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 2 Cl 4 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 \( \approx 70\% \) 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 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 2 Cl 4 [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, and NOx (averaged into 90-s intervals [Sandholm et al., this issue]). Samples for peroxycarboxylate (PAN) and acetone ((CH 3 ) 2 CO) and a second determination of C 2 Cl 4 were acquired over \( \approx 60 \) s at \( \approx 2 \) 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 (\( \approx 90 \) 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 2 Cl 4 were also elevated, and vice versa. Concentrations of C 2 Cl 4 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 2 Cl 4, 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 (ELQ) 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 ELQ, 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.
Fig. 1. Concentrations of C2Cl4 and CH3CCl3 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 C2Cl4

Concentrations of C2Cl4 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 [Harris 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 C2Cl4, within ±30% in most cases. Directly over source regions, ratios for CO:C2Cl4 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 C2Cl4, were similar to observations over the source regions (flights 21 and 22; see Table 1), including species such as C2H6 and NOx, with lifetimes as short as ~5 days. According to Bakwin et al. [this issue], significant quantities of NOx and other pollutants were transported to Schefferville (55°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 NOy, or that decompose at low altitudes, such as PAN. For example, variations of NOy and PAN are either uncorrelated with C2Cl4 or variance ratios are inconsistent between U.S. and Canadian flights.
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 \((\text{CH}_3)\text{CO}\), 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 strong evidence that the variance ratios in Table 1 are characteristic of industrial/urban sources.

Data for \(\text{C}_2\text{H}_6\) and \(\text{C}_3\text{H}_8\) over the United States show anomalies in which concentrations of both are markedly enhanced, without comparable elevation of \(\text{CH}_4\) 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 \(\text{C}_2\text{H}_6\) and \(\text{C}_3\text{H}_8\), especially in winter when \(\text{C}_2\text{H}_6/\text{C}_2\text{H}_2\) ratios are highly variable (A. H. Goldstein, private communication, 1993). Variance ratios of most other hydrocarbons are more uniform, relative to \(\text{C}_2\text{H}_2\), in all seasons. Therefore in the present paper we use emission ratios from Table 1, relative to \(\text{C}_2\text{Cl}_4\), neglecting anomalous points for \(\text{C}_2\text{H}_6\) and \(\text{C}_3\text{H}_8\). Thus we neglect these fuel-related sources and may slightly underestimate emissions of \(\text{C}_2\text{H}_6\) and \(\text{C}_3\text{H}_8\) from urban/industrial regions.

**Characteristic Emission Ratios for Tundra/Taiga Fires Versus \(\text{C}_2\text{H}_2\)**

Hydrocarbon emissions from biomass fires and ratios to \(\text{CO}\) and \(\text{C}_2\text{H}_2\) 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 \((\text{CH}_3)\text{CO}\) to be generated.

The ratio \(\text{C}_2\text{H}_2/\text{CO}\) 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,
TABLE 2a. Industrial/Urban Sources of C₂Cl₄ and CO

| Region          | USA+Canada | Europe (E+W) | Units |
|-----------------|------------|--------------|-------|
| Emission Rates  |            |              |       |
| C₂Cl₄          | 154        | 293          | kt/yr |
| CO             | 77         | 161          | Mt/yr |
| Emission Ratios|            |              |       |
| From inventories | 3000      | 3200         | mol/mol |
| From ABLE3B data | 3800      | -            | mol/mol |

aEuropean Chlorinated Solvent Association [1992]; P. Midgely (private communication, 1992).
bNAPAP, 1985; D. Jacob, J. Logan (private communication, 1992).

TABLE 2b. Anthropogenic Emission/Enhancement Ratios
Relative to CO 10⁻³ mol/mol

| Species | Emission Ratio | Arctic Enhancement |
|---------|----------------|--------------------|
| C₂H₂    | 3.6            | 2.4 (2-3.1)        |
| C₂H₆    | 4.8            | 8.1 (3.7-30)       |
| C₃H₈    | 4.5            | 2.6 (1.9-11)       |
| (CH₃)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 C₂H₂, 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/CO₂ 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 NOₓ are much lower than in most other biomass combustion or in pollution, reflecting the prevalence of smoldering combustion; the associated low NOₓ/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 C₂H₂ and the ratios from Table 3a to assess hydrocarbon inputs from biomass fires. The relatively large emission ratios for (CH₃)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 C₂H₂:C₂Cl₄ from Table 1 was employed to account for input of C₂H₃ from by pollution sources (for flights with enhancements of C₂Cl₄). We selected C₂H₂ as the index species, instead of CO, to preserve correlations.
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 covered and the bias in selecting grab samples. Figure 7 shows the relationship between concentrations of C2H6 and C3H8 over the East Coast of the United States, flights 21 and 22. The deviant samples with enhanced C2H6 (Figure 4a) are enhanced also in C3H8, consistent with a natural gas release.

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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, C2H2, and C2H6 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[species]/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 ABLE 3B and ABLE 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 NOx or HNO3 (Table 3).
TABLE 3a. Enhancement of Hydrocarbons Relative to CO from Boreal Biomass Burning

| Flight | CH4 | C2H2 | C2H4 | C3H6 | C3H8 | i-C4H10 | n-C4H10 | n-C6H14 | C6H6 | C7H8 |
|--------|-----|------|------|------|------|---------|---------|---------|------|------|
|        |     |      |      |      |      |         |         |         |      |      |
| HBL    |     |      |      |      |      |         |         |         |      |      |
| 04     | 0.65| 2.35 | 8.38 | 5.40 | 1.83 | 1.30    | 0.09    | 0.43    | 0.21 | 0.15 |
| 06     | 3.70| 5.08 | 6.49 | 0.71 | 1.87 | 0.07    | 0.31    | 0.12    | 0.09 | 1.57 |
| 07     | 3.44| 7.96 | 6.17 | 0.82 | 1.49 | 0.07    | 0.45    | 0.21    | 0.12 | 1.81 |
| 08     | 0.42| 2.29 | 1.02 | 0.28 | 2.55 |         |         |         |      |      |
| 09     | 0.30| 2.49 | 0.61 | 0.91 | 0.61 | 0.26    | 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    | 0.31    | 0.14    |      | 0.13 |
| ±(1σ)  | 0.14| 0.55 | 0.48 | 0.44 | 0.13 | 0.04    |         | 0.04    |      | 0.31 |

β = C2H2 / C2H6

β, ratio to CH2, used in Table 5. Means assumed = 0 for short-lived, high-variance species.

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

| Species | Tundra | BERING | U.S. East Coast | Amazon | Taiga | Flight 21 | Flight 22 |
|---------|--------|--------|----------------|--------|-------|-----------|-----------|
| CH4     | 0.18   | 0.41   | 0.66           | 0.08   | 0.42  | 0.56      | 0.75      |
| C2H2    | 0.019  | 0.020  | 0.0017         | 0.03   | 0.0028| 0.0043    | 0.0028    |
| C2H4    | NA     | NA     | NA             | NA     | --    | 0.0024    | 0.0005    |
| C3H6    | 0.055  | 0.0096 | 0.04           | 0.007  | 0.0062| 0.0040    | 0.0014    |
| C3H8    | NA     | NA     | NA             | NA     | --    | 0.0002    | 0.0005    |
| C4H8    | NA     | NA     | NA             | NA     | --    | 0.0019    | 0.0047    |
| n-C6H10 | 0.0043 | 0.015  | 0.0014         | 0.0014| 0.0019| 0.0047    | 0.0069    |
| n-C6H12 | 0.0001 | 0.0046 | NA             | NA     | 0.0005| 0.0071    | 0.0032    |
| NOy     | 0.0056 | 0.023  | 0.008          | 0.016  | 0.018 | 0.025     | 0.031     |
| PAN     | 0.0017 | NA     | NA             | NA     | 0.0036| 0.0076    | 0.0057    |

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

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Haze layers with negligible enhancement of C2Cl4: 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^-3 mol/mol, except for CH4 (mol/mol). Ratios not reported for correlation coefficients < 0.4. β, ratio to C2H2, used in Table 5. Means assumed = 0 for short-lived, high-variance species.

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 [C2Cl4], is the background concentration (cm^-3), Δ[C2Cl4] is the change during observation period Δt, k_C2Cl4 is the rate coefficient for reaction of OH with C2Cl4 (1.3·10^-13 cm^3 sec^-1), Δ[C2Cl4] is the concentration difference between 40 and 60°N latitudes, and τex 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
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$_2$Cl$_4$ for latitudes $> 56^\circ$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$^\circ$N, while most North American sources are south of 48$^\circ$. Emission rates for C$_2$Cl$_4$ at high latitudes evidently exceed rates of consumption due to reaction with OH. The quantity of C$_2$Cl$_4$ 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

$$\alpha_iP_{\text{ind}} + \beta_iP_{\text{bb}} + P_{\text{in situ}} = \frac{\Delta[i]}{\Delta t} + \frac{A[i]}{v_{\text{eff}}}$$

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

The input of C$_2$H$_2$ from biomass fires, $P_{\text{bb}}$ (C$_2$H$_2$ = 3.8 ppt/d), was obtained by assuming balance in equation (2) for i = C$_2$H$_2$ (see Table 5). The source due to biomass fires is about twice as large as inputs from industrial/urban pollution. Since C$_2$H$_2$ has a shorter chemical lifetime than C$_2$Cl$_4$ (5 times faster reaction with OH), transport and time-dependence terms are considerably smaller for C$_2$H$_2$ than for C$_2$Cl$_4$, 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$_2$Cl$_4$ and C$_2$H$_2$, combined with budgets for C$_2$Cl$_4$ and C$_2$H$_2$ 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<CO<120 | Mean of 80<CO<120 | Trimmed Mean 80<CO<120 |
|---------|-----------------|-------------------|---------------------|-------------------|------------------------|
| CO      | 110 ppb         | 102               | 99                  | 99                | 99                     |
| CH$_4$  | 1751 ppb        | 1752              | 1750                | 1750              | 1749                   |
| C$_2$Cl$_4$ | 12 ppt       | 12                | 12                  | 12                | 12                     |
| CH$_3$CCl$_3$ | 155 ppt   | 155               | 154                 | 154               | 154                    |
| C$_2$H$_6$ | 807 ppt      | 758               | 738                 | 759               | 745                    |
| C$_2$H$_8$ | 105 ppt       | 78                | 69                  | 83                | 74                     |
| C$_2$H$_2$ | 126 ppt       | 86                | 80                  | 93                | 83                     |
| C$_3$H$_6$ | 56 ppt        | 39                | 36                  | 43                | 38                     |
| (CH$_3$)$_2$CO | 1040 ppt   | 1214              | 1192                | 1147              | 1156                   |
| CHCl$_3$ | 5.1 ppt        | 5.1               | 5.1                 | 5.2               | 5.0                    |
| F-113   | 79.2 ppt       | 79                | 79                  | 79                | 79                     |

*Mean of data between 10th and 90th percentiles for data selected as given for corresponding CO concentration (adopted as summertime background concentrations).
to terms on the left-hand side. The mean of these ratios (excluding C2Cl4 and C2H2), 0.8 (±0.2) (column 13 in Table 5), indicates remarkable consistency, with relative contributions of biomass fires and pollution defined to ±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 $\tau_{\text{a}}$ and $\Delta t$, all the terms in equation (2) scale with [OH] (the $k_{\text{a}}k_{\text{OH}}$, $P_{\text{ind}}$, and $P_{\text{bb}}$ terms in equation (1)), and $P_{\text{bb}}$ CO, 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 $\alpha P_{\text{bb}}$ Cl appear to correspond to similar fractions of emission inventories for hydrocarbons (Table 2b), except for (CH3)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 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-C4H0). 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: Simultaneous Sources and Sinks for Hydrocarbons and CO in the Subarctic (ppb)

| Gas        | CO        | CH4       | NMHCs     | Anthropogenic Sources/Sinks | Time Dependence | OH Rate | kOH[OH] | $\tau_\text{a}$ | $\tau_\text{x}$ | $\Delta t$ | $\Delta t$ |
|------------|-----------|-----------|-----------|-----------------------------|-----------------|---------|---------|-----------------|-----------------|-----------|-----------|
| C2Cl4      | 0.12      | 0.04      | 0.7       | $\alpha P_{\text{ind}}$     | $k_{\text{OH}}A_{\text{H}}$ | 62.3    | 0.015   | 0.15            | 0.25            | -0.02     | 0.09      |
| C2H2       | 0.04      | 0.02      | 0.3       | $P_{\text{ind}}$            | $k_{\text{OH}}I_{\text{B}}$     | 89.4    | 0.13    | 0.13            | 0.25            | -0.02     | 0.09      |
| C2H4       | 0.04      | 0.02      | 0.3       | $P_{\text{ind}}$            | $k_{\text{OH}}I_{\text{B}}$     | 89.4    | 0.13    | 0.13            | 0.25            | -0.02     | 0.09      |
| n-C4H10    | 0.04      | 0.02      | 0.3       | $P_{\text{ind}}$            | $k_{\text{OH}}I_{\text{B}}$     | 89.4    | 0.13    | 0.13            | 0.25            | -0.02     | 0.09      |
| (CH3)2CO   | 0.12      | 0.04      | 0.7       | $\alpha P_{\text{ind}}$     | $k_{\text{OH}}A_{\text{H}}$ | 62.3    | 0.015   | 0.15            | 0.25            | -0.02     | 0.09      |
| CO         | 0.12      | 0.04      | 0.7       | $\alpha P_{\text{ind}}$     | $k_{\text{OH}}A_{\text{H}}$ | 62.3    | 0.015   | 0.15            | 0.25            | -0.02     | 0.09      |

Numbers in italic denote balances assumed in the budget analysis: budget region = 56°-90°N (1.1x10^6 mol of air in the troposphere); ND, not determined; $\alpha$, molar emission ratio relative to C2H4 from industrial pollution (Table 5); $\Delta t$, chemical lifetime (days). Mean [OH] = 1 x 10^6 cm^-3. Sputnik.
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), C2H2 (ppt), and C2Cl4 (scaled ×10); (b) hydrocarbons (ppt), scaled as shown in the legend; (c) nitrogen oxides (ppt); 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 CH4 concentrations provides an important indirect human influence on CO concentrations. If two thirds of the source from CH4 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 NOx. 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 (CH3)2CO associated with anthropogenic pollution arises from atmospheric oxidation of hydrocarbon precursors. Biomass fires provide a very strong source of (CH3)2CO 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       | $\int_{[OH]}[X]k_x\, dz$ ($10^6$ cm$^{-2}$s$^{-1}$) | CO yield/Carbon Atom | $P_{CO}$ $dz$ ($10^6$ cm$^{-2}$s$^{-1}$) |
|---------------|-------------------------------------------------|---------------------|---------------------------------|
| C$_2$Cl$_4$   | 16                                              | 1                   | 31                              |
| CHCl$_3$      | 4                                               | 1                   | 4                               |
| C$_2$H$_2$    | 598                                             | 0.6                 | 717                             |
| C$_2$H$_6$    | 1639                                            | 0.55                | 1803                            |
| C$_3$H$_8$    | 710                                             | 0.61                | 1300                            |
| n-C$_4$H$_{10}$ | 345                                         | 0.54                | 745                             |
| i-C$_4$H$_{10}$ | 132                                         | 0.72                | 380                             |
| n-C$_4$H$_{12}$ | 180                                         | 0.53                | 477                             |
| C$_6$H$_6$    | 456                                             | 0.09                | 81                              |
| C$_7$H$_8$    | 488                                             | 0.09                | 88                              |
| (CH$_3$)$_2$CO | 2320                                            | 0.67                | 4663                            |
| Isoprene*     | $\approx$16000                                  | 1.15                | $\approx$16900                   |
| Total NMHC    | 21490                                           | -                   | 27190                           |
| CH$_4$        | 78750                                           | 1                   | 78750                           |
| Total atmosphere | 100240                                         | -                   | 106040                          |
| CO            | 220000                                          | -                   | -                               |

Yield of CO/molecule from Altshuller [1991].
*Mean isoprene emission rate, 50°-90°N (D. J. Jacob, private communication, 1992).

TABLE 6b. Annual Areas Burned in Canada

| Year   | Area (10$^6$ 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].

Biomass fires represent major sources for nonmethane hydrocarbons, CO, and (CH$_3$)$_2$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$_2$Cl$_4$, 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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