UNIVERSITY OF NEW HAMPSHIRE

Complex Systems Research Center
Institute for the Study of
Earth, Oceans, and Space
Science and Engineering Research Building
Durham, New Hampshire 03824-3525
(603) 862-1792
FAX: (603) 862-1915

LANGLEY
GRANT
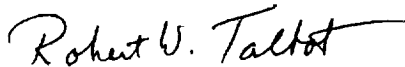*IN - 45 - CR*
51900
P-32

November 26, 1991

NASA Scientific and Technical Information Facility
Attn: Document Processing Section
800 Elkridge Landing Road
Linthicum Heights, MD 21090

re: Final Technical Report for NASA Grant NAG-1-936

To Whom it May Concern,

Enclosed is a copy of the final technical report for the grant entitled, "Organic Acids and Selected Nitrogen Species for ABLE-3" (NAG-1-936), awarded to the University of New Hampshire. Additional copies have been sent to R. J. Bendura, technical officer, and R. J. Siebels, grants officer, both at Langley Research Center in Hampton, VA.

Sincerely,

Robert W. Talbot
Research Associate Professor

FINAL TECHNICAL REPORT

Organic Acids and Selected Nitrogen Species for ABLE-3

NASA Research Grant NAG-1-936

(December 1, 1988 - November 30, 1991)

awarded to

Institute for the Study of Earth, Oceans and Space
University of New Hampshire
Durham, New Hampshire 03824

Robert W. Talbot
Principal Investigator

November 1991

1.0 Introduction

The research investigation funded through this grant to the University of New Hampshire was performed during two large field expeditions conducted by the NASA Tropospheric Chemistry Program. The NASA Global Tropospheric Experiment (GTE) executed airborne science missions aboard the NASA Wallops Electra (NA429) in the North American high latitude (>45 °N) atmosphere during July-August 1988 and July-August 1990. These missions were part of GTE's Atmospheric Boundary Layer Experiment. The 1988 mission (ABLE-3A) examined the ecosystems of Alaska as a source and/or sink for important tropospheric gases and particles, and gained new information on the chemical composition of the Arctic atmosphere during the summertime. During 1990 the second high latitude mission (ABLE-3B) focused on the Hudson Bay Lowland and Labrador regions of Canada. Both of these missions provided benchmark data sets on atmosphere-biosphere exchange and atmospheric chemistry over largely uninhabited regions of North America.

In support of the GTE/ABLE-3A and -3B field missions, the University of New Hampshire flew instrumentation aboard the Wallops Electra research aircraft to provide measurements of the trace gases nitric (HNO_3), formic (HCOOH), and acetic (CH_3COOH) acid. In addition, measurements were conducted to determine the major water-soluble ionic composition of the atmospheric aerosol. For ABLE-3B, ground-based measurements of the acidic trace gases were also performed from the NASA micrometerological tower situated at Schefferville, Laborador. These measurements were aimed at assessing dry deposition of acidic gases to the taiga ecosystem in the Laborador region of Canada. The salient features of these measurements during the ABLE-3A and -3B missions are highlighted in this report. Preliminary results were reported at two American Geophysical Union meetings (May 1989 and May 1991). Peer-reviewed professional publications have or will result from work performed under this grant. A listing of professional meeting abstracts and journal publications are included in the last section of this report. The reader is strongly encouraged to review the special issues of the Journal of Geophysical Research-Atmospheres to appreciate the overall scientific findings and benefits of the ABLE-3 program.

2.0 Results from ABLE-3A

The Arctic Boundary Layer Experiment (ABLE-3A) was conducted in Arctic and sub-Arctic regions of North America and Greenland during July-August 1988 (Figure 1). This was the first comprehensive investigation of the sources, sinks, and distribution of trace gases and aerosol chemical species in a northern high latitude region during the summer months. The ABLE-3A experimental design focused on assessing biosphere-atmosphere interactions as a dynamic process influencing the chemical composition of the troposphere.

The Arctic is a source of air masses which influence both air quality and climate over extensive areas of North America, Eurasia, and northern oceanic regions. It is particularly important to understand the chemistry of unpolluted high latitude air masses before they are influenced directly by mid-latitude emissions. The measurements performed by the University of New Hampshire during ABLE-3A provide information on the large-scale distribution of important acidic trace gases and aerosol composition in the North American Arctic and sub-Arctic atmospheres.

The average concentration of selected acidic gases and aerosol chemical species in the high latitude atmosphere are presented in Table 1. The data are grouped into four categories which represent boundary layer (0.15-2 km altitude) and free tropospheric (2-6 km altitude) regions in the Arctic and sub-Arctic atmospheres. In the sub-Arctic there was significant enrichment in the concentration of aerosol species in the boundary layer compared to the free troposhere. The reverse condition existed in the high Arctic; at low altitude the average concentration of aerosol particle NO_3^-, SO_4^{2-}, and NH_4^+ was about 2-fold lower at 0.15 km compared to 6 km altitude.

Over the Arctic Ocean pack ice we found that low level fog banks and stratus clouds were important for controlling the aerosol species concentrations. Under such atmospheric conditions the concentration of aerosol species below 2 km altitude were usually below detectable levels of a few parts per trillion by volume (molar mixing ratio in 10^{12}). With clear air conditions the concentration of most aerosol species over the pack ice was essentially invariant with altitude. It appears that the occurrence of stratus clouds and fog are principal factors controlling aerosol species concentrations at low altitude
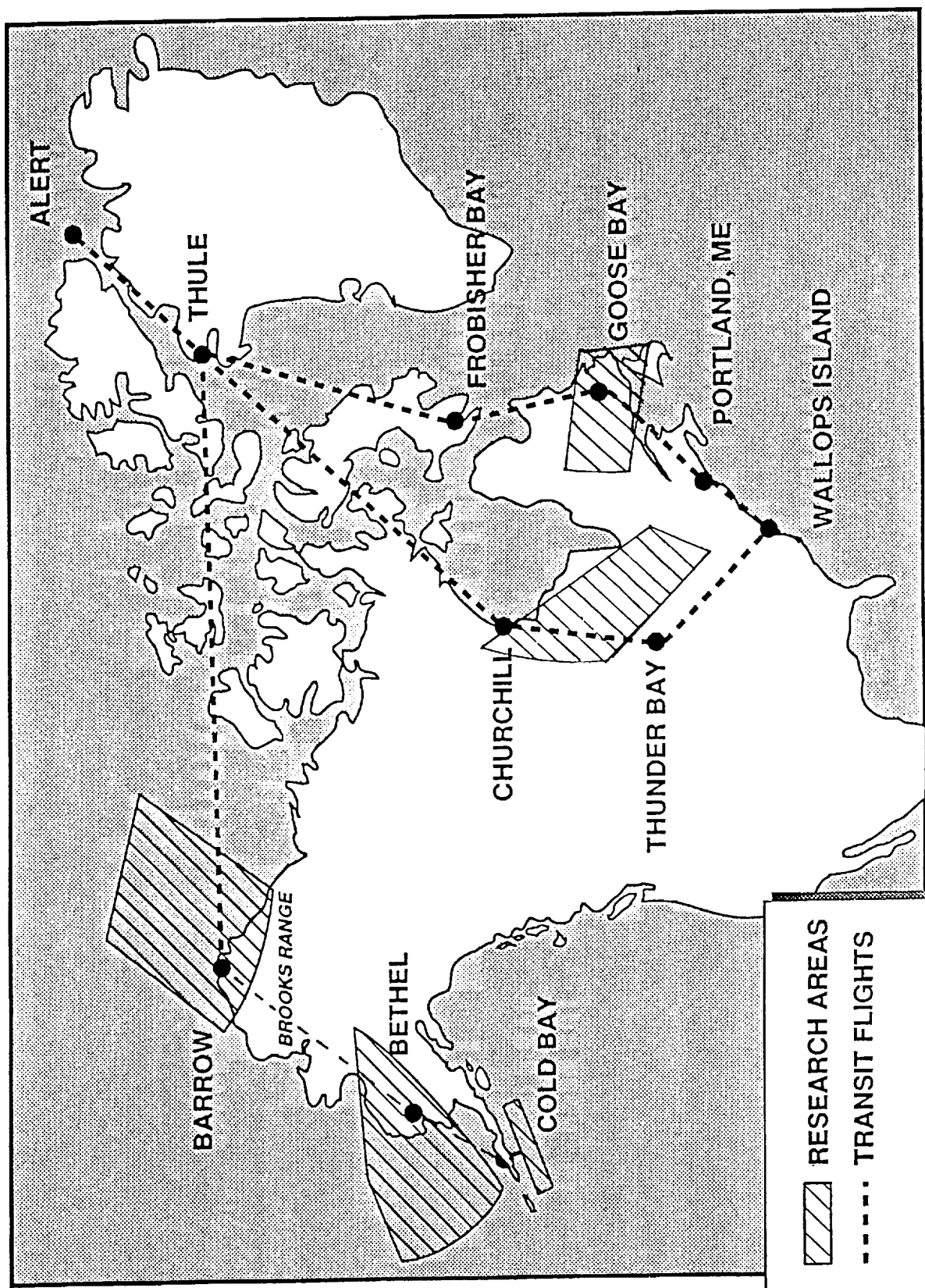
3

Figure 1. Location of GTE/ABLE-3A and -B study areas.

Table 1. Average Concentration of Selected Acidic Gases and Aerosol Species in the Summer Arctic Troposphere

Region	HCOOH	CH$_3$COOH	HNO$_3$	NO$_3^-$	SO$_4^{2-}$	Cl$^-$	C$_2$O$_4^{2-}$	NH$_4^+$	Na$^+$	K$^+$
	--- Gases (ppt) ---			------- Aerosol Species (ppt) --------						
High Arctic (>60°N)										
(N=12) BL:$\overline{X}$	270	277	45	11	29	<15	5.3	53	18	5.2
σ	97	53	20	9	14		3.6	39	14	6.2
(N=28) FT:$\overline{X}$	163	206	45	22	65	<15	4.2	75	8.5	5.4
σ	106	102	25	12	·31		2.5	33	9.3	5.2
SubArctic (50-60°N)										
(N=20) BL:$\overline{X}$	275	210	59	30	128	20	8.0	137	40	7.2
σ	128	93	25	19	77	10	7.0	76	·32	4.7
(N=17) FT:$\overline{X}$	191	225	58	15	40	<15	5.2	52	8.4	3.7
σ	72	70	32	7	22		3.0	15	10	3.3

BL means boundary layer and FT free troposphere.

N refers to the number of observations.

in the near-surface Arctic summer troposphere.

Over sub-Arctic tundra we observed 2- to 3-fold enhancement in the concentration of aerosol species in the boundary layer compared to free tropospheric levels. In addition, the aerosol number density was enhanced 5-fold in boundary layer air (G. L. Gregory, personal communication). Our primary study area was approximately 100 km inland from the Bering Sea. Many of the air masses that we sampled over subArctic tundra near Bethel, Alaska, moved inland after having been out over the North Pacific for at least several days prior. Despite the potential for significant influence from sea salt on aerosol composition over sub-Arctic tundra near Bethel, there appeared to be only minor effects. Based on an average aerosol Na^+ concentration of 40 pptv, the average concentration of sea salt should have been around 0.13 $\mu g\ m^{-3}$ in boundary layer air near Bethel. On average, ≥98% of the aerosol SO_4^{2-} was of non-sea salt (nss) origin over the tundra. An important source of SO_4^{2-} over the tundra region appears to originate from biogenic dimethyl sulfide (DMS) gas released from the highly productive Bering Sea. In general, high values for the mole ratio methyl sulfonate (MSA)/nss SO_4^{2-} were observed over the Bering Sea (average was 0.41) and occasionally over sub-Arctic tundra (up to 0.45). A detailed discussion of the high latitude sulfur budget is provided by Li et al. (in press, see section 4.0 for full citation).

An important finding of my investigation is that the chemical composition of the atmospheric aerosol in the Arctic summer troposphere is remarkably uniform on a large spatial scale; the water-soluble composition is essentially the same in the boundary layer and free troposphere over both the high Arctic and sub-Arctic regions of North America (Table 2). The data indicate that SO_4^{2-} comprises 75% of the aerosol anionic composition. Nitrate, Cl^-, and $C_2O_4^{2-}$ are minor high latitude aerosol particle constituents. For the cation species, NH_4^+ accounted for 70-80% of the measured composition. It is likely that H^+, although not measured, can account for a significant percentage of the missing cation composition (see below).

An interesting aspect of the aerosol composition is that the anion-to-cation ratio indicates nearly a factor of two deficit in cations except in the boundary layer over the pack ice (Table 2). Both the anion/cation ratio and the ratio $(SO_4^{2-} + NO_3^-)/ NH_4^+$ suggest that partial neutralization of aerosol acidity

Table 2. Aerosol Compositional Summary for the
Arctic Summer Troposphere

	Boundary Layer		Free Troposphere	
	neq. m^{-3}	% Total	neq. m^{-3}	% Total
High Arctic (>60°N)				
SO$_4$	2.6	67	5.8	78
NO$_3$	0.49	13	0.98	13
Cl	0.30	8	0.30	4
C$_2$O$_4$	0.47	12	0.37	5
	$\Sigma = 3.9$		$\Sigma = 7.5$	
SO$_4$+NO$_3$/NH$_4$ =	1.31		2.02	
Anion/Cation = 1.15		(70)[a]	1.89	(84)
SubArctic (50-60°N)				
SO$_4$	11.4	80	3.6	72
NO$_3$	1.3	9	0.67	13
Cl	0.89	6	0.30	6
C$_2$O$_4$	0.71	5	0.46	9
	$\Sigma = 14.3$		$\Sigma = 5.0$	
SO$_4$+NO$_3$/NH$_4$ =	2.08		1.84	
Anion/Cation = 1.74		(74)	1.75	(81)

[a]Represents the percentage of the cation composition attributed
to NH$_4$.

widespread patches (red/brown color) of apparently decaying organic materials of marine origin dominated much of the pack ice surface landscape. It is hypothesized that NH_3 is released to the atmosphere during decomposition of these materials and incorporated directly into sulfate aerosols or by aqueous phase scavenging during cloud/fog events. Rotting sea ice may also release trace gases, such as NH_3, to the atmosphere. The acidic aerosols in the Arctic appear to be an effective sink for basic atmospheric gases like NH_3. Further speculation leads to the possibility that the decaying organic materials may contribute to fog and stratus cloud formation over the pack ice by providing nuclei from direct release of particles and conversion of volatile organic matter to particles.

The mean concentrations of HNO_3, $HCOOH$, and CH_3COOH in the Arctic and sub-Arctic atmospheres during the summertime are given in Table 1. The concentration of the carboxylic acids was usually a factor of 4-5 higher than the concentration of HNO_3. Indeed, $HCOOH$ and CH_3COOH are principal components of sub-Arctic precipitation in the summertime (see below).

In the Arctic and sub-Arctic atmospheres $HCOOH$ and CH_3COOH concentrations appear to be correlated linearly in both the boundary layer and free troposphere (Figure 2). The results of a reduced major axis (RMA) regression analysis of these data are presented in Table 3. The values for the slope of the regression lines indicate that $HCOOH$ was significantly enriched in boundary layer air compared to CH_3COOH. The greatest enhancement occurred at low altitude over the Arctic Ocean pack ice. It is hypothesized that $HCOOH$ is produced and released to the gas phase from fog and stratus clouds in this region. Due to the acidic atmosphere in the Arctic, it is likely that the fog and cloud droplet pH is below 5, which should lead to loss of $HCOOH$ to the gas phase following its production in the aqueous phase. Production of CH_3COOH in the atmosphere is uncertain at this time. Over sub-Arctic tundra both of these carboxylic acids may be directly released from the biosphere or formed from hydrocarbon emissions (Figure 3). Indeed, there is a strong gradient in the concentration of $HCOOH$ and CH_3COOH in the boundary layer progressing inland from over the Bering Sea to tundra to boreal forest. The increased concentrations of these carboxylic acids over land compared to the ocean suggests a dominant continental source for $HCOOH$ and CH_3COOH.
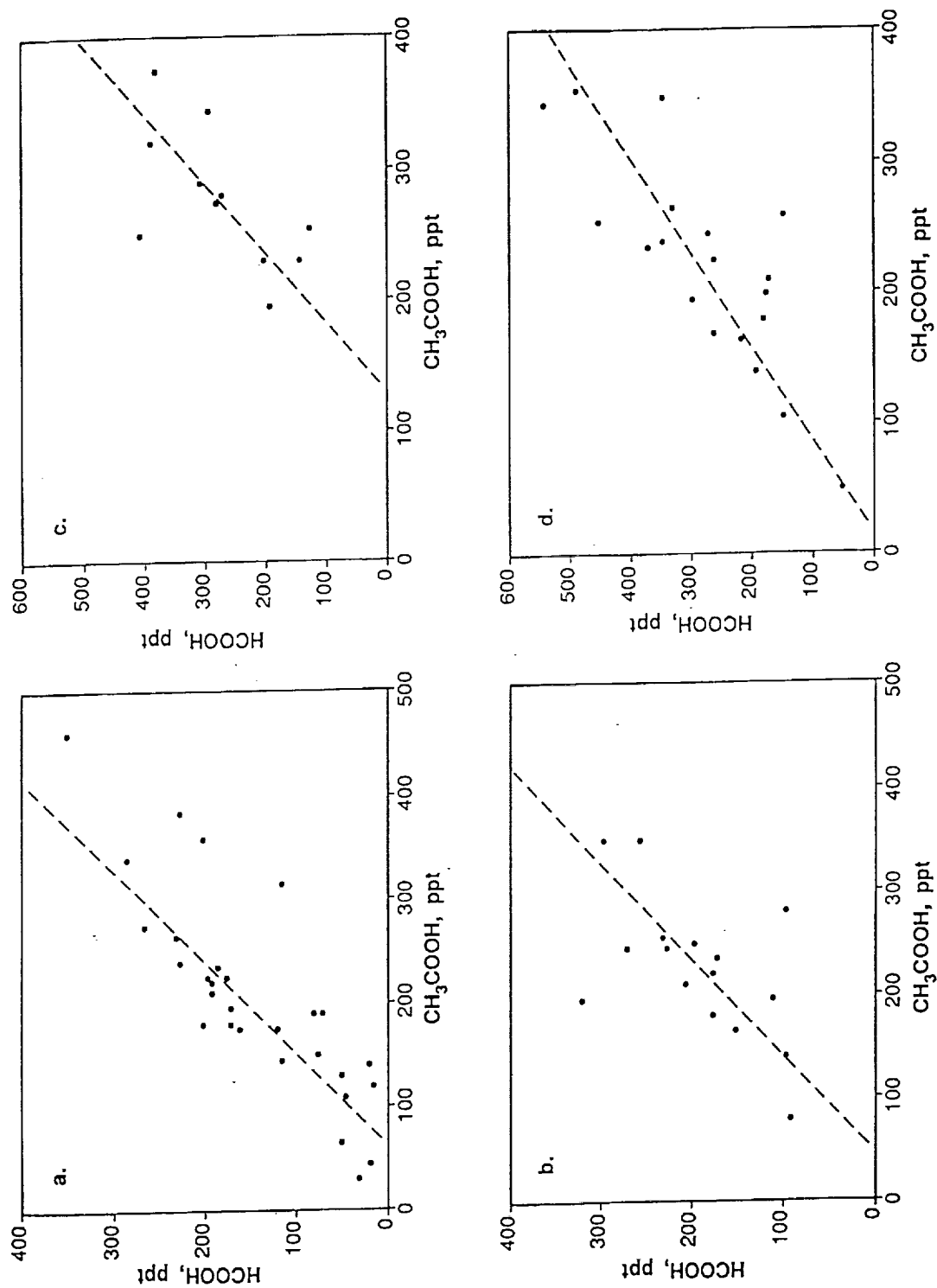
Figure 2. Relationship between the concentration of the gas phase carboxylic acids in: a. high Arctic free troposphere, b. sub-Arctic free troposphere, c. high Arctic boundary layer, d. sub-Arctic boundary layer. The dashed line represents the RMA regression fit.

Table 3. Results of RMA Regression Analysis

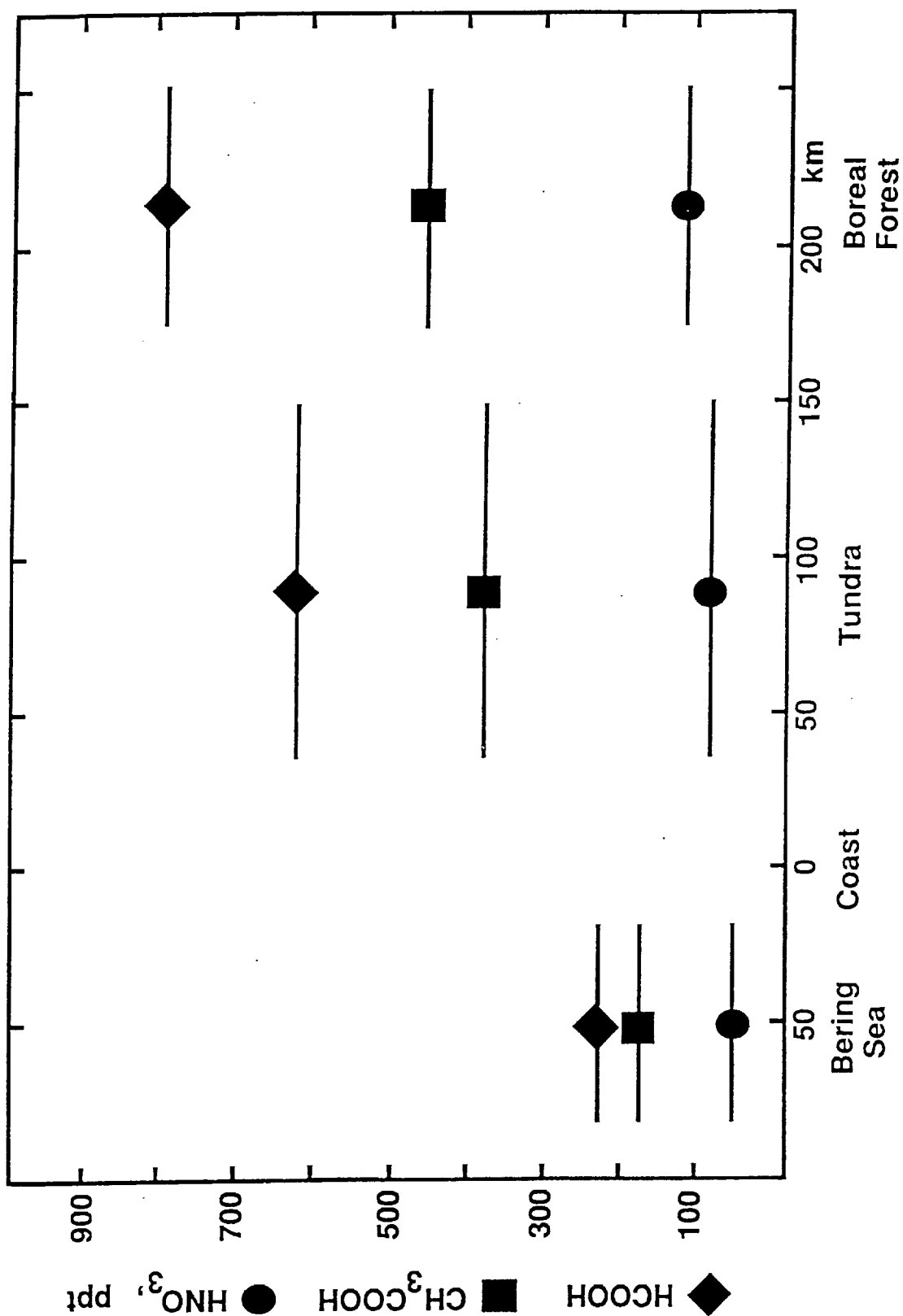| Region	Nitric Acid versus Nitrate			Formic versus Acetic		
	slope	intercept	r^2	slope	intercept	r^2
High Arctic (>60°N)						
Boundary Layer	1.23	+31	0.48	1.82	-234	0.71
Free Troposphere	2.01	+ 0.78	0.13	1.12	- 68	0.68
SubArctic (50-60°N)						
Boundary Layer	1.33	+19	0.05	1.40	- 19	0.72
Free Troposphere	4.35	- 7	0.39	1.04	- 43	0.73

Figure 3. Distribution of acidic gases in the boundary layer across a geographic track from the Bering Sea to the sub-Arctic tundra and over the adjacent boreal forest. The concentration trends suggest a continental source for these species (see text).

The geographic distribution of HNO_3 in the boundary layer (Figure 3) suggests that it has a continental source. Since the aerosol NO_3^- concentration was not significantly different over ocean and land, the apparent trend in HNO_3 does not simply reflect loss of it to sea salt aerosols over the Bering Sea. Biogenic emissions of nitric oxide (NO) over the tundra were very low (P. Bakwin, Harvard University, personal communication). It appears that decomposition of peroxyacetylnitrate (PAN) subsiding from aloft may be the source of nitrogen oxides (NO and NO_2) and subsequently HNO_3 in the boundary layer (D. Jacob, Harvard University, personal communication). This source may also be augmented by emissions from regional forest fires (see below).

THe relationship between HNO_3 and aerosol NO_3^- in the Arctic and sub-Arctic atmospheres is shown in Figure 4. Out of 74 samples, 68 showed that the concentration of HNO_3 was greater than that of aerosol NO_3^-. The results of RMA regressions for the boundary layer and free troposphere are given in Table 3. The following generalities were observed: (1) there was poor correlation between HNO_3 and aerosol NO_3^- concentrations in the Arctic and sub-Arctic atmospheres, (2) the phase partitioning in boundary layer air showed on the average that the concentration of HNO_3 was 25-30% higher than that of aerosol NO_3^-, (3) in the Arctic free troposphere the concentration of HNO_3 was 2-fold higher than that of aerosol NO_3^-, and (4) in the sub-Arctic free troposphere HNO_3 concentrations were enhanced 4-fold over aerosol NO_3^- levels.

To chemically characterize the various anthropogenic sources influencing the Arctic summer free troposphere, I utilized data obtained directly within plumes or highly contaminated air masses. For comparison, data collected in present day "clean background Arctic air" was summarized from air masses encountered with low CO ($\sim$95 ppbv) and NO_x ($\leq$ 25 pptv) levels (Table 4). Such "background" air masses were rarely encountered during ABLE-3A. The composition of the various pollution sources characterized during ABLE-3A are shown in Table 5 as enhancements over the "background" levels (Table 4). The common occurrence of these pollution plumes suggest that they may be important in determining the large-scale distribution of acidic gases and aerosol chemical species in the high latitude North American atmosphere. Emissions from forest fires in central Alaska were highly enriched in the carboxylic
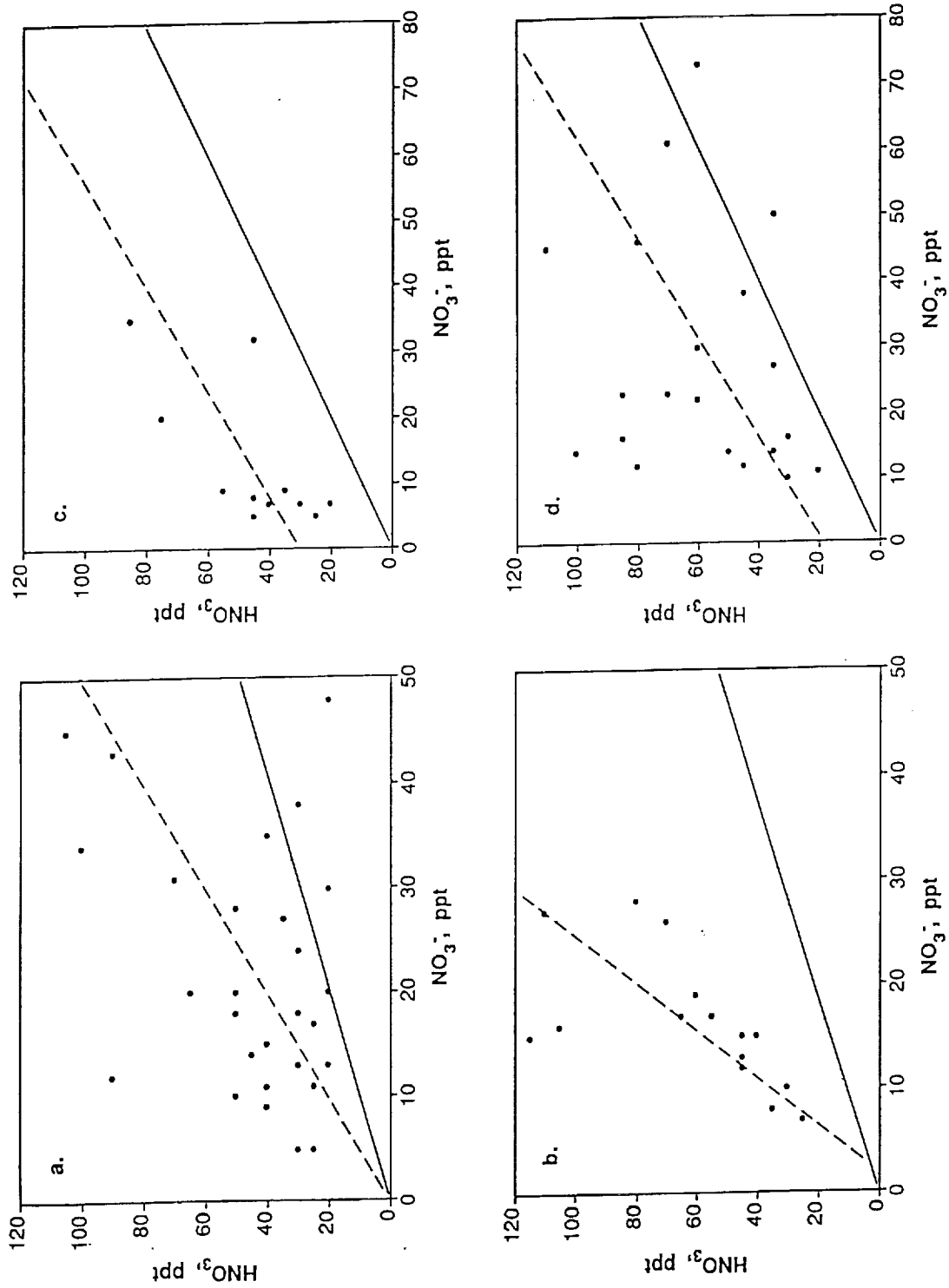
12

Figure 4. Relationship between nitric acid and aerosol nitrate in: a. high Arctic free troposphere, b. sub-Arctic free troposphere, c. high Arctic boundary layer, d. sub-Arctic boundary layer. The dashed line represents the RMA regression fit. The solid line corresponds to a ratio of 1.0.

Table 4. Summertime Characterization of North American

Arctic Free Tropospheric Composition

HFo	HAc	HNO$_3$	NO$_3^-$	SO$_4^{2-}$	Cl$^-$	C$_2$O$_4^{2-}$	NH$_4^+$	Na$^+$	K$^+$
Grand Average (N = 45)									
166	215	48	22	61	<15	4.5	68	12	5.7
± 81	± 90	±29	±17	±30		±2.7	±30	±7.5	±6.7
"Clean Background"									
			High Arctic (>60°N)						
50	65	30	5	38	<15	2.9	50	<20	<3
			SubArctic (50-60°N)						
90	80	45	13	10	<15	4.7	56	<20	<3

Atmospheric concentrations are stated in ppt.

High Arctic "clean background" concentrations are mean value

observed during missions 11 and 12 (July 20 and 21, 1988).

SubArctic "clean background" concentrations are mean value observed

during missions 20 and 21 which were flown on the same day (August

3, 1988).

Table 5. Enhancement Above "Clean Background" Concentration of Selected Acidic Gases and Aerosol Species in the Arctic Free Troposphere by Anthropogenic Sources During the Summertime

	HFo	HAc	HNO_3	NO_3^-	SO_4^{2-}	Cl^-	$C_2O_4^{2-}$	NH_4^+	Na^+	K^+
North American Signal (N = 3)										
	160	230	80	70	135	20	17	170	50	30
North Pacific Signal (N = 4)										
	320	400	300	10	40	0	6	40	0	10
Alaskan Forest Fires (N = 4)										
	570	410	185	60	150	15	10	315	30	20

Values (ppt) represent the source mean concentration minus the average "clean background" concentration in the Arctic free troposphere (see Table 4).

HFo means formic acid and HAc acetic acid.

acids and NH_4^+ while contaminated North Pacific air masses contained high concentrations of acidic gases but showed little enrichment of aerosol species (Table 5). For aerosol SO_4^{2-} the stratosphere may be an important source. Elevated SO_4^{2-} levels were observed at 6 km on several occasions (Figure 5). Outside of identifiable air mass types or plumes the anthropogenic (or stratospheric) influences are chemically diffuse and variable, making it very difficult to quantitatively ascertain the magnitude of the effects.

One final component of my ABLE-3A work was characterization of precipitation composition and wet deposition at Bethel, Alaska. The volume-weighted chemical composition of precipitation during the July 11 - August 11, 1988, study interval is shown in Table 6. The rain water pH at this site was 4.69. The carboxylic acids, HCOOH and CH_3COOH, can account for a maximum of 52% of the free acidity at this site. Sulfuric acid can contribute up to 43%, while nitric acid can only provide about 18%. The volume-weighted NO_3^-/SO_4^{2-} ratio was 0.86 in rain water at this site, compared to an average of 0.23 in the atmospheric aerosol. This observation suggests that HNO_3 must be effectively incorporated into precipitation during the summertime at this site.

The wet deposition fluxes of N and S over sub-Arctic tundra near Bethel, Alaska, were calculated using the volume-weighted rain water concentrations and the actual precipitation amount recorded by the National Weather Service at Bethel. The fluxes are shown in Table 7 for the July-August 1988 study period. Because the study period was abnormally warm and dry, the average deposition fluxes based on climatological mean percipitation for June-August were also calculated. The estimated wet fluxes show approximately 2-fold higher deposition of N (NO_3^- + NH_4^+) compared to S. The fluxes are similar to values measured at remote locations around the world.

At the Bethel tower site the surface deposition of total reactive nitrogen (NO_y) was measured using the eddy correlation technique. The average flux was found to be $1.4 \pm 0.8 \times 10^9$ molecules $cm^{-2} s^{-1}$, which is believed to represent primarily dry deposition of HNO_3 (P. Bakwin, Harvard University, personal communication). In comparison, wet deposition of NO_3^- was 4×10^9 molecules $cm^{-2} s^{-1}$, about 3-fold greater than the NO_y flux at this site. Based on the climatological mean precipitation amount, on average
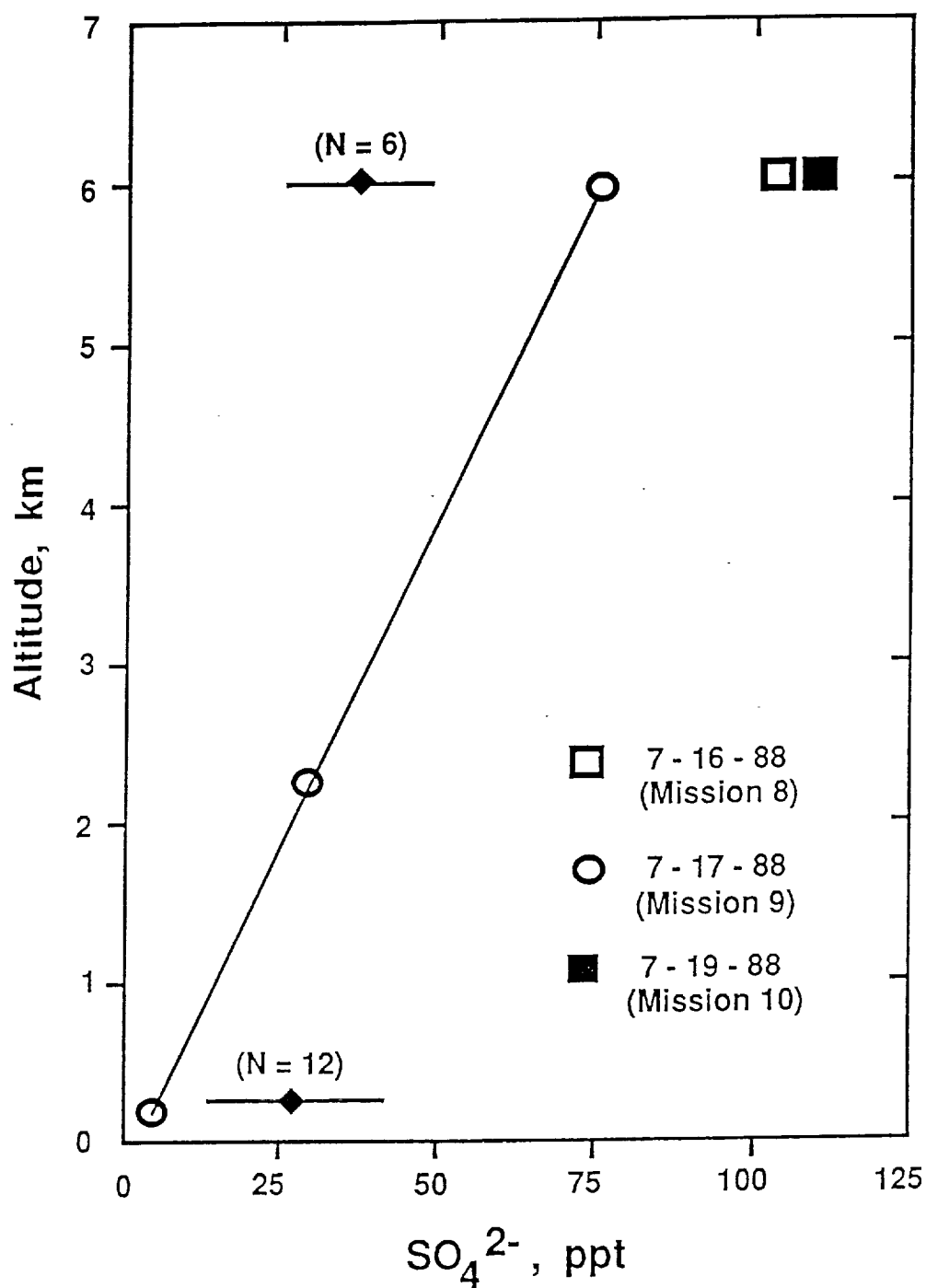
Figure 5. Vertical distribution of aerosol sulfate over the
Arctic Ocean pack ice during July 1988. The mean
values are shown for all flights north of Point
Barrow, AK. Enhanced concentrations of sulfate
were observed at 6 km altitude during missions 8,
9, and 10.

Table 6. Volume-Weighted Mean Composition of Precipitation
Over SubArctic Tundra near Bethel, Alaska,
From July 11 to August 11, 1988.

Species	μeq. L^{-1}
$HCOO_T$	7.9
CH_3COO_T	7.0
CH_3COCOO_T	0.15
SO_4	8.6
NO_3	3.7
Cl	9.4
Br	0.06
PO_4	0.05
C_2O_4	1.4
MSA	0.31
NH_4	5.1
Na	4.6
K	1.6
Ca	4.2
Mg	1.8
H	20.2

Table 7. Summertime Wet Deposition Fluxes Over SubArctic Tundra

| Species | ---------- mmol N or S m^{-2} yr^{-1} ---------- | |
	July 11-Aug. 11,1988 (48 mm)	Summertime Based on Climatological Mean (176 mm)
NO_3^-	2.1	7.5
NH_4^+	2.9	10.3
SO_4^{2-}	2.4	8.7

Climatological mean rainfall amount at Bethel, Alaska, for the months of June-August [taken from National Weather Service Records, Anchorage, Alaska].

this difference is probably even greater.

3.0 Results from ABLE-3B

The analysis and interpretation of the data obtained during ABLE-3B is currently ongoing with the focus at this time primarily on the reactive nitrogen cycle. Compared to ABLE-3A, the ABLE-3B data are being analyzed by individuals using data from virtually all groups involved in the experiment. I am taking the lead working on the large scale distributions and relationships of the reactive nitrogen family members. As such, the data have been merged to represent actual measurements of all species with equal sampling time resolution. At this time the data interpretation is being conducted with the goal of producing manuscripts for the March 1, 1992, deadline pertaining to the ABLE-3B special issue of the Journal of Geophysical Research-Atmospheres. In this report I briefly describe the types of results that were obtained by the University of New Hampshire during ABLE-3B. The reader should review the journal special issue for detailed interpretation of the ABLE-3B results .

The ABLE-3B experiment was conducted in the Hudson Bay Lowlands region of Ontario and the Schefferville area of Laborador (Figure 1). The objectives of ABLE-3B were essentially the same as for ABLE-3A, except that the experiment focused on other important ecosystems at high latitude in North America. Some flight tracks purposely sampled regions examined during ABLE-3A to re-visit certain air mass types for building links between these two large-scale experiments.

To illustrate the distribution of HNO_3 over central Canada during ABLE-3B I have selected data from various flights in the study regions. These data are plotted as a function of altitude in Figure 6. The Hudson Bay Lowlands region was impacted significantly by forest fire emissions in Ontario and other areas of western Canada and Alaska. Within biomass burning plumes the concentration of HNO_3 approached 1000 pptv compared to 100 pptv or less outside the directly impacted air masses. In the Schefferville region the effects of forest fires were much less resulting in significantly lower concentrations of HNO_3 compared to the Hudson Bay area (Figure 6). During missions to Frobisher Bay we sampled "clean background" Arctic air. In these air masses the HNO_3 concentration was invariant with altitude remaining between 15-30 pptv.
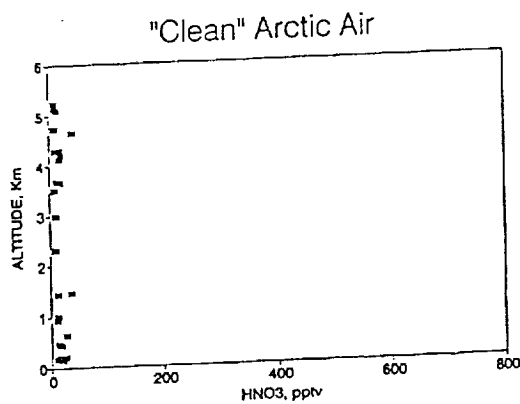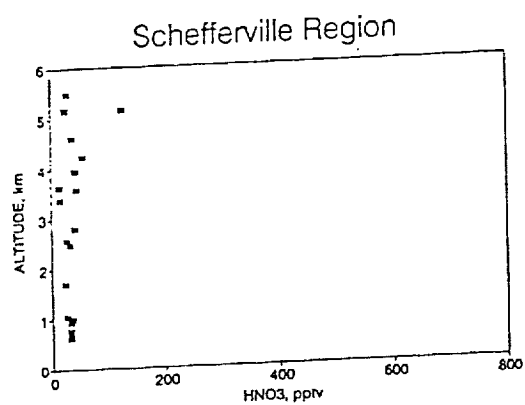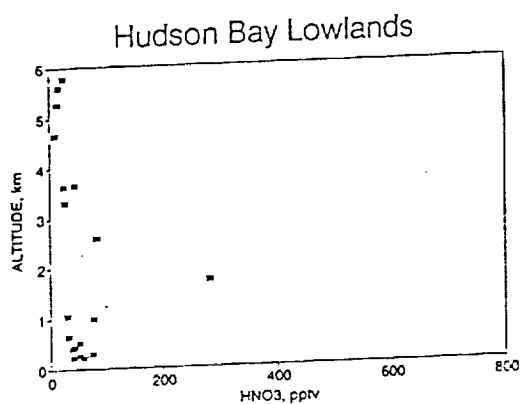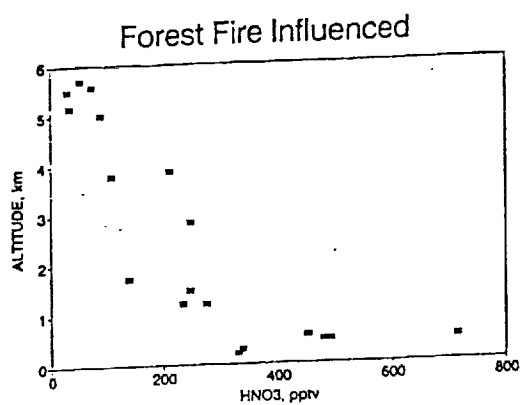
Forest Fire Influenced

Hudson Bay Lowlands

Schefferville Region

"Clean" Arctic Air

Figure 6. Vertical distribution of HNO_3 in selected air

masses during ABLE 3B.

21

Using the NO_y data obtained by the Georgia Institute of Technology group (J. Bradshaw and S. Sandholm) during ABLE-3B, I have examined the relationship of HNO_3/NO_y for the air masses depicted in Figure 6. These relationships are shown graphically in Figure 7 as a function of altitude. Nitric acid composed the largest fraction of NO_y in air masses impacted significantly by biomass burning emissions. The fraction of NO_y represented by HNO_3 appeared to decrease with increasing altitude. I am currently examining the suite of ABLE-3B data to see if this effect is related to plume age or instead reflects physical removal (e.g., precipitation scavenging) of soluble species like HNO_3 from the impacted air masses. The approach is to use long-lived hydrocarbon species to assess differences in nitrogen plume chemistry.

In general, HNO_3 comprised a larger fraction of NO_y in the Schefferville region than in the over the Hudson Bay Lowlands. This was the case despite the fact that the HNO_3 concentration was lower over Schefferville than the Hudson Bay Lowlands. The reason for this is unclear. One possible explanation can be put forth based on our measurements of nitrogen chemistry in "clean background" Arctic air masses near Frobisher Bay. Using data from two flights in this region I have found that in air masses with the lowest levels of NO_y (< 100 pptv) the value of the ratio HNO_3/NO_y tends to increase (Figure 8). The same thing happens in the case of NO and NO_2, but PAN/NO_y decreases. Looking at this as a function of altitude, it appears that the largest changes in the various ratios occurs in boundary layer air (< 2 km altitude). These data might be showing the slow thermal decomposition of PAN as it subsides from aloft providing a source of NO and NO_2 and subsquently HNO_3 at lower altitudes. Air masses in the Schefferville region were commonly feed with air coming from higher laltitudes. Thus, the regeneration of NO_x and HNO_3 from PAN decomposition could be influencing the partitioning of NO_y over the Laborador study region. The Hudson Bay Lowlands were rarely influenced by these high latitude air masses during our study period. Instead, the air masses were usually moving into the region from the south or west directions. The major impact of biomass burning on air chemistry in Ontario would also tend to obscure influences from "clean" air chemistries. I am currently examining this hypothesis in detail to see if it is a plausible explanation for our observations.
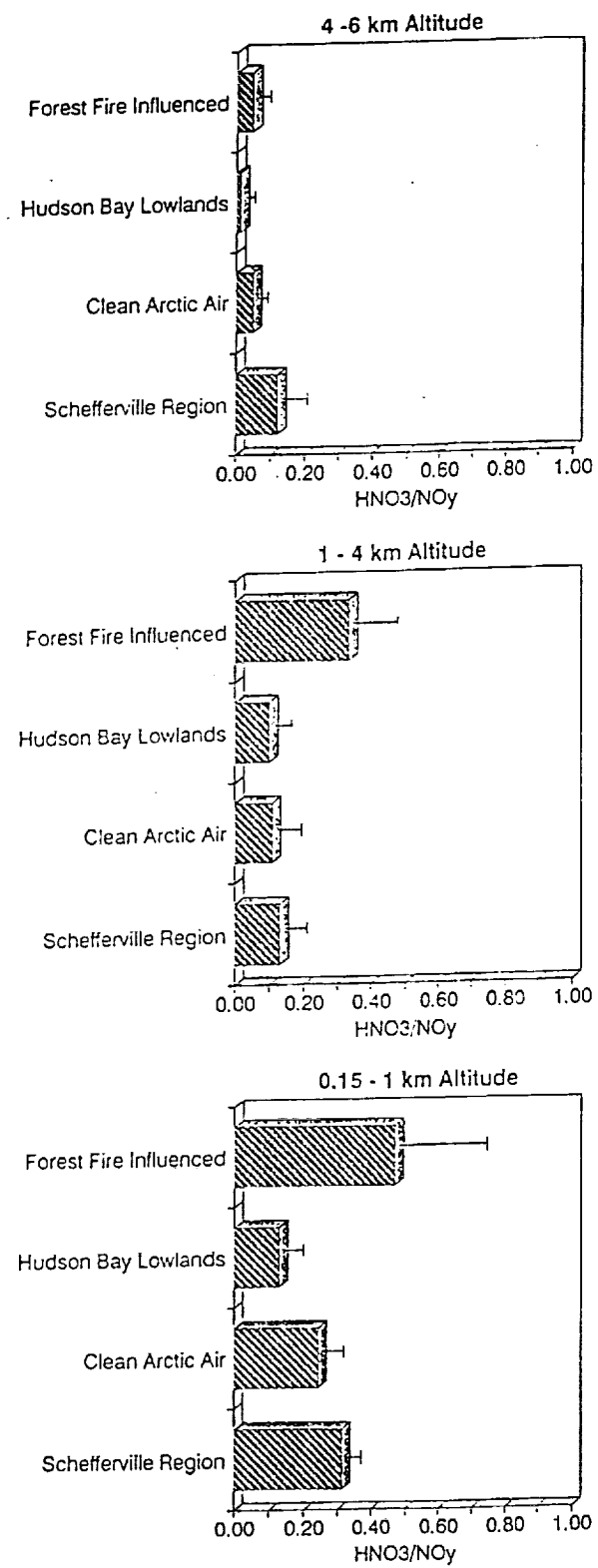
4 -6 km Altitude

HNO3/NOy

1 - 4 km Altitude

HNO3/NOy

0.15 - 1 km Altitude

HNO3/NOy

Figure 7. Relationship of HNO_3 / NO_y as a function of altitude in selected air masses during ABLE 3B. NO_y data courtesy of Georgia Institute of Technology.
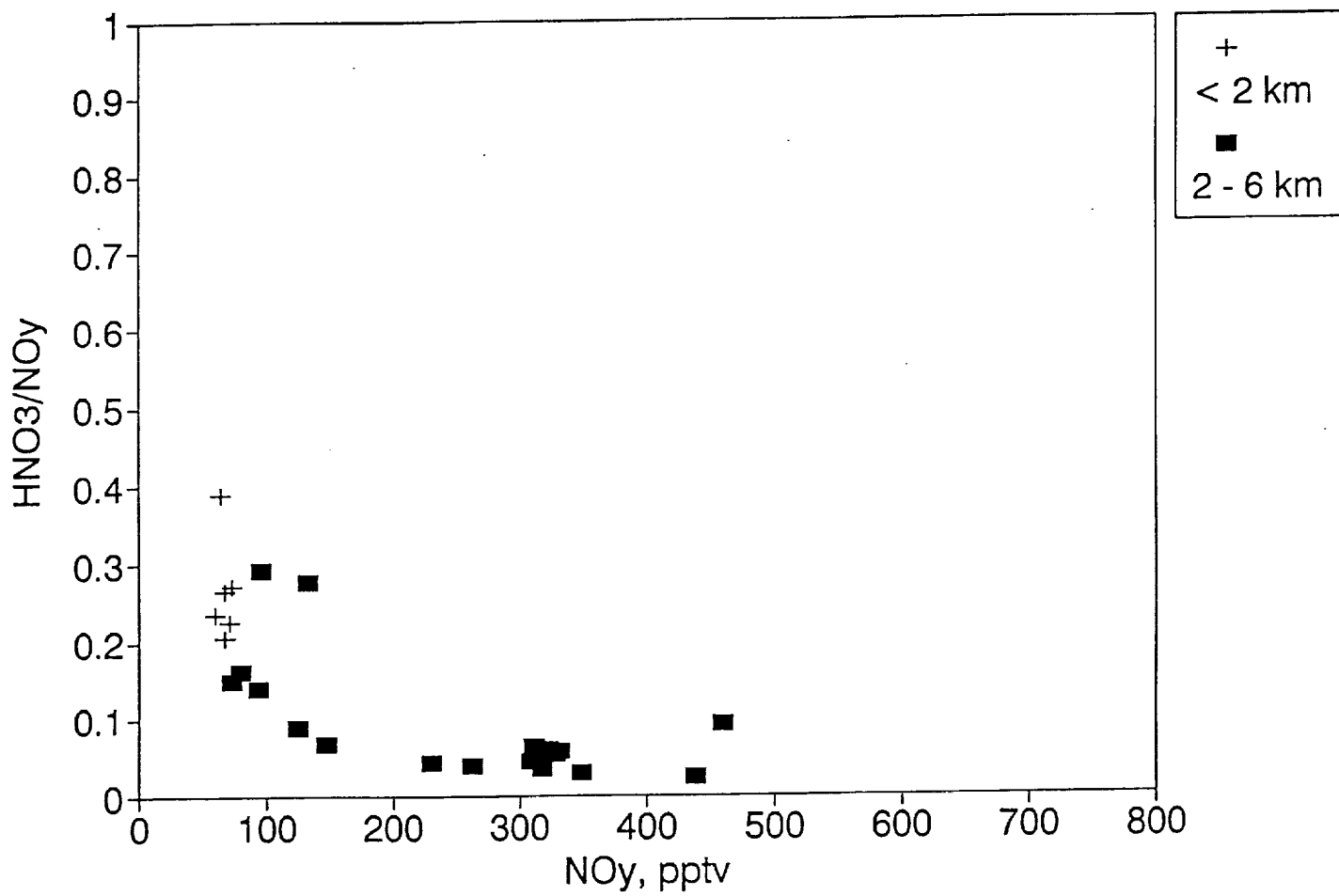
23

Figure 8. Relationship of HNO_3/ NO_y in "clean background" Arctic air.

The University of New Hampshire group is also working on interpreting data collected on the carboxylic acids, HCOOH and CH_3COOH. In the Hudson Bay region, the distribution of HCOOH and CH_3COOH was driven to a large extent by emissions from forest fires. An example of this effect is shown in Figure 9 for a plume encountered between 4-5 kn altitude. The concentrations of these carboxylic acids within plume were commonly elevated 3-10 times over air masses outside direct plume influences. The concentrations of HCOOH and CH_3COOH were much greater than that of HNO_3, both within and outside of biomass burning plumes. Typically the carboxylic acids were observed at concentrations of 2-10 times higher than that of HNO_3. This trend is the same as what we observed for these acidic trace gases in ABLE-3A, except that their concentrations are 2-3 times higher on average over Canada than in the high Arctic atmosphere. A graduate student (B. Lefer) is currently working on interpreting the carboxylic acid data set from ABLE-3B.

A large data set was also obtained on the chemistry of the atmospheric aerosol over central Canada during ABLE-3B. A research scientist (K. Gorzelska) at the University of New Hampshire has just begun to examine the aerosol compositional data. In addition, we are working on assessing the surface exchange of acidic gases at the Schefferville tower site. A research scientist formerly at the University of New Hampshire (O. Klemm) is leading this effort. He has now returned to F. R. Germany, but we are still colloborating on the interpretation of this unique data set for a remote region. The results of these analyses are not yet available, but we plan to submit manuscripts which describes the aerosol chemistry and the effects of biomass burning on it and the surface exchange work to the ABLE-3B special issue of the Journal of Geophysical Research-Atmospheres.
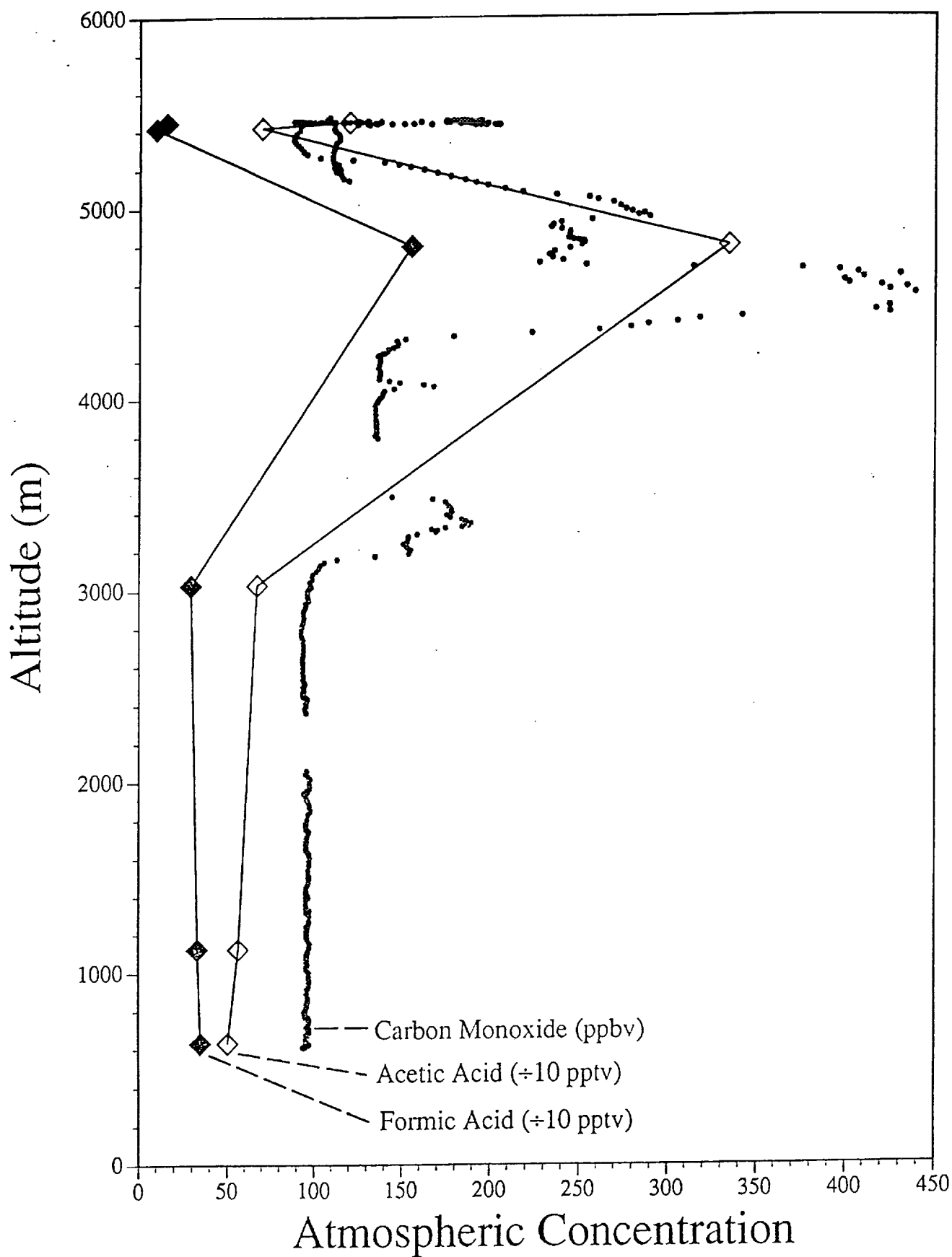
Figure 9. Vertical distribution of carboxylic acids over central Canada during ABLE 3B showing influence of biomass burning emissions above 3 km altitude. CO data courtesy of Glen Sachse.

4.0 Professional Abstracts and Journal Publications for Work Performed Under NAG-1-936

The following abstracts appeared in EOS Trans. 70, 15, 1989:

Talbot, R. W., R. C. Harriss, A. S. Vijgen, and M. R. Scott, Aerosol and precipitation chemistries in the North American Arctic during ABLE-3A.

Singh, H. B., D. O'Hara, D. Herlth, J. D. Bradshaw, S. T. Sandholm, D. D. Davis, R. Talbot, and G. L. Gregory, Atmospheric distribution of PAN and other organic nitrates at high latitudes: Aircraft measurements during ABLE-3A.

Bradshaw, J. D., S. T. Sandholm, E. Browell, G. Sachse, G. Gregory, J. Barrick, M. Shipham, R. Talbot, R. Harriss, H. Singh, D. Blake, J. Nordeman, and S. Wofsy, Characterization of continental and maritime polar air masses impact on the troposphere over ALaska.

Sandholm, S., G. Chen, J. Schendel, J. Bradshaw, R. Talbot, H. Singh, and D. Herlth, Shortfall reactive odd-nitrogen budget observed during NASA/GTE-ABLE-3A field program.

Wofsy, S. C., R. C. Harriss, R. W. Talbot, J. Bradshaw, S. Sandholm, E. Browell, G. Gregory, J. Barrick, M. Shipham, S. Bachmeier, D. Nordeman, H. Singh, and D. Blake, Enhanced trace gas and aerosol concentrations in the free troposphere over Alaska, July-August 1988.

The following abstracts appeared in EOS Trans. 72, 44, 1991:

Gregory, G. L., B. E. Anderson, M. C. Shipham, E. V. Browell, and R. W. Talbot, Size characteristics of tropospheric aerosols as observed during periods of haze and biomass burning over Canada during the summer of 1990.

Bradshaw, J. D., S. T. Sandholm, R. W. Talbot, and H. Singh, Summertime tropospheric spatial distribution of reactive odd-nitrogen compounds over Canada.

Talbot, R. W., J. D. Bradshaw, S. T. Sandholm, and H. Singh, Tropospheric NO_y partitioning during sumertime over Canada.

Sandholm, S. T., J. D. Bradshaw, R. W. Talbot, H. Singh, G. L. Gregory, B. E. Anderson, J. D. Barrick, M. C. Shipham, G. W. Sachse, J. Collins, and A. S. Bachmeier, The odd-nitrogen budget from observations made during ABLE-3B.

Singh, H. B., D. O'Hara, D. Herlth, J. D. Bradshaw, S. T. Sandholm, R. Talbot, D. Blake, and G. L. Gregory, Reactive nitrogen distribution and photochemistry during ABLE-3B.

Anderson, B. E., G. L. Gregory, S. Bachmeier, E. V. Browell, M. Shipham, D. R. Blake, J. D. Bradshaw, S. Sandholm, G. W. Sachse, J. Collins and R. Talbot, Low ozone events in the mid-troposphere over Canada during summer 1990.

The following papers are "in press" for publication in a special issue of the Journal of Geophysical Research-Atmospheres on ABLE-3A:

Talbot, R. W., A. S. Vijgen, and R. C. Harriss, Soluble species in the Arctic summer troposphere: Acidic gases, aerosols, and precipitation.

Jacob, D. J., S. C. Wofsy, P. S. Bakwin, S. -M. Fan, R. C. Harriss, R. W. Talbot, J. D. Bradshaw, S. T. Sandholm, H. B. Singh, G. L. Gregory, G. W. Sachse, M. Shipham, D. R. Blake, and D. R. Fitzjarrald, Summertime photochemistry of the troposphere at high northern latitudes.

Wofsy, S. C., G. W. Sachse, G. L. Gregory, D. R. Blake, J. D. Bradshaw, S. T. Sandholm, H. B. Singh, J. A. Barrick, R. C. Harriss, R. W. Talbot, M. A. Shipham, E. V. Browell, D. J. Jacob, and J. A. Logan, Atmospheric chemistry in the Arctic and subArctic: Influence of natural fires, industrial emissions, and stratospheric inputs.

Singh, H .B., D. Herlth, D. O'Hara, K. Zahnle, 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: Influences of reservoir species on NO_x and O_3.

Dibb, J. E., R. W. Talbot, and G. L. Gregory, [7]Be and ^{210}Pb in the western hemisphere Arctic atmosphere: Observations from three recent aircraft-based sampling programs.

Sandholm, S. T., J. D. Bradshaw, G. Chen, H. B. Singh, R. W. Talbot, G. L. Gregory, D. L. Blake, G. W. Sachse, E. V. Browell, J. A. Barrick, M. A. Shipham, A. S. Bachmeier, D. Owen, S. C. Wofsy, and R. C. Harriss, Arctic tropospheric observations related to N_xO_y distributions and partitioning: ABLE-3A.

The following papers are "in preparation" for publication in a special issue of the Journal of Geophysical Research-Atmospheres on ABLE-3B:

Talbot, R. W., J. D. Bradshaw, S. T. Sandholm, and H. B. Singh, Distribution and partitioning of reactive nitrogen over Canada in summertime.

Bradshaw, J. D., S. T. Sandholm, R. W. Talbot, and H. B. Singh, Shortfall in reactive nitrogen over Canada in summertime.

Klemm, O., R. W. Talbot, and K. Klemm, Surface exchange of acidic trace gases over a taiga ecosystem in Canada.

Gorzelska, K., R. W. Talbot, K. Klemm, B. Lefer, and O. Klemm, Composition of the atmospheric aerosol over central Canada during summertime.

Singh, H. B., D. O'Hara, D. Herlth, J. D. Bradshaw, S. T. Sandholm, R. W. Talbot, and G. L. Gregory, Distribution and photochemistry of PAN and other reactive nitrogen over Canada.

Lefer, B., R. W. Talbot, K. Klemm, and O. Klemm, Observations of gas phase phosphoric and oxalic acids in biomass burning plumes over Canada.

Wofsy, S. C., G. W. Sachse, G. L. Gregory, D. R. Blake, J. D. Bradshaw, S. T. Sandholm, R. C. Harriss, R. W. Talbot, M. Shipham, E. V. Browell, and D. J. Jacob, Influence of forest fire emissions on atmospheric chemistry over Canada in summertime.

Anderson, B. E., G. L. Gregory, S. Bachmeier, E. V. Browell, J. D. Bradshaw, S. T. Sandholm, D. L. Blake, R. W. Talbot, M. Shipham, G. Sachse, and J. Collins, Low ozone air masses in the mid-troposphere over central Canada during summer 1990.

Other Publications:

Li, S. -M., R. W. Talbot, L. A. Barrie, and R. C. Harriss, Seasonal and geographic variations of methanesulphonic acid in the Arctic troposphere, submitted to Atmospheric Environment, 1991.