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Atmospheric Chemistry in the Arctic and Subarctic: Influence of Natural Fires, Industrial Emissions, and Stratospheric Inputs

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Haze layers with perturbed concentrations of trace gases, believed to originate from tundra and forest wild fires, were observed over extensive areas of Alaska and Canada in 1988. Enhancements of CH_4, C_2H_2, C_2H_6, C_3H_8, and C_4H_{10} were linearly correlated with CO in haze layers, with mean ratios (mole hydrocarbon/mole CO) of 0.18 (± 0.04 (1 σ)), 0.0019 (± 0.0001), 0.0055 (± 0.0002), 0.0008 (± 0.0001), and 1.2 $\times 10^{-4}$ ($\pm 0.2\times 10^{-4}$), respectively. Enhancements of NO_y were variable, averaging 0.0056 (± 0.0030) mole NO_y/mole CO, while perturbations of NO_x were very small, usually undetectable. At least 1/3 of the NOy in the haze layers had been converted to peroxyacetyl nitrate (PAN), representing a potential source of NOx to the global atmosphere; much of the balance was oxidized to nitrate (HNO_3 and particulate). The composition of sub-Arctic haze layers was consistent with aged emissions from smoldering combustion, except for CH_4, which appears to be partly biogenic. Inputs from the stratosphere and from biomass fires contributed major fractions of the NO_y in the remote sub-Arctic troposphere. Analysis of aircraft and ground data indicates relatively little influence from mid-latitude industrial NO_y in this region during summer, possibly excepting transport of PAN. Production of O_3 was inefficient in sub-Arctic haze layers, less than 0.1 O_3 molecules per molecule of CO, reflecting the low NO_x/CO emission ratios from smoldering combustion. Mid-latitude pollution produced much more O_3, 0.3 - 0.5 O_3 molecules per molecule of CO, a consequence of higher NO_x/CO emission ratios.

1. INTRODUCTION

The Arctic and sub-Arctic regions of Alaska, Canada, and Greenland represent a vast wilderness with extremely low levels of human activity, one of the largest such land areas remaining in the world. Anthropogenic emissions are negligible over most of the region, except for oil operations on the North Slope [*Blake et al.*, this issue]. Atmospheric composition is regulated mainly by natural processes and by long-range transport of pollution. Natural influences include stratosphere-troposphere exchange [*Gregory et al.*, this issue; *Browell et al.*, this issue], tundra and forest wild fires, and uptake of reactive chemical species by vegetation [*Jacob et al.*, this issue]. Anthropogenic pollutants have been observed at particularly high levels in late winter and spring, during the "Arctic haze" period [*Rahn*, 1981; *Rahn and McCaffrey*, 1980; *Barrie and Hoff*, 1985; *Hansen et al.*, 1989].

Natural fires occur throughout the boreal zone during summer, representing a potentially dominant source of hydrocarbons, NO_x, and particulates. Most previous studies of fires have focussed on mid-latitudes or on tropical burning [e.g., *Hegg et al.*, 1990; *Seiler and Crutzen*, 1980, *Andreae et al.*, 1988; *Crutzen et al.*, 1985; *Ward and Hardy*, 1991; *Greenberg et al.*, 1984; *Cofer et al.*, 1988], with only a few investigations in the boreal zone [*Cofer et al.*, 1989].

The present paper investigates layers with enhanced concentrations of trace gases intercepted by the NASA Electra aircraft over Alaska during the Arctic Boundary Layer Expedition (ABLE 3A) in July-August 1988. The summer of 1988 was notably hot and dry over Alaska and the haze layers are believed to have originated from natural fires that were widespread in the region [*Shipham et al.*, this issue]. Data from the haze layers are examined to define primary emission factors from boreal wild fires and to delineate the course of chemical aging. The chemical signatures of these haze layers are found to be remarkably consistent with emissions from smoldering combustion observed in the laboratory [*Lobert et al.*, 1991], and notably different from emissions from flaming combustion.

We also assess the relative importances of natural and anthropogenic sources in regulating trace gas concentrations over southern Alaska. Analysis of data for background air indicates that input from the stratosphere provided a dominant source for O_3 [*Gregory et al.*, this issue]. We argue that the stratosphere provided a significant source for NO_y and that natural fires were also important. Long-range transport of pollution from mid-latitudes may have affected vertical distributions of C_2–C_4 alkanes and CO but could not be detected unambiguously for NO_y or O_3.

2. SUMMERTIME HAZE LAYERS IN THE SUB-ARCTIC

Plate 1 shows lidar images from several flights during ABLE 3A, and Figure 1 shows the corresponding flight paths and locations of fires on the day of Flights 14 and 20/21. Flight 14, on July 26, 1988 (Plate 1*a*), shows an extensive haze layer between 2 and 3km altitude, as indicated by dark areas in the aerosol image. This layer was sampled near 2-km and again at 4-km altitude in a vertical profile at point 2 (see Figure 2). Weak ozone enhancement may have been associated with the aerosol layer (for example, examine the lidar data near Point 1). A fire covering several square kilometers was burning about 100 km to the north, and a number of very large fires were burning to the east; visibility had

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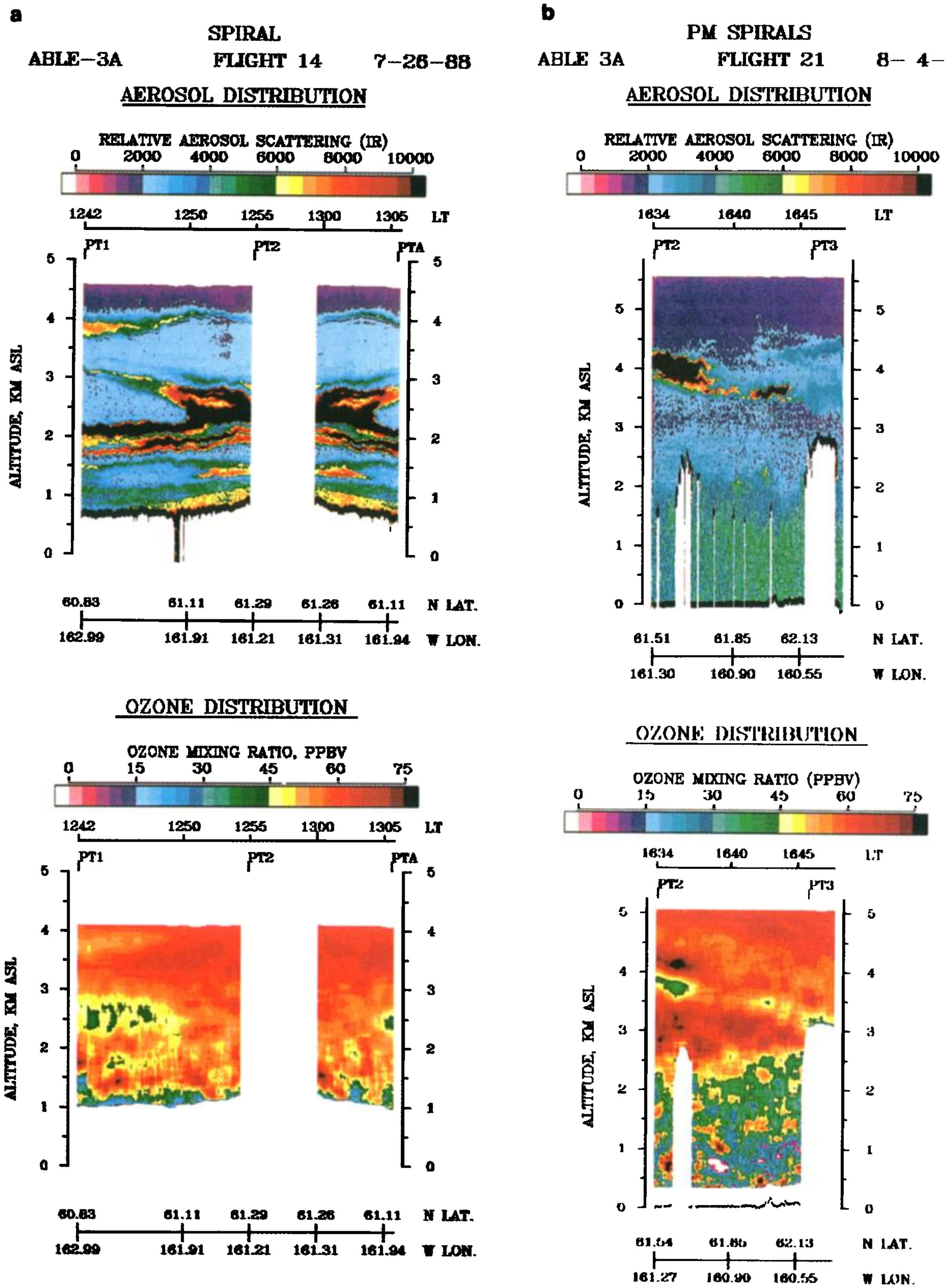


Plate 1. LIDAR images of aerosol extinction at 1 μm (upper panels) and ozone mixing ratio (lower panels) for (a) Flight 14 (July 26, 1988, and (b) Flight 21 (August 4, 1988), showing haze layers in the region near Bethel, Alaska. (c) Data for Flight 33 (August 17, 1988) cover the coastal transect from Portland, Maine, to Wallops Island, Virginia.

been reduced by smoke during the previous few days in Bethel [*Shipham et al.*, this issue]. The high aerosol burden suggests that a biomass fire was the main source; however the origin cannot be uniquely traced. Elevated NO_x (see S.T. Sandholm et al., Summertime Arctic troposphere observations related to N_xO_y distribution and partitioning: ABLE 3A, submitted to *Journal of Geophysical Research*, 1991) for experimental detail) was observed (see Figure 2 and Table 1), indicating relatively recent emissions, and

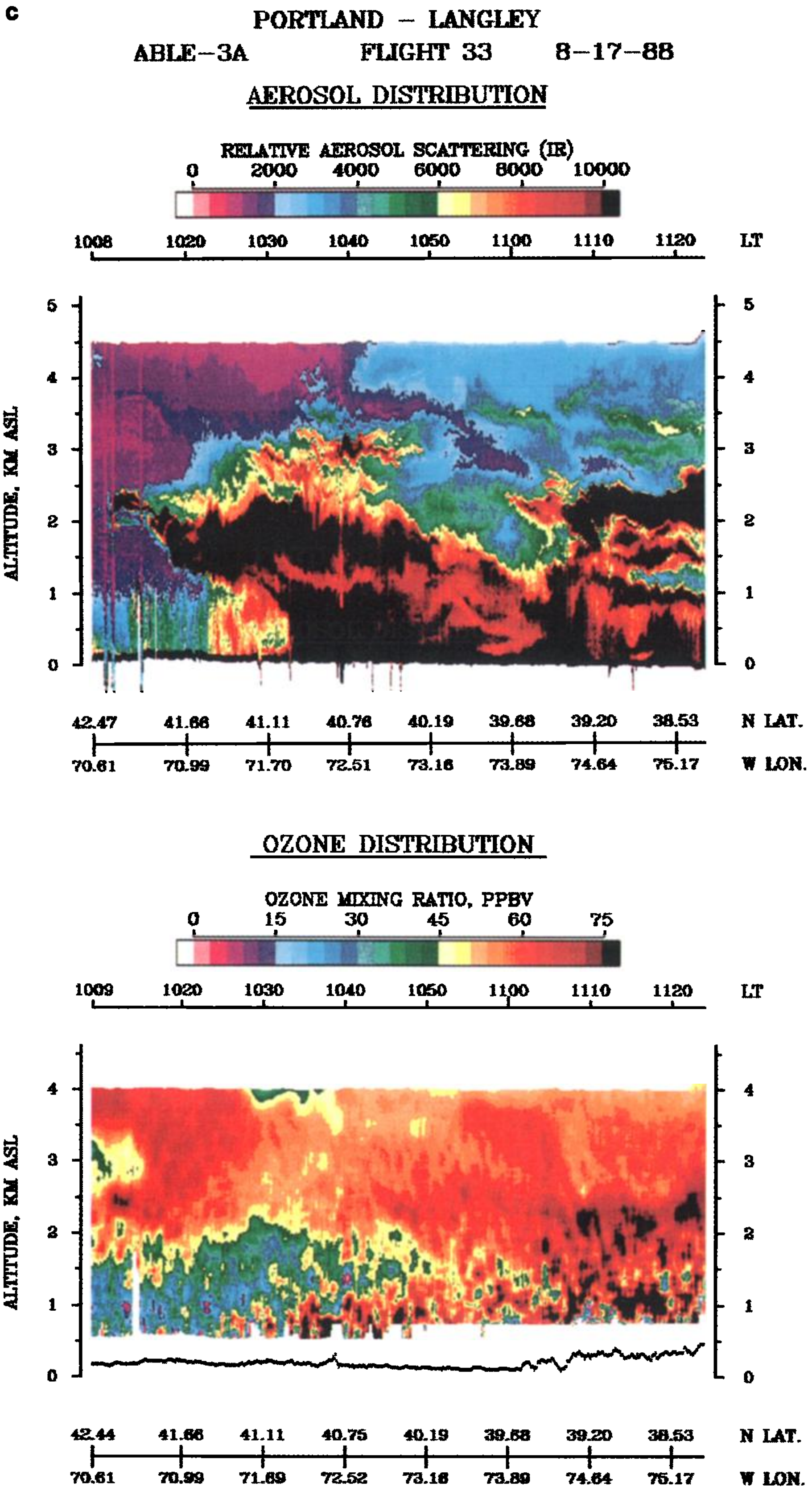
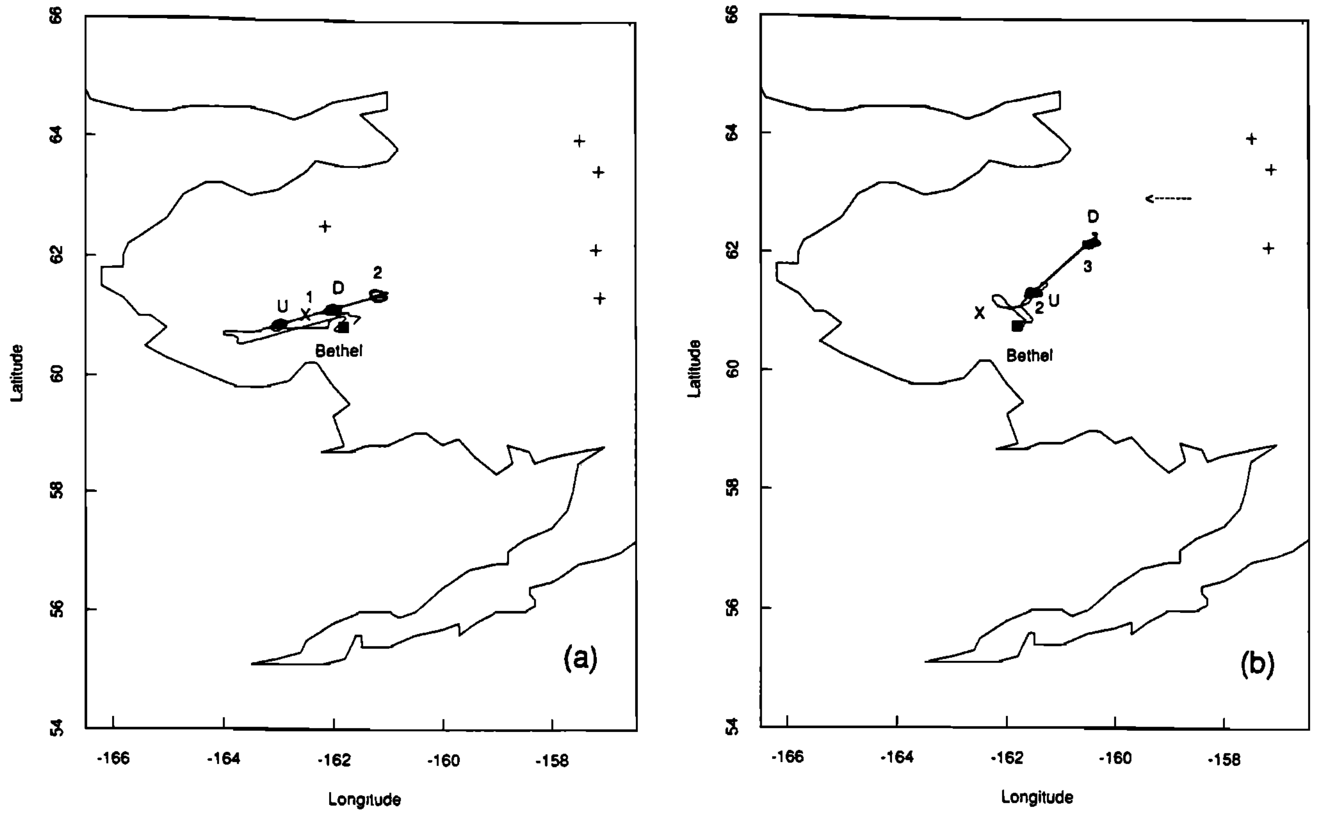


Plate 1 (continued)

the town of Bethel (population 4000, 30 - 100 km distant) may have contributed.

On Flights 20 and 21 (August 3, 1988) a haze layer was observed between 3 and 4.5km altitude (Plate 1*b* and Figure 3). Back trajectories passed over numerous and extensive fires identified in satellite images 200 - 1000 km to the east and northeast (see Figures 34 and 35 in *Shipham et al.* [this issue]. Enhancements of CO and C_2 hydrocarbons were similar on Flights 14 and



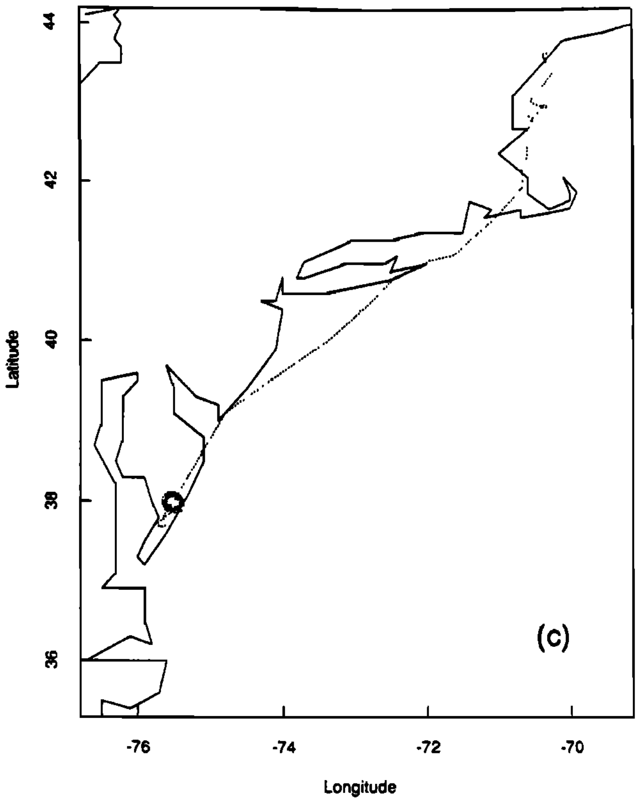


Fig. 1. Flight tracks for (a) Flight 14 and (b) Flight 20/21 near Bethel, Alaska, and (c) Flight 33 along the east coast of the United States. The numbers correspond to points in the LIDAR images in Plate 1. The locations of spirals are indicated by D (first spiral, descending) and U (second spiral, ascending). The tower site is denoted by X; locations of major active fires by crosses. The arrow denotes direction of motion of air parcels from trajectory calculations for Flights 20/21 [*Shipham et al.*, this issue], for the 300 K level (close to the haze layer altitude).

20/21, but NO was not perturbed and NO_y was only slightly elevated on Flights 20/21.

Carbon monoxide, measured continuously by the differential absorption CO measurement (DACOM) instrument [*Harriss et al.*, this issue], provides the most sensitive indicator for combustion, to which other concentrations may be ratioed to obtain emission factors. Correlations between CO and C_2H_6, and between CO and C_2H_2, were remarkably uniform for the haze layers. Figure 4 shows linear regressions for composite data from Flights 14, 20 and 21 (20 grab samples analyzed for hydrocarbons [*Blake et al.*, this issue]), giving $r^2= 0.97$ for both, i.e., linear dependence on CO could account for 97% of the variance observed for C_2H_2 and C_2H_6. Propane was more variable than acetylene and ethane, relative to CO, but a significant correlation (r^2=0.82) was still obtained in the composite data set (Figure 4c) and for individual haze layers (see Table 1). The uniformity of hydrocarbon/CO ratios in Flights 14 and 20/21 argues strongly for a similar origin for haze layers encountered on these flights.

Concentrations of butane were not correlated with CO in the composite set, however consistent correlations, with similar proportionality coefficients, were found in individual layers (Table 1). The variable results likely reflect the difficulty in making measurements at very low concentrations, and atmospheric losses could also play a role. The lifetime for C_4H_{10} is only a few hours in the daytime, and layers more than a day old might lose the signature of primary emissions.

We define emission factors from fires by focussing on haze layers with well-defined boundaries, believed to represent fire plumes. Primary emission ratios are preserved within the haze

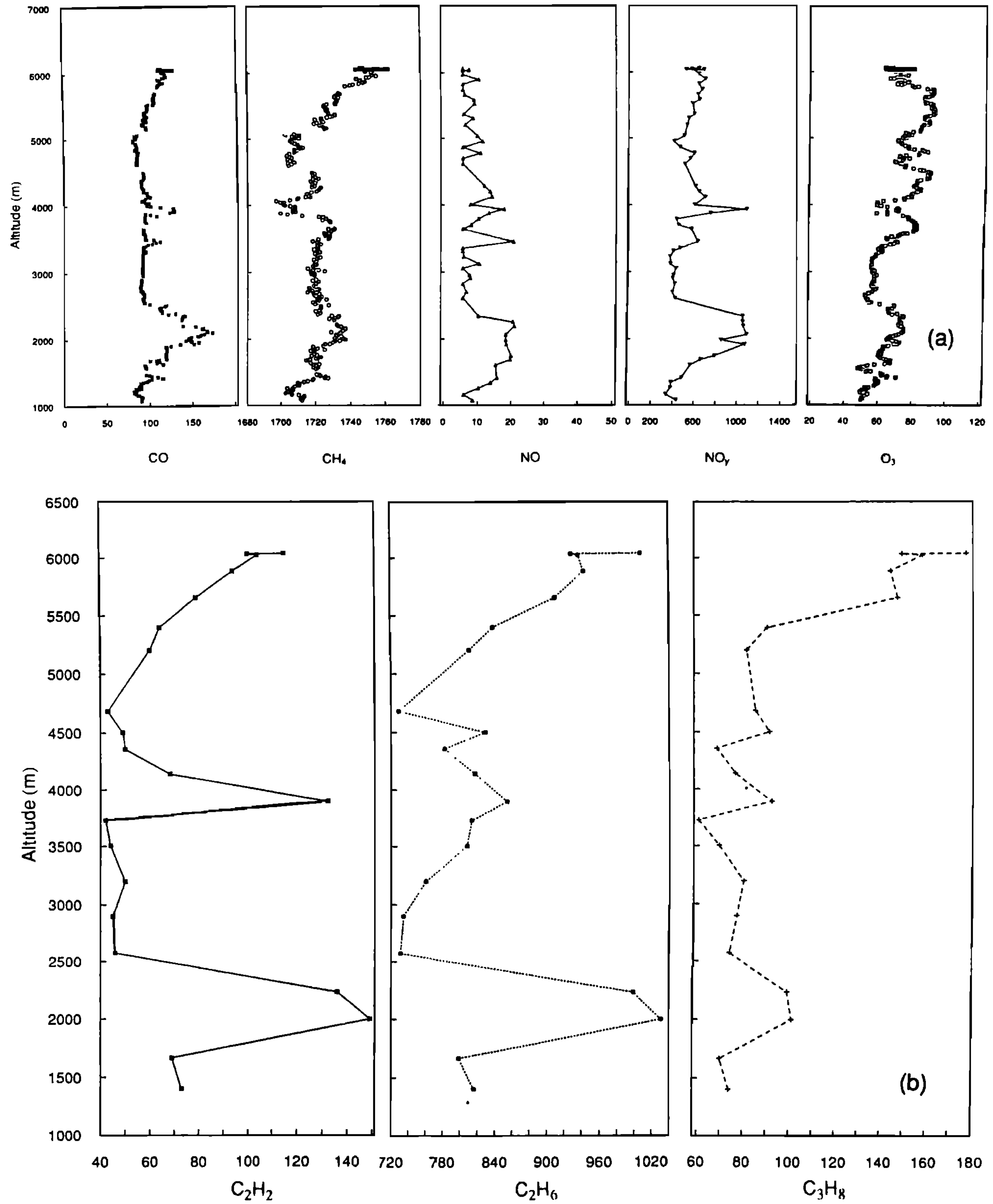


Fig. 2. Vertical profiles for trace gases on Flight 14, at Point U (spiral 2) in Plate 1*a*. Data for CO, CH_4 and O_3 represent 10-s averages; data for NO and NO_y are 1-min averages, and data for nonmethane hydrocarbons represent grab samples.

layer as clean air is entrained. The uniform ratios obtained for C_2H_2 and C_2H_6 support the validity of this framework.

Table 1 summarizes observations of trace gas concentrations in haze layers encountered in the Bethel region (Flights 14, 20, and 21) and over the Bering Sea (Flight 23). Linear correlations between trace gases and CO were derived from the slope of the regression of Δi against ΔCO, where Δ denotes the excess of i over a background obtained by linear interpolation between altitude lim-

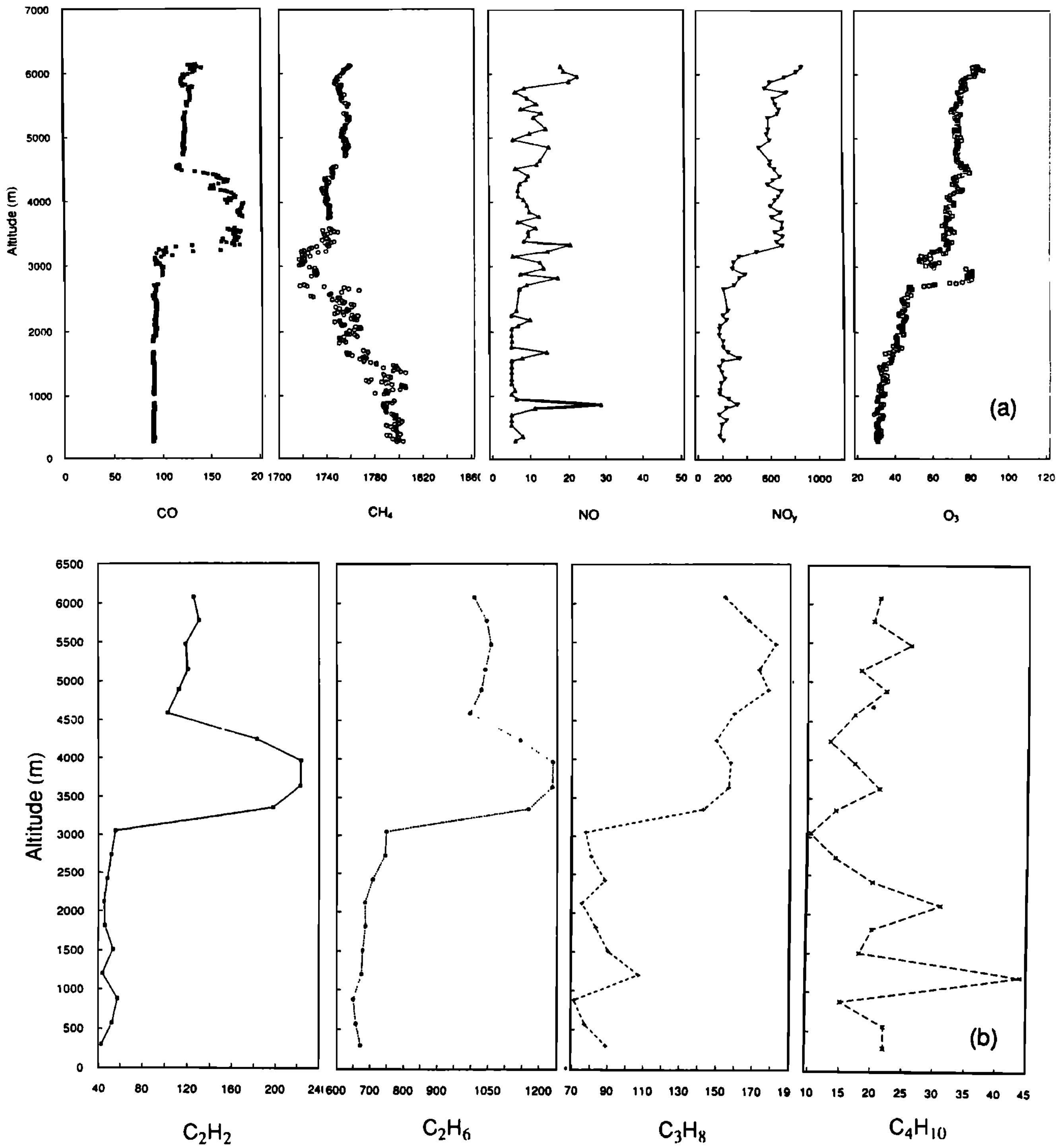


Fig. 3. (*a* and *b*) Vertical profiles on Flight 21 at Point 3 (descending) in Plate 1*b*. (*c* and *d*) Profiles on Flight 21 at point 2 (ascending) in Plate 1*b*.

its for the polluted layer defined by the CO enhancement. For each intercepted layer, results for two profiles were averaged (descending and ascending spirals).

Examples of regressions against ΔCO are given in Figure 5 for the vertical profile at Pt. D on Flight 14 (Plate 1a). Values of r^2 for hydrocarbons and NO_y typically exceeded 0.7 and in many cases, were larger than 0.9. Small enhancements of NO were observed for Flights 14 and 23, but none for Flights 20/21. Values of r^2 for O_3 were relatively low, and ratios $\Delta O_3/\Delta CO$ were variable.

Relationships between CO and nonmethane hydrocarbons were remarkably consistent with laboratory data for smoldering combustion of biomass material [*Crutzen and Andreae*, 1990; *Cofer et al.*, 1989; *Lobert et al.*, 1991]. In fact, observed ratios fell within 10% of laboratory means for C_2H_2/CO and C_2H_6/CO. Laboratory data for flaming combustion show more than 3 times

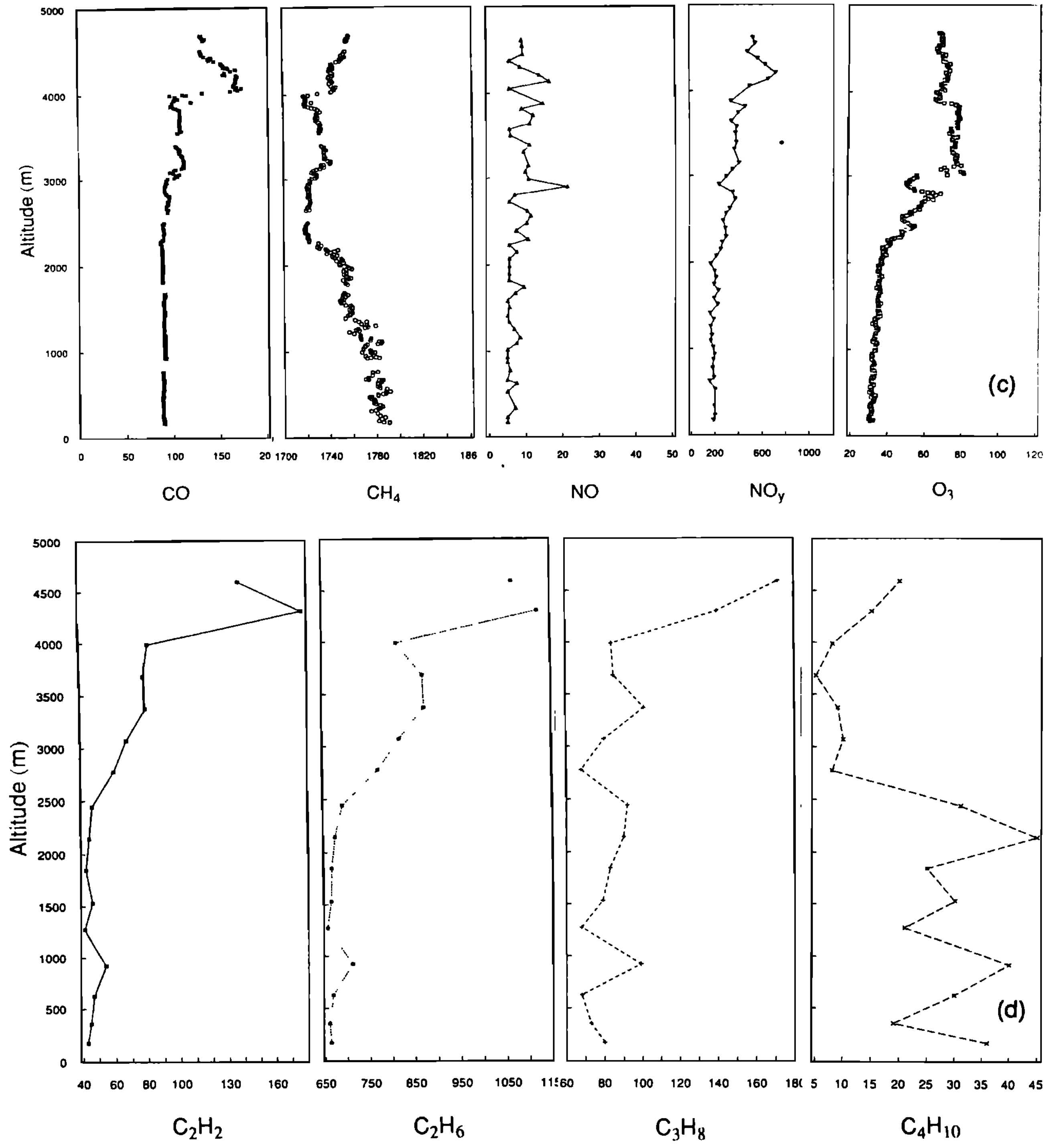


Fig. 3. (continued)

higher emissions of C_2H_2, and 3 times lower of C_2H_6, relative to CO [*Lobert et al.*, 1991].

Arctic haze layers contained less NO_y than observed in association with fires in the Amazon or at mid-latitudes (see Table 1*a*), consistent with a dominant role for smoldering combustion. Most NO_y from biomass fires evolves during flaming combustion, by oxidation of fuel nitrogen [*Lobert et al.*, 1991]. Arctic vegetation is notably low in nitrogen [*Chapin and Shaver*, 1985]. The variance of NO_y ratios to CO suggests variable contributions from small areas of flaming combustion. Background levels of NO_y are very low in the Arctic, and the small yields of NO*y* from tundra fires can nevertheless represent a significant source.

Enhancements of ozone are small in the haze layers, even negative in some, reflecting the low NO_x emissions typical of smoldering fires [*Jacob et al.*, this issue]. Significant positive correlation between O_3 and CO was observed only in a layer with detectable enhancement of NO_x and relatively high $\Delta NO_y/\Delta CO$ (Flight 14). The small values for $\Delta O_3/\Delta CO$ in Arctic haze layers, about 0.1 (Table 1*a*), may be contrasted with values averaging 0.4 in urban/industrial pollution (Table 2 and Figure 7).

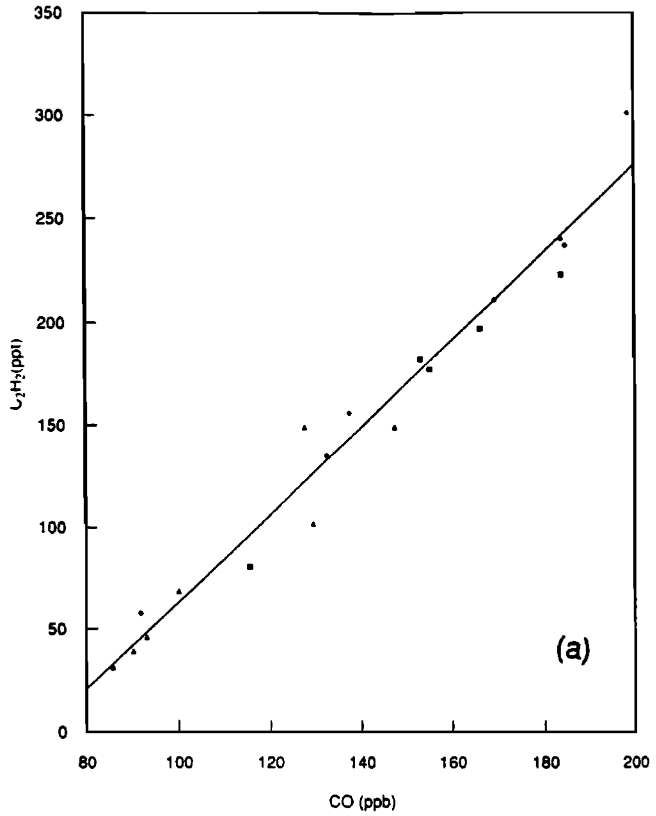


Fig. 4*a*. (*a*) Relationship between CO (ppb) and C_2H_2 (ppt) obtained from composited data for haze layers from Flights 14 (triangle), 20 (diamond) and 21 (square). The regression line shown, with slope 0.0021 (± 0.03) mole C_2H_2 per mole CO, gives r^2=0.97.

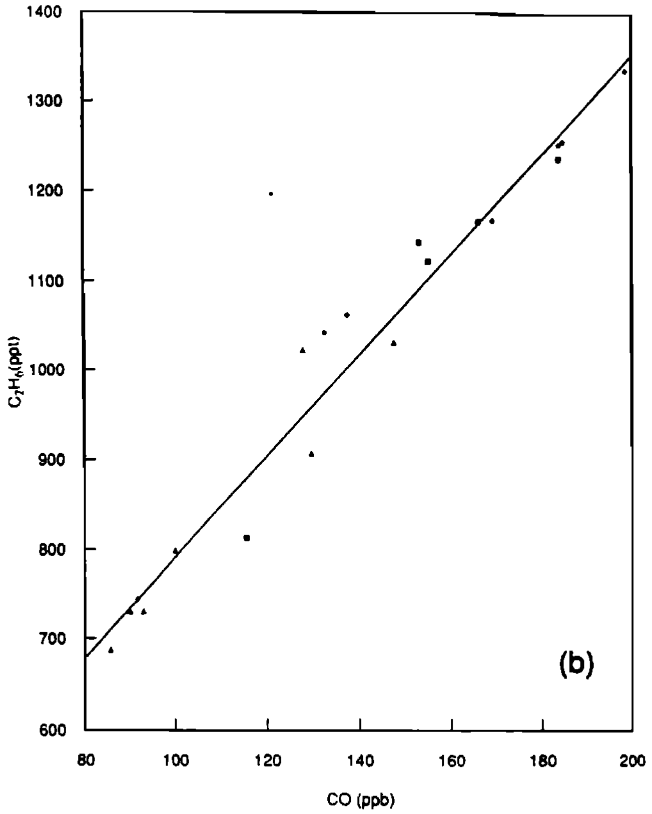


Fig. 4*b*. Same as for Figure 4*a*, for C_2H_6. Regression has slope 0.0055 (± 0.002) mole/mole, r^2 = 0.96.

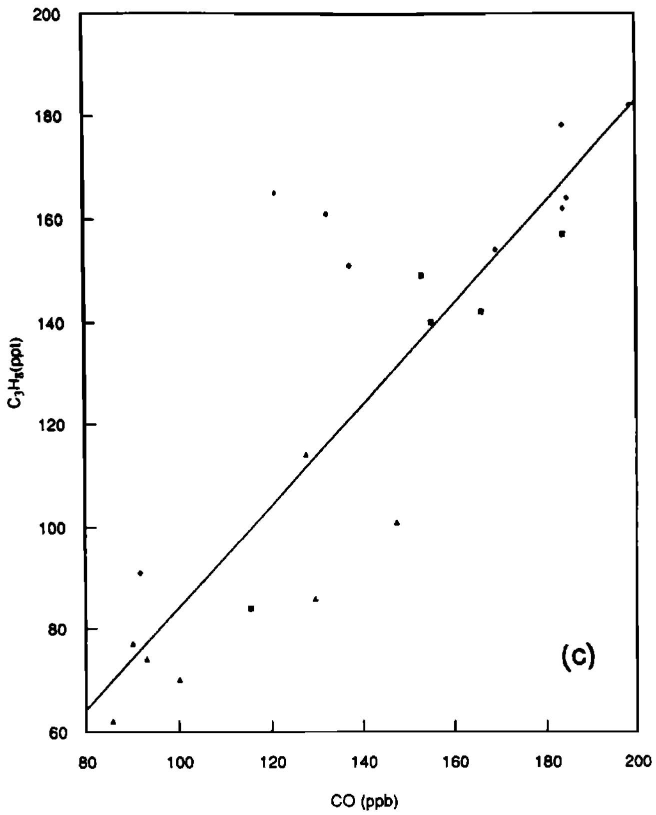


Fig. 4*c*. Same as for Figure 4*a*, for C_3H_8. Regression has slope 0.0010 (± 0.002) mole/mole, r^2 = 0.82.

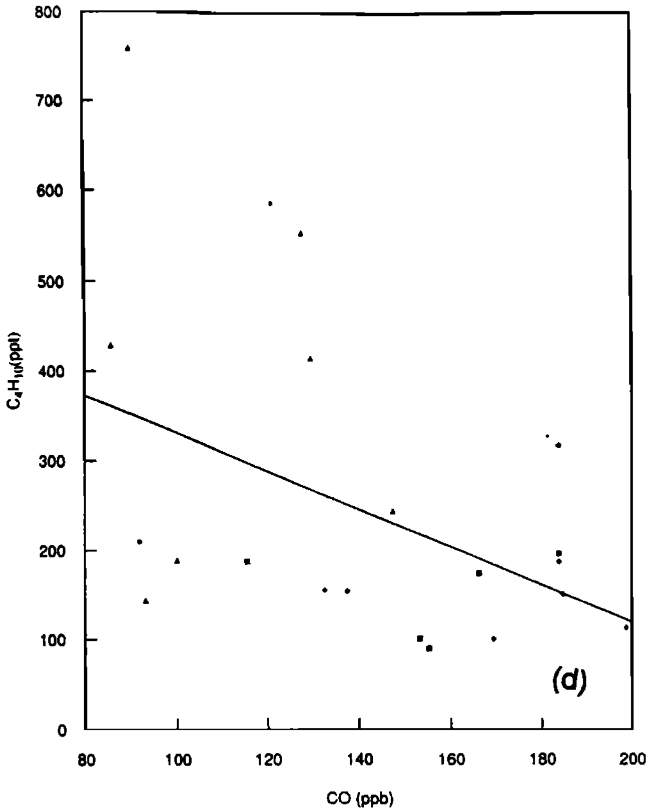


Fig. 4*d*. Same as for Figure 4*a*, for C_4H_{10}. Regression is not statistically valid.

TABLE 1*a*. Enhancement Ratios in Biomass Burning and Pollution Plumes

Flight	NO_y	NO	C_2H_2	C_2H_6	C_3H_8	C_4H_{10}	CH_4	O_3	PAN
14(Bethel)	0.0084	0.0003	0.0020	0.0057	0.0006	0.00011	0.23	0.175	0.31
20(Bethel)	0.0036	<0.00002	0.0019	0.0054	0.0008	0.00010	0.17	(0.076)	0.23
21(Bethel)	0.0032	<0.0001	0.0019	0.0055	(0.0009)	0.00015	0.19	(0.040)	0.38
Mean	0.0056	<0.0001	0.0019	0.0055	0.0008	0.00012	0.18	0.095	0.30
Bethel	±0.0003		±0.0001	±0.0002	±.0001	±.00002	±.04	±0.06	±0.05
23(Bering)	0.023	0.0002	0.0020	0.0096	0.0043	0.0046	0.41	0.137	NA
29(80°N)	-	-	-	-	-	-	0.44	-0.9	-
Amazon*	0.016	0.014	0.03†	0.007	0.0014	NA	0.08	0.056(.042‡)	NA
N. America*	0.042	0.042	0.0026	0.00516	0.00264	0.0011	0.032	0.037	

All ratios are given relative to CO (mole/mole) except PAN, which is ratioed to NO_y. Flights 14, 20, 21 were near Bethel, Alaska, Flight 23 over the Bering Sea, Flight 29 over polar sea ice north of Greenland. Proportionality coefficients were computed by averaging results for two plume encounters on each flight. "Mean Bethel" is the average of the coefficients from individual flights. Marginally significant correlations are given in parentheses. C_2H_2:C_2H_6=0.3 (in Anchorage, C_2H_2:C_2H_6=1.15).

*Previous data for forest and savanna fires. Mean values for the Amazon from *Andreae et al.* [1988] for NO and NO_y (computed as 4 ($\Delta NO/\Delta CO$) for fresh plumes) and from *Greenberg et al.* [1984] for hydrocarbons. Data for forest and brush fires in the United States and Canada from *Hegg et al.* [1990], with NO_x~NO_y assumed in fresh plumes.

†For all alkynes, from *Greenberg et al.* [1984].

‡The $\frac{\Delta O_3}{\Delta CO}$ ratio in heavy pollution over the cerrado was 0.056 [*Greenberg et al.*, 1984], the average value was lower (0.042 ±.030) in aged plumes over the Amazon Basin [*Andreae et al.*, 1988].

TABLE 1*b*. Acid and Aerosol Concentrations (pptv) in Plumes and Background

	Gaseous Acids			Aerosol Components							
Flight	HNO_3	HCOOH	CH_3COOH	NO_3^-	$SO_4^=$	$C_2O_4^=$	MSA*	Na^+	K^+	NH_4^+	$[NO_y]$†
14(plume, 2.2 km)	335	350	540	103	169	20	11	33	33	577	1030
14(4-5 km)	110	230	255	27	23	5	<1	7	3	67	600
ΔC	235	120	295	76	146	15	10	26	30	490	430
23(plume, 3-4 km)	375	295	350	17	18	13	<1	<10	3	56	1150
23(3-5 km)	90	180	240	20	66	6	<1	50	10	50	690
ΔC	285	115	110	-3	-48	7	<1	<-40	-7	6	460

*Methane sulfonic acid.

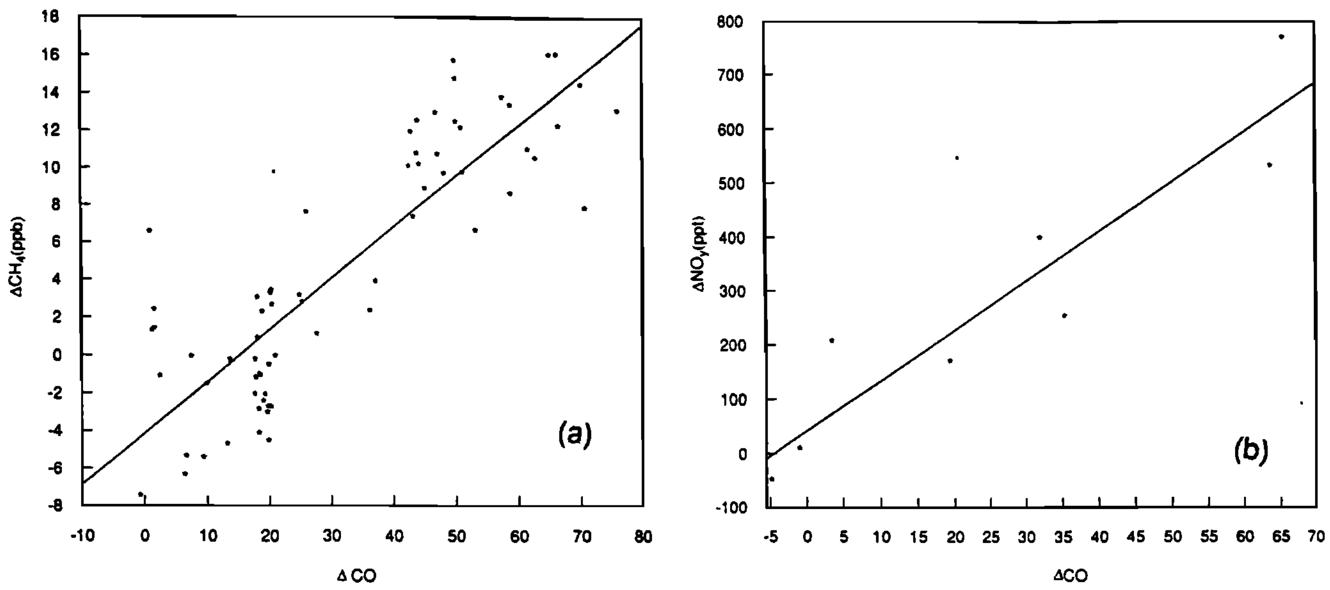
†Total nitrogen oxides (gaseous and aerosol).

Peroxyacetyl nitrate (PAN) is an important reservoir for odd nitrogen, representing up to half the NO_y above 4 km [*Singh et al.*, this issue]. Much of the NO_x emitted by fires appears to be converted to PAN, which accounted for 30(±5)% of the NO_y enhancement in haze layers (Table 1*a*). This efficient conversion to PAN can be explained by the low NO_x/hydrocarbon emission ratios in the fires and the low atmospheric temperatures [*Jacob et al.*, this issue]. Decomposition of this PAN provided a small but potent source of NO_x, mainly in warmer layers of the atmosphere at low altitude [*Singh et al.*, this issue; *Jacob et al.*, this issue].

Samples integrated over 30-60 min were obtained for gaseous acids and aerosols [*Talbot et al.*, this issue] on Flights 14 and 23, in haze layers and in unperturbed air. Concentrations and enhancements are summarized in Table 1*b*. Concentrations of HNO_3 were elevated by factors of 2-3 in the haze layers, accounting for 55 and 65% of the enhancement of NO_y. The sum of PAN and HNO_3 accounted for ~85% of NO_y on Flight 14, with the balance due to particulate NO_3^-. Conversion of NO_x to reservoir species is evidently very rapid: recent results obtained near Hudson's Bay [*Singh*, 1991; *Bradshaw et al.*, 1991] found NO_x in a smoke plume converted to nonradicals within minutes, apparently due to the overwhelming quantities of reactive hydrocarbons emitted by smoldering fires.

The aerosol data in Table 1*b* show that the the haze layer in Flight 14 is rich in NH_4^+, K^+, and Na^+. Ammonium more than offsets the acidity associated with HNO_3, HCOOH, and CH_3COOH, as observed also in haze layers attributed to Amazonian fires [*Andreae et al.*, 1988] and in laboratory studies of smoldering fires [Lobert et al., 1991]. These observations support the view that large biomass fires may be recorded as spikes of ammonium and acetate in Greenland ice cores [*Legrand et al.*, 1992].

Enhancements observed for CH_4, 0.17-0.23 mole CH_4/mole CO, were significantly higher than emission ratios observed in the laboratory from either flaming or smoldering combustion ([0.03 or 0.08 mole/mole, respectively [*Lobert et al.* 1991), in Amazon fires (0.08, [*Greenberg et al.*, 1984]) or in boreal forest fires (0.097 [*Cofer et al.*, 1989]). The data suggest that methane associated with tundra fires could represent in part biogenic methane



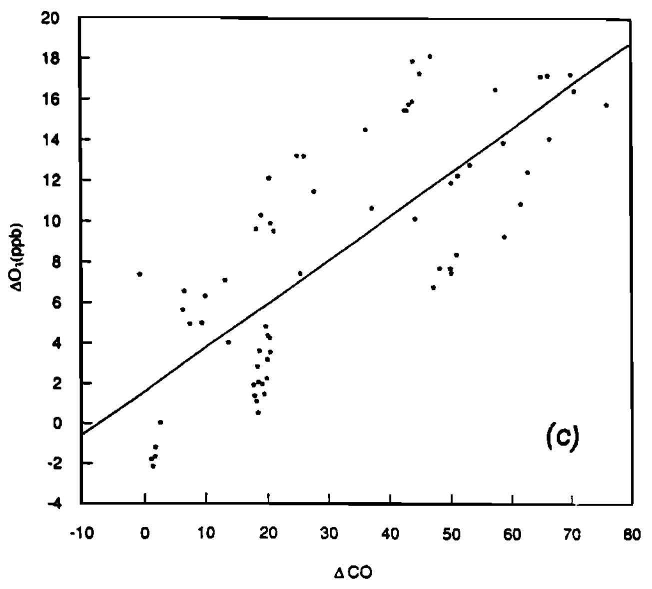


Fig. 5. Relationships between ΔCO and (*a*) ΔCH_4, (*b*), ΔNOy, and (*c*) ΔO_3 for the haze layer encountered at point 1 on Flight 14 (Plate 1*a*).

released from the ground, e.g., in response to heating. (Note that this CH_4 would be depleted in ^{13}C relative to combustion-derived methane.)

The Electra encountered several layers with anomalous trace gas concentrations that did not appear to be from biomass fires, for example, on Flight 23 between 3 and 4 km (Table 1). Trajectory calculations suggest a distant source, in central Siberia, and pollution aerosols were absent (see Table 1*b*). However, NO levels were enhanced, consistent with recent emissions, and ozone was elevated as in Flight 14. The origin of the pollution observed in this area remains unclear.

Figure 6 shows anomalous data obtained during another flight, over the polar ice cap at 80°N. Concentrations of CH_4 and CO were markedly enhanced, and O_3 apparently depressed. There were no data for NO_y or hydrocarbons for this segment. It is apparent from Flight 33 (Table 2) that industrial pollution contains about twice as much methane, relative to CO, as haze layers attributed to biomass burning. *Conway and Steele* [1989] and *Hansen et al.* [1989] previously reported a strong association of CH_4 with combustion products over the high Arctic, and relatively fresh industrial pollutants were observed to be advected off the northeast coast of Canada during ABLE 3B [*Blake et al.*, this issue]. The high $\Delta CH_4/\Delta CO$ ratio in Figure 6, 0.5, suggests episodic transport of industrial pollution to this remote area.

3. NO_x, NO_y, AND HYDROCARBONS OVER THE EASTERN UNITED STATES

Strong pollution influence was observed in the middle troposphere between Portland, Maine. and Wallops Island, Virginia., on Flight 33 (see Plate 1c), as summarized in Figure 7 and Table 2. Trajectories indicated probable origin from industrial midwestern regions [*Shipham et al.*, this issue]. Polluted layers were rich in CH_4 and O_3 (both enhanced by 40–60 ppb) and in CO (elevated by 60–80 ppb), except in the boundary layer where ozone was apparently depleted by surface deposition. The average molar ratio $\Delta O_3/\Delta CO$ was 0.4 (excluding the boundary layer), similar to values observed elsewhere over the continental United States, [*Pickering et al.*, 1989] and in marine areas influenced by pollution inputs [*Fishman and Seiler*, 1983; *Chameides et al.*, 1987]. The average molar ratio $\Delta CH_4/\Delta CO$ was about 0.5, twice as large as in Alaskan haze layers but similar to observations over the ice cap (Figure 6) and over the Bering Sea (Table 1).

Enhancements of NO_y on Flight 33 were small, about 0.8 ppb, corresponding to 0.007 moles N_y/mole CO (see Figure 7). Concentrations of NO_x were typically less than 100 ppt, and were not correlated with CO. The observed $\Delta NO_y/\Delta CO$ is much smaller than found near urban complexes [*Parrish et al.*, 1991]. For example, at Niwot Ridge [*Fahey et al.*, 1986], NO_y concentrations exceeded 5 ppb when O_3 exceeded 70 ppb, nearly an order of magnitude more NO_y than observed in Flight 33. In rural central Massachusetts, ΔNOy/ΔCO is typically 0.03-0.05 when pollution is advected from New York City (J. W. Munger, P. S. Bakwin, B. C. Daube, S.-M. Fan, and S. C. Wofsy, unpublished data, 1992). Most of the nitrogen oxide radicals (NO_x) and (~75%) of the NO_y were apparently removed in transit from industrial sources to the aircraft, demonstrating the potential for rapid oxidation followed by deposition.

TABLE 2. Convariance Ratios (Relative to CO) Over the Northeastern United States (Flight 33)

Flight Segment	NO_y	C_2H_2	C_2H_6	C_3H_8	CH_4	O_3
A 3-4 km	-	-	-	-	0.48	0.32
A 2.8-4.2 km	-	-	-	-	0.48	0.47
A <1.5 km	-	-	-	-	0.55	-0.16
B >4.5km	0.0081	0.0017	0.	0.	0.57;0.27	0.63;0.17
C 1-4.5km	0.0089	0.0017	0.037	0.015	0.76	0.43

A, spiral departing from Portland; covariance of CO with O_3 differed in the mixed layer from altiutdes above;
B, transit, Portland to Wallops Island; Two distinctly different values were noted for the covariance of CH_4 and O_3 with CO, with higher values north of about 40°N; C, descent into Wallops Island.

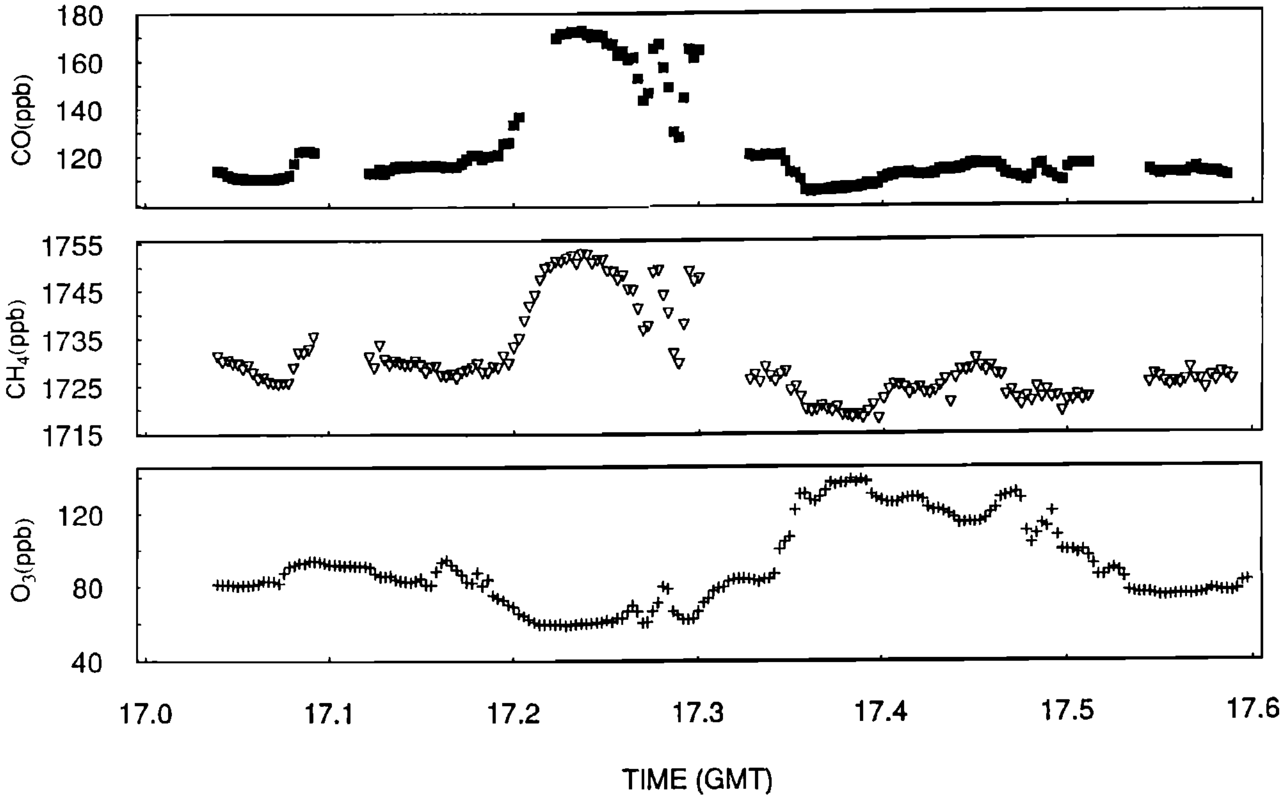


Fig. 6. Enhancements of CH_4 and CO, and reduction of O_3 observed during level flight at 80°N latitude over the polar ice cap on Flight 29. Concentrations of H_2O were high [see also *Gregory et al.*, this issue].

4. DISCUSSION

Figure 8 shows average vertical profiles for the Bethel area, using data only for flights where no distinct haze layers were encountered (11-13, 15-17, and 25) to define the background atmospheric composition over sub-Arctic Alaska. Flights over the Bering Sea were not included, due to the pollution encountered there. Steep gradients, extending over the entire altitude range, were observed for NO_y (Figure 8a) and O_3. Strong evidence indicates that vigorous stratosphere-troposphere exchange [*Gregory et al.*, this issue; *Browell et al.*, this issue; *Danielsen and Hipskind*, 1980] represents the dominant ozone source in this region during summer. Photochemical production of O_3 is small or negative, in the background atmosphere and also in haze layers (see above and *Jacob et al.* [this issue]). We were unable to detect significant correlations between O_3 and CO outside of haze layers (see Figures 8b, 9b, and *Gregory et al.* [this issue]). These data differ markedly from aircraft observations over the North Pacific and the North Atlantic, which indicate positive correlations between O_3 and CO [*Fishman and Seiler*, 1983; *Fishman et al.*, 1987; *Chameides et al.*, 1987, 1989; *Marenco and Said*, 1989].

Mean profiles for CO, C_2H_2, and C_2-C_4 alkanes show signifi-

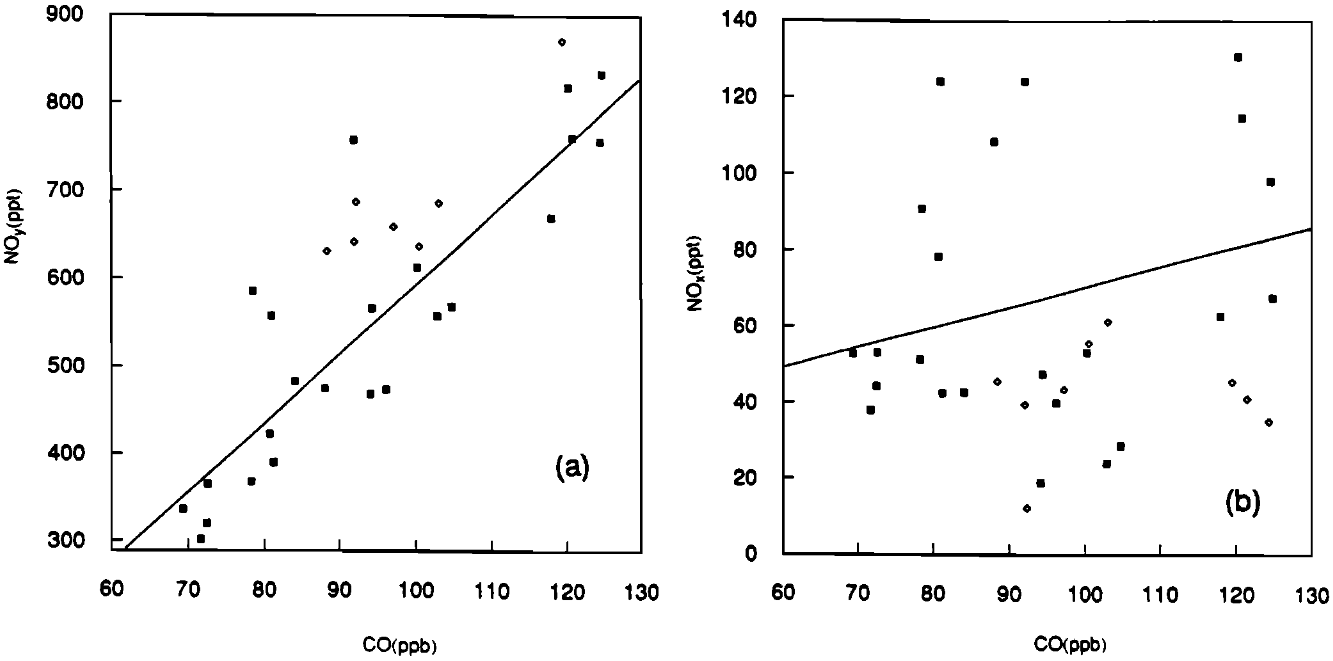


Fig. 7. Measurements of (*a*) NO_y (*b*) and NO_x observed during level flight above 4500-m altitude between Portland, Maine. and Wallops Island, Virginia. (solid squares), and during the descent into Wallops (open diamonds). The least squares line was fit to the data above 4500-m only.

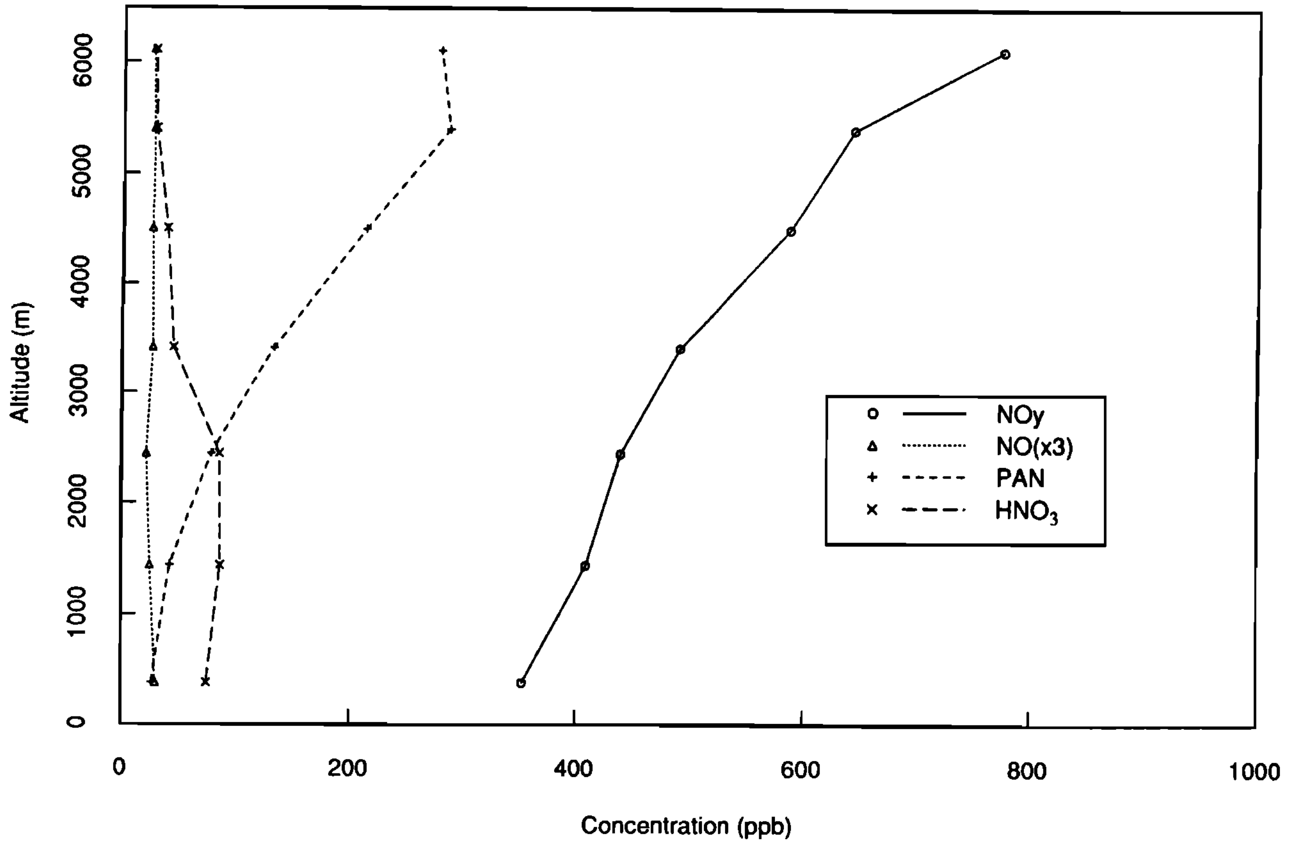


Fig. 8. Average vertical profiles for flights in the Bethel area defining "background" concentrations (11-13, 15-17, 25), excluding those where distinct haze layers were encountered (14, 20, 21): (*a*), nitrogen oxides (note NO scaled by factor 3); (*b* CO (ppb) and hydrocarbons (ppt) (note scaling of C_2H_6).

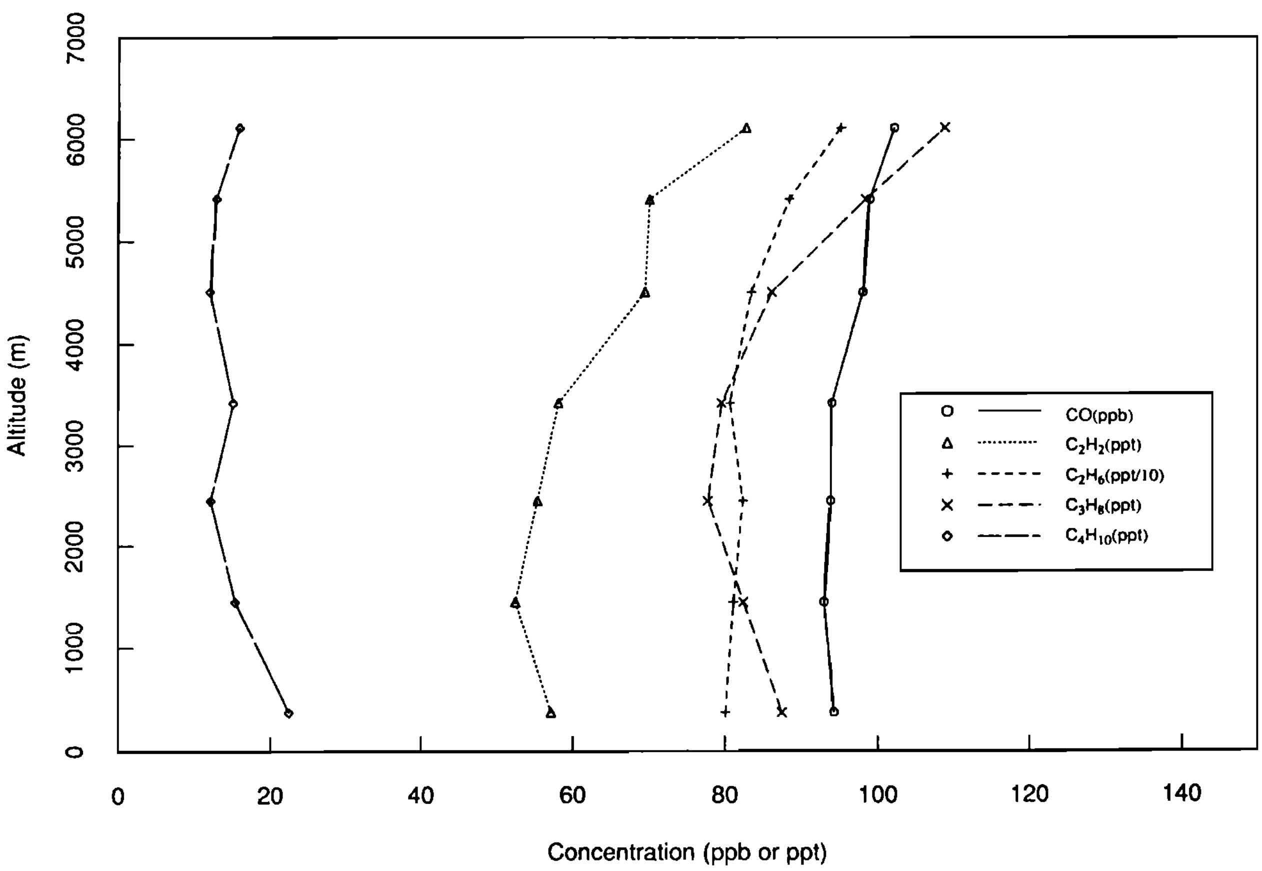


Fig. 8. (continued)

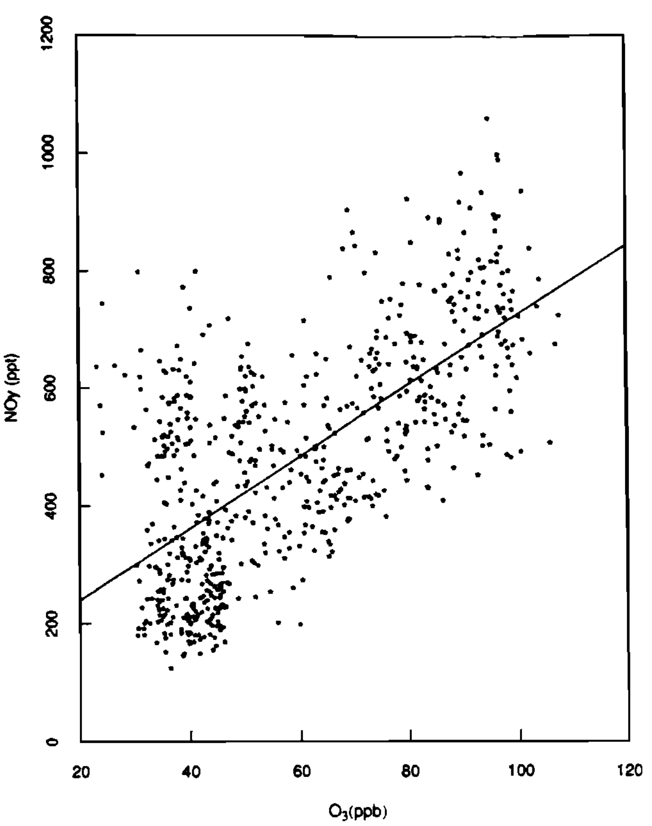


Fig. 9*a*. Scatterplot for NO*y* and O_3 observed for all measurements on "background" Bethel flights (11-13, 15-17, 25). The regression line, NO_y(ppt)=118+6.05(±0.26)O_3 (ppb), accounts for 44% of the variance.

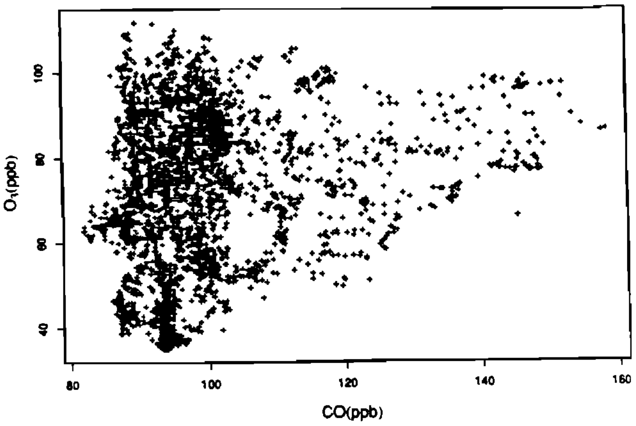


Fig. 9*b*. Scatterplot for CO against O_3, for the flights above and altitudes > 3 km. There is no significant correlation.

cant increase with altitude above 4 km, in addition to suggestion of ground-level inputs. The stratosphere cannot be the source of hydrocarbons at altitude, and these C-shaped profiles indicate the influence of long-range transport of combustion by-products in the middle troposphere. The pattern of correlations between CO, CH_4, and alkanes suggests that boreal fires, arctic gas operations, and mid-latitude pollution could all contribute (see Table 3). Vertical profiles for gases with the longest lifetimes (CO, C_2H_6, C_2H_2) were nearly well-mixed, except when haze layers were present.

Correlations between concentrations of NO_y, NO_x, O_3, and hydrocarbons can help us to evaluate relative contributions to back-

TABLE 3. Relationships Among NO_y, Hydrocarbons, CO, and O_3 (Equation (1))

Grabsample Subset

Species	a_1 (ppt/ppb) x O_3	a_2(ppt/ppb) x CO	r^{2*}	Flights
NO_y	5.2 (±0.4)	3.4 (±0.6)	0.43 {0.38}	11-17,20,21,25 (includes haze layers, no Bering Sea data)
C_2H_6	1.6 (±0.4)	6.0 (±0.14)	0.74 {0.27}	
C_2H_2	0.12 (±0.03)	2.4 (±0.05)	0.89 {0.13}	
C_3H_8	0.05(±0.04)	1.6(±0.09)	0.5{0.10}	
NO_y	5.1 (±0.5)	2.9 (±1.3)	0.34 {0.33}	11-13,15-17,25 (no haze, no Bering)
NO_y	11.2 (±0.8)	4.6 (±1.2)	0.46 {0.43}	19,22,23 (Bering Sea)

Full Data Set

Species	a_1 (ppt/ppb)	a_2(ppt/ppb)	r^{2*}	Flights
NO_y	5.7 (±0.27)	4.0 (±0.7)	0.47	11-13,15-17,25 (no haze, no Bering)
NO_y	6.05 (±0.26)	--	{0.44}	
CH_4	--	0.4	0.02	
CH_4	-0.5	0.4	0.02	
NO_y	5.5 (±1.3)	-5.4 (±2.9)	0.47	11-13,15-17,25 (5-6 km only)
NO_y	5.0 (±0.9)	--	{0.38}	
CH_4	--	1.1	0.58	
NO_y	7.2 (±1.0)	--	{0.91}	mean vertical gradient

*Value for r^2, fraction of the variance removed by the two parameter fit. If in braces, r^2 for O_3 the only independent variable.

ground levels that may be attributed to biomass fires, industrial emissions, and inputs from the stratosphere. If travel times are short compared to loss rates, ratios to CO should reflect the emission ratios for principal combustion sources. Correlation analysis cannot uniquely identify a source, since sinks can be quite different, as in the case of wet deposition which removes NO_y but leaves CO unchanged. Nevertheless, near sources CO and NO_y are correlated (see Figures 2,3, 5b and 7a) and analysis of NO_y/CO correlations provides useful constraints on possible sources of NO_y.

We examine correlations among various species measured over southern Alaska using the linear form

$$Y = a_0 + a_1[O_3] + a_2[CO]. \qquad (1)$$

Here Y is the concentration of the species, and the coefficients a_i are determined by linear regression. The indicator species CO and O_3 are uncorrelated (Figure 9*b*). If concentrations correlate strongly with O_3, we suspect a contribution from the stratosphere, or perhaps from high-flying aircraft, while correlations with CO suggest a combustion component.

Table 3 shows best fit coefficients in Eq. (1) obtained using data for the Bethel area. The top panel of the table uses data corresponding to available hydrocarbon measurements (grab sample set, 130 data points), and the lower panel employs the larger subset (700 data points) with data available for O_3, CO, and NO_y. Results are shown for "background" air (no identifiable haze layers on the flight: Flights 11-13, 15-17, 25), for "background" air plus flights with haze layers (14 and 20/21), but with data excluded from the haze layers themselves, and for all these flights including haze layer data. Flights over the Bering Sea are considered separately. Results in braces denote fits using only ozone as an independent variable, indicating how much of the variance (r^2) is associated with O_3.

Figure 9*a* shows the correlation between NO_y and O_3 for all "background" observations. As much as 30-45% of the variance of NO_y is linearly related to O_3 in the Bethel area, but there is no significant correlation with CO. Particularly striking is the result for level flight legs at high altitude, where nearly half the variance can be explained by correlation with O_3 alone (see rows labeled "5-6 km only" in the lower panel of Table 3). The average molar ratio, $\Delta NOy/\Delta O_3$, lies between 0.005 and 0.007, strikingly close to the ratio in the lower stratosphere [*Hubler et al.*, 1990; *Kawa et al.*, 1990].

Input of NO_y from biomass fires could be detected on days when distinct haze layers were encountered (Table 1), but on other days, only a small part of the NO_y variance was correlated with CO. The behavior of NO_y over southern Alaska contrasts with the hydrocarbons, all of which correlated strongly with CO but weakly, or not at all, with O_3.

These results point to the stratosphere as an important source for NO_y in this region, just as it is the main source of ozone [*Danielsen and Hipskind*, 1980; *Gregory et al.*, this issue; *Browell et al.*, this issue]. *Levy et al.* [1980] and *Liu et al.* [1980] proposed that the stratosphere should provide a major fraction of tropospheric NO_y, while *Logan* [1983] and *Kasibhatla et al.* [1991] concluded that stratospheric input could account for only a small fraction of the NO_y deposition flux at the surface. In ABLE 3A, the measured NO_y deposition flux was 2-5 $\times 10^9$ $cm^{-2}s^{-1}$ [*Jacob et al.*, this issue; *Bakwin et al.*, this issue], about 10x larger than the global mean flux of NO_y from the stratosphere. Dry deposition, a major fraction of the total, occurs mostly over land, hence the mean stratospheric input could account readily for 15-20% of the total. Stratosphere-troposphere exchange at high latitudes is more vigorous than the mean [*Browell et al.*, this issue; *Danielsen and Hipskind*, 1980], and it seems reasonable for the stratosphere to supply 40% or more of NO_y. Analysis of fire occurrence during the summer of 1988 indicated that ~30% of the regional deposition flux could be provided by NO_y from biomass fires [*Jacob et al.*, this issue]. We argue therefore that NO_y is provided mainly by stratospheric inputs and by biomass fires. If these inferences are correct the anthropogenic component of NO_y would be smaller than natural influences in this region during summer. We could rationalize this result by citing the rapid removal of industrial NO_y demonstrated by the data from Flight 33 (Figure 7).

Singh et al. [this issue] argue that PAN, a major component of NO_y, is influenced by combustion. This interpretation is not necessarily inconsistent with our analysis; PAN may well derive from hydrocarbons released by pollution or biomass burning, while the inorganic component of NO_y may originate from the stratosphere. Haze layers attributed to tundra fires are certainly very rich in PAN, and they are found at the altitudes where PAN concentrations peak. Nitric acid is also produced efficiently in the haze layers but would have a short lifetime against deposition. Assessment of factors influencing NO_y is inhibited by the fragmentary understanding of NOy chemistry in the troposphere. Concentrations of HNO_3 are low, and major components of NO_y remain unidentified.

Methane concentrations at high altitude were strongly correlated with CO (r^2=0.58), with a molar ratio of 1.1 moles CH_4/mole CO, but were uncorrelated with O_3 (Table 3, lower panel). This ratio was more than 5 times larger than observed from tundra fires, suggesting an input from CH_4-rich industrial sources such as gas fields or mid-latitude pollution. Mean concentrations of propane increased by about 20 ppt where CO rose by only 5-7 ppb, corresponding also to a source rich in alkanes. There was no significant correlation between CH_4 and CO in the boundary layer, where biogenic sources of CH_4 were dominant [e.g., *Bartlett et al.*, this issue].

5. CONCLUSIONS

Haze layers apparently associated with boreal fires were enriched in hydrocarbons and NO_y, with emission factors corresponding closely to laboratory data for smoldering combustion. We argue that atmospheric composition was strongly modified by wild fires during several periods of the ABLE 3A mission. The associated enhancement of NO_y was smaller than observed for most other combustion processes, but was nonetheless significant in the context of very low background concentrations.

Ozone production in fire plumes was negligible because NO_x emissions were low and because NO_x was rapidly oxidized to HNO_3 and PAN. Eventual decomposition of pyrogenic PAN in the regional atmosphere may have a widespread effect on O_3 levels by slowing down the rate of photochemical loss [*Jacob et al.*, this issue]. The low NO_x/CO emission ratio suggests that tundra fires could depress OH concentrations on the regional scale.

Ambient O_3 was supplied by the stratosphere, with little direct input from mid-latitude sources during summer. We argued that NO_y was supplied about equally by the stratosphere and by wildfires. Hydrocarbons and CO appear to derive from biomass fires and from human activities, including gas extraction in the Arctic and long-range transport of mid-latitude pollution. Anthropogenic inputs of hydrocarbons may shift the speciation of NO_y toward PAN, thus facilitating long-range transport of NO_y with resulting perturbation to NO_x in the remote atmosphere [*Crutzen*, 1979; *Kasting and Singh*, 1986].

If areas burned in tundra fires increase, as noted in response to climate warming in northern Ontario between 1960 and 1990 [*Schindler et al.*, 1990], enhancements might be expected in levels of O_3 and NO_y. Should climate warm in response to global increases in greenhouse gases, we can expect increased fires and associated perturbations to oxidant and aerosol chemistry to be among the diverse environmental impacts.

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