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Concentrations and Snow-Atmosphere Fluxes of Reactive Nitrogen at Summit, Greenland

J. W. Munger D. J. Jacob, S.-M. Fan[1], A. S Colman[2],

Harvard University,

Division of Engineering and Applied Sciences and

Department of Earth and Planetary Sciences

J. E. Dibb

Institute for the Study of Earth Oceans and Space

University of New Hampshire

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Corresponding author:
J. W. Munger
Harvard University
Dept. of Earth and Planetary Sci.
20 Oxford St.
Cambridge, MA 02138

email (jwm@io.harvard.edu)
617-495-5361 617-495-2768 (fax)

[1] Now at Princeton University

[2] Now at Yale University

Abstract. Concentrations and fluxes of NO_y (total reactive nitrogen), ozone concentrations and fluxes of sensible heat, water vapor and momentum were measured from May 1 to July 20, 1995 at Summit, Greenland. Median NO_y concentrations declined from 947 ppt in May to 444 ppt by July. NO_y fluxes were observed into and out of the snow, but the magnitudes were usually below 1μmol m^{-2} hr^{-1} because of the low HNO_3 concentration and weak turbulence over the snow surface. Some of the highest observed fluxes may be due to temporary storage by equilibrium sorption of PAN or other organic nitrogen species on ice surfaces in the upper snowpack. Sublimation of snow at the surface or during blowing snow events is associated with efflux of NO_y from the snowpack. Because the NO_y fluxes during summer at Summit are bi-directional and small in magnitude, the net result of turbulent NO_y exchange is insignificant compared to the 2 μmol m^{-2} d^{-1} mean input from fresh snow during the summer months. If the arctic NO_y reservoir is predominantly PAN (or compounds with similar properties) thermal dissociation of this NO_y is sufficient to support the observed flux of nitrate in fresh snow. Very low HNO_3 concentrations in the surface layer (1% of total NO_y) reflect the poor ventilation of the surface layer over the snowpack combined with the relatively rapid uptake of HNO_3 by fog, falling snow, and direct deposition to the snowpack.

Index terms: 0365 (Tropospheric composition and chemistry), 1863 (Snow and ice)

1. Introduction

Concentration records of NO_3^- in snow and ice cores have been used to infer variations of atmospheric nitrogen loading and inputs from anthropogenic NO_x emissions, biomass burning, solar activity, and stratospheric denitrification [*Legrand and Delmas,* 1986; *Mayewski et al.*, 1990; *Wolff,* 1995]. Inferences from the ice-core nitrate record, however, have been called into question because the chemical and physical processes controlling transport and speciation of N in the atmosphere, deposition to snow, and ultimate preservation in glacial ice are not fully understood [*Wolff,* 1995]. Our ability to invert the ice-core nitrate record to infer global atmospheric nitrogen concentrations and emission rates depends on a quantitative understanding of which nitrogen species are transported to the arctic; what processes control conversion and deposition of N; and how extensively post-depositional processes alter the record. The lifetimes for NO_y species (we define NO_x = NO +NO_2; NO_y = NO_x + HNO_3 + NO_3 + N_2O_5 + peroxyacetylnitrate (PAN) + other organic nitrates + particulate nitrate) vary from a few days to deposit HNO_3 from the boundary layer to several months to decompose peroxyacetylnitrate (PAN) in the upper troposphere. The amount of NO_y that reaches the polar regions depends strongly on the form of NO_y that is transported, but the long-lived species, such as PAN, that are transported effectively may not deposit efficiently. *Dibb et al*., [1994] point out the dilemma that HNO_3 concentrations measured above Summit, Greenland are very low yet NO_3^- is the dominant anion in the snow. Furthermore, the ratio of NO_3^- to SO_4^{2-} in snow at Summit exceeds the ratio of those ions (as HNO_3 and aerosol SO_4^{2-}) in air. They suggest that rapid dry deposition of HNO_3 from a shallow boundary layer depletes the gas-phase

HNO_3 or that species other than HNO_3 are deposited and convert to nitrate in the snowpack. Concentration profiles in the surface snow from Antarctica and Greenland indicate that NO_3^- may migrate within the snowpack (distorting seasonal and interannual variations) or be returned to the atmosphere [*Fischer, et al*., 1998a,b; *Mayewski and Legrand*, 1990; *Mulvaney et al.,* 1998; *Neubauer and Heumann*, 1988], particularly at low-accumulation sites. Volatilization of HNO_3 from snow is in apparent contradiction to laboratory studies showing irreversible uptake of HNO_3 on ice surfaces [*Abbatt*, 1997; *Laird and Sommerfeld*, 1995; *Zondlo et al.*, 1997]. Better understanding of the processes controlling HNO_3 removal is needed to objectively distinguish long-term trends in NO_3^- deposition [*Mayewski et al.,* 1986; 1990] from post-depositional loss where both processes are important.

This paper presents results from the first measurements of total nitrogen oxides (NO_y) mixing ratios and eddy fluxes above the surface of a polar glacier at Summit, Greenland. The goals of this work were to determine the ambient mixing ratios of NO_y, to quantify the direction and magnitude of NO_y fluxes at the snow-atmosphere interface, and identify processes that control exchange of reactive nitrogen with the snow surface. A previous paper [*Dibb et al.,* 1998] presented a subset of the 1995 NO_y data and HNO_3 concentration gradients above the snow surface. Nitric acid was 1% of the total NO_y. Measurable gradients of HNO_3 were observed and were frequently in opposition to the NO_y eddy flux, suggesting that N exchange with the snow was more complex than a simple adsorption/desorption of HNO_3. Large apparent deposition velocities for HNO_3 suggest that NO_y species other HNO_3 may be exchanging with the snowpack. In this paper we present the complete NO_y concentration and flux results for the May-June, 1995 summer field season, along with an examination of turbulent exchanges over the snowpack. We consider what nitrogen species are present, how they are transformed and deposited to the snowpack, and whether they are stable in the snow.

2. Methods

During the 1994 field season an 18 m tower was installed 270 m south of the main camp at Summit (elev. 3200 m 38.4°E, 72.55°N). Measurements were made during the summer season in both 1994 and 1995, however, we will not discuss the 1994 data here because contamination by local combustion sources affected too much of the data. Winds from the clean sector were more frequent and polluting activities were restricted during the 1995 field season. A 3-axis sonic anemometer (Solent Research Anemometer, Gill Instruments) and sampling inlets for NO_y, H_2O and O_3 measurements were mounted at 17.5 m facing the clean-air sector to the south and east. Instruments and data acquisition and control systems were housed in a covered snow trench at the tower base. Ventilation at the trench ceiling was required to discharge waste heat from the instrumentation and prevent the walls from melting. The instrument rack was enclosed to maintain a moderate operating temperature despite the room temperature being < 0°C. Operating temperatures for the instrument were in fact more stable than is often achieved in field measurements. NO_y was measured by catalysis on a heated gold surface with H_2 and O_3-chemiluminescent detection following methods described by *Bakwin et al.* [1994] and *Munger et al*. [1996]. The hot-gold catalyst quantitatively converts all species of NO_y to NO. The catalyst was mounted on the tower with no additional inlet to avoid inlet retention problems for species such as HNO_3. The sample line was attached to a heating cable and sheathed in foam insulation to prevent ice formation downstream from the catalyst. Temperature of the tubing was controlled by manually adjusting the voltage applied to the heating cable. The system was calibrated several times daily by addition of NO in N_2; isopropylnitrate (IPN) was added as a check on the catalyst conversion efficiency. Post-season tests indicated that the catalyst also converted HCN, which adds a degree of uncertainty to the true level of the lowest NO_y concentrations, but should not affect the fluxes. A fast-response CO_2/H_2O analyzer (LiCor 6262) was used to measure H_2O mixing ratios. The instrument response was checked using a dewpoint calibrator before and after the sampling season and found to be constant. Ozone was determined by UV-absorbance (Dasibi 1008). Dry zero air was supplied to the inlet several times a day to determine the zero offsets for both H_2O and O_3.

The anemometer and concentration signals were recorded at 4 Hz and auxiliary data on pressures and flows used to calibrate the sensors were recorded at 0.5 Hz by a PC-based data acquisition and control system. The data were downloaded to a separate computer daily and processed to generate initial concentration, flux and quality assurance data. Air temperature was computed from the speed of sound reported by the sonic anemometer. Fluxes of NO_y, H_2O, heat and momentum were calculated for 10-minute intervals from the covariance of fluctuations in vertical wind velocity (w') and trace-gas concentration (C'), temperature (T') or horizontal wind velocity (u') after removing the linear trend and offsetting the data to account for delays in the sample tubing [McMillen, 1988].

Data-quality criteria. Because the source of contamination at Summit was so close to the sensor, data rejection based on wind sector alone may not be reliable, particularly when winds are light and variable. In order to objectively exclude periods with contamination from camp activities, the NO_y mixing ratio data were rejected if the signal variance was too large. A few additional observations were rejected because the signal changed too much between successive intervals. (see Table 1). The computed eddy fluxes were rejected if rime ice was present or the wind was blowing through the tower. A small number of periods with in-sector winds and valid temperatures still had anomalous wind data and were rejected (Table 1). Between May 1 and July 19, the data system was operational 82% of the time. The wind velocity and NO_y mixing ratio data were acceptable for 66% and 60% of the time, respectively; the NO_y fluxes were acceptable for 50% of the possible observations (Table 1).

3. Results

3.1. Meteorological conditions

During the summer months the sun never sets at Summit; at the solstice, the noon sun is ≈ 41° above the horizon and the midnight sun is 5° above the horizon. Air temperatures exhibited diel variation in response to sun angle superimposed on seasonal and synoptic trends (Figure 1). Tethered-balloon temperature soundings (not shown) revealed that a strong temperature inversion (temperature increases of up to 10°C) existed at or near (within tens of meters) of the surface on many days. Maximum temperatures during the measurement period never exceeded 0°C.

Except for wind storms on 10-11 June and 3-4 July the momentum flux was generally between 0 and -0.1 m^2s^{-2}; these low values demonstrate the weak turbulence above the cold, aerodynamically smooth snow surface (Figure 2). *Grelle and Lindroth,* [1996] reported problems with heat fluxes calculated from a Solent sonic anemometer at wind speeds > 10 m s^{-1} due to noise in the virtual temperature signal. Less than 10% of the observations at Summit were in this range and they showed no apparent anomalies. If this problem is due to oscillation or vibration of the sensor it may depend on specific properties of the mounting and tower configuration. Sensible heat fluxes above the snow were small; 90% of observations had absolute values <20 W m^{-2}. Negative sensible heat fluxes and decreasing air temperatures were usually observed between the hours of 1600 and 0800, which we refer to here as "night". Peak values of latent heat (evaporation) flux during midday were < 15 Wm^{-2} (0.3 mmol-H_2O $m^{-2}s^{-1}$; 5.4 mg $m^{-2}s^{-1}$). Mean water vapor fluxes during the afternoon were 5 Wm-2 (0.1 mmol H_2O m^{-2} s^{-1}). Measurable negative values (condensation) were consistently observed at night, due to formation of frost and ground fog. Note that periods of larger water vapor deposition may be under represented because the wind sensor did not function during fog. Water vapor concentrations were generally near the saturation vapor pressure (Figure 1, panel 2). The small magnitude of water vapor fluxes and rapid diel variations in H_2O concentration imply that surface layer was fairly shallow and, if air above the inversion was dry, that the entrainment rate was small. Vertical profiles of water vapor concentration that would allow quantification of the water budget and entrainment rates could not be measured accurately in this sub-zero environment with the available sounding equipment.

3.2. NO_y and O_3 Mixing ratios

The variance-based criteria used to reject periods of local contamination removes the high NO_y concentration outliers from the data, leaving a population that fits a log-normal distribution (Figure 3). From May 3, to July 19, 1995 NO_y mixing ratios at Summit ranged from <100 ppt to 4900 ppt (ppt = 10^{-12} mol NO_y/mol air). Mixing ratios of NO_y were highest in May (Figure 4). Median mixing ratios decreased by a factor of 2 from May to July, and other statistical measures of the concentration distribution decreased similarly (Table 2).

Ozone concentrations declined from values near 70 ppb in early May to a minimum about 30 ppb in mid June, then rose again to 70 ppb (Figure 4). In general O_3 concentrations had a maximum in the late afternoon, as is typical of sites where surface deposition is balanced by entrainment of high O_3 from aloft. The diel variations in O_3 concentration at Summit were only 5-15 ppb.

3.3. Fluxes

The NO_y flux observations averaged over hourly intervals are about equally divided between periods of net deposition ($F_{NO_y} < 0$) and net emission ($F_{NO_y} > 0$) (Figure 5, Table 2). We estimate that the absolute value for the smallest observable flux (defined as twice the standard deviation during periods of very small flux) is 0.03 μmol m^{-2} hr^{-1}. The absolute values in general are small; 25% were below the 0.03 μmol m^{-2} hr^{-1} detection limit and only 10% exceeded 1 μmol $m^{-2}hr^{-1}$ (Figure 6). The frequency of fluxes with larger absolute value is highest in June. The NO_y fluxes are generally weak in July, resulting in the minimum range between 10% and 90% quantiles. In comparison to NO_y flux, snow deposition of NO_3^- averages 3.8 μmol m^{-2} per event [*Bergin, et al.*, 1995]; total snow deposition of NO_3^- for the period April 28-July 12, 1995 was 149 μmol m^{-2} (J. Dibb unpublished data).

4. Discussion

4.1. Nature and Origin of NO_y At Summit

Previous observations in the arctic show a seasonal spring peak in NO_y concentration with peroxyacetylnitrate (PAN) being the dominant contributor to NO_y [*Bottenheim and Gallant,* 1989; *Bottenheim et al.,* 1986; *Bottenheim et al.,* 1993; *Dickerson,* 1985; *Honrath and Jaffe*, 1992; *Honrath et al.,* 1996; *Solberg et al.,* 1997]. Enhanced PAN background concentrations are also observed in the northern mid-latitudes during the winter months [*Brice et al.,* 1988]. Aircraft measurements in the arctic during July and August indicate an increase of PAN concentrations with altitude *Singh et al*. [1992a,b], see Table 3). At the end of winter, however, vertical profiles of NO_y and PAN [reported by *Honrath et al.,* 1996] show concentrations decreasing with altitude up to 6 km.

Results from a three-dimensional chemical transport model that includes a detailed chemical mechanism for reactive N [*Wang et al.,* 1998] (Table 4) predict that PAN is the dominant NO_y species in the arctic middle troposphere. In the model, PAN over Summit is mostly derived from long-range transport in the free troposphere of PAN produced at northern mid-latitudes from anthropogenic NO_x. Even a small yield of PAN can lead to a substantial accumulation during the winter and early spring because the lifetime is very long. Emissions from forest and tundra fires during summer may contribute to additional PAN at high latitudes [*Singh et al.,* 1992a]. The spring maximum in the model most likely results from a combination of high emissions of biogenic hydrocarbons (precursors of PAN) and relatively low temperatures (suppressing PAN decomposition) [*Liang et al.*, 1998]. Because natural sources of NO_x (soils, lightning, forest fires) are at a minimum in winter, the NO_y peak in spring is most likely of anthropogenic origin. Simulated PAN concentrations exceed 500 ppt in April and decline to levels < 200 ppt by July. A vertical gradient of increasing PAN concentrations with altitude develops over the summer, reflecting the dominance of high-altitude transport of pollution as was observed in the ABLE-3A aircraft mission over the Arctic [*Harriss et al.,* 1992]. HNO_3 concentrations are depressed in the bottom model layer by deposition. Both the model and aircraft observations have higher HNO_3 concentrations and HNO_3:NO_y ratios than are observed in the surface layer at Summit. The differences between predicted and observed HNO_3 can be reconciled if the surface layer is shallow and the lifetime for HNO_3 deposition is shorter than the flushing time for air in the mixed layer. The lifetime for HNO_3 in a 100 m surface layer with a deposition velocity 0f 0.7 cm s^{-1} (the median V_d computed from aerodynamic resistance) is < 4 hours and decreases linearly as mixing height decreases. The ratio of H_2O concentration changes and the evaporation fluxes imply that evaporated water is mixed into a very shallow layer that does not mix effectively with dry air from aloft (see section 3.1). Modeled NO_x concentrations are low (10-20 ppt) throughout the spring and summer due to the ~1 day lifetime for NO_x oxidation.

The NO_y observations from this study (Table 2) exceed the model predictions by a factor of 2-4, but show similar trends. The median NO_y concentration observed at Summit during July (444 ppt) is within the range of NO_y concentrations measured in the free troposphere during ABLE-3A, and a factor of 2 higher than the corresponding PAN concentration (see Table 3). Concentrations of NO_y and PAN at Spitsbergen [*Solberg et al*., 1997] (elev. 474 m) exhibit the same decreasing trend from spring to summer as we observed at Summit, but the concentrations are about a factor of 5 less, which might result from differences in elevation. The results of this and previous studies taken together with the model predictions point to the accumulation of a reactive N reservoir during winter and spring in the arctic. The dominant identified species is PAN [*Singh et al.*, 1992b], but other compounds such as alkyl nitrates are also present at small concentrations [*Muthuramu et al.*, 1994]. The NO_y concentrations measured during ABLE3A were a factor of 2 higher than the sum concurrently measured concentrations of NO_x, PAN, and HNO_3, and issues about measurement artifacts [*Bradshaw et al.*, 1998] or unidentified species have not been resolved. As temperatures in the middle and lower troposphere warm, PAN (and other organic nitrogen species) thermally decomposes and the resulting NO_2 is quickly converted to HNO_3 [*Fan et al.*, 1994]. The reservoir concentration declines over summer through reaction and dilution by mixing with NO_y-depleted air.

We next examine whether the distinct episodes of elevated mixing ratio lasting for hours at a time (Figure 4) can be attributed to specific sources or transport patterns. The magnitude of these episodes decreases from May to July. Analysis of isentropic back trajectories indicates that about 50% of the air parcels arriving at Summit during the May-July, 1995 period had passed over northern Canada or the Arctic Ocean within the previous 5 days [*Kahl et al.*, 1997] (unpublished trajectory analysis for 1995, J Kahl, Univ. of Wisconsin, Milwaukee). Parcels that had been over the Atlantic Ocean or stagnated over Greenland for the previous 5 days accounted for an additional 23% and 12%, respectively. Trajectories from mid-latitude regions of North America, Europe or Asia that could have been significantly influenced by anthropogenic emissions or forest fires within 5 days had a combined frequency of 10% during the summer of 1995. NO_y events that occur on timescales of a few hours were not clearly associated with the back trajectories calculated at 12-hour intervals. Large day-to-day variability in aerosol ^{7}Be and ^{210}Pb at Summit have been attributed to short-term fluctuations in vertical mixing between the surface layer and free troposphere [*Dibb,* 1990]. The same process of intermittent vertical mixing could dominate the variability in the NO_y data at Summit.

4.2. Factors Contributing to NO_y Flux

Storage The vertical flux of NO_y measured at 18m (F_{18}) is equal to the flux at the snow surface, F_0, plus any change in concentration (storage) in the 0-18m column,

$$F_{18} = F_0 + \frac{\partial}{\partial t}\int_0^h C(z)dz \qquad (1)$$

where C(z) is the number density of NO_y at height z, and h = 18 m. Because snow is porous the lower boundary should be below the surface, but we ignore this contribution because only the upper 0.1 to 1 m is rapidly ventilated [*Colbeck*, 1989; *Waddington et al.*, 1996], and air space in the snowpack is reduced by the volume of ice. We estimate the magnitude of the storage term by assuming a uniform concentration below the sensor. For the range of observed hourly concentration changes the storage term would be between -1 and 1.5 μmol m^{-2} hr^{-1}; 50% of the data, however, have an absolute value < 0.05 μmol m^{-2} hr^{-1}. Although the storage term can have a large magnitude at times, the surface exchange, F_0 is not consistently different from the flux at 18 m. More importantly, the storage term does not bias the results; the least-squares fit of F_0 vs. F_{18} has a slope of 0.99 and an intercept not different from 0.

HNO_3 Uptake Laboratory studies [*Abbatt*, 1997; *Laird and Sommerfeld*, 1995; *Zondlo et al.*, 1997] show very efficient uptake of HNO_3 by ice up to monolayer coverage. Slower adsorption corresponding to formation of a multilayer or surface rearrangement is observed as well. Diffusion of HNO_3 through ice crystals is discounted by *Sommerfeld et al.,* [1998], however. Adsorption of a HNO_3 monolayer is largely irreversible [*Abbatt,* 1997; *Laird and Sommerfeld,* 1995; *Zondlo et al.,* 1997]. The capacity for monolayer HNO_3 adsorption is weakly temperature dependent and decreases by only a factor of 4 as temperature increases from 208K to 248K [*Abbatt,* 1997]. As seen below this apparent contradiction between laboratory measurements of HNO_3 adsorption and HNO_3 volatilization in the field can be reconciled by considering the surface-to-volume relationship of ice grains and the temperature dependence of HNO_3 uptake.

Sommerfeld et al., [1998] report that HNO_3 will be predominantly on the surface of ice grains. The concentration (mol g^{-1}) and surface density (mol cm^{-2}) of HNO_3 for an ice grain are related by the S/V ratio, and density of ice. As snow ages its S/V ratio decreases from > 100 mm^{-1} for new snow, to <5 mm^{-1} for fully developed depth hoar in summer (B. Davis, CRREL, personal communication) [*Davis et al.,* 1996] For the mean snow concentration of 3 nmol g^{-1} [*Dibb et al.,* 1998] the surface coverage increases from 0.016 x 10^{14} molecules cm^{-2} to 0.33 x10^{14} molec. cm^{-2} and the concentration corresponding to the monolayer uptake at 248 K (0.7 x 10^{14} molec cm^{-2}) [*Abbatt* 1997] decreases from 130 nmol g^{-1} to 6 nmol g^{-1} .as the snow ages. New snow has a capacity for HNO_3 adsorption well in excess of the observed ambient concentrations, but older coarse-grained snow approaches the monolayer adsorption limit (for ice at 248K), and may exceed that threshold if the HNO_3 uptake coefficient is even smaller at the warmer temperatures in the summer snowpack. Temperature profiles in the snow can be complex and vary over diel and seasonal timescales. Ice evaporates in the warmer layers and the vapor is either redeposited in colder layers or escapes entirely [*Davis et al*., 1996]. The fate of HNO_3 liberated from evaporated ice grains depends on whether the vapor encounters other ice surfaces or is quickly ventilated to the surrounding air. Snow metamorphism could redistribute HNO_3 within the snowpack and modify seasonal layers. This mechanism could account for the large enhancement of NO_3^- in the surface snow and the damping of seasonal cycles in older snow [*Fischer and Wagenbach*, 1996; *Mulvaney et al.*, 1998]. Increasing NO_3^- inventories of surface snow layers over the course of several days that have been interpreted as evidence of dry deposition [*Bergin et al*., 1995; *Dibb et al.*, 1998] may actually be redeposition of HNO_3 migrating from deeper layers. Evaporation at the surface of the snowpack, or sublimation from blowing snow [*Pomeroy and Jones,* 1996], however, would release HNO_3 to the atmosphere (see section 4.3). The extent of NO_3^- loss from the snowpack would depend on the length of time a layer was near the surface where it is subject to thermal gradients and ventilation and on the frequency of high winds.

PAN adsorption. Laboratory measurements (R. Friedl, JPL, personal communication) indicate that PAN is reversibly adsorbed on ice at 193 °K and shows no evidence of chemical reaction. The adsorption coefficient, K_{ads}, is K_{ads} = 30 cm (defined as the ratio of PAN adsorbed (molecules cm^{-2}) to the concentration in the overlying air (molecules cm^{-3})). For our application the mass of adsorbed PAN in a volume of snow is determined by the gas-phase concentration, adsorption constant and the bulk surface area of the snow. The unadsorbed PAN in the pore space is the gas-phase concentration adjusted for the volume of snowpack filled by ice. Hence the ratio of adsorbed PAN to gaseous PAN in a volume of snow is given by;

$$\frac{C \times K_{ads} \times SV}{C \times \left(1 - \frac{\rho_s}{\rho_i}\right)} \qquad (2)$$

where C is the gas-phase concentration (molecule cm^{-3}), SV is the bulk surface area of the snowpack (typically 30 mm^{-1} for wind-packed surface snow [*Davis et al.*, 1996] (B. Davis, CRREL, unpublished data)), ρ_s is the bulk density of snow (typically 0.4 g cm^{-3} for wind-packed surface snow [*Davis et al.*, 1996] (B. Davis, CRREL, unpublished data)), and ρ_i is the density of ice (0.9 g cm^{-3}). For the conditions given, which correspond to layer of small, closely packed grains, adsorbed PAN exceeds PAN in the pores by a factor of 16000. For the snow morphology given above and the adsorption coefficient determined at 193 °K a 1 cm layer of snow would hold 2.85 nmol of PAN per m^2 at equilibrium with a 1 ppt gas-phase concentration. Temporal variations in NO_y concentration range from -400 ppt hr^{-1} to 400 ppt hr^{-1} (90% of data), which translates to fluxes of -1.1µmol m^{-2} hr^{-1} to 1.1µmol m^{-2} hr^{-1} if ventilation of the snowpack and PAN equilibration at the ice surfaces are rapid and all NO_y is (or behaves like) PAN. This range is comparable to the measured fluxes, however, it is probably an overestimate because concentration changes in the snowpack may be damped relative to variations in the overlying air and the adsorption coefficient for PAN at temperatures relevant for Summit is probably less than the value for 193°K. This analysis suggests however, that the porous snowpack provides a mechanism to at least temporarily sequester a relatively large mass of PAN. Adsorption and desorption of PAN in response to changes in ambient concentration provides a mechanism to explain NO_y eddy fluxes that are in opposition to observed HNO_3 concentration gradients [*Dibb et al.*, 1998]. The NO_y flux measurement would not distinguish uptake and release of PAN from PAN conversion and release as a different compound (e.g. NO_x). The adsorption constant and reactivity for PAN on ice at temperatures relevant to polar snow needs to be determined. As pointed out by *Dibb et al*., [1998], conversion of only a small fraction of the NO_y passing through the snow could be a large term in the snow nitrate budget.

4.3. Illustrative Case Studies

The processes of HNO_3 and PAN adsorption noted above suggest there should be correlation between NO_y fluxes and physical parameters such as temperature, evaporation rate or changes in ambient concentration. Loss of HNO_3 by sublimation of blowing snow [*Pomeroy and Jones,* 1996] is indicated by consistently positive NO_y and water vapor flux and negative sensible heat flux for the periods with the largest momentum fluxes (Figure 7). The ratio of NO_y to H_2O fluxes corresponds to evaporation of snow with a NO_3^- ratio of about 20 nmol g^{-1}. This is higher than the observed mean NO_3^- concentration in snow at Summit, but surface snow may have enhanced NO_3^- concentrations, or partial evaporation of ice grains may preferentially release HNO_3.

The interactions between controlling variables at Summit are complex and correlation plots between NO_y fluxes and any single factor were generally confounded by the effects of other factors. Physical factors such as snow density, porosity or surface temperature that may affect the NO_y flux are difficult to quantify routinely over the large upwind area that contributes to the eddy flux. Defining quantitative relationships between NO_y flux and any single variable is difficult because the data set is too limited to identify trends by binning of the data to selectively hold the other factors constant. Instead we illustrate processes that affect NO_y exchange by examining selected periods of the data. A pulse of NO_y deposition immediately precedes a 1500 ppt increase in NO_y concentration the afternoon of June 22 (Figure 8) and is followed by a period of positive NO_y flux during the night. This pattern of alternating deposition and efflux is consistent with temporary storage by reversible surface adsorption. Positive NO_y fluxes continue during the afternoon of June 23 accompanied by wind speeds that peak at 12 m s^{-1} and observations of snow and blowing snow. Latent heat fluxes that exceed the sensible heat flux suggest strong evaporation and liberation of HNO_3. Another period of high wind on June 24, which only stirred up a layer of blowing snow just above the surface, is associated with a consistent small negative NO_y flux. Evaporation rates are smaller during this period and the sensible heat flux is larger. The increased sensible heat flux and warmer surface temperatures would weaken the surface inversion and allow mixing over a deeper layer and allow HNO_3 from aloft to reach the surface. Water vapor concentrations decrease throughout the day on June 24 despite the evaporation from the surface, suggesting there is a deeper mixed layer or entrainment of dry air across the inversion. Subtle differences in the consolidation of surface snow or shifts in the energy balance can affect the direction of NO_y fluxes.

Several hours of NO_y uptake, with a peak of 1 μmol m^{-2} hr^{-1} is associated with a 1500 ppt increase in NO_y concentration on July 1 (Figure 9). Consistent small NO_y efflux is observed from mid-morning on July 1 to the night of July 2 that is again associated with high wind speed, warmer temperatures, increasing water vapor concentrations, and low ambient NO_y concentration, suggesting evaporation of snow along into a relatively clean well mixed surface layer. A short pulse of NO_y deposition occurs on July 3 along with rising NO_y concentration that suggests surface adsorption. The temperature is colder during this period than during the NO_y concentration increase on 1 July and the surface snow has been densely packed by the wind storm on the previous day. In addition, the slight positive heat flux may enhance vertical mixing and entrainment of air that has a higher proportion of HNO_3.

Nitrate scavenging by snow. In this section we consider whether the levels of nitrate observed in snow at Summit are consistent with the NO_y concentrations and fluxes. Based on the recent laboratory investigations of HNO_3 adsorption and evaluation of HNO_3 uptake by cirrus clouds [*Abbatt*, 1997; *Zondlo et al.*, 1997] (see 4.2) we expect that HNO_3 is completely scavenged by the ice surface during formation of clouds and snowflakes. Even if a quasi-liquid layer [*Conklin and Bales*, 1993] were present HNO_3 uptake would be efficient because of its high solubility and dissociation constants. Although some PAN could adsorb on the fresh snowflakes, the surface area of ice in the cloud is too small for this process to significantly alter the gas-phase concentrations. The final concentration of NO_3^- in fresh snow depends on the initial concentration of HNO_3 in the air and the mass of water that freezes, which can be computed from the temperatures before and after cloud formation. This mechanism differs from the co-deposition process considered by *Silvente and Legrand* [1995] because all the HNO_3 present in an air parcel is partitioned into the small fraction of water vapor that freezes. For an HNO_3 concentration of 6 ppt, cooling saturated air from -12 °C to -12.5°C is sufficient to produce nitrate concentrations of 3.5 nmol g^{-1} in snow (Figure 10). Even the low HNO_3 observed in the surface layer could account the mean NO_3^- concentrations in fresh snow, without any additional input from dry deposition.

Budget considerations. We next evaluate whether an NO_y reservoir composed of PAN, can account for the observed total deposition of NO_3^- during summer. The lifetime (1/k) for PAN decomposition below -10° C exceeds 4 weeks, (decay rate ≤ 4% d^{-1}) but it decreases rapidly to 3 days as temperature warms above 0° C (decay rate ≥ 31% d^{-1}) [*Roberts and Bertman,* 1992]. The lifetime for OH oxidation of NO_2 to HNO_3 at pressure and temperature of Summit and an OH concentration of 1x 10^6 molecule cm^{-3} is 1 day. *Fan et al.* [1994] conclude that PAN is extensively decomposed and converted to HNO_3 in subsiding air parcels. Using mid-day mean air temperatures measured at the surface, the monthly median NO_y concentrations (assuming that NO_y is PAN), and temperature coefficients for PAN decomposition from *Roberts and Bertman* [1992] we compute a maximum source of NO_x from PAN of 13 ppt d^{-1}, 34 ppt d^{-1}, and 31 ppt d^{-1} in the surface layer for May, June and July, respectively. Thermal decomposition of PAN followed by oxidation of NO_x to HNO_3 in a 3 km layer above Summit could thus yield 153 μmol m^{-2} of deposited NO_3^- for the period May 1 to July 15 (1 μmol m^{-2} d^{-1}, 2.7 μmol m^{-2} d^{-1}, and 2.5 μmol m^{-2} d^{-1} for the months May, June, and July, respectively). From April 28 to July 12, 1995 the nitrate accumulation in snow was 149 μmol m^{-2} (J Dibb, unpublished data). Such close agreement between the NO_3^- accumulation rate in fresh snow and PAN decomposition is fortuitous considering the gross simplification in our assumptions about vertical structure of temperature and PAN concentration. The surface temperatures lie between the inversion temperature and the temperatures in the free troposphere above.. Nevertheless, the calculation demonstrates that production of HNO_3 from PAN can potentially account for the NO_3^- deposited in snow. As noted in section 4.1, PAN transport and thermal decomposition account for HNO_3 concentrations of 80-90 ppt just above the surface layer. The seasonal pattern for PAN decomposition is consistent with the observed summertime peak in snow NO_3^- [*Davidson et al.,* 1989; *Whitlow et al.,*1992] despite the decline in ambient concentrations over the summer.

Our observations of small offsetting fluxes of NO_y from the snowpack are consistent with the observations by *Bergin et al.* [1995] that measured inputs in fresh snow and fog accounted for 99% of the NO_3^- present in the snowpack at the end of the season, leaving little room for significant dry deposition or revolatilization of HNO_3. Although the flux observations from Summit do not indicate consistent revolatilization of HNO_3 during the summer leading to a net loss of nitrate from the snowpack they do not address redistribution of NO_3^- within the snow or losses in other seasons or at other sites.

5. Conclusions

The concentration of NO_y at Summit, Greenland declined over the summer from a median of 950 ppt in May to 440 ppt in July. Nitric acid in the surface layer was typically only 1% of the observed NO_y. Predictions based on current understanding of reactive N chemistry indicate that PAN should accumulate in early spring in the arctic troposphere. Thermal decomposition rates for PAN as temperatures warm in the summer are adequate to supply fresh NO_x that is oxidized to HNO_3 and scavenged by fresh snow. Variations in the ice-core nitrate record should be interpreted with respect to variations in the long-range transport of PAN to the Arctic, which depends on the supply of precursor hydrocarbons, photochemical activity, temperatures, as well as variations in NO_x emissions.

The turbulent fluxes of NO_y at Summit were bi-directional, but the magnitudes were small. Most of the time NO_y fluxes were < 1 μmol m^{-2} hr^{-1}. Neither emission or dry deposition dominated the NO_y flux and the overall net exchange was insignificant compared to the flux of NO_3^- via snow deposition, which contributed 149 μmol m^{-2} over 75 days. Water vapor concentrations were close to the saturation vapor pressure and responded quickly to variations in temperature, which demonstrates that the boundary layer is shallow and infrequently mixed with the overlying atmosphere. Even the very small HNO_3 deposition that we observed at Summit can account for the small HNO_3 concentrations if the limiting process is entrainment of HNO_3 from aloft. If the process that limits HNO_3 dry deposition is its entrainment from aloft the small fluxes that we observed would be sufficient to maintain very low concentrations in the surface layer.

Pulses of NO_y exchange into and out of the snow that follow ambient concentration changes suggest that reversible adsorption of compounds such as PAN on the ice surfaces may temporarily store reactive N in the snowpack. However, we cannot rule out adsorption of one species followed by conversion and release as a different compound. Upward fluxes of NO_y and H_2O during high wind events point to sublimation as a mechanism for releasing NO_3^- from the snowpack. Nitric acid is tightly bound to ice surfaces up to a monolayer coverage, but may be liberated as the snow ages and the individual grains increase in size. Once liberated, this HNO_3 may redeposit on fine-grained layers near the surface or be lost from the snowpack if it is released near the surface and is quickly ventilated. The tendency for NO_y efflux during windy periods that evaporate the snow indicates that post-depositional losses of NO_3^- from the snowpack could be more important in drier or windier seasons and sites.

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Figure Legends

Figure 1. Meteorological parameters at Summit Greenland during the summer of 1995. The top panel shows virtual temperature measured by the sonic anemometer. The second panel shows H_2O concentrations as black lines superimposed on the saturation vapor pressure for the observed air temperature. The third and fourth panels show wind speed and direction, respectively.

Figure 2. Momentum, sensible and latent heat (water vapor) fluxes measured at Summit Greenland during May - July 1995.

Figure 3. Probability distribution for NO_y concentrations measured at Summit, Greenland during the 1995 field season, May - July. The dashed line is fit to the 25% and 75% quantiles. Log-Normally distributed data would follow a straight line in this plot.

Figure 4. NO_y (black line with dots) and O_3 (gray lines) concentrations at Summit Greenland during May - July of 1995 are shown for 20-day periods. Downward pointing tick marks indicate noon of each day (local time).

Figure 5. Distribution of NO_y fluxes measured at Summit, Greenland during the summer of 1995.

Figure 6. Time series of NO_y fluxes at Summit, Greenland. Each dot represents a 1-hour average flux. Downward pointing tick marks indicate noon of each day (local time).

Figure 7. Fluxes of NO_y sensible heat and water vapor (latent heat) are plotted vs. the momentum flux (F_{MOM} = <u'w'>) when the magnitude of F_{MOM} exceeds 0.1 m^{-2} s^{-2} . Day-time hours are indicated by filled symbols. The mean NO_y fluxes and standard deviations are computed over F_{MOM} intervals of 0.05 m^{-2} s^{-2} and shown as vertical segments connected by the long-dashed line in the upper panel.

Figure 8. (top) Concentration of NO_y (dots) and NO_y flux (plusses connected by lines) are shown for a four day period beginning on June 21, 1995. Vertical bars indicate the HNO_3 concentration x 10. (middle) Wind direction (solid line), wind speed (plusses connected by dashed line), and u*, the friction velocity, x10 (triangles) are plotted against time of day. (third panel) For the same period sonic temperature (dots), sensible heat flux (plusses), (fourth panel) latent heat flux and H_2O concentration.

Figure 9. Same as Figure 8**,** but for four days commencing June 30, 1995**.**

Figure 10. The concentration of NO_3^- in increases as temperature decreases because cold air holds less water. Nitrate concentration in snow that formed with an ambient HNO_3 concentration of 0.27 nmol m^{-3} (6ppt) [*Dibb et al.,* 1998] is plotted on the vertical axis against the saturation temperature on the horizontal axis. The symbols indicate different temperature differences associated with snow formation. The ice formed by cooling saturated air 0.5C to -12 C would have a nitrate concentration of 3.5 nmol g^{-1}. The dashed horizontal line shows the mean nitrate concentration in snow [*Dibb et al.,* 1998].

Table 1. Summary of Data Rejection.

Criteria	Hours
Overall duration of campaign (May 1 - July 20, 1995)	1923
NO_y Mixing ratios	
Instrument in sampling mode	1553
Instruments on	1535
Variance indicates clean conditions[4]	1320
ΔNO_y indicates clean conditions	1311
After exclusion of warm-up time and miscellaneous failures	1280
Mixing ratios Acceptable	1280
Wind Velocities	
Instrument Operational[1]	1574
Sonic data valid - frost free (T<0°C)	1255
In-sector winds[2]	1187
Valid friction velocity[3]	1168
Downward momentum flux	1164
Wind Data Acceptable	1164
Eddy Flux ($w'NO_y'$) acceptable	944

[1] Excluding power shutdowns and maintenance; [2] Tower not upwind of the sensors; [3] $u^* < 0.0046 + 0.045 \times \bar{u}$ (m s^{-1}), $u^* = (-1 * \langle u'w' \rangle)^{1/2}$; [4] $21 < \sigma_{NO_y} < 1250$ and $\sigma_{NO_y}^2 / NO_y < 200$.

[5] $|\Delta NO_y| < 1450$. NO_y thresholds are based on the raw photon count data sampled at 4 Hz in units of counts (or counts^2 for the variance).

Table 2. NO_y (ppt) HNO_3 and O_3 (ppb) mixing ratios and NO_y fluxes (μmol $m^{-2}hr^{-1}$) between May 3 and July 19, 1995 at Summit, Greenland

	percentile							
Period (N)	10%	25%	33%	median	67%	75%	90%	mean
				NO_y (ppt)				
Overall (1280)	330	469	547	740	939	1072	1508	850
May (507)	574	751	828	985	1252	1363	1849	1145
June (429)	329	448	518	683	858	965	1242	748
July (344)	233	331	363	444	571	651	947	544
				O_3 (ppb)				
Overall (943)	37	46	50	55	58	61	68	54
May (318)	49	53	54	58	63	65	72	59
June (601)	33	43	45	51	56	58	63	50
				HNO_3 at 8m [1] (ppt)				
4/25-7/8 (225)	2.7	4.2	4.9	6.4	9.9	11.2	18.3	9.6
May (69)	3.4	5.5	7.4	10.4	13.4	15.7	24.1	12.8
June (134)	2.5	4	4.4	5.5	7.1	8.8	12.6	8.2
July (22)	3.7	4.4	4.6	8.3	10.2	12	14.5	8.3
				NO_y flux (μmol m^{-2} hr^{-1})				
overall (944)	-0.703	-0.151	-0.053	0.002	0.066	0.146	0.717	0.008
May (316)	-0.468	-0.095	-0.041	0.001	0.063	0.178	0.973	0.140
June (339)	-1.154	-0.409	-0.270	0.007	0.126	0.305	0.898	-0.070
July (289)	-0.318	-0.051	-0.022	0.000	0.030	0.066	0.206	-0.045

[1] Dibb et al., 1998

Table 3. ABLE3A mean concentrations for July-August arctic and subarctic flights.

Altitude (km)	NO_x (ppt)[1,3]	HNO_3 (ppt)[2]	PAN (ppt)[3]	NO_y (ppt)[1,3]	O_3 (ppb)[4]
2-4	26	78	140	518	36
4-6	34	70	285	860	57

[1]Sandholm et al., 1992. [2]Talbot et al. [1992], [3] Singh et al., [1992a]. [4]Gregory et al., [1992].

Table 4. Reactive N mixing ratios (ppt) simulated over Summit, Greenland by a global 3-dimensional model.

Month	NO_x		PAN		HNO_3		NO_y	
Altitude, km[1]	0-0.4	1.0-2.3	0-0.4	1.0-2.3	0-0.4	1.0-2.3	0-0.4	1.0-2.3
April	8	11	547	547	80	162	688	769
May	14	19	257	306	78	187	381	543
June	15	18	191	233	77	197	300	469
July	14	20	133	180	94	207	253	421
August	14	19	132	176	96	199	258	411

[1] Mean model results from Wang et al., [1998] for the atmosphere over Summit. The model was sampled in vertical levels 1 and 3, corresponding to 0-0.4 km and 1-2.3 km above the surface at Summit, which is at 3 km above sea level.

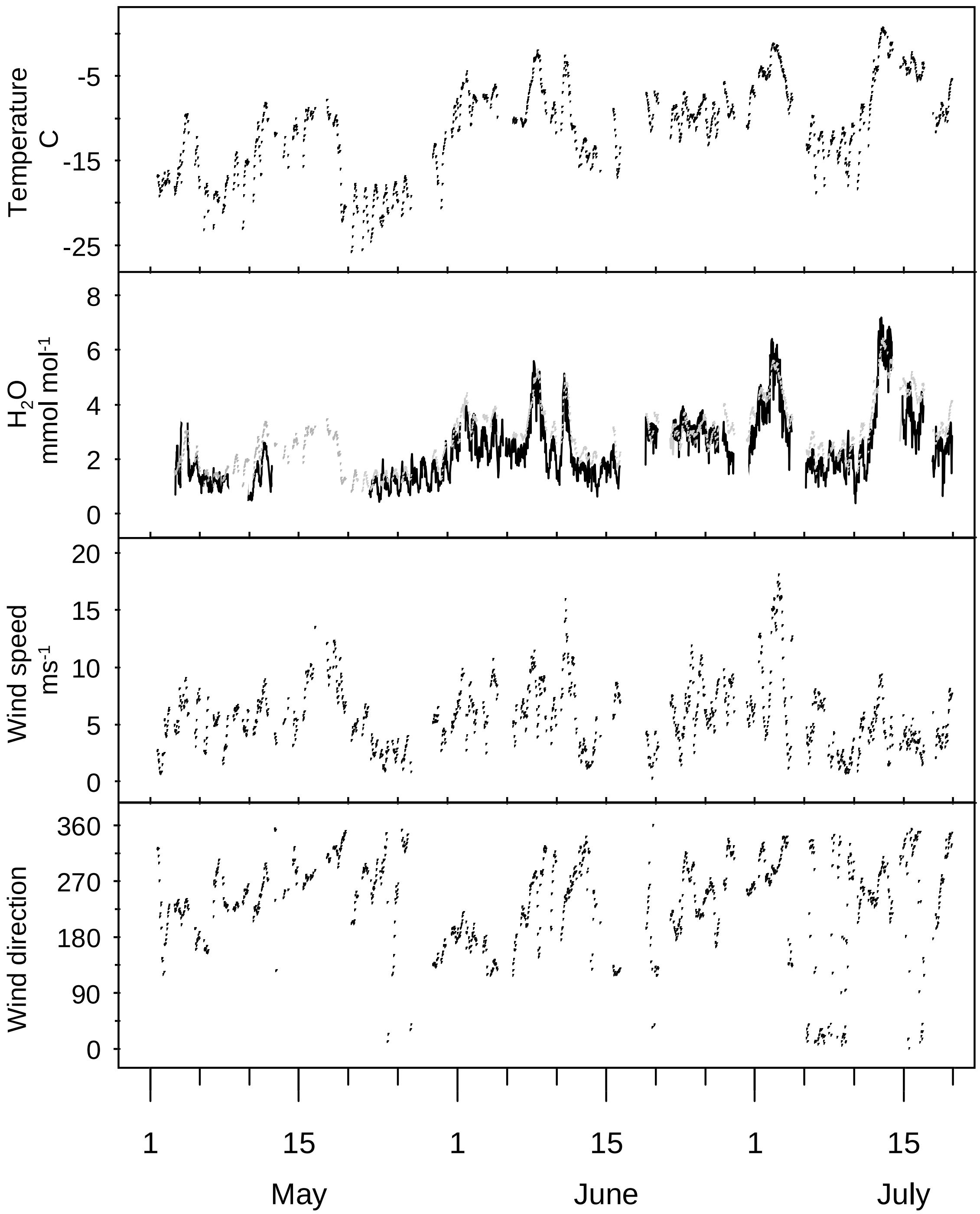

Figure 1 Meteorological parameters at Summit Greenland during the summer of 1995. The top panel shows virtual temperature measured by the sonic anemometer. The second panel shows H_2O concentrations as black lines superimposed on the saturation vapor pressure for the observed air temperature. The third and fourth panels show wind speed and direction, respectively.

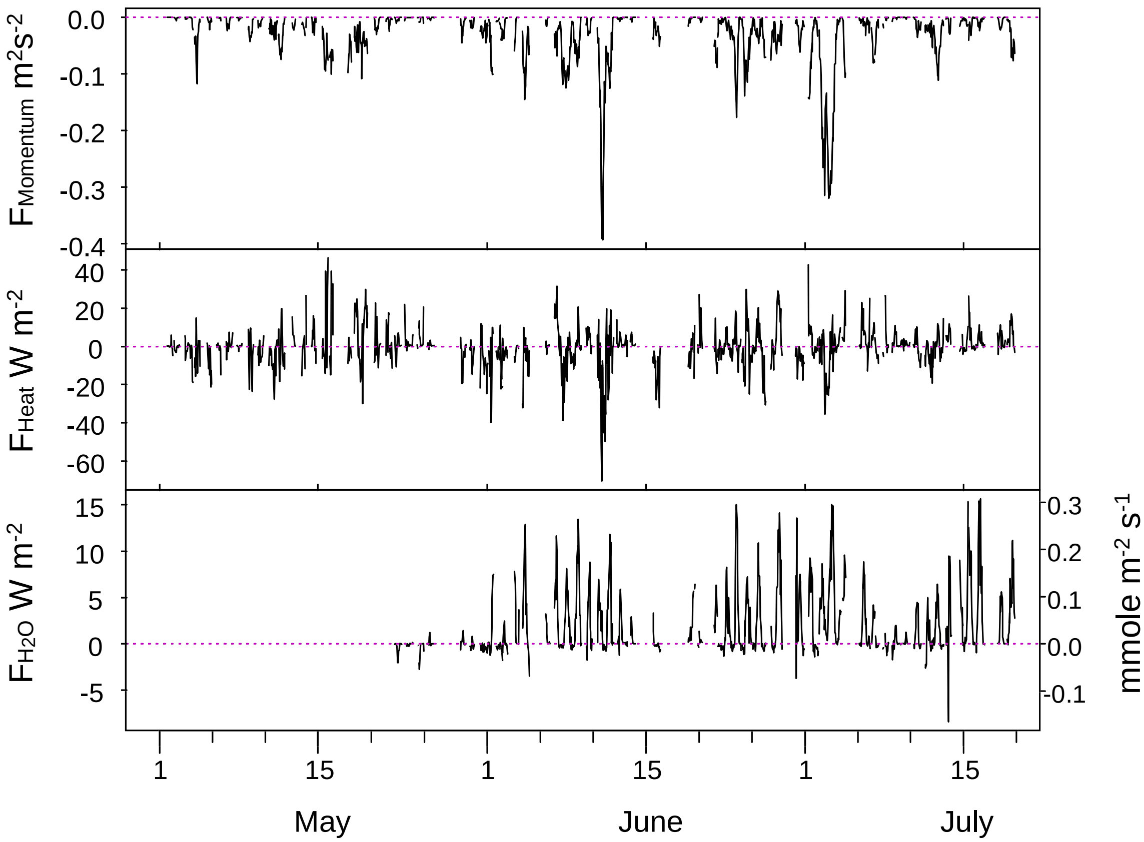

Figure 2 Momentum, sensible and latent heat (water vapor) fluxes measured at Summit Greenland during May - July 1995.

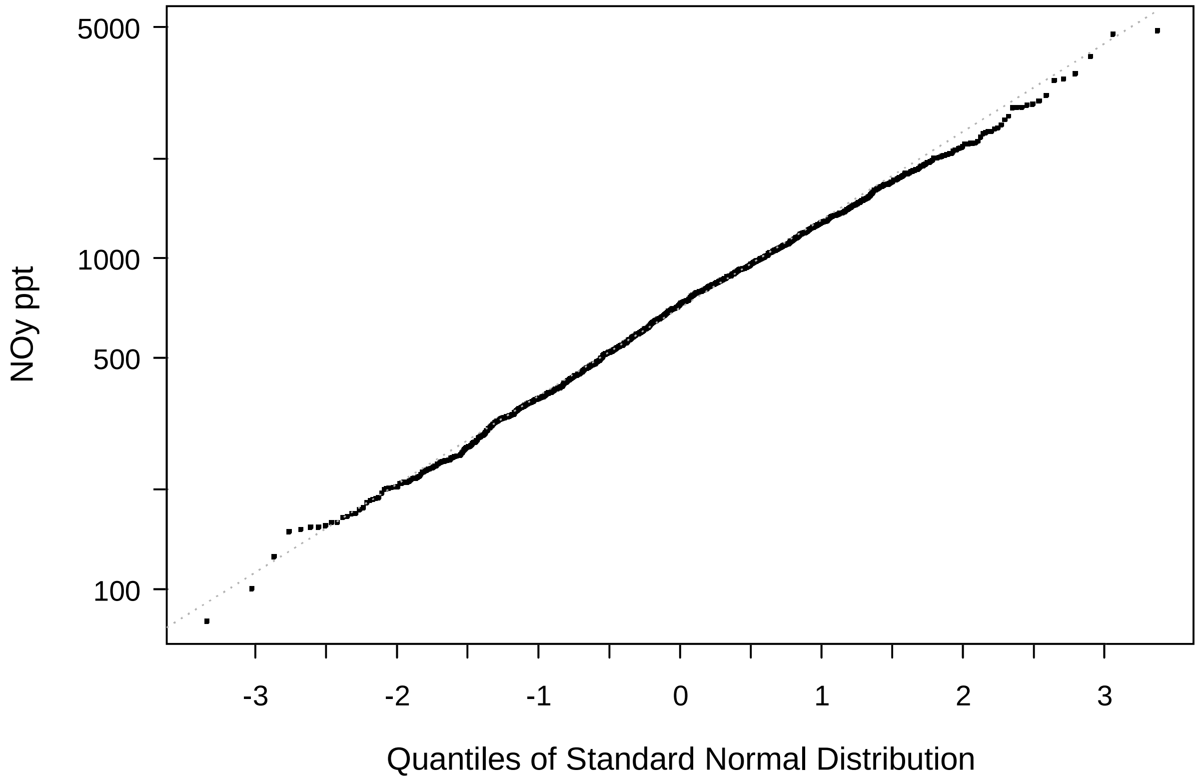

Figure 3 Probability distribution for NO_y concentrations measured at Summit, Greenland during the 1995 field season, May - July. The dashed line is fit to the 25% and 75% quantiles. Log-Normally distributed data would follow a straight line in this plot.

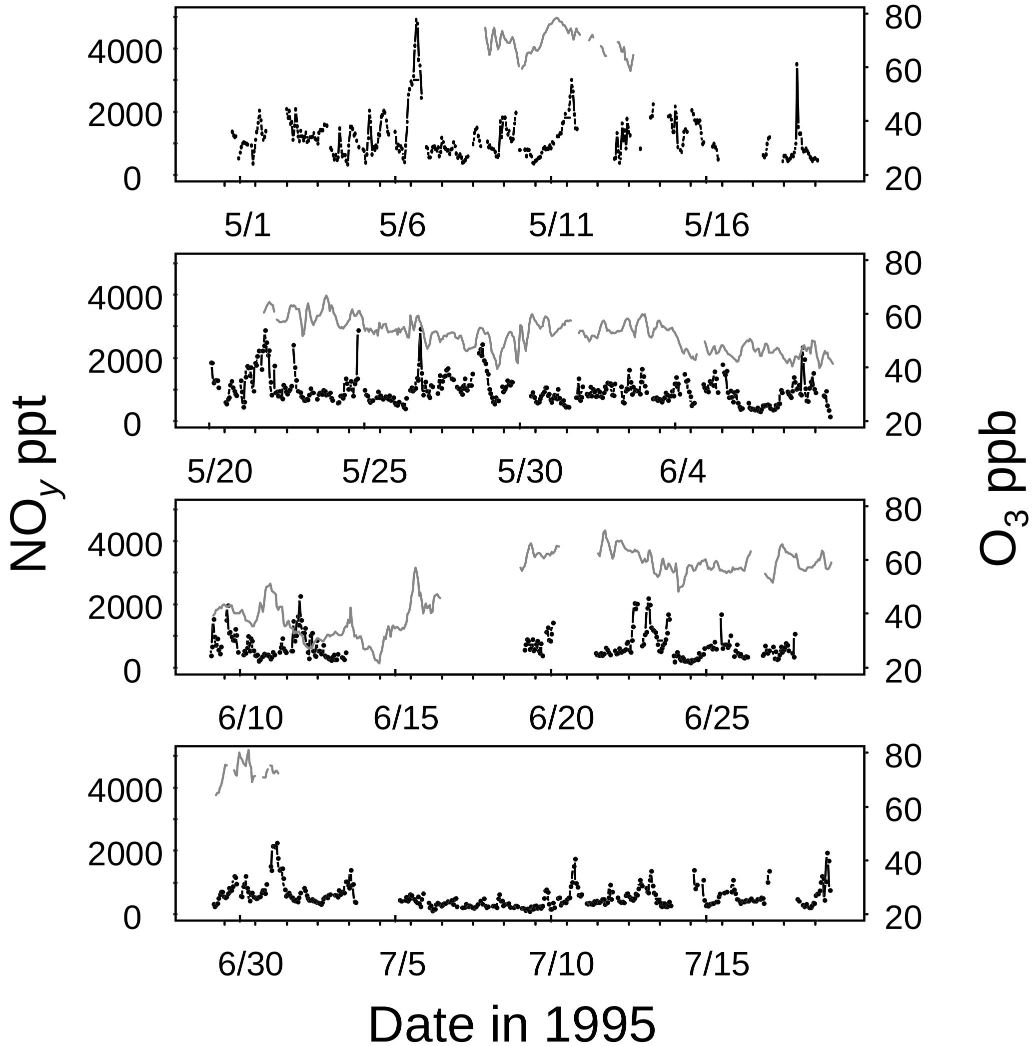

Figure 4. NO$_y$ (black line with dots) and O$_3$ (gray lines) concentrations at Summit Greenland during May - July of 1995 are shown for 20-day periods. Downward pointing tick marks indicate noon of each day (local time).

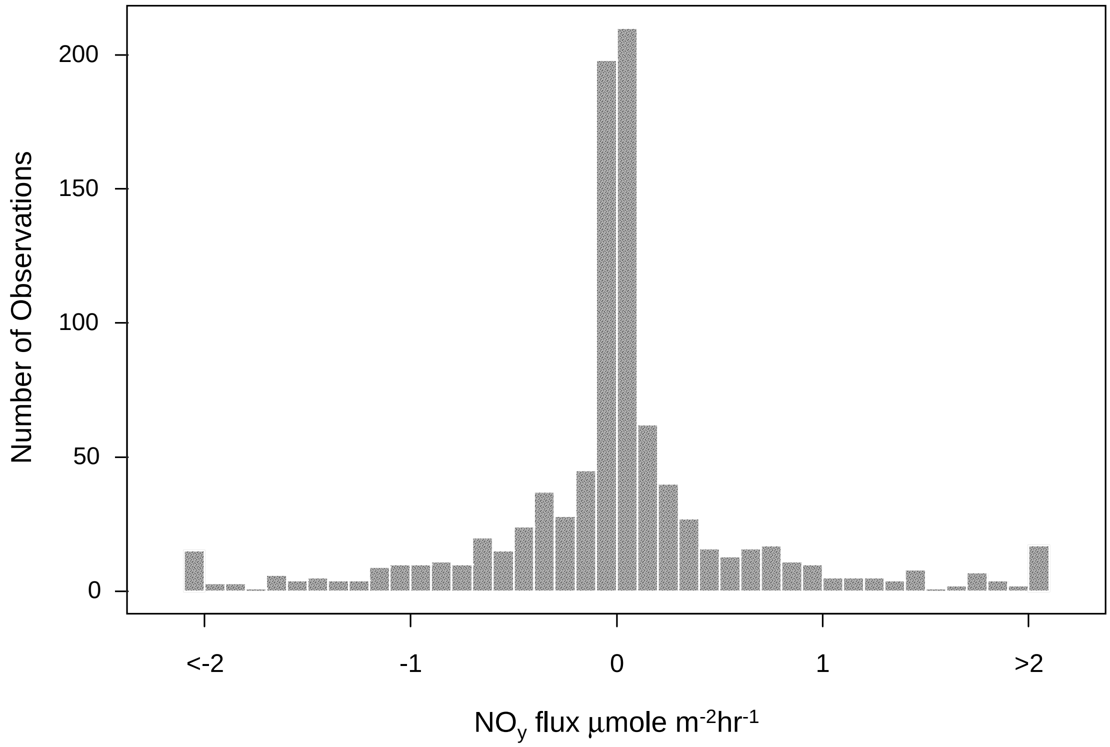

Figure 5. Distribution of NO_y fluxes measured at Summit, Greenland during the summer of 1995.

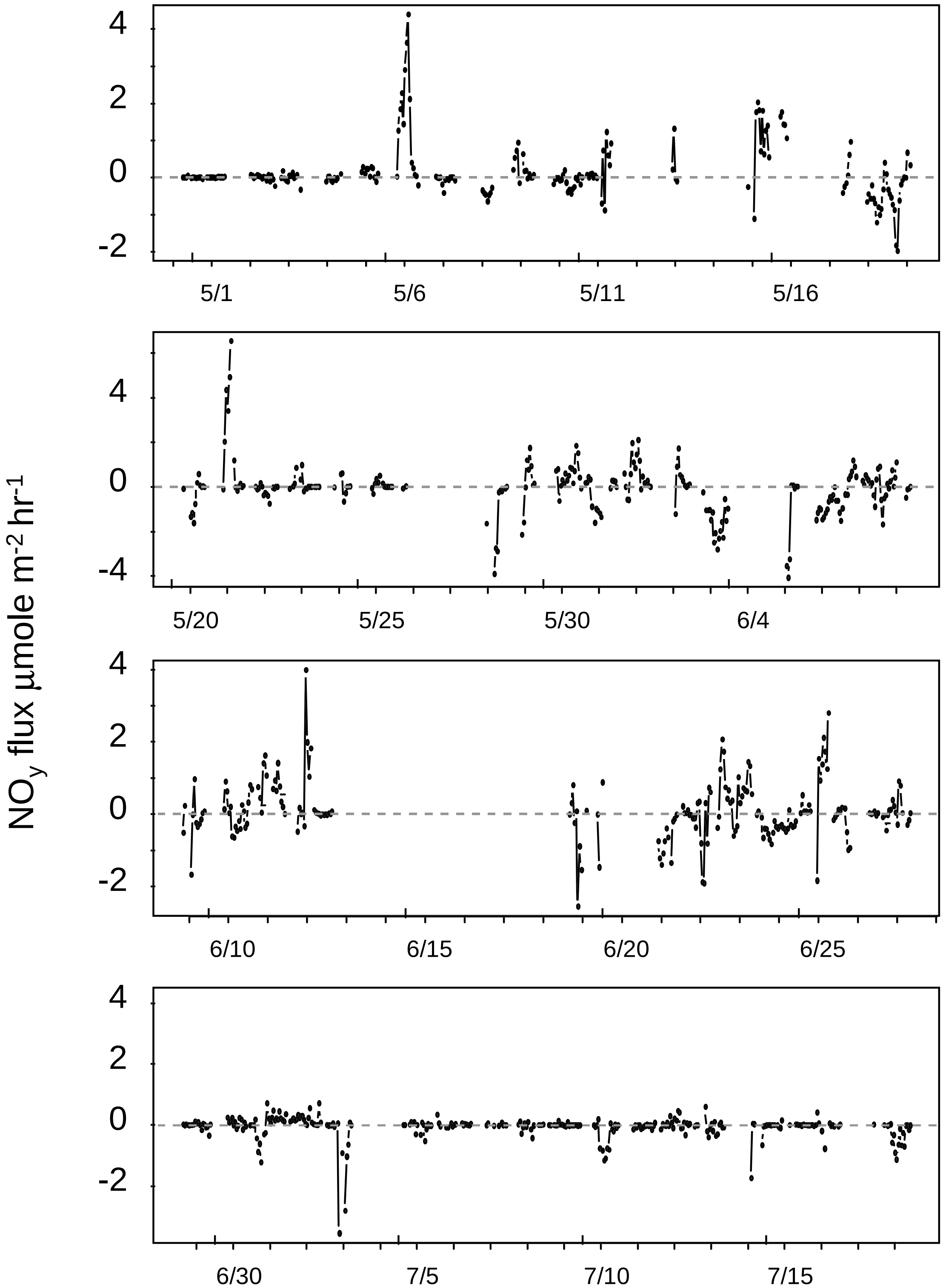

Figure 6 Time series of NO_y fluxes at Summit, Greenland. Each dot represents a 1-hour average flux. Downward pointing tick marks indicate noon of each day (local time).

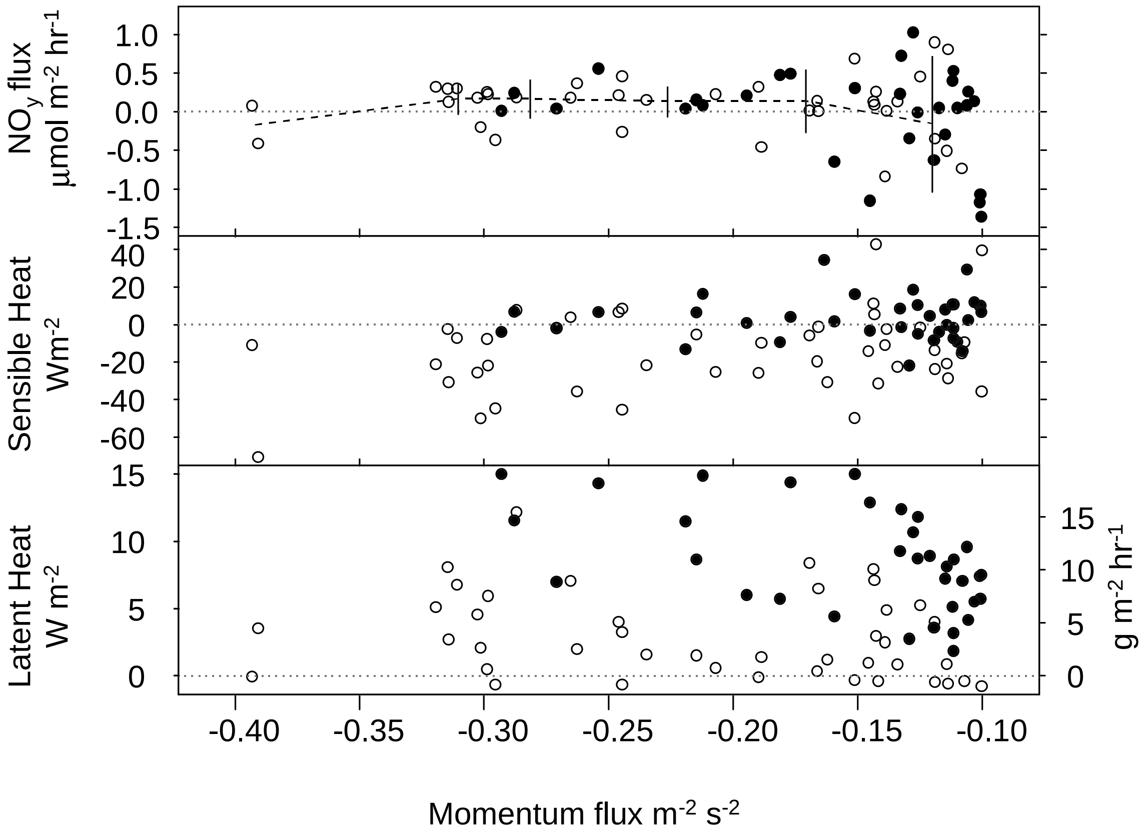

Figure 7 Fluxes of NO_y sensible heat and water vapor (latent heat) are plotted vs. the momentum flux (F_{MOM} = <u'w'>) when the magnitude of F_{MOM} exceeds 0.1 m^{-2} s^{-2} . Daytime hours are indicated by filled symbols. The mean NO_y fluxes and standard deviations are computed over F_{MOM} intervals of 0.05 m^{-2} s^{-2} and shown as vertical segments connected by the long-dashed line in the upper panel.

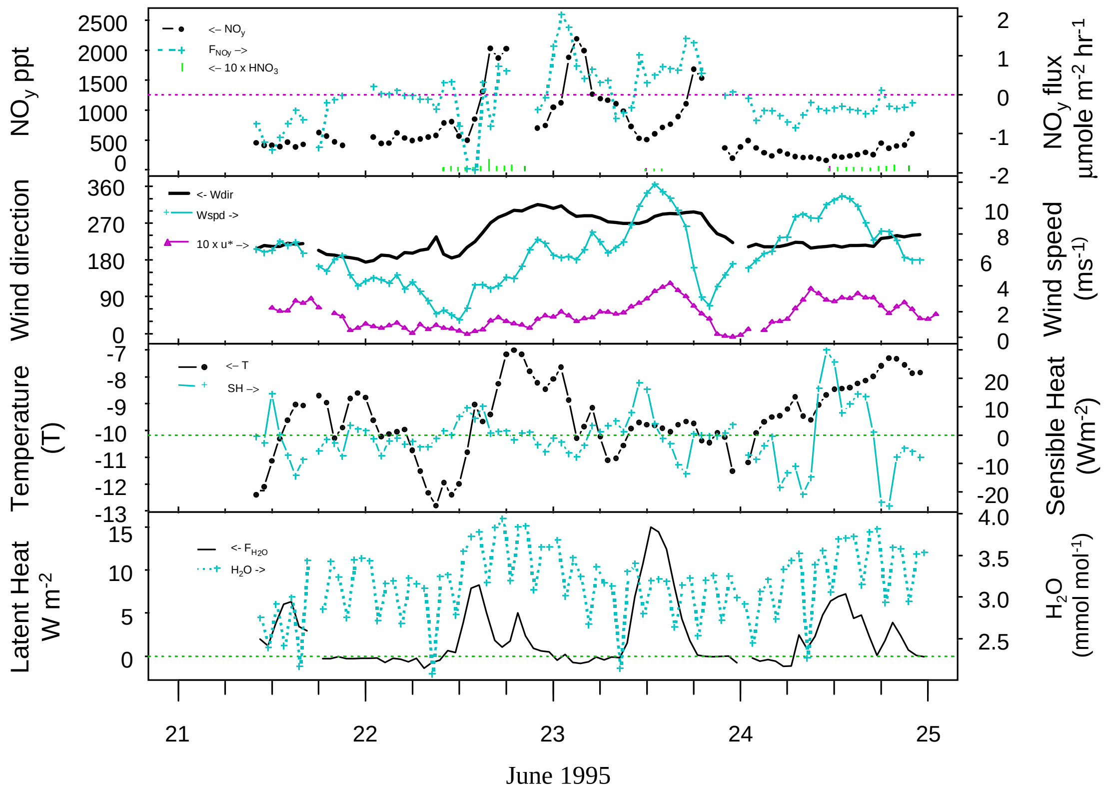

Figure 8 (top) Concentration of NO_y (dots) and NO_y flux (plusses connected by lines) are shown for a four day period beginning on June 21, 1995. Vertical bars indicate the HNO_3 concentration x 10. (middle) Wind direction (solid line), wind speed (plusses connected by dashed line), and u*, the friction velocity, x10 (triangles) are plotted against time of day. (third panel) For the same period sonic temperature (dots), sensible heat flux (plusses), (fourth panel) latent heat flux and H_2O concentration.

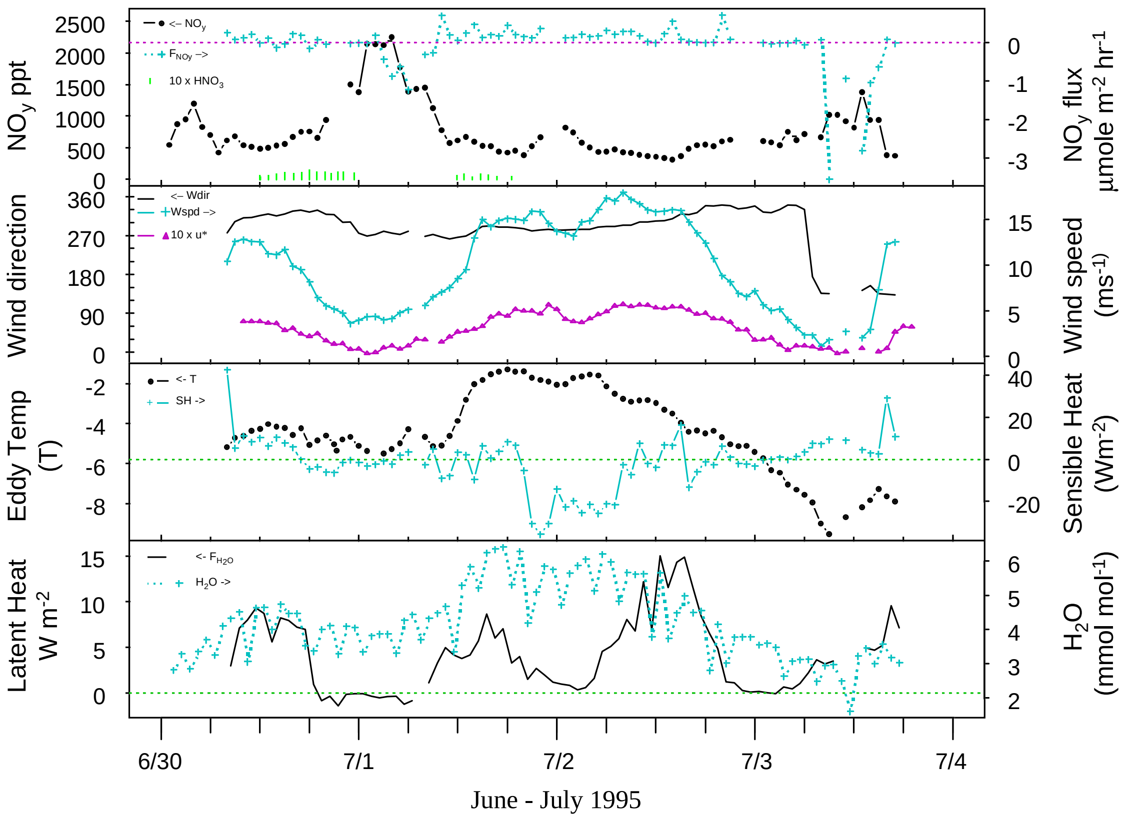

Figure 9. Same as Figure 8, but for four days commencing June 30, 1995.

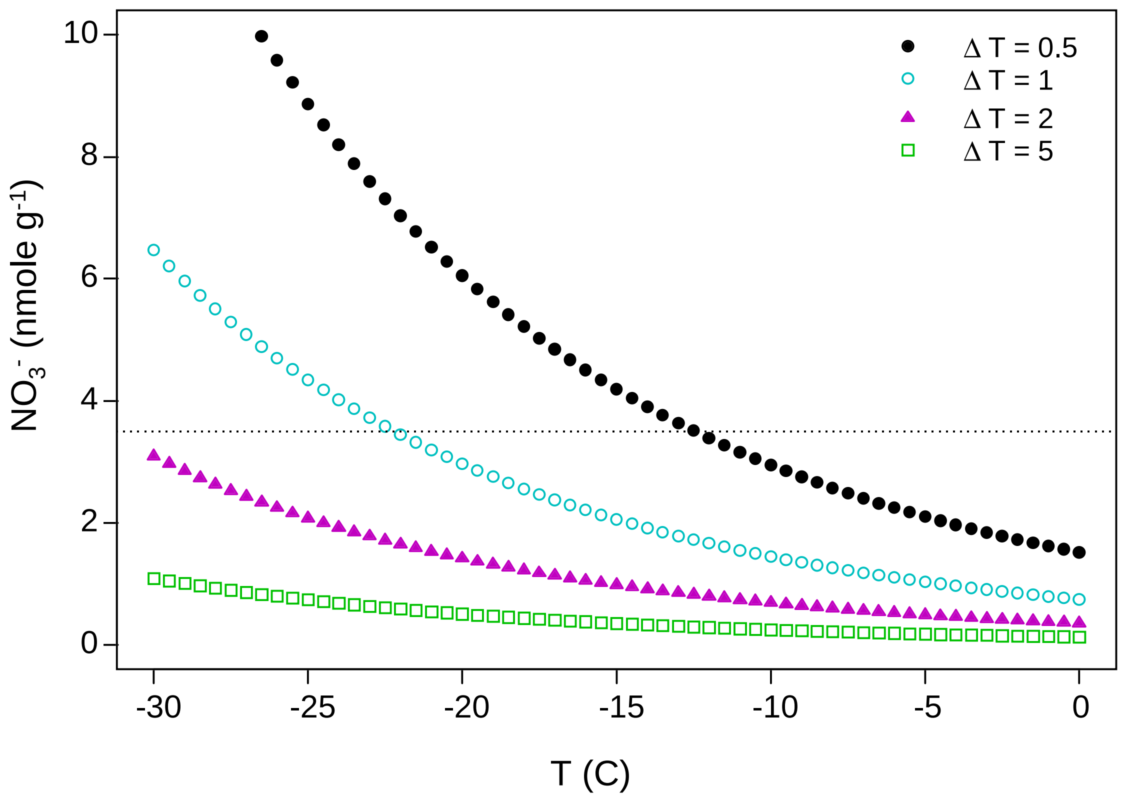

Figure 10**.** The concentration of NO_3^- in increases as temperature decreases because cold air holds less water. Nitrate concentration in snow that formed with an ambient HNO_3 concentration of 0.27 nmol m^{-3} (6ppt) [*Dibb et al.*, 1998] is plotted on the vertical axis against the saturation temperature on the horizontal axis. The symbols indicate different temperature differences associated with snow formation. The ice formed by cooling saturated air 0.5C to -12 C would have a nitrate concentration of 3.5 nmol g^{-1}. The dashed horizontal line shows the mean nitrate concentration in snow [*Dibb et al.*, 1998].].