

## Summertime Photochemistry of the Troposphere at High Northern Latitudes

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The budgets of O<sub>3</sub>, NO<sub>x</sub> (NO+NO<sub>2</sub>), reactive nitrogen (NO<sub>y</sub>), and acetic acid in the 0-6 km column over western Alaska in summer are examined by photochemical modeling of aircraft and ground-based measurements from the Arctic Boundary Layer Expedition (ABLE 3A). It is found that concentrations of O<sub>3</sub> in the region are regulated mainly by input from the stratosphere, and losses of comparable magnitude from photochemistry and deposition. The concentrations of NO<sub>x</sub> (10-50 ppt) are sufficiently high to slow down O<sub>3</sub> photochemical loss appreciably relative to a NO<sub>x</sub>-free atmosphere; if no NO<sub>x</sub> were present, the lifetime of O<sub>3</sub> in the 0-6 km column would decrease from 46 to 26 days because of faster photochemical loss. The small amounts of NO<sub>x</sub> present in the Arctic troposphere have thus a major impact on the regional O<sub>3</sub> budget. Decomposition of peroxyacetyl nitrate (PAN) can account for most of the NO<sub>x</sub> below 4-km altitude, but for only 20% at 6-km altitude. Decomposition of other organic nitrates might supply the missing source of NO<sub>x</sub>. The lifetime of NO<sub>y</sub> in the ABLE 3A flight region is estimated at 29 days, implying that organic nitrate precursors of NO<sub>x</sub> could be supplied from distant sources including fossil fuel combustion at northern mid-latitudes. Biomass fire plumes sampled during ABLE 3A were only marginally enriched in O<sub>3</sub>; this observation is attributed in part to low NO<sub>x</sub> emissions in the fires, and in part to rapid conversion of NO<sub>x</sub> to PAN promoted by low atmospheric temperatures. It appears that fires make little contribution to the regional O<sub>3</sub> budget. Only 30% of the acetic acid concentrations measured during ABLE 3A can be accounted for by reactions of CH<sub>3</sub>CO<sub>3</sub> with HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>. There remains a major unidentified source of acetic acid in the atmosphere.

### 1. INTRODUCTION

The Arctic Boundary Layer Expedition (ABLE 3A) surveyed the composition of the North American Arctic and sub-Arctic troposphere from the surface to 6 km altitude during July-August 1988 [Harriss *et al.*, this issue (a)]. Aircraft measurements included concentrations of O<sub>3</sub>, NO, NO<sub>2</sub>, peroxyacetyl nitrate (PAN), HNO<sub>3</sub>, total reactive nitrogen (NO<sub>y</sub>), CO, non-methane hydrocarbons (NMHCs), and organic acids. We examine in this paper the photochemical activity of the regional atmosphere documented by the ABLE 3A data, with focus on the budgets of O<sub>3</sub>, NO<sub>x</sub> (NO+NO<sub>2</sub>), and NO<sub>y</sub>.

Our principal objective is to explain the ~ 1% yr<sup>-1</sup> rise of O<sub>3</sub> concentrations observed in the Arctic troposphere over the past two decades [Logan, 1985; Oltmans and Komhyr, 1986]. This rise is most pronounced in summer, averaging 3% yr<sup>-1</sup> at Barrow in July for the period 1973-1984 [Oltmans and Komhyr, 1986]. Anthropogenic influence would provide a logical explanation. However, the ABLE 3A data clearly point to a stratospheric rather than to a pollution origin for O<sub>3</sub> in the region [Browell *et al.*, this issue; Gregory *et al.*, this issue]. This source attribution is based on three pieces of evidence: (1) concentrations of O<sub>3</sub> in the middle troposphere were anticorrelated with concentrations of aerosol, H<sub>2</sub>O, and CO; (2) well-defined layers of pollution were only marginally enriched in O<sub>3</sub>; and (3) high-O<sub>3</sub> episodes were usually associated with stratospheric intrusions (documented by lidar). The NO<sub>x</sub> concentrations measured in ABLE 3A were in the range 10-50 ppt [Sandholm *et al.*, this issue], sufficiently low that photochemistry should provide a net sink for O<sub>3</sub>. As discussed below, our analysis of the ABLE 3A data indicates that O<sub>3</sub> concentrations in the summertime Arctic troposphere represent largely a balance between input from the stratosphere, and losses of comparable magnitude from photochemistry and deposition.

A major point of the present paper is to show that anthropogenic influence on O<sub>3</sub> levels in the Arctic may manifest itself not by long-range transport of pollution-derived O<sub>3</sub>, but rather by a decrease of the regional photochemical sink due to the presence of small amounts of NO<sub>x</sub>. The low concentrations of NO<sub>x</sub> measured in ABLE 3A were sufficient to reduce the rate of photochemical loss appreciably relative to a NO<sub>x</sub>-free atmosphere, thus increasing the O<sub>3</sub> lifetime. We show below that decomposition of PAN can account for most of the NO<sub>x</sub> measured below 4-km altitude, but for only 20% at 6-km altitude. Decomposition of other organic nitrates might provide the missing source of NO<sub>x</sub> at high altitude. Sandholm *et al.* [this issue] found that about half of total NO<sub>y</sub> in ABLE 3A could not be accounted for by NO<sub>x</sub>, PAN, or HNO<sub>3</sub>, suggesting that unidentified organic nitrates made a large contribution to the NO<sub>y</sub> budget.

We estimate below a lifetime of 29 days for NO<sub>y</sub> in the ABLE 3A flight region, suggesting that PAN and other organic nitrate precursors of NO<sub>x</sub> could have been transported from distant sources. Singh *et al.* [this issue (a)] have argued that long-range transport from northern mid-latitudes was a major source of NO<sub>y</sub> in ABLE 3A, and our analysis lends some support to that view. Concentrations of NO<sub>y</sub> in the Arctic troposphere have therefore probably increased over the past few decades, reflecting the rise in fossil fuel combustion at northern mid-latitudes [Dignon and Hameed, 1989]. Decomposition of this anthropogenic NO<sub>y</sub>, providing a source of NO<sub>x</sub> in the Arctic troposphere, could then explain the observed increase of O<sub>3</sub> concentrations in the region.

Biomass burning emissions at high northern latitudes have also

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probably increased over the past two decades, as suggested by forest fire statistics for Canada [Van Wagner, 1988; Schindler *et al.*, 1990; Stocks, 1991], but the effect on the regional  $O_3$  budget appears to be small. The aged fire plumes sampled during ABLE 3A were only slightly enriched in  $O_3$  [Wofsy *et al.*, this issue]. The  $\Delta O_3/\Delta CO$  ratios in the plumes, where  $\Delta$  represents the concentration enrichment relative to background, were in the range 0.04-0.18. In comparison,  $\Delta O_3/\Delta CO$  ratios in the range 0.3-0.5 were observed in urban plumes sampled off the east coast of the United States during ABLE 3A transit flights. Andreae *et al.* [1988] previously documented  $\Delta O_3/\Delta CO$  ratios in the range 0.01-0.09 for biomass fire plumes over Amazonia, as compared to 0.34 in the Manaus urban plume. Andreae *et al.* [1992] reported an average ratio of 0.14 in biomass fire plumes over the Congo. It appears that  $O_3$  production from biomass fires, when normalized to CO emissions, is low compared to production from fossil fuel combustion. We will explain this result as due to low  $NO_x/CO$  and  $NO_x/NMHC$  emission ratios in biomass fires;  $O_3$  production is  $NO_x$ -limited, and  $NO_x$  is rapidly oxidized to organic nitrates. The relatively low  $NO_x$  emissions in biomass fires may result from low burn temperatures, particularly under smoldering conditions, and also at high latitudes from the low nitrogen content of vegetation [Chapin and Shaver, 1985].

Talbot *et al.* [this issue] measured acetic acid concentrations in the range 100-400 ppt during ABLE 3A. Acetic acid is produced by  $CH_3CO_3$  + peroxy reactions [Moortgat *et al.*, 1989a,b]. If these reactions were the dominant sources of acetic acid in the atmosphere, as has been suggested by Madronich *et al.* [1990], then acetic acid would be an interesting tracer of photochemical activity. However, we report below that only ~30% of the acetic acid measured in ABLE 3A can be accounted for in that manner. There remains a major unidentified source of acetic acid in the atmosphere.

The paper is organized in two sections. In section 2 we construct budgets of  $O_3$ ,  $NO_x$ ,  $NO_3$ , and acetic acid in the ABLE 3A flight region, using photochemical model statistics based on the aircraft observations. In section 3 we use a Lagrangian model to reconstruct the photochemical history of two aged biomass fire plumes sampled by the ABLE 3A aircraft. Concluding remarks are in section 4.

## 2. REGIONAL PHOTOCHEMICAL BUDGETS

### Approach

We use a merged data base of chemical and meteorological measurements from ABLE 3A flights 11-25 over western Alaska (Figure 1). The data base includes 475 points in space and time for which simultaneous aircraft measurements of atmospheric composition are available. We reconstruct the local photochemical state of the atmosphere at each point, using the mechanism described in the appendix, and obtain as model products the instantaneous production and loss rates of  $O_3$ ,  $NO_x$ , PAN,  $HNO_3$ , and acetic acid, as well as the local concentrations of short-lived species (e.g., OH). We then derive spatial and temporal averages for these products, and document the ensemble of conditions found in the regional photochemical environment.

The following measurements are used as independent variables to define the photochemical state of the atmosphere at each point: concentrations of  $O_3$ , NO, PAN,  $HNO_3$ , CO, ethane, propane, and butanes; and temperature, dew point, altitude, and solar zenith angle. The concentration of NO is selected as independent variable rather than the concentration of  $NO_x$  because of the sparsity of data for  $NO_2$ . All radicals other than NO are assumed to be in

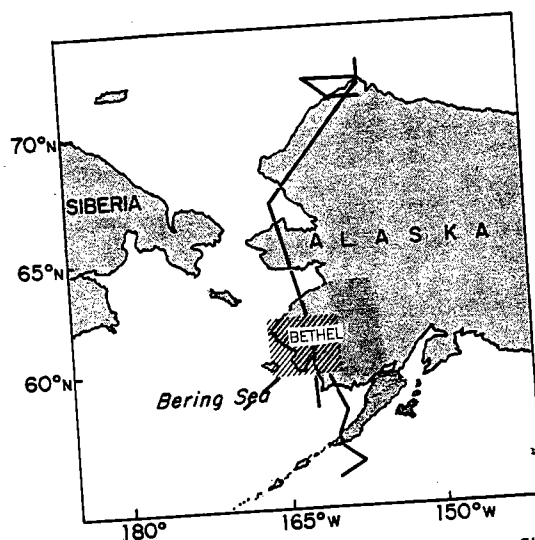


Fig. 1. ABLE 3A sampling region over western Alaska on flights 11-25 (July 19 to August 7, 1988). The dashed area around the town of Bethel was heavily sampled; additional flight tracks outside that area are shown as thick lines.

chemical steady state (including OH, peroxy species, and  $NO_2$ ). Steady state is assumed also for oxygenated hydrocarbons with lifetimes of a few days or less (carbonyls, peroxides) and for other short-lived compounds (e.g.,  $HNO_2$ ,  $HNO_4$ ). A fixed acetone concentration of 120 ppt is adopted [Arnold *et al.*, 1986]. The UV radiation field is computed on the basis of the local altitude, solar zenith angle, and albedo, assuming clear-sky conditions (see appendix). Proper accounting of cloud effects is not possible from the data available; averaging over a large number of points should at least reduce the associated uncertainty.

The 475 points in the data base were selected on the basis of NMHC data availability. Each NMHC grab sample [Blake *et al.*, this issue] was matched with 10-s average data for  $O_3$ , CO, and meteorological variables [Gregory *et al.*, this issue; Harriss *et al.*, this issue (b); National Aeronautics and Space Administration, 1989], 1-min average data for NO and  $NO_3$  [Sandholm *et al.*, this issue], grab sample data for PAN [Singh *et al.*, this issue (a)], and 15 to 60 min average data for  $HNO_3$  and acetic acid [Talbot *et al.*, this issue]. Figure 2 shows the mean vertical distributions of species concentrations in the data base. Also shown in Figure 2 are the model-calculated concentrations of OH,  $NO_x$ , and  $RNO_x$ . Here  $RNO_x$  is the residual  $NO_y$ , i.e., the fraction of observed  $NO_y$  that cannot be accounted for by measured concentrations of NO, PAN, and  $HNO_3$  or model concentrations of  $NO_2$ ,  $NO_3$ ,  $N_2O_5$ ,  $HNO_2$ , and  $HNO_4$ . This residual  $NO_y$  is speculated to represent unidentified organic nitrates, hence the  $RNO_x$  notation; it accounts for about half of total  $NO_y$ .

The principal products of our analysis are the diurnally and vertically averaged photochemical rates obtained by (1) binning the individual points into 1-km altitude bands and 2-hour time intervals, (2) averaging within each bin the rates computed at individual points, and (3) averaging again over either the diurnal cycle or the 0 to 6-km column, or both. The ensemble of 475 data points covers the altitude range 0.1-6.2 km and the temporal range 0600-1915 solar time (ST); here solar time is defined by a maximum solar elevation at noon. The vertical and temporal distribution of points is shown in Figure 3. The diurnal cycle of OH concentrations in the 0 to 1-km band, where the density of points is highest, indicates a time window of active photochemistry extending from 6 to 18 ST (Figure 4).

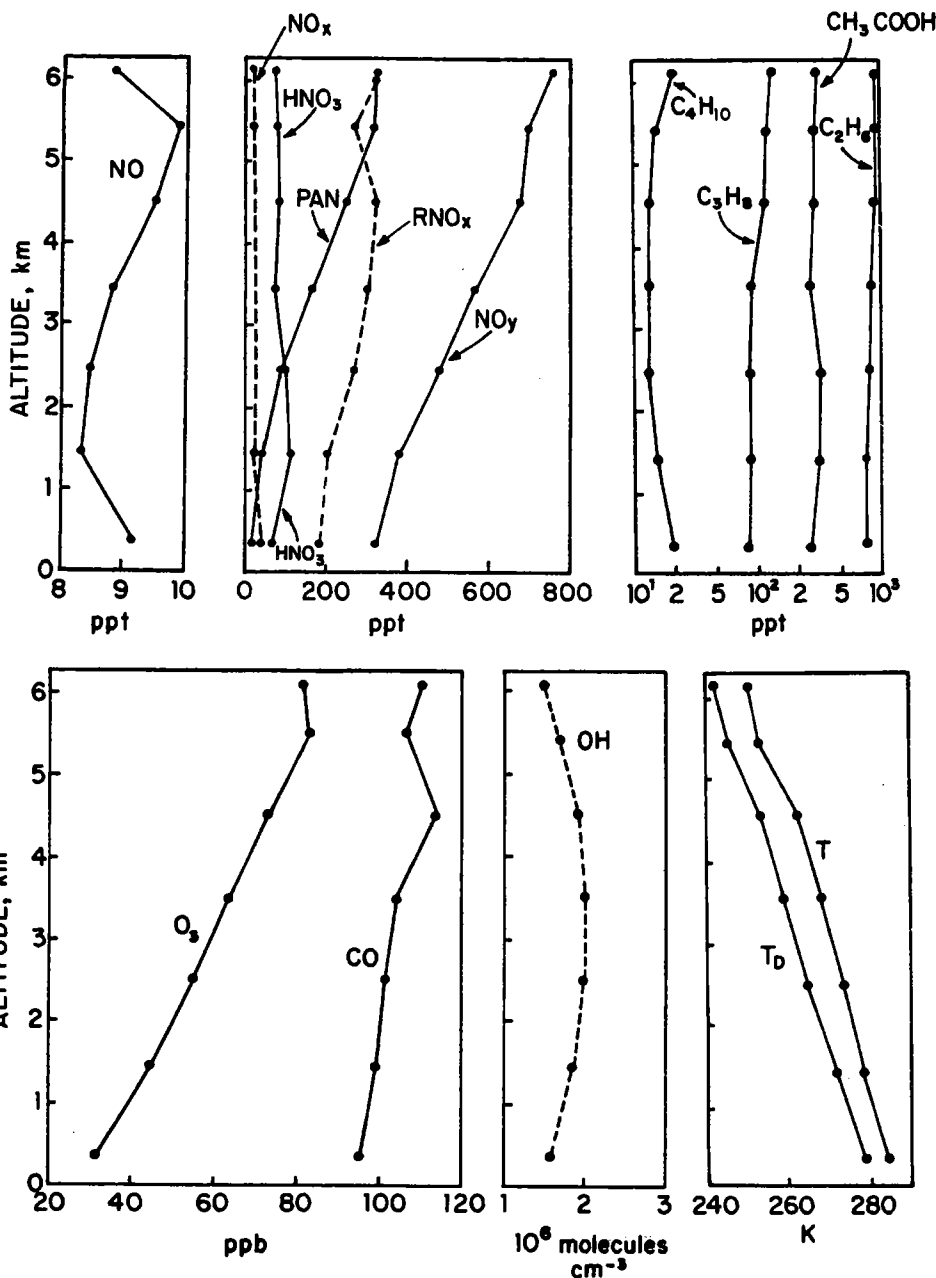


Fig. 2. Vertical distributions of species concentrations on flights 11-25 over western Alaska. The data are averages over 1-km altitude bands. Concentrations of OH, NO<sub>x</sub>, and RNO<sub>x</sub> (residual NO<sub>y</sub>) are model results

and are shown as dashed lines. The OH concentration is a daytime average computed over the time window 6-18 solar time (ST). Temperature (T) and dew point (T<sub>D</sub>) are also shown.

Inspection of Figure 3 indicates that portions of the altitude-time domain were only sparsely sampled by the aircraft. To increase the density of points, we calculate the photochemical rates for each point above 2 km altitude over a range of solar angles from 6 to 18 ST. The underlying assumption is that there should be little covariance between solar zenith angle and the other independent variables. Such an assumption would be inappropriate below 2 km because of diurnal variations driven by surface fluxes, but there is less need for increasing the density of points in that altitude range.

**Ozone**

Figure 5 shows the net photochemical production rate of O<sub>3</sub>, (P-L)<sub>O<sub>3</sub></sub>, as a function of altitude. Values are 24-hour averages computed by assuming (P-L)<sub>O<sub>3</sub></sub> = 0 outside the 6-18 ST time win-

dow. Net O<sub>3</sub> loss takes place over the entire 0 to 6-km column, and is maximum between 2 and 5 km. The 24-hour average column loss rate is 8.0x10<sup>10</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>, comparable in magnitude to the mean O<sub>3</sub> deposition flux of 8.2x10<sup>10</sup> molecules cm<sup>-2</sup> s<sup>-1</sup> estimated by Jacob *et al.* [this issue] for the world north of 60°N in summer. Photochemistry and deposition add up to an estimated total sink of 1.6x10<sup>11</sup> molecules cm<sup>-2</sup> s<sup>-1</sup> for O<sub>3</sub> in the summertime Arctic troposphere. The mean 0 to 6-km column concentration of O<sub>3</sub> measured during flights 11-25 was 6.4x10<sup>17</sup> molecules cm<sup>-2</sup>, from which we infer an O<sub>3</sub> column lifetime of 46 days. This lifetime is relatively short; we conclude that the regional O<sub>3</sub> budget represents largely a balance between stratospheric input on the one hand, and losses from photochemistry and deposition on the other hand.

The importance of photochemical loss as a regional sink for O<sub>3</sub>

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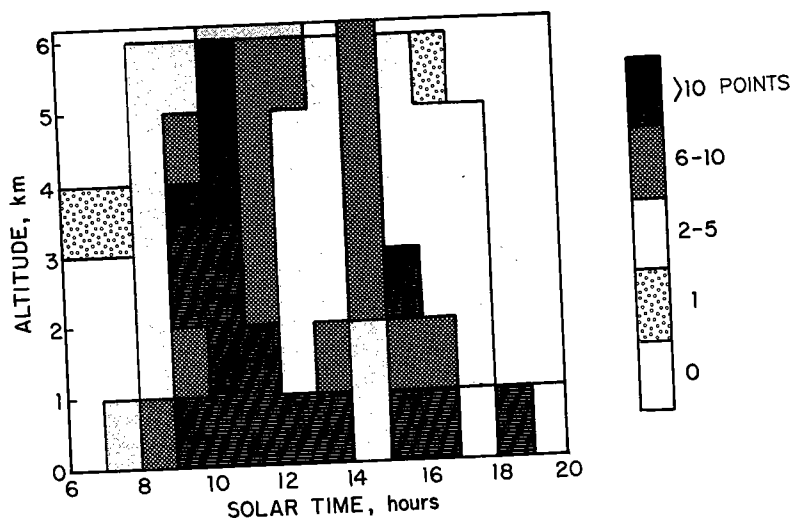


Fig. 3. Vertical and temporal distribution of the 475 points in the data base for flights 11-25.

implies that small anthropogenic perturbations to  $\text{NO}_x$  could have a major effect on  $\text{O}_3$  levels. In the low- $\text{NO}_x$  regime of interest here,  $(\text{P-L})_{\text{O}_3}$  increases linearly with increasing  $\text{NO}_x$  concentration [Fishman et al., 1979]. To assess the sensitivity of  $(\text{P-L})_{\text{O}_3}$  to  $\text{NO}_x$ , we repeated our calculations for the 475 points with  $\text{NO}$  and  $\text{PAN}$  concentrations set to zero. The 24-hour average photochemical column loss rate of  $\text{O}_3$  rose to  $2.0 \times 10^{11}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ , 2.5 times larger than in the standard calculation (Figure 5). The  $\text{O}_3$  lifetime dropped to 26 days, 43% shorter than in the standard calculation, because of the faster photochemical loss.

**Nitrogen oxides**

The origin of the small amounts of  $\text{NO}_x$  measured during ABLE 3A thus emerges as a major issue in the regional  $\text{O}_3$  budget. We expect this  $\text{NO}_x$  to represent on average a steady state between chemical sources and chemical sinks, because the lifetime against oxidation is short ( $\sim 1$  day) and emission sources are remote. The low variability of  $\text{NO}$  concentrations observed over the course of the expedition [Sandholm et al., this issue] supports the argument that  $\text{NO}_x$  did not originate from direct emissions. The major chemical sources of  $\text{NO}_x$  are

- (R1)  $\text{PAN} \xrightarrow{\text{T}} \text{NO}_2 + \text{CH}_3\text{CO}_3$
- (R2)  $\text{PAN} + \text{OH} \rightarrow \text{NO}_2 + \text{products}$
- (R3)  $\text{HNO}_3 + \text{h}\nu \rightarrow \text{NO}_2 + \text{OH}$
- (R4)  $\text{HNO}_3 + \text{OH} \xrightarrow{\text{h}\nu, \text{O}_2} \text{NO}_2 + \text{H}_2\text{O} + \text{O}_3$
- (R5)  $\text{RNO}_x \xrightarrow{\text{T, OH, h}\nu} \text{NO}_x + \text{products}$

and the major chemical sinks of  $\text{NO}_x$  in the daytime are

- (R6)  $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$
- (R7)  $\text{NO}_2 + \text{CH}_3\text{CO}_3 + \text{M} \rightarrow \text{PAN} + \text{M}$

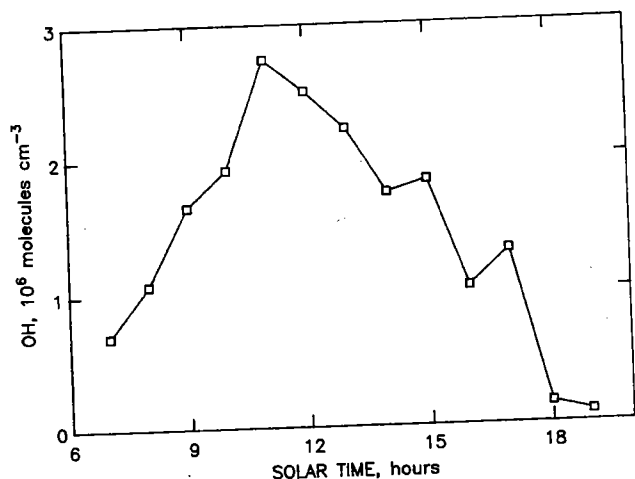


Fig. 4. Mean diurnal variation of OH concentrations below 1-km altitude on flights 11-25.

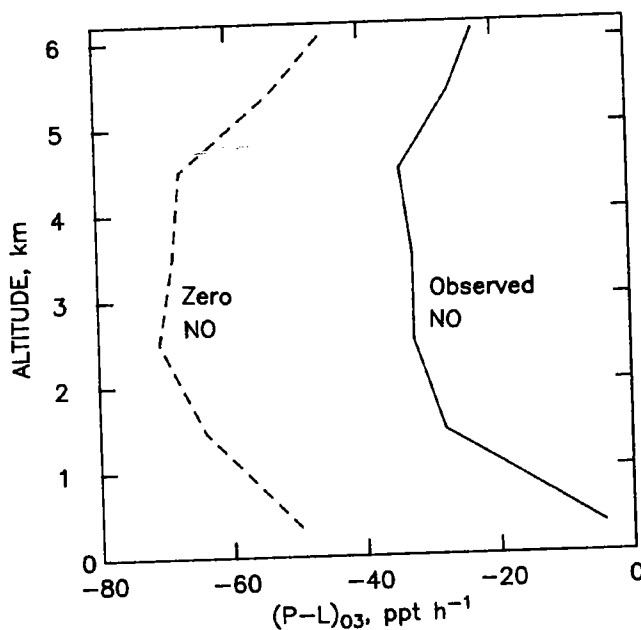
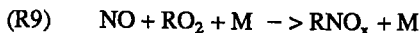
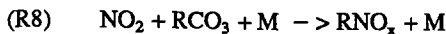


Fig. 5. Net photochemical production rates of  $\text{O}_3$  as a function of altitude, calculated for flights 11-25 and shown as 24-hour averages for each 1-km altitude band. All values are negative, indicating net loss. The dashed line shows results from a sensitivity calculation with  $\text{NO}$  and  $\text{PAN}$  concentrations set to zero.

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where  $\text{RCO}_3$  represents peroxyacyl radicals other than  $\text{CH}_3\text{CO}_3$ ,  $\text{RO}_2$  represents organic peroxy radicals, and  $\text{RNO}_x$  represents organic nitrates other than PAN. Reaction (R9) is a low-yield branch of the oxidation of  $\text{NO}$  by  $\text{RO}_2$  [Lurmann et al., 1986].

Nighttime sinks of  $\text{NO}_x$  include oxidation of NMHCs by  $\text{NO}_3$ , and hydrolysis of  $\text{N}_2\text{O}_5$  in clouds. If these sinks were important,  $\text{NO}_x$  should be depleted at night. Although no aircraft flights were conducted during the nighttime hours, the daytime  $\text{NO}_x$  data do not indicate a depression of concentrations in the early morning, or a gradual increase of concentrations from morning to afternoon, that would be suggestive of nighttime  $\text{NO}_x$  depletion (S. T. Sandholm, personal communication, 1990). We infer that nighttime chemistry probably had only a small effect on the budget of  $\text{NO}_x$  during ABLE 3A.

For each point in the data base, we calculate the instantaneous rates of reactions (R1) through (R9) with the exception of (R5). The production of  $\text{NO}_x$  from (R5) cannot be calculated due to uncertainties on the identities, concentrations, and reactivities of the  $\text{RNO}_x$  species. We choose therefore to test the hypothesis that PAN and  $\text{HNO}_3$  were the main sources of  $\text{NO}_x$ , i.e., that (R5) was negligible. If this hypothesis is correct, then the  $\text{NO}_x$  loss rate

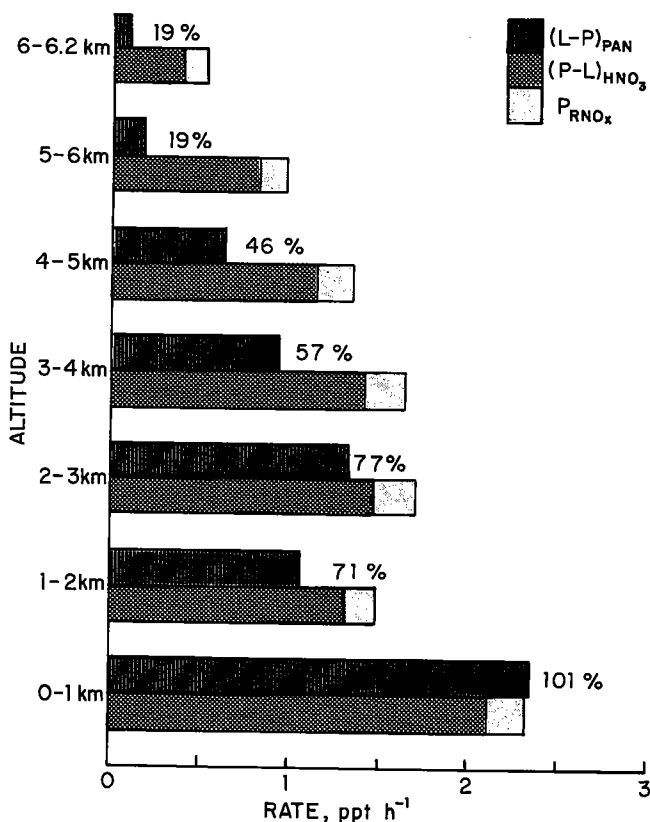


Fig. 6. Chemical production and loss rates of  $\text{NO}_x$  as a function of altitude, calculated for flights 11-25 and shown as daytime averages (6-18 ST) for each 1-km altitude band. The net production rate of  $\text{NO}_x$  from decomposition of PAN,  $(\text{L-P})_{\text{PAN}}$ , is compared to the net loss rate of  $\text{NO}_x$  from oxidation to  $\text{HNO}_3$ ,  $(\text{P-L})_{\text{HNO}_3}$ . The additional loss term for  $\text{NO}_x$ ,  $\text{P}_{\text{RNO}_x}$ , represents production of organic nitrates other than PAN from oxidation of propane and butanes. Numbers to the right of the  $(\text{L-P})_{\text{PAN}}$  bars give the percent of the total loss rate of  $\text{NO}_x$  that is balanced by decomposition of PAN.

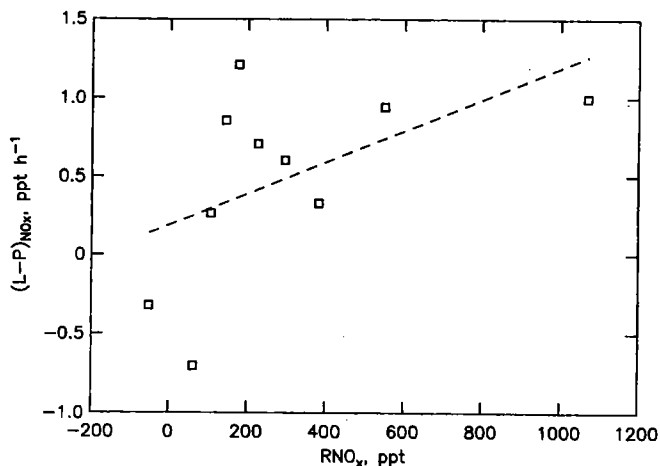


Fig. 7. Missing source of  $\text{NO}_x$ ,  $(\text{L-P})_{\text{NO}_x}$ , as a function of residual  $\text{NO}_y$ ,  $(\text{RNO}_x)$ . The concentration of  $\text{RNO}_x$  is calculated as the difference between the concentration of  $\text{NO}_y$  and the sum of the concentrations of  $\text{NO}_x$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_2$ ,  $\text{HNO}_4$ , PAN, and  $\text{HNO}_3$ . Negative concentrations of  $\text{RNO}_x$  reflect uncertainties in the measurements. Results are from the 475 points in the data base for flights 11-25, ranked in order of increasing  $\text{RNO}_x$  concentration and then averaged over 50-point clusters. The dashed line is the linear regression ( $r = 0.54$ ).

computed from  $(\text{R6})+(\text{R7})+(\text{R8})+(\text{R9})$  should balance the  $\text{NO}_x$  production rate computed from  $(\text{R1})+(\text{R2})+(\text{R3})+(\text{R4})$ , when averaged over a large number of points and over the daytime hours (to remove transient effects from accumulation and transport terms in the  $\text{NO}_x$  budget).

Results of the analysis are shown in Figure 6, where the rates are given as averages over 1-km altitude bands and over the time window 6-18 ST. The net PAN loss rate,  $(\text{L-P})_{\text{PAN}}$ , is defined as  $(\text{R1})+(\text{R2})-(\text{R7})$ ; the net  $\text{HNO}_3$  production rate,  $(\text{P-L})_{\text{HNO}_3}$ , is defined as  $(\text{R6})-(\text{R3})-(\text{R4})$ . Also shown in Figure 6 is the production rate  $\text{P}_{\text{RNO}_x}$  of  $\text{RNO}_x$  species generated in the model by oxidation of propane and butanes. We find that net chemical loss of PAN, and net chemical production of  $\text{HNO}_3$ , take place on average throughout the 0 to 6-km column. Below 3 km there is a close balance between production of  $\text{NO}_x$  from PAN decomposition on the one hand, and loss of  $\text{NO}_x$  by oxidation to  $\text{HNO}_3$  and  $\text{RNO}_x$  on the other hand. At higher altitudes, however, a large fraction of the  $\text{NO}_x$  loss is not balanced by decomposition of PAN. The source of  $\text{NO}_x$  from PAN decomposition decreases rapidly with altitude because of the stability of PAN at low temperatures; the sink of  $\text{NO}_x$  from oxidation to  $\text{HNO}_3$  decreases also with altitude but at a slower pace.

The missing source of  $\text{NO}_x$ ,  $(\text{L-P})_{\text{NO}_x}$ , could conceivably represent decomposition of organic nitrates other than PAN. In that case we might expect a positive correlation between  $(\text{L-P})_{\text{NO}_x}$  and the  $\text{RNO}_x$  concentration. We examined the data base for such a correlation; the analysis was done by grouping the 475 points into clusters of 50, in order of increasing  $\text{RNO}_x$  concentration, to reduce influences of local deviations of  $\text{NO}_x$  from steady state. The resulting scatter diagram indicates some positive correlation (Figure 7), although the coefficient of linear correlation is not significant at the 95% level. Changing the clustering of points did not significantly affect the result.

The atmospheric lifetime of  $\text{NO}_y$  in ABLE 3A can be estimated by assuming that deposition of  $\text{HNO}_3$  is the only  $\text{NO}_y$  sink, and calculating the  $\text{HNO}_3$  deposition flux needed to balance the net production rate  $(\text{P-L})_{\text{HNO}_3}$  in Figure 6. The resulting 24-hour

average  $\text{HNO}_3$  deposition flux is  $2.3 \times 10^9$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ . The mean 0 to 6-km column concentrations of  $\text{HNO}_3$  and  $\text{NO}_y$  measured on flights 11-25 were  $8.9 \times 10^{14}$  and  $5.7 \times 10^{15}$  molecules  $\text{cm}^{-2}$ , respectively, from which we infer  $\text{HNO}_3$  and  $\text{NO}_y$  column lifetimes of 4.5 and 29 days, respectively.

The long lifetime of  $\text{NO}_y$  implies that distant sources could make major contributions to the  $\text{NO}_y$  budget. Singh *et al.* [this issue (a)] and Wofsy *et al.* [this issue] point to three possibly important sources of  $\text{NO}_y$  in ABLE 3A: fossil fuel combustion at mid-latitudes, biomass fires, and stratosphere-troposphere exchange. An estimate of the regional  $\text{NO}_y$  source from biomass fires can be made by using the average  $\Delta\text{NO}_y/\Delta\text{CO}$  ratio of 0.0056 reported by Wofsy *et al.* [this issue] for the ABLE 3A fire plumes, and a CO emission inventory of  $4 \times 10^6$  tons/month for fires north of  $60^\circ\text{N}$  in July (J.A. Logan, personal communication, 1992). The resulting source of  $\text{NO}_y$  is  $5 \times 10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ , balancing only 20% of the  $\text{NO}_y$  sink computed above. The Logan emission inventory is based on mean fire statistics for 1975-1985, while ABLE 3A took place in 1988, but data for Canada indicate that the area burned in 1988 was about equal to the 1975-1985 average [Stocks, 1991]. It appears that biomass fires represent a significant but not dominant component of the  $\text{NO}_y$  budget at high northern latitudes.

Stratospheric input probably made a significant contribution to the  $\text{NO}_y$  budget in ABLE 3A, as indicated by the negative correlation between  $\text{NO}_y$  and CO concentrations observed in some regions of the atmosphere [Wofsy *et al.*, this issue]. However, the low  $\text{HNO}_3/\text{NO}_y$  concentration ratio at 6-km altitude (Figure 2) argues against a dominant stratospheric influence. Most of the  $\text{NO}_y$  in the lower stratosphere is present as  $\text{HNO}_3$  [Russell *et al.*, 1988; Fahey *et al.*, 1990], and conversion of  $\text{HNO}_3$  to organic nitrates in the upper troposphere is thought to be slow [Kasting and Singh, 1986]. It seems therefore that biomass fires and stratospheric input cannot account fully for the  $\text{NO}_y$  budget in ABLE 3A. Sources from fossil fuel combustion at northern mid-latitudes were probably important.

### Acetic Acid

Our model calculations provide statistics for (1) the chemical production rate  $P_A$  of acetic acid from the reactions  $\text{CH}_3\text{CO}_3 + \text{HO}_2$  and  $\text{CH}_3\text{CO}_3 + \text{CH}_3\text{O}_2$ , and (2) the loss rate  $L_A$  of acetic acid from reaction with OH. We still need to estimate the deposition flux of acetic acid in order to construct a regional budget. Talbot *et al.* [this issue] reported mean  $\text{CH}_3\text{COOH}/\text{HNO}_3$  concentration ratios of 5 in the atmosphere and 2 in the rain, from which we infer that the lifetime of acetic acid against wet deposition was 2.5 times that of  $\text{HNO}_3$ . The same factor may be assumed for dry deposition also [Wesely, 1989]. The lifetime of acetic acid against deposition in each 1-km altitude band is then scaled to the lifetime of  $\text{HNO}_3$ , which is in turn calculated to balance the net production rate  $(P-L)_{\text{HNO}_3}$  in that band.

Figure 8 shows the resulting acetic acid budget. Deposition and reaction with OH are sinks of comparable importance, leading to a 24-hour average total loss rate of  $6.0 \times 10^9$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  in the 0 to 6-km column. The resulting column lifetime of acetic acid is 5.7 days, sufficiently short that concentrations should be near steady state. Figure 8 indicates, however, that production of acetic acid from  $\text{CH}_3\text{CO}_3$  + peroxy reactions can balance only 30% of the loss rate at all altitudes. Additional sources of acetic acid must therefore be important. Candidates include other permutation reactions of organic peroxy and peroxyacyl radicals [Madronech and Calvert, 1990], biogenic emissions [Keene and Galloway, 1986; Talbot *et al.*, 1990], and emissions from biomass fires [Talbot *et al.*, 1988]. A rough estimate of the regional emission

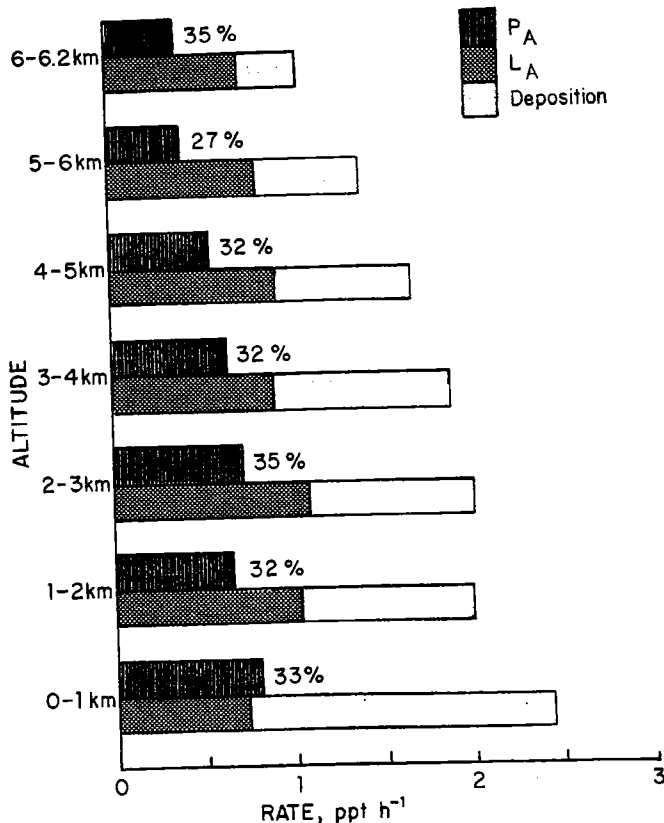


Fig. 8. Production and loss rates of acetic acid as a function of altitude, calculated for flights 11-25 and shown as 24-hour averages for each 1-km altitude band. The photochemical production rate  $P_A$  from reactions  $\text{CH}_3\text{CO}_3 + \text{HO}_2$  and  $\text{CH}_3\text{CO}_3 + \text{CH}_3\text{O}_2$  is compared to loss rates from reaction with OH ( $L_A$ ) and deposition. Numbers to the right of the  $P_A$  bars give the percent of the total loss rate of acetic acid that is balanced by photochemical production.

from biomass fires can be made by using the enrichment ratio  $\Delta\text{CH}_3\text{COOH}/\Delta\text{CO} = 0.006$  reported by Wofsy *et al.* [this issue] and the CO emission inventory cited above. We obtain an emission flux of  $6 \times 10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ , balancing only 10% of the acetic acid loss rate. It would appear that emission from biomass fires is only a minor source of acetic acid on the regional scale.

### 3. PHOTOCHEMISTRY IN BIOMASS FIRE PLUMES

#### Approach

On August 3, the ABLE 3A aircraft sampled two well-defined pollution layers at 4 km altitude over the town of Bethel (Plate 1). Trajectory analyses suggest that the layers originated from thunderstorm-generated forest fires, and had traveled for 1-2 days in the middle troposphere before interception by the aircraft [Wofsy *et al.*, this issue]. The mechanism by which the fire plumes were pumped to the middle troposphere is unknown; the trajectories suggest that this pumping took place shortly after emission, possibly in the convective activity associated with the thunderstorms. The chemical composition of the pollution layers is discussed in detail by Wofsy *et al.* [this issue]. Average concentration enrichments of CO and  $\text{NO}_y$  were  $\Delta\text{CO} = 80$  ppb and  $\Delta\text{NO}_y = 270$  ppt. The  $\Delta\text{PAN}/\Delta\text{NO}_y$  ratio was 0.23 in one layer and 0.38 in the other. No detectable enrichments of NO were observed. Enrichments of  $\text{O}_3$  were slight, 3-6 ppb.

We reconstruct the photochemical history of these pollution layers by using a Lagrangian plume model constrained to repro-

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AEROSOL DISTRIBUTION

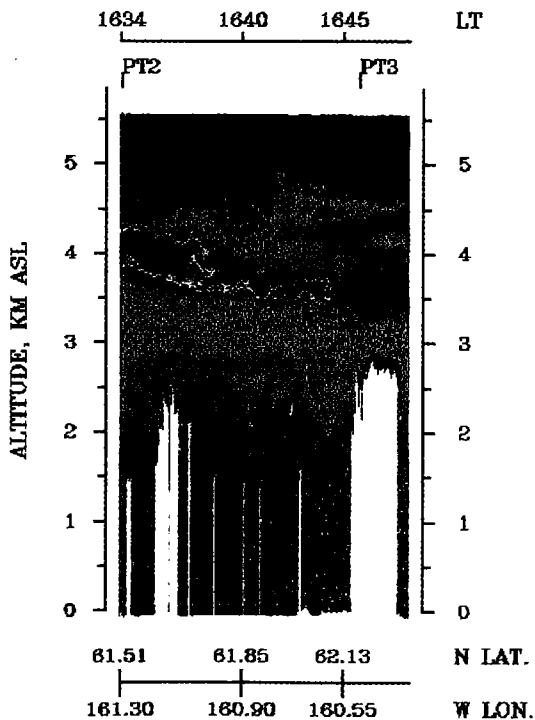
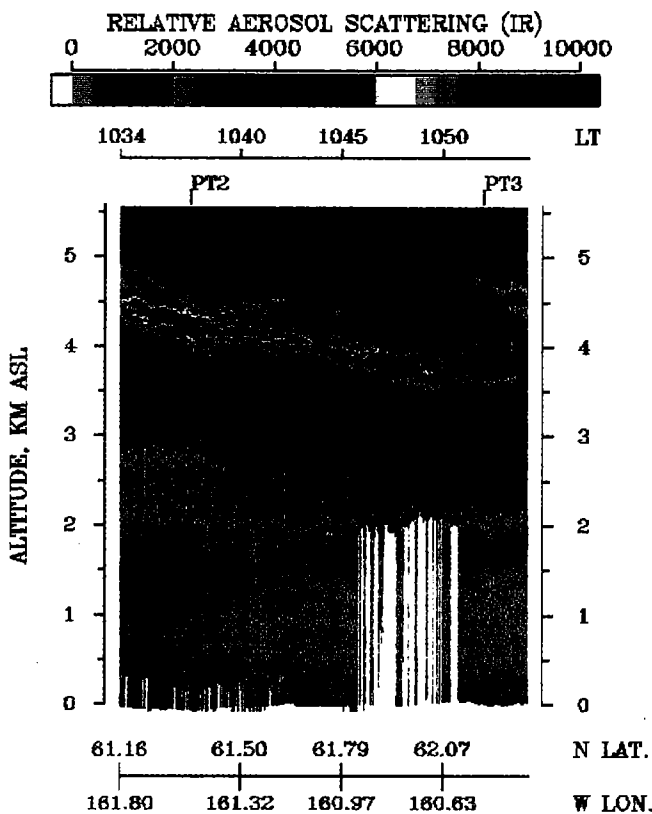


TABLE 1. Model Conditions for the Biomass Fire Plume Simulations

Species	Unit	Initial Concentration (Fresh Plume)		Background Concentration
		Diluted Plume	Diluting Plume	
CO	ppb	170	12,000	90
O <sub>3</sub>	ppb	50	50	50
NO <sub>x</sub>	ppt	300	40,800	25
PAN	ppt	200	200	200
HNO <sub>3</sub>	ppt	50	50	50
Ethane	ppt	1400	97,000	800
Propane	ppt	500	60,000	100
Butanes	ppt	100	12,000	20
Ethylene	ppt	1200	170,000	0
Propene	ppt	370	48,000	0
Butene	ppt	90	12,000	0
Benzene	ppt	140	16,000	30
Toluene	ppt	80	7,200	30
Xylene	ppt	20	2,400	0

Background concentrations are taken from ABLE 3A observations on August 3, 1988, except for benzene and toluene concentrations, which are taken from Rasmussen and Khalil [1983]. The choice of initial concentrations is discussed in the text.

duce the observed enrichments ΔCO and ΔNO<sub>y</sub> after a travel time of 2 days at 4-km altitude. Two simple schemes are used to model plume dilution: (1) instantaneous dilution upon emission, with no further dilution over the 2-day trajectory (diluted plume) and (2) horizontal dilution at a constant rate (diluting plume). These two schemes provide reasonable limiting cases; neither can pretend to capture the plume dynamics in a realistic manner, but comparison of the two gives a measure of the sensitivity of plume photochemistry to dilution rates. The width Y(t) of the diluting plume at time t is computed following Sillman et al. [1990]:

$$Y(t) = [Y(0)^2 + 8K_y t]^{1/2} \quad (1)$$

where Y(0) is the width of the fire and K<sub>y</sub> is a constant cross-flow diffusion coefficient. Concentrations in the diluting plume are adjusted at each model time step by entrainment of background air (Table 1).

Initial conditions for the calculations (Table 1) are selected by assuming that NO<sub>y</sub> is emitted in the fire as NO<sub>x</sub> and that CO and NO<sub>y</sub> are conserved over the 2-day travel time. The observed ratio ΔNO<sub>y</sub>/ΔCO = 0.0034 [Wofsy et al., this issue] then defines the NO<sub>x</sub>/CO emission ratio. In the diluting plume case we further assume an initial CO concentration of 12 ppm and a fire width Y(0) = 1 km, based on data from Cofer et al. [1989] for a boreal forest fire in Ontario. We then adjust K<sub>y</sub> to obtain ΔCO = 80 ppb after 2 days, corresponding to a plume width of 150 km. The resulting K<sub>y</sub> = 1.6x10<sup>4</sup> m<sup>2</sup> s<sup>-1</sup> is consistent with values recommended by Gifford [1982] for plume widening calculations.

Initial concentrations of NMHCs are selected by assuming a NMHC/CO emission ratio of 0.10 ppbC/ppb, taken from the boreal forest fire data of Cofer et al. [1989]. This ratio appears typi-

Plate 1. Aerosol vertical profiles measured by downward-pointing lidar in the morning (top) and afternoon (bottom) of August 3. "LST" is local standard time (two hours ahead of solar time). Results are shown in a false color display with the relative amount of atmospheric backscattering defined by the color scale. Black represents values greater than the maximum of the color scale, i.e., strongly scattering environments (clouds, pollution layers). The black layers at 4 km altitude (top and bottom panels) are biomass fire plumes. Regions of no data, e.g., under a cloud, are shown in white.

sition

of altitude, each 1-km reactions from the P<sub>A</sub> bars and by photo-

ment ratio in this issue] an emission of 30% of the biomass scale.

Well-defined (Plate 1). lifted from 1-2 days after [Wofsy] the plumes the trajectory emission, thunderstorms is disorganized ΔNO<sub>y</sub> = 0.38 in the model. En-

pollution to reproduce

cal of biomass fires in general, as indicated by data for selva and cerrado fires in Brazil [Greenberg *et al.*, 1984], and for a chaparral fire in California [Cofer *et al.*, 1989]. The speciation of NMHCs among alkanes, alkenes, and aromatic species is taken from Greenberg *et al.* [1984]. Initial concentrations of all secondary species (including  $O_3$  and PAN) are assumed equal to background. Fixed temperature (268 K) and dew point (263 K) are adopted from aircraft measurements. The chemical evolution of the plume is simulated for 48 hours using the mechanism described in the appendix. The simulations are initialized at noon; initialization at midnight produced no significant differences in results.

#### Loss of $NO_x$

The  $NO_x$  concentrations in the model plumes decrease to 50 ppt during the first day of travel and drop to below background (25 ppt) by the middle of the second day (Figure 9a). The lifetime of  $NO_x$  in the fresh plumes is only 5-7 hours, consistent with the lack of a detectable  $\Delta NO_x$  in the aircraft observations. The oxidation

of  $NO_x$  on the first day produces roughly equal proportions of  $HNO_3$  and PAN, plus small amounts of other organic nitrates (Figure 9b). The high yield of PAN reflects the low  $NO_x/NMHC$  emission ratio and the low temperatures. As the plumes age on the second day, slow decomposition of PAN takes place, because of the paucity of  $NO_x$ , shifting the composition of the  $NO_y$  pool towards  $HNO_3$  and  $RNO_x$ . The  $\Delta PAN/\Delta NO_x$  ratios after 2 days are 0.28 in the diluted plume and 0.38 in the diluting plume; both values fall within the range of observations.

#### Ozone production

Figure 9c shows the time evolution of  $O_3$  concentrations in the model plumes. Photochemical production of  $O_3$  is modest and confined mainly to the first day of travel when  $NO_x$  concentrations are relatively high. The decline of  $O_3$  concentrations in the diluting plume as the plume ages is due to entrainment of background air. Simulated enrichments  $\Delta O_3$  after 2 days of travel are 4 ppb in both plumes, consistent with observations.

Photochemical production of  $O_3$  in the model plumes is strongly  $NO_x$ -limited. Increasing  $NO_x$  emissions by a factor of 10 causes  $\Delta O_3$  to increase by a factor of 5, while increasing NMHC emissions has little effect on  $O_3$  (Table 2). This result reflects the low  $NO_x/NMHC$  emission ratio in the fire (0.034), which can be compared to typical  $NO_x/NMHC$  emission ratios of 0.1-1 in U.S. cities [Environmental Protection Agency, 1989]. The  $NO_x/CO$  emission ratio in the fire (0.0034) is also low compared to typical urban values (0.05-0.1). Our finding that  $O_3$  production in the ABLE 3A fire plumes was  $NO_x$ -limited may be applicable to biomass fire plumes in general. The review of biomass burning emissions by Crutzen and Andreae [1990] gives  $NO_x/CO$  emission ratios in the range 0.002-0.05 for various types of fires; these values are low compared to urban pollution. A likely explanation is that temperatures in biomass fires are relatively low. The particularly low  $NO_x/CO$  emission ratios in the ABLE 3A fires may reflect in addition the low nitrogen content of vegetation at high latitudes [Chapin and Shaver, 1985].

The above discussion implies that the relatively low  $\Delta O_3/\Delta CO$  ratios previously reported for biomass fire plumes in the tropics [Andreae *et al.*, 1988, 1992] can be explained simply by low  $NO_x/CO$  emission ratios. The  $\Delta O_3/\Delta NO_x$  ratio is an alternate measure of  $O_3$  production in the plumes. Assuming that  $O_3$  and  $NO_x$  are conserved in the plume, and that  $NO_y$  is emitted as  $NO_x$ , then the  $\Delta O_3/\Delta NO_x$  ratio measures the number of  $O_3$  molecules produced per molecule of  $NO_x$  emitted, i.e., the " $O_3$  production efficiency" [Liu *et al.*, 1987; Lin *et al.*, 1988]. The  $\Delta O_3/\Delta NO_x$  ratios measured in the ABLE 3A fire plumes ranged from 12 to 21 [Wofsy *et al.*, 1991], and our model gives a value of 13 (Table 2). These values are low compared to the  $O_3$  production efficiencies of 30-40 reported by Lin *et al.* [1988] from photochemical simulations of pollution plumes with same initial inputs of  $NO_x$  and NMHCs as in Table 1. Part of the difference appears to reflect the low temperatures in the ABLE 3A plumes, promoting conversion of  $NO_x$  to PAN.

We can estimate roughly the contribution of biomass fires plumes to the regional  $O_3$  budget at high northern latitudes by assuming an  $O_3$  production efficiency of 13 in the plumes, and a regional average  $NO_y$  emission flux of  $5 \times 10^8$  molecules  $cm^{-2} s^{-1}$  (section 2). The resulting  $O_3$  source is  $7 \times 10^9$  molecules  $cm^{-2} s^{-1}$ , small relative to the  $O_3$  sink of  $1.6 \times 10^{11}$  molecules  $cm^{-2} s^{-1}$  derived in section 2. Additional  $O_3$  production may take place on the regional scale following dispersion of  $NO_y$  emitted from fires and eventual decomposition to  $NO_x$ . In section 2 we estimated that biomass fires could account for 20% of the  $NO_y$  budget in

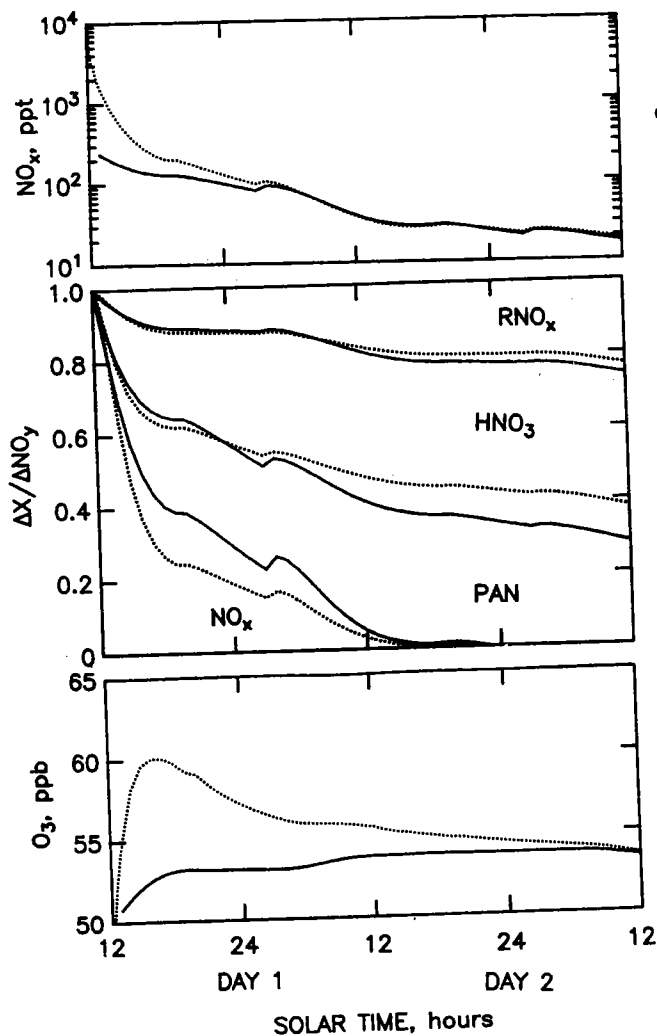


Fig. 9. Simulated chemical history of the biomass fire plumes sampled by the ABLE 3A aircraft on August 3. The calculations assume a 2-day travel time of the plumes starting at noon at the location of the fire, and ending at noon 2 days later at the location of the ABLE 3A aircraft. Results are shown for the diluted plume (solid lines) and for the diluting plume (dotted lines). (Top): Concentrations of  $NO_x$ . (Middle): Cumulative contributions of  $NO_x$ , PAN,  $HNO_3$ , and  $RNO_x$  to  $\Delta NO_y$ . (Bottom): Concentrations of  $O_3$ .

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TABLE 2. Concentration Enrichments in the August 3 Biomass Fire Plumes

	$\Delta\text{PAN}/\Delta\text{NO}_y$ ppb/ppb	$\Delta\text{O}_3$ ppb	$\Delta\text{O}_3/\Delta\text{NO}_y$ ppb/ppb	$\Delta\text{O}_3/\Delta\text{CO}$ ppb/ppb
Observations	0.23-0.38	3-6	12-21	0.04-0.08
Model				
1. Diluted plume	0.28	4	13	0.04
2. Diluting plume	0.38	4	13	0.04
3. $\text{NO}_x$ emissions $\times 10$	0.12	19	7	0.24
4. NMHC emissions $\times 10$	0.41	2	8	0.03

$\Delta X$  is the concentration enrichment of species X in the plume relative to background. Observations are from *Wofsy et al.* [this issue]. Model results are shown for 2-day old plumes. The sensitivity simulations 3 and 4 were conducted with the diluted plume assumption.

ABLE 3A, suggesting that the overall influence of fires on the regional  $\text{O}_3$  budget remains minor.

#### 4. CONCLUSIONS

Modeling of observations from the ABLE 3A expedition indicates that the  $\text{O}_3$  concentrations in the summertime Arctic troposphere reflect mainly a balance between input from the stratosphere, and losses of comparable magnitude from photochemistry and deposition. The observed concentrations of  $\text{NO}_x$  (10-50 ppt) are sufficiently high to reduce the  $\text{O}_3$  photochemical loss rate by a factor of 2.5 relative to a  $\text{NO}_x$ -free atmosphere. We estimate an atmospheric lifetime of 46 days for  $\text{O}_3$  in the 0-6 km column sampled during ABLE 3A; this lifetime would drop to 26 days if no  $\text{NO}_x$  were present. The small amounts of  $\text{NO}_x$  observed in ABLE 3A have thus a major effect on the regional  $\text{O}_3$  budget.

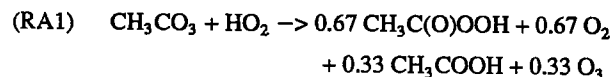
We find that decomposition of PAN can account for most of the  $\text{NO}_x$  observed in ABLE 3A below 4-km altitude, but for only 20% at 6 km altitude. The missing source of  $\text{NO}_x$  at high altitudes may be due to decomposition of unidentified organic nitrates. The atmospheric lifetime of  $\text{NO}_y$  is estimated at 29 days, implying that organic nitrate precursors of  $\text{NO}_x$  could be transported from distant sources. Long-range transport of mid-latitudes pollution probably made a substantial contribution to the  $\text{NO}_y$  budget. Decomposition of anthropogenic  $\text{NO}_y$  in the Arctic, providing a source of  $\text{NO}_x$ , could possibly explain the increase of tropospheric  $\text{O}_3$  concentrations observed in that region over the past two decades.

Biomass fires appear to be only a minor source of  $\text{O}_3$  in the Arctic because  $\text{NO}_x$  emissions from fires are weak. Production of  $\text{O}_3$  in the biomass fire plumes sampled during ABLE 3A was strongly  $\text{NO}_x$ -limited. The enrichment ratios  $\Delta\text{O}_3/\Delta\text{CO}$  observed in the ABLE 3A fire plumes are consistent with values previously reported for biomass fire plumes in the tropics, and are much lower than values for urban and industrial pollution. This result may be explained by the generally low  $\text{NO}_x/\text{CO}$  emission ratio from biomass burning relative to fossil fuel combustion.

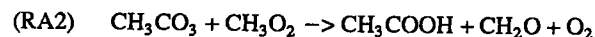
Only 30% of the acetic acid concentrations measured in ABLE 3A can be explained by reactions of  $\text{CH}_3\text{CO}_3$  with  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$ . Another 10% can be explained by emissions from biomass fires. There remains a major unidentified source of acetic acid in the atmosphere.

#### APPENDIX: CHEMICAL MECHANISM

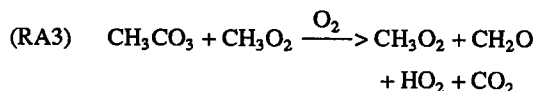
All chemical computations use the detailed mechanism of *Lurmann et al.* [1986], modified for low- $\text{NO}_x$  conditions as described by *Jacob and Wofsy* [1988, 1990]. The modifications include in particular acetic acid production from the  $\text{CH}_3\text{CO}_3 + \text{HO}_2$  and  $\text{CH}_3\text{CO}_3 + \text{CH}_3\text{O}_2$  reactions [*Moortgat et al.*, 1989a,b]:



$$k = 4.3 \times 10^{-13} e^{1040/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



$$k = 4.1 \times 10^{-15} e^{2100/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



$$k = 1.8 \times 10^{-9} e^{-1800/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Loss of PAN by reaction with OH [*Wallington et al.*, 1984] is also included:



$$k = 1.2 \times 10^{-12} e^{-653/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Reaction with OH dominates over thermal decomposition as a sink for PAN above 5 km. Photolysis of PAN [*Senum et al.*, 1984] is negligibly slow at all altitudes of concern.

The UV radiation field is computed with a standard six-stream algorithm for the Rayleigh scattering atmosphere. The stratospheric  $\text{O}_3$  column is  $8.75 \times 10^{18}$  molecules  $\text{cm}^{-2}$  (mean value for July 1988 measured at Poker Flats, Alaska). The UV albedo is 0.02 over tundra and ocean, and 0.8 over stratus decks (flight 14) and sea ice (north of  $71^\circ\text{N}$ ). Scattering by aerosols is included with an optical depth of 0.1 at 310 nm, varying inversely with wavelength.

The calculations of section 2 solve the system of coupled algebraic equations describing the mass balances of species at steady state, with fixed input concentrations of  $\text{O}_3$ ,  $\text{NO}$ , PAN,  $\text{HNO}_3$ ,  $\text{CO}$ , methane, ethane, propane, butanes, and acetone. The time-dependent calculations of section 3 integrate the chemical mechanism over time with an implicit finite difference method.

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