared to those in "background" air (medians of 165 and 263 pptv). This enhancement dropped to around 50% in the 3- to 6-km altitude range (median of 522 versus 769 pptv). Similar comparisons between biomass-burning impacted and "background" air masses over Quebec/Labrador showed  $\text{NO}_y$  enhancements of <50% below 3 km but approaching a factor of 2 in the 3- to 6-km altitude range. Air masses influenced by the composition of the upper troposphere/lower stratosphere had  $\text{NO}_y$  mixing ratios (median = 569 pptv) that were similar to those in "background" air over Ontario (median = 522 pptv at 3-6 km) but were almost twofold larger than "background" air values observed over Quebec/Labrador (median 313 pptv at 3- to 6-km).

#### 4. DISCUSSION

##### 4.1. Correlation Among Species

To illustrate the relationship between CO and selected species in the troposphere over central Canada, a series of plots are presented in Figure 3. These plots show data obtained in various air mass categories over the Quebec/Labrador region. Although there were a few mixing ratios of CO between 150-400 ppbv (~15 data points for the biomass-burning category), we have selectively plotted the data below 150 ppbv CO in Figure 3 to minimize compression of the CO scale. There is a significant correlation between CO and  $\text{CH}_4$  mixing ratios that extends across the spectrum of air mass types encountered. Methane mixing ratios in the tropical and biomass-burning impacted air masses are quite distinct and different from values in the mixed, "background", and upper tropospheric/lower stratospheric air masses. Mixing ratios of  $\text{CH}_4$  in the latter three air mass categories are not significantly different ( $p=0.05$ ). It appears that the relationship

illustrated in Figure 3 between CO and  $\text{CH}_4$  primarily reflects the differing loss rates of these species from oxidation by OH across a spectrum of air mass sources and ages [Sandholm *et al.*, this issue]. These data are discussed in detail in a companion paper [Harriss *et al.*, this issue (b)].

There is no apparent correlation ( $r^2 < 0.3$ ) between mixing ratios of  $\text{O}_3$ , individual reactive odd nitrogen species, or  $\text{NO}_y$  and those of CO in the suite of air mass categories considered here. Specific examples are shown in Figure 3 for  $\text{O}_3$ ,  $\text{NO}_x$ , and  $\text{NO}_y$ . Disparity in mixing ratios of CO and  $\text{NO}_y$  was also observed during the late spring 1988 Mauna Loa Observatory Photochemistry Experiment (MLOPEX) experiment in Hawaii [Hübner *et al.*, 1992]. Because many of the air masses sampled over central Canada were probably aged at least a few days since the last combustion inputs, the lack of correlation between  $\text{NO}_x$  and CO is not surprising. Another factor influencing this relationship is that emissions from smoldering smoky boreal fires seem to be CO rich and  $\text{NO}_x$  poor [Wofsy *et al.*, 1992; Crutzen and Andreae, 1990]. Indeed, the  $\text{CO}/\text{NO}_y$  ratio values over the Canadian study regions were much higher than those usually found in tropical biomass-burning plumes or urban air [Sandholm *et al.*, this issue; Wofsy *et al.*, this issue]. There appears to be minimal photochemical production of  $\text{O}_3$  over this region even though  $\text{O}_3$  enhancements were sometimes evident within plumes [Browell *et al.*, this issue]. This may extend the region of low- $\text{NO}_x$ -net- $\text{O}_3$ -destruction observed in the North American Arctic and subarctic [Gregory *et al.*, 1992; Jacob *et al.*, 1992] southward to around  $52^\circ$  N latitude. The lack of a correlation between  $\text{NO}_y$  and CO is somewhat unexpected, but it potentially points to the importance of different sources and sinks for these species. For example,  $\text{NO}_y$  is removed from the troposphere by both photochemical and heterogeneous processes, whereas CO has predominantly a net photochemical loss. Carbon monoxide is clearly derived primarily from combustion sources over central Canada [Harriss *et al.*, this issue (b)]. The vertical distribution of  $\text{NO}_y$  over central Canada (Tables 1 and 3, Figure 1) suggests that it might have an important source from aloft. This possibility is explored in a latter section of this paper.

The species  $\text{NO}_y$ , PAN, and to a lesser extent  $\text{NO}_x$  exhibit a correlation but only in the sense that their mixing ratios increase with increasing altitude. This altitudinal relationship also exists between these odd nitrogen species and  $\text{O}_3$ . At low altitudes there is a general lack of correlation among the above species. These altitudinal dependencies may imply a high-altitude source relationship and/or thermal stability in the case of PAN. The stratosphere is certainly an important source of  $\text{O}_3$  [Browell *et al.*, this issue; Anderson *et al.*, this issue], but for reactive odd nitrogen the source is unclear. Definitely determining whether the  $\text{NO}_y$  source is due to long-range transport of natural (e.g., biomass-burning, stratosphere/troposphere exchange or lightning) or anthropogenic inputs, or even the result of high-altitude aircraft emissions is probably beyond the interpretive understanding that can be achieved with the present data set.

##### 4.2. Uncertainties Regarding the "Mixed" and "Tropical" Air Masses

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  $\text{HNO}_3$  and concomitantly  $\text{NO}_y$  at low altitudes (Table 3). This suggests possible removal of  $\text{HNO}_3$  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  $\text{NO}_y$  mixing ratios (below 50 pptv) observed in these air masses at altitudes below 3 km. Interestingly, the  $\text{NO}_x$  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  $\text{NO}_x$ , as this mechanism appears to provide an important source of  $\text{NO}_x$  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 on 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

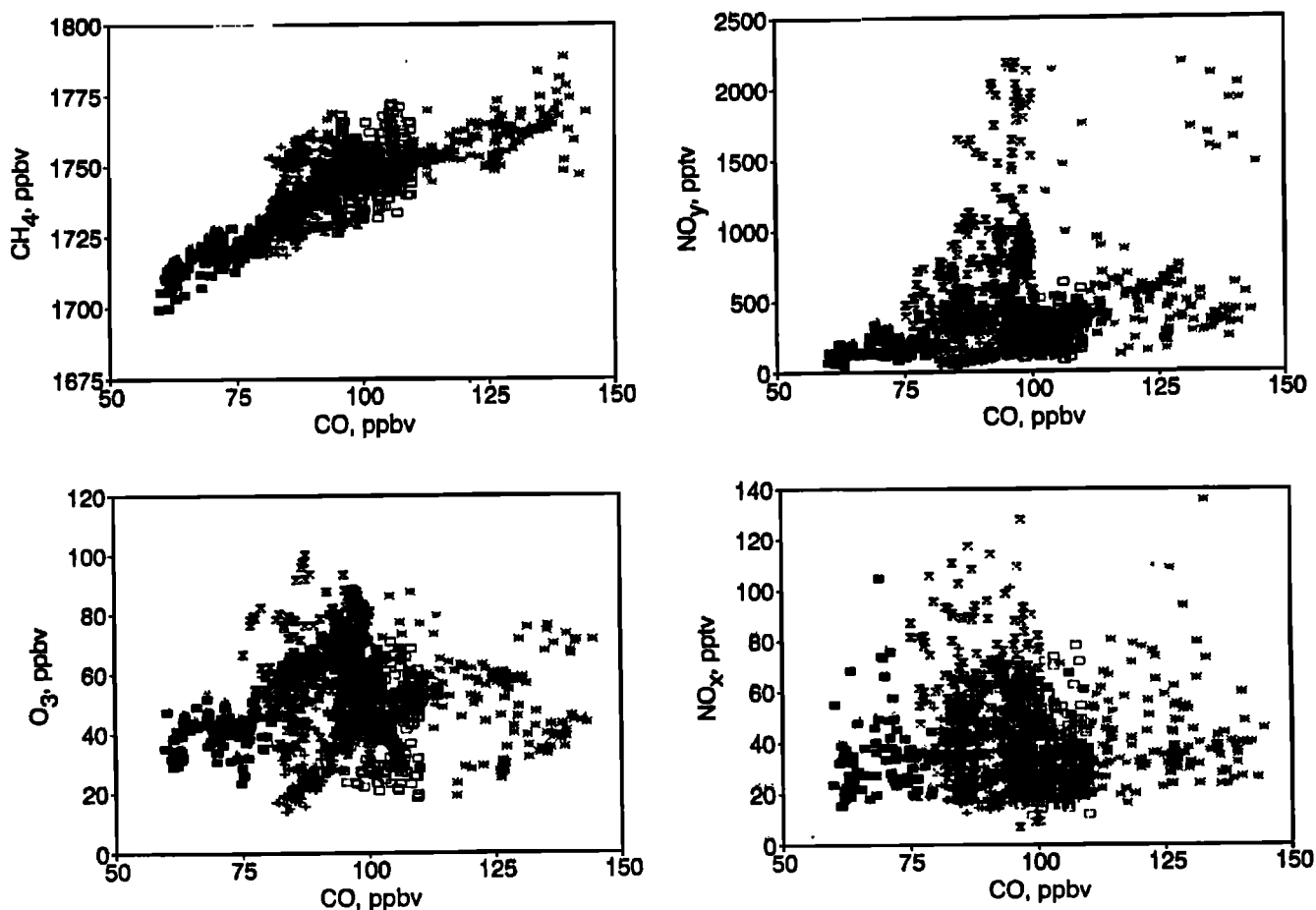


Fig. 3. Concentrations of  $\text{CH}_4$ ,  $\text{O}_3$ ,  $\text{NO}_y$ , and  $\text{NO}_x$  in various air mass categories over Quebec/Labrador defined by various CO mixing ratio brackets (see text) over the gradient 50-150 ppbv. Symbols are defined as follows: solid square, tropical; plus, mixed; open square, background; asterisk, biomass burning; hour glass, upper tropospheric/lower stratospheric.

nitrogen budget for this region and subsequent depositional inputs of fixed nitrogen to underlying boreal ecosystems.

#### 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  $\text{NO}_y$  were averaged over the time span of the  $\text{HNO}_3$  measurements. This data set was used to examine  $\text{NO}_y$  budget shortfalls [Sandholm *et al.*, this issue] and relationships of PAN and  $\text{HNO}_3$  with  $\text{NO}_x$  in this paper.

**PAN/NO<sub>x</sub>.** Values of the ratio PAN/NO<sub>x</sub> 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/NO<sub>x</sub> is driven largely by the steep gradient in PAN mixing ratios. In the 3- to 6-km altitude range, PAN/NO<sub>x</sub> values were 6-10, except in the Quebec/Labrador tropical air mass where it was about 3. Indeed, low values of PAN/NO<sub>x</sub> 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/NO<sub>x</sub> 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 over 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  $\text{NO}_x$  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/NO<sub>x</sub>, 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/NO<sub>x</sub> (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  $\text{NO}_x$ -limited aged air masses. In the boundary layer, release of peroxyacetyl (PA) radicals from PAN decomposition and subsequent PA-related chemistry under such  $\text{NO}_x$ -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/NO<sub>x</sub> 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/NO<sub>x</sub> ratio values in various air mass categories over the Quebec/Labrador region illustrates this point (Figure 4b). Even in "background" air the PAN/NO<sub>x</sub> ratio exhibited fivefold variability. The upper tropospheric/lower stratospheric air masses also showed a wide range of values, indicating variable influence on PAN/NO<sub>x</sub> ratio values in the 3- to 6-km altitude range over central Canada.

In general, the PAN/NO<sub>x</sub> 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/NO<sub>x</sub> ratios observed at high latitudes during GTE/ABLE 3A. PAN/NO<sub>x</sub> 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/NO<sub>x</sub> 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

TABLE 5. Altitudinal Distribution of PAN/NO<sub>x</sub> Ratio as a Function of Air Mass Categories

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	—	—	—	—	—	6.9	2.9	6.4	1.6-12	35
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  $\text{NO}_x$ -limited "background" air masses [Singh *et al.*, 1992] should have elevated PAN/ $\text{NO}_x$  ratios over Ontario. Air masses originating from remote lower-latitude regions typically exhibit much lower PAN/ $\text{NO}_x$  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.

$\text{HNO}_3/\text{NO}_x$ . Tropospheric chemical models predict that in continental regions the  $\text{HNO}_3/\text{NO}_x$  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  $\text{HNO}_3$ , and the presence of  $\text{NO}_x$  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  $\text{HNO}_3/\text{NO}_x$  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  $\text{HNO}_3/\text{NO}_x$  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-latitude air over Alaska exhibited  $\text{HNO}_3/\text{NO}_x$  values of 2-4 without a perceivable trend with altitude [Sandholm *et al.*, 1992]. Thus the values of  $\text{HNO}_3/\text{NO}_x$  (and  $\text{HNO}_3$  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

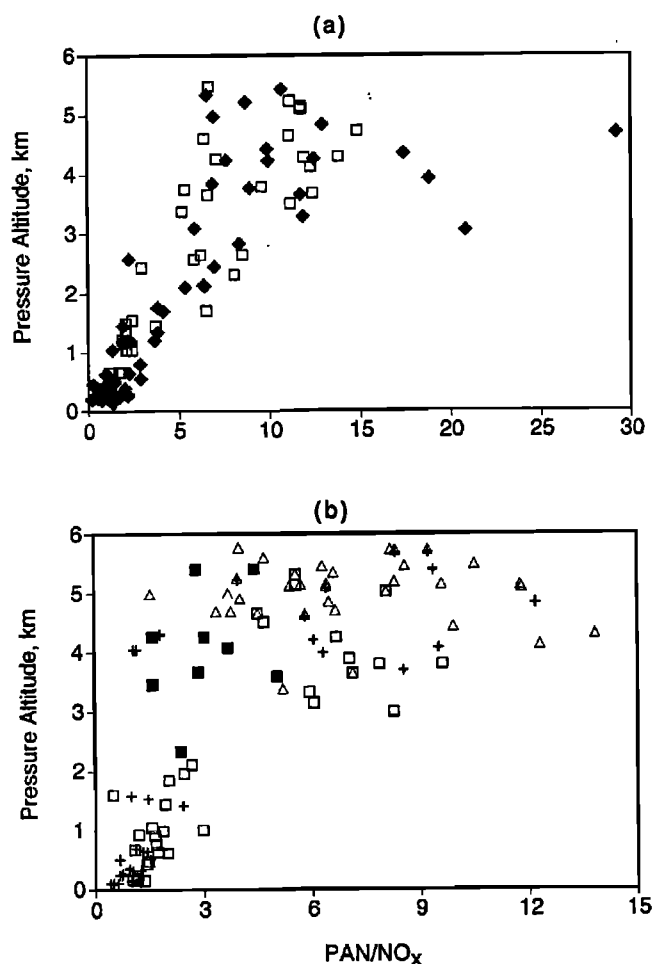


Fig. 4. Vertical distribution of the ratio PAN/ $\text{NO}_x$  in selected air mass categories. (a) Ontario: open square, "background"; diamond, biomass burning. (b) Quebec/Labrador: open square, "background"; diamond, mixed; solid square, tropical; triangle, upper tropospheric/lower stratospheric.

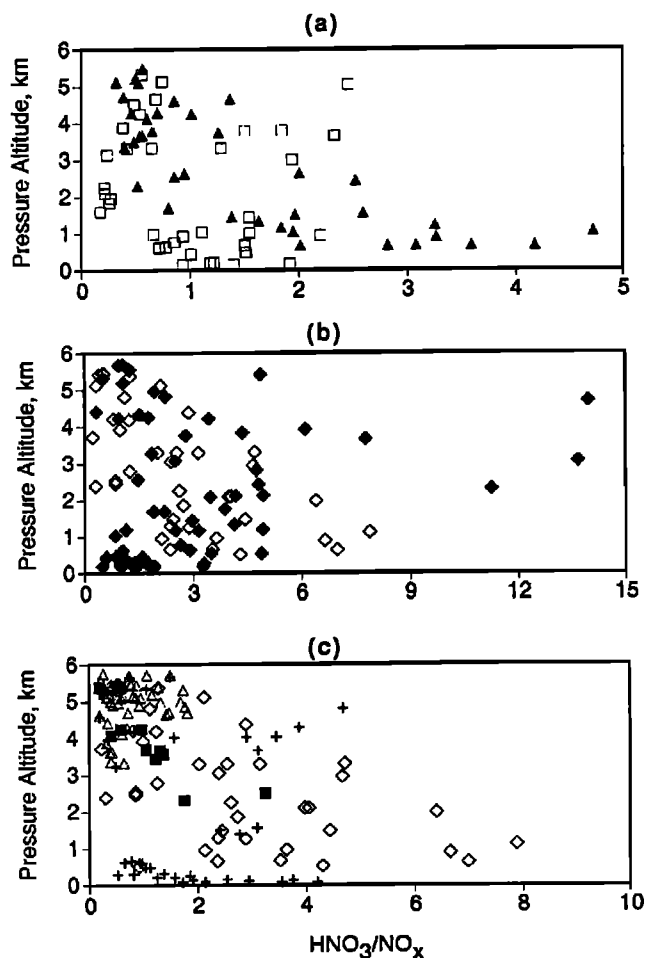


Fig. 5. Vertical distribution of the ratio  $\text{HNO}_3/\text{NO}_x$ . (a) "background": solid triangle, Ontario; open square, Quebec/Labrador. (b) biomass burning: solid diamond, Ontario; open diamond, Quebec/Labrador. (c) Quebec/Labrador: plus, mixed; solid square, tropical; open diamond, biomass burning; open triangle, upper tropospheric/lower stratospheric.

*et al.*, this issue]. Mixing ratios of  $\text{HNO}_3$  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  $\text{HNO}_3$  mixing ratios and  $\text{HNO}_3/\text{NO}_x$  ratio values 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  $\text{HNO}_3/\text{NO}_x$ , presumably due to biomass-burning inputs and precipitation scavenging of  $\text{HNO}_3$ .

The observed values of  $\text{HNO}_3/\text{NO}_x$  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  $\text{HNO}_3$  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  $\text{HNO}_3$  (~40%) but larger  $\text{NO}_x$  (~70%) mixing ratios [*Sandholm et al.*, 1992; *Talbot et al.*, 1992]. These shifts in relative abundance translate to a twofold decrease in the  $\text{HNO}_3/\text{NO}_x$  ratio over central Canada compared to Alaska. Again, the increase in  $\text{NO}_x$  going from the Alaska to Canada could be attributed to thermal decomposition of PAN producing  $\text{NO}_x$  more effectively, coupled with a higher precipitation scavenging rate of  $\text{HNO}_3$  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  $\text{HNO}_3/\text{NO}_x$  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  $\text{HNO}_3/\text{NO}_x$ . Subsidence of these high-altitude air masses to lower altitudes should result in reduced  $\text{HNO}_3/\text{NO}_x$  ratios in the midtroposphere. The low value of the ratio in upper tropospheric/lower stratospheric air masses was driven primarily by increased  $\text{NO}_x$  mixing ratios.

TABLE 6.  $\text{HNO}_3/\text{NO}_x$  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  $\text{HNO}_3/\text{NO}_x$  were found in biomass-burning impacted air masses. With reference to "background" air there were marginal increases in  $\text{HNO}_3/\text{NO}_x$  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  $\text{HNO}_3/\text{NO}_x$  values greater than about 2.5 (Figure 5c).

$\text{NO}_y/\text{O}_3$ . The ratio of  $\text{NO}_y/\text{O}_3$  (ppbv/ppbv) was used to examine the relative abundance of  $\text{NO}_y$  with respect to  $\text{O}_3$  (Figure 6). In aged air masses this ratio should shift to lower values as the  $\text{NO}_x$  reservoir is lost to  $\text{HNO}_3$  and subsequent wet and dry deposition of atmospheric nitrate. As previously stated,  $\text{NO}_y$  and  $\text{O}_3$  were correlated in the sense that their mixing ratios increased with increasing altitude. Over Alaska the value of the ratio  $\text{NO}_y/\text{O}_3$  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  $\text{NO}_y$  and  $\text{O}_3$  mixing ratios reported for the midtroposphere over the eastern Pacific Ocean [see *Hübler et al.*, 1992; *Ridley*, 1991, for summary] indicate that the  $\text{NO}_y/\text{O}_3$  ratio there typically has a value around 0.007. This value is similar to what we observed over Alaska and Canada.

The  $\text{NO}_y/\text{O}_3$  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  $\text{NO}_y/\text{O}_3$  exhibiting a range of values from 0.003 to 0.016, in contrast to the tight distribution around 0.005 over Ontario. Significantly higher  $\text{O}_3$  mixing ratios were observed in the boundary layer over Ontario compared to those over Quebec/Labrador, while those of  $\text{NO}_y$  were about equal (Tables 1 and 3). Thus the incidence of higher values of  $\text{NO}_y/\text{O}_3$  over Quebec/Labrador seems to be caused primarily by the smaller  $\text{O}_3$  mixing ratios there. Over Ontario the median mixing ratios of  $\text{O}_3$  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,  $\text{O}_3$  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  $\leq 20\%$  enhancement in  $\text{O}_3$  concentration associated with biomass-burning emissions (Tables 1 and 3). The large values in the ratio of  $\text{NO}_y/\text{O}_3$  (Figure 6) seem to result primarily from  $\text{NO}_y$  enhancements associated with biomass-burning emissions. Over Quebec/Labrador this influence was most pronounced at altitudes of 3-6 km. The  $\text{NO}_y/\text{O}_3$  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  $\text{NO}_y/\text{O}_3$  was about 0.05 over both Canadian study regions. Even though boreal fires seem to be  $\text{NO}_x$  poor, they still appear to cause significant enhancement of

$\text{NO}_y$  mixing ratios over those in "background" air. There appears to be rapid photochemical conversion of  $\text{NO}_x$  to other  $\text{NO}_y$  species in boreal fire plumes [Jacob *et al.*, 1992; Wofsy *et al.*, 1992]. At lower altitudes, much of the  $\text{NO}_y$  was in the form of  $\text{HNO}_3$ , whereas above 3-km altitude the PAN component dominated  $\text{NO}_y$ .

Anthropogenically influenced air masses a few hundred kilometers from point sources typically show  $\text{NO}_y/\text{O}_3$  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  $\text{O}_3$ . Urban plumes usually have  $\text{NO}_x$ -rich hydrocarbon mixtures which promote photochemical  $\text{O}_3$  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  $\text{O}_3$  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,  $\text{NO}_y/\text{O}_3$  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  $\text{NO}_y$  than  $\text{O}_3$ . Besides containing elevated  $\text{NO}_x$ , the chemical form of the  $\text{NO}_y$  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  $\text{NO}_y$  to the midtroposphere over central Canada and cause enhancements of  $\text{NO}_y/\text{O}_3$  values over those observed in "background" air over these regions. Just the opposite effect resulted from the tropical air masses which exhibited  $\text{NO}_y/\text{O}_3$  ratios  $< 0.01$  over Quebec/Labrador (Figure 7b). The small  $\text{NO}_y/\text{O}_3$  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  $\text{NO}_y/\text{O}_3$  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  $\text{NO}_y/\text{O}_3$  ratios tightly bound around the median value of 0.004 (Figure 7c). The decreased ratio values at low altitudes most likely reflect removal of  $\text{HNO}_3$  by precipitation, as discussed earlier in Section 4.2. The mixed and tropical air mass over

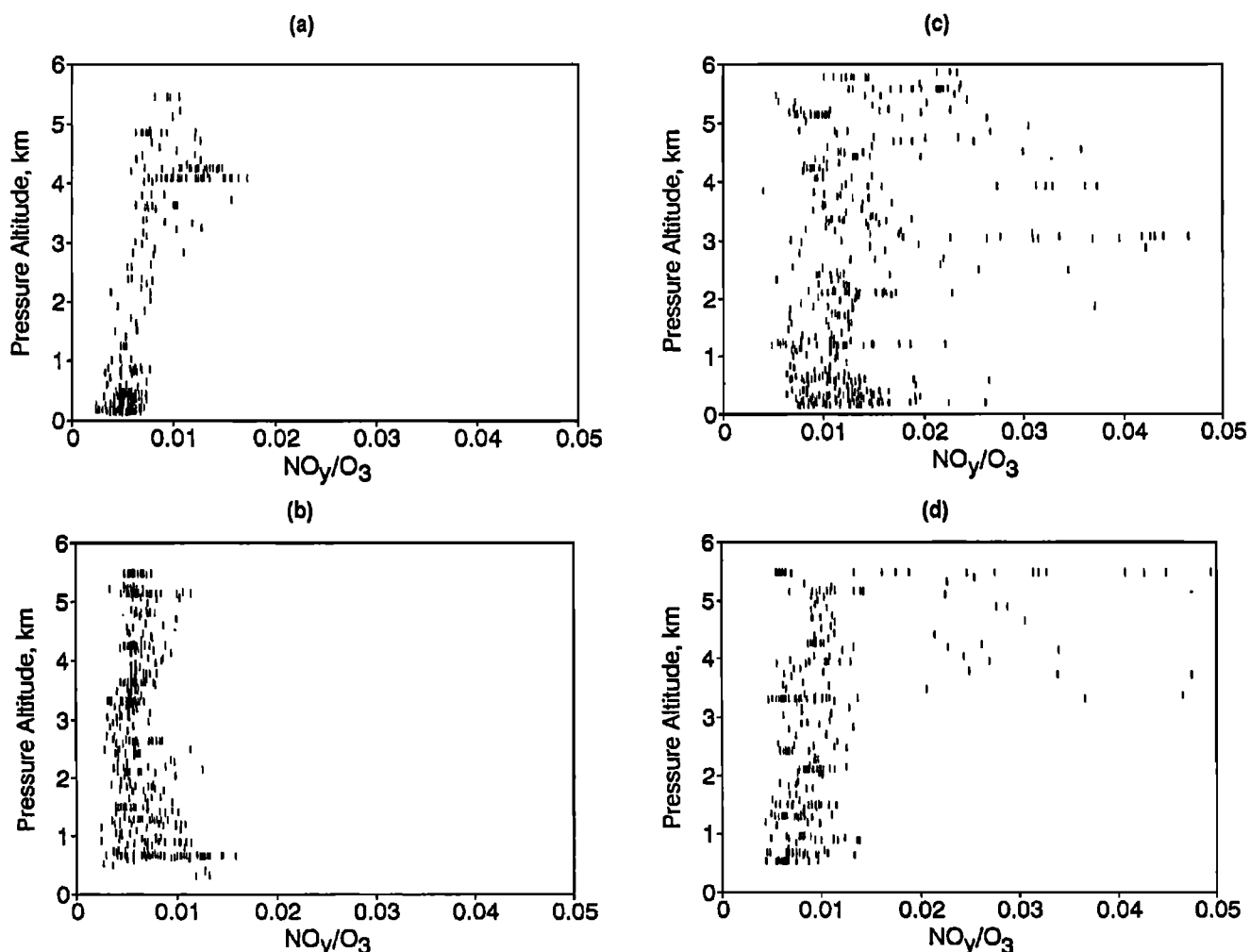


Fig. 6. Vertical distribution of the ratio  $\text{NO}_y/\text{O}_3$  in selected air mass categories: (a) Ontario "background"; (b) Quebec/Labrador "background"; (c) Ontario biomass burning; (d) Quebec/Labrador biomass burning.

Quebec/Labrador were quite depleted of  $\text{NO}_y$  (and  $\text{O}_3$ ), and their occurrence decreased the ratio  $\text{NO}_y/\text{O}_3$  at various altitudes. Both of these air masses had chemical signatures consistent with the characteristics expected of aged air that was cloud processed.

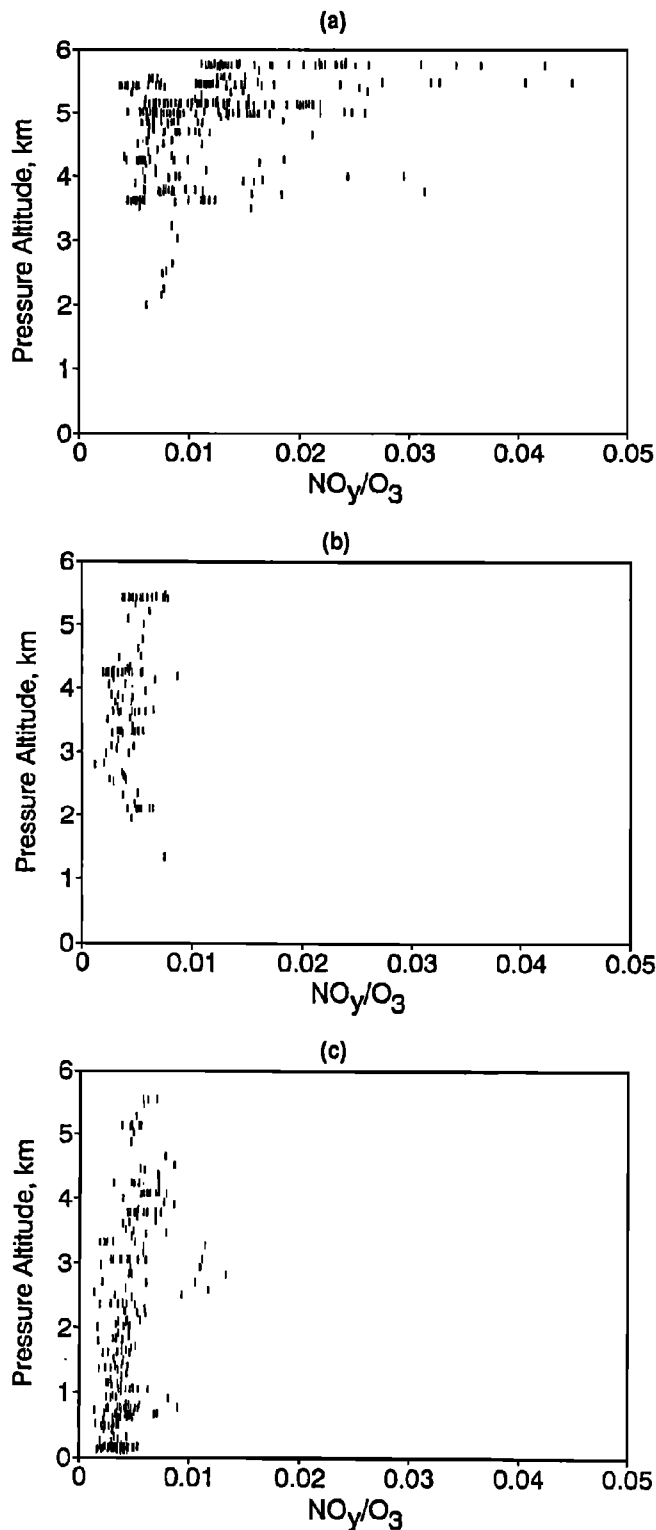


Fig. 7. Vertical distribution of the ratio  $\text{NO}_y/\text{O}_3$  in selected air mass categories: (a) upper tropospheric/lower stratospheric; (b) Quebec/Labrador tropical; (c) Quebec/Labrador mixed.

Our data analysis revealed the relatively high abundance of  $\text{NO}_y$  relative to  $\text{O}_3$  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  $\text{NO}_y/\text{O}_3$  would be expected [McElroy and Salawitch, 1989]. Recent extensive measurements of  $\text{NO}_y/\text{O}_3$  in the upper troposphere and lower stratosphere (5- to 21-km 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  $\text{HNO}_3$  mixing ratios should also be found in stratospherically influenced air masses [Russell *et al.*, 1988], unless it is rapidly removed by heterogeneous processes.

The  $\text{NO}_y$  and  $\text{O}_3$  mixing ratios and thus  $\text{NO}_y/\text{O}_3$  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  $\text{NO}_x$  mixing ratios were somewhat larger, while those of  $\text{HNO}_3$ ,  $p\text{-NO}_3^-$ , 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  $\text{CH}_4$  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  $\text{C}_2\text{Cl}_4$  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,  $\text{C}_2\text{Cl}_4$ , 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  $\text{O}_3$  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  $\text{O}_3$  air masses appeared to be associated with tropical air masses characterized by uniformly small  $\text{O}_3$  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  $\text{O}_3$  appeared to have both small (Plate 2) and large (Plate 3) aerosol loadings associated with them. The regions of low  $\text{O}_3$  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  $\text{O}_3$  regions that were observed over Ontario. This plate illustrates an apparent stratospheric fold penetrating a tropospheric region exhibiting small  $\text{O}_3$  mixing ratios. Frequently, we also observed

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

Air Mass	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> Cl <sub>4</sub>	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

well-defined regions of higher aerosol burden imbedded within low O<sub>3</sub>-containing air masses (Plate 3). 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., NO<sub>y</sub>), to higher altitudes. Note that in the far right portion of Plate 3 there is a region with relatively large O<sub>3</sub> mixing ratios but low aerosol concentrations. This region of enhanced O<sub>3</sub> may have been photochemically derived. If so, it is in direct contrast to the lack of significant photochemical O<sub>3</sub> production in biomass-burning plumes at lower altitudes. We also observed other tropospheric regions with relatively large O<sub>3</sub> 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 NO<sub>y</sub> and O<sub>3</sub> 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 NO<sub>y</sub> 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 NO<sub>y</sub> mixing ratios. It may be that the NO<sub>y</sub> mixing ratios over Quebec/Labrador were consistently diluted in the upper troposphere by intrusion of NO<sub>y</sub>-depleted tropical air. Subsiding air over this region may have reflected inputs of stratospheric O<sub>3</sub> mixed into an upper tropospheric region with low NO<sub>y</sub> (and CO, CH<sub>4</sub>, and O<sub>3</sub>).

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 NO<sub>x</sub> and NO<sub>y</sub> sources. It appears that other sources of NO<sub>x</sub> and NO<sub>y</sub> 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 NO<sub>x</sub> and NO<sub>y</sub> 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].

The proposed mechanism involves direct photolysis of HNO<sub>3</sub> yielding NO<sub>2</sub> (and thus NO<sub>x</sub>). If this NO<sub>2</sub> was converted to labile reactive odd nitrogen compounds more rapidly than competing reformation of HNO<sub>3</sub>, an air mass in the upper troposphere could possibly age losing much more O<sub>3</sub> than NO<sub>y</sub>. Thermally stable HO<sub>2</sub>NO<sub>2</sub> was hypothesized by Sandholm *et al.* [this issue] to be a dominant component of upper tropospheric NO<sub>y</sub> over the Canadian study regions. In addition, HNO<sub>3</sub> photolysis and HO<sub>2</sub>NO<sub>2</sub> 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 ABLE 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

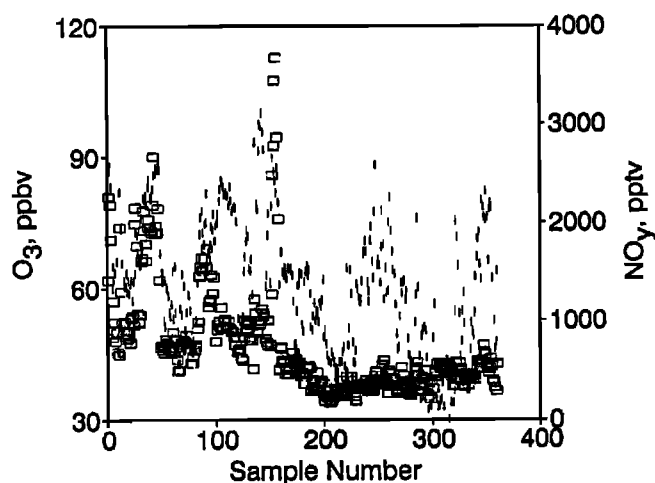
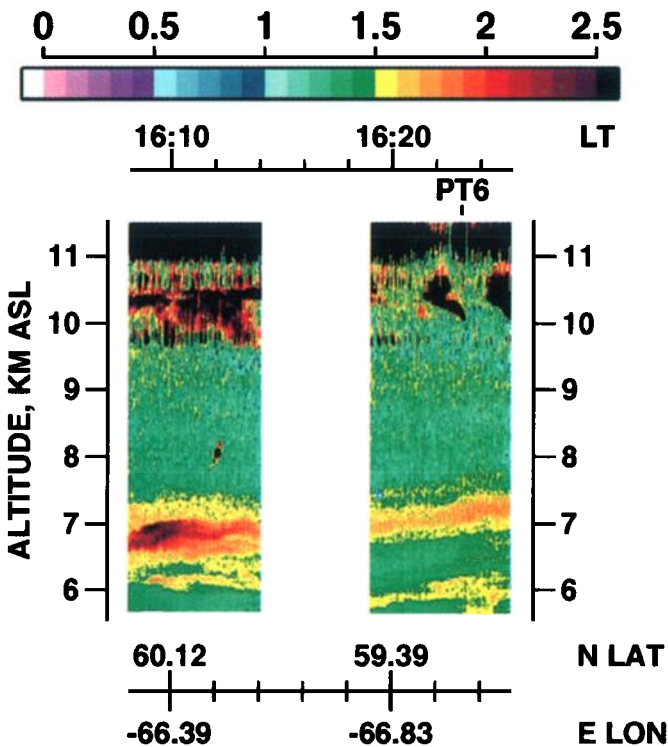


Fig. 8. Coincident NO<sub>y</sub> (square) and O<sub>3</sub> (dashes) mixing ratios in the air masses presumably subsiding from the upper troposphere/lower stratosphere.



# LATITUDINAL SURVEY FROBISHER BAY TO GOOSE BAY ABLE-3B FLIGHT 19 13 AUG 1990

RELATIVE AEROSOL SCATTERING X 1000 (IR)



OZONE (PPBV)

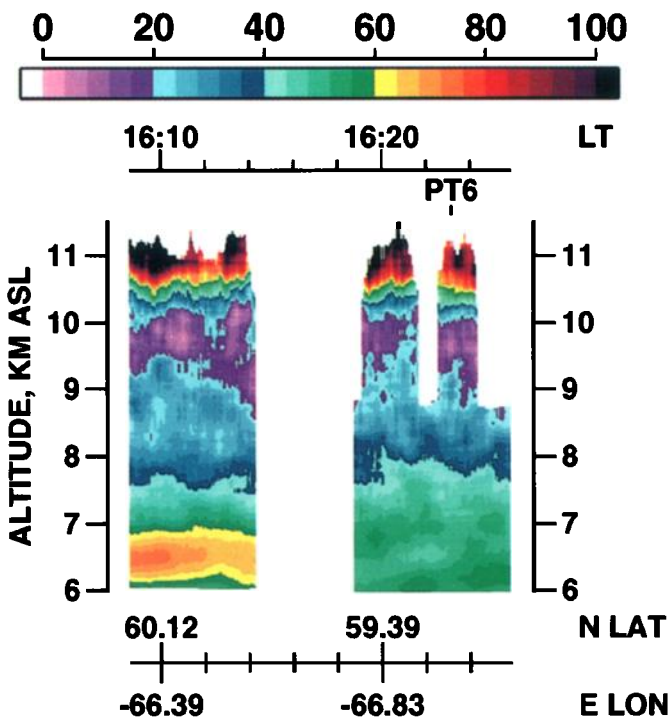
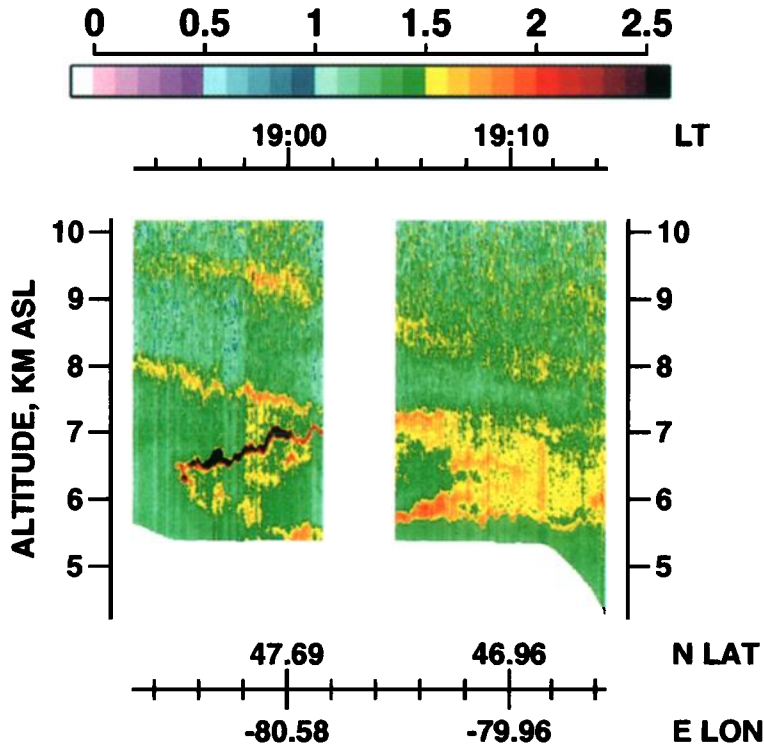


Plate 1. UV differential absorption lidar (DIAL) representation of the aerosol and O<sub>3</sub> vertical distributions (6- to 11-km altitudes) over eastern North America during mission 19, August 13, 1990.

**FLUX SURVEY HUDSON BAY LOWLAND - KINOSHEO LAKE  
ABLE-3B FLIGHT 2 9 JUL 1990**

**RELATIVE AEROSOL SCATTERING X 1000 (IR)**



**OZONE (PPBV)**

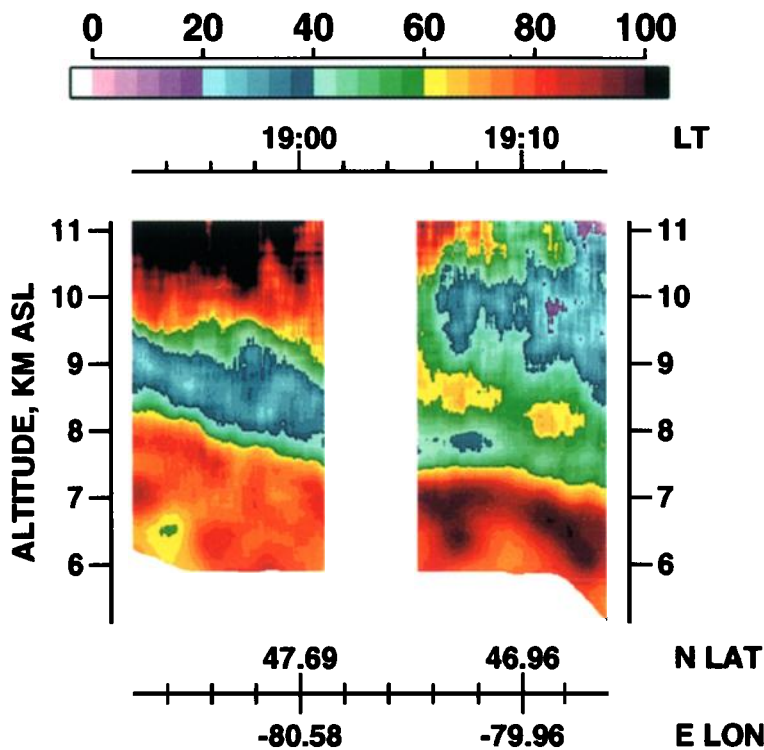


Plate 2. UV DIAL representation of the aerosol and O<sub>3</sub> vertical distributions (5- to 10-km altitudes) over Ontario during mission 2, July 9, 1990.

**FLUX SURVEY HUDSON BAY LOWLAND**  
**ABLE-3B FLIGHT 3 11 JUL 1990**

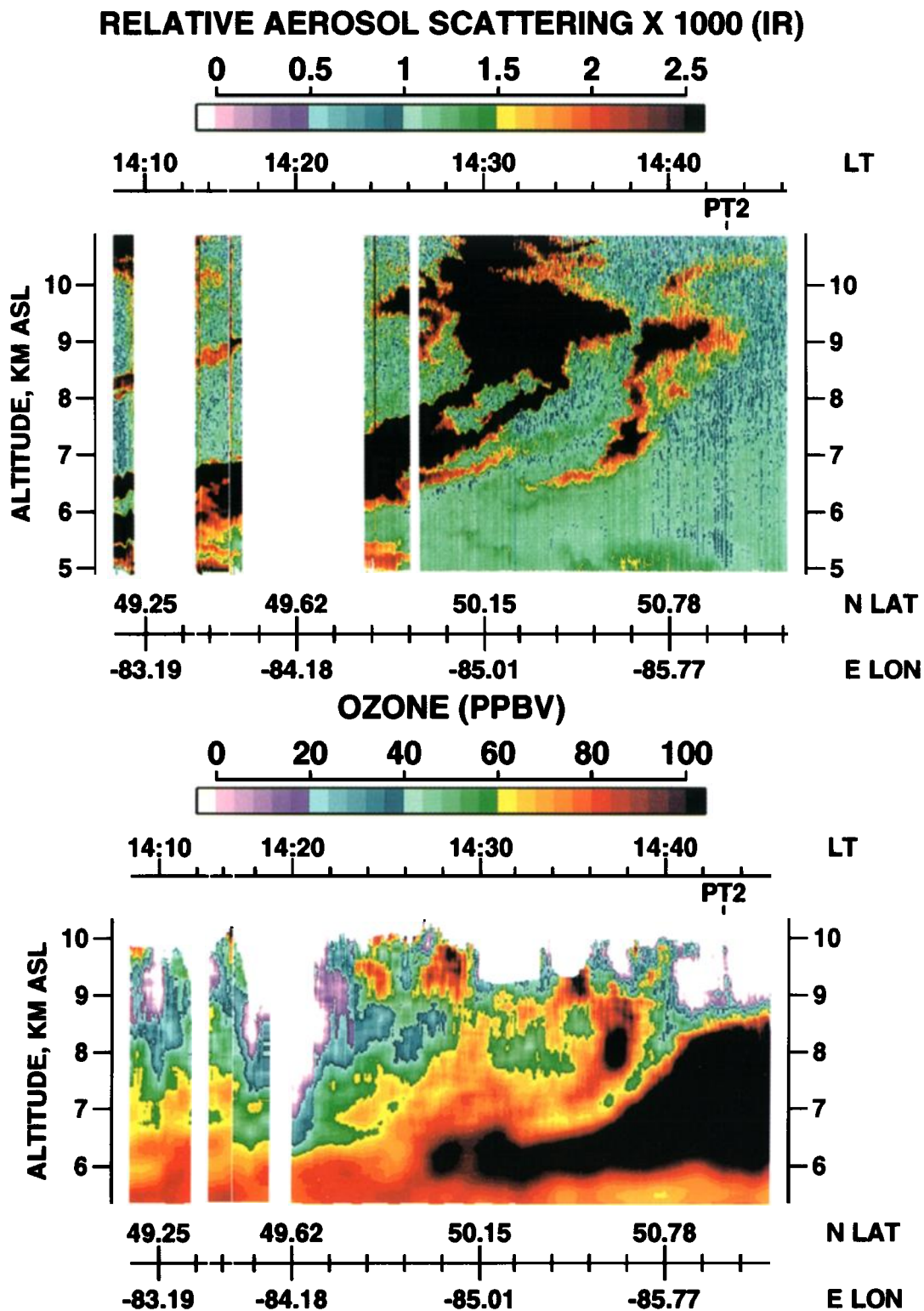
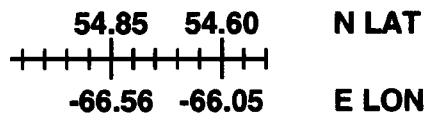
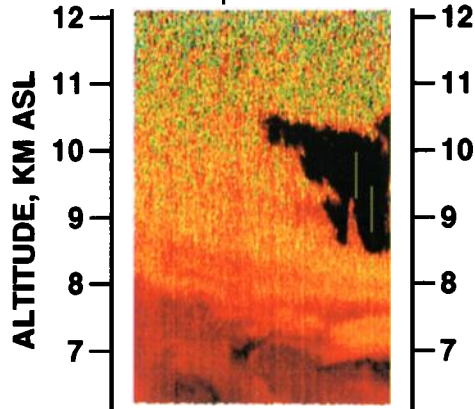
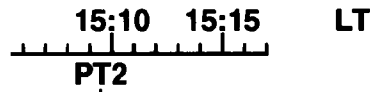
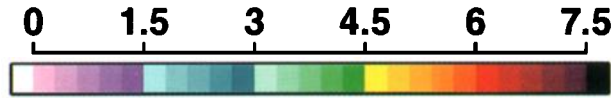


Plate 3. UV DIAL representation of the aerosol and O<sub>3</sub> vertical distributions (5- to 10-km altitudes) over Ontario during mission 3, July 11, 1990.

**FLUX SURVEY SCHEFFERVILLE, QUEBEC**  
**ABLE-3B FLIGHT 11 1 AUG 1990**

**RELATIVE AEROSOL SCATTERING X 1000 (IR)**



**OZONE (PPBV)**

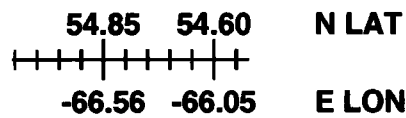
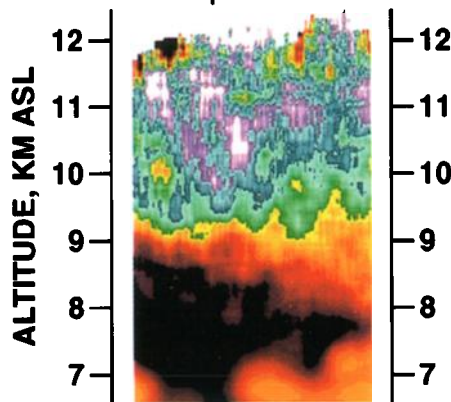
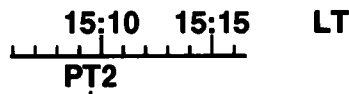
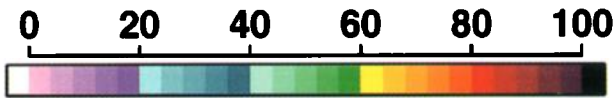


Plate 4. UV DIAL representation of the aerosol and O<sub>3</sub> vertical distributions (7- to 12-km altitudes) over northern Quebec/Labrador during mission 11, August 1, 1990.

TABLE 8. Selected Chemical Characteristics of Air Masses at 3-6 km Altitude Over Alaska During July-August 1988

Species	North Siberian					Arctic Pack-Ice				
	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
NO <sub>2</sub>	14	7	11	7-36	42	15	5	15	8-25	16
NO <sub>x</sub>	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
NO <sub>y</sub>	550	140	560	254-829	75	700	160	700	429-984	37
O <sub>3</sub>	75	25	75	50-283	102	80	10	85	53-99	45
CO	95	5	95	63-106	74	100	5	100		37
CH <sub>4</sub>	1725	10	1725	1658-1745	83	1725	5	1725	1713-1732	36

Species	Gulf of Alaska					Mid-Siberian				
	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N
NO	5	5	5	4-20	34	15	5	15	6-22	30
NO <sub>2</sub>	15	5	12	9-25	19	15	10	15	6-29	26
NO <sub>x</sub>	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
NO <sub>y</sub>	600	530	450	178-2688	34	1030	350	1000	625-1764	30
O <sub>3</sub>	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
CH <sub>4</sub>	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.

those observed over Canada. The air masses characterized here appeared to have origins from over the northern edge of Siberia, the center of the Arctic packice, the midsection of Siberia, and the Gulf of Alaska [Sandholm *et al.*, 1992].

The air masses indicated as originating from the northern edge of Siberia and the Arctic packice had nearly identical chemical signatures. The small increases in O<sub>3</sub>, CO, and NO<sub>y</sub> mixing ratios observed in the Arctic pack-ice air masses (i.e., O<sub>3</sub>, 85 versus 75 ppbv; CO, 100 versus 95 ppbv; NO<sub>y</sub>, 700 versus 560 pptv) may reflect a slightly stronger influence from Eurasian anthropogenic sources. The maritime polar air masses indicated as originating from the Gulf of Alaska (and the edge of the North Pacific Ocean) had smaller mixing ratios of PAN, O<sub>3</sub>, and NO<sub>y</sub> (i.e., PAN, 75 versus 240 pptv; O<sub>3</sub>, 50 versus 75 ppbv; and NO<sub>y</sub>, 450 versus 700-560 pptv) than the northern Siberian or Arctic pack-ice cases. The chemical signatures of these three air masses exhibited median CO mixing ratios in the range of 90 - 105 ppbv and are very chemically similar to those air masses that were classified as "background" over the Canadian study regions.

The air masses indicated as originating from the interior of Siberia are believed to have been influenced primarily by biomass-burning emissions [Sandholm *et al.*, 1992], even though anthropogenic emissions may also contribute a significant portion of both the CO and NO<sub>y</sub> budgets for latitudes > 60°N over Alaska [Jacob *et al.*, 1992]. The Siberian air masses that were observed in the 3- to 6-km altitude range over Alaska possess chemical signatures remarkably similar to those air masses observed over Canada that were characterized as having been significantly influenced by biomass-burning emissions. Certainly there are many intriguing aspects and potential connections of the ABLE 3A and ABLE 3B data sets which need to be explored in more detail.

## 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- to 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/

Labrador area. We find little direct evidence over central Canada for enhancement of mixing ratios of reactive odd nitrogen species and  $\text{NO}_y$  above those in "background" air by anthropogenic emissions. Generally, this region appears to be dominated by  $\text{NO}_x$ -limited aged air masses. Even when the chemistry was apparently driven primarily by biomass-burning impacts,  $\text{NO}_x$  concentrations were typically  $<50$  pptv. Biomass-burning emissions influencing the Canadian study regions appear to be several days old or from  $\text{CO}$ -rich- $\text{NO}_x$ -poor smoldering local fires. Within the boundary layer  $\text{NO}_x$  appears to be efficiently converted to  $\text{HNO}_3$ , but in the free troposphere,  $\text{NO}_x$  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  $\text{CO}$  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  $\text{NO}_y$ . 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  $\text{NO}_y$  abundance so high compared to  $\text{O}_3$  in the "upper tropospheric/lower stratospheric" air masses?

2. Are intrusions of  $\text{NO}_y$ -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  $52^\circ\text{N}$  latitude to the high Arctic?

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

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