Origin of tropospheric NO\textsubscript{x} over subarctic eastern Canada in summer

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Abstract. The origin of NO\textsubscript{2} in the summertime troposphere over subarctic eastern Canada is investigated by photochemical modeling of aircraft and ground-based measurements from the Arctic Boundary Layer Expedition (ABLE 3B). It is found that decomposition of peroxyacetyl nitrate (PAN) can account for most of the NO\textsubscript{x} observed between the surface and 6.2 km altitude (aircraft ceiling). Forest fires represent the principal source of PAN in the region, implying the same origin for NO\textsubscript{2}. There is, however, evidence for an unidentified source of NO\textsubscript{x} in occasional air masses subsiding from the upper troposphere. Isoprene emissions from boreal forests maintain high NO\textsubscript{x} concentrations in the continental boundary layer over eastern Canada by scavenging OH and NO\textsubscript{3}, thus slowing down conversion of NO\textsubscript{2} to HNO\textsubscript{3}, both in the daytime and at night. This effect is partly compensated by the production of CH\textsubscript{3}CO\textsubscript{2} radicals during isoprene oxidation, which slows down the decomposition of PAN subsiding from the free troposphere. The peroxy radical concentrations estimated from concurrent measurements of NO and NO\textsubscript{2} concentrations during ABLE 3B are consistent with values computed from our photochemical model below 4 km, but model values are low at higher altitudes. The discrepancy may reflect either a missing radical source in the model or interferences in the NO\textsubscript{2} measurement.

1. Introduction

Nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}) control the tropospheric production of O\textsubscript{3} and OH. Knowledge of the processes that govern tropospheric NO\textsubscript{x} concentrations is essential to understanding the present, past and future oxidizing capacity of Earth's atmosphere [Isaksen and Hov, 1987; Crutzen and Zimmerman, 1991; Thompson, 1992]. Distributions of NO\textsubscript{x} in the global troposphere have been simulated using two or three-dimensional chemistry, transport, and deposition models and estimated inventories of NO\textsubscript{x} emissions [Levy and Maxim, 1987; Penner et al., 1991; Kuhl et al., 1992; Kasibhatla et al., 1993]. However, the origin of NO\textsubscript{x} in the remote troposphere remains uncertain. Transport of primary NO\textsubscript{x} from source regions is limited, because NO\textsubscript{x} is oxidized to HNO\textsubscript{3}, in a matter of a few days. It appears that diffuse chemical sources must be responsible for maintaining the NO\textsubscript{x} levels in the remote troposphere.

Peroxyacetyl nitrate (PAN, CH\textsubscript{2}C(O)OONO\textsubscript{2}), which is produced in the oxidation of hydrocarbons, represents an ubiquitous reservoir of NO\textsubscript{x} in the remote troposphere [Singh et al., 1986, 1990, 1992, 1994a]. Since PAN is stable at the low temperatures of the upper troposphere, it may provide a vehicle for the long-range transport of NO\textsubscript{x} from source regions [Crutzen, 1979; Singh and Hanst, 1981]. The importance of PAN decomposition as a source of NO\textsubscript{x} in the remote troposphere has been evaluated recently in photochemical model analyses of observations taken over western Alaska in summer (Arctic Boundary Layer Expedition (ABLE) 3A) and at Mauna Loa, Hawaii (Mauna Loa Observatory Photochemistry Experiment (MLOPEX)). Jacob et al. [1992] found that PAN decomposition in ABLE 3A could account for most of the NO\textsubscript{x} observed below 4 km but not above. Liu et al. [1992] and Walega et al. [1992] found that PAN decomposition could provide only a minor source of NO\textsubscript{x} in MLOPEX. The origin of NO\textsubscript{x} in MLOPEX remains uncertain (R. R. Chatfield. The anomalous HNO\textsubscript{3}/NO\textsubscript{2} ratio of remote tropospheric air: Is there conversion of nitric acid to formic acid and NO\textsubscript{2}? submitted to Geophysical Research Letters, 1994).

We present here a photochemical investigation of the NO\textsubscript{x} budget in the troposphere over eastern Canada in summer, using data from the ABLE 3B expedition conducted in July-August, 1990 [Harriss et al., 1994]. This expedition offered a comprehensive documentation of air chemistry over the region including mixing ratios of O\textsubscript{3}, NO, NO\textsubscript{2}, PAN, NO\textsubscript{3}, CO, and hydrocarbons measured from aircraft up to 6.2 km altitude and biosphere-atmosphere exchange fluxes measured from an instrumented tower at a boreal woodland site near Schefferville, Quebec (see special section "The Northern Wetlands Study and the Arctic Boundary Layer Expedition 3B: An International and Interdisciplinary Field Campaign" in Journal of Geophysical Research, 99 (D1), 1421-1539, 1994). We analyze the origin of NO\textsubscript{x} in ABLE 3B by using a combination of zero-dimensional (0-D) and one-dimensional (1-D) models constrained with the observations (details presented in section 2). The 0-d model calculations are used for the free tro-
osphere, yielding an ensemble of snapshots of local photochemistry along the aircraft flight tracks from which regional statistics for the NO$_2$ budget can be obtained. The 1-D model calculations are used for the continental boundary layer (CBL) over the boreal woodland and account for diel variations in vertical mixing and biogenic isoprene emissions. The woodlands of eastern Canada are large sources of isoprene [Blake et al., 1994]. The ABLE 3B data provide a rare chance to study the chemistry of isoprene under the low NO$_2$ conditions which are characteristic of the CBL over remote regions.

The NO$_2$ budgets in the free troposphere and in the continental boundary layer are presented in sections 3 and 4, respectively. Conclusions are in section 5. The appendix provides discussion on the feasibility of using the concurrent measurements of NO and NO$_2$ in ABLE 3B to calculate the concentration of peroxy radicals and test the accuracy of photochemical models.

2. Methods

A map of the ABLE 3B region is shown in Figure 1. Air masses of various chemical compositions were encountered by the aircraft, reflecting influences from forest and tundra fires, industrial and urban pollution, stratospheric intrusions, and tropical outflow (Table 1). The ABLE 3B mission design placed particular emphasis on sampling biomass fire plumes. Air masses influenced by biomass fire emissions, as diagnosed by CO concentrations greater than 120 ppb [Falbot et al., 1994], accounted for about 30% of the aircraft observations in the free troposphere. Lidar measurements of aerosol concentrations in the 2 to 6 km column during the expedition suggest that air influenced by biomass burning occupied, on average, 13% of the free troposphere, background air, 42%, stratospherically influenced air, 35%, and other types, 12% [Browell et al., 1994].

We use a 0-D model to calculate the concentrations of radicals and other secondary species at chemical steady state in the free troposphere. The calculations are constrained with the ensemble of measurements taken aboard the aircraft including temperature, dew point, pressure, UV radiation fluxes (zenith and nadir), and concentrations of NO, PAN, HNO$_3$, O$_3$, CO, acetone, C$_1$-3 alkenes, C$_3$-5 alkenes, benzene, and toluene. Measurements of NO are more reliable than those of NO$_2$ owing to possible interference in the NO$_2$ measurement (see appendix). The calculations are conducted for 3-min averaging intervals in the aircraft observations, representing the time resolution of the NO measurement. There are 165 intervals in the free troposphere (2.5-6.2 km) where concurrent measurements are available for all the above input variables except acetone. The data are sparse for acetone; missing data are filled based on the correlation between acetone and CO (Figure 2) (see also Singh et al. [1994b]).

The 0-D model is inadequate in the continental boundary layer (CBL) (below 2.5 km), where the concentrations of radicals are sensitive to the abundance of biogenic isoprene and its oxidation products [Jacob and Wofsy, 1990]. The lifetime of isoprene is only a few hours, while the carbonyls produced successively in the isoprene oxidation chain have lifetimes of a few hours to a few days. One cannot assume that the isoprene oxidation products are in local chemical steady state with the isoprene concentrations measured aboard the aircraft. We use therefore a time-dependent, 1-D model for the CBL, following Trainer et al. [1987, 1991] and Jacob and Wofsy [1988, 1990], and apply this model to simulate observations over the Schefferville tower site on August 7 when detailed measurements from the tower and from an aircraft spiral over the tower are available. The tower site is 0.5 km above sea level. The CBL in our 1-D model extends to 2.25 km above ground level, representing the afternoon maximum of mixed layer depth as measured locally from rawinsondes [Fitzjarrald and Moore, 1994]. Photochemical calculations are conducted at seven grid points (0.01, 0.1, 0.2, 0.5, 1.0, 1.5, and 2.0 km above the canopy). Vertical transport is simulated with an eddy diffusion parameterization based on local measurements of the mixed layer depth $z$, and of the fluxes of momentum and sensible heat [Lamb et al., 1975]. The eddy diffusion coefficient between $z$ and 2.25 km is adjusted to reproduce the observed vertical profiles of O$_3$ mixing ratio, resulting in a ventilation lifetime of 4.5 days for the CBL.

![Figure 1](image)

**Figure 1.** Map of the Arctic Boundary Layer Experiment (ABLE) 3B study region. The hatched areas indicate regions of intensive aircraft flight. The tower site was located near Schefferville, Quebec.
Table 1. Mean Characteristics of Air Masses Observed in the Free Troposphere Over Eastern Canada in Summer 1990

<table>
<thead>
<tr>
<th>Type 1, Altitude, km</th>
<th>Type 2, Altitude, km</th>
<th>Type 3, Altitude, km</th>
<th>Type 4, Altitude, km</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5-3.5</td>
<td>3.5-4.5</td>
<td>4.5-6.2</td>
<td>2.5-3.5</td>
</tr>
<tr>
<td>( n )</td>
<td>24</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>( T, , ^\circ C )</td>
<td>-3</td>
<td>-6</td>
<td>-13</td>
</tr>
<tr>
<td>( DPT, , ^\circ C )</td>
<td>-8</td>
<td>-17</td>
<td>-18</td>
</tr>
<tr>
<td>NO</td>
<td>6</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>20</td>
<td>29</td>
<td>27</td>
</tr>
<tr>
<td>PAN</td>
<td>190</td>
<td>200</td>
<td>320</td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>41</td>
<td>57</td>
<td>51</td>
</tr>
<tr>
<td>NO(_x)</td>
<td>260</td>
<td>510</td>
<td>530</td>
</tr>
<tr>
<td>( O_3 )</td>
<td>46</td>
<td>54</td>
<td>61</td>
</tr>
<tr>
<td>CO</td>
<td>100</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>Ethyne</td>
<td>80</td>
<td>82</td>
<td>99</td>
</tr>
<tr>
<td>Ethene</td>
<td>24</td>
<td>24</td>
<td>39</td>
</tr>
<tr>
<td>Ethane</td>
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<td>Propane</td>
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</tr>
<tr>
<td>Butane</td>
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<td>15</td>
<td>16</td>
</tr>
<tr>
<td>Benzene</td>
<td>35</td>
<td>34</td>
<td>43</td>
</tr>
<tr>
<td>Acetone</td>
<td>1200</td>
<td>1100</td>
<td>1100</td>
</tr>
<tr>
<td>( \Delta N\text{O}_3, , % )</td>
<td>2</td>
<td>40</td>
<td>22</td>
</tr>
</tbody>
</table>

Air mass types are defined following Talbot et al. [1994] as 1. Regional background; 2. biomass burning influence; 3. tropical outflow; and 4. stratospheric influence. The mean characteristics are computed from aircraft observations for the 165, 3-min intervals used in our photochemical modeling calculations. Volume mixing ratios are in parts per trillion (ppt) except for CO, \( O_3 \) in parts per billion. Unlisted species were generally near or below their detection limits; 10 ppt propane, 5 ppt toluene, and 2 ppt for \( \geq 4 \) alkanes. Abbreviations are \( n \), number of observations; \( T \), temperature; DPT, dew point; PAN, peroxyacetyl nitate.

\( \Delta N\text{O}_3 \) is the percent of NO not accounted for by observations of NO\(_x\), PAN, and HNO\(_3\); negative values indicate that the sum of concentrations of these species exceeded the observed concentration of NO\(_x\). For further details on the NO\(_x\) mass balance, see Sandholm et al. [1994].

The CRI model uses as upper boundary conditions the mean concentrations of \( O_3 \), NO, NO\(_x\), and PAN measured between 2.5-3.0 km above sea level and the mean concentrations of peroxydes and carboxyls calculated in the 0-D model under background conditions. Vertical profiles of HNO\(_3\), CO, and hydrocarbons other than isoprene are specified using observations from the aircraft spirals below 2 km. The diurnal variations of temperature and relative humidity are specified based on interpolation of aircraft measurements and hourly ground measurements. The deposition flux of \( O_3 \) to the surface is calculated on the basis of the hourly mean \( O_3 \) deposition velocities measured at the tower, typically 0.33 cm s\(^{-1}\) during the day and 0.03 cm s\(^{-1}\) at night (J. W. Munger et al., manuscript in preparation, 1994). We assume that PAN and peroxydes have the same deposition velocity as \( O_3 \). Soil emission of NO and dry deposition of NO\(_x\) were negligibly small (Bakwin et al., 1994). The dry cycle of isoprene emission is specified according to Jacob et al. [1993], assuming a leaf area index of 2 and with the midday emission rate adjusted to match the isoprene concentrations measured in the CBL during the aircraft spiral. The resulting 24-hour average emission flux of isoprene is 6.1x10\(^{10}\) molecules cm\(^{-2}\) s\(^{-1}\). In comparison, Klinger et al. [1994] estimated a mean isoprene emission rate of 5.5x10\(^{10}\) molecules cm\(^{-2}\) s\(^{-1}\) along a successional gradient in the Hudson Bay lowlands.


Aerosol chemistry is not included in our calculations. Nighttime hydrolysis of N\(_2\)O\(_5\) in aqueous aerosols is a sink for NO\(_x\) [Heikes and Thompson, 1983; Dentener and Crutzen, 1993]. However, the NH\(_3\)/SO\(_4\) equivalent ratio in ABL 3B averaged 1.4 for background air [Gorzelnska et al., 1994], implying that sulfate aerosol would be present as solid (NH\(_4\))\(_2\)SO\(_4\) [Tang et al., 1978]. Conversion of N\(_2\)O\(_5\) to HNO\(_3\) on solid aerosols is negligibly slow [Mozurkewich and Calvert, 1988].

In the 0-D model the NO\(_x\) photolysis rate coefficient \( J_{\text{NO}_x} \) is obtained from the UV measurements by zenith and nadir Eppley radiometers [Madronich, 1987; Chameides et al., 1990]. Photolysis rate coefficients for other species are calculated using a six-stream radiative transfer model for the clear sky, Rayleigh-scattering atmosphere [Logan et al., 1981] and are scaled by the ratio of \( J_{\text{NO}_x} \) calculated with the model to \( J_{\text{NO}_x} \) derived from the UV measurements. In these calculations, surface albedo is fixed at 0.06, a value obtained from extrapolation of Eppley measurements to ground level. The overhead ozone column is taken from daily satellite measurements at a resolution of 1° latitude by 1° longitude (total ozone mapping spectrometer) and ranges from 290 to 360 Dobson units. The ratio of \( J_{\text{NO}_x} \) obtained from Eppley meas.
Figure 2. Relationship of acetone with CO. The line represents a least squares fit through the data. Mixing ratios of CO were averaged to measurement intervals of acetone. Data include all acetone measurements over eastern Canada during ABLE 3B.

Figure 3. Sources and sinks of NOx in the free troposphere (2.5-6.2 km) during ABLE 3B. Values are daytime means obtained by averaging the rates (parts per trillion per hour) computed for individual 3-min intervals, first according to time of day (2-hour bins, with morning/afternoon folding) and then over 12 hours from 0600 to 1800 UT. The data were segregated by air mass type (Table 1). The number of data points used in the computation are, respectively, 16 for all data, 82 for background air, 33 for stratospheric influence, 16 for tropical outflow, and 34 for biomass burning influence. The top abscissa scale is for the case of biomass burning influence, and the bottom abscissa scale is for all other cases.

3. NOx in the Free Troposphere

Mean production and loss rates of NOx in the free troposphere during daytime are shown in Figure 3 for individual air mass types. The reaction rates calculated for each 3-min interval were first averaged according to time of day (2-hour bins, with morning/afternoon folding to overcome a lack of measurements in the early morning) and then averaged over daytime hours (0600-1800 LT). Nighttime chemistry is assumed negligible in the free troposphere for reasons discussed above. We find that sources and sinks of NOx are in close balance in background air (Table 1, type 1). Decomposition of PAN represents the largest source for NOx, and therefore can explain most of the observed NOx during ABLE 3B. Photoxduction of HNO3 to NOx is negligibly slow.

The effect of uncertainties in measured concentrations and rate constants must be considered in our NOx mass balance. The rates for PAN formation and thermal decomposition are estimated to have uncertainties of 20% at 298 K [Atkinson et al., 1992]. The precision and accuracy of the PAN measurement are estimated to be 10% and 25%, respectively, of PAN mixing ratios [Singh et al., 1994a]. The principal sources of the CH3CO2 precursor to PAN in the model are photoxulation of acetone, oxidation of acetaldelyde, and decomposition of PAN. The error caused by inferring acetone concentrations from observations of CO can be estimated to be 0.25 ppb (Figure 2), which would cause a mean error of 0.2 parts per trillion per hour (hereafter, ppb h⁻¹) in the computation of PAN production. Although the above uncertainties are substantial, they are not so large as to affect our central conclusion that PAN decomposition can account for most of the NOx observed during ABLE 3B.

Forest and tundra fires were found to be the major source for PAN, acetone, and other nonmethane hydrocarbons during ABLE 3B [Singh et al., 1994b; Talbot et al., 1994; Wofsy et al., 1994]. Long-range transport of midlatitude pollution was found to be of secondary importance. Nitrogen oxides emitted from biomass burning are efficiently converted to PAN in the fire plumes, because of the abundance of reactive hydrocarbons [Jacob et al., 1992], and additional PAN is formed in the regional scale following photoxulation of pyrogenic acetone.

Air masses sensibly influenced by biomass burning in ABLE 3B (Table 1, type 2) showed indication of rapid decomposition of
PAN (Figure 3). The resulting net source for NO\textsubscript{2} in Figure 3 is 10 ppt h\textsuperscript{-1}, but the mean concentration of NO\textsubscript{2} in these air masses was only 40-50 parts per trillion (hereafter, ppt). Reconciling the model NO\textsubscript{2} budgets with the observed NO\textsubscript{2} concentrations would require rapid dilution of the air masses with the regional background. However, an underestimate of PAN formation is also possible, because many primary and secondary species, particularly oxygenated hydrocarbons, may be present in type 2 air masses but not included in the model. Such species could decompose to yield CH\textsubscript{3}CO\textsubscript{2} radical and promote PAN formation.

Tropical air masses originating from the Pacific Ocean (Table 1, type 3) showed a near balance between chemical sources and sinks of NO\textsubscript{2} (Figure 3). However, the total NO\textsubscript{2} was exceeded by the sum of individual NO\textsubscript{2} species in these air masses. Reasons for the abnormal NO\textsubscript{2} composition are unclear; measurement errors could not be ruled out, though it is unlikely that possible errors can account for all of missing NO\textsubscript{2} [Sandholm et al., 1994].

Air masses subsiding from the upper troposphere (Table 1, type 4) represent the only case where decomposition of PAN was insufficient to account for the observed NO\textsubscript{2}. One possible explanation for the missing NO\textsubscript{2} source is decomposition of unidentified nitrogen compounds. Nearly 50% of total NO\textsubscript{2} in type 4 air masses was unaccounted for by measurements of NO\textsubscript{2}, PAN, and HNO\textsubscript{3} (Table 1). Figure 4 shows the relation between the net loss of NO\textsubscript{2} computed in the model, equivalent to a missing source of NO\textsubscript{2}, and the NO\textsubscript{2} deficit in air of type 4. The missing source of NO\textsubscript{2} appears to increase with the NO\textsubscript{2} deficit. The NO\textsubscript{2} budget would be balanced if the missing species representing the NO\textsubscript{2} deficit were converted to NO\textsubscript{2} in the free troposphere with chemical lifetime of a few weeks. A remarkable feature of air masses of type 4 was the low mixing ratio of HNO\textsubscript{3} (42 ppt on average). Such a concentration would be obtained in about 3 days from oxidation of NO\textsubscript{2} (Figure 3). Reduction of HNO\textsubscript{3} to NO\textsubscript{2} on a timescale of 3 days would balance the NO\textsubscript{2} budget (Figure 3), but the chemical lifetime of HNO\textsubscript{3} against photolysis and reaction with OH is about 2 weeks.

One way to explain the NO\textsubscript{2} and HNO\textsubscript{3} budgets as well as the missing NO\textsubscript{2} species in air masses of type 4 would be by reaction of CH\textsubscript{3}O with HNO\textsubscript{3} on concentrated sulfuric acid aerosols, producing methylene glycol nitrates (HOC\textsubscript{2}HONO\textsubscript{3}, CH\textsubscript{2}H(ONO\textsubscript{2})\textsubscript{2}) [Travaglini, 1938]. Methylene glycol nitrates have low solubility and would volatilize from the aerosols to the gas phase. They are likely photodissociated to release NO\textsubscript{2} by analogy with methyl nitrate; they would have a lifetime of the order of a few weeks. Sandholm et al. [1994] found the observed NO\textsubscript{2} deficit species to increase with O\textsubscript{3} concentration (or altitude) and to increase with the photochemical age of the air mass as measured by the CO:C\textsubscript{2}H\textsubscript{2} ratio. These observations seem consistent with possible formation of HOC\textsubscript{2}HONO\textsubscript{3} and CH\textsubscript{2}H(ONO\textsubscript{2})\textsubscript{2} in the upper troposphere.

A comparison can be made between the NO\textsubscript{2} budgets in ABLE 3B and those in ABLE 3A. Free troposphere concentrations of NO\textsubscript{2}, PAN, and O\textsubscript{3} were similar in both expeditions [Sandholm et al., 1992, 1994; Singh et al., 1992, 1994] temperatures were also similar. Therefore we expect PAN decomposition to also have accounted for most of the NO\textsubscript{2} in ABLE 3A. In their modeling of ABLE 3A data, Jacob et al. [1992] argued that PAN decomposition could account for the NO\textsubscript{2} below about 4 km but not at higher altitudes. They used a PAN decomposition rate constant taken from Lurmann et al. [1986] that is about 30% lower than used here [Atkinson et al., 1992].

4. NO\textsubscript{2} in the Continental Boundary Layer

We now turn to an analysis of the origin of NO\textsubscript{2} in the continental boundary layer (CBL) over the boreal woodland at Schefferville using the 1-D model for August 7 described in section 2. We address the following questions. (1) Does decomposition of PAN subsiding from the free troposphere account for NO\textsubscript{2} in the CBL? (2) How does vegetative emission of isoprene affect NO\textsubscript{2} and PAN? (3) How sensitive is the NO\textsubscript{2} budget in the CBL to the RO\textsubscript{2} + HO\textsubscript{2} reactions? The last question is motivated by the lack of kinetic data for the reactions of organic peroxy radicals (RO\textsubscript{2}) arising from photochemical oxidation of isoprene. Reactions of these peroxy radicals with each other are probably slow [Madronich and Calvert, 1990], but reactions with HO\textsubscript{2} may be rapid [Atkinson, 1990]. The reaction products are assumed to be organic peroxides (ROOH) which may photolyze, react with OH, or be removed by deposition. The latter two sinks would represent real loss of radicals from the atmosphere.

To address the above questions, we present here results from three simulations (1) a standard run including isoprene emission, RO\textsubscript{2} + HO\textsubscript{2} reactions with a rate constant $k = 3.4 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ taken from Atkinson [1990], and ROOH photolysis at a rate twice that for CH\textsubscript{3}OOH, (2) a sensitivity run with twice isoprene emission; and (3) another sensitivity run with isoprene emission but without the RO\textsubscript{2} + HO\textsubscript{2} reactions. Our definition of RO\textsubscript{2} here does not include the CH\textsubscript{3}O radicals, for which kinetic measurements of the reaction with HO\textsubscript{2} are available.
Figure 5 shows aircraft measurements of ambient temperature, absolute humidity, and mixing ratios of CO over the tower site on the afternoon of August 7. The air mass below 2 km originated from the Hudson Bay region 5 days prior to aircraft measurements and was not modified by rain or combustion emissions during the transit period [Shipham et al., 1994]. The composition of that air mass is typical of the regional background (Table 1). Tropical influence from the Pacific is apparent above 2 km and is manifested in Figure 5 by the low mixing ratios of CO (<80 ppb). This tropical influence was transitory [Shipham et al., 1994]; therefore, we assume that the boundary layer had been in contact with a free troposphere of background composition in the few days before being overridden by the tropical air. This assumption dictates our choice of upper boundary conditions (section 2).

Figure 6 shows the comparisons of model mixing ratios of isoprene, O3, NO, NO2, and PAN with observations. The model simulates NO, NO2, and PAN within the measurement uncertainties. The vertical distribution of isoprene is controlled by turbulent mixing and by OH oxidation in the boundary layer (the isoprene emission flux was adjusted to match the observed isoprene concentrations.) Concentrations of O3 are controlled mainly by transport from the free troposphere and deposition. The net photochemical production of O3 in the CBL is small, about 20% of the flux from the free troposphere.

The sensitivity simulation without isoprene emission yields O3, NO, and NO2 within the range of measurements. However, the PAN mixing ratio in the CBL falls below the measurement by a factor of more than 2. In the standard simulation, oxidation of isoprene yields high concentrations of the CH2CO radical. As a result, PAN decomposition is compensated by rapid PAN formation. Our simulation with no isoprene predicts concentrations of NO2 and PAN close to observed in the CBL over Alaskan tundra during AHE 3A [Bakwir, 1992; Sandholm et al., 1992; Singh et al., 1992]. Isoprene is not emitted by the major tundra plants (lichens and mosses).

The sensitivity simulation without RO3 + HO2 reactions yields mixing ratios of NO a factor of 2 lower than the standard simulation and significantly lower than the measurements. The afternoon mixing ratio of total peroxy radicals (2RO2) in this simulation is higher than 100 ppt (Figure 7).

Figure 8 shows the simulated NOx and PAN budgets in the boundary layer for the standard simulation. The formation of HNO3 is nearly balanced by decomposition of PAN subsiding from the free troposphere; net exchange of NOx between the CBL and the free troposphere is small. The production of HNO3 occurs mostly in the daytime. At night, isoprene reacts rapidly with NO3, producing isoprene nitrate radicals [Atkinson et al., 1988; DiSalvo et al., 1989] which release NO2 upon further reactions after sunrise [Paulson and Seinfeld, 1992]; this effectively prevents the nighttime formation of N2O5 and hence the loss of NO3 to HNO3 via N2O5 hydrolysis. Thus isoprene suppresses formation of HNO3 by depleting OH during nighttime (Figure 7) and by reacting with NO3 at night. As a result, the lifetime of NO3 in the CBL is considerably longer than without isoprene, 2.9 versus 1.2 days. Loss of NO3 in the former case could be more rapid than computed here if isoprene nitrate radicals react on aerosols to yield HNO3.

5. Summary

The origin of NOx in the summertime subarctic troposphere over eastern Canada was studied by modeling aircraft and ground observations from the ARLF 3R expedition. It is found that decomposition of PAN can account fully for the observed NOx concentrations in the free troposphere below 6 km except in occasional air masses subsiding from the upper troposphere. There is evidence that other organic nitrates are present in these air masses, and their decomposition may provide significant sources for NOx. We speculate that HNO3 may react with CH3O in concentrated sulfuric acid aerosols to produce HOC12ONO2 and CH3(ONO2)2 and that these nitrates would photolize on a timescale of weeks to release NOx.

Decomposition of PAN subsiding from aloft appears to provide the primary source of NOx in the continental boundary layer (CBL) over eastern Canada woodlands. The NOx budget in the CBL is strongly influenced by isoprene emission from vegetation. On the one hand, isoprene increases the lifetime of NO3 in the CBL by scavenging OH in the daytime and NO3 at night (the isoprene nitrate radicals produced at night are assumed to return
Figure 6. Comparisons of model mixing ratios of (a) isoprene, (b) O₃, (c) NO, (d) NO₂, and (e) peroxyacetyl nitrate (PAN) with measurements taken from aircraft during a descending spiral over the Schefterville tower site at 1310-1330 LT on August 7. The squares show mean measurements over 3-min intervals. The lines show model results (solid line, standard simulation; dotted line, no isoprene; and dashed line, no RO₂ + HO₂ reactions). The upper boundary conditions at 2.5 km above ground are 0 parts per trillion (ppt) isoprene, 40 ppb O₃, 6 ppt NO, 20 ppt NO₂, and 150 ppt PAN.

NO₂ upon sunrise). On the other hand, the production of CH₃CO radicals from isoprene oxidation slows down PAN decomposition and hence the source of NO₂. For the conditions in ABLE 3B, the net effect of isoprene is to increase NO₂ concentrations in the boundary layer, providing thus a small boost for O₃ production.

Forest fires appeared to be the most important source for PAN during ABLE 3B. Formation of PAN occurs in fresh biomass burning plumes and also in the regional atmosphere following dispersal of pyrogenic acetone and other hydrocarbons. Subsequent transport and decomposition of PAN can then maintain a uniform distribution of NO₂ in the troposphere.

Appendix: Constraints on Peroxy Radicals

A critical variable in predictions of the photochemical activity of the atmosphere is the total concentration of peroxy radicals (ΣRO₂). Concurrent measurements of NO, NO₂, and O₃ concentrations, together with JNO₂, allow, in principle, a direct computation of ΣRO₂ concentrations [Rüter et al., 1979; Kelly et al., 1980; Parrish et al., 1986; Volf et al., 1988; Chameides et al., 1990; Ridley et al., 1992; Davis et al., 1993]. Rapid cycling of NO and NO₂ occurs in the daytime through the following reactions:

Figure 7. Concentrations of (a) OH and (b) ΣRO₂ (sum of peroxy radicals, values in parts per trillion) at 1.0 km above ground for the simulations described in Figure 6.
\[ \text{O}_3 + \text{NO} \xrightarrow{k_1} \text{NO}_2 + \text{O}_2 \]  
\[ \text{R}_i \text{O}_2 + \text{NO} \xrightarrow{k_{i,i}} \text{NO}_2 + \text{R}_i \text{O} \]  
\[ \text{NO}_2 + \text{h}_\nu \xrightarrow{} \text{NO} + \text{O}_3 \]

where \( k_{i,i} \) is the rate constant of reaction (2) for the \( i \)th peroxy radical. Photochemical steady state between NO and NO\(_2\) is established on a timescale of a few minutes. The steady state relation is given by

\[ J_{\text{NO}_2}[\text{NO}_2] = (k_i[\text{O}_3] + \sum_i k_{i,i}[\text{R}_i \text{O}_2])/k_2 \]  

The values of \( k_{i,i} \) for \( \text{CH}_3\text{O}_2, \text{CH}_2\text{O}_3 \), and other organic peroxy radicals are within 20\% of that for \( \text{HO}_2 \) for the range of observed temperatures (-30°C to 20°C) [Atkinson et al., 1992]. We choose the rate constant of the \( \text{HO}_2 + \text{NO} \) reaction, simply denoted \( k_2 \), as an approximation of \( k_{i,i} \) values. We represent the sum of peroxy radicals by

\[ \Sigma \text{RO}_2 = \sum_i [\text{R}_i \text{O}_2] = \frac{J_{\text{NO}_2}[\text{NO}_2]}{k_2[\text{NO}] - k_i[\text{O}_3]} \]  

which may be evaluated from measurements of ambient temperature, \( J_{\text{NO}_2} \), and concentrations of \( \text{O}_3, \text{NO}, \) and \( \text{NO}_2 \). We call this quantity "implied" \( \Sigma \text{RO}_2 \).

Errors for this implied \( \Sigma \text{RO}_2 \) may be estimated from measurement errors for the individual variables,

\[ \Delta \Sigma \text{RO}_2 = \left[ \frac{\Delta J_{\text{NO}_2}}{J_{\text{NO}_2}} + \frac{\Delta [\text{NO}]}{[\text{NO}]} + \frac{\Delta [\text{NO}_2]}{[\text{NO}_2]} \right] \]  

\[ \Sigma \text{RO}_2 + k_1[\text{O}_3] \]

Measurement errors for \( \text{O}_3 \) are small and therefore neglected. The uncertainties on \( k_1 \) and \( k_2 \) are respectively 20 and 25\% [Atkinson et al., 1992] but are neglected as they also occur in model calculations. The values of \( k_1/k_2[\text{O}_3] \) averaged 65 ppt in the free troposphere during ARIPE 3R. Stated measurement precisions for 3-min averaging intervals were about 20\% for NO at 10 ppt and 20\% for NO\(_2\) at 30 ppt [Sardaholm et al., 1994]. Measurement uncertainties on \( J_{\text{NO}_2} \) are about 20\% [Madronich, 1987; Shetter et al., 1992]. Hence a typical measurement error for the \( \Sigma \text{RO}_2 \) concentration would be at least 60\%. Much larger errors for \( \Sigma \text{RO}_2 \) are expected when measured mixing ratios of NO fall below 10 ppt and NO\(_2\) below 30 ppt, respectively. Therefore it is not instructive to compare model \( \Sigma \text{RO}_2 \) with the implied \( \Sigma \text{RO}_2 \) at 3-min averaging intervals. We reduce the uncertainty in the implied \( \Sigma \text{RO}_2 \) by averaging over a large number of intervals.

Figure A1 shows the implied \( \Sigma \text{RO}_2 \) mixing ratios as a function of NO averaged over all intervals for which data are available for constraining the model. Values of \( \Sigma \text{RO}_2 \) increase with decreasing NO and exceed 200 ppt for NO less than 5 ppt. Concentrations of \( \Sigma \text{RO}_2 \) of a few 100 ppt would result in rapid \( \text{O}_3 \) production (of the order of 1 ppbv h\(^{-1}\)), which seems inconsistent with the concentrations of \( \text{O}_3 \) typically observed in the free troposphere. Further, this high level of \( \Sigma \text{RO}_2 \) could not be maintained by known sources of odd hydrogen radicals. On the other hand, possible unknown errors in the NO measurements have been estimated to be at or below 3.5 ppt [Sardaholm et al., 1994], so the implied \( \Sigma \text{RO}_2 \) at a few ppt NO may not be reliable. Figure A2 compares simulated and implied mixing ratios of \( \Sigma \text{RO}_2 \) for the subset of data with NO above 10 ppt (i.e., x5 measurement noise). The implied \( \Sigma \text{RO}_2 \) mixing ratios show large variances and appear to increase with altitude. The model underpredicts the implied \( \Sigma \text{RO}_2 \) by a factor of 2.3 above 4 km; the discrepancy is less at lower altitudes.

The discrepancy could conceivably reflect a large missing source of odd hydrogen radicals in the model at high altitudes.

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**Figure A1.** Observed \( \Sigma \text{RO}_2 \) versus NO concentrations (both values in parts per trillion). The circles indicate median \( \Sigma \text{RO}_2 \), and vertical bars indicate quartiles for binned NO intervals shown by horizontal bars. Data between 0900 and 1500 LT and mixing ratios of NO and NO\(_2\) above 20 (instrumental noises) are selected.

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**Figure R.** Diel mean budgets of NO\(_2\) and PAN computed for the boundary layer over Schefferville, Quebec. Rates (parts per trillion per hour) and concentrations (parts per trillion) are shown (note that the model specifies 70 ppt HNO\(_3\)). Exchange of NO\(_2\) with the surface is considered negligible [Balswin et al., 1994].
Alternatively, it is possible that interferences in NO$_2$ measurements, increasing with altitude, may be responsible. In particular, HNO$_3$ could heterogeneously decompose in the sampling tubing [Ridley et al., 1988; Sandholm et al., 1992, 1994]. Our model predicts significant levels of HNO$_3$ in the free troposphere, with HNO$_3$/NO$_2$ concentration ratios increasing from 0.2 at 3 km to 0.9 at 6 km, on the average. To illustrate the potential effect of an HNO$_3$ interference, we recalculated ΣRO$_2$ mixing ratios using adjusted NO$_2$ (which equals observed NO$_2$ minus simulated HNO$_3$). The agreement between simulated and implied mixing ratios of ΣRO$_2$ is somewhat improved (Figure A2). Concentrations of PAN also increased with altitude and were many times larger than those of NO$_2$ [Singh et al., 1994a]. If a few percent of PAN decomposed in the sampling tubing, the interference on the NO$_2$ measurement would be significant. For the instrument configuration used in ABLE 3B the wall reaction efficiency would need to be approximately 1 x 10$^{-4}$ for a 50% conversion efficiency of HNO$_3$ → NO$_2$ + H$_2$O and 1 x 10$^{-5}$ for a 5% conversion efficiency of PAN.

Measurements of NO are more reliable and were therefore chosen as constraint in the O-D model calculations. Since the disagreement between implied and modeled ΣRO$_2$ concentrations is less at lower altitudes, we also use the NO$_2$ measurements as model constraints in the boundary layer calculations.

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