

Studies of Peroxyacetyl nitrate (PAN) and its interaction with the snowpack at Summit, Greenland

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[1] Peroxyacetyl nitrate (PAN) was measured in ambient and snowpack interstitial air at Summit, Greenland, in June and July of 1998 and 1999 and at a rural/forest site in the Keewenaw Peninsula of Michigan in January of 1999. At Summit, we found that PAN typically represented between 30 and 60% of NO_y . In the summer of 1999, a significant diel variation in both PAN/NO_y and NO_x/NO_y was observed, but this was much less pronounced in 1998. Experiments during SNOW99 near Houghton, Michigan, indicated that PAN undergoes weak uptake onto snow grain surfaces. At Summit, we found that PAN concentrations in the snowpack interstitial air were significantly elevated (by as much as 2–5 times) relative to ambient levels, implying a flux of PAN out of the snowpack during the study period. We also observed evidence that PAN can be photochemically produced in snow that is exposed to polluted air. These observations indicate that interactions with the snowpack can have a significant impact on PAN concentrations in the boundary layer and point to potential difficulties associated with investigation of long-term changes in PAN uptake into ice cores because of the impact of postdepositional processes. **INDEX TERMS:** 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 1863 Hydrology: Snow and ice (1827); 1827 Hydrology: Glaciology (1863); **KEYWORDS:** PAN, snowpack, nitrate, air-snow exchange, photochemistry, flux

1. Introduction

[2] Glacial ice core nitrate records have been used to determine long-term changes in atmospheric nitrogen composition and the relative magnitude of the anthropogenic input [Mayewski *et al.*, 1990; Wolff, 1995; Dibb and Jaffrezo, 1997]. However, using the ice core record in such a way is problematic, as the physical and chemical processes leading to uptake and storage of nitrogen in the glacial ice are complex and not fully understood [Wolff, 1995]. A problem that has been identified is that current levels of gas phase nitric acid (HNO_3) deposition cannot account for the NO_3^- in the surface snowpack. Bergin *et al.* [1995] found that most of the NO_3^- uptake in the firn can be accounted for via wet deposition. However, Dibb *et al.* [1998] observe a significant increase in surface snow NO_3^- over a 6 day period during which there was no precipitation or ice fog; because of the low levels of gas phase HNO_3 and the stability of the air over the ice sheet, it was concluded that dry deposition of HNO_3 could not account for the increase and that the most plausible explanation was that PAN (peroxyacetyl nitrate; $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$) or organic nitrates are converted in the ice to NO_3^- . It was also suggested by Bergin *et al.* [1995] that PAN and/or organic nitrates might contribute to the flux of NO_3^- associated with ice fog.

[3] Understanding the surface enhancement of NO_3^- is complicated by recent studies [Dibb *et al.*, 1998] that indicate rapid loss of NO_3^- from fresh fallen snow. This situation has been further complicated by the observations of Honrath *et al.* [1999, 2000a, 2000b] who demonstrated that NO_3^- photolysis can produce NO_x ($\text{NO} + \text{NO}_2$) in the snowpack, which in turn will influence boundary layer NO_x concentrations. It now seems clear that snow and glacial firn are quite dynamic with respect to nitrogen exchange with the atmosphere and that the source of the surface enhancement of NO_3^- is ill defined.

[4] The possibility that PAN heterogeneous decomposition on snow grain surfaces could be a source of NO_3^- in the snowpack has been recently discussed by Munger *et al.* [1999]. PAN is a product of biogenic and anthropogenic volatile organic compound (VOC) oxidation in the presence of NO_x ($\text{NO} + \text{NO}_2$), and decomposes via reaction (1) below. Reaction (1) is highly



temperature dependent, with a reported $k_1 = 4.0 \times 10^{16} e^{-13600/T_S - 1}$ [Atkinson *et al.*, 1999]. At $T = 258$ K (typical for Summit during the timeframe of this study), the PAN thermal lifetime (i.e., $1/k_1$) is ~ 23 days. At higher altitudes (i.e., lower T values), PAN's lifetime

can be quite long. Thus PAN made from continental pollution sources can be readily transported to remote, NO_x -clean environments, such as Summit [Singh and Hanst, 1981]. Although PAN has been measured in Antarctica [Jacobi et al., 2000] and in the Arctic [Singh et al., 1992, 1994; Bottenheim et al., 1993; Beine and Krognnes, 2000], to date there have been no measurements of PAN at the surface in Greenland, and the nature of the interaction of PAN with snow crystals and its transport and fate in the snowpack/interstitial air has not been investigated. The only information available is a report that PAN is reversibly adsorbed on ice [Munger et al., 1999].

[5] Here we report measurements of PAN at Summit, Greenland, during June and July of 1998 and 1999. We also report the results of studies of PAN interactions with fresh snowfall near Houghton, Michigan, in January 1999. In this paper we discuss the impact of PAN on the NO_y budget at Summit and the extent to which PAN may be a possible source of NO_3^- in the glacial firn.

2. Experimental

[6] The studies of PAN's contribution to NO_y (total reactive nitrogen) and its interactions with snow were made at the surface at Summit, Greenland (72.33°N, 38.75°W, 3210 m above sea level), between 30 June and 7 July 1998 (Summit 98) and between 3 July and 16 July 1999 (Summit 99). At this time of year, the sun is above the horizon continuously but with a strong diel cycle in radiant intensity. Studies of the interaction of PAN with fresh fallen snow were conducted near Houghton, Michigan (47.35°N, 88.40°W) between 10 and 16 January 1999, during the project Snow Nitrogen and Oxidants in Winter (SNOW99; Honrath et al. [2000a]). PAN concentrations were determined using capillary gas chromatography with electron capture detection (GC-ECD). During SNOW99 and Summit98 the detector contained a Shimadzu ^{63}Ni source, while during Summit99 the detector was a Valco Xe Pulsed Discharge Electron Capture Detector (Model D-2). Samples were injected into the column via a two position, six-port loop flow valve (Hamilton Valve and Fitting) with a 3.2 mm OD PFA 2 cm^3 sample loop. The column was a DB-210 0.53 mm ID capillary column (J&W Scientific) and was maintained isothermally at 17°C. Samples were drawn through 6.4 mm OD PFA Teflon tubing from typically 1 m above the snow surface into the sampling trench that extended to ~3 m below the snowpack surface, using a diaphragm pump and MKS mass flow controller, typically at 1930 cm^3/min . The instruments used were automated to sample at a rate of six samples/h.

[7] Calibration of the instrument was done directly using synthesized PAN/zero air mixtures during Summit98 and SNOW99. PAN was added to the inlet by passing a low flow of zero air over a diffusion tube capillary filled with a solution of PAN in dodecane [Nielsen et al., 1982; Gaffney et al., 1984], controlled to 0°C using an ice bath. The output of the diffusion cell was determined using the MTU NO_y instrument in 1998 and in 1999 using a TECO model 42C NO_x monitor (converter temperature at 350°C) that had an NO_2 converter efficiency determined on-site to be 98%. In 1999 the output was also cross calibrated with the instrumentation used to collect NO_y data and determined to agree to within 5%. The output of the diffusion cell was simultaneously injected into the GC-ECD for calibration. During Summit 99, the instrument was calibrated directly and then changes in the absolute sensitivity of the detector were tracked for the 11 day period after that using an internal standard of perchloroethylene (PCE). A 1.2 mL/min flow (regulated with a mass flow controller, yielding a gas phase standard concentration of 930 ppt) of a 1.46 (± 0.09) ppm PCE/ N_2 mixture (prepared in-house in a deactivated aluminum cylinder) was mixed with every ambient sample injection. The injected PCE concentrations are hundreds of times greater than expected concentrations in a sunlit Northern Hemisphere free

troposphere [Atlas et al., 1992] and thus the signal will not be significantly influenced by ambient PCE. The PCE/PAN relative ECD responses were determined during absolute calibration on site, from calibration curves for both species, to be 1.66 ± 0.14 . This procedure allowed for improved uncertainties during the 1999 study, as a continuously varying sensitivity was used. When discrete absolute PAN sensitivities are used, it is necessary to interpolate between determined sensitivities. However, the PCE (and thus PAN) sensitivities sometimes changed significantly, over short timescales, perhaps due to changes in the temperature of the trench from which measurements were conducted. Thus having a running sensitivity enabled us to improve the uncertainty of the determination. We note, however, that only 11 days elapsed from the time of the absolute calibration (6 July) and the end of the study, and over that period the average sensitivity did not change significantly. We estimate from propagation of errors that the uncertainty in the PAN determinations was $\pm 25\% + 10$ ppt for Summit98 and SNOW99, and $\pm 20\% + 10$ ppt for Summit99. The limit of detection was 10 ppt, at Summit pressure. As discussed in section 3, the average PAN concentrations were not significantly different for the two years.

[8] Snow chamber experiments were conducted using a 34 L Teflon snow chamber described by Honrath et al. [2000a]. The chamber was lined with FEP Teflon, filled with fallen or artificial snow, and sealed with a transparent FEP Teflon film. The flow rate through the snow chamber was 30 L/min at SNOW99 and 20 L/min at Summit99 (unless otherwise stated). Snow samples from the chamber were obtained for ion chromatographic determination of nitrite and nitrate ions.

[9] Vertical profiles of PAN concentration were obtained during Summit99 from a meter above to a few tens of centimeters below the snow surface. For some of the measurements, we used a firm probe, designed to enable measurements of the firm air without downward mixing of the ambient air to the sample inlet. The probe consisted of a PFA inline filter pack (25 mm diameter; 10 μm Teflon filter) held inside the end of a 5 cm diameter stainless steel tube by machined Teflon supports, which also restricted airflow through the steel tube. The filter was designed to prevent snow from entering the sample line. PFA 6.4 mm OD tubing was attached to the filter pack for sampling from the end of the probe. An adjustable aluminum support held the firm probe perpendicular to the snow surface. A type K thermocouple was used to measure the temperature ~5 mm above the bottom of the probe. To test for the possibility that the stainless steel probe might conduct heat from solar radiation and thus heat the snow near the probe edges, we used an alternative method for sampling the firm air. The Teflon tube and the filter pack from the probe were inserted into the hole to near the base. Snow was then backfilled into this hole down to the inlet. These two methods were directly compared during one night, using independent holes, at the same depths, and produced similar PAN concentrations. This backfilled hole method was used for the 16 July 2000 daytime vertical profile discussed in section 3.

[10] The NO_x and NO_y data discussed here were determined as discussed by Peterson and Honrath [1999] and Honrath et al. [1999]. During the 1998 Summit campaign, the NO_x/NO_y inlets were located 10 m above the snowpack surface, while during the 1999 Summit campaign, the inlets were at 80 cm above the surface. However, tests conducted during the 1999 campaign indicated no NO_x gradient between the two inlet heights; that is, the NO_x concentrations were not significantly different at these two heights.

3. Results and Discussion

3.1. Ambient Measurements

[11] A principal objective of this study was to investigate the contribution of PAN to NO_y at the surface of the Greenland glacier, as no PAN data have previously been available. The PAN

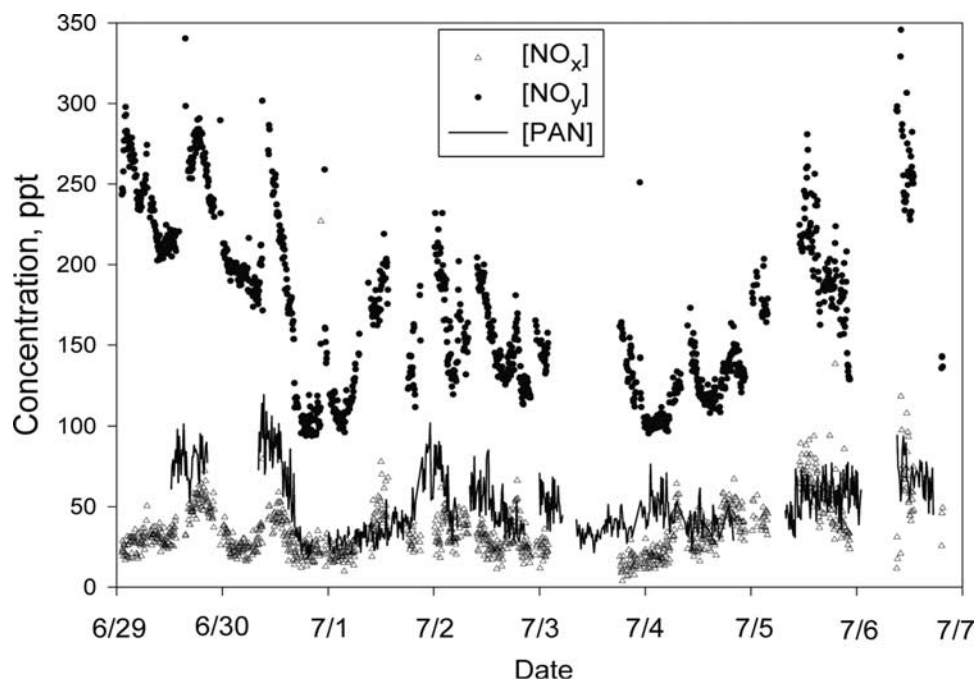


Figure 1. Ambient NO_x , NO_y , and PAN concentrations during Summit 98.

and NO_y measurement data are shown in Figures 1 and 2 for Summit98 and Summit99, respectively. The PAN concentrations 1 m above the snow surface ranged from ~ 20 to 150 ppt. The average concentrations were 52 ± 19 ppt in 1998 and 74 ± 26 in 1999. These values are smaller than those reported by *Singh et al.* [1992, 1994], for similar latitudes and altitudes during the same time of year, from aircraft-based measurements, as part of the ABLE3A and ABLE3B studies. *Singh et al.* [1994] reported PAN concentrations ranging from ~ 100 to 300 ppt. However, their measurements, although made at comparable altitudes, were not within the surface boundary layer. *Beine and Krognes* [2000] reported summer mean concentrations at Ny-Alesund, Svalbard to

be ~ 80 ppt, which are quite comparable to what is observed at Summit, although we expect that snowpack interactions (discussed in section 3), as well as different turbulent mixing rates in the boundary layers in these two environments make the measured concentrations at Summit and Svalbard not necessarily directly comparable.

[12] NO_y concentrations typically ranged from 100 to 300 ppt, while the ABLE3B data indicate NO_y in eastern Canada of ~ 250 –700 ppt [*Singh et al.*, 1994]. The fractional contribution of PAN to NO_y is shown for Summit98 and Summit99 in Figures 3a and 4a, respectively. PAN generally represents the largest fraction of NO_y , with considerable variability, ranging from 10 to 80%. However,

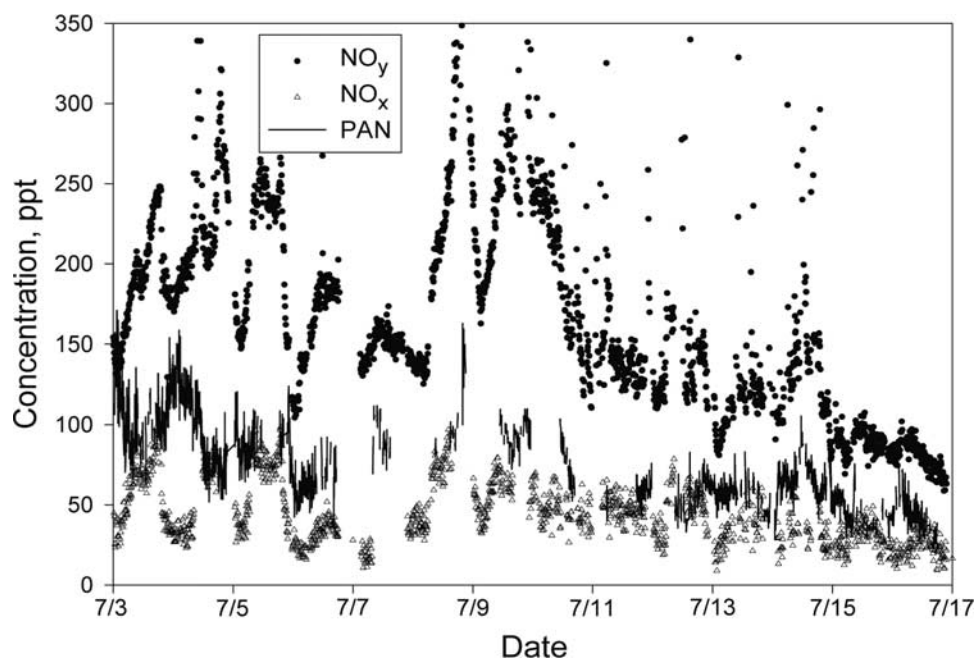


Figure 2. Ambient NO_x , NO_y , and PAN concentrations during Summit 99.

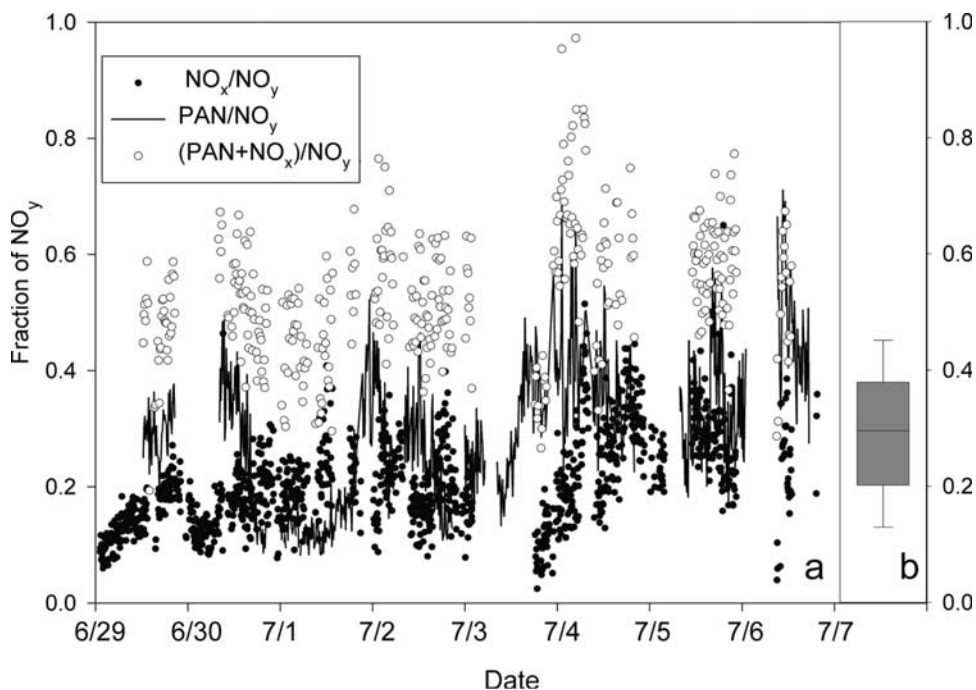


Figure 3. (a) NO_x/NO_y, PAN/NO_y, and (PAN + NO_x)/NO_y, during Summit 98. (b) Box and whisker plot of PAN/NO_y, Summit 98.

the observations differ significantly between Summit98 and Summit99. Figure 3b shows PAN/NO_y ranges from 10 to 60% during Summit98, with a median of 30%; the second and third quartiles cover a range of only 25–36%. For that year, NO_x/NO_y was typically 10–40%, and (PAN + NO_x)/NO_y is 50–80%, with a median of 53%. This implies that some other specie(s) made a substantial contribution to NO_y in 1998. In contrast, Figure 4b shows that for Summit99, PAN/NO_y ranged from ~40 to 80% with a median of 55%; the second and third quartiles range from 46 to 65%. NO_x/NO_y ranged from 10–70%, with a median value of 33%. The sum of PAN and NO_x frequently accounted for all the NO_y, within the measurement uncertainty, as shown in Figure 4a.

The 1999 PAN/NO_y ratios were comparable to those observed by Singh *et al.* [1992, 1994].

[13] There is no apparent diel cycle for PAN concentrations at Summit, although NO_x exhibits a distinct diel cycle, correlating with radiation [Honrath *et al.*, 1999]. NO_x exhibited a stronger diel cycle in 1999, with significantly higher solar noon maxima. As discussed above, although the NO_x inlet was much lower in 1999, we do not attribute this difference to sampling height differences. The diel averages for PAN/NO_y and NO_x/NO_y are shown in Figures 5 and 6, for Summit98 and Summit99, respectively. PAN/NO_y did exhibit a diel cycle, which was out of phase with the NO_x/NO_y diel cycle; PAN/NO_y reached a

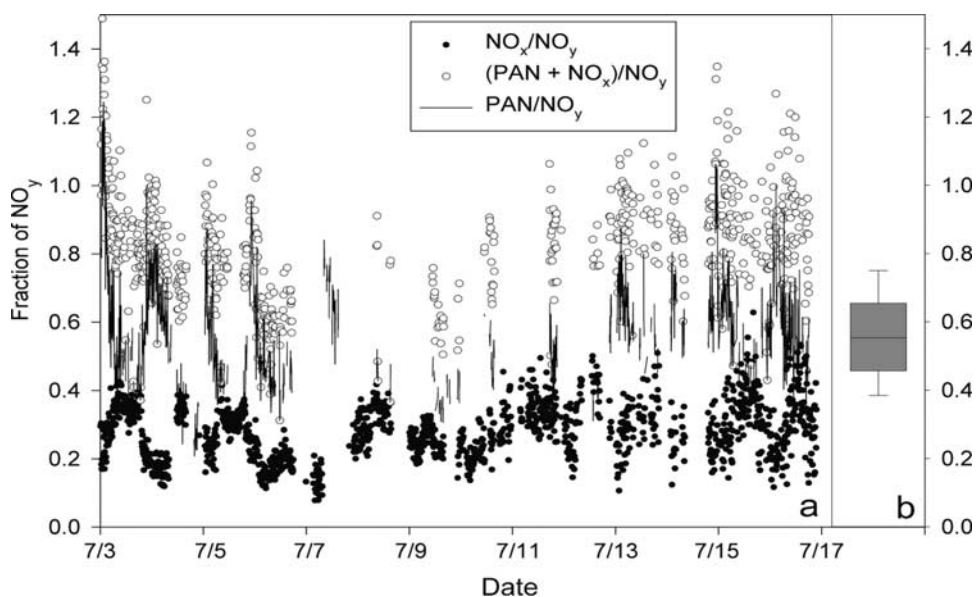


Figure 4. (a) NO_x/NO_y, PAN/NO_y, and (PAN + NO_x)/NO_y, during Summit 99. (b) Box and whisker plot of PAN/NO_y, Summit 99.

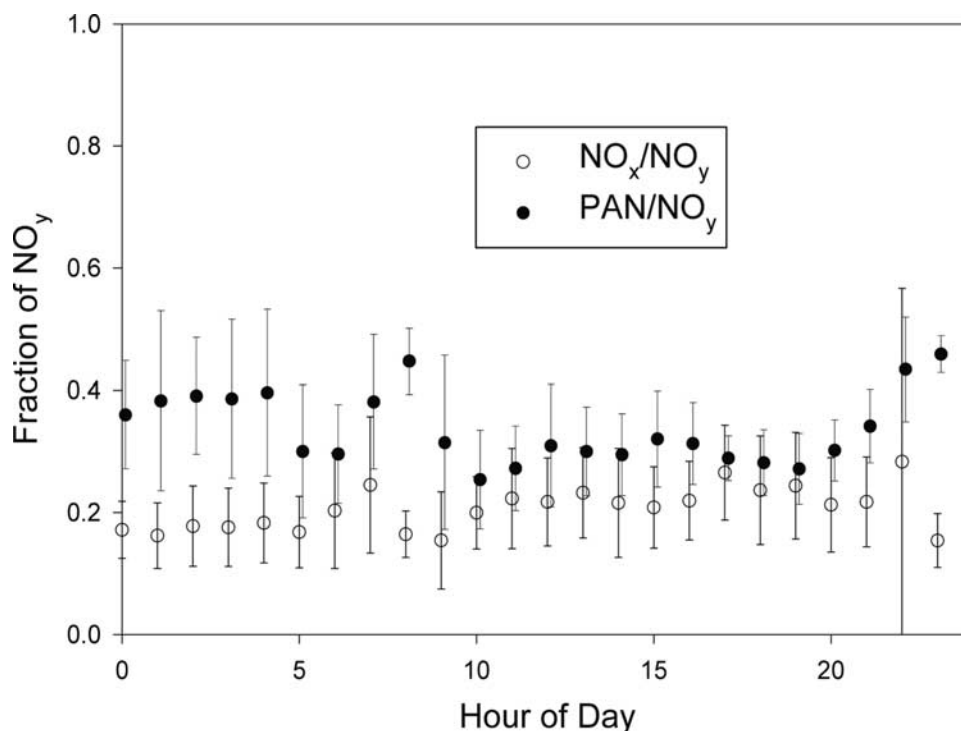


Figure 5. Diel average of NO_x/NO_y and PAN/NO_y in hourly bins; Summit 98.

maximum at minimum radiation, while NO_x/NO_y maximized at solar noon. This pattern likely reflects the dilution of the PAN contribution to NO_y by NO_x emissions through snow phase photoproduction of NO_x [Honrath *et al.*, 2000b] and loss of NO_y components to the snowpack, for example, HNO_3 , at night. As shown in Figures 1 and 2, there is some diel variability in NO_y , which follows the pattern of NO_x emission from the

snowpack. However, the amplitude of the diel cycle in NO_y is for some days significantly larger than that for NO_x indicating that other NO_y species contribute significantly to the NO_y diel cycle. This is in contrast to what was previously observed for snowpack interstitial air at Summit [Honrath *et al.*, 1999], in which the observed NO_y increase with radiation could be accounted for by the NO_x enhancement.

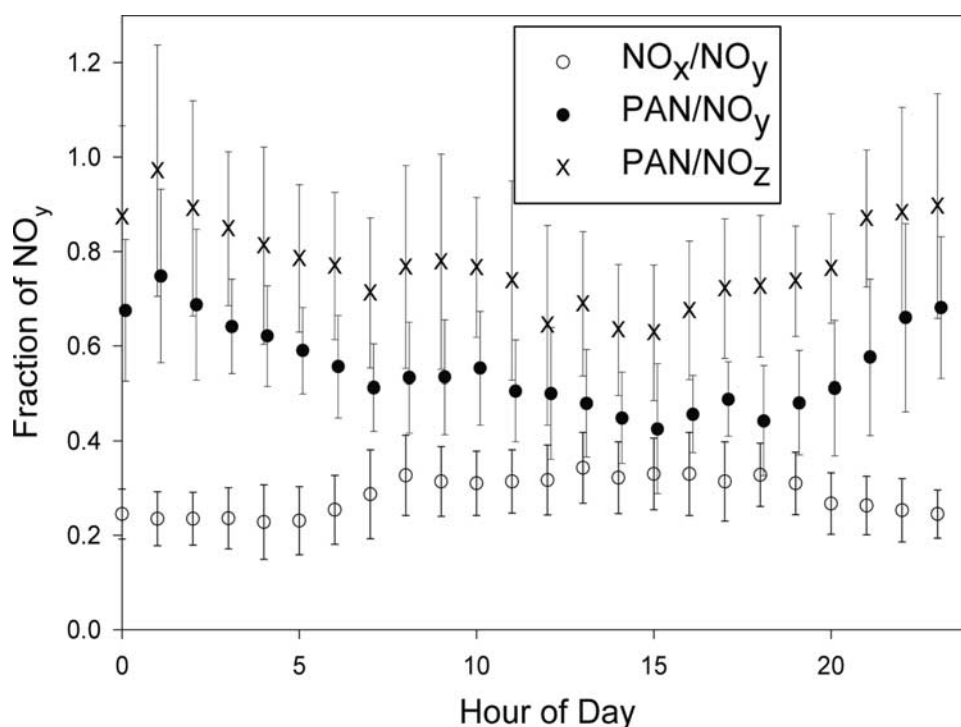


Figure 6. Diel average of NO_x/NO_y , PAN/NO_y , and $\text{PAN}/(\text{NO}_y - \text{NO}_x)$ in hourly bins; Summit 99.

[14] The diel variation in NO_x implies that there is a mechanism for uptake of NO_x in the evening, which could in part be related to conversion to HNO_3 via reaction (R2). A modeling study by *Yang et al.* [2002] indicated substantial OH radical concentrations in the near-surface air. This would likely be followed by deposition of HNO_3 to the snowpack in the evening,



which would account for some of the evening decrease in NO_y . To account for the observed rate of NO_x loss (i.e., conversion to HNO_3) requires substantial OH concentrations, i.e., $\geq 5 \times 10^6$ molecules/cm³. Although *Dibb et al.* [1998] observe a diurnal variation in HNO_3 , its gas phase concentration is typically of the order of 10 ppt, i.e., a relatively small fraction of the NO_y variability. But in 1999, the HNO_3 levels were high during the period shown in Figure 2, i.e., with daytime maxima as high as ~ 80 ppt and nighttime minima of less than 10 ppt. For example, for 5 July 1999, NO_y decreases by ~ 150 ppt in the late evening, while the NO_x decrease is about a third of that. HNO_3 for that day reached a maximum of 55 ppt ($\sim 22\%$ of NO_y) and decreased through the evening. Thus some, but clearly not all, of the NO_y decay is due to loss of HNO_3 to the surface. There is also recent evidence that HONO is produced photochemically in the snowpack at Summit [*Dibb et al.*, 2002] and that there is a diurnal cycle in ambient HONO, which could also account for a fraction of the NO_y diurnal variability. The PAN/ NO_z data presented in Figure 6 indicate that near solar noon as much as 30% of the NO_z (i.e., NO_x oxidation products) is other than PAN but that PAN is nearly all of the NO_z near midnight, presumably in part due to deposition of HNO_3 and HONO. It is also possible that some of the diel cycle is caused by HO_2NO_2 .

[15] In light of the finding of the snow surface photochemistry impact on ambient air NO_x concentrations, as well as recent reports of the impact of snow phase photochemistry [*Sumner and Shepson*, 1999] and temperature dependent uptake/release [*Hutterli et al.*, 1999] on HCHO in the Arctic, the question arises as to the potential impact of uptake and/or chemistry on snow crystal surfaces on atmospheric PAN concentrations, as well as on one of its potential decomposition products, NO_3^- [*Munger et al.*, 1999]. We first address the likelihood of NO_3^- production via PAN composition.

3.2. PAN Adsorption and Decomposition on Snow

[16] As discussed in section 3.1, it is currently unknown what may cause an increase in NO_3^- in the snowpack in the absence of precipitation. As proposed by *Munger et al.* [1999], some PAN may decompose, presumably on the snow grain surfaces, to produce NO_3^- . A simple calculation of the contribution from PAN can be obtained by assuming that PAN on the snow grain surface is at Henry's Law equilibrium and that it undergoes hydrolysis to produce NO_3^- at the known aqueous phase rate. Caution should be exercised, as there is evidence that indicates that uptake on snow surfaces is not Henry's Law controlled [*Dominé et al.*, 1995; *Thibert and Dominé*, 1998; *Couch et al.*, 2000]. However, making this assumption will provide an upper limit nitrate production rate from PAN decomposition, to the extent that it occurs via known chemistry. The Henry's Law constant for PAN at 255 K is ~ 80 M/atm [*Kames and Schurath*, 1995]. Using snowpack interstitial air [PAN] = 200 ppt (see data presented in Figure 9) leads to $[\text{PAN}]_{aq} = 1.1 \times 10^{-8}$ M. The first-order rate coefficient for hydrolysis of PAN is $8.8 \times 10^{-6} \text{ s}^{-1}$ at 255 K [*Kames and Schurath*, 1995]. Given these two values, we calculate $d[\text{NO}_3^-]/dt = 9.7 \times 10^{-14}$ M/s in the surface disordered layer of the snow grains, assuming that NO_3^- is the only product of PAN hydrolysis. From *Conklin and Bales* [1993] we estimate that the surface disordered layer thickness corresponds to 0.2% of the bulk snow mass. This equates to a nitrate production rate of 7.0×10^{-16}

moles $\text{NO}_3^-/\text{gram snow/hr}$, within the bulk snow. Thus assuming PAN is at Henry's Law equilibrium and that the aqueous phase hydrolysis rate constant applies to the surface disordered layer leads one to conclude that aqueous PAN hydrolysis to produce nitrate ions is an insignificant process, relative to the observed snowpack NO_3^- increase (i.e., $\sim 1.5 \times 10^{-11}$ moles $\text{NO}_3^-/\text{gram snow/hr}$) reported by *Dibb et al.* [1998].

[17] It is known that the snowpack is photochemically active, producing both NO_x [*Honrath et al.*, 1999, 2000a, 2000b] and HONO [*Zhou et al.*, 2002; *Dibb et al.*, 2002]. HONO photolysis can produce significant snowpack interstitial air OH concentrations, and this gas phase OH can in turn react with NO_2 to produce HNO_3 , which will in turn undergo uptake into the snow grains. However this process only acts to recycle snowpack NO_3^- , as NO_3^- is believed to be the precursor to photochemical production of snowpack NO_x .

[18] To further investigate the role of PAN as a snowpack nitrogen source, studies of PAN interaction with the snowpack were conducted as part of SNOW99 [*Honrath et al.*, 2000a; *Couch et al.*, 2000]. To study PAN interaction with snow in a controlled manner, we conducted experiments during which the Teflon coated snow chamber was allowed to fill with snow during a snowstorm. The snow in the filled chamber was then sampled to enable nitrate determination by ion chromatography. The chamber was then sealed, and zero air, to which a constant amount of PAN from a PAN/dodecane impinger was added, was allowed to be pumped through the snow-filled chamber at constant flow rate. PAN concentrations were then measured at the inlet and outlet for a ~ 6 hour period. At the end of this experiment, snow samples were collected from the chamber and were again analyzed for NO_3^- concentration. Interestingly, the nitrate concentration decreased from 9.67 nmoles/mL at the beginning of the experiment to 7.23 nmoles/mL at the end. This decrease could be explained by the process of snow metamorphism [*Hobbs*, 1974; *Colbeck*, 1983; *Hanot and Dominé*, 1999]. Specifically, during the experiment, the snow surface area decreases, causing loss of HNO_3 from the surface simultaneous with the loss of water vapor. Rapid emission of HNO_3 from surface snow at Summit has been observed as discussed by *Dibb et al.* [1998]. Thus it is not possible to draw any specific conclusions about PAN decomposition to NO_3^- on the snow surface from this experiment.

[19] During the last four hours of this experiment, the inlet concentration of PAN ranged from 1.0 to 1.6 ppb. As shown in Figure 7a, there was no discernible difference between the inlet and outlet PAN concentrations (e.g., from examination of the data between 1540 and 1700), indicating relatively little uptake of PAN onto the snow grain surfaces. For much of that period, the opaque cover over the Teflon film top was removed, and it is apparent that, for the low radiation levels present on this day, there was no evidence for a photochemical influence on PAN in the chamber. However, the residence time of unretained species in the chamber was quite short; tests with a pulse of NO added to the chamber inlet indicate an actual residence time, mediated by channeling of the airflow paths, of ~ 30 s [*Honrath et al.*, 2000a].

[20] At the end of the experiment, the PAN addition was stopped, while zero air continued to flow at constant flow rate. As shown in Figure 7b, PAN was observed to decay exponentially but with a calculated chamber lifetime of 13 min. In contrast, the lifetime for flushing NO (an unretained species) from the chamber was only 2.2 min., making the observed lifetime of PAN in the snow chamber ~ 6 times greater. This implies that PAN is weakly adsorbed on snow grain surfaces, consistent with the statements by *Munger et al.* [1999]. When compared to the carbonyl compounds formaldehyde, acetaldehyde and acetone (snow chamber lifetimes of 5.2, 2.3, and 2.9 hour., respectively [*Couch et al.*, 2000]), PAN is relatively weakly adsorbed. This is consistent with the relatively low solubility of PAN in water, with a calculated Henry's Law

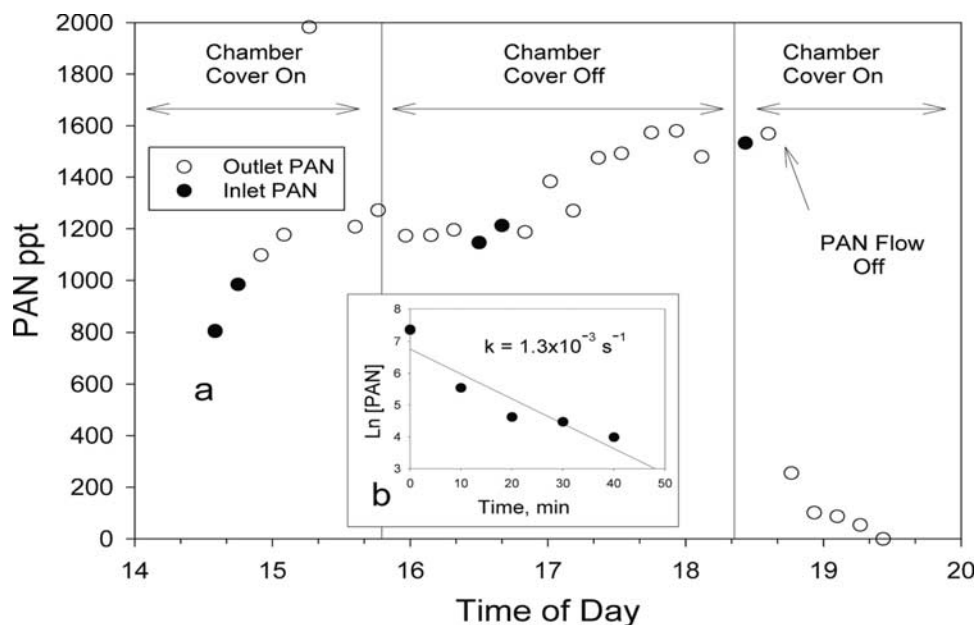


Figure 7. (a) [PAN] at the outlet of a snow chamber to which a constant PAN/air mixture was added. (b) Determination of the PAN decay constant during a snow chamber experiment.

coefficient of $\sim 80 \text{ M/atm}$ at 255 K [Kames and Schurath, 1995]; however, Couch *et al.* [2000] indicated that the observed decay lifetimes may be largely a function of the rate of water loss during their zero air experiment.

3.3. Snowpack Photochemistry

[21] Given that we know that CH_3CHO is elevated in snowpack interstitial air [Couch *et al.*, 2000; Guimbaud *et al.*, 2002], as is NO_x and that HCHO, O_3 , and HONO photolysis (mainly HONO) in the interstitial air will generate abundant OH radicals, it is reasonable to ask whether PAN production, for example, from reactions (R3)–(R5) followed by -1 , in the illuminated snowpack is



possible. During several experiments during Summit99, PAN was measured from the inlet and exit of the filled 34 L snow chamber under dark and sunlit conditions, and no significant change in [PAN] was seen. However, the short residence time for those experiments makes it difficult to see any impact from photochemistry. For sunlit snowpack near-surface interstitial air, we can estimate the OH radical concentration by applying the steady state assumption. From measurements at Summit [Dibb *et al.*, 2002] and at Alert during ALERT2000 [Zhou *et al.*, 2002], we believe that the dominant source of gas phase OH in the snowpack is HONO photolysis, followed by consumption in reactions (R4) and (R6)–(R8). The snowpack interstitial air



steady state [OH] can then be calculated as in equation (1) below; using a calculated $J_3 = 1.74 \times 10^{-3} \text{ s}^{-1}$

$$[\text{OH}]_{\text{SS}} = J_3[\text{HONO}] / \{k_6[\text{CO}] + k_7[\text{HCHO}] + k_4[\text{CH}_3\text{CHO}] + k_8[\text{CH}_4]\} \quad (1)$$

and [HONO] = 75 ppt [Dibb *et al.*, 2002], [CO] = 100 ppb [Chin *et al.*, 1994], [HCHO] = 250 ppt, [CH₃CHO] = 250 ppt [Guimbaud *et al.*, 2002], and [CH₄] = 1.7 ppm [Dlugokencky *et al.*, 1994] yields $[\text{OH}]_{\text{SS}} = 5.0 \times 10^6 \text{ molecules/cm}^3$. Using this [OH] applied to the snow chamber interstitial air, [CH₃CHO] = 250 ppt, using the measured NO and NO₂ in snowpack interstitial air, and taking into account reaction (R9), we calculate a PAN production rate of 75 ppt/hr.



Although this is a very significant result for the snowpack itself, it corresponds to only 1 ppt of PAN produced on the timescale of the chamber residence time during these experiments. We note that this is just the maximum gas phase production rate in the snowpack interstitial air. The actual observed $d[\text{PAN}]/dt$ in the snowpack air is of course a combination of the production and loss terms; for the snowpack, the important “loss” term is likely adsorption onto snow grain surfaces. Given the precision of our method and background concentrations at the inlet of ~ 100 ppt, the change in PAN concentrations during snow chamber experiments with a short residence time was too small to detect. Thus during one experiment, conducted 12 July 1999, we connected only the PAN instrument (which sampled at 1.8 slpm) to the snow-filled chamber, resulting in a ~ 10 fold increase in the chamber air residence time. The results of this experiment are shown in Figure 8, in which we plotted ambient PAN and NO_y (i.e., at the chamber inlet), and the PAN concentration in the chamber exit air. From 0900 to 1700 the ambient (inlet) PAN mixing ratio was reasonably constant at 52 ± 9 ppt. Although the chamber effluent was initially indistinguishable from these concentrations, at 1000, local generator exhaust impacted on the area around the chamber inlet, and the measured ambient NO_y rose

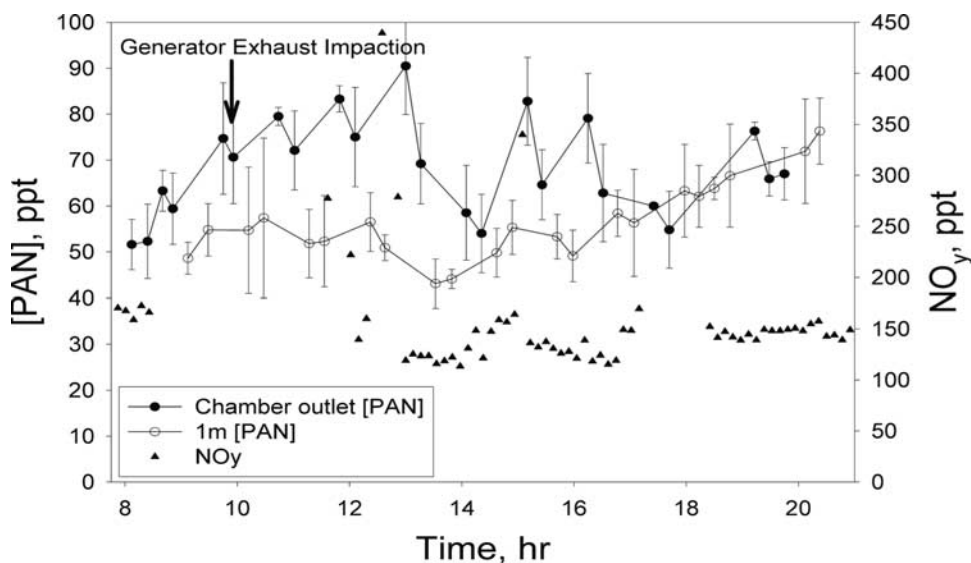
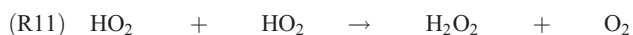


Figure 8. Snow chamber experiment during Summit 99; ambient air was contaminated with generator exhaust from 1000 to 1300.

dramatically. From 1000 to 1700, all PAN measurements from the chamber effluent indicated greater concentration than the inlet air, by typically 25–30 ppt, even though there was no change in ambient [PAN]; that is, the generator air was not elevated in [PAN]. For many of the measurements, the difference was statistically significant, as shown in Figure 8. We attribute the impact of the generator plume on the snow chamber effluent air [PAN] to an increase in the rate of OH production in the snowpack air, caused by the presence of NO_x . This can result from promoting reaction (R10) rather than the termination reaction (R11), or perhaps equally likely, from production of HONO from NO_2 reaction



on snow surfaces, as has been seen during high NO_x episodes during Alert2000 [Zhou *et al.*, 2001]. It thus seems possible that PAN could be produced in photochemically active snowpack interstitial air, especially after long range transport events that bring elevated NO_x (and CH_3CHO) to the site.

3.4. Vertical Profiles

[22] During Summit99, vertical profiles of the PAN concentration, sampling typically from 1 m above the air/snow interface to 70 cm below the surface within the firn interstitial air were obtained. In Figure 9 we show the ambient air and snow interstitial air PAN concentrations as a function of depth relative to the snow-air interface, for experiments conducted on 9 July and 16 July. For the 16 July experiment, the profile was measured twice, at midnight and noon, each time over a period of 3 hours. As shown in

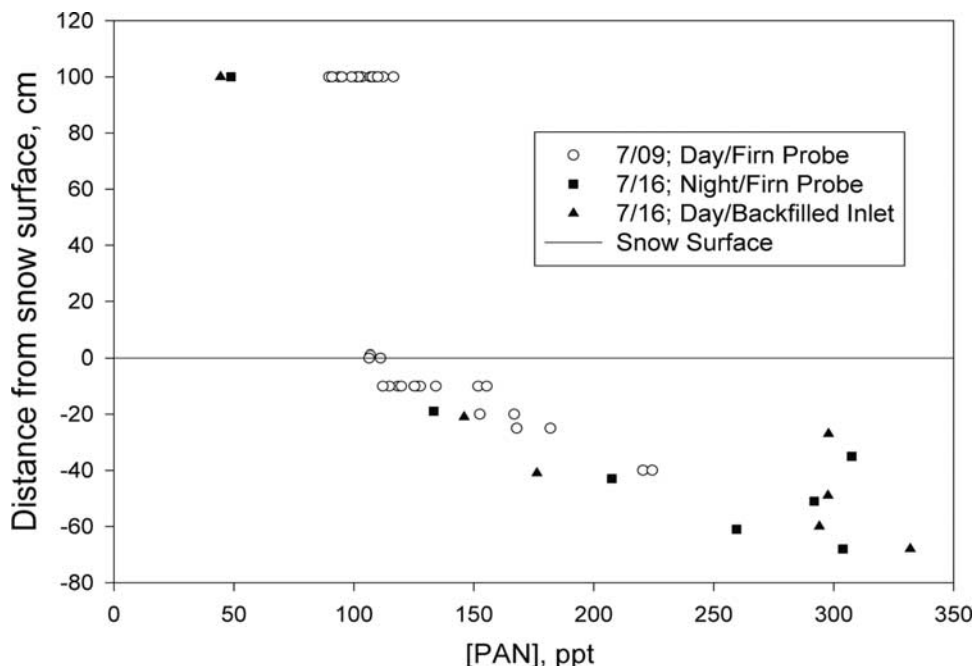


Figure 9. Vertical profiles of PAN during Summit 99.

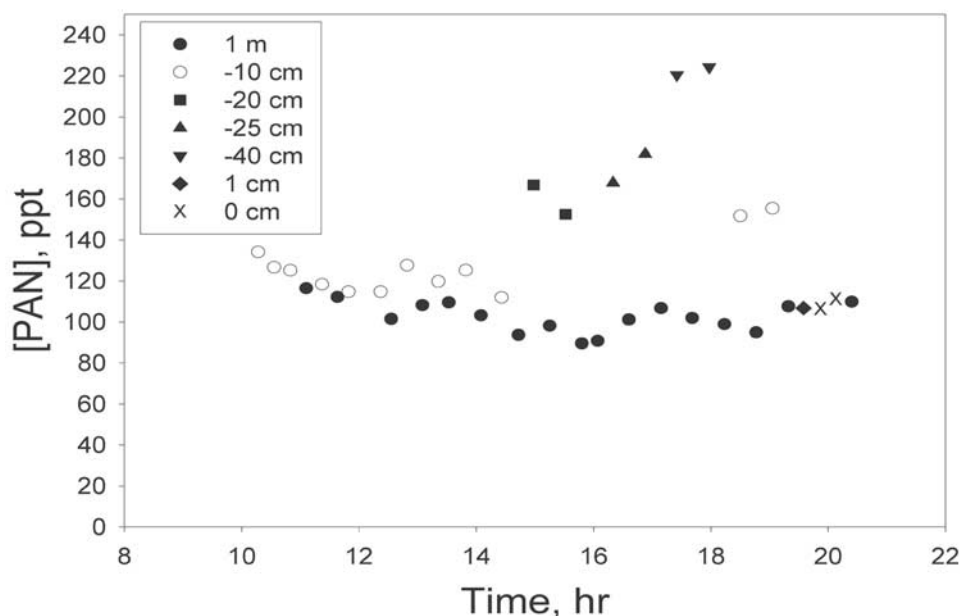


Figure 10. Concentrations of PAN in firm air at various depths on 9 July 1999.

Figure 9, although the gas phase PAN concentration 1 m above the snowpack surface was stable (the 1 m [PAN] was identical at midnight and noon, at ~ 50 ppt), it increased dramatically across the snowpack surface to between ~ 130 and 300 ppt at depths between -20 and -70 cm, i.e., as much as 6 times greater at -70 cm. For comparison, we also show in Figure 9 the profile data for the 9 July experiment, which is discussed below and presented in Figure 10. Given the magnitude of the gradient, it is important that the two profiles from the 16 July experiment were very reproducible and that the profiles are similar using two different sampling methods, implying that they are not biased by sampling artifacts. The fact that PAN in the firm air is elevated is perhaps not too surprising, given our observations that PAN is weakly adsorbed to snow surfaces and that PAN can be produced in the snowpack.

[23] To carefully examine the reproducibility of the firm air PAN measurements, PAN vertical profiles were measured on 9 July 1999, during which we alternated measurements between a height of 1 m above the air-snow interface and at various depths over a 10 hour period. In Figure 10 we present the results of those measurements. As shown in the Figure 10, in this experiment, the ambient [PAN] at 1 m was very stable at 103 ± 8 ppt. PAN concentrations in the firm air were always greater than at 1 m; indeed the PAN concentration exhibited a distinct gradient, being equivalent to 1 m levels down to the surface but increasing with depth in the firm air, to ~ 220 ppt at -40 cm. We can also see from Figure 10 that the concentrations were quite reproducible at each depth.

[24] Although the profiles cannot be fully explained, possible important factors should be discussed. First, wind pumping can transfer the components of the air aloft to a depth of ~ 50 cm on a timescale of ~ 6 hours (M. R. Albert and E. Shultz, Ventilation measurements and modeling at Summit, Greenland, submitted to *Journal of Geophysical Research*, 2000). Thus if the snowpack was exposed to PAN at relatively low temperatures and then warmed, the interstitial air could exhibit, at least temporarily, elevated PAN concentrations relative to ambient air, due to temperature dependent adsorption/desorption. Typically, the measured snowpack temperature (most often in the range -10° to -15°C) during these experiments was comparable to ambient temperatures during the day and several degrees warmer than the ambient temperatures at night. We note, however, that over the entire study period during Summit99, ambient PAN concentrations were never

as high as the firm air concentrations at -50 cm. Thus such a mechanism requires relatively long-term PAN storage in the snowpack. However, this depth corresponds to a midwinter snowfall, when the temperatures were much lower. Thus if PAN were incorporated into fresh snowfall, for example, through codeposition and then could undergo temperature dependent release, this could in principle account for the observations. At -50 cm, exchange with the atmosphere is very slow, and PAN is quite thermally stable at the low temperatures in this environment. Unfortunately, to date there is no information about [PAN] in precipitation or the bulk snow phase at the surface.

4. Conclusions

[25] As expected, PAN was found to be a major component of NO_y in the Greenland ice cap boundary layer. No diel cycle was found in [PAN], indicating that the ambient PAN is predominantly transported to Summit. The results presented here indicate that PAN interaction with the snowpack surface is likely important and is likely to influence the PAN concentration above snow covered surfaces, although the magnitude of the impact is unclear. These limited experiments did not show PAN decomposition in the snowpack to be a significant source of NO_3^- . Whether or not PAN decomposition on ice does yield NO_3^- should be explored through careful laboratory experiments. To improve our understanding regarding PAN's interactions with the snow, the temperature dependence of the PAN adsorption/desorption equilibrium constant on ice should be determined. It seems likely that PAN production could occur in snowpack interstitial air, owing to the likelihood of enhanced photochemistry in that air, related to increased concentrations of various inorganic and organic chromophores and significant levels of radiation in the near surface snowpack [Peterson *et al.*, 2002]. To explain the PAN vertical profiles within the snowpack will require determinations of its concentrations in precipitating snow and within the surface bulk snow. For PAN as well as other photochemically active gases that can be both photochemically produced or destroyed, extreme care will be required to interpret ice core concentrations, as the degree of this processing is likely highly variable, depending on season and the transport history (e.g., deposition of HNO_3) of air arriving at the site.

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