Summertime photochemistry of the troposphere at high northern latitudes

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Summertime Photochemistry of the Troposphere at High Northern Latitudes


The budgets of O₃, NOₓ (NO+NO₂), reactive nitrogen (NOₓ), 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 Experiment (ABLE 3A). It is found that concentrations of O₃ in the region are regulated mainly by input from the stratosphere, and losses of comparable magnitude from photochemistry and deposition. The concentrations of NOₓ (10-50 ppb) are sufficiently high to slow down O₃ photochemical loss appreciably relative to a NOₓ-free atmosphere; if no NOₓ were present, the lifetime of O₃ in the 0-6 km column would decrease from 46 to 26 days because of faster photochemical loss. The small amounts of NOₓ present in the Arctic troposphere have thus a major impact on the regional O₃ budget. Decomposition of peroxyacetyl nitrate (PAN) can account for most of the NOₓ below 4-km altitude, but for only 20% at 6-km altitude. Decomposition of other organic nitrates might supply the missing source of NOₓ. The lifetime of NOₓ in the ABLE 3A flight region is estimated at 29 days, implying that organic nitrate precursors of NOₓ 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 O₃; this observation is attributed in part to low NOₓ emissions in the fires, and in part to rapid conversion of NOₓ to PAN promoted by low atmospheric temperature. It appears that fires make little contribution to the regional O₃ budget. Only 30% of the acetic acid concentrations measured during ABLE 3A can be accounted for by reactions of CH₃COH with NOₓ and CH₂O. There remains a major unidentified source of acetic acid in the atmosphere.

1. INTRODUCTION

The Arctic Boundary Layer Experiment (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]. Aircraft measurements included concentrations of O₃, NO, NOₓ, peroxyacetyl nitrate (PAN), HNO₃, total reactive nitrogen (NOₓ), 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 O₃, NOₓ (NO+NO₂), and NOₓ.

Our principal objective is to explain the ~1% yr⁻¹ rise of O₃ 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⁻¹ 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 O₃ 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 O₃ in the middle troposphere were anticorrelated with concentrations of aerosol, H₂O, and CO₂; (2) well-defined layers of pollution were only marginally enriched in O₃; and (3) high-O₃ episodes were usually associated with stratospheric intrusions (documented by lidar). The NOₓ concentrations measured in ABLE 3A were in the range 10-50 ppb [Sandholm et al., this issue], sufficiently low that photochemistry should provide a sink for O₃. As discussed below, our analysis of the ABLE 3A data indicates that NOₓ 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 O₃ levels in the Arctic may manifest itself not by long-range transport of pollution-derived NOₓ, but rather by a decrease of the regional photochemical sink due to the presence of small amounts of NOₓ. The low concentrations of NOₓ measured in ABLE 3A were sufficient to reduce the rate of photochemical loss appreciably relative to a NOₓ-free atmosphere, thus increasing the O₃ lifetime. We show below that decomposition of PAN can account for most of the NOₓ measured below 4-km altitude, but for only 20% at 6-km altitude. Decomposition of other organic nitrates might provide the missing source of NOₓ at high altitude. Sandholm et al. [this issue] found that about half of total NOₓ in ABLE 3A could not be accounted for by NOₓ, PAN, or HNO₃, suggesting that unidentified organic nitrates made a large contribution to the NOₓ budget.

We estimate below a lifetime of 29 days for NOₓ in the ABLE 3A flight region, suggesting that PAN and other organic nitrate precursors of NOₓ could have been transported from distant sources. Singh et al. [this issue] have argued that long-range transport from northern mid-latitudes was a major source of NOₓ in ABLE 3A, and our analysis lends some support to that view. Concentrations of NOₓ 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 NOₓ, providing a source of NOₓ in the Arctic troposphere, could then explain the observed increase of O₃ concentrations in the region.

Biomass burning emissions at high northern latitudes have also
probably increased over the past two decades, as suggested by forest fire statistics for Canada [Van Wagner, 1986; Schindler et al., 1990; Stocks, 1991], but the effect on the regional O₃ budget appears to be small. The aged fire plumes sampled during ABLE 3A were only slightly enriched in O₃ [Wofsy et al., this issue]. The ΔO₃/ΔCO ratios in the plumes, where Δ represents the concentration enrichment relative to background, were in the range 0.04-0.18. In comparison, ΔO₃/ΔCO 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 ΔO₃/ΔCO 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 O₃ production from biomass fires, when normalized to CO emissions, is lower compared to production from fossil fuel combustion. We will explain this result as due to low NOₓ/CO and NOₓ/NH₃ emission ratios in biomass fires; O₃ production is NOₓ-limited, and NOₓ is rapidly oxidized to organic nitrates. The relatively low NOₓ 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 CH₃COOH + 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 O₃, NOₓ, NOₓ, 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 O₃, NOₓ, PAN, HNO₃, 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 O₃, NO, PAN, HNO₃, 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 NOₓ because of the sparsity of data for NO₂. All radicals other than NO are assumed to be in chemical steady state (including OH, peroxy species, and NO₂). Steady state is assumed also for oxygenated hydrocarbons with lifetimes of a few days or less (carbonyls, peroxydis) and for other short-lived compounds (e.g., HNO₂, HNO₃). 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 NHMC data availability. Each NHMC grab sample [Blake et al., this issue] was matched with 10-s average data for O₃, CO, and meteorological variables [Gregory et al., this issue; Harris et al., this issue (b); National Aeronautics and Space Administration, 1989], 1-min average data for NO and NOₓ [Sandholm et al., this issue], grab sample data for PAN [Singh et al., this issue (a)], and 15 to 60 min average data for HNO₃ 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, NOₓ, and RNOₓ. Here RNOₓ is the residual NOₓ, i.e., the fraction of observed NOₓ that cannot be accounted for by measured concentrations of NO, PAN, and HNO₃ or model concentrations of NOₓ, NO, N₂O, HNO₂, HNO₃, and HNO₄. This residual NOₓ is speculated to represent unidentified organic nitrates, hence the RNOₓ notation; it accounts for about half of total NOₓ.

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).
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 O₃, (P–L)O₃, as a function of altitude. Values are 24-hour averages computed by assuming (P–L)O₃ = 0 outside the 6-18 ST time window. Net O₃ 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 8.0x10ⁱ⁹ molecules cm⁻² s⁻¹, comparable in magnitude to the mean O₃ deposition flux of 8.2x10⁹ molecules cm⁻² s⁻¹ 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 1.6x10¹¹ molecules cm⁻² s⁻¹ for O₃ in the summertime Arctic troposphere. The mean 0 to 6-km column concentration of O₃ measured during flights 11-25 was 6.4x10¹⁷ molecules cm⁻³, from which we infer an O₃ column lifetime of 46 days. This lifetime is relatively short; we conclude that the regional O₃ 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 O₃...
implies that small anthropogenic perturbations to NO$_x$ could have a major effect on O$_3$ levels. In the low-NO$_x$ regime of interest here, (P–L)$_{O_3}$ increases linearly with increasing NO$_x$ concentration [Fishman et al., 1979]. To assess the sensitivity of (P–L)$_{O_3}$ to NO$_x$, we repeated our calculations for the 475 points with NO and PAN concentrations set to zero. The 24-hour average photochemical column loss rate of O$_3$ rose to 2.0x10$^{11}$ molecules cm$^{-2}$ s$^{-1}$, 2.5 times larger than in the standard calculation (Figure 5). The 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 NO$_x$ measured during ABLE 3A thus emerges as a major issue in the regional O$_3$ budget. We expect this NO$_x$ to represent on average a steady state between chemical sources and chemical sinks, because the lifetime against oxidation is short (~1 day) and emission sources are remote. The low variability of NO concentrations observed over the course of the expedition [Sandholm et al., this issue] supports the argument that NO$_x$ did not originate from direct emissions. The major chemical sources of NO$_x$ are:

(R1) PAN $\rightarrow$ NO$_2$ + CH$_3$CO$_3$
(R2) PAN + OH $\rightarrow$ NO$_2$ + products
(R3) HNO$_3$ + hv $\rightarrow$ NO$_2$ + OH
(R4) HNO$_3$ + OH $\xrightarrow{hv, O_3}$ NO$_2$ + H$_2$O + O$_3$
(R5) RNO$_x$ $\xrightarrow{T, OH, hv}$ NO$_2$ + products

and the major chemical sinks of NO$_x$ in the daytime are:

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

![Fig. 3. Vertical and temporal distribution of the 475 points in the database for flights 11-25.](image)

![Fig. 4. Mean diurnal variation of OH concentrations below 1-km altitude on flights 11-25.](image)

![Fig. 5. Net photochemical production rates of 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 NO and PAN concentrations set to zero.](image)
(R8) \[ \text{NO}_2 + \text{RCO}_3 + M \rightarrow \text{RNO}_x + M \]
(R9) \[ \text{NO} + \text{RO}_2 + M \rightarrow \text{RNO}_x + M \]

where RCO₃ represents peroxycetyl radicals other than CH₂CO₂, RO₂ represents organic peroxy radicals, and RNOₓ represents organic nitrates other than PAN. Reaction (R9) is a low-yield branch of the oxidation of NO by RO₂ [Lurmann et al., 1986].

Nighttime sinks of NOₓ include oxidation of NMHCs by NOₓ and hydrolysis of N₂O₅ in clouds. If these sinks were important, NOₐ should be depleted at night. Although no aircraft flights were conducted during the nighttime hours, the daytime NOₐ 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 NOₐ depletion (S. T. Sandholm, personal communication, 1990). We infer that nighttime chemistry probably had only a small effect on the budget of NOₐ 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 NOₓ from (R5) cannot be calculated due to uncertainties on the identities, concentrations, and reactivities of the RNOₓ species. We choose therefore to test the hypothesis that PAN and HNO₃ were the main sources of NOₓ, i.e., that (R5) was negligible. If this hypothesis is correct, then the NOₓ loss rate computed from (R6)+(R7)+(R8)+(R9) should balance the NOₐ production rate computed from (R1)+(R2)+(R3)+(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 NOₐ 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, (L-P)PAN, is defined as (R1)+(R2)+(R7); the net HNO₃ production rate, (P-L)HNO₃, is defined as (R6)-(R3)-(R4). Also shown in Figure 6 is the production rate P RNOₓ of RNOₓ species generated in the model by oxidation of propane and butanes. We find that net chemical loss of PAN, and net chemical production of HNO₃, take place on average throughout the 0 to 6-km column. Below 3 km there is a close balance between production of NOₓ from PAN decomposition on the one hand, and loss of NOₐ by oxidation to HNO₃ and RNOₓ on the other hand. At higher altitudes, however, a large fraction of the NOₓ loss is not balanced by decomposition of PAN. The source of NOₓ from PAN decomposition decreases rapidly with altitude because of the stability of PAN at low temperatures; the sinks of NOₓ from oxidation to HNO₃ decreases also with altitude but at a slower pace.

The missing source of NOₓ, (L-P)RNOₓ, could conceivably represent decomposition of organic nitrates other than PAN. In that case we might expect a positive correlation between (L-P)RNOₓ and the RNOₓ 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 RNOₓ concentration, to reduce influences of local deviations of NOₓ 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 NOₓ in ABLE 3A can be estimated by assuming that deposition of HNO₃ is the only NOₓ sink, and calculating the HNO₃ deposition flux needed to balance the net production rate (P-L)HNO₃ in Figure 6. The resulting 24-hour...
average HNO₃ deposition flux is $2.3 \times 10^9$ molecules cm$^{-2}$ s$^{-1}$. The mean 0 to 6-km column concentrations of HNO₃ and NO₂ measured on flights 11-25 were $8.9 \times 10^4$ and $5.7 \times 10^5$ molecules cm$^{-2}$, respectively, from which we infer HNO₃ and NO₂ column lifetimes of 4.5 and 29 days, respectively.

The long lifetime of NO₂ implies that distant sources could make major contributions to the NO₂ budget. Singh et al. [this issue (a)] and Wofsy et al. [this issue] point to three possibly important sources of NO₂ in ABLE 3A: fossil fuel combustion at mid-latitudes, biomass fires, and stratosphere-troposphere exchange. An estimate of the regional NO₂ source from biomass fires can be made by using the average ANO₂/ΔCO ratio of 0.0056 reported by Wofsy et al. [this issue] for the ABLE 3A fire plumes, and a CO emission inventory of $4 \times 10^4$ tons/month for fires north of 60°N in July [J.A. Logan, personal communication, 1992]. The resulting source of NO₂ is $5 \times 10^8$ molecules cm$^{-2}$ s$^{-1}$, balancing only 20% of the NO₂ 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 NO₂ budget at high northern latitudes.

Stratospheric input probably made a significant contribution to the NO₂ budget in ABLE 3A, as indicated by the negative correlation between NO₂ and CO concentrations observed in some regions of the atmosphere [Wofsy et al., this issue]. However, the low HNO₃/NO₂ concentration ratio at 6-km altitude (Figure 2) argues against a dominant stratospheric influence. Most of the NO₂ in the lower stratosphere is present as HNO₃ [Russell et al., 1988; Fahey et al., 1990], and conversion of HNO₃ 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 NO₂ 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 CH₃CO + HO₂ and CH₂CO + CH₂O₂, 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 CH₃COOH/HNO₃ 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 HNO₃. 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 HNO₃, which is in turn calculated to balance the net production rate ($P_A - L_A$)HNO₃ 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 $6 \times 10^8$ molecules cm$^{-2}$ 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 CH₃CO + 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 permutational reactions of organic peroxy and peroxyxy radicals [Martinich and Calvert, 1990], biogenic emissions [Keele and Goloway, 1986; Talbot et al., 1990], and emissions from biomass fires [Talbot et al., 1988]. A rough estimate of the regional emission from biomass fires can be made by using the enrichment ratio $\Delta$CH₃COOCH/ΔCO = 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 cm$^{-2}$ 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 NO₂ were $\Delta$CO = 80 ppb and $\Delta$NO₂ = 270 ppb. The $\Delta$PAN/$\Delta$NO₂ ratio was 0.23 in one layer and 0.38 in the other. No detectable enrichments of NO were observed. Enrichments of O₃ were slight, 3-6 ppb.

We reconstruct the photochemical history of these pollution layers by using a Lagrangian plume model constrained to repro-
TABLE 1. Model Conditions for the Biomass Fire Plume Simulations

<table>
<thead>
<tr>
<th>Species</th>
<th>Unit</th>
<th>Initial Concentration (Fresh Plume)</th>
<th>Background Concentration</th>
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<td></td>
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<td>Diluted Plume</td>
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<tr>
<td>O₃</td>
<td>ppb</td>
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<td>ppt</td>
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</table>

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

duce the observed enrichments ΔCO and ΔNO₂ 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]:

$$Y(t) = [Y(0)]^2 + 4K_p t^2$$

where $Y(0)$ is the width of the fire and $K_p$ is a constant cross-flow diffusion coefficient. Concentrations in the diluting plume are adjusted at each model step by entrainment of background air (Table 1).

Initial conditions for the calculations (Table 1) are selected by assuming that NO₂ is emitted in the fire as NO₃ and that CO and NO₂ are conserved over the 2-day travel time. The observed ratio $\Delta NO₂/\Delta CO = 0.0034$ [Wofsy et al., this issue] then defines the NO₂/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 Cofe et al. [1989] for a boreal forest fire in Ontario. We then adjust $K_p$ to obtain $\Delta CO = 80$ ppb after 2 days, corresponding to a plume width of 150 km. The resulting $K_p = 1.6 \times 10^6$ m² s⁻¹ 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 0.1 ppbC/ppb, taken from the boreal forest fire data of Cofe 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.
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 [Cofe 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 O₃ 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 NOₓ**

The NOₓ 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 NOₓ in the fresh plumes is only 5-7 hours, consistent with the lack of a detectable ∆NOₓ in the aircraft observations. The oxidation of NOₓ on the first day produces roughly equal proportions of HNO₃ and PAN, plus small amounts of other organic nitrates (Figure 9b). The high yield of PAN reflects the low NOₓ/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 NOₓ, shifting the composition of the NOₓ pool towards HNO₃ and RNOₓ. The ∆PAN/∆NOₓ 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 O₃ concentrations in the model plumes. Photochemical production of O₃ is modest and confined mainly to the first day of travel when NOₓ concentrations are relatively high. The decline of O₃ concentrations in the diluting plume as the plume ages is due to entrainment of background air. Simulated enrichments ∆O₃ after 2 days of travel are 4 ppb in both plumes, consistent with observations.

Photochemical production of O₃ in the model plumes is strongly NOₓ-limited. Increasing NOₓ emissions by a factor of 10 causes ∆O₃ to increase by a factor of 5, while increasing NMHC emissions has little effect on O₃ (Table 2). This result reflects the low NOₓ/NMHC emission ratio in the fire (0.034), which can be compared to typical NOₓ/NMHC emission ratios of 0.1-1 in U.S. cities [Environmental Protection Agency, 1989]. The NOₓ/CO emission ratio in the fire (0.0034) is also low compared to typical urban values (0.05-0.1). Our finding that O₃ production in the ABLE 3A fire plumes was NOₓ-limited may be applicable to biomass fire plumes in general. The review of biomass burning emissions by Crutzen and Andreae [1990] gives NOₓ/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 NOₓ/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 ∆O₃/∆CO ratios previously reported for biomass fire plumes in the tropics [Andreae et al., 1988, 1992] can be explained simply by low NOₓ/CO emission ratios. The ∆O₃/∆NOₓ ratio is an alternate measure of O₃ production in the plumes. Assuming that O₃ and NOₓ are conserved in the plume, and that NOₓ is emitted as NOₓ, then the ∆O₃/∆NOₓ ratio measures the number of O₃ molecules produced per molecule of NOₓ emitted, i.e., the "O₃ production efficiency" [Liu et al., 1987, Lin et al., 1988]. The ∆O₃/∆NOₓ 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 O₃ production efficiencies of 30-40 reported by Lin et al. [1988] from photochemical simulations of pollution plumes with some initial inputs of NOₓ and NMHCs as in Table 1. Part of the difference appears to reflect the low temperatures in the ABLE 3A plumes, promoting conversion of NOₓ to PAN.

We can estimate roughly the contribution of biomass fires plumes to the regional O₃ budget at high northern latitudes by assuming an O₃ production efficiency of 13 in the plumes, and a regional average NOₓ emission flux of 5x10⁹ molecules cm⁻² s⁻¹ (section 2). The resulting O₃ source is 7x10⁹ molecules cm⁻² s⁻¹, small relative to the O₃ sink of 1.6x10¹¹ molecules cm⁻² s⁻¹ derived in section 2. Additional O₃ production may take place on the regional scale following dispersion of NOₓ emitted from fires and eventual decomposition to NOₓ. In section 2 we estimated that biomass fires could account for 20% of the NOₓ budget in...
TABLE 2. Concentration Enrichments in the August 3 Biomass Fire Plumes

<table>
<thead>
<tr>
<th></th>
<th>$\Delta$PAN/\Delta$NO_x$</th>
<th>$\Delta$O$_3$</th>
<th>$\Delta$O$_x$/\Delta$NO_x$</th>
<th>$\Delta$O$_y$/\Delta$O_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observations</td>
<td>0.23-0.38</td>
<td>3-6</td>
<td>12-21</td>
<td>0.04-0.08</td>
</tr>
<tr>
<td>Model</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Diluted plume</td>
<td>0.28</td>
<td>4</td>
<td>13</td>
<td>0.04</td>
</tr>
<tr>
<td>2. Diluting plume</td>
<td>0.38</td>
<td>4</td>
<td>13</td>
<td>0.04</td>
</tr>
<tr>
<td>3. NO$_x$ emissions x10</td>
<td>0.12</td>
<td>19</td>
<td>7</td>
<td>0.24</td>
</tr>
<tr>
<td>4. NMHC emissions x10</td>
<td>0.41</td>
<td>2</td>
<td>8</td>
<td>0.03</td>
</tr>
</tbody>
</table>

$\Delta X$ 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.

4. Conclusions

Modeling of observations from the ABLE 3A expedition indicates that the 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 NO$_x$ (10-50 ppt) are sufficiently high to reduce the O$_3$ photochemical loss rate by a factor of 2.5 relative to a NO$_x$-free atmosphere. We estimate an atmospheric lifetime of 46 days for O$_3$ in the 0-6 km column sampled during ABLE 3A; this lifetime would drop to 26 days if no NO$_x$ were present. The small amounts of NO$_x$ observed in ABLE 3A have thus a major effect on the regional O$_3$ budget.

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

Biomass fires appear to be only a minor source of O$_3$ in the Arctic because NO$_x$ emissions from fires are weak. Production of O$_3$ in the biomass fire plumes sampled during ABLE 3A was strongly NO$_x$-limited. The enrichment ratios $\Delta$O$_3$/\Delta$O$_x$ 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 NO$_x$/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 CH$_3$CO$_2$H with HO$_2$ and CH$_3$O. 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-NO$_x$ conditions as described by Jacob and Wofsy [1988, 1990]. The modifications include in particular acetic acid production from the CH$_3$CO$_2$H + HO$_2$ and CH$_3$CO$_2$H + CH$_3$O reactions [Moortgat et al., 1989a,b];

$($RA1$) \quad \begin{align*}
\text{CH}_3\text{CO}_2\text{H} + \text{HO}_2 & \rightarrow 0.67 \text{CH}_3\text{C(O)}\text{OOH} + 0.67 \text{O}_2 \\
& + 0.33 \text{CH}_3\text{COOH} + 0.33 \text{O}_3 \\
\end{align*}$

$k = 4.3 \times 10^{-15} \text{e}^{1000/kT} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$

$($RA2$) \quad \begin{align*}
\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{O}_2 & \rightarrow \text{CH}_3\text{COOH} + \text{CH}_2\text{O} + \text{O}_2 \\
\end{align*}$

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

$($RA3$) \quad \begin{align*}
\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{O}_2 & \rightarrow \text{CH}_2\text{O}_2 + \text{CH}_2\text{O} \\
& + \text{HO}_2 + \text{CO}_2 \\
\end{align*}$

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

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

$($RA4$) \quad \text{PAN} + \text{OH} \rightarrow \text{NO}_2 + \text{products}$

$k = 1.2 \times 10^{-12} \text{e}^{-650/kT} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$

Reaction with OH dominates over thermal decomposition as a sink for PAN above 5 km. Photoysis of PAN [Serum 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 O$_3$ column is 8.75 x 10$^{18}$ molecules 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°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 O$_3$, NO, PAN, HNO$_3$, 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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