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Measurements of PAN, alkyl nitrates, ozone, and hydrocarbons during spring in interior Alaska

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Abstract. Measurements of the atmospheric mixing ratios of ozone, peroxyacetylnitrate (PAN), hydrocarbons, and alkyl nitrates were made in a boreal forest ecosystem in the interior of Alaska from March 15 to May 14, 1993. During this period the mixing ratios of PAN, alkyl nitrates, and nonmethane hydrocarbons (NMHCs) generally decreased due to the influence of both meteorology and OH removal. Mean mixing ratios of ozone, PAN, C_2 - C_6 alkyl nitrates, and total C_2 - C_5 NMHC during southerly flow periods were 24.4 parts per billion (ppbv), 132.1 parts per trillion (pptv), 34 pptv, and 8.2 ppbCv, respectively. During a short period of northerly flow, mixing ratios of PAN and total NMHC were approximately 2 times the southerly flow mixing ratios. PAN is correlated with ozone, and alkyl nitrates are correlated with alkanes. PAN and ozone mixing ratios exhibit similar diurnal variations on a number of days with an early morning minimum and afternoon maximum. This is likely due to a diurnal cycle in the boundary layer - free troposphere exchange and loss processes in the boundary layer for both O_3 and PAN. Higher molecular weight (mw) hydrocarbons and alkyl nitrates are observed to decrease more quickly than the lower mw hydrocarbons, consistent with removal by OH as the primary loss process.

Introduction

NO and NO_2 ($NO + NO_2 \equiv NO_x$) are key species in tropospheric chemistry through their primary role in ozone production and influence on the lifetime of the hydroxyl radical [*Crutzen*, 1979. *Logan*, 1985]. Photochemistry in the troposphere oxidizes NO_x to reservoir species such as HNO_3, peroxyacetylnitrate (PAN), and other organic nitrates such as alkyl nitrates ($RONO_2$). The ultimate sink for NO_x is HNO_3, which contributes to acid rain. Photolysis or thermal degradation of these reservoir species can return NO_x to the atmosphere. During the Arctic winter, reduced temperature and/or insolation increases the atmospheric lifetimes of PAN, alkyl nitrates, and nonmethane hydrocarbons (NMHCs), so that they may be transported over large distances from midlatitudes into the Arctic. Subsequent warming and increased insolation at the onset of spring can lead to the decomposition of these reservoir species and a return of NO_x to the atmosphere. In this manner, thermal decomposition of PAN may be the most important NO_x source in the Arctic troposphere during the winter-spring transition [*Isaksen et al.*, 1985; *Penkett and Brice*, 1986] and thus may have an important effect on ozone production in the Arctic spring.

The Arctic atmosphere has some unusual features relative to chemistry in lower latitudes. Because the nitric acid reservoir is depleted during transport to the Arctic, organic nitrates are a major fraction of the NO_y ($\equiv NO_x + PAN + HNO_3 + RONO_2 + N_2O_5 + ..$) budget. PAN and alkyl nitrates have been reported to contribute 70-80% to NO_y during spring in

the high Arctic [*Bottenheim et al.*, 1993; *Muthuramu et al.*, 1994] In addition to the odd nitrogen reservoir species, elevated levels of NMHC are present in the high latitudes during spring [*Rasmussen et al.*, 1983; *Blake and Rowland*, 1985; *Penkett*, 1993; *Jobson et al.*, 1994b]. Furthermore, the decay of NO_y during spring has been found to coincide with a pulse in NO mixing ratios [*Honrath and Jaffe*, 1992]. The combination of enhanced NO_x and NMHC from anthropogenic sources may influence the ozone budget in the Arctic troposphere during spring.

Surface ozone mixing ratios observed at Barrow, Alaska, show a long-term increase of about 1%/year [*Oltmans and Levy*, 1994]. This trend may reflect increasing NO_x emissions and chemical processing of these anthropogenic pollutants. However, the long-term ozone trends reported by Oltmans are most pronounced during summer, rather than in spring when ozone produced from processing of anthropogenic precursors might be expected. A possible explanation is that ozone produced during late spring is sufficiently long lived to contribute to ozone trends in the summer. Alternatively, regional sources of NO_x may be responsible for the summer increase [*Jaffe*, 1993].

The broad objective of this work is to gain a better understanding of the sources and sinks of ozone and its precursors in the Arctic and, ultimately, to determine the primary factors affecting mixing ratios and trends of ozone in the Arctic troposphere. Here we present the measurements of trace gases related to oxidant chemistry and describe their trends and relationships during the winter-spring transition of 1993 at Poker Flat, Alaska. The trace gases we discuss are ozone, C_2-C_5 NMHC, PAN, and C_2-C_6 alkyl nitrates.

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Experiment

Measurements were made at Poker Flat Research Range, Alaska (64°11'N, 147°43'W, 501 m above mean sea level), from March 15 to May 14, 1993 (days of year 74 to 134) in a boreal forest ecosystem. A map of Alaska is shown in Figure
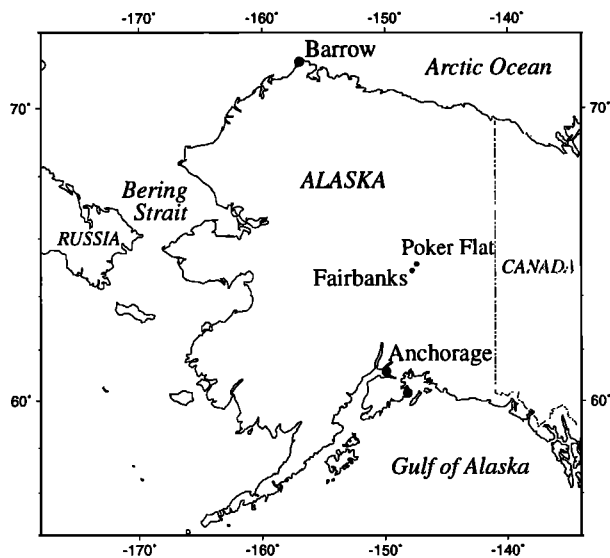
Figure 1. Map of Alaska

1. The research site is located on a ridge, 300 m above the Chatanika River valley. A Dasibi UV-analyzer (model 1003-PC) was used to measure ozone mixing ratios continuously A multi point calibration was carried out by titration of ozone with a NIST traceable NO standard (Scott-Marrin). A gas chromatograph with elecron capture detector (GC-ECD) was used for the PAN measurements. Samples (1 mL) were automatically injected every 15 min onto a 30-m, 0.53-mm ID capillary column with a stationary phase of DB-210. Calibrations were performed every 2 weeks using a diffusion tube containing PAN in tridecane. The standard was referenced against the NO standard, using a chemiluminescence NO/NOy instrument [*Honrath and Jaffe*, 1992]. In the calibration system, PAN was detected as NO following reduction by CO in a 300°C catalytic gold converter [*Bollinger et al.*, 1983] The precision of the measurements, determined by propagation of error, was 11% and 2.5% for PAN and ozone, respectively. Alkyl nitrates (C_2 - C_6) were collected for 6 hours on charcoal traps 4 times each day and analyzed by GC-ECD and gas chromatography - mass spectrometry (GC-MS) [*Atlas and Schauffler*, 1991]. The precision is estimated to be 5 to 8 %. Whole air ambient pressure samples were collected approximately every other day and later analyzed by GC-FID for C_2 - C_5 NMHC [*Blake et al.*, 1996]. The precision is the larger of 5% or 5 pptv. Isobaric back trajectories were calculated daily for 0000 and 1200 GMT at 1000 and 850 hPa [*Harris*, 1982].

Results

Time series for PAN, ozone, total NMHC, and alkyl nitrate mixing ratios show the general decline in mixing ratios during the winter-spring transition (Figure 2). On two days the isopentane mixing ratio was anomalously high The measurements on these days appear to have been influenced by an unidentified source. Isopentane is therefore not included in the sum of NMHC.

Surface pressure, 850 mbar height, and isobaric back trajectories indicate primarily southerly flow with an Arctic influence on the site only once during this campaign. Days 82 to

86 show airflow from the Arctic into the interior of Alaska After this period until the middle of May, trajectories indicate transport from the south and southeast. The unusual persistence of southerly flow during this period contributed to the higher than usual ambient air temperatures in Fairbanks The daily mean temperature during the entire campaign (5 8°C) was 4.8°C higher than the 30 year mean for this period. The data set is therefore divided into three groups. days 82 to 86 (Arctic flow) and the period before and after this time (southerly flow).

Statistics for the three different groups are given in Tables 1a-1c. Measurements of alkyl nitrates and ozone did not start until days 89 and 100, respectively; they are therefore not included in Tables 1a and 1b.

Mixing ratios are higher during the period of Arctic flow than during southerly flow. Elevated levels of both gases and aerosols in connection with airflow from the Arctic and possible long-range transport from Eurasian sources (in winter and spring) have been reported previously [e.g., *Raatz and Shaw*, 1984; *Barrie*, 1986; *Jaffe et al.*, 1991] and may account for the increases in mixing ratio here   Individual NMHC mixing ratios are near those reported for Alert, North West Territories, during the same season [*Jobson et al.*, 1994b], but PAN mixing ratios are significantly lower.

After day 125 until the end of the campaign, higher molecular weight alkane and unsaturated hydrocarbon mixing
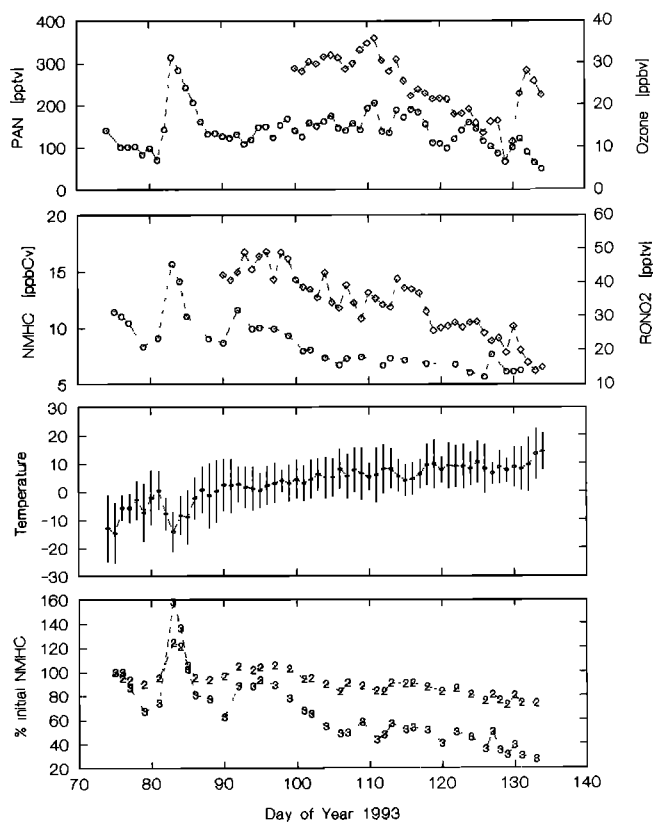
Figure 2. Daily averages of peroxyacetylnitrate (PAN) (circles, top panel, left axis), ozone (diamonds, top panel, right axis), total nonmethane hydrocarbons (circles), total alkyl nitrates (diamonds), temperature (the bars extend to the daily minimum and maximum), ethane (2) and propane (3) (bottom panel, as percent of the initial concentration on day 75 (100%). The initial concentrations were 2320 and 841 pptv for ethane and propane, respectively).

Table 1a. Statistics of Hourly Averages for Measured Values of PAN and Daily Samples for Total NMHC for Days 74-81 (Southerly Flow)

Species	N	Mean	s.d	Median	Minimum	Maximum
PAN, pptv	135 hours	96	21	95	52	158
Total NMHC, ppbCv	5 days	10.1	1.3	10 5	8.4	11 5

Table 1b. Statistics of Hourly Averages for Measured Values of PAN and Daily Samples for Total NMHC for Days 82-86 (Arctic Flow)

Species	N	Mean	s d	Median	Minimum	Maximum
PAN, pptv	86 hours	241	80	256	49	371
Total NMHC, ppbCv	3 days	13 7	2 4	14.2	11 1	15 7

Table 1c. Statistics of Hourly Averages for Measured Values of PAN and Ozone. Daily Samples for Total NMHC, and 6-hour Samples of Alkyl Nitrates for Days 87-134 (Southerly Flow)

Species	N	Mean	s.d	Median	Minimum	Maximum
PAN, pptv	1053 hours	138	40	136	27	301
Total NMHC, ppbCv	24 days	7 7	1 5	7.3	5 6	11 6
Alkyl Nitrates, pptv	154 6-hrs.	34	10	33	11	66
Ozone, ppbv	869 hours	27.3	12.6	26 7	0	72 0

ratios are highly variable, and daily minimum ozone mixing ratios are low, probably due to nearby anthropogenic pollution sources.

Alkyl nitrates and NMHC mixing ratios decreased steadily during the measurement period. As expected from their atmospheric lifetimes [*Roberts*, 1990], alkyl nitrates with high

Figure 3. Correlation of 10th percentiles of PAN and ozone. The data were ordered by the ozone mixing ratios. The line shows a linear regression, weighted by the standard deviation in the ordered ozone averages, with a slope of 1.96 (pptv PAN/ppbv O₃).

molecular weight decreased faster than those with low molecular weight. Both PAN and ozone showed an increase in their mixing ratios during the first month of the campaign and reached a maximum on day 110 after which the mixing ratios decreased. The trajectories do not explain the observed PAN and ozone increases, though the isobaric trajectories do not provide information on altitude variations or vertical mixing the air masses may have encountered en route.

For northern latitudes a general decrease from spring to summer in the mixing ratios of NO_y species, ozone, and NMHC have been reported [*Honrath and Jaffe*, 1992; *Oltmans*, 1993; *Blake and Rowland*, 1985; *Penkett et al.*, 1993], our results are in general agreement with those earlier reports.

Discussion

Trace gas trends at Poker Flat showed two main features during this campaign (1) An abrupt transition related to changing air mass back trajectories between days 82 and 86, and (2) a slow decline in mixing ratios from late winter to early spring. During the short period of flow from the north, PAN mixing ratios were the highest observed in this campaign but at the low end of mixing ratios observed at a Canadian Arctic site during spring [*Barrie et al.*, 1989; *Bottenheim et al.*, 1993]. Also, the maximum PAN mixing ratio observed at Poker Flat on day 83 (315 pptv) was significantly lower than mixing ratios measured during the same time period at Alert, North West Territories (500-600 pptv), as part of the Polar Sunrise 1992 Experiment (PSE 92) [*Muthuramu et al.*, 1994]. Maximum mixing ratios of most NMHC at Poker Flat, however, were near those found at Alert [*Jobson et al.*, 1994b]. While one should expect variable mixing ratios of both PAN and NMHC over the Arctic region, observations at Poker Flat are consistent with PAN decomposition or deposi-
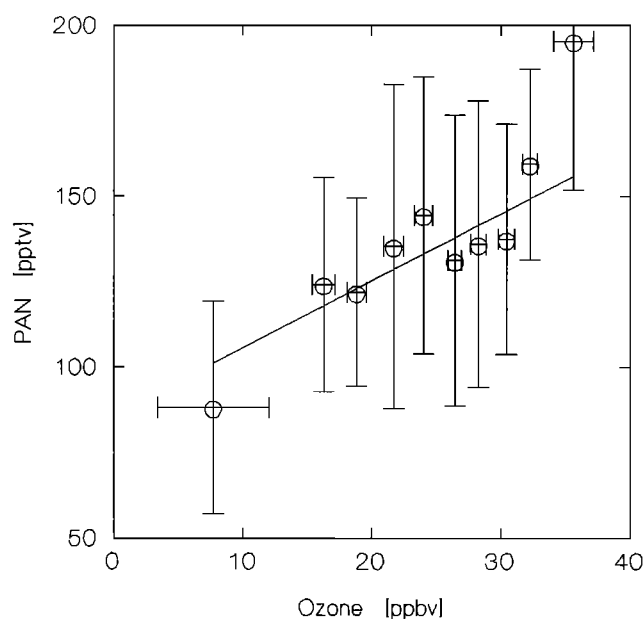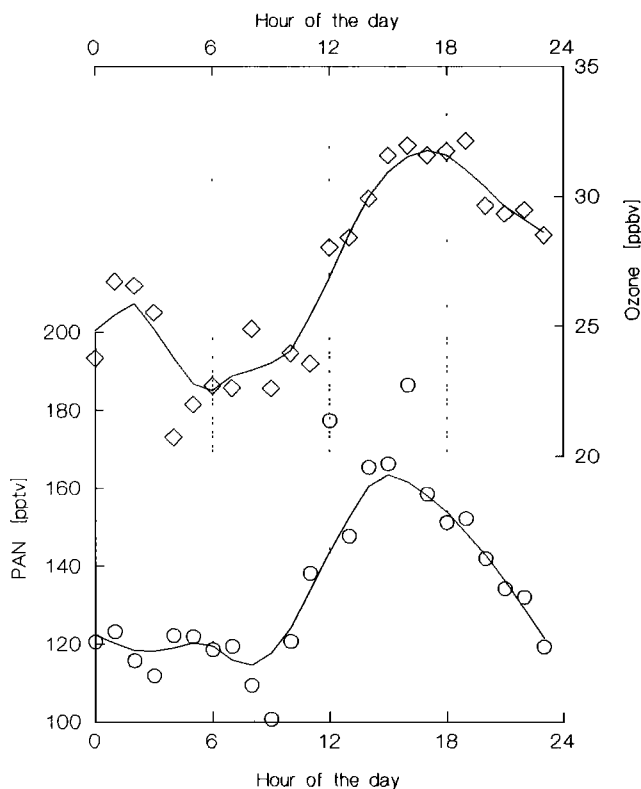
Figure 4. Median diurnal cycle for ozone (diamonds, top panel), and PAN (circles, bottom panel) for 10 days when the ozone/PAN correlation was significant at the 95% level. Those days were 102, 103, 104, 108, 110, 119, 120, 127, 130, and 131. The lines show lowess smoothing (tension is equal to 0 25)

Table 2. Maximum Temperature and PAN/Ozone Slope for the 10 Days When the PAN/Ozone Correlation Was Significant at the 95% Level

T max. [°C]	pptv PAN/ ppbv O₃	R^2	N	Day
10.0	21.52	0.746	21	110
10.0	1.48	0.323	20	127
11.1	4.67	0.352	24	102
11.7	6.65	0.227	20	103
12.2	10.13	0.690	23	104
12.2	3 14	0.622	24	120
15.6	3.47	0.453	23	108
15.6	2.94	0 438	20	130
15.6	4.10	0.753	21	131
18.3	-2 83	0.216	21	119

tion during transport from more northerly latitudes. Decreased mixing ratios of PAN could be related to increased rates of thermal decomposition encountered during transport south with a minor effect due to increases in the NO/NO₂ ratio. Lifetimes of PAN with respect to thermal decomposition will decrease from near 3 months at -20°C (typical of Alert) to about 8.6 hours at 10°C No correlation of PAN mixing ratios with local temperatures is apparent, although a general decline of PAN with increasing temperature was found.

The mixing ratios of ozone and PAN were strongly correlated during our campaign. Figure 3 shows a plot of PAN versus ozone where both data sets were ordered and grouped by the ozone mixing ratio. A linear regression, weighted by the standard deviation of the grouped ozone averages, shows a slope of 1.96 (pptv PAN/ppbv ozone) ($r^2 = 0.997$), corresponding to 510 molecules ozone per molecule PAN. During summertime clean westerly flow at Niwot Ridge, Colorado, the ratio of PAN to O₃ was found to be about 5 - 9 (pptv PAN/ppbv ozone) [*Ridley et al.*, 1990]. *Bottenheim et al.* [1994] report for background air at a rural site in Canada 5.01 (pptv PAN/ppbv ozone). Ratios for easterly flow at Niwot Ridge and in Boulder are about one order of magnitude higher (39 and 48, respectively) due to fresh emissions of NOₓ and therefore recent PAN production [*Ridley et al.*, 1990].

PAN and ozone mixing ratios exhibit diurnal cycles during our campaign, which are often correlated. On 10 days during our campaign the correlation between hourly averaged PAN

and ozone mixing ratios was significant at the 95% level. A median diurnal cycle for both PAN and ozone is shown in Figure 4 for those 10 days. The diurnal ozone variation is of the order of 10 ppbv. The diurnal variation in PAN is about 60 pptv

During days when the surface temperature exceeded 10°C, growth in the boundary layer mixes air with higher mixing ratios of both PAN and O₃ from above. This boundary layer-free troposphere exchange apparently is less pronounced on cooler days. Table 2 lists the maximum temperature and the PAN/ozone slope for the 10 days when this slope was statistically significant at the 95% level. No clear picture emerges; however, part of the data seem to suggest that on days with highest temperatures PAN may be decomposing thermally to an increasing extent, leading to a small or even negative PAN/ozone slope. The maximum ratio during periods of concurrent downward mixing was 21.5. The slope of 1 96 found when using all of the data as in Figure 3 indicates that during most times, thermal decomposition during transport results in PAN lifetimes which are shorter than the ozone lifetime.

That PAN and O₃ are correlated in both daily averages for the whole campaign and the hourly averages on many days is probably a result of several causes First, the daily averages for both reflect the similar seasonal cycles, whereby both PAN and O₃ show a recurrent April maximum [e.g., *Barrie et al.*, 1989; *Bottenheim et al.*, 1993; *Oltmans and Levy*, 1994]. Whether the accumulated PAN reservoir causes the O₃ maximum, as proposed by *Isaksen et al.* [1985] and *Penkett and Brice* [1986], is not clear from these data. The role of boundary layer exchange in transporting both PAN and ozone to the surface is apparent from the diurnal cycle on a number of days and the good correlation on those days.

Sounding data from the Fairbanks international airport indicate median mixing heights during the afternoons of around 1400 m. Every night, low-level surface inversions formed. However, at the Poker Flat site, which is located about 50 km from Fairbanks and on a ridge, the situation is unclear. The nighttime loss of both PAN and O₃ shown in Figure 4 suggest rapid deposition in a shallow inversion layer. Thus we conclude that in general the boundary layer is a sink for both O₃ and PAN. Deposition of both on snow surfaces is not likely to be a substantial loss process. In April, loss of both to vegetation probably became more important as the snow disappeared.
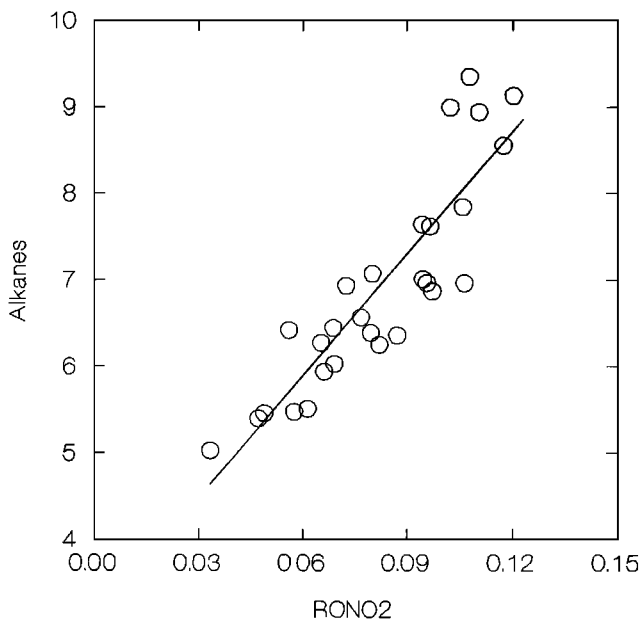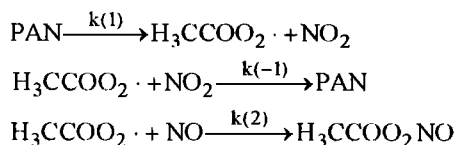
Figure 5. Correlation of alkanes versus alkyl nitrates. Units are (10^{10} molecules). The linear regression shows a slope of 47 (molecules alkanes/molecules alkyl nitrates).

An estimation of the thermal PAN decomposition can be made from simple kinetics. The three most important reactions for formation and loss of PAN are

$$PAN \xrightarrow{k(1)} H_3CCOO_2 \cdot + NO_2$$

$$H_3CCOO_2 \cdot + NO_2 \xrightarrow{k(-1)} PAN$$

$$H_3CCOO_2 \cdot + NO \xrightarrow{k(2)} H_3CCOO_2 NO$$

Finlayson-Pitts and Pitts [1986] calculated the thermal PAN decomposition rate at a given temperature from the first order rate constant $k_{(1)}$, where $k_{(1)} = 1.95 \times 10^{16}$ $e^{(-13,543/T)}$ [s^{-1}] [*Atkinson and Lloyd*, 1984]. This method ignores the reformation of PAN. However, it is probably an acceptable approach at Poker Flat, given that NO_x mixing ratios are low.

The highest median PAN mixing ratio of about 170 pptv occurs at 1500 in the afternoon (Figure 4). The mixing ratio drops subsequently over the next 10 hours to 120 pptv. This drop is possible from thermal decomposition alone at about 3°C, using the approach discussed above. At temperatures of 10°C, which were frequently seen during our campaign, thermal decomposition alone would result in a drop from 170 pptv

to about 50 pptv over 10 hours. Therefore for PAN, thermal decomposition in the boundary layer, when the temperature is above 0°C, is also increasingly important.

In spring, diurnal boundary layer variations are relatively large in interior Alaska. Daytime solar heating occurs during the many clear days, resulting in growth in the mixed layer. At night, strong temperature inversions reform due to radiative cooling. Thus in the boundary layer we believe the observed mixing ratios result from the difference between the source from above and the boundary layer losses. Although the meteorological and chemical situation was rather different, a similar conclusion was also reached from measurements taken during the summer of 1988 as part of the ABLE 3A campaign in Bethel, Alaska [*Jacob et al.*, 1992].

Total alkyl nitrates correlate well with alkanes (Figure 5). The other NMHC show little or no correlation with alkyl nitrates. The slope of the linear regression is 47 (molecules alkanes/molecules alkyl nitrates). Alkyl nitrates are produced from alkanes when sufficient NO_x is present. The primary removal process for alkanes is OH attack on the carbon chain, for alkyl nitrates it is both photolysis and OH attack. The chemical lifetime of an alkyl nitrate is within 50% of that of the corresponding alkane, the differences are mainly due to different photolysis rates [*Atlas et al.*, 1992]. The correlation therefore suggests that the ratio of pollutants in the source region is a controlling factor on the NMHC/alkyl nitrates ratio observed at Poker Flat. Total NMHC and PAN are correlated only for the time of Arctic flow to the site. For the southerly flow regime no correlation is apparent, indicating different removal processes for PAN and alkanes, thermal decomposition, and OH attack, respectively.

The ratio of PAN to alkyl nitrates and the variation of this ratio can suggest the processes affecting these organic nitrates during transport from a common source. Through oxidation of hydrocarbons in the presence of NO_x, both PAN and alkyl nitrates are associated with anthropogenic pollution. In addition, PAN and not alkyl nitrates may be produced from the oxidation of biogenic hydrocarbons or photolysis of acetone [*Singh et al.*, 1994]. Biogenic hydrocarbons were measured as early as April at Fraserdale, Ontario, [*Jobson et al.*, 1994a], which is in a similar ecosystem as Poker Flat. As already noted, the major PAN sink in the atmosphere is thermal decomposition, while alkyl nitrates have mainly photochemical sinks via photolysis and reaction with OH radicals [*Roberts*, 1990]. Thus in principle, changes in the ratio of PAN to alkyl nitrates should reflect source variations and the relative lifetimes. The PAN/alkyl nitrate ratios increased steadily from about 2 to a maximum of around 6 on day 110, after that it

Table 3. PAN to Alkyl Nitrate Ratio (pptv PAN / pptv $RONO_2$)

Campaign	Day of Year	Mean	Median	Range	Reference
Poker Flat 1993	74 - 134	4.11	4.17	2.04 - 6.09	this work
PSE 88	60 - 98	2.05	2.05	1.4 - 3.3	*Bottenheim et al.* [1993]
PSE 92	22 - 112			3.3 - 10	*Muthuramu et al.* [1994]
Ontario, Spring 1990	85 - 117	7.7			*Shepson et al.* [1993]
Scotia, Summer 1988	197 - 243	15.15	14.57	7 - 18.75	*Buhr et al.* [1990]
Mauna Loa	spring 1988	5.40			*Atlas et al.* [1992]
	fall 1991		6.25		E. Atlas, unpublished data,
	winter 1991/1992		3.57		[1993]
	spring 1992		10.0		
	summer 1992		5.55		

varied greatly. The overall mean is 4.1, with a standard deviation of 0.95. No correlation with local daily mean or maximum temperatures was found.

The PAN/RONO₂ ratio from different measurements varies over a wide range, depending greatly on geographic location, season, and proximity to pollution sources (Table 3). At Alert the ratio ranged from 1.4 to 3.3 during the PSE 88 [*Bottenheim et al.*, 1993], while *Muthuramu et al.* [1994] report ratios of 3.3 to 10 during PSE 92. *Shepson et al.* [1993] report a mean value of about 7.7 for a rural site in Ontario that is influenced by local NOₓ emission, and higher ratios were measured in a rural site in the SE United States which is largely influenced by biogenic hydrocarbon emissions [*Buhr et al.*, 1990]. Free tropospheric air at Mauna Loa, Hawaii, shows PAN and alkyl nitrate mixing ratios that are 1 order of magnitude lower than the ones reported here, but surprisingly, the ratio during spring at Mauna Loa Observatory (MLO) (5.4 for downslope air) is near that reported for continental sites [*Atlas et al.*, 1992]. In other seasons a ratio between 3.5 and 10 was found at MLO, with the highest during spring 1992. The comparison suggests, in general, that higher ratios are found in more polluted environments. However, no clear picture emerges from this comparison.

The primary removal for saturated NMHC is via reaction with the OH radical. Since higher molecular weight NMHCs have larger OH reaction rates, we would expect to see a faster falloff in their mixing ratio during the winter-spring transition at high latitudes. This was observed during this campaign for ethane, propane, and n-pentane (the bottom panel in Figure 2 shows ethane and propane only). Ethane mixing ratios drop by about 28% from March to May, whereas propane and n-pentane drop by approximately 73 and 85 %, respectively, over the same time period. For these hydrocarbons the percent decrease is consistent with their OH reactivity. I-butane and n-butane, however, decreased by only 63 and 70%, respectively, which compared to the other hydrocarbons is not in accord with their OH reactivity. This suggests that the butanes have additional sources on the transport path, or were influenced by local sources.

The measured species seem to fall into two groups: Ozone is very strongly correlated with PAN, and alkyl nitrates with the alkanes. The correlation between the two groups is weaker but still statistically significant. The very different mixing ratios found for the short period of northerly flow supports the view that synoptic meteorology has a strong influence on pollution mixing ratios.

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