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Summertime Measurements of Selected Nonmethane Hydrocarbons in the Arctic and Subarctic during the 1988 Arctic Boundary Layer Expedition (ABLE 3A)

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Approximately 1000 whole air samples were collected and assayed for selected C_2-C_5 hydrocarbons during the 6-week Arctic Boundary Layer Expedition (ABLE 3A). Transit flights enabled latitudinal (40°N to 83°N) and longitudinal (70°W to 155°W) profiles to be obtained for altitudes between 4000 and 6000 m yielding summertime background mixing ratios for ethane, ethyne, propane and n-butane of 1050±200, 100±40, 120±80 and 10±8 pptv, respectively. Drilling associated with oil exploration in the Alaskan North Slope area is suggested to be a probable source of the enhanced levels of alkanes observed in the Arctic region within a radius in excess of 300 km from Prudhoe Bay, Alaska. A significant number of pollution plumes were encountered which could be attributed to wildfires. Factors describing the emissions caused by biomass burning relative to ethane for ethyne (0.40) and propane (0.08) were determined. An increase of hydrocarbon mixing ratios with altitude was observed during all but two of the missions. Therefore, the Arctic and sub-Arctic are significantly influenced by the long-range transport of pollutants from nonlocal sources. A single vertical profile made in the vicinity of Wallops Island, Virginia, revealed elevated levels of isoprene, numerous hydrocarbons of the types associated with the leakage of natural gas and fossil fuel combustion, and substantial concentrations of nitrogen oxides and ozone. This implies that long-range transport of various gases from urban areas, combined with local biogenic emissions of isoprene, are significant sources of regional tropospheric ozone.

INTRODUCTION

Nonmethane hydrocarbons (NMHC) are found in the troposphere with low mixing ratios ranging from ppbv (parts in 10^9 by volume) to pptv (parts in 10^{12} by volume). The dominant mechanism for the removal of these hydrocarbons from the atmosphere, and for the removal of many atmospheric components, has, as its first step, reaction with hydroxyl radicals (HO). In regions where NMHC are at the low end of their concentration range, the two relatively unreactive but abundant species carbon monoxide (CO) and methane (CH_4) dominate HO photochemistry [*Levy*, 1971; *Wofsy*, 1976; *Crutzen and Fishman*, 1977; *Singh and Zimmerman*, 1992]. However, in regions with higher NMHC concentrations, such as are encountered routinely in urban locations, the rate of hydroxyl radical attack on the various NMHC is sufficiently fast to allow them to play a critical role in atmospheric photochemical reaction cycles. The interaction of reactive decomposition fragments with nitrogen oxides to form additional ozone is well known. In addition, these fragments can act as carriers of active nitrogen in the troposphere through in situ formation of molecules such as peroxyacetyl nitrate (PAN) [*Singh and Hanst*, 1981; *Aikin et al.*, 1982; *Singh*, 1987; *Singh et al.*, this issue]. Urban sources of hydrocarbons include emissions from incomplete combustion or leakage of fossil fuels. Significant levels of NMHC can also be found in nonurban regional environments such as boreal and coniferous forests, which release many highly reactive unsaturated hydrocarbon species including isoprene and several terpenes [*Rasmussen*, 1970; *Greenberg et al.*, 1985; *Rasmussen and Khalil*, 1988]. The many other qualitatively identified natural sources of NMHC include biological emissions from other types of vegetation, from soil and from seawater. Biomass burning can also provide a significant regional source of numerous NMHC compounds [*Crutzen et al.*, 1979; *Greenberg et al.*, 1984; *Wofsy et al.*, this issue].

The atmospheric lifetimes of nonmethane hydrocarbons range from months to less than 1 hour and vary with season, latitude, and altitude. The less reactive hydrocarbons (e.g., ethane [C_2H_6], ethyne [C_2H_2] and propane [C_3H_8]) can be used as tracers for atmospheric transport over time scales of days to weeks [*Gidel*, 1983; *Ehhalt et al.*, 1985; *Zimmerman et al.*, 1988; *Jacob et al.*, this issue]. By contrast, highly reactive species such as isoprene (C_5H_8) and most terpenes are rarely encountered above the planetary boundary layer. In general, the greater atmospheric reactivity of NMHC compounds induces much larger relative concentration gradients than are found for CO or CH_4. Despite their importance, relatively few data on the spatial or temporal variations of NMHC are available [*Robinson*, 1978; *Singh et al.*, 1979, 1988; *Rudolph and Ehhalt*, 1981; *Rudolph et al.*, 1981, 1984, 1989; *Penkett*, 1982; *Singh and Salas*, 1982; *Rasmussen and Khalil*, 1982, 1988; *Duce et al.*, 1983; *Greenberg and Zimmerman*, 1984; *Ehhalt et al.*, 1985; *Isaksen et al.*, 1985; *Tille et al.*, 1985; *Blake and Rowland*, 1986; *Rudolph*, 1988; *Zimmerman et al.*, 1988; *Greenberg et al.*, 1990; *Lightman et al.*,1990; *Rudolph and Johnen*, 1990].

Polar regions represent more than 10% of the Earth's surface and are projected to be particularly sensitive to the effects of any greenhouse warming [*Ingram et al.*, 1989]. Furthermore, it has been suggested that biotic and biogenic processes may be affected during episodes of winter ozone depletion [*Karentz*, 1988]. Studies [e.g., *Barrie*, 1986] have documented that in wintertime, meteorological conditions favor transport processes bringing to the Arctic pollutants from sources in Europe, Asia, and the continental United States, leading to the phenomenon known as "Arctic haze." However, very little is known about the summertime composition of the Arctic or sub-Arctic troposphere and, in particular, the relative importance of emissions from local sources such as the tundra, boreal and coniferous forests, and from the extensive areas of natural gas and petroleum drilling, versus transport from other latitudes [*Rudolph and Ehhalt*, 1981; *Rasmussen et al.*, 1983; *Hov et al.*, 1984; *Ehhalt et al.*, 1985; *Blake and Rowland*, 1986]. Therefore, it is a matter of great importance that the composition and interactions of the Arctic and sub-Arctic atmosphere receive increased scientific attention.

In this paper, the concentration distributions of several NMHC in the Arctic and sub-Arctic regions of Alaska are discussed. These data were obtained during July and August of 1988 as part of the Arctic Boundary Layer Expedition (ABLE 3A), one of a series of missions comprising the NASA Global Tropospheric Experiment (GTE). Numerous vertical profiles in the altitude range 150 to 6000 m were flown over the polar icecap, selected ocean areas, and various land sites covered by different types of vegetation. Data gathered during the transit flights to and from locations in Alaska are presented also to show the large-scale distribution of NMHC during varying meteorological conditions [Harriss et al., this issue (b)].

EXPERIMENT

Sample Canisters

The collection and analysis within a 6-week period of some 1000 discrete air samples necessitated the fabrication of 350 new 2-L stainless steel sampling canisters, each equipped with a single Nupro SS-4BG-STHT metal bellows valve. These canisters were prepared according to the procedure described in Blake [1984] except that, because of unavoidable delays, they could not be baked in air prior to first use. The usual procedure has yielded canisters which maintain ambient air over periods in excess of 1 month with no detectable change in the mixing ratios of most low molecular weight hydrocarbons and halocarbons. However, during the field portion of the project, 72 air samples, which were collected on three separate flight missions early in the ABLE 3A program, were reassayed 1 week after their initial analysis. These samples revealed that although there was no change in the concentrations of ethane, propane, n-butane, ethyne, and isoprene, the mixing ratios of the simple alkenes, i.e., ethene (C_2H_4) and propene (C_3H_6), had increased in these samples by a factor of 2 or more from 50-300 pptv to 150-600 pptv. Consequently, the original alkene concentrations for these samples cannot be specified with any confidence, although the concentrations found in the first measurement do place upper limits on the olefinic influence in these air samples. The alkene augmentation decreased substantially on missions later in ABLE 3A as the canisters became conditioned by usage, and the later flights were probably not severely impacted. This canister problem was solved subsequent to the mission by baking them in air. However, the uncertainties are sufficient that the only alkene data discussed here are for samples collected on mission 33 along the east coast of the United States at the very end of ABLE 3A.

Throughout the 6-week ABLE 3A project an additional three to five canisters from each mission were set aside and returned to the home laboratory at the University of California, Irvine (UCI). The samples selected for retention, approximately 150 pressurized canisters in all, were representative of both background and augmented air. Reanalysis 1 year after the completion of the field project showed that the mixing ratios of these samples exhibited no statistically significant departure from the original assay for ethane, ethyne, propane, and n-butane concentrations, while those for isoprene were lower by about 20%.

Sample Filling Procedure

On board the NASA Electra aircraft, the stainless steel canisters were handled in fixed sets of 24 arranged in three parallel rows of eight canisters. All were attached in series to a common 1/4-inch stainless steel inlet tube, which was in turn connected to an air intake mounted on top of the fuselage above and forward of the wing section. The gas handling manifold and the two-stage, metal bellows pumps (Metal Bellows Company, MB-602), also connected in series, were configured to allow the system to be operated within the

subambient to 60 psig pressure range. After a 24-canister set was installed, and the aircraft was airborne, the pump system was used to pressurize and depressurize the manifold 10 times in order to expel cabin air from the system. Outside air was pumped through the manifold, flushing the approximately 200-mL volume of the manifold and canister system with more than 100 L of outside air. This adequately expelled the cabin air from the system. Each individual air sample was collected by first closing the venting valve to prevent back-flow and then opening the valve between the canister and the manifold until a pressure of approximately 75 psig had been attained. The time required to achieve this was 30 to 60 s, depending on the ambient pressure. Each canister, therefore, contained an air sample which represented an integration over a horizontal distance of several kilometers, or an altitudinal range of up to 150 m. Limited storage space on the aircraft during these missions restricted the number of samples that could be collected on each flight to a maximum of 48.

Integrity and contamination studies were performed on the pumping system using pressurized ambient air (Irvine, California), humidified zero air, the ABLE 3A secondary standard (dry ambient air collected at Niwot Ridge, Colorado, by Paul Steele of NOAA-CMDL), ultrahigh purity (UHP) helium and UHP nitrogen. Each test gas was analyzed for hydrocarbons and halocarbons, pressurized through the pump, collected, and reanalyzed. No detectable mixing ratio changes were observed for any of the test gases. The pump performance at different altitudes was also tested and found to produce no observable artifacts.

After the conclusion of each sampling flight, the filled canister sets were shipped by air cargo on commercial airlines to our field laboratory which had been assembled at the Chemistry Department of the University of Alaska, Anchorage (UAA). Typically these air samples were initially assayed within 48 hours of collection and always within 96 hours. The canisters to be employed on further sampling missions were then evacuated at the UAA laboratory to a pressure of 10^{-2} torr and shipped back to the aircraft.

Chemical Analysis

Each sample was analyzed for ethane, ethene, ethyne, propane, propene, n-butane, i-butane, n-pentane, i-pentane, and isoprene using a Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector (FID). A 30-m 0.53-mm GSQ megabore column (J & W Scientific) with a helium carrier flow rate of 15-mL/min was used for component separation. Methane and carbon monoxide were not measured in these air samples because such data were taken on board the aircraft with a laser-based analytical system [Harriss et al., this issue (a)].

Approximately 1150 torr of air from each sample canister was transferred to a 2-L stainless steel storage vessel, which was fixed permanently to the vacuum line. The hydrocarbons were trapped using a vacuum pump to pull the air sample through a preconcentration loop (8 inch x 1/4-inch O.D. stainless steel) filled with 1-mL-diameter glass beads and immersed in liquid nitrogen. After 1000 torr of the sample had passed through the glass beads, the trap was isolated and heated with warm water. Then the helium carrier was redirected to flush the previously trapped contents from the loop to the separation column. The temperature of the column then was increased from -80°C to 240°C at a rate of 30°/min and held at the final temperature for 5 min. A chromatogram of a sample collected in the boundary layer of the sub-Arctic is shown in Figure 1. The time required for one complete cycle of the analytical temperature program, including sample preconcentration and subsequent oven cool-down, was about 25 min. Continuous operation of the gas chromatographic
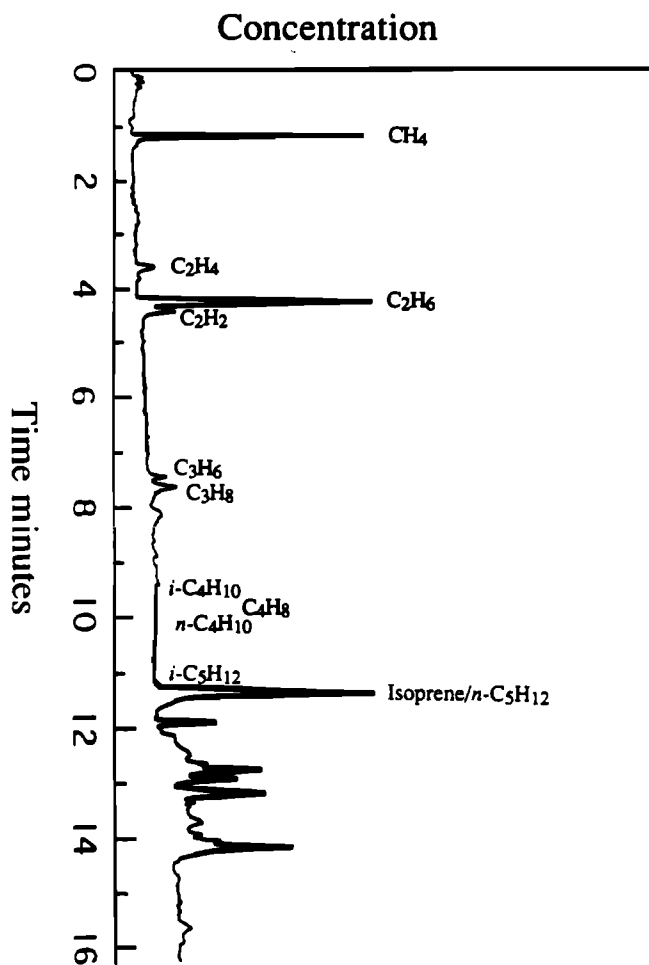
Concentration

Fig. 1. Hydrocarbon chromatogram with the GSQ column for a sample collected in the planetary boundary layer over a boreal forest located in central Alaska.

apparatus allowed approximately 50 air samples to be analyzed per 24-hour period.

The gas chromatograph was interfaced to a Spectra Physics 4270 computing integrator and a PC computer for data storage and reduction. While the computer-controlled data storage was adequate for preliminary data output, the variations in baseline behavior and retention times required subsequent visual examination of each chromatogram.

A clean, partially dried (3 ppmv H_2O), whole air sample contained in an Aculife-treated Luxfer cylinder pressurized to about 2000 psi was used throughout this project as a working standard. It was assayed after every eight air samples in the same manner and procedure used to analyze the samples. Repetitive comparisons with several gas mixtures employed as reference standards demonstrated that the selected gases in this working standard exhibited no statistically significant changes in their mixing ratios over the course of the ABLE 3A project. Reference standards with a stated accuracy of 2% (95% confidence limit) were obtained from Scott Specialty Gases (Plumsteadville, Pennsylvania). The mixing ratio of propane in the Scott standard was in turn confirmed by comparison to a methane-propane mixture provided by the National Bureau of Standards (SRM 1660A) with a stated accuracy of 1% (95% confidence limit). We have assumed the FID response for isoprene (C_5H_8) and n-pentane (C_5H_{12}) to be the same. The accuracy of the calibration procedure is estimated to be 5%.

Although the GSQ column utilized during the Alaskan phase of measurement did not resolve n-pentane and isoprene,

a series of later experiments were carried out on the Alaskan samples at UCI with an Al_2O_3 porous layer open tubular (PLOT) column (Chrompak) which provided a clean separation of these two C_5 molecules, as shown in Figure 2. When very low concentrations were observed for C_3H_8 and n-C_4H_{10} in the atmospheric samples and isoprene concentrations were elevated to the ppbv range, n-pentane was a very small interference (< 5 pptv). While such n-pentane/isoprene reanalyses were carried out on numerous Alaskan air samples, most of them were no longer available for reanalysis. Therefore, in the samples analyzed only in Alaska on the GSQ column, large isoprene/n-pentane peaks were assigned as isoprene when accompanied by n-butane near the detection limits. With slightly higher n-butane mixing ratios, the n-pentane mixing ratios by inference represented only a minor fraction of the combined peak and were assigned from the n-butane/n-pentane ratios in isoprene samples collected well outside the planetary boundary layer.

The precision of the air sample measurements were estimated to be as follows: Ethane, ethene, ethyne, propane and propene (3%); n-butane, i-butane, and i-pentane (8%); and n-pentane/isoprene (10%). The qualitative detection limit for the C_2-C_4 hydrocarbons was estimated to be about 2 pptv, while the detection limit of the C_5 hydrocarbons was estimated to be about 10 pptv.
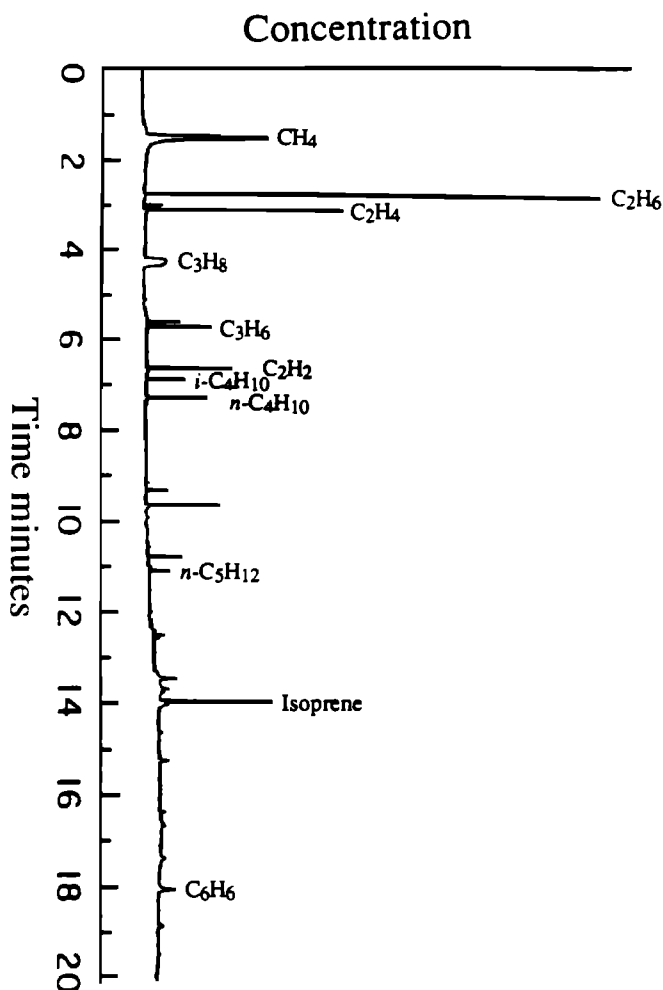
Concentration

Fig. 2. Hydrocarbon chromatogram with the Al_2O_3 PLOT column for a sample collected in the planetary boundary layer over a boreal forest located in central Alaska.
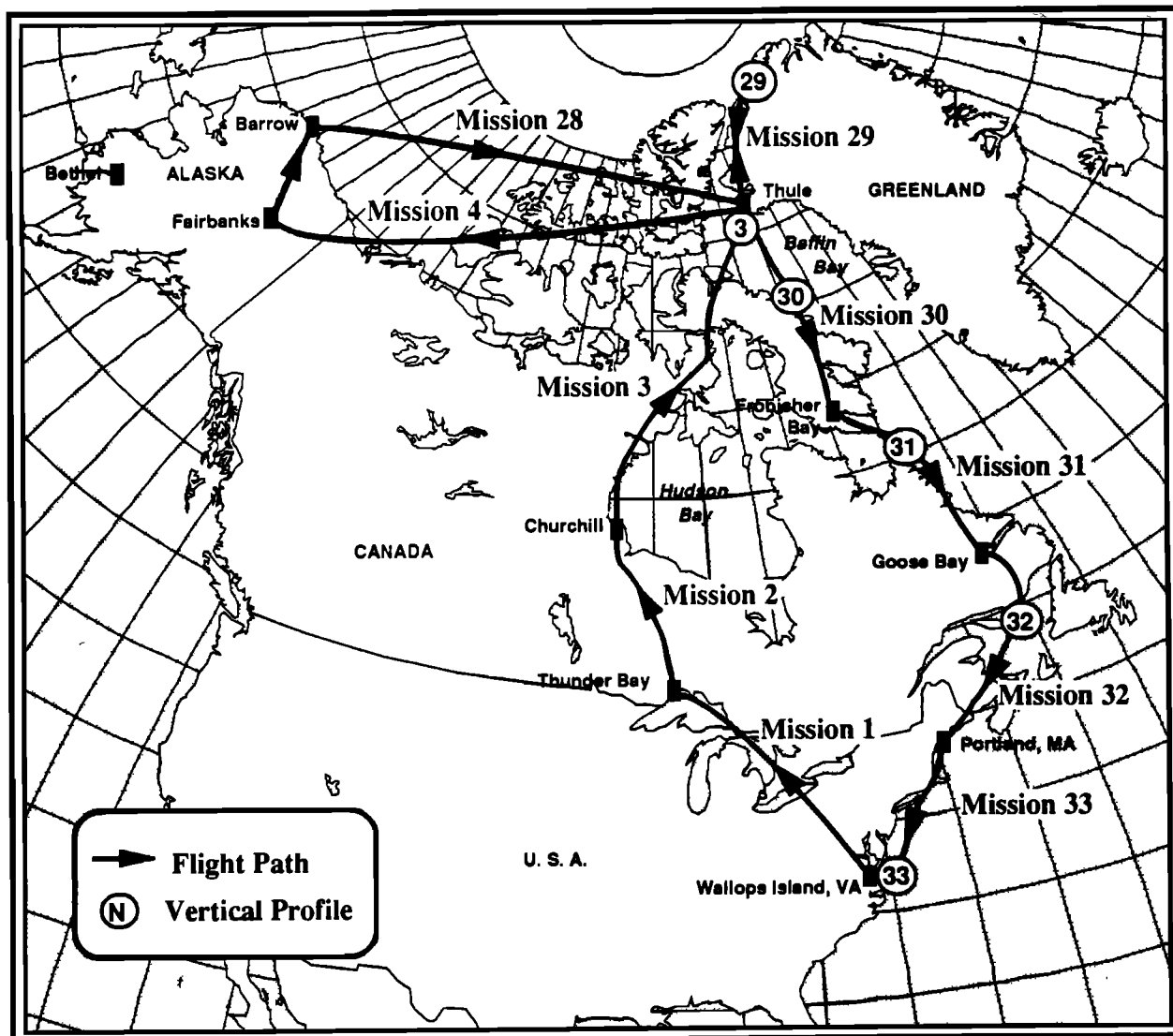
Fig. 3.   Map showing flight paths and vertical profiles for the transit between the aircraft base, Wallops Island, Virginia, and the Alaskan sampling region.

RESULTS: OVERVIEW OF FLIGHTS

More than 1000 air samples were collected during the 33 missions flown during this GTE project. The typical collection patterns produced series of air samples representing flights at various constant altitudes and of vertical profiles from ascending or descending tight spirals over fixed points. Figures 3 and 4 show flight paths and campaign areas and Table 1 summarizes information for each vertical profile made. Commencing in early July, the first four missions constituted the transit from Wallops Island, Virginia (37.9°N, 75.5°W), to northern Alaska via Thule, Greenland (76.6°N, 68.8°W). Samples were collected in the middle free troposphere between 4500 and 6000 m to furnish the latitudinal and longitudinal profiles shown in Figures 5 and 6 and data given in Table 2. In these and all subsequent figures, the mixing ratios for isoprene are only reported if one or more of the samples showed concentrations sufficiently elevated over background to insure that the chromatographic peak was not plausibly attributable to n-pentane. No such samples were encountered prior to flights over the Alaskan boreal forest.

One vertical profile was made near Thule (Figure 7). On arrival in Alaska, missions 5 - 12 were flown over the Arctic Ocean and tundra around Barrow (71.3°N, 156.8°W) and

included 14 vertical profiles in the altitude range 150 - 6200 m. The observed mixing ratios from the profiles considered to have been background conditions for the region (10 profiles from missions 8, 9, 11, and 12) are shown as a composite in Figure 8 (and see Table 3). The remainder of the data are shown individually in Figures 9 to 11.

Next, the focus of the research flights shifted to the sub-Arctic regions around Bethel, Alaska (60.8°N, 161.8°W) where many similar vertical profiles were made over the boreal forest, tundra, and the northern Pacific Ocean. A composite profile representing sub-Arctic background conditions (six profiles of missions 13, 15, 17, and 25) is shown in Figure 12. The remaining profiles made near Bethel are shown in Figures 13 to 19, and Figure 20 shows a composite of all the Arctic and sub-Arctic background vertical profile data (Table 3). The project was concluded with the return transit to Wallops Island made in mid-August (missions 28-33) when further longitudinal, latitudinal, and vertical profile samples were collected, the results of which are shown in Figures 21 to 27. Further details of the individual flights and their categorization can be found in subsequent sections of this paper and in the overview paper of *Harriss et al.* [this issue (b)]. All references to meteorological data and air mass trajectories are derived from *Shipham et al.* [this issue]. All of
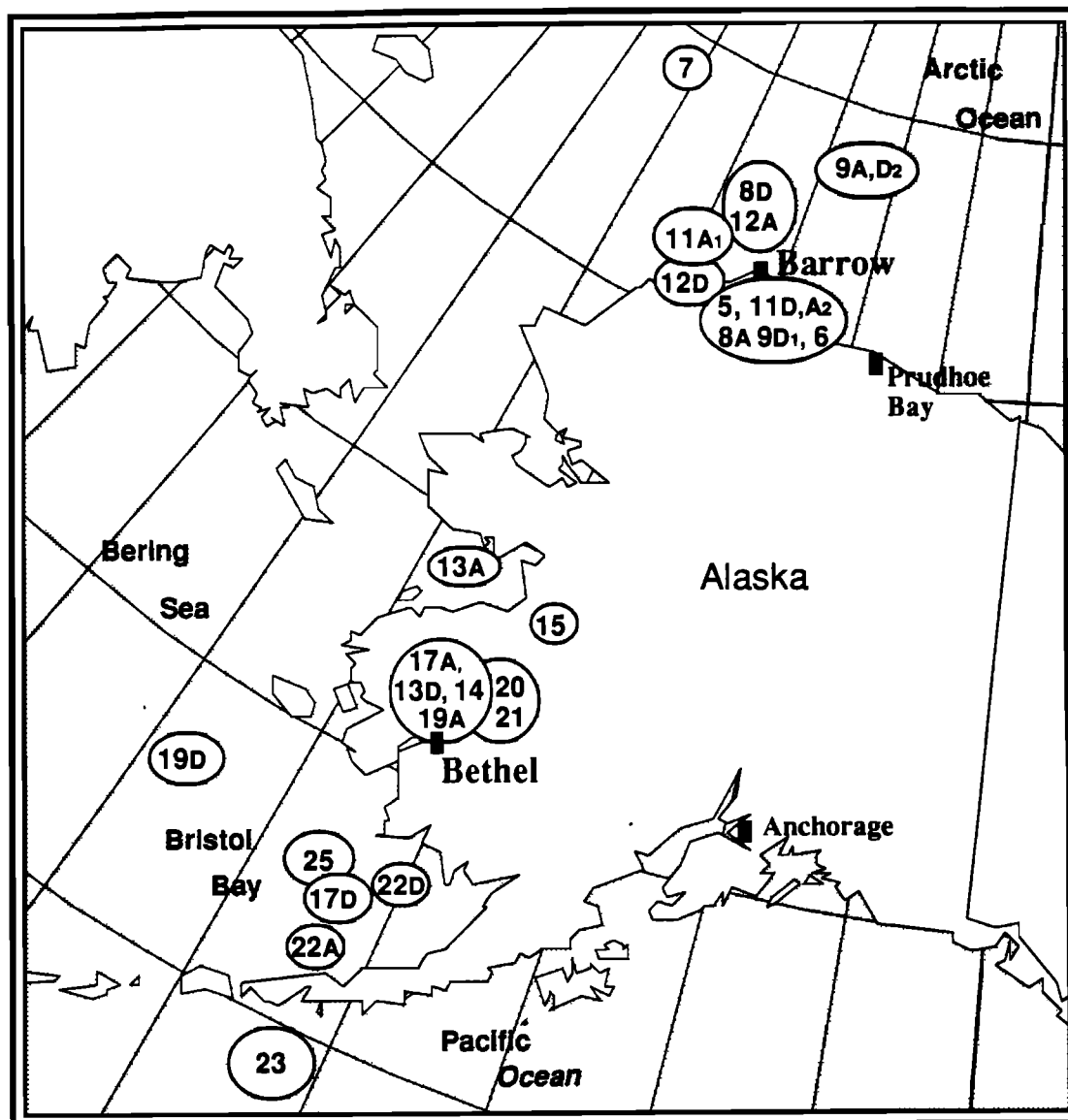
Fig. 4.   Map showing locations of the hydrocarbon vertical profiles made in the Alaskan region during the ABLE 3A field campaign.

the flights were made during daylight hours and, therefore, represent conditions of strong photochemical influence. (Most of these flights were carried out for latitudes and seasons in which sunlight hours represent most or all of the 24-hour intervals.)

The Arctic and sub-Arctic vertical profiles revealed background planetary boundary layer mixing ratios for ethane, ethyne, propane and n-butane of 819±42, 49±13, 49±12, and 8±4 pptv, respectively, while the mixing ratios at altitudes of greater than 4 km were 891±95, 74±23, 66±30, and 9±8 pptv, respectively. An increase of mixing ratio with altitude was observed during all but two missions for C_2H_6, C_2H_2 and C_3H_8. The mixing ratios of n-C_4H_{10} were generally so close to the detection limit that trends with altitude are of marginal statistical significance.

DISCUSSION

Hydrocarbon Source Signatures

More than 90% of the air samples contained mixing ratios of the four hydrocarbons, ethane, ethyne, propane, and n-butane, which fell within a rather well-defined pattern, e.g.,

ethane between 600 and 1200 pptv. Much of the variation within this group can be assigned to temporal and altitudinal variation, i.e., lower mixing ratios at lower altitudes and later in the summer. Within this generalized background, it is difficult to isolate any specific input sources. However, among the remaining 10% of the air samples, some easily noticeable mixing ratio variations are observable which identify specific NMHC sources. The most obvious source is the boreal forest, with isoprene as its unique marker. The atmospheric lifetime of isoprene against HO reaction is only an hour or two, and the marker is therefore not found very far from its local source. The experimental data show that isoprene emission is observed only on flights over or adjacent to the boreal forest, demonstrating by its absence that neither the polar ocean nor the tundra are isoprene sources.

None of the other four measured hydrocarbons are exclusively associated with any specific NMHC source, making it necessary to establish variations in the patterns of multiple hydrocarbon emissions to identify additional sources. n-Butane with its relatively short lifetime can more easily exhibit large percentage variations in mixing ratio, although complicated by the low concentrations and relatively low

TABLE 1. Vertical Profiles During Which Multiple Air Samples Were Collected

Mission No.	Date in 1988	Local Time of Day	Location	North Latitude	West Longitude	No. of Samples	Range m	Vertical Spiral*
3	July 8	1430±13	Baffin Bay/near Thule	75.9°±0.5	69.9°±1.0	7	5200-300	D
5	July 10	1400±10	Tundra/S of Barrow	70.6°±0.2	157.0°±0.2	16	4900-150	D
6	July 12	1503±14	Tundra/SE of Barrow	70.4°±0.2	153.5°±0.2	16	4100-150	A
		1715±23	Tundra/E of Barrow	70.7°±0.2	153.7°±0.3	17	6100-100	D
7	July 13	1304±13	Arctic Ocean	74.0°±0.2	166.0°±0.2	8	4400-150	D
8	July 15	1328±16	Arctic Ocean	72.8°±0.2	157.8°±0.3	16	4200-200	D
		1456±15	Tundra/SE of Barrow	70.7°±0.2	155.0°±0.7	14	6100-2600	A
9	July 17	1028±10	Arctic Ocean	73.8°±0.2	152.0°±0.3	5	6100-4000	A
		1147±08	Tundra/SE of Barrow	71.0°±0.2	155.2°±0.2	6	4500-2300	D_1
		1250±10	Arctic Ocean	73.8°±0.2	152.0°±0.5	7	2400-150	D_2
11	July 19	1231±40	Ocean near Barrow	71.5°±0.2	160.5°±0.3	15	6100-150	A_1
		1416±38	Tundra/S of Barrow	70.4°±0.1	155.8°±0.3	16	5800-150	D
		1547±40	Tundra/S of Barrow	70.7°±0.1	158.0°±0.2	16	6200-200	A_2
12	July 22	1527±39	Ocean/N of Barrow	72.3°±0.2	157.0°±0.3	18	6100-450	A
		1717±39	Tundra/SW of Barrow	70.6°±0.1	159.0°±0.3	20	6000-200	D
13	July 24	1150±42	Norton Sound	64.0°±0.2	163.3°±0.2	19	6100-150	A
		1343±41	Tundra/near Bethel	61.1°±0.1	161.9°±0.2	21	6100-150	D
14	July 26	1235±27	Tundra/plus Lake Able†	61.1°±0.1	162.0°±0.2	16	5200-1100	D
		1347±30	Tundra/near Bethel	60.8°±0.2	162.9°±0.2	21	6000-1400	A
15	July 28	1702±22	Tundra and Forest	63.6°±0.1	158.5°±0.2	10	3500-150	D
17	July 29	1050±16	Tundra/NW of Bethel	61.8°±0.2	163.0°±0.2	18	4900-150	A
		1306±36	Bristol Bay	57.5°±0.2	163.0°±0.2	9	5000-150	D
19	Aug 2	1048±17	Tundra/near Bethel	61.1°±0.1	162.0°±0.1	9	5000-100	A
		1254±21	Bering Sea	58.3°±0.1	168.0°±0.2	14	6100-150	D
20	Aug 3	1042±41	Tundra and Forest	62.2°±0.2	160.3°±0.3	22	6100-200	D
		1217±48	Tundra/N of Bethel	61.3°±0.2	161.3°±0.3	23	6100-150	A
21	Aug 3	1628±43	Tundra and Forest	62.2°±0.2	160.4°±0.2	21	6100-300	D
		1811±41	Tundra/N of Bethel	61.3°±0.2	161.3°±0.3	19	6200-200	A
22	Aug 7	1102±23	Bristol Bay	57.9°±0.2	159.9°±0.3	11	5300-150	D
23	Aug 7	1543±36	Pacific Ocean	54.3°±0.1	160.8°±0.3	13	5600-150	D
		1731±41	Pacific Ocean	53.6°±0.1	162.5°±0.3	17	6100-150	A
25	Aug 9	1932±31	W Bristol Bay	57.4°±0.1	162.9°±0.2	12	5000-150	D
29	Aug 13	1144±33	Ice/Greenland	83.0°±0.2	56.0°±1.0	18	5200-150	D
30	Aug 15	954±32	Baffin Bay	72.0°±0.2	68.7°±0.3	9	5500-500	D
31	Aug 15	1443±35	Labrador Sea	61.1°±0.2	65.9°±0.3	10	5100-150	D
32	Aug 16	1111±33	Gulf of St. Lawrence	49.8°±0.2	61.0°±0.2	10	5200-150	D
33	Aug 17	1111±34	near Wallops Island	37.9°±0.2	75.5°±0.2	8	5300-150	D

* Spiral direction with A, ascending; D, descending.

† "Lake Able" was the colloquial designation for the small body of water which was the site for the ground portion of ABLE 3A [Harriss et al. this issue(b)].

signal/noise ratio usually found in its measurement. However, very few data were previously available on the emission patterns that would enable us to identify individual local hydrocarbon sources. Thus, a number of samples were collected to represent the fingerprint composition of four different potential NMHC emission sources in the Alaskan air shed: urban, leakage from natural gas operations, oil exploration drilling, and biomass burning. The results of these analyses are summarized in Table 4 and are employed throughout the remainder of the paper. Because CO and CH_4 data were not available for some aircraft missions, the excess source composition and air sample enhancements are reported relative to ethane.

First, natural gas samples were collected from the Alaskan North Slope area. The NMHC composition of natural gas is known to be variable, depending on whether it is derived from the biogenic decomposition of organic matter or is associated with crude oil or coal deposits. These Alaskan samples had a particularly low concentration of NMHC compounds (99.5% CH_4 by volume of total hydrocarbons) and contained 0.4% ethane, 0.05% propane, 0.02% n-butane, and no measurable ethyne (<0.001%).

Anchorage, the largest urban area in Alaska, was chosen to represent Arctic and sub-Arctic cities. Four samples collected in July 1989 upwind of Anchorage yielded average background mixing ratios of 1770 ppbv for methane and 750, 50, 50, and 30 pptv of ethane, ethyne, propane, and n-butane, respectively. These values were subtracted from the average

mixing ratios of 12 samples collected at locations throughout the city to yield average excess mixing ratios of approximately 150,000, 750, 2250, 150, and 450 pptv for methane, ethane, ethyne, propane and n-butane, respectively. From these values, the urban NMHC ratios relative to ethane reported in Table 4 were calculated. The several-fold higher excess contribution from ethyne versus ethane is known to be particularly characteristic of fossil fuel combustion.

Furthermore, sets of air samples were collected on two separate occasions upwind and downwind of the oil drilling activities located near Prudhoe Bay, Alaska. The upwind samples yielded average background concentrations of 1780 ppbv for methane, and 802, 60, 71, and 49 pptv for ethane, ethyne, propane, and n-butane, respectively. The downwind samples yielded average mixing ratios of 1785 ppbv for methane and 1408, 181, 492, and 295 pptv for ethane, ethyne, propane, and n-butane, respectively, from which the excess ratios given in Table 4 were calculated. The precision of the CH_4 measurements is estimated as ±4 ppbv, making the downwind concentrations marginally higher than the upwind values. The other gases were clearly augmented on the downwind side. The Prudhoe Bay samples had the lowest ratios relative to ethane for methane and ethyne (8±4 and 0.2) and the highest propane ratio (0.7) of any sampled source.

The fourth possible local source of NMHC was biomass burning. Because of the unusually hot, dry summer experienced in parts of Alaska during 1988, numerous fires occurred south of the Brooks range (approximately 68°N)
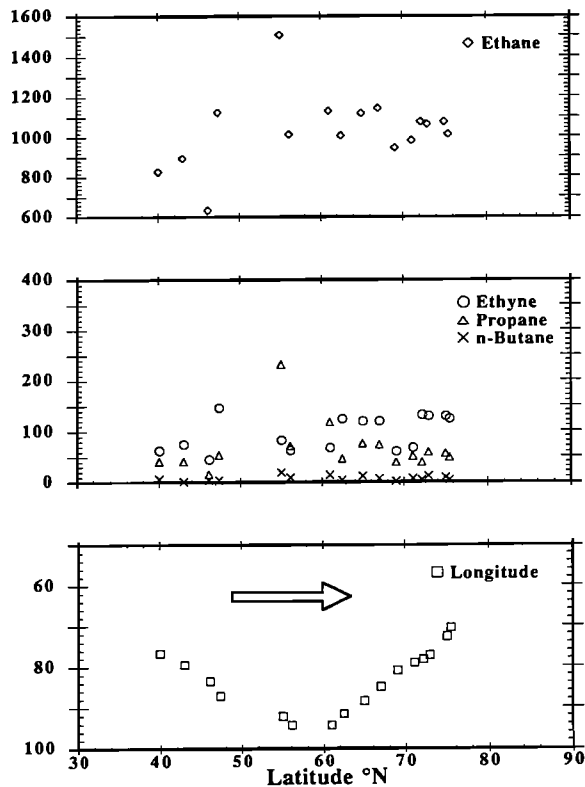
Fig. 5. Latitudinal profile of ethane, ethyne, propane, n-butane (in pptv), and longitude (in degrees west) collected during transit missions 1-3, flown between Wallops Island, Virginia, and Thule, Greenland, on July 7-8, 1988.
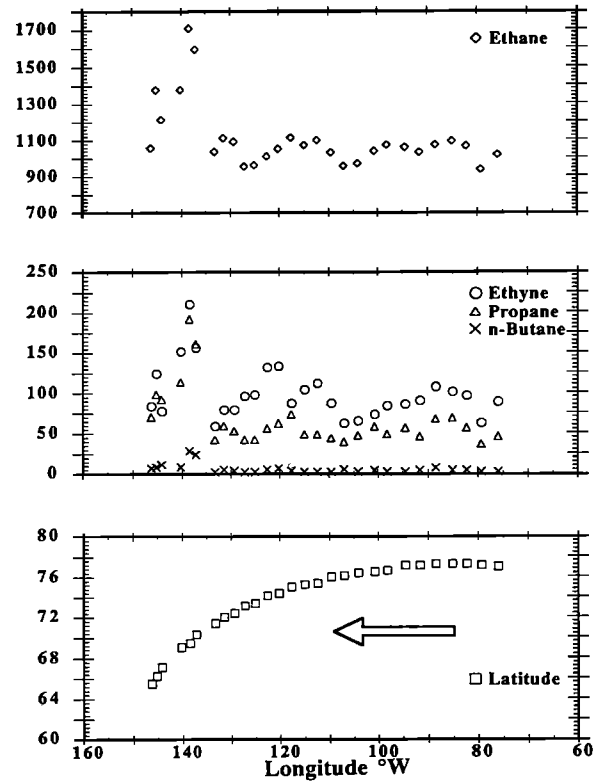
Fig. 6. Longitudinal profile of ethane, ethyne, propane, n-butane (in pptv), and latitude (in degrees north) collected during transit mission 4, flown between Thule, Greenland, and northern Alaska on July 9, 1988.

throughout the period of the project. Thus, a significant number of well-defined layers or "plumes" exhibiting elevated levels of many gases were encountered during about half of the missions of the ABLE 3A project, and can be attributed to biomass burning. Wildfire mapping and back trajectory analysis [Shipham et al., this issue], as well as airborne Lidar images and aerosol data, support this conclusion [Browell et

TABLE 2. Observed Mixing Ratios in pptv for Four Hydrocarbons on ABLE 3A Transit Flights Between Wallops Island, Virginia, Thule, Greenland, and Alaska, with Comparisons to Other Northern Latitude Summertime Studies

	Ethane	Ethyne	Propane	n-Butane
40-56°N (missions 1-2)	1030±185	95±35	95±35	10±5
61-76°N (mission 3)	1053±65	108±29	61±25	9±4
37-83°N (missions 29-33)	980±120	105±30	150±60	6±2
4-6 km				
Blake and Rowland [1986] W. coast, United States (30-75°N) June 1985, ground	930±120			
Rudolph [1988] E. coast, United States (40-70°N) June 1984, 0 - 6 km	1500-2000	50-500	100-500	50-500
Rudolph et al. [1982] Ireland (52°N) early June, 1.2 - 6.6 km	1350±250	75±15	120±50	20±8

al., this issue; Gregory et al., this issue]. Gas and aerosol enhancements in biomass plumes are specifically dealt with in a separate paper [Wofsy et al., this issue].

Several profile samples collected in the sub-Arctic during missions 14, 20, and 21 exhibited enhanced hydrocarbon concentrations which can, as described above, be circumstantially associated with biomass burning. The increased mixing ratios of all four hydrocarbons are readily apparent at 2000 m in both vertical profiles of mission 14 (Figure 13). Similarly, excesses of these hydrocarbons are found at 4000 m in both profiles of mission 20 (Figure 16) and the first profile of mission 21 (Figure 17). The assignment of "background" hydrocarbon concentrations is an important aspect in the evaluation of the "excess" hydrocarbon concentration ratios presented individually in Table 5 and in summary in Table 4. The error estimates shown in Table 5 have been evaluated from the standard deviations of a linear fit to the background air samples. For example, four samples above and four below the fire enhanced layer samples collected during the descending spiral of mission 20 were employed to evaluate the background concentrations and errors.

Of the measured NMHC, ethane and ethyne exhibited the greatest enhancements from biomass burning and were remarkably uniform between different plumes. These two NMHC also have the longest atmospheric lifetimes and would be expected to be the least diminished during the time elapsed between emission from the fire and collection of the samples. The propane and n-butane excesses were relatively small so that n-butane could not provide reliable enhancement ratios, only being reported as less than 0.01. This is consistent with the fact that propane and n-butane are shorter lived (and, by the same reasoning, would be expected to have lost a substantial fraction of their initial concentrations during the transit time between emission and sampling, estimated from trajectory
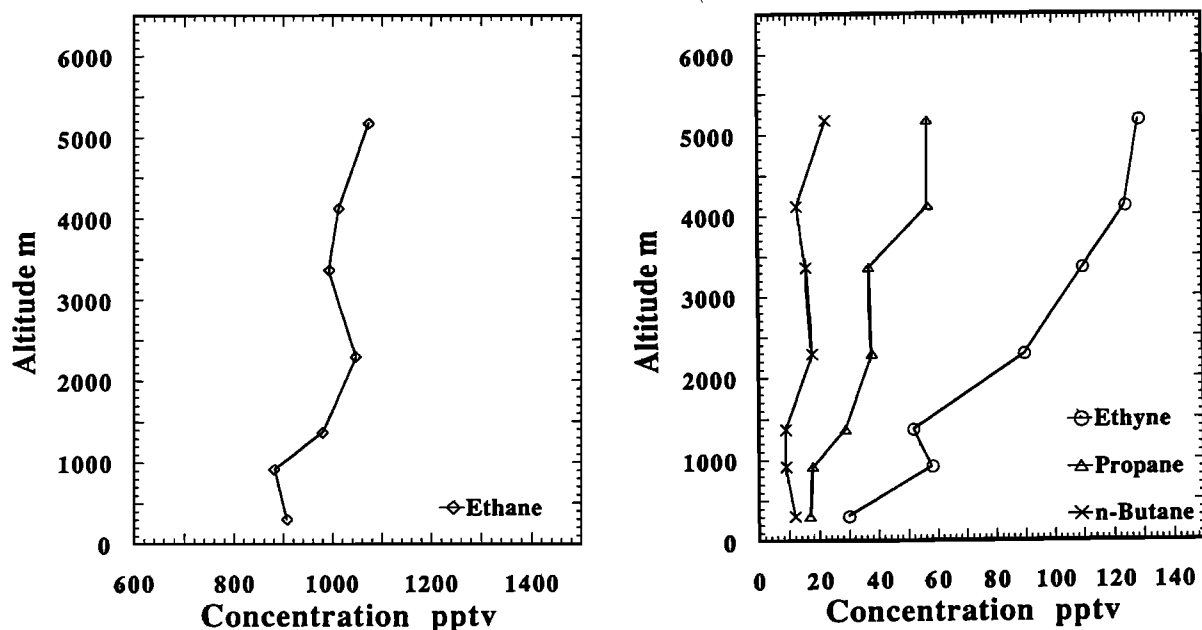
Fig. 7. Vertical profile of ethane, ethyne, propane, and n-butane for samples collected during mission 3, flown on July 8, 1988, at 75.9°N, 69.9°W over Baffin Bay near Thule, Greenland.

analysis to be 25-50 hours). The correspondingly lower mixing ratios of these gases also make it more difficult to assign baseline values. These factors were accordingly taken into account in the error calculation. Thus, it is suggested that the range of values given in Tables 4 and 5 provide emission factors for longer-lived gases which will encompass most scenarios for Alaskan wildfires.

Previous studies of biomass burning events have usually focussed on the tropics [e.g., Greenberg et al., 1984; Andreae et al., 1988], and very few report speciated hydrocarbon measurements. Those that are available indicate that emissions of individual hydrocarbons vary significantly according to the type of vegetation burned. Greenberg et al. [1984] measured relatively high ethyne emissions from Amazonian fires, but the emission of ethyne reported by Hegg et al. [1990] for the burning of forests and brush in the United States and Canada were more consistent with our Alaskan findings (Table 4). Both papers quote somewhat higher propane and lower methane ratios to ethane.

Two other prominent regions of enhanced hydrocarbon concentrations can be identified in the vertical profiles for mission 23 near 4000 m (Figure 19, descending data only) and for mission 29 near 3000 m (Figure 23). The relative excesses of the hydrocarbons from these two profiles are calculated in Table 6. The data from profile 23D were collected from an air mass over Bristol Bay, while the vertical spiral on mission 29 was over the northern edge of Greenland and completely dissociated from possible Alaskan forest fire contributions.

Enhanced NMHC contributions were also noted in level flight for missions 4 and 28, as shown in Figure 6 (C_2H_6 mixing ratio >1500 versus 1100 average) and Figure 22 (C_2H_6 mixing ratio >1200 versus 950 average). The samples with the largest NMHC excesses in each of these missions are also described in Table 6.

Longitudinal Surveys

Between 1.5 and 6.0 hours into mission 4, the Electra followed an isoentropic surface at approximately 6000 m above mean sea level from 80°W over the Arctic ice cap, the barren Queen Elizabeth Islands, and the Arctic Ocean to 133°W

longitude. Trajectory analysis suggests that the air mass sampled during this period passed over central Siberia approximately 72 hours earlier [Shipham et al., this issue]. The mixing ratios of ethane, ethyne, propane, and n-butane were fairly constant during this section of the flight (Figure 6), with average mixing ratios $\pm 1\sigma$ of 1035$\pm$50, 85$\pm$20, 60$\pm$8, and 5$\pm$2 pptv, respectively. All other assayed NMHC were below their detection limit.

The aircraft then flew over the very northernmost corner of Canada (MacKenzie Bay) before entering Alaskan territory. As shown in Figure 6 and Table 6, the C_2 to C_4 hydrocarbons exhibited a sharp increase in their mixing ratios near 138°W longitude and 70°N latitude, suggesting that the air mass encountered during mission 4 had been enhanced by one or more NMHC sources. The ratios of the excess NMHC concentrations to ethane for each of the three augmented air samples collected in this area are given in Table 6. Comparison of these with the hydrocarbon source fingerprints given in Table 4 suggests that neither natural gas nor urban emissions, both of which exhibit characteristically large methane/ethane ratios, are the likely source of these enhancements. The meteorological trajectories indicate that the air mass had passed over the Prudhoe Bay, Alaska, region, during which time the air parcel could have been augmented with alkanes emitted by oil drilling activity located there. Aerosol data and visual observations revealed that there was also some haze in the MacKenzie Bay area at the time the samples were collected [Gregory et al., this issue]. It has been suggested that this haze was the result of the numerous fires known to have been burning in the region north of Fairbanks, Alaska, prior to and during mission 4 [Shipham et al., this issue]. It therefore seems most likely, because neither biomass burning nor oil drilling processes alone can account for the measured excesses, that the sampled air parcel, already enhanced by biomass burning, passed through the Prudhoe Bay region, where it was further augmented by emissions associated with oil drilling processes.

Mission 28, the transit flight from Barrow, Alaska, to Thule, Greenland, made about 5 weeks after the mission 4 flight, again exhibited enhanced concentrations of all four
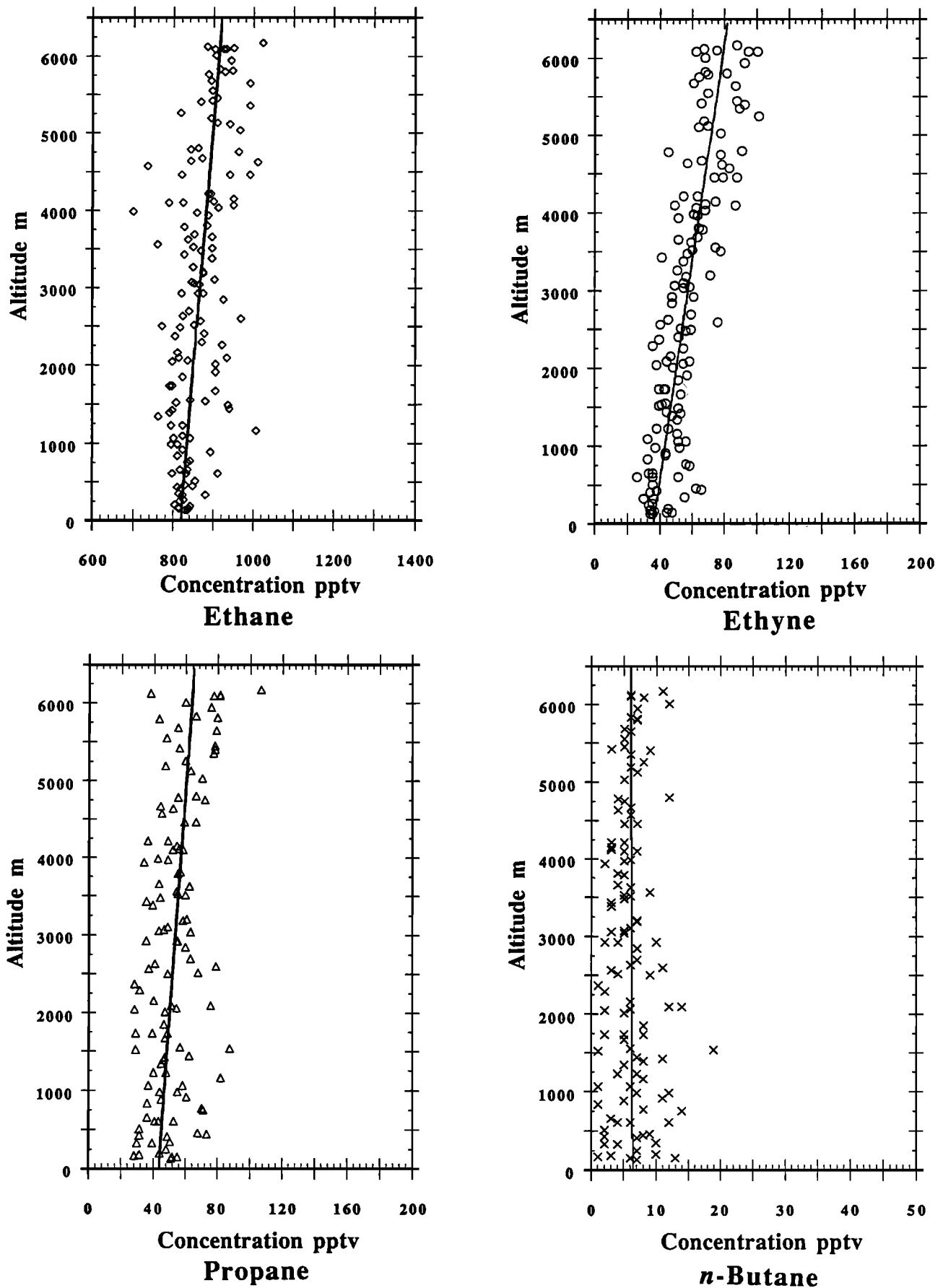
Fig. 8.   Composite vertical profiles of ethane, ethyne, propane, and n-butane for samples collected in background conditions near Barrow during missions 8, 9, 11, and 12, flown on July 15, 17, 19, and 22, 1988, respectively.

TABLE 3. Observed Mixing Ratios in pptv for Four Hydrocarbons During ABLE 3A on Arctic and Sub-Arctic Flights During July/August 1988, With Comparisons to Other Northern Latitude Summertime Studies

	Ethane	Ethyne	Propane	n-Butane
Average Arctic and Sub-Arctic missions 8, 9, 11-13, 15, 17, 25	847±72	59±18	54±21	8±6
Average Arctic (Barrow) missions 8, 9, 11, 12	865±59	57±17	53±15	6±3
Average sub-Arctic (Bethel) missions 13, 15, 17, 25	821±80	62±18	55±26	10±8
0.1-6.2 km				
Rasmussen et al. [1983] Barrow (71°N) June 1982, ground	1015	106	86	NA
Hov et al. [1984] Norwegian Arctic (74°-79°N) July 1982, ground	1195±27	67±18	87±30	<20

NA, not available.

NMHC in the region northeast of Prudhoe Bay (Figure 22). The excess hydrocarbon ratios relative to ethane for each of the two samples collected in this region (153°W - 145°W) (see Table 6) show that they represent two distinct air masses. Comparison of these hydrocarbon ratios with the source ratios of Table 4 indicates that the sample collected northwest of Prudhoe Bay (153°W) exhibited hydrocarbon ratios that were within a factor of 2 of those representative of biomass burning plumes, making it consistent with significant NMHC contributions from forest fires. By contrast, the second sample, collected 40 min later and 300 km northeast of Prudhoe Bay (at 145°W), appears to be more characteristic of an air mass enhanced by emissions from the Prudhoe Bay oil fields.

The remaining hydrocarbon data shown in Figure 22 clearly reveal that the air mass sampled between 140°W and 70°W appears to have had a completely different origin from that encountered in the same area during mission 4. The average ethane, ethyne, propane and n-butane mixing ratios ±1σ for this portion of mission 28 were 950±40, 120±10,

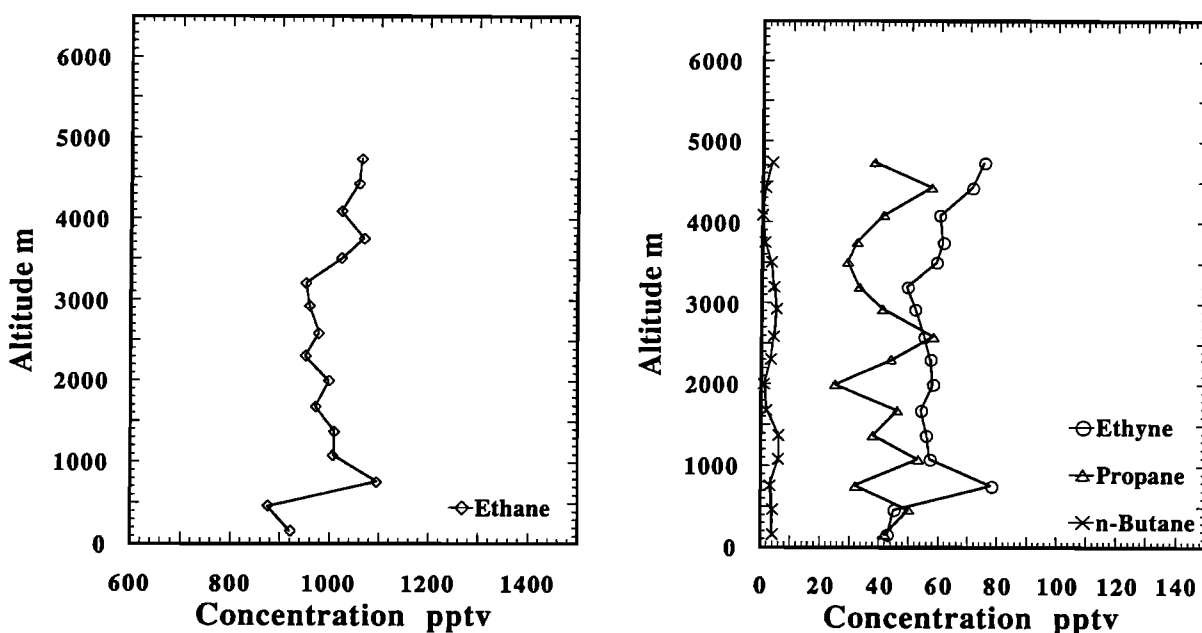Fig. 9. Vertical profile of ethane, ethyne, propane, and n-butane for samples collected during mission 5, flown on July 10, 1988, at 70.6°N, 157.0°W, south of Barrow, Alaska.
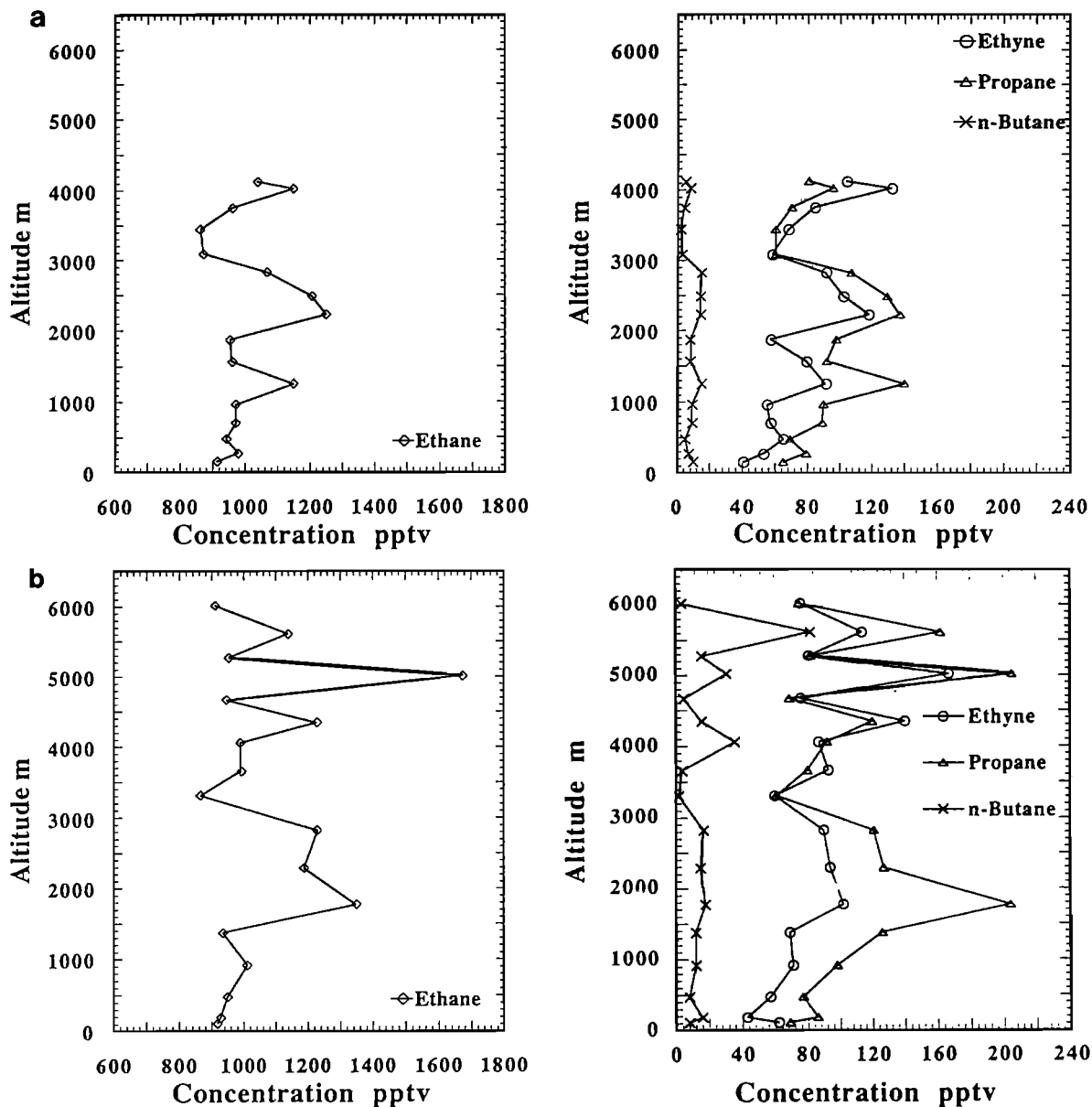
Fig. 10. Vertical profiles of ethane, ethyne, propane, and n-butane collected during mission 6, flown on July 12, 1988 (a) at 70.4°N, 153.5°W and (b) at 70.7°N, 153.7°W, southeast of Barrow, Alaska.
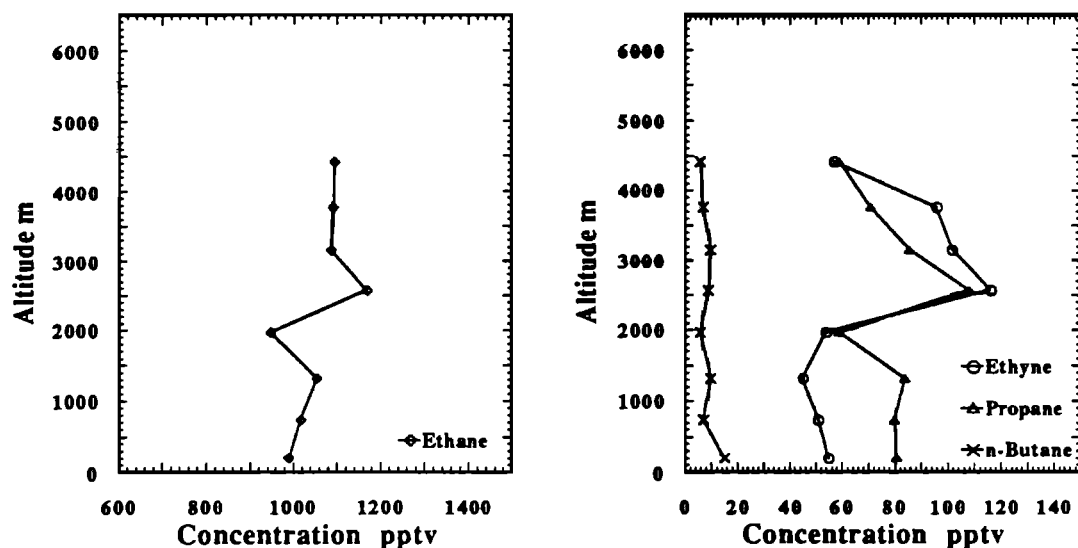

Fig. 11. Vertical profile of ethane, ethyne, propane, and n-butane for samples collected during mission 7, flown on July 13, 1988, at 74.0°N, 166.0°W over the Arctic Ocean north of Barrow, Alaska.
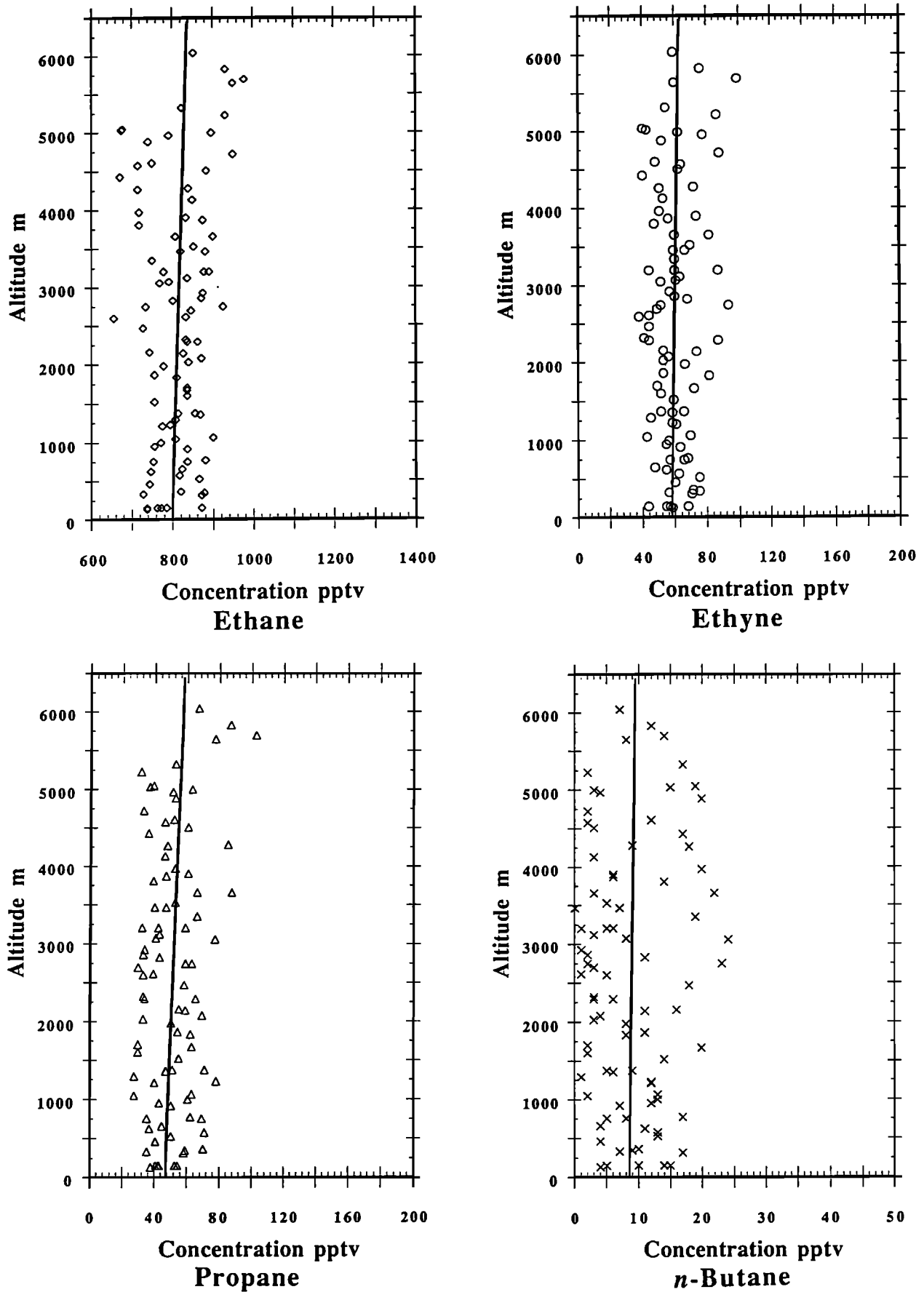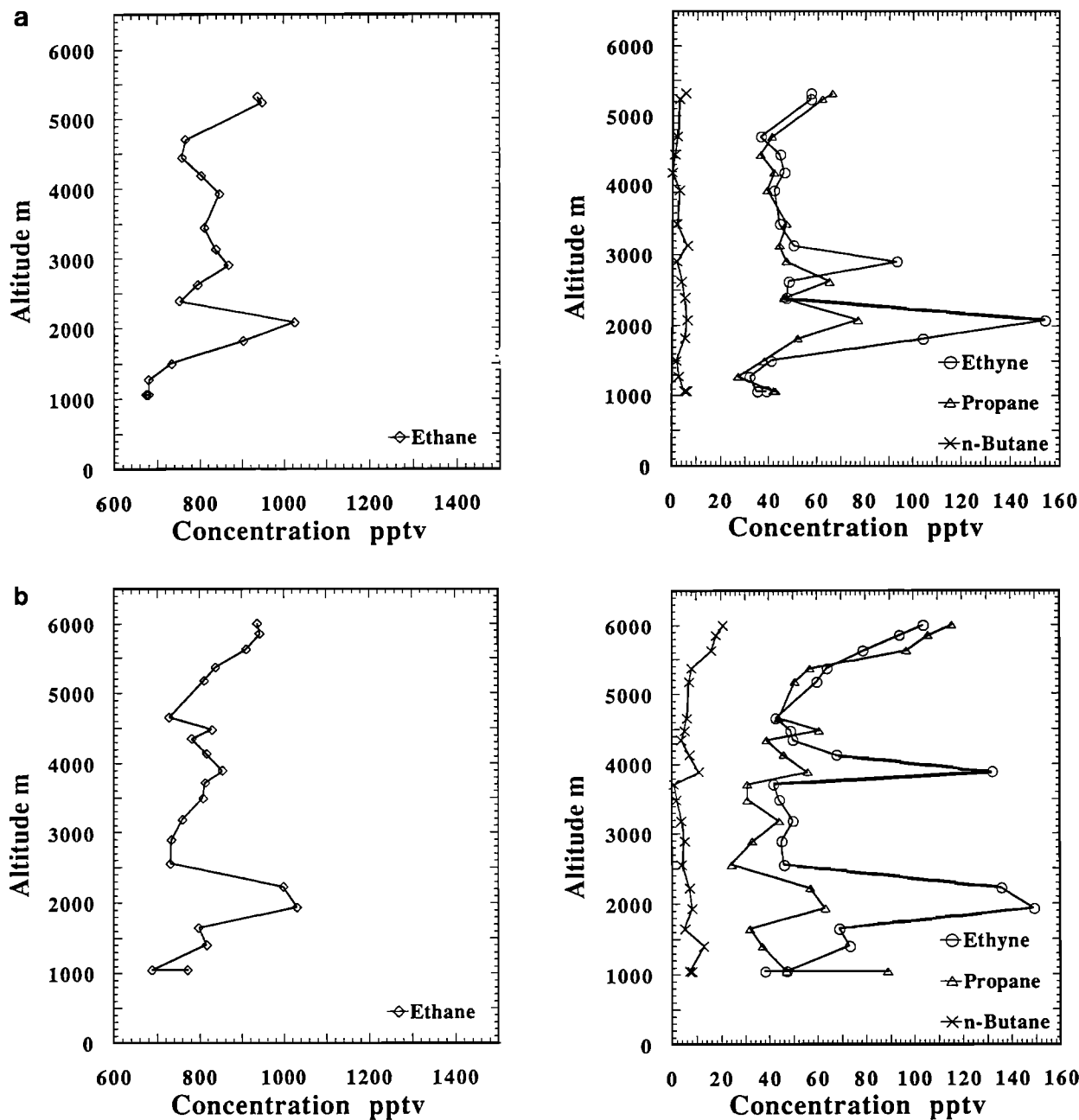
Fig. 12.   Composite vertical profiles of ethane, ethyne, propane, and n-butane for samples collected in background conditions near Bethel, Alaska,   during missions 13, 15, 17 and 25 flown on July 24, 28, 29 and August 9, 1988, respectively.

Fig. 13. Vertical profiles of ethane, ethyne, propane, and n-butane for samples collected during mission 14 flown on July 26, 1988, at (a) 61.1°N, 162.0°W and (b) 60.8, 162.9°W, northwest of Bethel, Alaska.

120±15, and 15±7 pptv, respectively, showing that although the ethane concentrations are similar for both missions 4 and 28, the ethyne, propane, and n-butane levels measured for mission 28 are considerably higher. This observation is consistent with the trajectory analysis, which indicates that the air mass encountered during this portion of mission 28 originated over the North American continent before it moved out over the Arctic Ocean. By contrast, the cleaner air mass sampled during mission 4 was of central Siberian origin [Shipham et al., this issue].

Latitudinal Surveys

The hydrocarbon mixing ratios encountered during the first latitudinal survey between 40°N and 56°N were quite variable (Figure 5); the mean ethane mixing ratio ±1σ was

1030±185 pptv, ethyne and propane were both in the 95±35 pptv region, and n-butane was 10±5 pptv (Table 2). Trajectory analysis suggests that the air mass encountered in this region had been stagnant over the Great Lakes region of the United States for several days. Augmented samples from continental urban emissions would be expected in an air mass subjected to such meteorological conditions. The much cleaner samples measured in this region were likely to have been collected in a stratospheric/tropospheric folding as suggested by the in situ ozone and dew point temperature instruments [Gregory et al., this issue]. Such a combination of samples representative of continental or of stratospherically influenced air would explain the large variations in the NMHC mixing ratios observed for these first two missions. In contrast, the air mass encountered between 61°N and 76°N had moved in from across
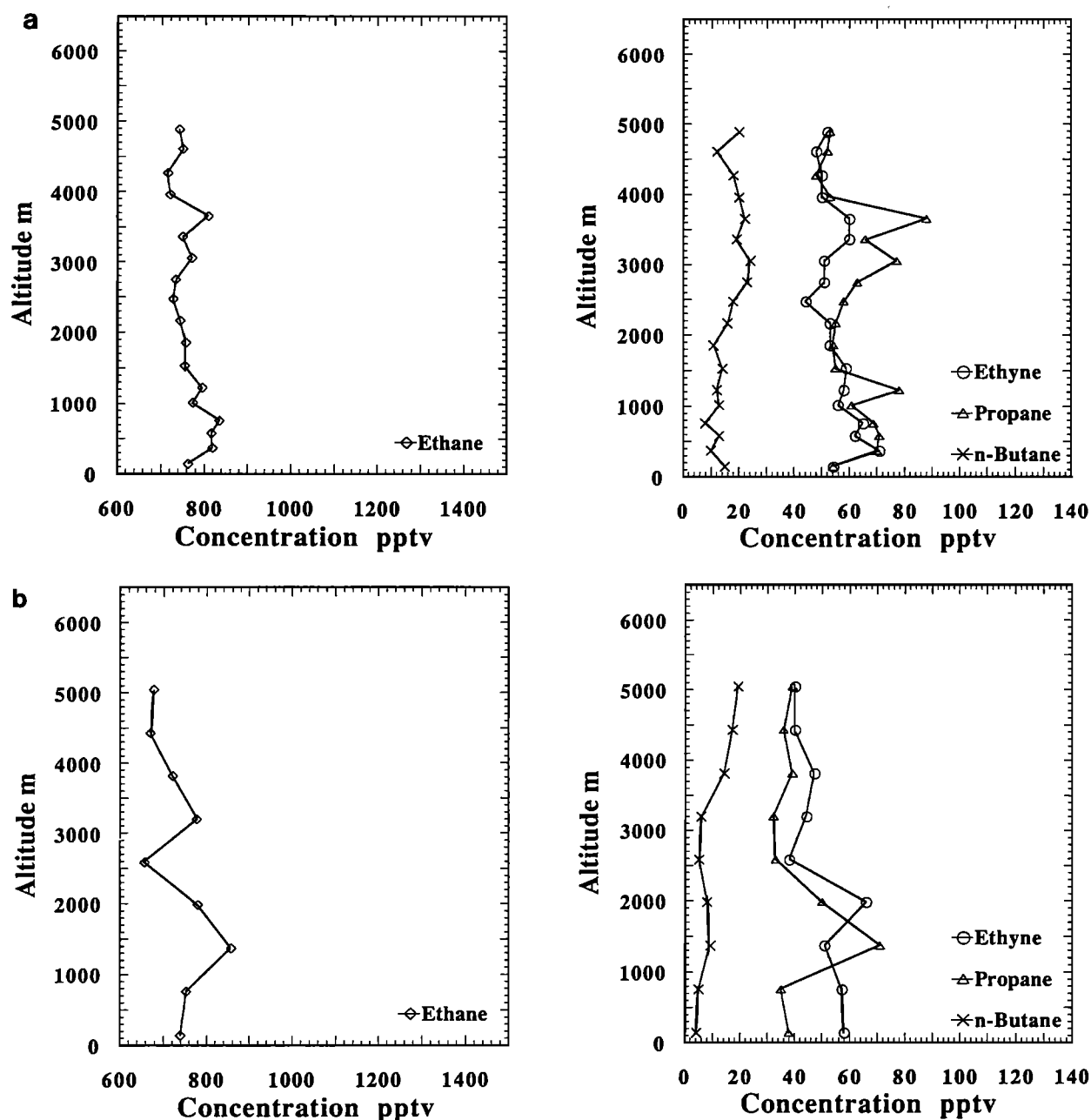
Fig. 14. Vertical profiles of ethane, ethyne, propane, and n-butane collected during mission 17, flown on July 29, 1988 (a) at 61.8°N, 163.0°W, north of Bethel, Alaska, and (b) at 57.5°N, 163.0°W over Bristol Bay, Alaska.

the Arctic Ocean [Shipham et al., this issue]. Consistent with this trajectory analysis, lower concentrations with relatively minor variability (±1σ) of the assayed NMHC (1053±65, 108±29, 61±25 and 9±4 pptv for ethane, ethyne, propane, and n-butane, respectively) were observed for this mission, although some stratospheric component may have been encountered once again.

The average mixing ratios ±1σ for the latitudinal range covered by the second latitudinal survey during the return to Virginia were 980±120, 105±30, 150±60, and 6±2 pptv for ethane, ethyne, propane, and n-butane, respectively (Figure 21 and Table 2). The northernmost air mass encountered (between 78° and 83°N) was suggested to be of a single Arctic origin, with the probable exception of the air mass containing enhanced hydrocarbon concentrations at the 3000 m level in the vertical profile (Figure 23 and Table 6). Consequently,

only minor variations in the concentrations of the gases were observed (Figure 21). For the remainder of the flights, the air masses were of stratospheric and/or continental origin and showed much greater variability. The observed variation in the mixing ratios of the selected gases displayed in Figure 21 supports the trajectory analyses.

In conclusion, neither of the latitudinal surveys, which were performed 6 weeks apart in this summertime experiment, revealed any statistically significant dependence of the measured hydrocarbons within this range of latitude. This observation is consistent with the latitudinal profiles that have been observed in surface samples collected during the same season at similar latitudes by Blake and Rowland [1986 and unpublished data, 1990]. Table 2 shows that the mixing ratios are within and mostly at the low end of the ranges observed by other studies made in this latitude band in summer
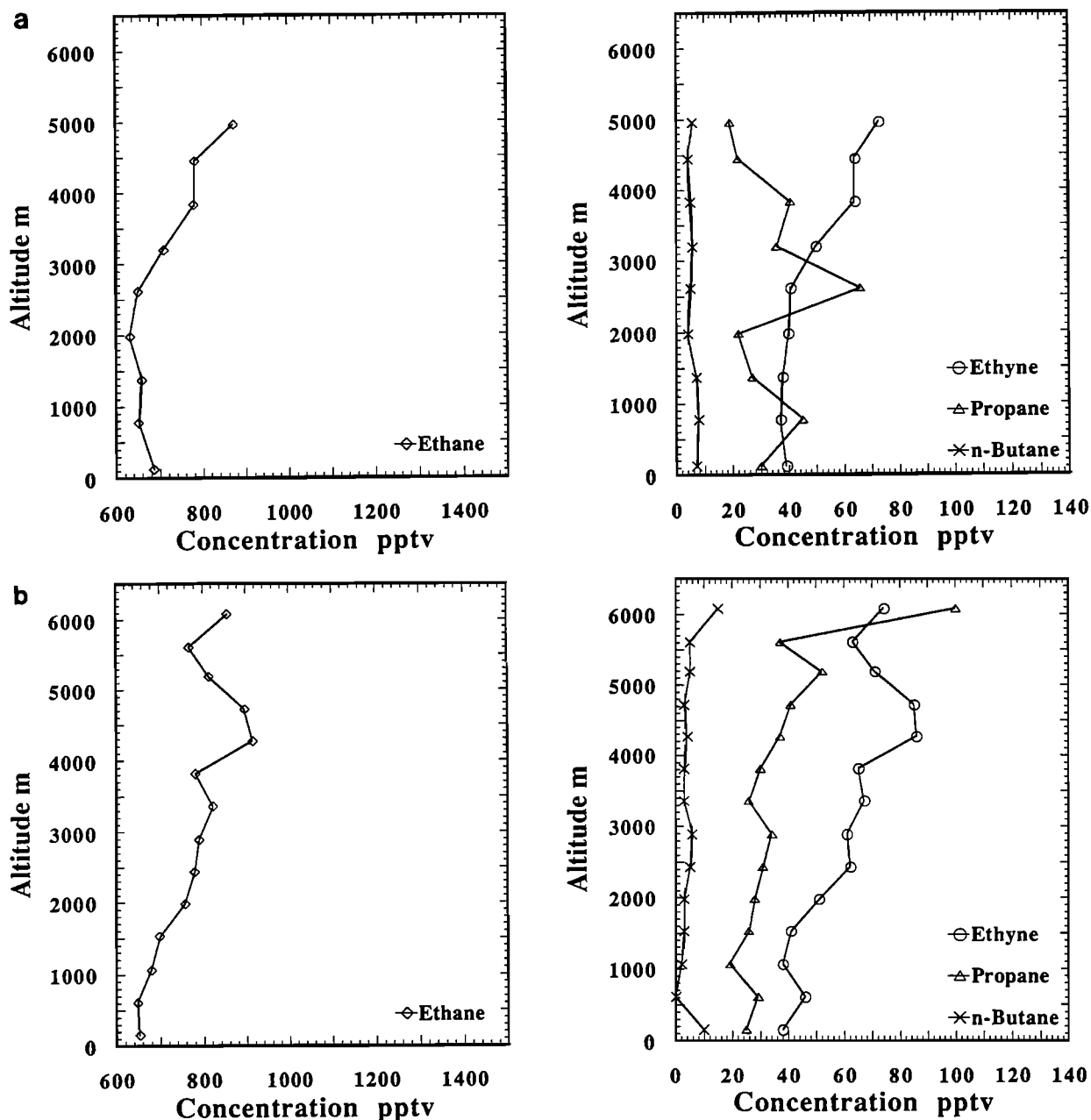
Fig. 15. Vertical profiles of ethane, ethyne, propane, and n-butane collected during mission 19, flown on August 2, 1988 (a) at 61.1°N, 162.0°W over Bristol Bay, north of Bethel, Alaska, and (b) at 58.3°N, 168.0°W over the Bering Sea.

[*Blake and Rowland*, 1986; *Rudolph*, 1988; *Rudolph et al.*, 1982]. The cumulative exposure to high HO concentrations is expected to reduce NMHC concentrations as the summer progresses, as illustrated by the lower values found in mid-August versus early July.

Vertical Profiles

Almost every mission flown during the ABLE 3A project contained at least one vertical profile. In all, 37 spiral vertical profiles were made between 150 and 6200 m (Table 1). Various profile locations were chosen in order to examine unpolluted regions of the lower troposphere and to investigate regional phenomena such as emissions from biomass burning, long-range transport of pollutants, and emissions from tundra and forested areas.

A principal objective of the ABLE 3A project was

characterization of the air above the pristine Alaskan environment. However, even in this remote region, only about half of the Alaskan flights showed little or no evidence of recent emissions from such sources as biomass burning and urban activity including fossil fuel combustion [*Wofsy et al.*, this issue; *Jacob et al.*, this issue]. The missions flown in the Arctic and sub-Arctic regions of Alaska which showed evidence of local contamination from Alaskan biomass burning were missions 4, 5, 6, 14, 19, 20, 21, 22, and 28. Those that appeared to have been augmented by emissions from biomass burning and/or from Siberian sources such as the Siberian coal fields and fires were missions 7, 22, and 23. The remaining Alaskan missions which exhibited background concentrations and represented 222 discrete samples from 16 individual profiles were 8, 9, 11, 12, 13, 15, 17, and 25 and are shown as a composite in Figure 20. A single sample from mission 13
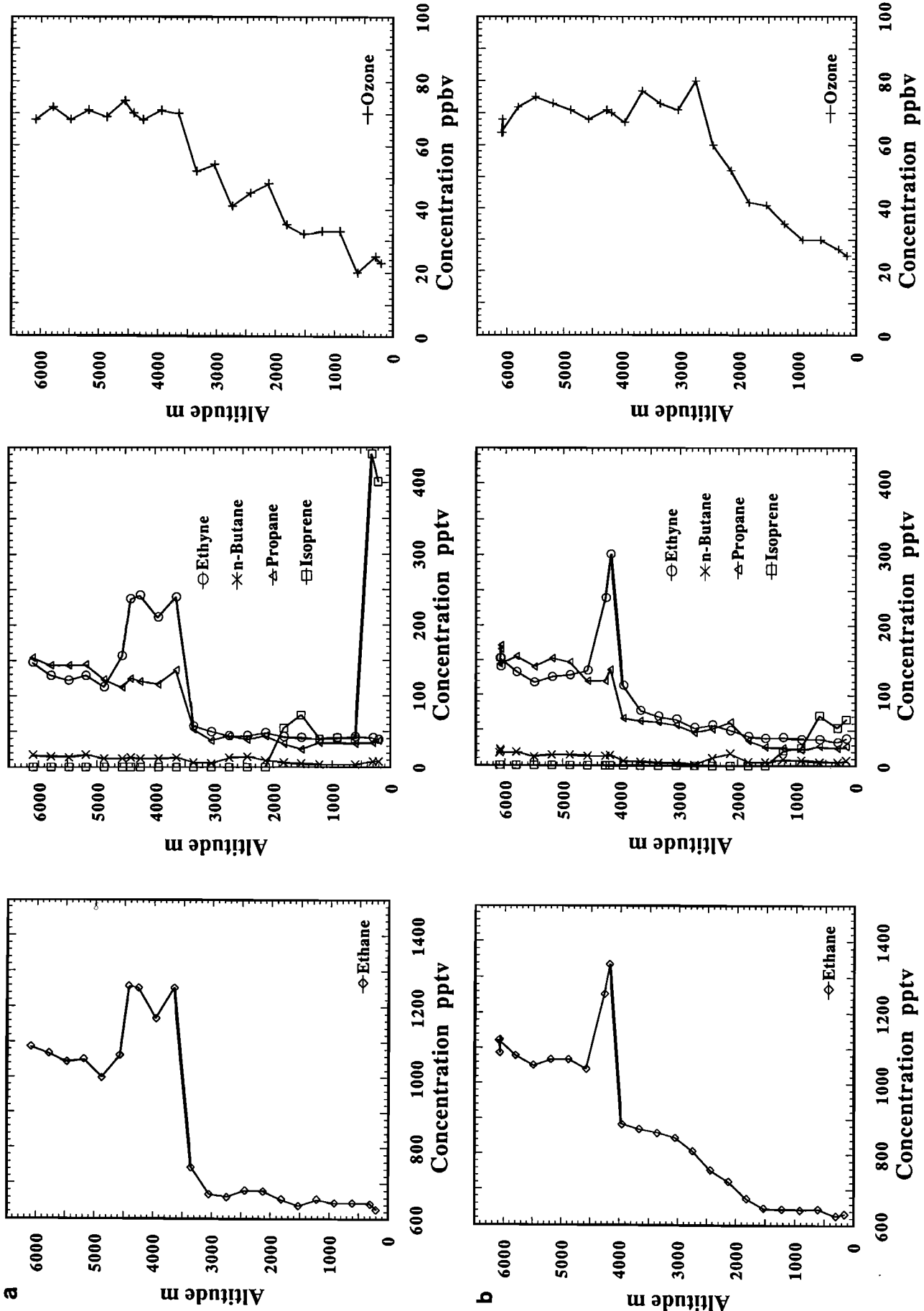
Fig. 16.   Vertical profiles of ethane, ethyne, propane, n-butane, isoprene, and ozone (Gregory et al., this issue) collected during mission 20, flown on August 3, 1988 (a) at 62.2°N, 160.3°W and (b) at 61.3°N, 161.3°W, near Bethel, Alaska.
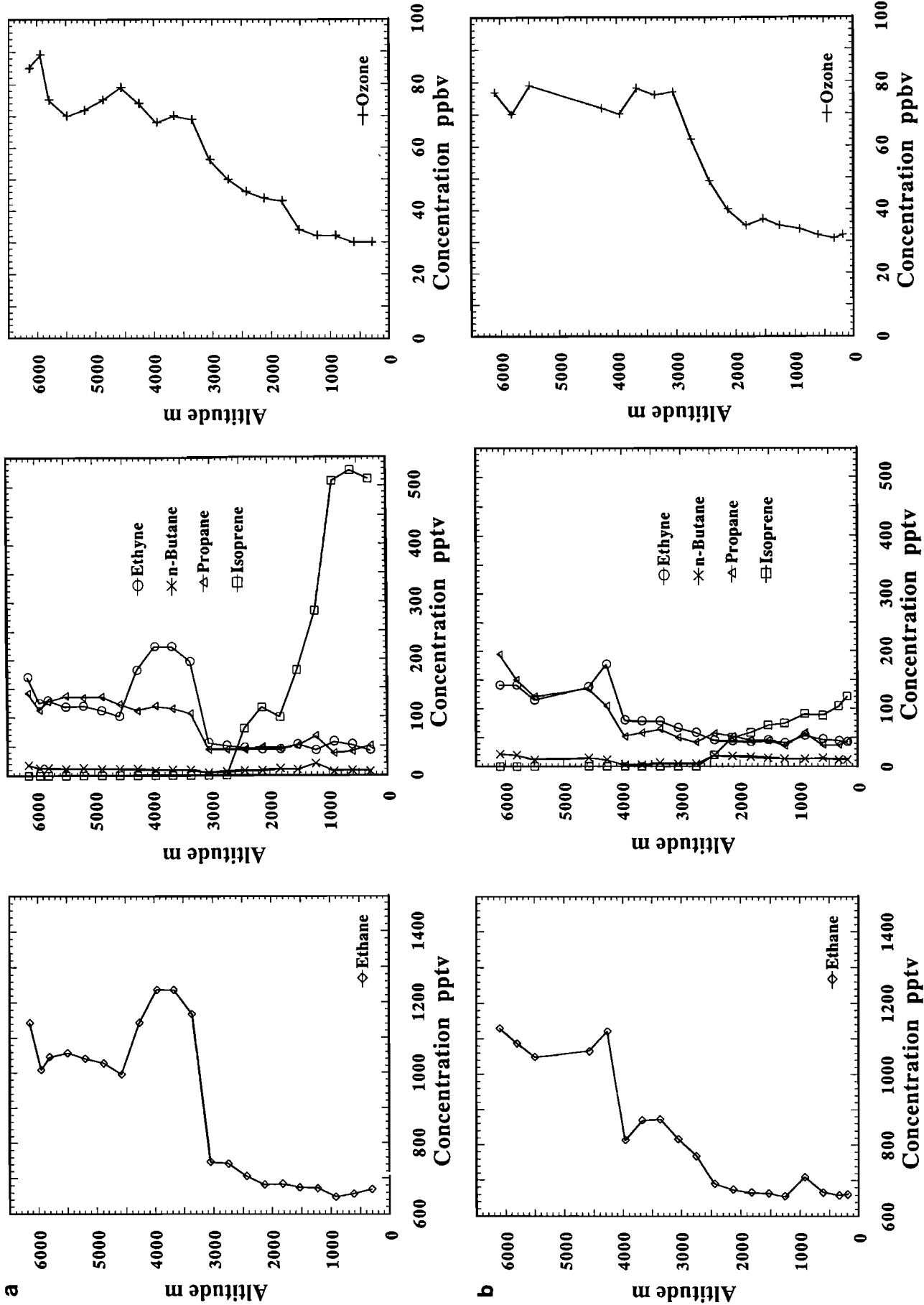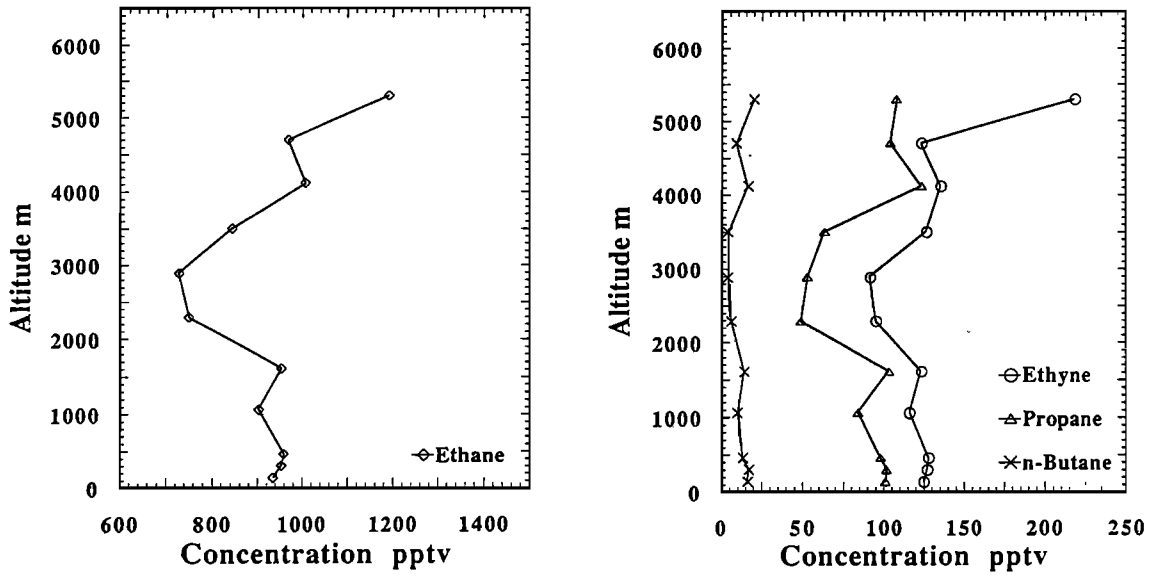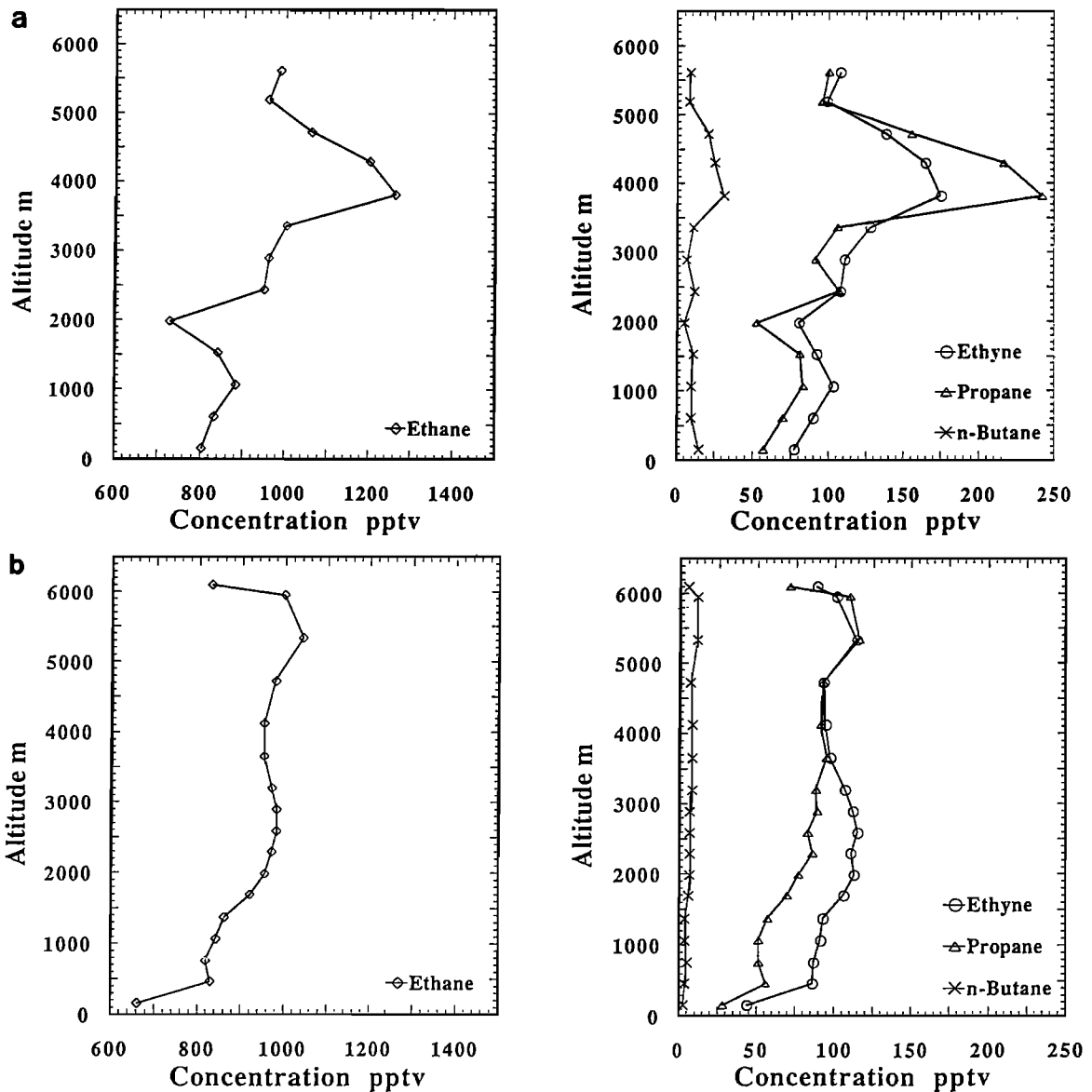
Fig. 17. Vertical profiles of ethane, ethyne, propane, n-butane, isoprene, and ozone (*Gregory et al.*, this issue) collected during mission 21, flown on August 3, 1988 (*a*) at 62.2°N, 160.4°W and (*b*) at 61.3°N, 161.3°W, near Bethel, Alaska.

Fig. 18. Vertical profile of ethane, ethyne, propane, and n-butane for samples collected during mission 22, flown on August 7, 1988, at 57.9°N, 159.9°W, over Bristol Bay (22D, descending).

Fig. 19. Vertical profiles of ethane, ethyne, propane, and n-butane collected during mission 23, flown on August 7, 1988 (a) at 54.3°N, 160.8°W and (b) at 53.6°N, 162.5°W over the Pacific Ocean, south of the Aleutian Islands.
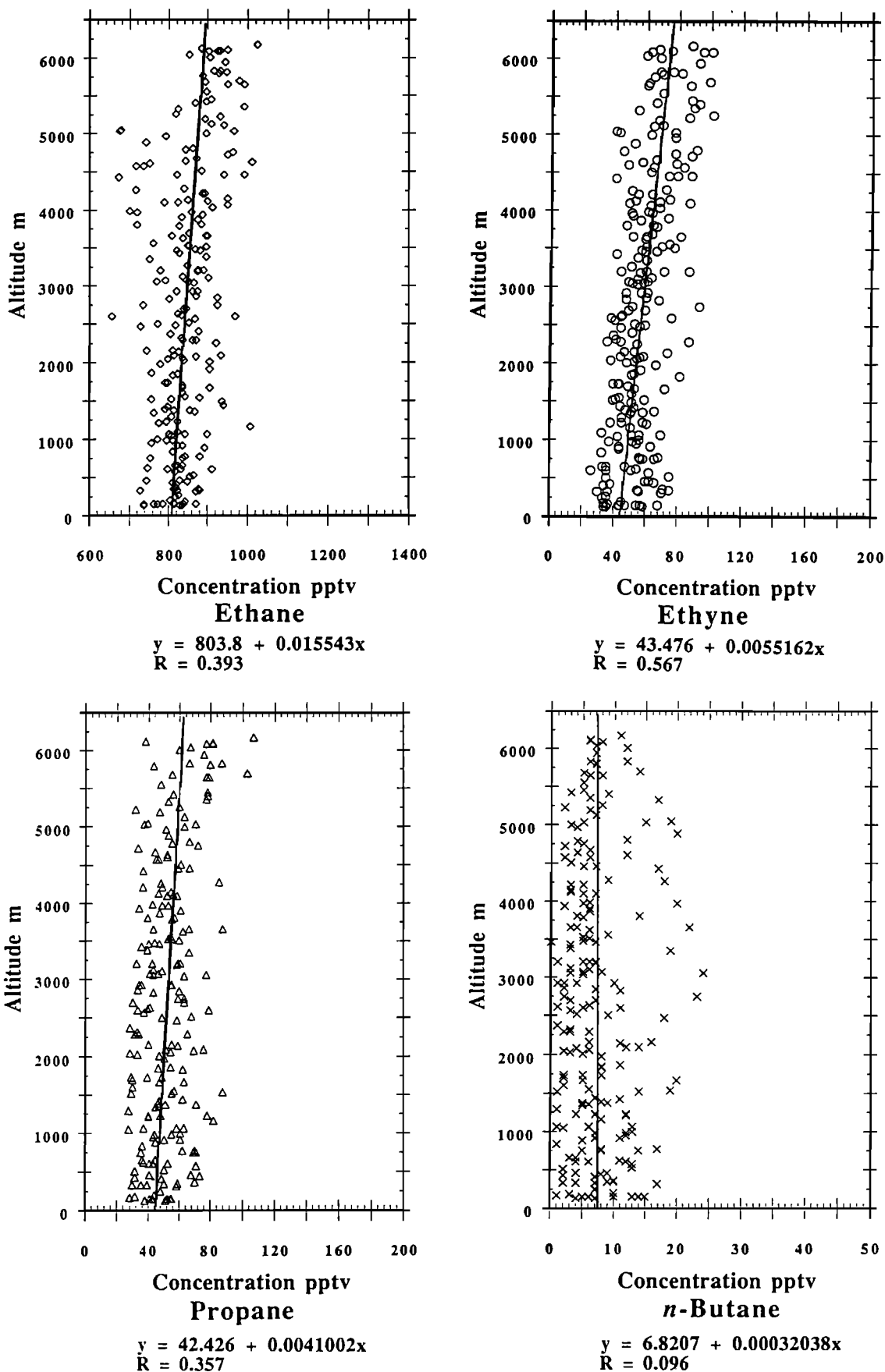
Fig. 20. Composite vertical profiles of ethane, ethyne, propane, and n-butane for samples collected in background conditions in the Alaskan Arctic and sub-Arctic during missions 8, 9, 11, 12, 13, 15, 17, and 25, flown on July 15, 17, 19, 22, 24, 28, 29 and August 9, 1988, respectively.
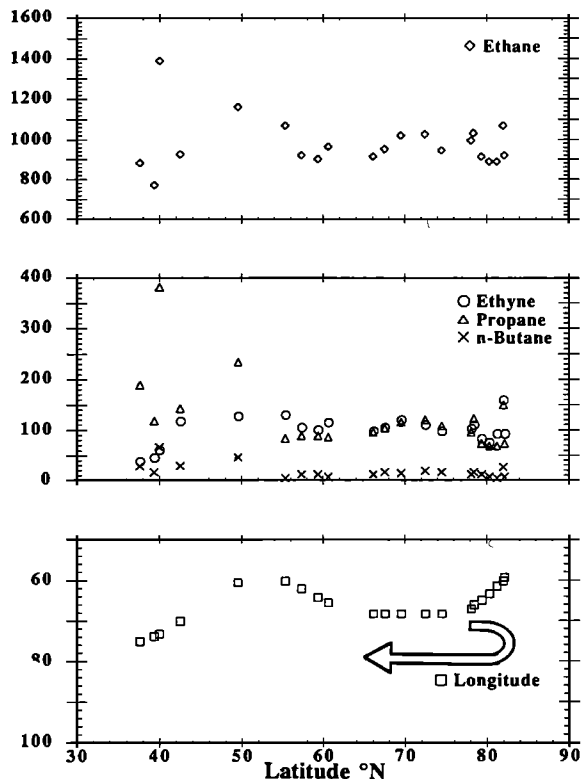
Fig. 21. Latitudinal profile of ethane, ethyne, propane, *n*-butane (in pptv) and longitude (in degrees west) collected during transit missions 29-33, flown between August 13 and 17, 1988, between Greenland and Wallops Island, Virginia.
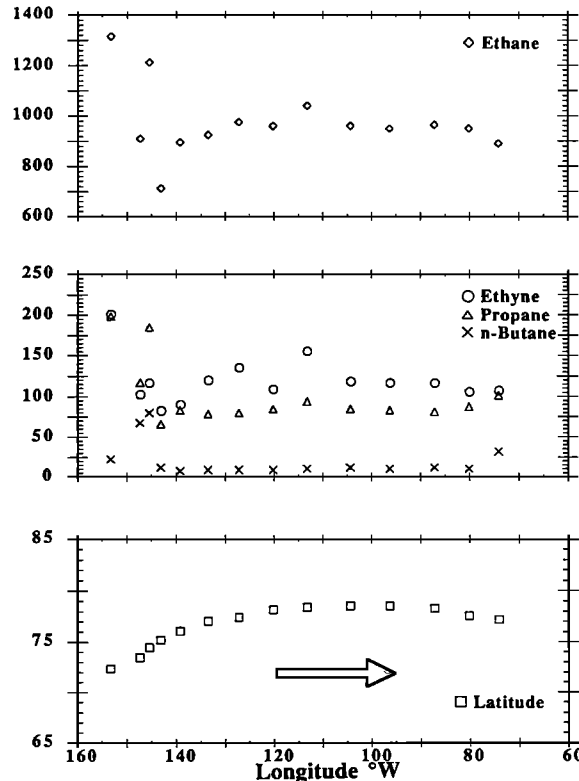
Fig. 22. Longitudinal profile of ethyne, ethane, propane, *n*-butane (in pptv), and latitude (in degrees north) for samples collected during transit mission 28, flown on August 12, 1988, between Alaska and Thule, Greenland.

has been removed from the data set as it obviously had been augmented by some local source. Trajectory analysis indicates that the background air sampled near Barrow was continental polar in origin. The background vertical profiles made near Bethel were both marine polar and continental polar in character. The average concentrations of each hydrocarbon are

shown in Table 3, where they are seen to compare well with other Arctic measurements made during summertime (see Table 3 for references).

Increase of hydrocarbon concentrations with altitude. The most marked characteristic, which was observed in all but mission 17 during the entire sub-Arctic campaign, was the
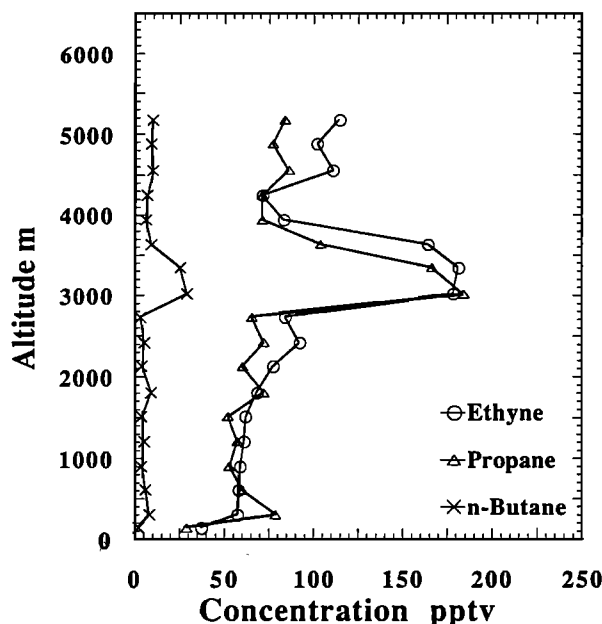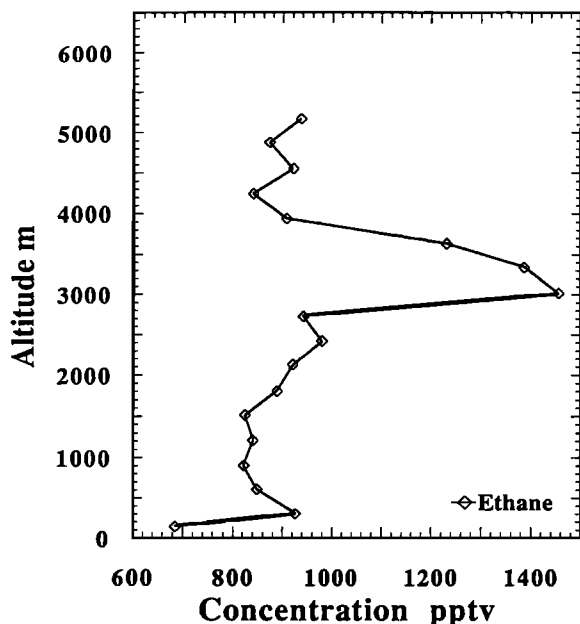

Fig. 23. Vertical profile of ethane, ethyne, propane, and *n*-butane for samples collected during mission 29, flown on August 13, 1988, at 83.0°N, 56.0°W near the northern edge of Greenland.
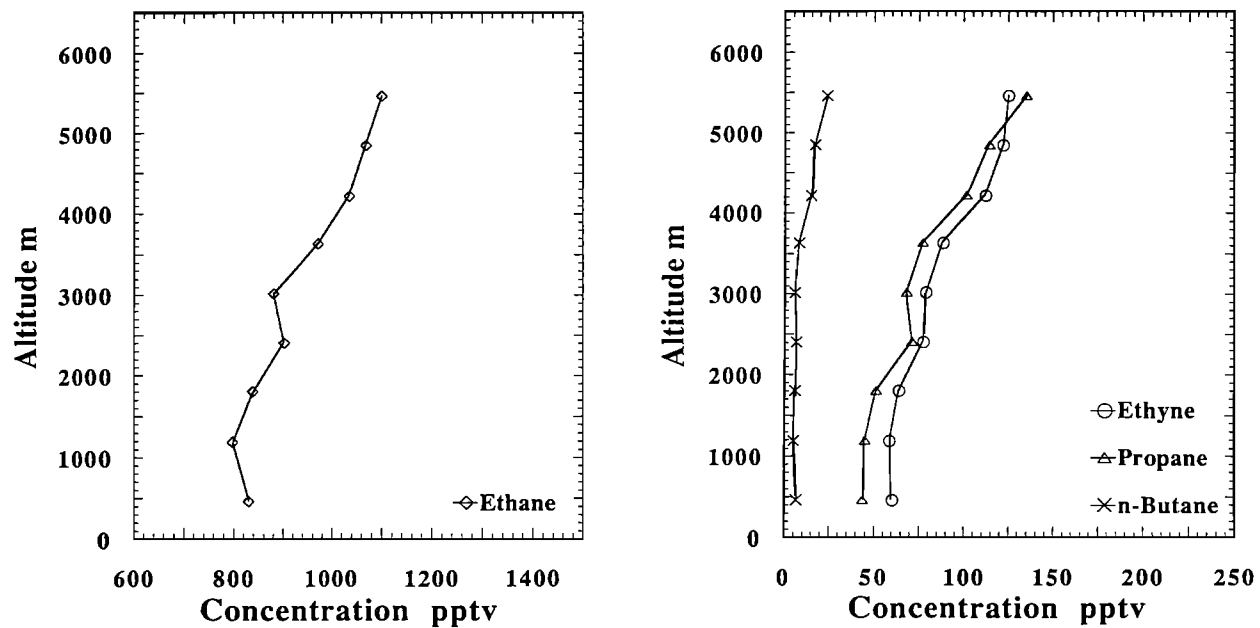
Fig. 24. Vertical profile of ethane, ethyne, propane, and n-butane for samples collected during mission 30, flown on August 15, 1988, at 72.0°N, 68.7°W over Baffin Bay.

general increase in hydrocarbon mixing ratios with increasing altitude. (The vertical profile of mission 33 exhibited a negative correlation with altitude but is excluded from this discussion because it took place at 38°N latitude.) Mixing ratios increased in the background Arctic and sub-Arctic profiles over the altitude range from 150 to 6000 m by approximately 11% for ethane and 50-70% for propane and ethyne. The data also suggest an increase in n-butane mixing ratio at the higher altitudes, but the scatter is too large to conclude statistical significance. When the changes are expressed as logarithms of mixing ratios, the slopes for C_2H_2 and C_3H_8 are about 5 and 4 times larger, respectively, than for C_2H_6. Because the only known atmospheric sources of these

hydrocarbon species are located at the Earth's surface, some mechanism must exist by which the pollutants are transported from the source areas into the mid-troposphere above the Arctic. In the summer months the northerly location of the polar front is thought to prevent access to the lower Arctic troposphere of polluted air from mid-latitudes [Iverson, 1984]. Indeed, none of the low-altitude surveys in ABLE 3A exhibited the much higher concentrations which are characteristic of the mid-latitude source regions, with the exceptions of isoprene from the forests and the specific plume events discussed above.

The single vertical profile made during mission 30, which was flown on August 15, 1988, over the Baffin Bay area during the return transit of the NASA Electra to Wallops Island,
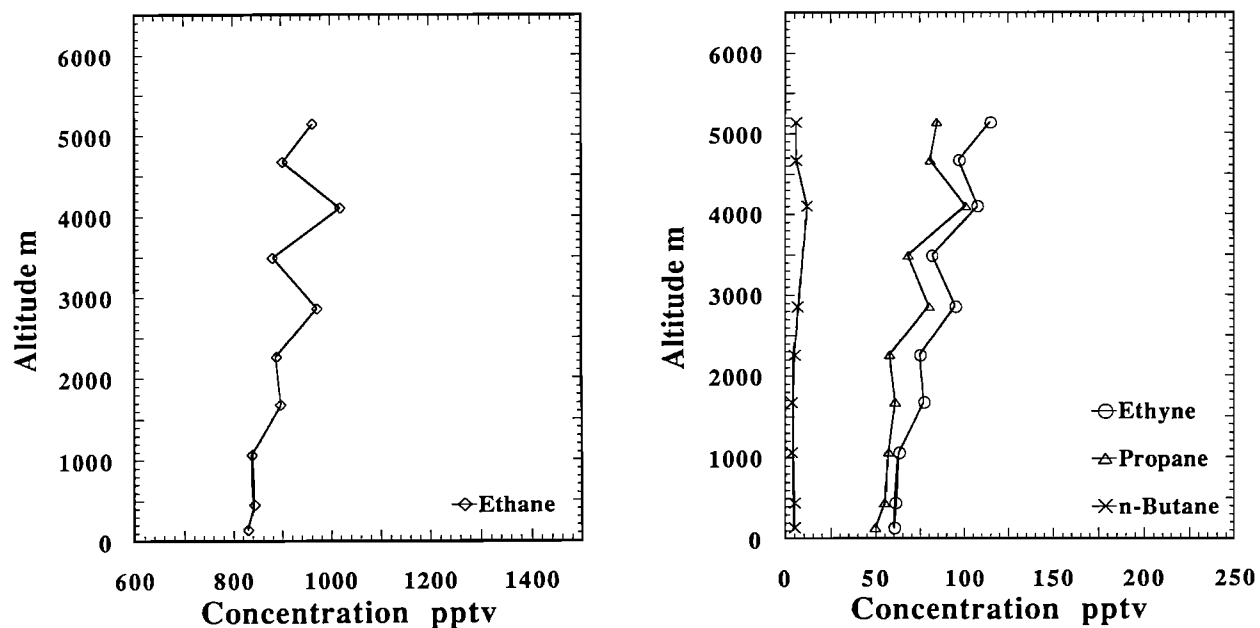

Fig. 25. Vertical profile of ethane, ethyne, propane, and n-butane for samples collected during mission 31, flown on August 15, 1988, at 61.1°N, 65.9°W over the Labrador Sea.
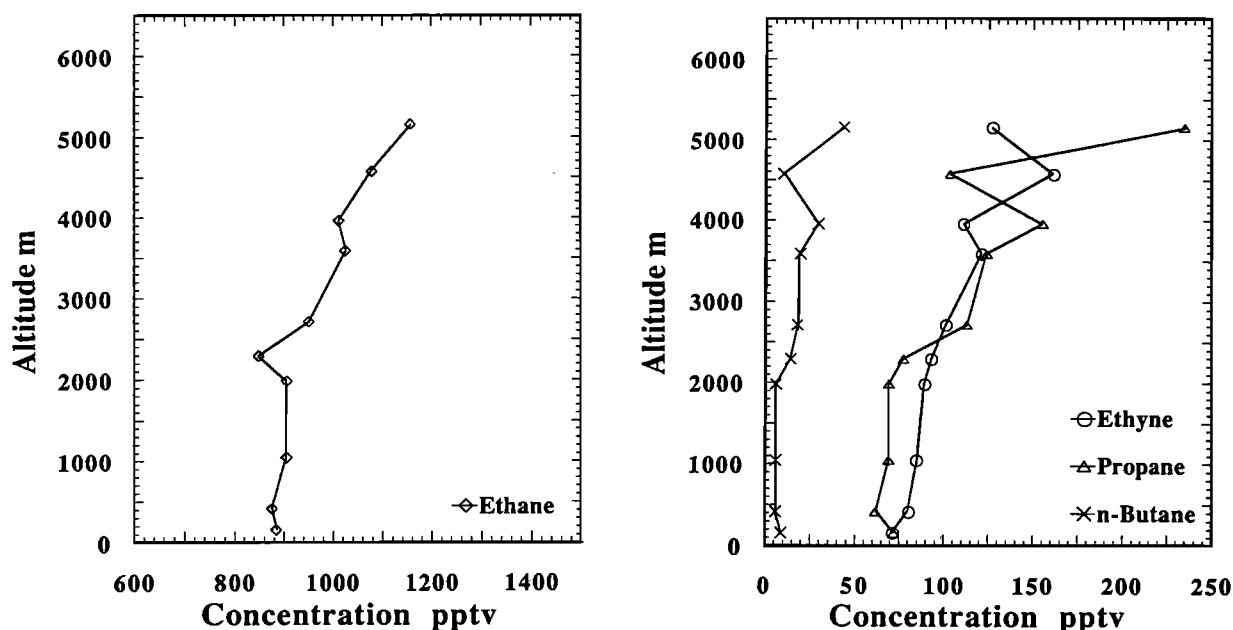
Fig. 26. Vertical profile of ethane, ethyne, propane, and n-butane for samples collected during mission 32, flown on August 16, 1988, at 49.8°N, 61.0°W over the Gulf of St. Lawrence.

clearly illustrates the phenomenon in which the NMHC concentrations were positively correlated with altitude (Figure 24). Trajectory analysis indicates that the air sampled during this spiral was continental polar in origin, but during the previous week had been confined to a tight circulation within a low-pressure system located over Baffin Island [*Shipham et al.*, this issue]. The top of the planetary boundary layer (PBL) was at about 2700 m. The mixing ratios of all four hydrocarbons correlate very well with increasing altitude and with one another. The correlations of the mixing ratio of ethane with each of the other three hydrocarbons are illustrated in Figure 28 for a linear plot and in Figure 29 in a natural log-log plot. The r^2 values for C_2H_2, C_3H_8, and n-C_4H_{10} versus C_2H_6 are 0.97, 0.95, and 0.83 for Figure 28 and 0.98, 0.96, and 0.92 for Figure 29. The slopes in Figure 29 are 2.5 for C_2H_6 versus C_2H_2, 3.1 for C_2H_6 versus C_3H_8, and 4.8 for C_2H_6 versus n-C_4H_{10}. A third comparison of relative changes in hydrocarbon mixing ratios is illustrated for ethane versus ethyne in the natural log-log plot of Figure 30 with the nonplume air samples of missions 20 and 21. Again, the correlation is excellent, with r^2 of 0.97 and a slope of 2.3.

The frequent observation of very high correlation coefficients among hydrocarbons in a vertical profile, with higher concentrations at higher altitudes, indicates the operation of a rather consistent mechanism for simultaneous alteration of all of the mixing 'ratios. For all four of these hydrocarbons, the primary atmospheric sink is reaction with HO radical, as in (1) and (2), thereby providing the needed

$$HO + RH \rightarrow H_2O + R \qquad (1)$$

$$HO + C_2H_2 + M \rightarrow C_2H_2OH + M \qquad (2)$$
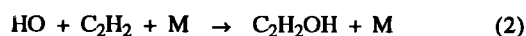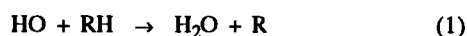
correlated sink. The reactions with these hydrocarbons of other atmospheric oxidants are much too slow to play significant roles in their atmospheric removal [*Atkinson*, 1990]. With an isolated air mass, the concentrations of all four hydrocarbons can be expected to diminish logarithmically versus integrated exposure to the atmospheric level of HO.

The reaction of HO with the three alkanes all have activation energies for hydrogen abstraction, as in (1) [*Jet Propulsion Laboratory (JPL)*, 1990; *Atkinson*, 1990]. On the other hand, HO attack on ethyne proceeds by a third-body reaction through addition and stabilization as in (2) and is both pressure and temperature dependent [*JPL*, 1990]. The variations among these reaction rate constants are summarized in Table 7 for the observed atmospheric conditions encountered between 200 and 6000 m altitude during mission 21 near Bethel. If an isolated air mass were exposed steadily to hydroxyl radical attack, with no opportunity for additional hydrocarbon input, then the logarithmic slopes of decreasing hydrocarbon mixing ratios would fall in the ratios of these rate constants. In a hypothetical air mass held steadily at 293 K, these rate constant ratios versus C_2H_6 would then be 3.1 for C_2H_2, 4.2 for C_3H_8, and 9.6 for n-C_4H_{10}.

In the actual atmosphere, however, these completely isolated, constant temperature conditions do not hold. In addition there will be some contribution from dilution. Nevertheless, the measured slopes of the logarithmic plots are not too different from the calculated rate constant ratios in Table 7 for C_2H_2 and C_3H_8, and all four logarithmic hydrocarbon loss rates fall generally in the same relative order characteristic of the rate constants at the lower altitudes. The very high correlation coefficients strongly suggest that all of the hydrocarbons (other than isoprene) in these air masses at different altitudes in a vertical profile tend to have a generic common origin subjected later to diminution in mixing ratios by HO attack. This common origin is primarily assumed to be release of the hydrocarbons in the inhabited areas of the temperate latitudes. At these lower latitudes, the air masses generally show decreasing mixing ratios of hydrocarbons with increasing altitude, so that the subsequent reversal to the opposite tendency requires even more hydroxyl processing than if the starting profiles had exhibited no change with altitude.

The formation of tropospheric HO is initiated by ozone absorbing ultraviolet radiation energetic enough to produce $O(^1D)$ atoms by (3) which then react with water vapor by (4) to form two hydroxyl radicals. The yield of HO from $O(^1D)$ is
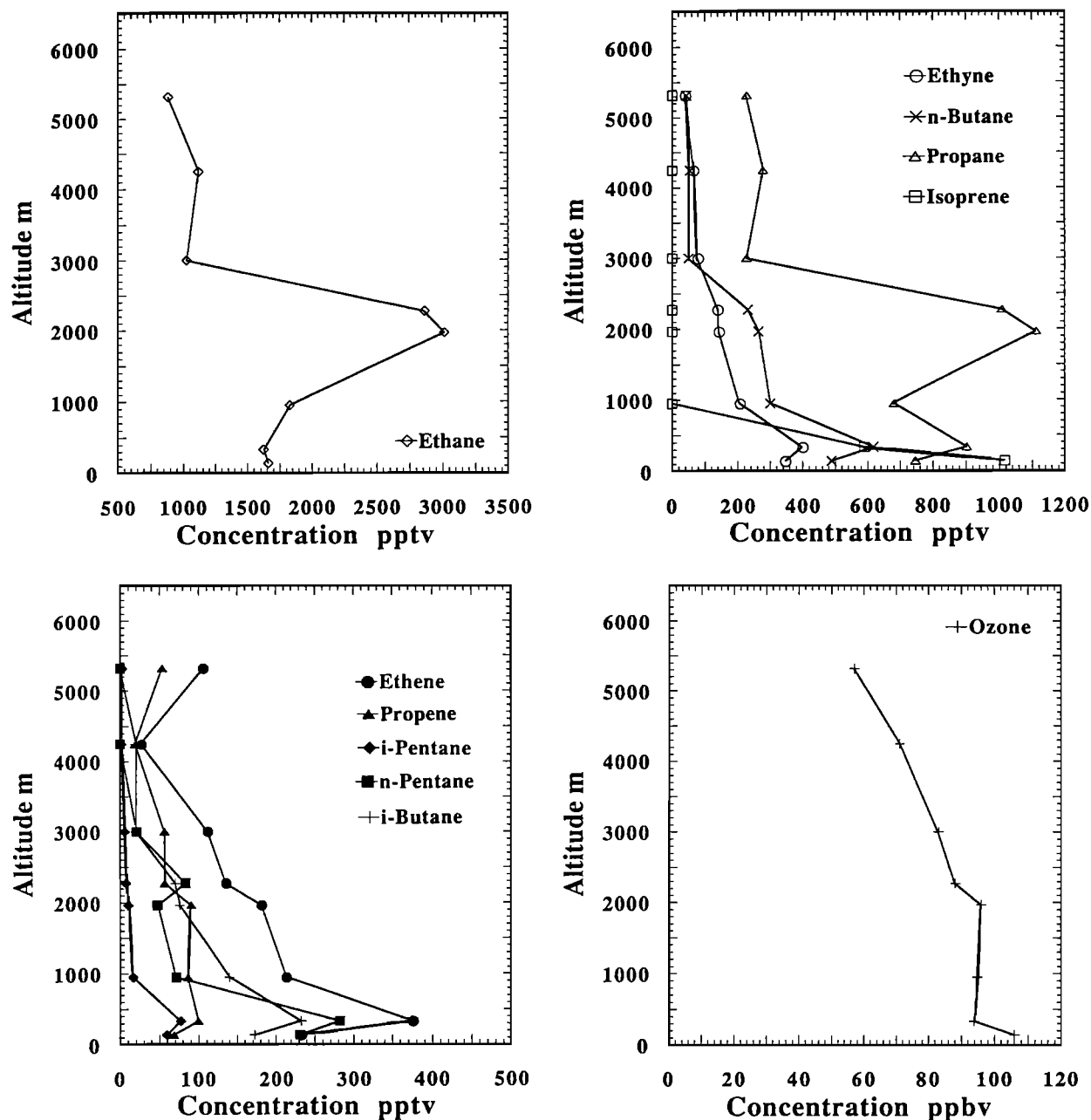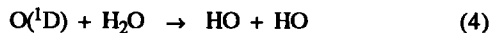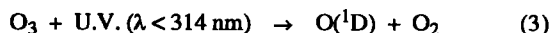
Fig. 27. Vertical profile of ethane, ethyne, propane, n-butane, isoprene, ethene, propene, i-butane, i-pentane, n-pentane, and ozone (*Gregory et al.*, this issue) for samples collected during mission 33, flown on August 17, 1988, at 37.9°N, 75.5°W near Wallops Island, Virginia.

$$O_3 + U.V. (\lambda < 314\,nm) \rightarrow O(^1D) + O_2 \qquad (3)$$

$$O(^1D) + H_2O \rightarrow HO + HO \qquad (4)$$

dependent upon the relative concentration of H_2O as compared to those of N_2 and O_2 which can de-excite $O(^1D)$ to $O(^3P)$ atoms incapable of (4). The total production of HO is dependent upon the availability of solar UV radiation and upon the water vapor mixing ratio, with higher yields in the tropics and during the temperate and polar summers. No measurements of steady state HO concentrations versus altitude are available, but atmospheric models tend to suggest higher steady state levels of HO nearer the surface.

Accepting the hypothesis that the relative hydrocarbon mixing ratios for all of the air masses encountered in a single vertical profile were initially rather similar, as required by the high correlations observed in their concentrations, the mixing ratio differences indicate that the air masses at lower altitudes have received larger integral exposures to HO radicals than have those at higher altitudes.

Three different types of meteorological conditions can be suggested, each of which might account for these differences in integrated hydroxyl radical exposure, with more extensive exposure for air masses at lower altitude. First, if air masses which were vertically homogeneous in hydrocarbon mixing ratios were advected toward the Arctic from a distant source region, then higher steady state hydroxyl radical concentrations at low altitudes could cause significantly greater depletion of hydrocarbons there, leaving vertical profiles with positive correlations of mixing ratios versus altitude. Second, if air masses from higher altitudes tended to

TABLE 4. Emission Ratios of Methane, Ethyne, Propane, and n-Butane Relative to Ethane (= 1.0) for Various NMHC Sources

	CH4	C2H2	C3H8	n-C4H10
Natural gas Barrow (1989)	250	0	0.12	0.05
Urban emissions Anchorage (1988)	200	3	0.2	0.6
Prudhoe Bay (1988 and 1989)	8±4	0.2	0.7	0.4
Biomass burning missions 14, 20 and 21	33	0.38	0.08	< 0.01
Hegg et al. [1990] North America	6.2	0.50	0.51	0.21
Greenberg et al. [1984] Amazon	11.4	4.3[*]	0.2	NA

NA, not available.
[*] For all alkynes.

travel more rapidly from the source region than those from lower altitudes, then less exposure time to HO attack could have accumulated upon reaching a particular Arctic latitude and longitude, and the initial hydrocarbon ratios would be more nearly intact. Third, another variant of this possible differential exposure to hydroxyl is the suggestion of subsidence from higher to lower altitudes. This scenario invariably requires longer exposure to reach lower altitudes and, therefore, greater hydrocarbon losses.

This third explanation would begin with rapid upwelling into the upper free troposphere from the source region by some fast mechanism such as cloud pumping [Gidel, 1983]. As it moved aloft, a general subsidence of some portion of the air mass and subsequent mixing with cleaner low-altitude air could occur. Supporting this possibility is the argument that high-altitude, long-range transport of PAN, followed by subsidence and subsequent thermal decomposition, transports a significant fraction of NO$_x$ from urban sources areas to Arctic and sub-Arctic regions [Singh et al., this issue; Jacob et al.,

this issue; Sandholm et al., this issue]. While attractive as an explanation for NO$_x$ transport, this meteorology seems quantitatively incapable of producing the large concentration changes observed in most low-altitude air masses. Our data do not provide any definitive resolution among these meteorological mechanisms, nor is it likely that a single meteorology suffices. Whatever the meteorology, however, the dominant factor in explaining the strong correlations is chemical removal of the hydrocarbons by reaction with hydroxyl radicals.

The ABLE 3A missions can be compared with a number of vertical profiles from the STRATOZ II and STRATOZ III projects [Ehhalt et al., 1985; Rudolph, 1988]. Those experiments were flown in June of 1980 and 1984 and covered a latitudinal range from 70°N to 60°S at altitudes up to 12 km above the Atlantic Ocean. The longitudes involved in STRATOZ were those of Greenland and the east coast of North America. Their measured northern hemisphere concentrations were somewhat higher than presented here (Table 2). The profiles measured at mid-northern latitudes and throughout the southern hemisphere exhibited a general decrease in the mixing ratios of the selected NMHC with increasing altitude but, interestingly, both STRATOZ II and III showed the opposite trend at high northern latitudes. This increase of NMHC concentrations with altitude was interpreted in terms of fast mechanisms of upward transport such as the cloud pumping suggested by Gidel [1983]. The same phenomenon also has been observed in the Norwegian Arctic by Tille et al. [1985], and hydrocarbon "bulges" above the PBL have been reported in the region of Alaska by Rasmussen et al. [1983] and Greenberg et al. [1990]. The much more extensive collection of vertical profiles presented here has demonstrated that these scattered previous observations of vertical profiles are not anomalous, and have shown that the positive correlation of NMHC mixing ratios with altitude is a characteristic feature at high northern latitudes during late spring and summer.

Decrease of hydrocarbon concentrations with altitude. As previously mentioned, only two missions, 17 and 33, exhibited a general decrease in the levels of ethane, ethyne, and propane with altitude. Several similar vertical profiles were made in and around the Bethel region, but mission 17 was

TABLE 5. Emission Ratios Relative to Ethane (=1.0) of the Excess Concentrations of NMHC Measured in Samples Collected in Plumes Originating From Biomass Burning

Mission Number	Date	Profile	Altitude, m	Ethyne	Propane
14	July 26, 1988	14D	2090	0.41±0.02	0.08±0.04
			1820	0.38±0.04	0.06±0.06
		14A	1940	0.29±0.02	0.08±0.02
			2230	0.30±0.02	0.08±0.03
20	Aug. 3, 1988	20D	4570	0.42±0.12	0.03±0.07
			4420	0.40±0.04	0.07±0.03
			4270	0.41±0.04	0.07±0.03
			3960	0.40±0.05	0.10±0.03
			3660	0.37±0.03	0.14±0.02
		20A	4180	0.42±0.06	0.10±0.03
			4270	0.34±0.07	0.07±0.03
21	Aug. 3, 1988	21D	4270	0.42±0.05	0.04±0.05
			3960	0.40±0.03	0.07±0.03
			3660	0.38±0.02	0.08±0.03
			3360	0.36±0.03	0.09±0.03
Average values				0.38±0.04	0.08±0.03

TABLE 6. Excess Mixing Ratios Relative to Excess Ethane (= 1.0) of Methane, Ethyne, Propane, and n-Butane of 11 Samples Collected in NMHC Enhanced Air Masses

Mission	Date	Profile	Altitude m	CH_4	C_2H_2	C_3H_8	n-C_4H_{10}
4	July 9, 1988		6100	25	0.12	0.21	0.03
			6100	25	0.18	0.24	0.02
			6100	26	0.19	0.23	0.02
28	Aug. 12, 1988						
NW of Prudhoe Bay			5180	--	0.25	0.16	0.02
NE of Prudhoe Bay			5180	--	0.068	0.38	0.28
23	Aug. 7, 1988	23D	4720	52	0.29	0.65	0.14
			4300	47	0.23	0.52	0.07
			3810	50	0.21	0.49	0.08
29	Aug. 13, 1988	29	3630	--	0.26	0.11	0.01
			3280	--	0.21	0.21	0.04
			3020	--	0.18	0.23	0.05

Fig. 29. Ln-ln plot for ethyne, propane, and n-butane versus ethane for the vertical profile made during mission 30.

the only one to exhibit this negative correlation with altitude (Figure 14). This mission was flown on July 29, 1988, and consisted of two spirals. The first was made over the tundra near Bethel, and the second was made several hours later over the ocean at Bristol Bay, Alaska. The geography and terrain were very similar to that of mission 19 (Figure 15), but the meteorological conditions were quite different. On the day of mission 17, there was an aged, low-pressure system in the area which was fading away as it moved up over eastern Alaska and northwest Canada. One of the final effects of this system was to sweep air from the south and southwest into the sampling region [Shipham et al., this issue].

The altitude profiles of the several hydrocarbons showed only small variations during the two vertical profiles of mission 17, but these changes reflected different tendencies. The ethane concentrations. for which the signal/noise ratio
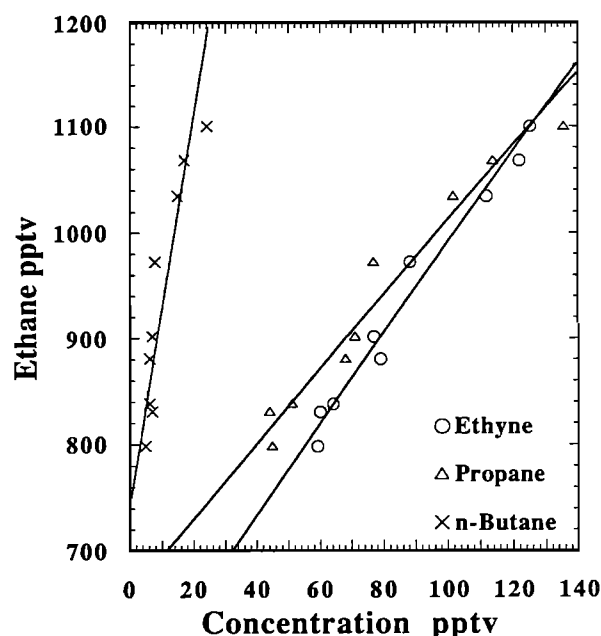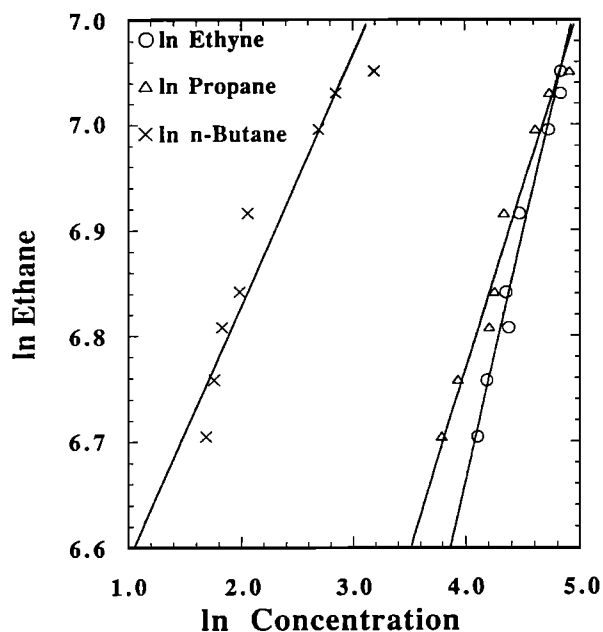
was highest, decreased with increasing altitude for both profiles (Figure 14), from about 800±40 pptv to 710 pptv on the first and 740 pptv to 680 pptv plus an alkane plume at 1500 m on the second. The mixing ratios for ethyne also decreased toward the higher altitudes, but n-butane at generally quite low mixing ratios showed the opposite behavior, with higher values at the higher altitudes. The propane data showed more variation, with several higher values well correlated with apparent excess ethane. These incremental excess propane concentrations were more significant on a percentage basis than similar additions for ethane because the background concentration of the latter was about twelve-fold higher than for propane. These incremental amounts of propane make its underlying correlation with altitude uncertain as to sign, but small in magnitude.

Fig. 28. Ethyne, propane, and n-butane (in pptv) versus ethane for the vertical profile made during mission 30.
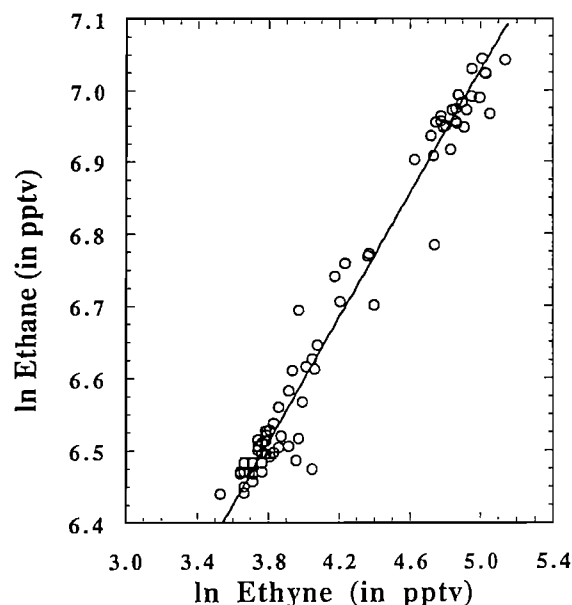

Fig. 30. Correlation of mixing ratios of ethane and ethyne for nonplume air samples of missions 20 and 21.

TABLE 7. Rate Constants for the Reactions of Hydroxyl Radicals With Selected Hydrocarbons
Under Background Tropospheric Conditions (Mission 21)

	Altitude, m							
	200	1000	2000	3000	4000	5000	6000	200*
	Conditions							
Temperature, K	293	285	277	274	268	264	257	302
Pressure, mbar	993	905	801	706	621	544	474	996
	Assumed HO Reaction Rate Constant, $10^{-13} cm^3/molecule\ s$							
C_2H_6	2.58	2.32	2.07	1.99	1.82	1.71	1.52	2.87
C_2H_2	7.92	8.33	8.77	8.91	9.25	9.46	9.89	7.48
C_3H_8	10.8	10.1	9.34	9.07	8.53	8.17	7.56	11.7
C_4H_{10}	24.8	23.9	23.0	22.7	22.0	21.6	20.9	25.8
$k_{C_2H_2}/k_{C_2H_6}$	3.08	3.59	4.23	4.49	5.10	5.54	6.50	2.61
$k_{C_3H_8}/k_{C_2H_6}$	4.20	4.35	4.50	4.57	4.70	4.79	4.97	4.06
$k_{C_4H_{10}}/k_{C_2H_6}$	9.63	10.3	11.1	11.4	12.1	12.7	13.7	8.97

Reaction rate constants from *JPL* [1990] except for n-butane from *Atkinson* [1990].

* Atmospheric conditions for mission 33; all others correspond to the measured temperatures and pressures for mission 21.

Apart from the considerable fluctuation of the carbon monoxide mixing ratio just above and below the top of the PBL, its general trend shown on these spirals was a systematic decrease from 100 ppbv at 150 m above sea level to approximately 90 ppbv at 5000 m. Similarly, methane exhibits a slight but steady decrease from 150 m to the highest sampling altitudes on mission 17 [*Harriss et al.*, this issue (a)].

It is clear from these observations that the air sampled during both spirals of mission 17 was quite different from all other Arctic and sub-Arctic air masses studied during the ABLE 3A project. Significantly, the decrease in the concentrations of NMHC with increasing altitude was accompanied by a unique trajectory indicating that air masses of southeastern origin (i.e., from the North American continent) are quite distinct in character from those that originate over either the Asian continent or the north-central Pacific. Among other possible factors is the likelihood of shorter exposure times to HO radicals at the lowest altitudes.

The only other profile that did not conform to the general pattern of increasing mixing ratio with altitude was made during the final mission (33), on August 17, 1988. The Electra passed over wetlands in the Wallops Island area and provided both the southernmost vertical sounding and the air mass with the highest NMHC concentrations sampled during the entire project. Altitude versus mixing ratio plots for ethane, ethene, ethyne, propane, propene, n-butane, i-butane, isoprene, i-pentane, n-pentane, and ozone are displayed in Figure 27, indicating a general decrease in mixing ratio with increasing altitude, plus a substantial alkane plume at 2000 m. A strong correlation between ethane and propane ($r^2 = 0.86$) suggests that the air mass was augmented by natural gas emissions. The ethyne/n-butane correlation ($r^2 = 0.92$) and elevated levels of ethene and propene imply strong combination influence. The air mass is further enhanced by local isoprene emissions. The negative correlations of the NMHC species with altitude displayed in Figures 14 and 27 are thought not to be solely the result of enhanced hydrocarbon levels at the surface, because these are coupled to unusually low concentrations in the air mass at the top of the profile.

The air mass encountered above 3 km on mission 33 was found to be particularly low in NMHC and was significantly different from that encountered at similar altitudes two days earlier during mission 30 (Figure 24). For example, the mixing ratios of ethane and ethyne of 884 pptv and 38 pptv, respectively measured at 5300 m during mission 33 were substantially lower than the 1100 pptv of ethane and 125 pptv of ethyne observed two days earlier during mission 30 at the same altitude. In addition, the methane levels observed during the high-altitude portions of missions 30 and 33 were 1660 and 1590 ppbv, respectively [*Harriss et al.*, this issue (a)], and a northern hemispheric methane mixing ratio for methane of only 1590 ppbv is low enough to imply that the air mass was of either stratospheric or tropical origin. The observations of low NMHC mixing ratios alone are consistent with both these possibilities; however, the relatively low in situ ozone data measured in this region [*Gregory et al.*, this issue] (Figure 27) considerably favor the case that the air sampled at high altitudes was of tropical origin. This conclusion is also supported by the available trajectory data [*Shipham et al.*, this issue].

Boundary Layer Measurements

The very high NMHC levels observed at lower altitude (in the PBL) during mission 33 are of interest. With the exception of isoprene and ethane, Table 8 shows that the mixing ratios of each NMHC were less at 135 m than at 330 m (see also Figure 27). Hydrocarbon oxidation in the presence of sufficient NO_x leads to the formation of tropospheric ozone where either the hydrocarbon or the NO_x concentration will be the factor limiting the total ozone production. However, ozone formation in a specific region is more strongly dependent on the reactivity of the hydrocarbons that are present, rather than on the total carbon concentration. This is especially true of isoprene, which is highly reactive toward HO radicals, and thus is a species of particular relevance to localized ozone production. The reaction rate constant for HO with isoprene is about a factor of 100 faster than for propane, so that lifetimes of only an hour or two are typical for the former.

TABLE 8. Observed Mixing Ratios (Mix) and Calculated Relative Hydroxyl Reaction Rates (Rel) for Selected Altitudes on Mission 33 off Chesapeake Bay

	Altitude, m							
	135		330		1970		5320	
	Mix	Rel	Mix	Rel	Mix	Rel	Mix	Rel
Ethane	1660	478	1630	458	3020	757	884	158
Ethene	233	1950	376	3180	181	1600	106	1070
Ethyne	347	259	399	302	143	114	38	35
Propane	690	806	820	942	1040	1110	200	169
Propene	68	1750	100	2610	90	2470	53	1700
n-Butane	465	1200	565	1450	205	503	35	77
i-Butane	173	410	233	549	76	173	0	0
n-Pentane*	112	463	136	558	49	194	(8)[a]	29
Isoprene	1140	112,300	735	73,300	0	0	0	0
Total rate		119,900		83,700		6,920		3,240
Isoprene, %		94		88		0		0
CH_4[b]	1.7×10^6	15,000	1.7×10^6	14,500	1.6×10^6	11,400	1.6×10^6	6,500
CO[b]	1.6×10^5	38,000	1.7×10^5	40,000	1.6×10^5	35,000	1.0×10^5	20,000
NO_x[c]	480		420		35		40	
O_3[d]	106		94		96		57	

Mix, observed mixing ratio of NMHC in pptv; Rel, relative rate of hydroxyl reaction with NMHC = (mixing ratio of NMHC) x (hydroxyl rate constant). (The units are pptv x k (in cm^3 $molecule^{-1}$ s^{-1})$x10^{12}$, but are only useful relative to other entries in the same column. Comparison across rows is not significant without correction for the atmospheric density and the variations in HO concentration, the latter not being measured.)

* Assumes n-pentane at 50% of the n-butane mixing ratio at the two lower altitudes. At the 1970-m altitude, the C_5 mixing ratio was less than half of the n-butane value. Therefore, all of the C_5 peak was assigned as n-pentane.

[a] Below detection limits, but inferred from observed n-C_4H_{10}.

[b] pptv, as measured by $Harriss$ et al. [this issue(a)].

[c] pptv, as measured by $Sandholm$ et al. [this issue].

[d] ppbv, as measured by $Gregory$ et al. [this issue].

A markedly negative correlation of ozone with altitude was observed for mission 33 (Figure 27). Of the hydrocarbons assayed, only isoprene was correlated with the high ozone concentrations observed below 1000 m. In order to establish whether this excess ozone could be the result of isoprene oxidation, the relative rates of reaction of each hydrocarbon with hydroxyl are calculated at selected altitudes and are given in Table 8. The mixing ratios of all the measured NMHC are also given for the samples, together with the corresponding concentrations of CH_4, CO, O_3, and NO_x measured by other research groups on the flight. Table 8 shows that the hydroxyl reaction rate above the PBL on mission 33 was dominated by reaction with CO and CH_4, with only 10-20% attributable to the reactions with NMHC compounds. On the other hand, within the PBL, the HO reactivity of the NMHC rises steeply, with about 90% of the increase caused by isoprene. In this case, the total reactivity is dominated by isoprene, with CO and CH_4 still playing important roles, while the reactivity of all of the other low molecular weight NMHC compounds has only a minor additional effect.

This profile also was modeled by I.S.A. Isaksen (personal communication, 1991) using a 2-dimensional channel model for the eastern United States with conditions corresponding as closely as possible to the observations of temperature, time of day, humidity, boundary layer depth, etc., for two scenarios, the only difference being the presence of high or very low isoprene emissions. The results of this modeling are shown in Figure 31, and they indicate that isoprene does make a significant difference to the ozone distribution, increasing it by almost 25 ppb in the boundary layer. It is, however, important to note that the particular air mass sampled during mission 33 contained NO_x concentrations that were in excess of 400 pptv (Sandholm et al., this issue). Although these concentrations are much higher than in the free troposphere, they are low enough that ozone production was still hydrocarbon limited.

By contrast, missions 20 and 21 were both flown in the sub-Arctic region near Bethel. Both missions consisted of two profiles each; the first was a descent over a boreal forested area, the second was an ascent over the Kuskokwim wetlands with only 6 hours separating the two pairs of profiles. Plots of altitude versus mixing ratio for ethane, ethyne, propane, n-butane, isoprene, and ozone for the two profiles of mission 20 are displayed in Figure 16, while the corresponding plots for mission 21 are shown in Figure 17. The concentrations of ethane, ethyne, and propane within the PBL, which was well mixed, exhibited no statistically significant variation with
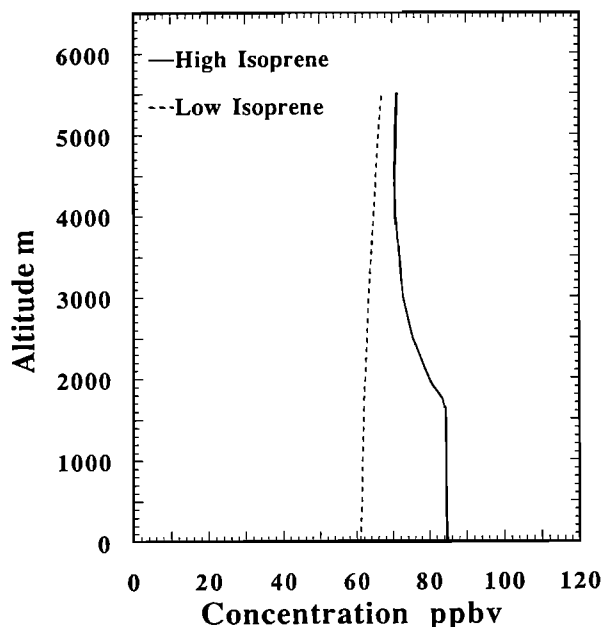
Fig. 31. Modeled vertical profile of ozone under conditions corresponding to mission 33 in the case of high and low isoprene emissions (I. S. A. Isaksen, personal communication, 1991).

altitude or in the transition from the boreal forest region to the wetland area.

These missions were interesting in terms of the well-defined biomass burning plumes, and also because the boreal forest area overflown on the descending spirals was populated by known isoprene emitters, such as white and black spruce, paper birch, balsam poplar, and aspen [*Rasmussen*, 1970]. Figures 16 and 17 show that the mixed samples collected in this forest region contained isoprene mixing ratios between 400 and 550 pptv at altitudes up to 300 m on mission 20 and up to about 1000 m on mission 21. By contrast, the samples collected at similar altitudes in the wetlands area near Bethel exhibited isoprene mixing ratios in the 50-120 pptv range. This observation is consistent with the fact that the moist tundra regions contain a much lower population of isoprene emitters.

The first spiral, made at 1000 local time over the boreal forest, yielded an isoprene profile which shows detectable concentrations of isoprene up to approximately 2000 m. Six hours later, during mission 21, isoprene was observed up to 2500 m. The available meteorological data for missions 20 and 21 indicate that the top of the mixed layer was between 1800 and 2000 m for mission 20 and between 1800 and 2400 m during mission 21. These observations are consistent with the fact that isoprene, with an atmospheric lifetime of an hour or two during daylight hours, is not expected to persist long enough to escape the PBL and be observed in the free troposphere. This is a good example of how vertical profiles of short-lived gases released at the surface can be used to corroborate meteorological analyses.

In addition, and notably unlike mission 33, Figures 16 and 17 show no ozone enhancement caused by the oxidation of isoprene. In fact, *Gregory et al.* [this issue] concluded that the fast reaction of isoprene with ozone was an efficient sink for ozone in the region of boreal forests. The major difference in the near-surface chemistry of missions 20 and 21 versus mission 33 lies not in the isoprene concentrations which are quite elevated in the PBL in all flights, but in the greatly enhanced NO_x levels in mission 33. The rate-determining step for formation of tropospheric ozone from isoprene emissions

involves the participation of the NO_x compounds in the reaction scheme.

CONCLUSIONS

The Arctic and sub-Arctic areas explored during ABLE 3A were significantly influenced by long-range transport of NMHC from distant source regions. Trajectory analysis suggests that the only high-latitude air masses that did not conform to the normally observed profiles were of a southern origin. Plume enhancement of some or all of the measured NMHC were observed on more than half of the 33 missions flown during this GTE project. The usual summer vertical profile of reactive hydrocarbons in these high latitudes has elevated concentrations at high altitudes, with mixing ratio variations largely controlled by hydroxyl radical reactions. Because of the very dry conditions prevailing during the project, wildfires were widespread and were established as a significant source of numerous NMHC. Biomass burning emission factors relative to ethane were established for ethyne (0.38±0.04) and propane (0.08±0.03). Activities associated with oil drilling are a probable source of the enhanced levels of alkanes that were observed as much as 300 km northeast of Prudhoe Bay, Alaska. Isoprene emissions from boreal forest regions of the Yukon Valley dominate local photochemical HO reactions. Biogenic production of isoprene in eastern Virginia, coupled with long-range transport of anthropogenically produced nitrogen oxides from urban areas, is responsible for significant production of regional tropospheric ozone.

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