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## Factors influencing atmospheric composition over subarctic North America during summer

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Elevated concentrations of hydrocarbons, CO, and nitrogen oxides were observed in extensive haze layers over northeastern Canada in the summer of 1990, during ABLE 3B. Halocarbon concentrations remained near background in most layers, indicating a source from biomass wildfires. Elevated concentrations of C<sub>2</sub>Cl<sub>4</sub> provided a sensitive indicator for pollution from urban/industrial sources. Detailed analysis of regional budgets for CO and hydrocarbons indicates that biomass fires accounted for ≈ 70% of the input to the subarctic for most hydrocarbons and for acetone and more than 50% for CO. Regional sources for many species (including CO) exceeded chemical sinks during summer, and the boreal region provided a net source to midlatitudes. Interannual variations and long-term trends in atmospheric composition are sensitive to climatic change; a shift to warmer, drier conditions could increase the areas burned and thus the sources of many trace gases.

### INTRODUCTION

Industrial and urban emissions provide massive inputs of pollutants to boreal and subarctic latitudes in winter and spring; rates for deposition and degradation are slow, and high pollutant concentrations are observed [Rahn, 1981; Barrie *et al.*, 1985; Barrie, 1986; Stonehouse, 1986; Bottenheim *et al.*, 1986; Li and Winchester, 1990]. Pollutant concentrations are much lower during summer [Harriss *et al.*, 1992]. Emissions from midlatitude sources appear to be efficiently scavenged during summer, and the influence of long-range transport is relatively weak. The composition of the atmosphere is most strongly affected by regional emissions, particularly boreal fires.

This paper summarizes observed concentrations of hydrocarbons, halocarbons, CO, and nitrogen oxides in the remote troposphere of subarctic central and eastern Canada in 1990, during the Arctic Boundary Layer Expedition (ABLE 3B). We use data for selected halocarbons and hydrocarbons to characterize emissions from urban/industrial sources and from wildfires, providing information on emission ratios for key species on the regional scale. We quantitatively assess the relative contributions of these sources to regional budgets, using a photochemical model. Wildfires appear to provide a major source for these gases during summer, as suggested earlier by data from Alaska [Blake *et al.*, 1992; Harriss *et al.*, 1992; Wofsy *et al.*, 1992]. The subarctic is a net global source for many trace species, reversing the source-sink relationships observed in other seasons.

### OBSERVATIONS

Hydrocarbons and halocarbons (including C<sub>2</sub>Cl<sub>4</sub>) [Blake *et al.*, this issue] were determined in grab samples, 40 - 50 electropolished canisters filled on each 5-hour flight, and analyzed in the laboratory using gas chromatography. Sample acquisition required 30 - 60 s. Samples were preferentially acquired during vertical profiles and in haze layers. Other species were measured continuously on board, including CO (averaged into 10-s intervals [Harris *et al.*, this issue, a]) and NO<sub>y</sub> and NO<sub>x</sub> (averaged into 90-s intervals [Sandholm *et al.*, this issue]). Samples for peroxyacetyl nitrate (PAN) and acetone ((CH<sub>3</sub>)<sub>2</sub>CO) and a second determination of C<sub>2</sub>Cl<sub>4</sub> were acquired over ≈ 60 s at ≈ 2 min intervals and analyzed using an on-board gas chromatograph [Singh *et al.*, this issue].

Tetrachloroethylene represents a sensitive indicator for anthropogenic emissions. Its lifetime (≈ 90 days in summer) is long enough to allow transport on a hemispheric scale but short enough to maintain a low background concentration. When air with elevated concentrations of CO and hydrocarbons was sampled, the anomaly could be attributed to long-range transport of pollution if concentrations of C<sub>2</sub>Cl<sub>4</sub> were also elevated, and vice versa. Concentrations of C<sub>2</sub>Cl<sub>4</sub> measured by the on-board chromatograph and in grab samples were in harmony at high concentrations (> 20 parts per trillion by volume (pptv)), but disagreed at low concentrations, reflecting different sampling times and possibly measurement and/or sampling artifacts. Correlations between C<sub>2</sub>Cl<sub>4</sub>, other halocarbons, and hydrocarbons were preserved in the grab samples at low concentrations, as shown in Figure 1, and we therefore focus on these measurements in our analysis.

Three areas were sampled extensively: Hudson Bay lowlands (HBL), Ontario (flights 4 - 9), central Labrador and Quebec (LBQ), and eastern Labrador (ELO) with adjacent coastal areas (flights 11 - 20). These areas were selected to allow study of atmospheric composition for a range of biomes, dry and fire prone in HBL, somewhat wetter and cooler in LBQ and ELO, both remote from large urban complexes. Identifiable smoke plumes from large fires were sampled over HBL on flights 4, 6, 7, and 8. Industrial/urban pollution was sampled twice over Canada (flights 10 and 16) and over the East Coast of the United States (flights 21 and 22), providing a signature for urban/industrial emissions.

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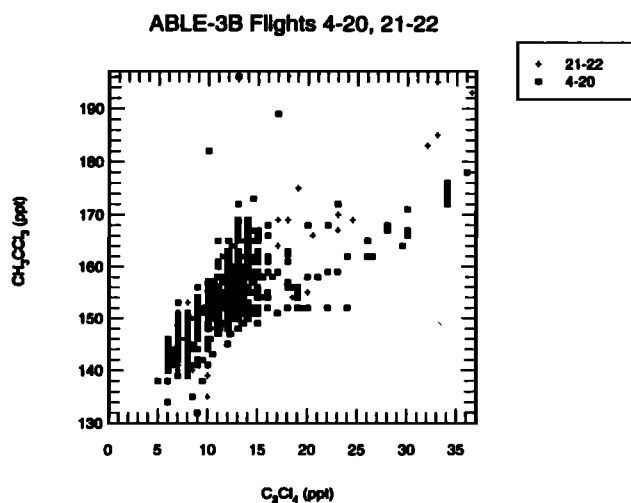


Fig. 1. Concentrations of  $C_2Cl_4$  and  $CH_3CCl_3$  observed in northeastern Canada (flights 4-20, squares) and over the East Coast of the United States (Maine - Virginia, flights 21 and 22, pluses).

#### Characteristic Urban/Industrial Emissions Ratioed Versus $C_2Cl_4$

Concentrations of  $C_2Cl_4$  were steady, 11-12 ppt, for most flights. Lower values were observed in air with tropical character (e.g., anomalously low CO) on flights 14-16 [Harriss *et al.*, this issue, *b*]. Enhancements were observed simultaneously with

elevated concentrations of other halocarbons and nonmethane hydrocarbons (NMHCs), as shown in Table 1, indicating urban/industrial pollution. Variance ratios were notably uniform relative to  $C_2Cl_4$ , within  $\pm 30\%$  in most cases. Directly over source regions, ratios for  $CO:C_2Cl_4$  were systematically lower, possibly reflecting incomplete oxidation of short-lived hydrocarbons that ultimately produce CO (see Figure 2).

Observations on flight 10 imply remarkably rapid advection of pollutants from midlatitude urban/industrial sources into the subarctic, confined largely within the planetary boundary layer (Figure 3). Variance ratios for pollutant species, relative to  $C_2Cl_4$ , were similar to observations over the source regions (flights 21 and 22; see Table 1), including species such as  $C_5H_{12}$  and  $NO_x$ , with lifetimes as short as  $\sim 5$  days. According to Bakwin *et al.* [this issue], significant quantities of  $NO_x$  and other pollutants were transported to Schefferville ( $55^\circ N$ ) within the boundary layer during the summer of 1990. However, Table 1 shows that this mode of transport is inefficient for some species, for example for gases that deposit to the surface, such as  $NO_y$  or  $O_3$ , or that decompose at low altitudes, such as PAN. For example, variations of  $NO_y$  and PAN are either uncorrelated with  $C_2Cl_4$  or variance ratios are inconsistent between U.S. and Canadian flights, reflecting the influence of surface deposition and atmospheric transformations.

Industrial/urban emissions north of  $45^\circ$  latitude, especially in Europe, are expected to contribute significantly to ambient concentrations of  $C_2Cl_4$  and CO in subarctic Canada. Source inventories for Europe (including the former USSR) indicate

TABLE 1. Variance Ratios Relative to  $C_2Cl_4$  (mol/mol)

Species	Mean Ratio (Pollution) $\alpha$	Flight 21 <sup>a</sup>		Flight 22 <sup>a</sup>		Flight 16 <sup>b</sup>		Flight 10 <sup>c</sup>	
		Ratio	$r^2$	Ratio	$r^2$	Ratio	$r^2$	Ratio	$r^2$
$CO^d$	3.80	2.96	0.45	4.09	0.77	8.90	0.63	3.80	0.87
$C_2H_2$	9.1	8.0	0.72	10.6	0.87	11.7	0.54	10.8	0.91
$C_2H_6$	31 <sup>e</sup>	43.5	0.80	110.5	0.52	14.8	0.22	19.3	0.67
$C_3H_8$	10 <sup>e</sup>	12	0.71	45	0.50	7.3	0.63	8.4	0.67
$n-C_4H_{10}$	3.7	2.3	0.86	4.6	0.62	3.7	0.73	4.2	0.67
$i-C_4H_{10}$	2.1	1.6	0.89	2.5	0.60	2.3	0.71	2.0	0.52
$n-C_5H_{12}$	1.6	1.2	0.93	1.5	0.46	2.0	0.69	1.9	0.85
$C_6H_6$	4.1	2.7	(0.22)	3.4	0.45	4.7	0.35	4.2	0.86
$C_7H_8$	2.1	-	note <sup>f</sup>	1.3	0.40	1.8	0.53	2.4	0.76
$CH_4^d$	3.50	3.86	0.63	3.10	0.75	3.60	0.75	2.80	0.83
$(CH_3)_2C=O$	65	48	0.76	88	0.71	61	0.97	ND	
$CHCl_3$	0.14	0.14	0.70	0.11	0.75	0.18	0.78	0.14	0.8
$CH_3CCl_3$	1.7	1.91	0.87	1.49	0.51	1.32	0.88	1.28	0.83
CFC-113	0.29	0.29	0.60	0.20	(0.13)	0.16	0.46	0.41	0.54
CFC-11	0.50	0.87	0.46	-	note <sup>f</sup>	0.31	0.32	0.33	0.30
$NO_y$	41	25.6	0.50	57.0	0.62	15	(0.16)	-	note <sup>f</sup>
$NO_x$	4.3	6.2	0.73	3.5	0.39	-	note <sup>f</sup>	3.4	0.62
PAN		17.6	0.40	16.8	0.68	-	note <sup>f</sup>	-12.8	0.60

Units, mol/mol, except for CO and  $CH_4$  which are 1000 mol/mol. Correlation coefficients ( $r^2$ ) in parentheses are marginally significant, not used to compute means or medians.  $\alpha$ , ratio to  $C_2Cl_4$  used in Table 5.

<sup>a</sup>Data were selected to eliminate near-source values by rejecting concentrations of  $C_2Cl_4 > 25$  ppt on flight 21, or altitudes  $< 2$  km on flight 22.

<sup>b</sup>Marine boundary layer.

<sup>c</sup>Within 100 km of Schefferville.

<sup>d</sup>Units are mol/mol  $\times 1000$ .

<sup>e</sup>Median value (see text).

<sup>f</sup>Insignificant correlation.

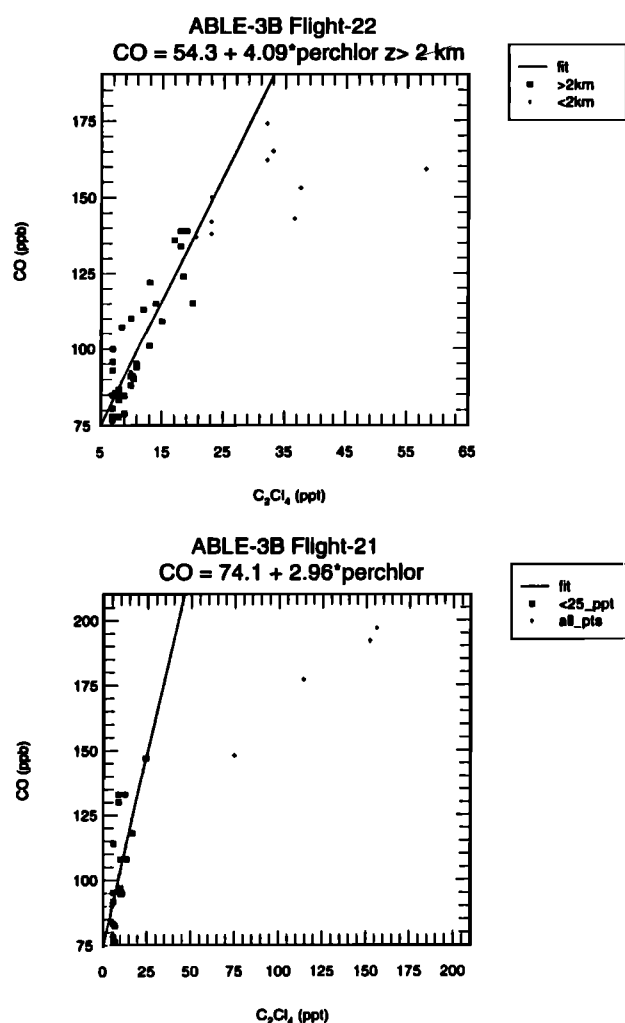


Fig. 2. Concentrations of  $C_2Cl_4$  and CO observed over the East Coast of the United States (Maine - Virginia, flight 22): altitudes > 2 km, squares ; < 2 km, pluses.

similar emission ratios as in North America and Canada (Table 2a), and emission inventories for both continents are consistent with observed atmospheric variance ratios (compare Tables 1 and 2b). The notable exception is  $(CH_3)_2CO$ , for which photooxidation of hydrocarbons dominates direct emissions [Singh *et al.*, this issue; see discussion below]. The consistency of observed enhancement ratios between flights and the harmony between emission inventories and ratios of concentration enhancements in the atmosphere provides evidence that the variance ratios in Table 1 are characteristic of industrial/urban sources.

Data for  $C_2H_6$  and  $C_3H_8$  over the United States show anomalies in which concentrations of both are markedly enhanced, without comparable elevation of  $CH_4$  or other hydrocarbons (Figures 4a, 4b, 4c). A fuel source such as liquified petroleum gas (LPG) may be responsible. Long term measurements of hydrocarbons in rural New England also suggest disparate sources of  $C_2H_6$  and  $C_3H_8$ , especially in winter when  $C_2H_6:C_2H_2$  ratios are highly variable (A. H. Goldstein, private communication, 1993). Variance ratios of most other hydrocarbons are more uniform, relative to  $C_2H_2$ , in all seasons. Therefore in the present paper we use emission ratios from Table 1, relative to  $C_2Cl_4$ , neglecting anomalous points for  $C_2H_6$  and  $C_3H_8$ . Thus we neglect these fuel-related sources and

may slightly underestimate emissions of  $C_2H_6$  and  $C_3H_8$  from urban/industrial regions.

#### Characteristic Emission Ratios for Tundra/Taiga Fires Versus $C_2H_2$

Hydrocarbon emissions from biomass fires and ratios to CO and  $C_2H_2$  are summarized in Table 3a, determined from haze layers with unperturbed halocarbon concentrations (flights 4, 6-9, 11; see Figure 5 for examples). Haze layers sampled on flights 18 and 19 (Table 3a, bottom panel) showed enhancements for long-lived species similar to those in flights 4, 6-9, and 11, but no enhancement of shorter-lived hydrocarbons. These haze layers had apparently aged long enough for short-lived species to be removed by photochemistry and for significant quantities of  $(CH_3)_2CO$  to be generated.

The ratio  $C_2H_2:CO$  was remarkably consistent among flights (e.g., Figure 5). Hydrocarbon/CO ratios closely matched laboratory observations from smoldering combustion [Lobert *et al.*, 1991], as observed for Alaskan fire emissions [Wofsy *et al.*, 1992; Blake *et al.*, 1992]. With the notable exception of methane,

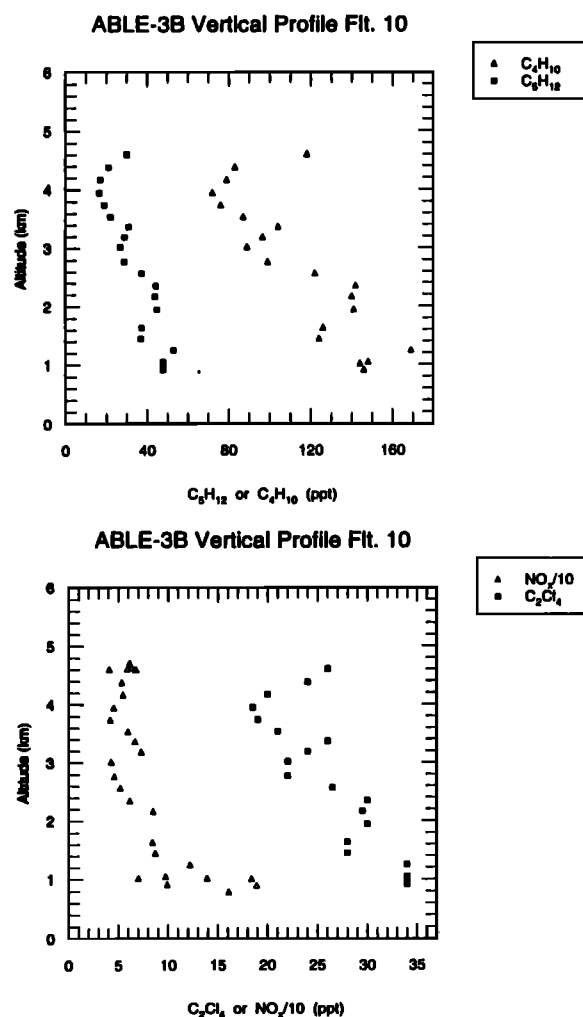


Fig. 3. (a) Vertical profiles of short-lived hydrocarbons ( $n-C_4H_{10}$ ,  $C_5H_{12}$ ) and (b)  $NO_x$  and  $C_2Cl_4$  on flight 10. Strong inputs of short-lived species was reflected in enhanced concentrations relative to background levels, throughout the column 0-6 km. Largest enhancements were observed at the lowest altitudes, indicating rapid low-level advection of pollutants from source regions to the south.

TABLE 2a. Industrial/Urban Sources of  $C_2Cl_4$  and CO

	Region		Units
	USA+Canada	Europe (E+W)	
<i>Emission Rates</i>			
$C_2Cl_4^a$	154	293	kt/yr
CO <sup>b</sup>	77	161	Mt/yr
<i>Emission Ratios</i>			
From inventories <sup>a,b</sup>	3000	3200	mol/mol
From ABLE3B data	3800	-	mol/mol

<sup>a</sup>European Chlorinated Solvent Association [1992]; P. Midgey (private communication, 1992).

<sup>b</sup>NAPAP, 1985; D. Jacob, J. Logan (private communication, 1992).

TABLE 2b. Anthropogenic Emission/Enhancement Ratios Relative to CO  $10^{-3}$  mol/mol

Species	Emission Ratio NAPAP	Arctic Enhancement Table 1 (Range)
$C_2H_2$	3.6	2.4 (2-3.1)
$C_2H_6$	4.8	8.1 (3.7-30)
$C_3H_8$	4.5	2.6 (1.9-11)
$(CH_3)_2CO$	0.8	17.1 (12-23)

NAPAP, National Acid Precipitation Assessment Program.

emission ratios for most hydrocarbons are remarkably similar, relative to CO or  $C_2H_2$ , from biomass fires in a wide range of environments, including tundra, taiga, midlatitudes, and the tropics (see Table 3b). It appears that smoldering combustion provides the dominant source for emissions of these reduced gases, even though the fraction of fuel consumed in smoldering varies considerably, as indicated by the CO/CO<sub>2</sub> ratio [cf. Laursen *et al.*, 1992, Lobert *et al.*, 1991]. Emission ratios for methane are much higher in boreal fires than in fires at midlatitudes [Laursen *et al.*, 1992] or in the tropics [Andreae *et al.*, 1988], reflecting release of biogenic methane from peat soils in boreal wildfires (Table 3b). Emissions of NO<sub>x</sub> are much lower than in most other biomass combustion or in pollution, reflecting

the prevalence of smoldering combustion; the associated low NO<sub>x</sub>/hydrocarbon ratio is responsible for the negligible rates of ozone photochemical production observed in boreal haze layers [Jacob *et al.*, 1992].

In the discussion below, we use concentrations of  $C_2H_2$  and the ratios from Table 3a to assess hydrocarbon inputs from biomass fires. The relatively large emission ratios for  $(CH_3)_2CO$  were taken from Table 3b, representing aged haze layers to account for secondary production from oxidation of labile olefins (e.g., propene). The observed variance ratio for  $C_2H_2:C_2Cl_4$  from Table 1 was employed to account for input of  $C_2H_2$  from by pollution sources (for flights with enhancements of  $C_2Cl_4$ ). We selected  $C_2H_2$  as the index species, instead of CO, to preserve correlations

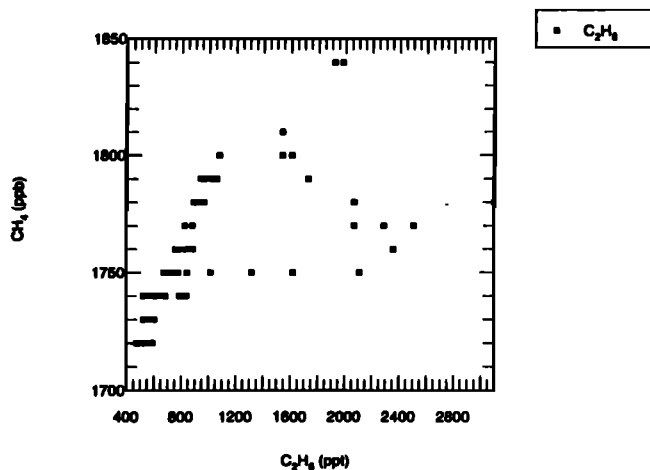
ABLE-3B  $C_3H_8 = -189 + .45 \cdot C_2H_6$   $r^2 = .85$  21&22

Fig. 4a. Relationships between concentrations of  $C_2H_6$  and  $CH_4$  over the East Coast of the United States, flights 21 and 22. Note the strongly deviant samples with greatly enhanced  $C_2H_6$ .

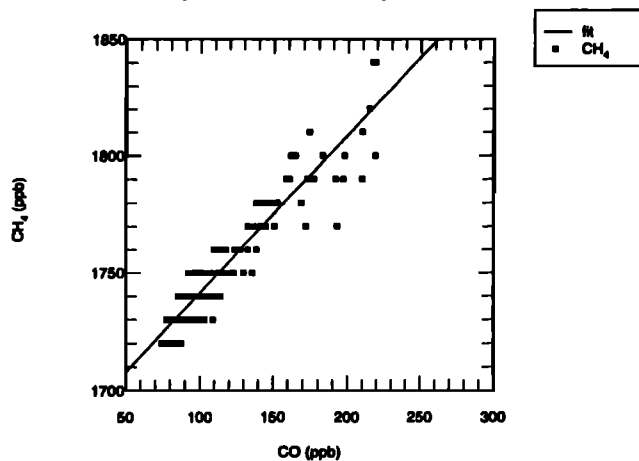
ABLE-3B  $CH_4 = 1674 + .675 \cdot CO$   $r^2 = .88$  21&22

Fig. 4b. Relationships between concentrations of CO and  $CH_4$  over the East Coast of the United States, flights 21 and 22. Note the absence of deviant samples evident in Figure 4a.

ABLE-3B C3H8 = -189 + .45 \* C2H6 r^2 = .85 21 & 22

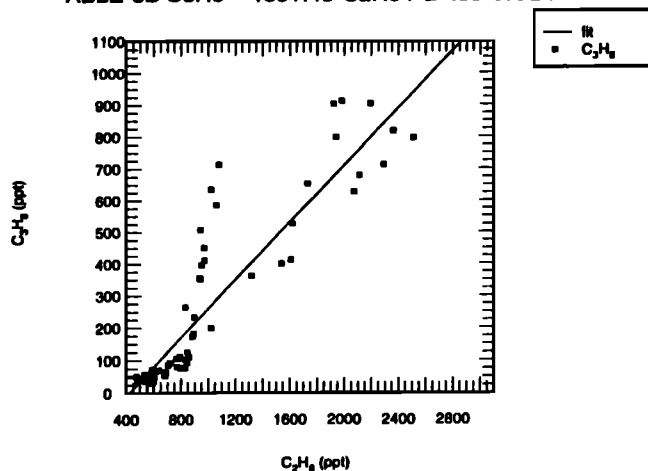


Fig. 4c. Relationships between concentrations of C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> over the East Coast of the United States, flights 21 and 22. The deviant samples with enhanced C<sub>2</sub>H<sub>6</sub> (Figure 4a) are enhanced also in C<sub>3</sub>H<sub>8</sub>, consistent with a natural gas release.

among species from the grab samples. In all of the measurements reported here, in ABLÉ 3A [Wofsy *et al.*, 1992], and in Harvard Forest (A. H. Goldstein, private communication, 1993), CO and C<sub>2</sub>H<sub>2</sub> are strongly correlated with uniform proportionality coefficient.

Background Concentrations

The background concentration is the characteristic value in the region, upon which anomalies reflecting local inputs or losses, or unusual transport events may be superimposed. The inputs, outputs, and chemical sources and sinks for a gas in a defined geographical region determine the regional budget. Both concepts are defined unambiguously for species with small spatial variance; neither is well defined for gases with short lifetimes and concentrated sources, since observed concentrations reflect particular circumstances of dilution, advection, and chemical reactions occurring after emission. The present analysis focuses

on gases with lifetimes of 1-12 weeks, long enough to establish a generally uniform background in the subarctic but short enough so that regional background concentrations are regulated significantly by chemical losses in the region.

Careful statistical analysis of observed concentrations is required in order to define regional background concentrations. For example, consider the cumulative distribution functions for CO and C<sub>2</sub>H<sub>2</sub> concentrations on plotted in Figure 6a for flights 4-20. Here we employ probability axes, where normally distributed data fall on a straight line and ±1σ corresponds to ± 1 quantile of standard normal. More than 50% of the CO observations lie within ±15% of the median, implying that the median of the aircraft observations represents a suitable background concentration. Anomalous high concentrations (> 1 standard quantile) represent primarily samples in haze layers.

For C<sub>2</sub>H<sub>2</sub> (lifetime ~17 days), the cumulative probability plot is curved at the median (Figure 6a), a notably different distribution than for C<sub>2</sub>H<sub>2</sub>. Grab samples were acquired preferentially in haze layers, accounting for 40-50% of the samples, in contrast to the continuous measurements of CO, and the distribution reflects this bias. There may be a nonzero background concentration for n-C<sub>4</sub>H<sub>10</sub> (lifetime 5 days), but the median concentration for C<sub>5</sub>H<sub>12</sub> (lifetime 4 days) was ≈0 and the regional budget is evidently not well defined (Figure 6b).

Background concentrations for species measured in grab samples were derived by examining the subset of grab samples with corresponding CO concentrations within ±20% of median CO, exploiting the more representative sampling for CO. We adopted the trimmed mean (average excluding the highest and lowest 10%) of this subset to define background concentrations; other conditional selection procedures yielded indistinguishable results (Table 4). As expected, background concentrations were notably lower than means of all grab samples and slightly lower (5-10%) than corresponding medians.

Estimates for changes in background concentrations during the mission are needed for the budget analysis. Only a rough determination is possible due to the limited geographic area covered and the bias in selecting grab samples. Figure 7 shows the tenth percentile measurement for CO, C<sub>2</sub>H<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub> for each flight in the subarctic. Flight 10 sampled grossly polluted air, and flights 14-16 were affected by an unusual influx of tropical air [Shipham *et al.*, this issue; Anderson *et al.*, this issue; Harriss *et al.*, this issue, b]. Data for CO from flights 4-9 and 17-20 indicate a decline of 5-6 ppb during the 28 days of the mission, approximately the seasonal change expected for CO in the subarctic over the period (J. A. Logan, private communication, 1993). Even the 10th percentile of data from the smaller set of grab samples appears to be affected by biomass fires on Flights 6-9. We adopt the difference between flights 4 and 5 and 17-19 as an estimate of the change in background concentrations over the period; the corresponding rates of change ((Δ[i]<sub>0</sub>/Δt) for species i) are shown in Table 5.

Figures 8 and 9 show meridional gradients for a variety of gases above the boundary layer (> 4 km) during transit flights on ABLÉ 3B and ABLÉ 3A, respectively. Concentrations of most species were higher in the subarctic than at midlatitudes during both missions for halocarbons and hydrocarbons but not for nitrogen oxides. This surprising result is consistent with the budget analysis given below. The latitudinal distribution for halocarbons indicates the influence of both European sources at high latitudes and inputs at midlatitudes from the United States. Boreal biomass fires provide a major source for hydrocarbons and PAN but have relatively little effect on NO<sub>x</sub> or HNO<sub>3</sub> (Table 3).

ABLE-3B Flts 4 & 6/ fire plumes

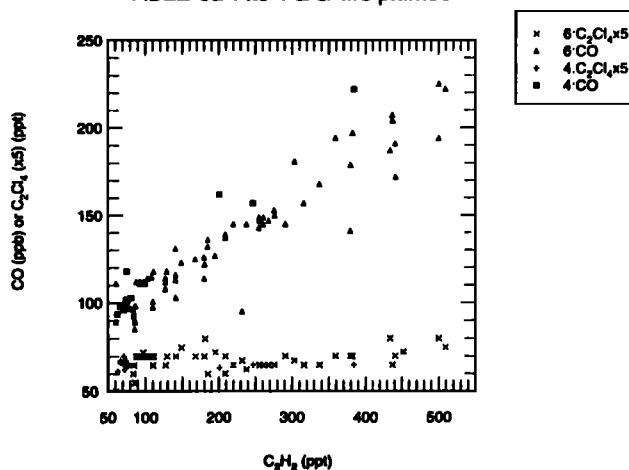


Fig. 5. Fire plumes observed on flights 4 and 6, showing strong correlations between C<sub>2</sub>H<sub>2</sub> and CO, with no corresponding changes in C<sub>2</sub>Cl<sub>4</sub>. Symbols are: triangle, CO (flight 6); square, (flight 4); cross, C<sub>2</sub>Cl<sub>4</sub> (x5 to expand the scale) (flight 6); plus, (flight 4).

TABLE 3a. Enhancement of Hydrocarbons Relative to CO from Boreal Biomass Burning

Flight	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	i-C <sub>4</sub> H <sub>10</sub>	n-C <sub>4</sub> H <sub>10</sub>	n-C <sub>5</sub> H <sub>12</sub>	n-C <sub>6</sub> H <sub>14</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>
<i>Fresh Haze Layers</i>												
HBL												
04	0.65	2.35	8.38	5.40	1.83	1.30	0.09	0.43	0.21	0.15	1.67	0.77
06	.	3.70	5.08	6.49	.	1.87	0.07	0.31	0.12	0.09	1.57	0.57
07	.	3.44	7.96	6.17	0.82	1.49	0.07	0.45	0.21	0.12	1.81	0.78
08	0.42	2.29	1.02	6.36	0.28	2.55	.	.	.	.	1.16	0.30
09	0.30	2.49	0.61	6.91	.	2.06	0.25	0.63	0.21	.	1.03	.
LBQ												
11	0.32	2.58	0.92	5.85	.	2.34	0.32	0.67	0.20	0.06	1.04	.
Mean	0.42	2.81	.	6.20	.	1.94	.	0.50	0.19	.	1.38	.
±(1σ)	0.14	0.55	.	0.48	.	0.44	.	0.13	0.04	.	0.31	.
β	0.15	1.00	.	2.2	.	0.69	.	0.18	0.068	.	0.49	.
Flight	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	i-C <sub>4</sub> H <sub>10</sub>	n-C <sub>4</sub> H <sub>10</sub>	n-C <sub>5</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	(CH <sub>3</sub> ) <sub>2</sub> CO	
<i>Aged Haze Layers</i>												
18	2.48	.	3.46	.	1.52	.	0.37	.	1.20	.	29	
19	2.00	.	4.40	.	1.74	.	0.51	.	0.65	.	26	

Haze layers with negligible enhancement of C<sub>2</sub>Cl<sub>4</sub>; HBL, Hudson Bay lowlands, Ontario; LBQ, Labrador and Quebec; aged haze layers are discussed by *Browell et al.* [1992] and *Blake et al.* [this issue]. Units, 10<sup>-3</sup> mol/mol, except for CH<sub>4</sub> (mol/mol). Ratios not reported for correlation coefficients < 0.4. β, ratio to C<sub>2</sub>H<sub>2</sub>, used in Table 5. Means assumed ≈ 0 for short-lived, high-variance species.

## REGIONAL BUDGETS OF TRACE SPECIES IN THE SUBARCTIC

The regional mass balance for C<sub>2</sub>Cl<sub>4</sub>, at latitudes > 56°N, may be derived by integrating the mass continuity equation over the volume of the subarctic region, the dividing by the volume to obtain an expression for the mean source of C<sub>2</sub>Cl<sub>4</sub> in the region, P<sub>ind</sub><sup>C<sub>2</sub>Cl<sub>4</sub></sup> (ppt/d),

$$P_{\text{ind}}^{\text{C}_2\text{Cl}_4} = [\text{C}_2\text{Cl}_4]_0 k_{\text{C}_2\text{Cl}_4} [\text{OH}] + \frac{\Delta[\text{C}_2\text{Cl}_4]}{\tau_{\text{ex}}} + \frac{\Delta[\text{C}_2\text{Cl}_4]_0}{\Delta t} \quad (1)$$

where the terms on the right hand side represent regional photochemical loss, net exchange with midlatitudes, and concentration change during the observation period, respectively. Here [C<sub>2</sub>Cl<sub>4</sub>]<sub>0</sub> is the background concentration (cm<sup>-3</sup>), Δ[C<sub>2</sub>Cl<sub>4</sub>]<sub>0</sub> is the change during observation period Δt, k<sub>C<sub>2</sub>Cl<sub>4</sub></sub> is the rate coefficient for reaction of OH with C<sub>2</sub>Cl<sub>4</sub> (1.3 · 10<sup>-13</sup> cm<sup>3</sup> sec<sup>-1</sup>), Δ[C<sub>2</sub>Cl<sub>4</sub>] is the concentration difference between 40 and 60°N latitudes, and τ<sub>ex</sub> is the meridional exchange time (≈ 1 month according to *Crutzen and Gidel* [1983]). The 24-hour mean [OH] concentration during summer for latitudes > 56°N, altitudes 0-6

TABLE 3b. Comparison of ABLE 3B Enhancement Ratios (Versus CO) to Data From Other Experiments

Species	ABLE3A <sup>a</sup>			ABLE2B <sup>b</sup>	ABLE3B			Middle Latitude Fire
	Tundra Fires	BERING Pollution	U.S. East Coast <sup>c</sup> Pollution	Amazon Fires	Taiga <sup>d</sup> Fires	Flight 21 <sup>e</sup> Pollution	Flight 22 <sup>f</sup> Pollution	
CH <sub>4</sub>	0.18	0.41	0.66	0.08	0.42	0.56	0.75	0.04
C <sub>2</sub> H <sub>2</sub>	0.0019	0.0020	0.0017	0.03	0.0028	0.0043	0.0028	0.0026
C <sub>2</sub> H <sub>4</sub>	NA	NA	NA	NA	--	0.0024	0.0005	NA
C <sub>2</sub> H <sub>6</sub>	0.0055	0.0096	0.04	0.007	0.0062	0.0040	0.0014	0.0061
C <sub>3</sub> H <sub>6</sub>	NA	NA	NA	NA	--	0.0002	0.0005	0.0066
C <sub>3</sub> H <sub>8</sub>	0.0008	0.0043	0.015	0.0014	0.0019	0.0047	0.0069	0.0023
n-C <sub>4</sub> H <sub>10</sub>	0.0001	0.0046	NA	NA	0.0005	0.0071	0.0032	0.0073
n-C <sub>5</sub> H <sub>12</sub>	NA	NA	NA	NA	0.00019	0.0020	0.0006	NA
C <sub>6</sub> H <sub>6</sub>	NA	NA	NA	NA	0.0014	0.0019	0.0010	NA
C <sub>7</sub> H <sub>8</sub>	NA	NA	NA	NA	--	0.0029	0.0006	NA
NO <sub>y</sub>	0.0056	0.023	0.008	0.016	0.018	0.025	0.031	0.038
PAN	0.0017	NA	NA	NA	0.0036	0.0076	0.0057	NA

ABLE, Arctic Boundary Layer Expedition. Double hyphens denote insignificant correlation with CO; NA, species not measured.

<sup>a</sup> *Blake et al.* [1992]; *Harriss et al.* [1992]; *Wofsy et al.* [1992].

<sup>b</sup> *Andreae et al.*, 1988.

<sup>c</sup> Coastal Maine to Virginia, anthropogenic pollution.

<sup>d</sup> Flights 4,6,7,8,9,11: haze layers attributed to biomass burning, i.e., with insignificant elevation of C<sub>2</sub>Cl<sub>4</sub>.

<sup>e</sup> Coastal Maine (pollution).

<sup>f</sup> Coastal Virginia (pollution). Forest and brush fires in the United States and Southern Canada, *Laursen et al.* [1992].

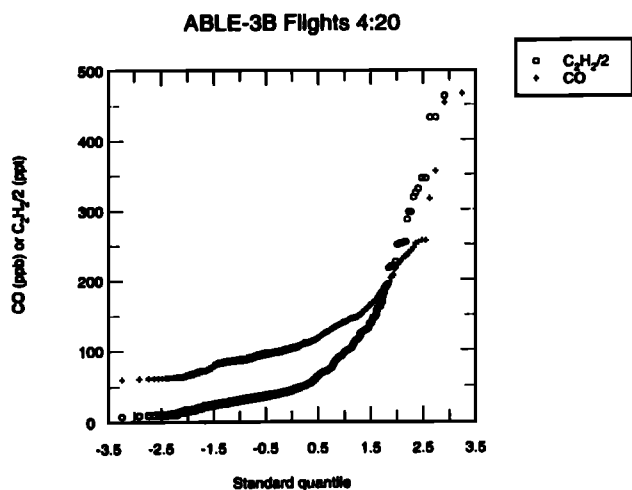


Fig. 6a. Cumulative probability distributions for CO (plus) and  $C_2H_2/2$  (circle, scaled by 1/2), for flights 4-20 in ABLE 3B. The x-axis gives the quantiles of standard normal ( $\pm 1$  denotes  $\pm 1\sigma$ ,  $\pm 2$  denotes  $\pm 2\sigma$ , etc.), such that a Gaussian distribution plots as a straight line.

km, is  $10^6 \text{cm}^{-3} \text{s}^{-1}$  according to model calculations [Spivakovsky *et al.*, 1990].

Table 5 shows our analysis of the budget for  $C_2Cl_4$  for latitudes  $> 56^\circ \text{N}$ . A mean input of 0.2 ppt/d is required to balance losses due to reaction with OH, transport to midlatitudes, and time dependence. This is equivalent to 120 kt/yr or about one fourth of European and North American emissions (Table 2a), a reasonable fraction since most European sources are located between  $48^\circ$  and  $60^\circ \text{N}$ , while most North American sources are south of  $48^\circ$ . Emission rates for  $C_2Cl_4$  at high latitudes evidently exceed rates of consumption due to reaction with OH. The quantity of  $C_2Cl_4$  exported from the subarctic cannot be determined accurately from our data due to the restricted spatial domain of the measurements, but the direction of net exchange is evident.

Table 5 summarizes regional inputs and losses for a number of species, given by

$$\alpha_i P_{\text{ind}}^{C_2Cl_4} + \beta_1 P_{\text{bb}}^{C_2H_2} + P_{\text{in situ}} = [i]_0 k_i [\text{OH}] + \frac{\Delta[i]}{\tau_{\text{ex}}} + \frac{\Delta[i]_0}{\Delta t} \quad (2)$$

where  $\alpha_i$  is the mean variance ratio for pollutant  $i$  from Table 1;  $\beta_1$

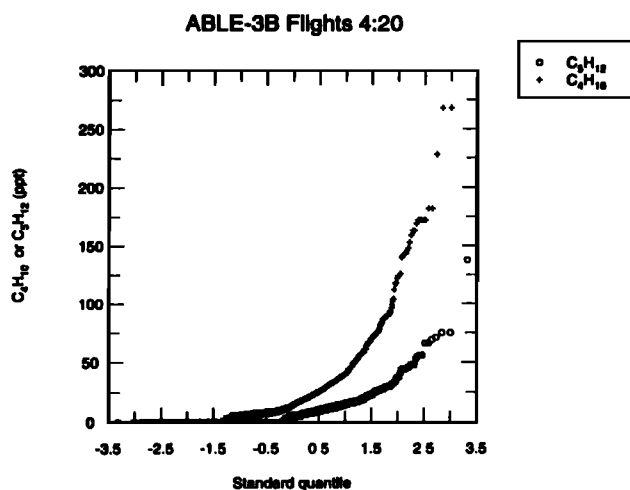


Fig. 6b. Same as Figure 6a, for  $n\text{-C}_4\text{H}_{10}$  (plus) and  $C_5\text{H}_{12}$  (circle) (ppt).

is the mean variance ratio for  $i$  relative to  $C_2H_2$  from Table 3; and  $P_{\text{in situ}}$  represents production of oxidized species such as CO and  $(\text{CH}_3)_2\text{CO}$  from photochemical degradation of hydrocarbon precursors. Photolysis provides an additional loss term in equation (2) for  $(\text{CH}_3)_2\text{CO}$  (24-hour mean rate =  $4.7 \times 10^{-7} \text{s}^{-1}$  at  $60^\circ \text{N}$ , July 15, overhead  $\text{O}_3$  column 330 Dobson Units (DU)).

The input of  $C_2H_2$  from biomass fires,  $P_{\text{bb}}^{C_2H_2}$  ( $= 3.8 \text{ ppt/d}$ ), was obtained by assuming balance in equation (2) for  $i = C_2H_2$  (see Table 5). The source due to biomass fires is about twice as large as inputs from industrial/urban pollution. Since  $C_2H_2$  has a shorter chemical lifetime than  $C_2Cl_4$  (5 times faster reaction with OH), transport and time-dependence terms are considerably smaller for  $C_2H_2$  than for  $C_2Cl_4$ , relative to regional chemical loss.

## DISCUSSION

Inputs of trace species to the region from biomass fires and pollution are computed in Table 5 using observed variances relative to  $C_2Cl_4$  and  $C_2H_2$ , combined with budgets for  $C_2Cl_4$  and  $C_2H_2$  constructed above using model OH distributions [Spivakovsky *et al.*, 1990]. We can test how well the sources thus defined account for observed background concentrations by examining the ratio of terms on the right-hand side in equation (2)

TABLE 4. Background Concentrations Defined by Various Conditional Averages (Flights 4-20)

Species	Mean of all data	Median of all data	Median of $80 < \text{CO} < 120$	Mean of $80 < \text{CO} < 120$	Trimmed Mean $80 < \text{CO} < 120^a$
CO	110 ppb	102	99	99	99
$\text{CH}_4$	1751 ppb	1752	1750	1750	1749
$C_2Cl_4$	12 ppt	12	12	12	12
$\text{CH}_3\text{CCl}_3$	155 ppt	155	154	154	154
$C_2H_6$	807 ppt	758	738	759	745
$C_3H_8$	105 ppt	78	69	83	74
$C_2H_2$	126 ppt	86	80	93	83
$C_6H_6$	56 ppt	39	36	43	38
$(\text{CH}_3)_2\text{CO}$	1040 ppt	1214	1192	1147	1156
$\text{CHCl}_3$	5.1 ppt	5.1	5.1	5.2	5.0
F-113	79.2 ppt	79	79	79	79

<sup>a</sup>Mean of data between 10th and 90th percentiles for data selected as given for corresponding CO concentration (adopted as summertime background concentrations).



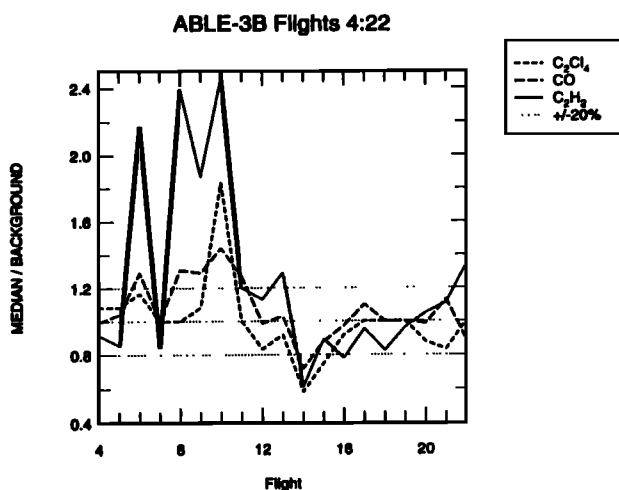


Fig. 7. Concentrations corresponding to the 10 th percentile, for each flight, for  $C_2H_2$  (ppt),  $C_2H_6$  (ppt, scaled by 0.05), and CO (ppb).

to terms on the left-hand side. The mean of these ratios (excluding  $C_2Cl_4$  and  $C_2H_2$ ),  $0.8 (\pm 0.2)$  (column 13 in Table 5), indicates remarkable consistency, with relative contributions of biomass fires and pollution defined to  $\pm 20\%$ . The inferences drawn here about the relative contributions of industrial sources and biomass burning are relatively insensitive to the value adopted for [OH]: apart from usually small terms involving  $\tau_{ex}$  and  $\Delta t$ , all the terms in equation (2) scale with [OH] ( $[i]_0 k_i [OH]$ ,  $P_{ind}^{C_2Cl_4}$  (equation (1)), and  $P_{bb}^{C_2H_2}$ , equation (2) with  $i=C_2H_2$ ).

An independent check on the budget analysis is provided by comparing mean inputs from industrial/urban sources in Table 5 to the emission inventory in Table 2. The industrial source for CO to the subarctic corresponds to annual input of  $85 \times 10^6 t yr^{-1}$ , 36 % of North American and European sources. This appears to be a reasonable value in light of the geographic distribution of sources. Values for  $\alpha_i P_{ind}^{C_2Cl_4}$  appear to correspond to similar fractions of emission inventories for hydrocarbons (Table 2b), except for  $(CH_3)_2CO$  (see below).

The results in Table 5 show that biomass fires provide the dominant contribution to ambient background concentrations of many hydrocarbons in the boreal zone during summer. Biomass fires and methane oxidation are the principal sources of xxx CO; there is a small additional source associated with oxidation of nonmethane hydrocarbons (Table 6a), mainly isoprene. Industrial/urban emissions play a smaller role, contributing 1/4 - 1/3 of total input (except 50% for  $n-C_4H_{10}$ ). Rates for photochemical removal are larger than loss terms associated with time dependence or flux divergence, indicating that the composition of the atmosphere does not depend strongly on antecedent conditions or on exchange with lower latitudes.

We were surprised initially to observe consistent excess concentrations of trace species in the "clean" subarctic, as compared to midlatitudes, above the boundary layer. According to our analysis, this distribution reflects inputs from biomass fires that exceed the regional rate of scavenging by OH. Note that areas burned in the boreal zone in 1988 were about 2 times larger than in 1990 (Table 6b); the latitude gradient for CO was correspondingly larger (Figure 9), providing strong support for this analysis.

TABLE 5. Summertime Sources and Sinks for Hydrocarbons and CO in the Subarctic (ppt/d)

Gas	Concentration	OH Rate, $cm^{-3} s^{-1}$	$\tau_c$ , Days	Sinks		Time Dependence		Transport		Sources			Anthropogenic	
				$k_i [OH] [i]$	hv	$\frac{\Delta [i]}{\Delta t}$	$\frac{\Delta [i]}{\tau_{ex}}$	$\alpha_i P_{ind}^{C_2Cl_4}$	$\beta_i P_{bb}^{C_2H_2}$	CH <sub>4</sub>	NMHCs	Sources/Sinks	Fraction, %	
$C_2Cl_4$	12 ppt	$1.3 \times 10^{-13}$	89	0.13		-0.02	0.09	0.20	0	1.00	100			
$C_2H_2$	83 ppt	$7.2 \times 10^{-13}$	16	5.2		-0.25	0.6	1.8	3.8	1.00	32			
$C_2H_6$	745 ppt	$2.2 \times 10^{-13}$	52	14.1		-3.5	5.5	3.4	8.4	0.73	29			
$C_3H_8$	74 ppt	$9.6 \times 10^{-13}$	12	6.1		-0.2	0.5	1.5	2.7	0.65	36			
$n-C_4H_{10}$	8 ppt	$2.3 \times 10^{-12}$	5	1.6		0	0.17	0.74	0.7	0.81	51			
$C_6H_6$	38 ppt	$1.2 \times 10^{-12}$	9.6	3.9		-0.3	0.6	0.8	1.9	0.64	29			
$(CH_3)_2CO$	1160 ppt	$2.0 \times 10^{-13}$	15.7	20.0	54.1	ND <sup>a</sup>	8.3	13	46.6	0.79	22	5.9 <sup>b</sup>		
CO	105 ppb	$2.2 \times 10^{-13}$	53	2000		-210	760	760	1330	1.17	25	227 <sup>c</sup>		

Numbers in italics denote balances assumed in the budget analysis; budget region  $56^\circ-90^\circ N$  ( $1.1 \times 10^{19}$  mol of air in the troposphere). ND, not determined.  $\alpha$ , molar emission ratio relative to  $C_2Cl_4$  from industrial pollution, Table 1;  $\beta$ , molar emission ratio relative to  $C_2H_2$  from boreal biomass fires, Table 3;  $\tau_c$ , chemical lifetime (days). Mean [OH],  $1 \times 10^6 cm^{-3}$  [Spirakovsky et al., 1990] for July. Reaction rates (at 280°K), from Atkinson [1990];  $\Delta [i] / \tau_{ex}$ , meridional exchange flux;  $\tau_{ex}$  = 30 days assumed; hv denotes photolysis;  $(\Delta [i] / \Delta t)$  denotes the rate of change of background concentration from day 198 → 226 (28 days).

<sup>a</sup> No measurements were obtained on flights 1-13.

<sup>b</sup> Oxidation of  $C_3H_8$  source in this column.

<sup>c</sup> Oxidation of isoprene provides 150 ppt/d, with the balance due to other nonmethane hydrocarbons.

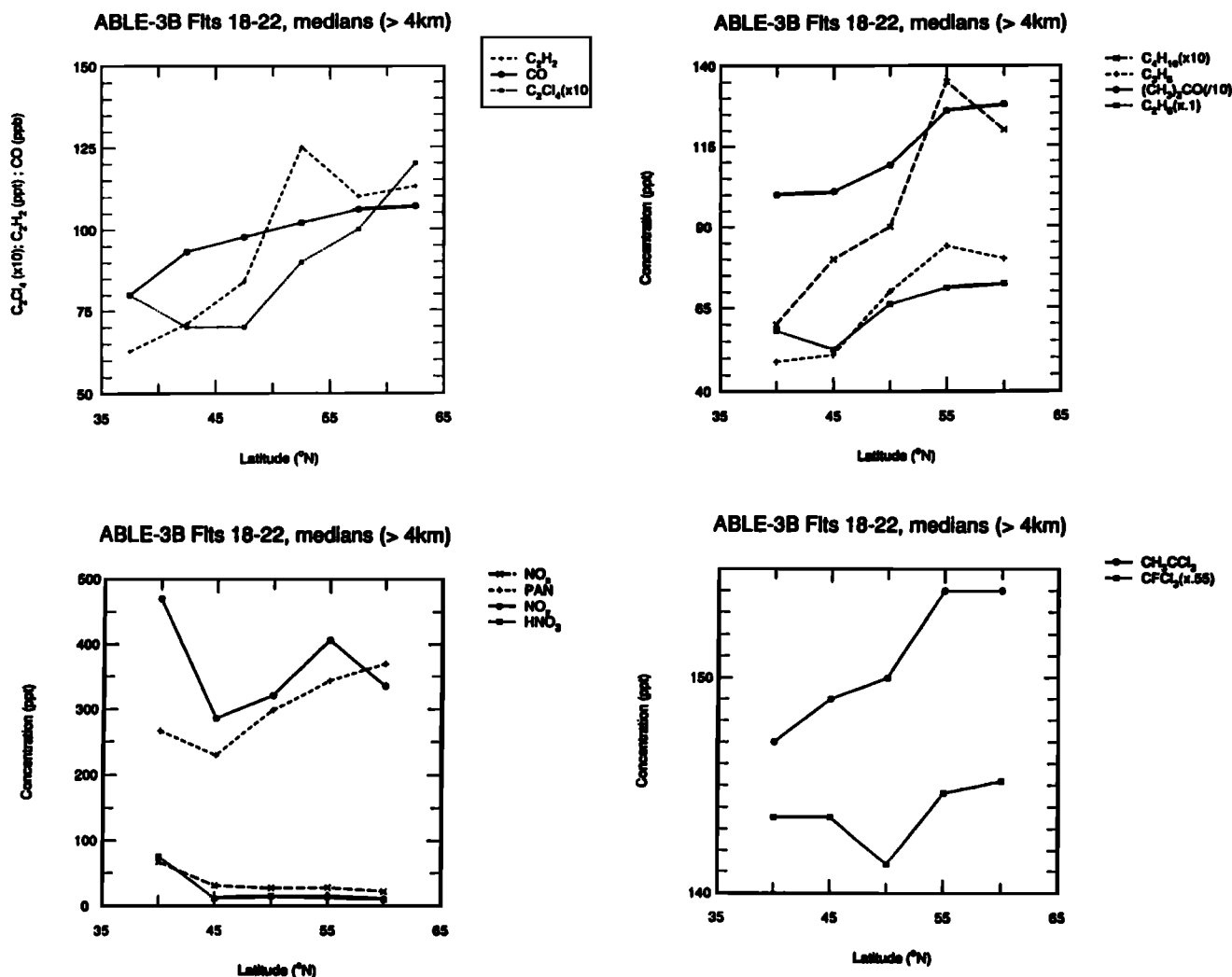


Fig. 8. Meridional distributions of median concentrations of trace gases above 4 km, for flights 18 - 22 in ABLE 3B, from Labrador to Virginia: (a) CO (ppb), C<sub>2</sub>H<sub>2</sub> (ppt), and C<sub>2</sub>Cl<sub>4</sub> (scaled ×10); (b) hydrocarbons (ppt), scaled as shown in the legend; (c) nitrogen oxides (ppb); and (d) long-lived halocarbons (ppt), scaled as shown in the legend.

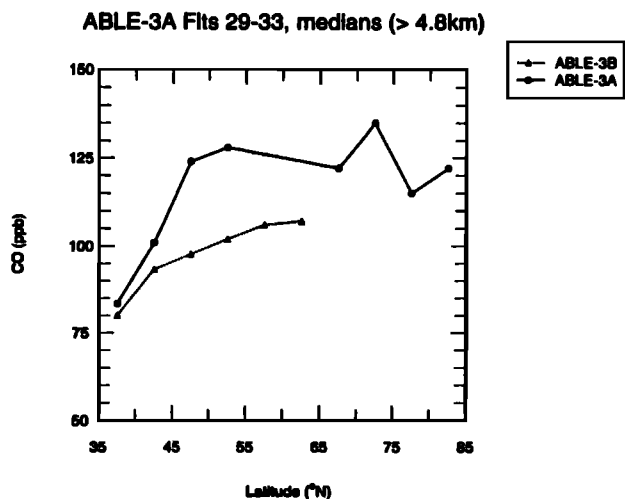


Fig. 9. Median concentrations in 5° latitude bins for CO (ppb): above 4 km, for flights 18 - 22 in ABLE 3B; above 4.8 km for flights 29 - 33 of ABLE 3A. These flights represent latitude transects along the East Coast of North America from Labrador to Virginia.

The global increase of CH<sub>4</sub> concentrations provides an important indirect human influence on CO concentrations. If two thirds of the source from CH<sub>4</sub> were attributed to anthropogenic increases, based on a preindustrial concentration of 0.6 ppm, the ratio of anthropogenic to natural inputs for CO would rise to about 0.6. The human influence might be higher if recent increases in areas burned annually [van Wagner, 1988] are associated with human activities. Hence CO concentrations appear to be strongly perturbed by global anthropogenic changes, even though direct pollution inputs are not large in the region during summer.

Acetone is a major source of acetylperoxy radicals, and it therefore plays an important role in producing PAN from NO<sub>x</sub>. Direct industrial sources are small (Table 2), but observed variance ratios (Table 1) suggest much larger pollution sources. According to Singh *et al.* [this issue], most of the (CH<sub>3</sub>)<sub>2</sub>CO associated with anthropogenic pollution arises from atmospheric oxidation of hydrocarbon precursors. Biomass fires provide a very strong source of (CH<sub>3</sub>)<sub>2</sub>CO in the boreal zone (Table 3 and 5), likely due to secondary production from oxidation of the rich suite of reactive hydrocarbons produced in smoldering combustion

TABLE 6a. OH Removal and Atmospheric Production of CO in the Arctic 56°-90° N Latitude, Entire Tropospheric Column, July

Species	$\int \frac{[\text{OH}][\text{X}]k_x}{10^6} dz \text{ (cm}^{-2}\text{s}^{-1}\text{)}$	CO yield/ Carbon Atom	$\int \frac{P_{\text{CO}}}{10^6} dz \text{ (cm}^{-2}\text{s}^{-1}\text{)}$
C <sub>2</sub> Cl <sub>4</sub>	16	1	31
CHCl <sub>3</sub>	4	1	4
C <sub>2</sub> H <sub>2</sub>	598	0.6	717
C <sub>2</sub> H <sub>6</sub>	1639	0.55	1803
C <sub>3</sub> H <sub>8</sub>	710	0.61	1300
n-C <sub>4</sub> H <sub>10</sub>	345	0.54	745
i-C <sub>4</sub> H <sub>10</sub>	132	0.72	380
n-C <sub>5</sub> H <sub>12</sub>	180	0.53	477
C <sub>6</sub> H <sub>6</sub>	456	0.09	81
C <sub>7</sub> H <sub>8</sub>	488	0.09	88
(CH <sub>3</sub> ) <sub>2</sub> CO	2320	0.67	4663
Isoprene <sup>a</sup>	≈14600	1.15	≈16900
Total NMHC	21490	-	27190
CH <sub>4</sub>	78750	1	78750
Total atmosphere	100240	-	106040
CO	220000	-	-

Yield of CO/molecule from *Altshuller* [1991].

<sup>a</sup>Mean isoprene emission rate, 50°-90°N (D. J. Jacob, private communication, 1992).

TABLE 6b. Annual Areas Burned in Canada

Year	Area (10 <sup>6</sup> ha)	Number of Fires
1988	1.36	10700
1990	0.93	10100
1981-90	2.1 (mean)	
1953-80	1.1 (mean)	
	0.5 (median)	

*Stocks* [1991]; B. *Stocks*, private communication, (1992).

[*Blake et al.*, this issue]. High (CH<sub>3</sub>)<sub>2</sub>CO concentrations associated with biomass fires could play a crucial role in regional NO<sub>x</sub> chemistry [*Jacob et al.*, 1992; *Singh et al.*, 1992], promoting preservation of reactive nitrogen as PAN over oxidation to rapidly deposited HNO<sub>3</sub>.

#### CONCLUSION

Biomass fires represent major sources for nonmethane hydrocarbons, CO, and (CH<sub>3</sub>)<sub>2</sub>CO in the subarctic during summer. Long-range transport of pollution, apparently originating primarily from high-latitude European sources, provides 1/3 - 1/4 of the total input to the region. Emissions of hydrocarbons, CO, and C<sub>2</sub>Cl<sub>4</sub>, from wildfires and industrial sources, exceed the rates for removal by reaction with OH, and the "clean" subarctic represents a net source of these species to midlatitudes.

The dominant role of emissions from biomass fires implies that regional concentrations for many gases should respond to variations in areas burned during the summer, a view supported by comparison of CO data from 1988 and 1990. Assessments of global environmental change should recognize the pervasive influence of biomass fires in the boreal zone and take into account long-term trends in fire frequency [*van Wagner*, 1988], which may be connected to climate warming [*Schindler et al.*, 1990], increased population, or other global phenomena.

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