Title
Atmospheric measurements of peroxyacetyl nitrate and other organic nitrates at high latitudes: Possible sources and sinks

Permalink
https://escholarship.org/uc/item/2bj546hf

Journal
Journal of Geophysical Research, 97(D15)

ISSN
0148-0227

Authors
Singh, HB
O'Hara, D
Herlth, D
et al.

Publication Date
1992-10-30

DOI
10.1029/91jd00889

Copyright Information
This work is made available under the terms of a Creative Commons Attribution License, available at https://creativecommons.org/licenses/by/4.0/

Peer reviewed
Atmospheric Measurements of Peroxyacetyl Nitrate and other Organic Nitrates at High Latitudes: Possible Sources and Sinks

H. B. Singh, D. O’Hara, D. Herlth, J. D. Bradshaw, S. T. Sandholm, G. L. Gregory, G. W. Sachse, D. R. Blake, P. J. Crutzen, M. A. Kanakidou

Aircraft measurements of peroxyacetyl nitrate (PAN) and other important reactive nitrogen species (NO, NO2, HNO3, peroxypropionyl nitrate (PPN), CH3ONO2, NOy) were performed at high latitudes over North America and Greenland during July-August 1988, at all altitudes between 0 and 6 km as part of an Arctic Boundary Layer Expedition (ABLE 3A). Complementing these were measurements of C1 to C5 hydrocarbons, O3, chemical tracers (C2Cl4, CO), and important meteorological parameters. PAN was found to be an important reactive nitrogen species in the free troposphere, with 95% of the mixing ratios falling in the range of 5 to 450 ppt. PAN increased systematically with height with mixing ratios of 100-700 ppt at 6 km and 0-50 ppt in the boundary layer. The free tropospheric PAN reservoir was present over the entire high-latitude region sampled (50° to 82°N latitude and 60° to 160°W longitude). In the boundary layer, PAN mixing ratios were higher over land than over the North Pacific Ocean. Significant levels of PAN were measured within stratospheric intrusions, forest fire plumes, and episodes of remote pollution. Other organic nitrates such as PPN and CH3ONO2 were found to be a small fraction of PAN (0-10%). PAN and O3 were strongly correlated both in their fine and gross structures, and the latitudinal distribution of PAN in the free troposphere followed that of O3. A two-dimensional global photochemical model is used to compare measurements and model results. Model simulations, correlations between reactive nitrogen species (e.g. PAN and NO3) and anthropogenic tracers (C2H2, CO, C2Cl4), and the composition of NOy itself support the view that the reactive nitrogen measured during ABLE 3A is predominantly of anthropogenic origin with a minor stratospheric component. Transported industrial pollution, biomass burning, and the unique seasonal dynamics of the Arctic/sub-Arctic region play a dominant role in defining this reactive nitrogen abundance. This PAN (and NOy) reservoir may contribute to the summertime maximum in deposited nitrate observed over Greenland.

INTRODUCTION

A long-term goal of the NASA Global Tropospheric Experiment (GTE) is to understand the atmospheric chemistry associated with Earth’s major ecosystems [McNeil et al., 1983]. The Arctic Boundary Layer Expedition (ABLE 3A) is a component part of GTE and was conceived to study the high-latitude (Arctic/sub-Arctic) environment of the northern hemisphere. It is now generally believed that despite the remoteness of the arctic atmosphere, significant human influences are beginning to impact this region especially in winter and early spring [Schnell, 1984; Rahn, 1985; Barrie, 1986]. Another reason for investigating the Arctic/sub-Arctic environment is the high predicted sensitivity of this region to climatic change resulting from human activities and the extreme paucity of available data from these regions. This aircraft and ground study, performed in the summer of 1988 (July–August), sought to investigate atmospheric photochemical and transport processes associated with the high latitude atmospheric system. An overview of the ABLE 3A field study has been provided by Harriss et al. [this issue].

It is well known that reactive nitrogen plays a central role in the chemistry of the atmosphere [Haagen-Smit, 1952; Levy, 1971; Logan et al., 1981]. The high-latitude environment has been insufficiently studied, and much of the available information is from the winter/spring Arctic haze period [Schnell, 1984; Rahn, 1985]. It is generally believed that summertime Arctic atmosphere is extremely clean [Barrie, 1986]. Although a body of data on organic nitrogen species has become available in recent years, very little of it is relevant to the free tropospheric environments of the high latitudes [Singh et al., 1986, 1990a, b; Rudolph et al., 1987; Bottenheim and Gallant, 1989]. ABLE 3A provided a unique opportunity to measure a large number of reactive nitrogen species (NO, NO2, CH3C(O)OONO2 peroxyacetyl nitrate, or PAN, C2H5C(O)OONO2 peroxypropionyl nitrate, or PPN, CH3ONO2, HNO3, and NOy (total odd nitrogen) to an altitude of 6 km during the summer (July–August) of 1988. A comprehensive set of related chemical [O3, C2–C5, NMHC (nonmethane hydrocarbons), CO, C2Cl4] and meteorological parameters were also measured. In this paper we describe the measurements of PAN and other reactive nitrogen species during ABLE 3A and use the transit flights to characterize their north-south and east-west gradients in the free troposphere. Relationships between the atmospheric concentrations of PAN and other key chemical parameters (such as NOx, NOy and O3) are explored to assess the sources and sinks of PAN and NOy.

EXPERIMENTAL

ABLE 3A utilized a Lockheed Electra for all aircraft measurements. Instrument integration and flight tests were performed at Wallops Island, Virginia. A total of 33 missions, including transit flights, were performed from July 7 to August 17, 1988. Aircraft missions were conducted from Barrow, Alaska (missions 6–13; July 12 to 24), Bethel/Cold Bay, Alaska (missions 14–26; July 26 to August 10), and Thule, Greenland (mission 29; August 13). The remainder were transit flights. A typical flight mission lasted approximately 5 hours.
Flight missions during ABLE 3A were divided into generic types that included boundary layer flux measurements, mid-tropospheric distributions and vertical profiles. Geographical extent covered during the ABLE 3A missions and a summary table of individual flights is provided in the overview paper by Harris et al. [this issue].

PAN was measured by an electron-capture gas chromatographic technique. Along with PAN, it was also possible to simultaneously obtain a PPN, CH$_3$ONO$_2$ and C$_2$Cl$_4$ measurement when detectable levels (1 to 5 ppt) were present. Typically, 100 to 200 mL of ambient air were pre-concentrated at a controlled -150°C temperature. PAN calibrations were performed by using a diffusion tube filled with liquid PAN in a n-tridecane matrix. For routine calibrations a diffusion tube (5 mm ID) was filled and held at ice-water temperature in a specially constructed dewar. Air flowed over this tube at a known rate. The PAN in the exit stream was measured by using an NO$_y$ detector. A nylon filter was inserted in line to remove any traces of nitric acid. A small correction (3 to 7%) was applied to account for trace quantities of methyl nitrate that were nearly always present. A two-step dynamic dilution system was used to generate low-ppt mixing ratios of PAN. A measurement sensitivity of better than 5 ppt PAN was achievable with a 100-mL air sample. Instrument precision and accuracy are estimated to be ±10% and ±25%, respectively. Additional details of this and similar techniques can be found elsewhere [Singh and Salas, 1983, Joos et al., 1986; Fehsenfeld et al., 1987; Singh et al., 1990a]. Methyl nitrate mixing ratios were calculated by using gas phase coulometry [Lillian and Singh, 1974]. Preliminary tests suggest that this should be accurate to ±50%. Nitric acid was measured by the mist chamber technique developed by Talbot et al. [this issue]. NO, NO$_2$, and NO$_y$ were measured by a laser-induced fluorescence (LIF) technique described by Sandholm et al. [this issue].

RESULTS AND DISCUSSION

This paper presents an analysis of the distribution and variability of PAN (also PPN and CH$_3$ONO$_2$) and its relationships with measured chemical and meteorological parameters for the high-latitude troposphere. A companion paper discusses the partitioning between active and total odd nitrogen [Singh et al., this issue]. Meteorological analyses involving synoptic conditions and 72-hour isentropic back trajectories are provided by Shipham and Bachmeier [this issue] and Drewry [1988]. Flights deployed from Barrow (71°N) and Bethel (61°N) are used to describe the "Arctic" (missions 6-13) and "sub-Arctic" (missions 14-26) distributions, respectively. The term "all data" is used for all flights north of 50°N (missions 2-32). Twelve transit flights (missions 1-5 and 27-33) provided opportunities for maximum latitudinal and longitudinal coverage. In this and the companion paper [Singh et al., this issue], latitudinal variations from 35° to 82°N are described based on transit missions 1-3 (July 7 to 8) and 29-33 (August 13 to 17). Longitudinal coverage (60° to 160°W) for the high-altitude environment (65° to 80°N) is described based on missions 4 (July 9) and 28 (August 12). Data in such instances are typically combined from altitude bands of 4 to 5.5 km. During the deployment there were also opportunities to sample plumes of air involving pollution episodes, forest fires, and stratospheric intrusions.

Some data selection procedures were necessary, since species were measured by multiple investigators, and sampling times often did not overlap. NO$_x$ data were generally available from direct measurements of NO and NO$_2$. In some instances where only NO data were reported, NO$_x$ was calculated by utilizing interpolations of the NO$_2$ to NO ratio. For the purposes of this and the companion paper all data were made to conform with the PAN sampling period. When sampling times did not exactly overlap, a linear interpolation was employed. This selection scheme led to a reasonable description of the original data, except in the case of HNO$_3$. To accommodate the extremely long sampling time for HNO$_3$, all other data were reduced to conform with this rather coarse time resolution. This file was used in all instances involving HNO$_3$ data. Model simulations are performed with a two dimensional global photochemical model described in Kanakidou et al. [1991].

**Mixing Ratios, Variabilities, and Vertical Structures**

**PAN.** Figure 1a shows the mean, minimum, and maximum mixing ratios of PAN measured during each of the ABLE 3A

![Graph 1a](Image)

**MISSIONS 2 THRU 32**

![Graph 1b](Image)

**MISSIONS 2 THRU 32**

![Graph 1c](Image)

Fig. 1. PAN mixing ratios during ABLE 3A. Solid squares (a) show mean PAN mixing ratios (ppt = 10$^{-12}$ v/v) for each mission. Vertical lines indicate maximum and minimum measured values. (b) Frequency distribution of PAN mixing ratios over high latitudes (missions 2-32). (c) Median PAN mixing ratios in 2-km altitude bands.
missions. The mean mixing ratios were typically in the 100-200 ppt range. Ninety percent of the measurements fell in a range of 0 to 350 ppt (Figure 1b) with a maximum value of 700 ppt. Mixing ratios of PAN, expressed in median values, increased with altitudes (Figure 1c). The vertical structure of PAN and \( \text{O}_3 \) for the Arctic and sub-Arctic region is shown in Figure 2. A superposition of PAN data from Barrow (Figure 2a) and Bethel (Figure 2c) shows that the vertical structures are nearly identical, supporting the conclusion that the high-latitude PAN reservoir is a large-scale phenomenon. It is further noted that the corresponding \( \text{O}_3 \) structures (Figures 2b and 2d) are very nearly identical. Overall, although PAN vertical profile is much steeper than that of \( \text{O}_3 \), both species increase rapidly with height between 50° and 75°N latitudes.

The low PAN concentrations in the boundary layer are probably associated with its rapid thermal dissociation rate at warmer surface temperature. The lifetime of PAN (\( \tau \)) can be defined by (1) [Singh, 1987]:

\[
\tau = \frac{1 + 0.43\text{[NO}_2\text{/NO]}}{k_1 + k_2\text{[OH]} + 0.43k_2\text{[OH]}\text{[NO}_2\text{/NO]}}
\]

where \( k_1 = 1.12 \times 10^6 \exp (-13,330/T) \text{ s}^{-1} \) and \( k_2 = 1.23 \times 10^{12} \exp (-651/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

Rate constants \( k_1 \) and \( k_2 \) are due to PAN thermal decomposition and reaction with OH, respectively. PAN lifetime in sunlit hours (\( \tau \)) from the above expression was derived by using temperature \( T \) and \( \text{[NO}_2\text{/NO]} \) ratio determined from direct measurements. July mean OH values as computed by Kanakidou et al. [1991] were employed. At 55°N, OH values were 2.1 x 10^6 molecule cm\(^{-3} \) and 1.7 x 10^6 molecule cm\(^{-3} \) for 0.3-km and 5.6 km altitudes, respectively. Mean temperatures during ABLE 3A were 282(±10)°K near the surface and decreased nearly linearly to 250(±7)°K at 6 km. It is evident from (1), that \( \tau \) is a strong function of temperature. Superimposed on the vertical profile of PAN is the computed value of its lifetime (Figures 2a and 2c). Although mixing processes modify the vertical profile of a trace gas, it is likely that the thermal dissociation of PAN is a major factor in defining its vertical structure. It is noted that the PAN lifetime at 6-km altitude is nearly a month compared to a few hours in the boundary layer. Hence a vertical structure such as the one observed is relatively easily established, provided a persistent source of PAN is available.

While there are good reasons for both PAN and \( \text{O}_3 \) mixing ratios to increase with height due to their increasing lifetime and the stratospheric source, respectively, such features were also found for a variety of other trace chemicals throughout the ABLE 3A program. Figure 3 shows an example of the vertical structure of \( \text{C}_2\text{H}_2, \text{CO}, \text{C}_2\text{H}_6, \) and \( \text{C}_2\text{Cl}_4 \) as measured over Barrow. In many instances the hydrocarbon vertical profile shows higher concentrations aloft in a pronounced manner as shown by Blake et al. [this issue]. All these species are of terrestrial origin with a significant anthropogenic component. A possible explanation for such a vertical structure is that industrial pollution is transported to this region from the industrial centers of the northern hemisphere via upper
tropospheric circulation. Superimposed on this are intrusions from the stratosphere and forest fire plumes. As we shall see later, the nitrogen and possibly O$_3$ chemistry of the Arctic is strongly affected by anthropogenic influences.

What is the possible source of this PAN (and NO$_y$) reservoir? A persistent source of PAN must come from either direct transport of PAN or NMHC/NO$_x$ photochemistry associated with the high-latitude environment. The primary emissions of NO$_x$ in the high-latitude region are small because of low population density, negligible soil fluxes (≈2 x 10$^8$ molecules/cm$^2$/s), and an extremely small lightning and stratospheric source [Bakwin et al., this issue; Isaksen and Hov, 1987]. Three-dimensional (3-D) models of the global troposphere show only a small amount of NO$_y$ coming from the stratosphere (10–80 ppt at 5.5 km and <1 ppt near the surface) and essentially all of it is in the form of HNO$_3$ [Levy et al., 1980; Kasibhatla et al., 1991], (J. Penner, private communication, 1991). Thus stratosphere is not likely to be a major source of PAN or NO$_y$. Also, as we shall see late, PAN mixing ratios behave in a manner that is similar to those of a variety of anthropogenic tracers. A conceptual model that is consistent with the available information is that high levels of pollution transported from industrial regions, with significant NMHC and NO$_x$ loading, are trapped in the stable Arctic atmosphere in winter and early spring ("arctic haze") and this charged reservoir photochemically generates significant quantities of PAN (and O$_3$) as sunlight and summer approach. Natural forest fire plumes also intermittently impact this region [Wofsy et al., this issue]. Measurements from Barrow (71°N) and Spitzbergen (76°–80°N) clearly show that high concentrations of C$_2$–C$_6$ NMHC (reactive alkenes, alkanes, and aromatics) are present in the springtime and are drastically lower in summer [Rasmussen et al., 1983; Hov et al., 1984]. Although no multiseasonal reactive nitrogen measurements were performed by these investigators, it is reasonable to assume that large amounts of NO$_y$ coexisted with these NMHC.

Limited ground level PAN measurements by Penkett and Brice,[1986] and NO$_y$ measurements by Honrath and Jaffe (The seasonal cycle of nitrogen oxides in the arctic troposphere at Barrow, Alaska, submitted to Journal of Geophysical Research, 1992) are also consistent with this conceptualized view.

Most 3-D models of the troposphere do not incorporate any PAN chemistry and incorrectly assume that the bulk of NO$_y$ is HNO$_3$ [Levy and Moxim, 1989; Penner et al., 1990]. A 2-D model of the troposphere with PAN synthesized from background levels of ethane and propane and a total NO$_x$ source of 38 Tg/yr (industrial emissions 20 Tg/yr; soil emissions 6 Tg/yr, biomass burning 6 Tg/yr, lightning 5 Tg/yr, stratosphere 1 Tg/yr) was used to simulate the reactive nitrogen chemistry of the troposphere [Kanakidou et al., 1991]. This model was unable to reproduce the large PAN mixing ratios observed during ABLE 3A (dark lines in Figures 2a and c), although O$_3$ vertical structures could be simulated. Such a model is inadequate to simulate the complex dynamics associated with the Arctic region over a 6–9-month period. The results further suggest that a far more complex array of NMHC are involved in PAN synthesis than are present in this model. A reasonable model simulation of O$_3$, with a significant stratospheric source, and a major under-prediction of PAN (and NO$_y$) further suggest that the stratosphere is not likely to be a major source of the observed NO$_y$. It is pertinent to note that the composition of this NO$_y$ [Singh et al., this issue; Sandholm et al., this issue] is substantially different from that of the high-latitude lower stratosphere, which is
principally made up of HNO$_3$ [Hübner et al., 1990; Kondo et al., 1990].

Davidson et al. [1989], based on sampling from snowpits at 2.6-km elevation, report a distinct summertime maximum in deposited nitrate over Greenland. During this time the airborne nitrate concentration at the three Canadian Arctic surface sites is nearly at a minimum. Measurements made during ABLE 3A clearly show that elevated sites can be exposed to a much higher concentration of reactive nitrogen. Direct deposition of PAN and other NO$_x$ species, along with their oxidation products (PAN $\rightarrow$ NO$_2$ $\rightarrow$ nitrate), and organic nitrate reservoir and their dry deposition could contribute in an important fashion to the observed summertime maximum in deposited nitrate in the Greenland snowpits.

PPN and CH$_3$ONO$_2$. PPN mixing ratios were extremely low and were typically only 5–10% of PAN. Given the PPN detection sensitivity of about 5 ppt, it could only be measured when PAN mixing ratios were 100 ppt or larger which was often the case only in the free troposphere. While the overall PPN structure is expected to be similar to PAN [Kasting and Singh, 1986; Kanakidou et al., 1991], its mixing ratios are only a small fraction of the available reactive nitrogen. Figure 4a shows the distribution of measured data with levels of 5–20 ppt in the upper troposphere.

The mixing ratios of CH$_3$ONO$_2$ were even smaller than those of PPN. It could often be measured only because of its nearly fourfold superior detection sensitivity compared to PPN. The distribution of CH$_3$ONO$_2$ was inverted compared to PAN and PPN, with highest mixing ratios in the boundary layer. Figure 4b shows its vertical distribution based on measured values only. Despite the preliminary nature of these data, it is evident that CH$_3$ONO$_2$ is probably not a significant component of the Arctic reactive nitrogen budget. The main source of this CH$_3$ONO$_2$ is likely to be from PAN decomposition (CH$_3$COONO$_2$ $\rightarrow$ CH$_3$ONO$_2$+CO$_2$). Unlike CH$_3$ONO$_2$, however, higher alkyl nitrates (>C$_2$) are favorably synthesized from the oxidation of higher hydrocarbons (RO$_2$+NO $\rightarrow$ RONO$_2$) and may exist in significant quantities. Because of the fundamentally different mechanism for CH$_3$ONO$_2$ and RONO$_2$ synthesis, the near absence of CH$_3$ONO$_2$ in no way implies that other alkyl nitrates are also absent. It is worth noting however, that the higher alkyl nitrates are somewhat more reactive and may be removed at a faster rate [Atkinson, 1990]. If the conceptualized mechanism for arctic PAN and NO$_x$ is correct, then significant quantities of simple and multifunctional organic nitrates must surely be present [Calvert and Madronich, 1987; Singh, 1987].

Latitudinal and Longitudinal Variations

As stated earlier, it was possible to arrange transit flights during outbound (missions 1 to 4) and inbound (missions 28-33) journeys in such a way as to gain maximum latitudinal (35° to 84°N) and longitudinal (60° to 160°W) coverage. These transit flights provided extensive opportunities for sampling in the free troposphere at around 5-km altitude.

Latitudinal profiles. The free tropospheric latitudinal profile of PAN during outbound (missions 1–3) and return (missions 29 to 33) transit flights is shown in Figure 5. Since PAN is not a conserved species, corresponding O$_3$, NO, and NO$_x$ mixing ratios are also shown. It is noted that north of 45°N, the mean temperature of the sampled air during missions 1–3 was 5° to 10°K warmer than that of missions 29–33. This is a result of both altitude variations and different synoptic meteorology. Figures 5a and 5c clearly show that PAN levels in the vicinity of 100 to 400 ppt were present in the free troposphere between 35° and 85°N latitudes. PAN concentrations are higher at northern latitudes only during the outbound flights (Figure 5a), but no such systematic gradient was observed during the inbound flights (Figure 5c). In both instances, a great deal of variability is present. PAN structure over the entire latitudinal belt is nearly coincident with the corresponding O$_3$ structure. Similar types of PAN-O$_3$ latitudinal behavior have been reported by Singh et al. [1990b] from lower latitudes (35°N to 0°N) in the northern hemisphere. It is becoming evident that atmospheric phenomena that define PAN distribution also define the corresponding O$_3$ behavior. It is also noted that while the NO$_x$ latitudinal profile consistently showed higher values at lower latitudes (Figures 5b and 5d), possibly because of proximity to sources, such was not the case for NO$_x$. NO$_x$, a more conserved quantity, showed only a small latitudinal gradient even though the NO$_x$ levels during missions 1–3 were nearly double those encountered during missions 29–33 (Figures 5b and 5d).

Also shown in Figure 5 (dashed line) is the systematic PAN, NO$_x$, and NO$_y$ latitudinal trend predicted by the ethane/propane model (5.6-km level) of Kanakidou et al. [1991]. As is discussed in the companion paper [Singh et al., this issue], NO$_x$ is roughly in equilibrium with PAN and under-prediction of PAN also ensures the same for NO$_y$. The model, probably because of its inability to simulate complex Arctic/sub-Arctic dynamics, also significantly under-predicts NO$_y$.
Figure 5. Latitudinal distribution of PAN as measured during outbound (missions 1 to 3) and inbound (missions 29 to 33) ABLE 3A transit flights. (a, c) Superimposed on PAN data is the corresponding O₃ profile shown by the dark line. (b, d) NOₓ and NOᵧ data are shown for comparison. All data are from 4 to 5.5-km altitude band. Mean temperatures during missions 1-3 were about 5°C warmer than missions 29-33. Dashed line is calculated for 5.6-km altitude from the ethane/propane 2-D model of Kanakidou et al. [1991].

Figure 6 shows similar latitudinal profiles of tracer molecules. In almost all these instances, species are more abundant at higher latitudes. However, air masses in the free troposphere appear to be relatively well mixed north of the typical summer jet stream position at 50°N. This is consistent with the distribution of NOᵧ, and implies that free tropospheric circulation, at least in the summer, results in rather rapid mixing between high and mid-latitudes. Overall, it appears that the Arctic is somewhat polluted in summer but a significant fraction of NOₓ has been oxidized to reservoir species.

**Longitudinal profiles.** PAN mixing ratios show no systematic trend as a function of longitude (Figure 7). Substantial variability throughout this latitude belt (65° to
Fig. 7. Longitudinal distribution of PAN in the high latitude (65° to 80°N) free troposphere. (b-d) Corresponding O₃, NOₓ
and NO₂ data are shown for comparison. Dark squares represent data from mission 4, and dark circles from mission 28.
Mission 4 data (65° to 77°N) are from an altitude band of 4.8 to 6.1 km and mission 28 data (70° to 80°N) are from a
somewhat lower 4.5- to 5.2-km altitude band.

80°N) is observed both in PAN and O₃ abundances. It is noted,
however, that a part of this variability is due to altitude
dissimilarities. For example, mission 4 (solid squares) data are
for an altitude band of 4.8 to 6.1 km, while mission 28 (solid
circles) data are from a lower altitude band of 4.5 to 5.2 km.
Figure 7a clearly shows that the high-latitude PAN reservoir is
a large-scale phenomenon that extends from 60° to 160°W
longitudes and probably beyond. These and the previously
published results [Singh et al., 1990a, b] leave little doubt that
a hemispheric-scale reservoir of PAN is present in the upper
troposphere.

Relationships With Chemical Parameters

Ozone. As stated earlier, PAN and O₃ showed similar
latitudinal and vertical behavior. Figure 8 shows significant
PAN-O₃ correlations for the entire high-latitude data set as well
as for the Arctic and sub-Arctic subsets. Such correlations have
also been previously reported from mid-latitudes and the
tropics [Singh et al., 1990a, b]. These correlations are
suggestive of a common source of PAN and O₃. The photo-
chemical oxidation of continental NMHC (natural and
anthropogenic) and NOₓ precursors, is most likely
responsible. The additional possibility that the large-scale
atmospheric structures of PAN and O₃ are similar (both increase
with altitude), and the observed correlations are largely due to
dynamical processes also needs to be investigated. It is highly
unlikely that the stratosphere is a cause of these correlations as
high PAN values are not expected there.

To investigate the reasons for these correlations we
performed limited studies with the 2-D photochemical model of
Kanakidou et al. [1991]. In this 2-D model, nearly all of O₃
resulted from stratospheric injections and CH₄/CO/NOₓ
chemistry, while PAN was synthesized exclusively from
C₂H₅/C₃H₈/NOₓ chemistry. The model-predicted PAN mixing
ratios were much lower than those measured. However, because
of the fairly detailed simulation of PAN and O₃ chemistry, it
was felt that the model may still capture the mean PAN and O₃
atmospheric structures. It was possible to generate some
similarities in the mean vertical structures of PAN and O₃ at
high latitudes [Kanakidou et al., 1991]. No such similarities
could be calculated for middle or low latitudes. The reasons for
the similarities in the large-scale structures are complex but
probably are related to the common NOₓ needed for both PAN
and O₃ synthesis, as well as some coincidental similarities in
sources and sinks. For example, PAN may be high in the upper
troposphere because of its thermal stability (long lifetime),
while O₃ may be high because of its stratospheric source.
Similarly, PAN may be low in the lower troposphere because of
its fast thermal dissociation (short lifetime), while O₃ may be
low because of surface deposition and, in the marine boundary
layer, net photochemical O₃ destruction due to insufficient
NOₓ.

It would seem that an important reason for PAN-O₃
correlations is due to the impact of continental precursors on
the Arctic/sub-Arctic photochemistry. However, dynamically
generated correlations due to similar mean vertical structures of
PAN and O₃ probably also play a role. Advanced 3-D models
of the troposphere and more atmospheric data on PAN, O₃, and
precursors are required to fully understand the reasons for the
observed correlations.

NOₓ. NOₓ is both a necessary precursor as well as a product
of PAN. Figure 9 shows the PAN-NOₓ relationships for the
high latitudes. PAN increases with increasing NOₓ for NOₓ
values up to about 60 ppt. At higher NOₓ values a decline is
observed. The reason for this behavior is not clear but may

| Longitude, øW | PAN, ppt | O₃, ppt | NOₓ, ppt | NO₂, ppt |
|--------------|---------|---------|---------|---------|
| 60           | 100     | 100     | 100     | 100     |
| 70           | 200     | 200     | 200     | 200     |
| 80           | 300     | 300     | 300     | 300     |
models show that at 60º to 70ºN, the stratospheric contribution to tropospheric NOy is in the 10 to 80 ppt range at 5.5 km and <1 ppt at the surface and is nearly all HNO3 [Levy et al., 1980; Kanakidou et al., 1991; Kasibhatla et al., 1991]; (J. Penner, private communication 1991). The substantial spread in free tropospheric estimates of 10 ppt (J. Penner, private communication, 1991) and 80 ppt [Kasibhatla et al., 1991] is a measure of uncertainty in 3-D models, largely due to the difficulties in rainout/washout parameterization processes.
especially since the amount of NO$_y$ injected from the stratosphere is nearly identical in these models (≈1 Tg/yr). Thus at high latitudes the stratospheric contribution to summertime tropospheric NO$_y$ is quite small. In addition, the composition of this Arctic/sub-Arctic NO$_y$, which is low in HNO$_3$ and high in PAN and possibly organic nitrates [Singh et al., this issue], is completely different from that of stratospheric NO$_y$ which is principally HNO$_3$ [Hübler et al., 1990; Kondo et al., 1990]. These arguments support the view that the Arctic/sub-Arctic NO$_y$ measured during ABLE 3A is predominantly of anthropogenic origin with a minor component from the stratosphere.

**Tracers.** Increasing PAN levels are generally associated with increasing concentrations of tracers such as C$_2$H$_2$ and CO, even though these relationships may not be linear. Figure 12 shows free tropospheric PAN-CO and PAN-C$_2$H$_2$ correlations. These relationships are similar to those for NO$_y$ and once again point to anthropogenic impacts.

Overall, the relationship of PAN with other chemical parameters during ABLE 3A is consistent with findings from other latitudes in the northern hemisphere [Singh, et al., 1990a, b]. The simplest association is between PAN and O$_3$. ABLE 3A data are consistent with the view that a substantial part of the reactive nitrogen budget at the high-latitude environments must find its original source in man-made pollution. A significant perturbation of the high-latitude troposphere is evident.

**Special Case Studies**

During the 33 ABLE 3A missions, a number of opportunities presented themselves to study specialized phenomenon. Here we present four cases involving stratospheric intrusions, sea and land differences, forest fires, and man-made pollution.

**Stratospheric Intrusion.** Stratospheric intrusions were encountered a number of times during ABLE 3A [Browell et al., this issue]. One of the strongest intrusion was sampled during mission 8 (July 15/16). Figure 13 shows the PAN, O$_3$, NO$_x$, and dew point behavior during mission 8. At an altitude of about 4.4 km around 2200 UT, O$_3$ values reached 270 ppb (NO$_y$ = 0.63 ppb) and the dew point temperature dropped to a low value of -41°C. NO$_x$ and NO$_y$ mixing ratios showed increases reflecting their stratospheric source. Tropospheric tracers such as C$_2$Cl$_4$ and C$_2$H$_2$ showed significant drops. As is evident from Figure 13, PAN levels slightly increased as the intrusion was intercepted. The O$_3$/NO$_y$ ratio of about 430 measured within this intrusion is much higher than the typical tropospheric values encountered during ABLE 3A (mean O$_3$/NO$_y$ = 124±48 for 0-4 km and 106±50 for 4-6 km) but closer to values of 200 to 500 found in the high-latitude lower stratosphere [Hübler et al., 1990; Kondo et al., 1990].
Although no measurements from the stratosphere have been published to date, these data suggest that substantial concentrations of PAN in the upper troposphere and lower stratosphere may exist.

Ocean-land variabilities. It was repeatedly observed that in the boundary layer, PAN over land was higher than over water. Figure 14 shows one such example (mission 19, August 2/3) when the aircraft flew over water and land at about 200-m altitude. PAN levels nearly doubled when the land mass approached. A similar increase when PAN levels increased from about 12 ppt to 26 ppt was also observed during mission 17. The reasons for this rapid transition are not likely to be associated with the additional soil sources of NO\textsubscript{x}, which are very small [Bakwin \textit{et al.}, this issue] and indeed both NO\textsubscript{x} and NO\textsubscript{y} did not perceptibly change during this transition. It is also noted that in virtually all such instances the land air temperature was warmer than the marine air; hence PAN was actually less stable over land than over water. A more plausible explanation lies in the more rapid vertical mixing, caused by warmer land temperatures, with the reservoir aloft. This is further supported by the observation that O\textsubscript{3} was also about 2 ppb higher over land than over water.

Forest fire plumes. Figure 15 shows PAN enhancement at around 2 km inside a haze layer intersected during the overland mission 14 (July 26/27). Inside the haze layer NO, O\textsubscript{3}, and CO showed concurrent increases. Other trace species such as C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} also showed significant excursions, while synthetic species such as C\textsubscript{2}Cl\textsubscript{4} were unchanged. It is likely that this haze layer consisted of residual smoke from forest fires that had been burning in the area during the previous several days [Drewery, 1988]. Within the plume a significant fraction of NO\textsubscript{x} had been converted to PAN. Forest fire plumes and their chemistry have been further studied by Wofsy \textit{et al.} [this issue] and Jacob \textit{et al.} [this issue].

North Pacific pollution episode. During the Cold Bay (Aleutian Islands) flight of mission 23 (August 7/8) a pollution episode was observed within the free troposphere over the North Pacific Ocean. PAN, O\textsubscript{3}, NO\textsubscript{x}, C\textsubscript{2}Cl\textsubscript{4} vertical profiles (Figure 16) show significant disturbance in the 4 to 6 km
Fig. 16. High-altitude pollution episode over the North Pacific Ocean (mission 23).

CONCLUSIONS

The ABLE 3A field study has shown that large concentrations of PAN and NO$_y$ are present in the Arctic/sub-Arctic troposphere of the northern hemisphere during the summer. Mixing ratios of PAN as well as a variety of other molecules are more abundant in the free troposphere compared to the boundary layer. Coincident PAN and O$_3$ atmospheric structures suggest that phenomena that define PAN also define the corresponding O$_3$ behavior. Unlike the lower stratosphere, where NO$_y$ is mostly made up of HNO$_3$, tropospheric Arctic/sub-Arctic NO$_y$ has little HNO$_3$. Model calculations, correlations between NO$_y$ and anthropogenic tracers, and the composition of NO$_y$ itself suggest that the Arctic/sub-Arctic reactive nitrogen measured during ABLE 3A is predominantly of anthropogenic origin with a minor component from the stratosphere. It is possible that high levels of pollution transported from industrial regions, with significant NMHC and NO$_x$ loading, are trapped in the stable Arctic atmosphere in winter and early spring and this charged reservoir photochemically generates significant quantities of PAN as summer approaches. Superimposed on this anthropogenically polluted reservoir are natural forest fire plumes and air of stratospheric origin. This view implies that important concentrations of simple and complex organic nitrates may also be present in the Arctic/sub-Arctic atmosphere. It is suggested that the tropospheric PAN (and NO$_y$) reservoir could be an important contributor to the summertime maximum in deposited nitrate observed over Greenland. Studies extending over several seasons, especially the spring-summer transition, are needed to fully understand the perturbations to the high-latitude troposphere.

Acknowledgments. This research was supported by the NASA Global Tropospheric Experiment. We acknowledge all ABLE 3A participants for their cooperation and support. Special thanks are due to the flight and ground crew of the Wallops Electra for making this effort a success. We greatly appreciate the computational assistance provided by D. Dempsey and B. Sliton of the Synemet Corporation.

REFERENCES

Atkinson, R., Gas-phase tropospheric chemistry of organic compounds: A review, Atmos. Environ., 24A, 1-41, 1990.
Bakwin, P. S., S. C. Wofsy, and D. R. Fitzjarrald, Measurements of NO$_x$ and NO$_y$ concentrations and fluxes over Arctic tundra, J. Geophys. Res., this issue.
Barrie, L. A., Arctic air pollution: An overview of current knowledge, Atmos. Environ., 20, 643-663, 1986.
Blake, D. R., D. F. Hurst, T. W. Smith, Jr., W. J. Shipple, T. Y. Chen, N. J. Blake, and F. S. Rowland, Summertime measurements of selected nonmethane hydrocarbons in the Arctic and sub-Arctic during the 1988 Arctic Boundary Layer Expedition (ABLE 3A), J. Geophys. Res., this issue.
Bartenheim, J. W. and A. G. Gallant, PAN over the Arctic: Observations during AGASP-2 in April 1986, J. Atmos. Chem., 9, 301-316, 1989.
Browell, E. V., C. F. Butler, S. A. Kooi, M. A. Fenn, R. C. Harris, and G. L. Gregory, Large-scale variability of ozone and aerosols in summertime Arctic and sub-Arctic troposphere, J. Geophys. Res., this issue.
Calvert, J. G., and S. Madronich, Theoretical study of the initial products of atmospheric oxidation of hydrocarbons, J. Geophys. Res., 92, 2211-2220, 1987.
Penkett, S. A., and K. A. Brice, *The spring maximum in photooxidants*

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, *McNeal, R. J., J.P. Mugler, Jr., R. C. Harriss, and J. M. Hoell, Jr., Lillian, D., and H. B. Singh, Absolute determination of atmospheric...* (Received June 12, 1990; revised March 18, 1991; accepted March 18, 1991.)