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Air-snow exchange of HNO3 and NOy at Summit, Greenland

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Abstract. Ice core records of NO_3^- deposition to polar glaciers could provide unrivaled information on past photochemical status and N cycling dynamics of the troposphere, if the ice core records could be inverted to yield concentrations of reactive N oxides in the atmosphere at past times. Limited previous investigations at Summit, Greenland, have suggested that this inversion may be difficult, since the levels of HNO_3 and aerosol-associated NO_3^- over the snow are very low in comparison with those of NO_3^- in the snow. In addition, it appears that some fraction of the NO_3^- in snow may be reemitted to the atmosphere after deposition. Here we report on extensive measurements of HNO_3, including vertical gradients between 1.5 and 7 m above the snow, made during the summers of 1994 and 1995 at Summit. These HNO_3 data are compared with NO_3^- concentrations in surface snow and the first measurements of the concentrations and fluxes of total reactive nitrogen oxides (NO_y) on a polar glacier. Our results confirm that HNO_3 concentrations are quite low (mean 0.5 nmol m^{-3}) during the summer, while NO_3^- is the dominant ion in snow. Daytime peaks in HNO_3 appear to be due at least partly to emissions from the snow, an assertion supported by gradients indicating a surface source for HNO_3 on many days. Observed short-term increases in NO_3^- inventory in the snow can be too large to be readily attributed to deposition of HNO_3, suggesting that deposition of one or more other N oxides must be considered. We found that the apparent fluxes of HNO_3 and NO_y were in opposite directions during about half the intervals when both were measured, with more cases of HNO_3 leaving the snow, against an NO_y flux into the snow, than the reverse. The concentrations of NO_y are generally about 2 orders of magnitude greater than those of HNO_3; hence deposition of only a small, non-HNO_3, fraction of this pool could dominate NO_3^- in snow, if the depositing species converted to NO_3^-, either in the snowpack or upon melting for analysis.

1. Introduction

Deposition of aerosol NO_3^- (p-NO_3^-) plus gaseous HNO_3 (denoted TIN herein for total inorganic nitrate) is generally believed to be the major atmospheric sink for total reactive nitrogen ($NO_y \equiv NO + NO_2 + HNO_3 + p$-$NO_3^- + N_2O_5$ + organic nitrates), [e.g., Logan, 1983; Platt, 1986]. Since NO and NO_2 regulate the production and destruction of O_3 and play central roles in the complicated set of reactions determining the mixing ratios of OH and HO_2 radicals (thereby strongly impacting all of the main oxidants in the troposphere), ice core records of NO_3^- (assumed to reflect deposition of TIN) accumulation could provide critical insight into past photochemical and especially oxidative states of the troposphere. In other words, if we understood how ice core records of NO_3^- accumulation are reflecting reactive N oxide concentrations and cycling in the overlying atmosphere, we would be able to provide powerful constraints for

reconstructing tropospheric chemical composition in past times. However, the relationship between NO_3^- concentration in snow and that of NO_y in the overlying atmosphere is probably not straightforward, nor is it certain that ice cores preserve a simple record of the deposition of TIN at the site [Wolff, 1995].

We have shown previously that during summer NO_3^- is the dominant ion in snow accumulating at Summit, Greenland (the site where the Greenland Ice Sheet Project 2 and Greenland Icecore Project deep drilling programs have recently produced the longest ice core records of NO_3^- accumulation possible for the northern hemisphere), with NO_3^- concentrations exceeding those of $SO_4^=$ (the next most abundant ionic species) by a factor of 5-10 [Dibb et al., 1994]. In air just above the snow we found that HNO_3 represents the dominant fraction of TIN at this site during summer but that the concentrations of TIN in the atmosphere are nearly always less than or equal to those of aerosol-associated sulfate (p-$SO_4^=$)[Dibb et al., 1994]. It is not immediately obvious that TIN should be incorporated into snow more than 10 times more efficiently than p-$SO_4^=$, so there appears to be a problem that could be described in two different ways depending on the point of view; (1) snow NO_3^- is very high in relation to atmospheric TIN, or (2) snow $SO_4^=$ is low in relation to p-

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$SO_4^=$. Comparisons of $SO_4^=$ scavenging ratios (concentration in precipitation/concentration in aerosol) from a range of different sampling programs [*Davidson*, 1989] indicate that Summit is not characterized by inefficient removal of p-$SO_4^=$, so we have interpreted these observations as indicating that there is too little TIN to readily explain the high concentrations of NO_3^- in Summit snow during summer [*Dibb et al.*, 1994].

At least two hypotheses that are not mutually exclusive can explain the combination of very high NO_3^- concentrations in surface snow and low TIN concentrations in the atmosphere above the snow. First, rapid loss of HNO_3 from near-surface air by deposition to the surface could readily account for these observations. Second, N species in addition to TIN could somehow be incorporated into snow and converted to NO_3^-. (Conversion to NO_3^- could occur in the snowpack, or when samples are melted for analysis.) The first of these hypotheses is consistent with the prevailing view that TIN deposition is the only significant sink of tropospheric reactive N oxides and source of NO_3^- in snow. The second directly questions the standard assumption regarding the source of NO_3^- in snow but does not necessarily imply that deposition of additional N species to Greenland snow represents a sink of any importance on the global scale. In this paper we present concurrent measurements of concentrations and gradients of HNO_3, concentrations and fluxes of NO_y, and concentrations and inventories of NO_3^- in surface snow, designed to illuminate the air/snow exchange of reactive nitrogen at Summit in summer.

2. Methods

2.1. Atmospheric Sampling

2.1.1. HNO$_3$. Nitric acid in the gas phase at Summit was measured with the mist chamber sampling technique and subsequent ion chromatographic analysis, as described previously by *Dibb et al.* [1994, 1996]. The mist chamber sampler concentrates soluble gases from the sampled airstream into a small volume of ultrapure water. A Teflon filter, in a custom made holder, is attached directly to the inlet of the sampler to exclude particles. Such a prefilter can cause either positive (due to dissociation of particulate NH_4NO_3 trapped on the filter) or negative (due to reaction with basic particles on the filter) artifacts in the derived HNO_3 concentrations. For the case of Summit during summer we suspect that any bias is likely to be toward higher values, since the levels of sea salt and dust are extremely low [*Bergin et al.*, 1995; *Kuhns*, 1997]. It is not possible to estimate how large any contribution from dissociation of NH_4NO_3 might be, but we assume that such a positive bias is generally very small on the basis of aerosol sampling at Summit that rarely found particulate NO_3^- to be detectable [*Dibb et al.*, 1994; *Bergin et al.*, 1995; *Kuhns*, 1997]. Of course, the dissociation of NH_4NO_3 would yield low values for particulate NO_3^-, so this is a circular argument. However, our main finding is that measured HNO_3 levels are problematically low, and correcting for any positive bias would accentuate this.

During the 1994 season all samples were collected 1.5 m above the snow surface at the base of an 18 m tall sampling tower. A total of 745 samples integrating for intervals of 30-50 min were collected between May 10 and August 10. In 1995, two mist chamber sampling systems were operated in parallel throughout the April 24 to July 8 sampling season.

One of the samplers was kept at 1.5 m above the snow for each of 402 sample collection intervals. The second system was deployed at 7 m above the surface to measure gradients during 230 of the intervals and at the 1.5 m height during all other intervals to establish the level of agreement between samplers when measuring the same air. The mist chamber that remained at 1.5 m (the "stationary mist chamber" herein) was located 3 m away from the sampling tower that supported the other system ("mobile mist chamber") and the Harvard sampling inlets and sonic anemometer described below.

During 1994, mist chamber sampling was conducted around the clock during several 3-4 day long intensive sampling periods and for at least 12 hours on most other days. In 1995 the bulk of the sampling was conducted between 1000 and 2400. Concentrations of HNO_3, plus CH_3COOH and $HCOOH$, were determined in a field laboratory within 12 hours (usually much less) of collection during both seasons. Errors in the measurement of sampled air volumes and in the ion chromatographic determination of concentrations in the stripping solution dominate uncertainty in the calculated atmospheric mixing ratios. We estimate this uncertainty to be of the order of 15-20% for the operating conditions at Summit, increasing to about 50% when the atmospheric mixing ratio of HNO_3 falls below 0.1 nmol m^{-3} STP.

2.1.2. NO$_y$. Details of the Harvard NO_y eddy correlation system and its operation are provided by J. W. Munger et al. (manuscript in preparation, 1998) (JWM, 1998 hereafter). Briefly, reactive N species are converted to NO by catalysis on a heated Au surface with H_2, and the NO is detected by O_3 chemiluminescence [*Bakwin et al.*, 1994; *Munger et al.*, 1996]. These NO_y measurements are made at 4 Hz, so that fluxes can be estimated from the covariance with vertical wind velocity measured with a sonic anemometer. The heated Au converter was mounted at 17.5 m on the tower, adjacent to the sonic anemometer. No inlet was used before the converter, so that line losses of sticky compounds such as HNO_3 were minimized. Detectors, pumps, controllers, and data acquisition systems were all located in a covered trench at the foot of the tower.

This system was operated at Summit for part of the 1994 season, but problems with icing of the NO_y sampling line (due to oxidation of H_2 in the convertor) and local pollution (presumably mainly NO_x from vehicles and a portable generator operated at the GISP2 drill dome within the clean air sector 500 m from the tower for several weeks) resulted in relatively sparse, discontinuous periods of valid data. The limited results from the Harvard instrument in 1994 will not be discussed herein. Additional heaters on the NO_y sampling line, and more favorable wind directions during periods when other experiments needed to operate generators at the dome, resulted in collection of valid data for most of the 1995 season (May 5 through July 19 for the Harvard instrument, beginning after and extending later than the mist chamber sampling).

For comparison with the HNO_3 measurements, all parameters measured by the Harvard instrument were averaged to the longer mist chamber sample integration intervals. Thus we focus only on the subset of NO_y data that corresponds to periods with HNO_3 data. Simultaneous measurements of HNO_3 and NO_y concentrations were made during 230 thirty to fifty minute intervals between May 5 and July 8, 1995. Measurements of HNO_3 at the two heights (gradient mode) were made for slightly more than half these intervals. Occasional loss of data from the anemometer, mainly due to riming of the sensor during overnight ice fog events, and periods when wake effects from the tower invalidated the air motion data reduced the number of common intervals that

included estimates of both HNO₃ gradients and NO_y flux to 64. (See JWM, [1998] for a more complete discussion of the full NO_y concentration and flux data sets)

2.2 Snow Sampling

Surface snow samples were collected for the determination of the concentrations of soluble ions following the rationale and protocols previously described by *Dibb et al.* [1994, 1996] and *Bergin et al.* [1995]. Careful attention to collecting the entire thickness of the uppermost stratigraphic layer, without including any of the underlying layer, allows calculation of the amount of each soluble ion contained in each unit area of the surface snow layer. This quantity is referred to as the inventory, with units of nmol cm^{-2}. During 1994 a major effort to characterize diurnal variations in snow composition was undertaken. This involved sample collection at least 3 times per day throughout the season and every 3 hours during the forementioned intensive sampling periods. In 1995 a single sampling was conducted each day, generally between 0800 and 1000.

In both seasons three adjacent replicate samples were collected during each sampling event. All samples were melted in the high-density polyethylene (HDPE) collection bottles in the field laboratory; aliquots were transferred into HDPE sample tubes that fit our autosampler and immediately refrozen. These aliquots remained frozen during shipment back to our laboratory and during short-term storage in New Hampshire. They were melted in small batches immediately prior to analysis, which occurred within 2 months of the completion of the summer field seasons.

3. Results

3.1 Nitric Acid in the Atmosphere

Concentrations of HNO₃ 1.5 m above the snow at Summit during the summers of 1994 and 1995 reached several nmol m⁻³ STP (1 nmol m^{-3} = 22.4 parts per trillion by volume or pptv) for short periods but were generally well below 1 nmol m^{-3} (Figures 1b and 2b). The spikes are felt to represent long-range transport events, since sampling was interrupted when the tower was clearly under the influence of local pollution sources. In 1994 and 1995 the baseline and frequency of spikes above background were higher in middle to late May than June. The increase in mean and median HNO₃ concentrations when the 2 month period common to both seasons (May 10 to July 8) is compared with the complete sampling seasons indicates that concentrations in middle to late May were also enhanced in relation to earlier in the summer (1995) and July-August (1994) (Table 1). Differences in HNO₃ concentrations between the two seasons were small, with 1994 showing slightly higher levels.

Despite the low ambient concentrations of HNO₃ at Summit in summer the agreement between two mist chamber samplers operating side by side at 1.5 m during 1995 was very good. The mean value of the ratio (HNO₃ measured with stationary mist chamber/HNO₃ measured with mobile mist chamber) (stationary/mobile) was 1.02, with a standard error of the mean of 0.03. This agreement when both samplers were at the same height indicates that values of the stationary/mobile ratio of >1.05 or <0.99 when the mobile sampler was at 7 m are likely to represent real gradients in
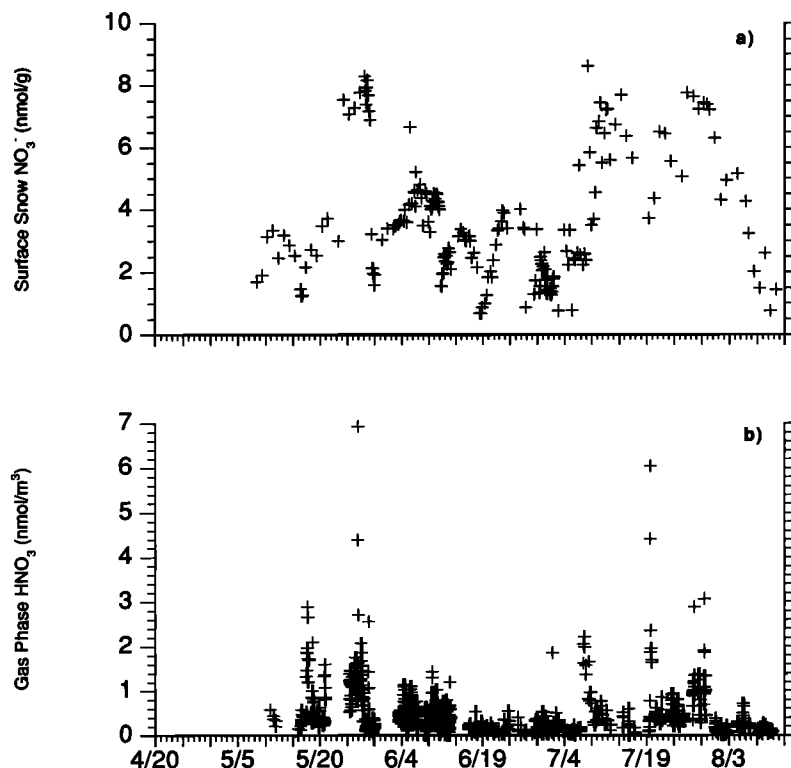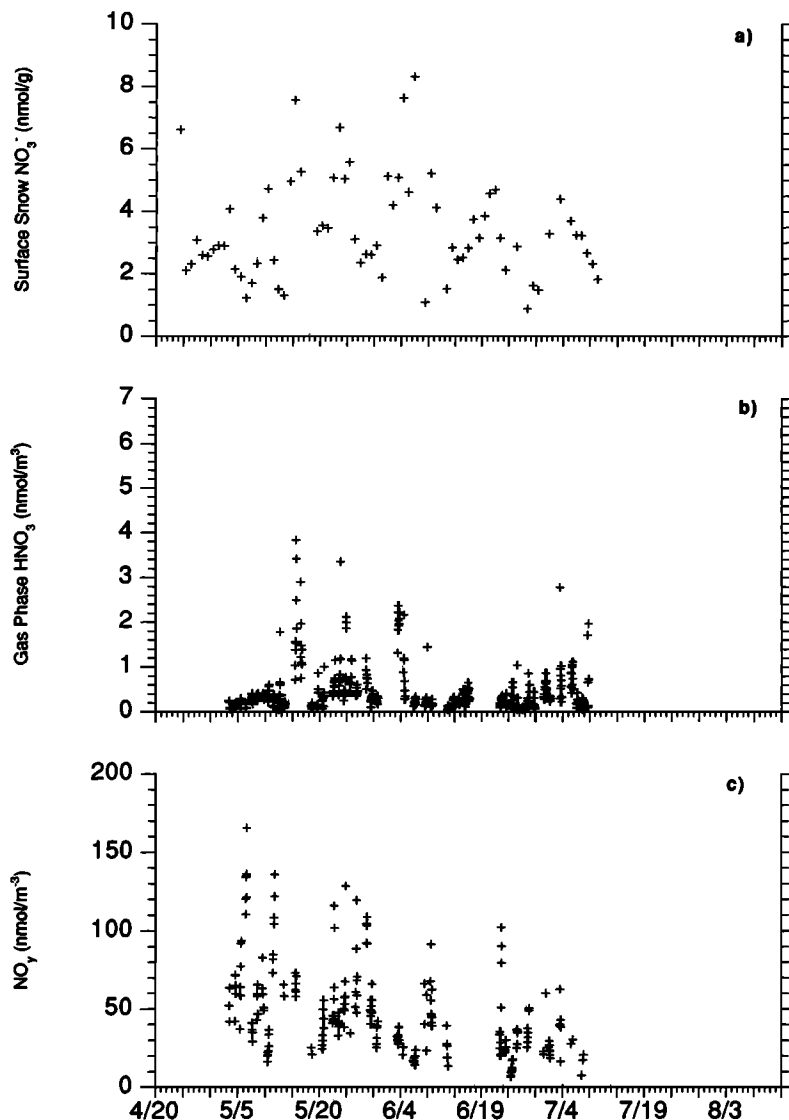

Figure 1. Concentrations of (a) NO₃⁻ in surface snow and (b) HNO₃ 1.5 m above the snow at Summit, Greenland, during summer 1994.

Figure 2. Concentrations of (a) NO_3^- in surface snow, (b) HNO_3 1.5 m above the snow, and (c) NO_y 17.5 m above the snow at Summit, Greenland, during summer 1995.

HNO_3 concentration, with confidence in the implied gradients increasing as the concentration ratio departs farther from 1.02.

3.2   Nitrate in Snow

Nitrate in surface snow during the summer also shows considerable short-term variability (Figures 1a and 2a) that is

not often readily related to variations in HNO_3 just above the snow. Direct comparison between the air and snow concentration time series requires careful filtering of the snow data set to identify periods reflecting newly fallen snow, deposition of rime, drifting of surface snow, and the length of time that a given layer of snow has been exposed at the surface since deposition. A thorough investigation of the causes for variation in concentrations of all soluble ions in surface snow

Table 1. Gas Phase Concentrations at Summit, Greenland

	HNO_3		NO_y		CH_3COOH		$HCOOH$	
	mean±s.d.	median	mean±s.d.	median	mean±s.d.	median	mean±s.d.	median
May 10 to Aug. 10, 1994	0.53±0.61	0.34	n.d.	n.d.	29.8±31.6	20.9	29.0±24.5	22.2
April 24 to July 8, 1995	0.45±0.52	0.28	47.6±29.1*	40.8	22.5±14.4	18.9	33.5±21.3	28.4
May 10 to July 8, 1994	0.55±0.59	0.36	n.d.	n.d.	21.8±13.6	18.6	23.0±12.0	20.4
May 10 to July 8, 1995	0.50±0.56	0.30	42.9±26.1	38.0	23.0±15.1	18.7	33.7±22.3	27.9

Season-long summaries for the 2 years are compared with the 2 month long period of overlap. Concentrations are in nanomoles per cubic meter. Abbreviations are as follows: s.d., standard deviation; n.d., no data.
*NO_y measurements began May 5.

Table 2. Concentrations of Soluble Ions in Surface Snow at Summit, Greenland

	NO3-	Cl-	SO4=	Na+	NH4+	K+	Mg2+	Ca2+
Entire season								
1994 mean	3.63	0.71	0.81	0.13	0.60	0.05	0.05	0.30
Median	3.33	0.64	0.69	0.11	0.51	0.04	0.03	0.18
1995 mean	3.40	0.62	0.78	0.17	0.89	0.07	0.09	0.54
Median	2.90	0.56	0.62	0.15	0.56	0.05	0.08	0.48
May 10 to July 8 overlap								
1994 mean	3.22	0.64	0.83	0.13	0.46	0.04	0.06	0.34
Median	2.99	0.61	0.69	0.12	0.42	0.03	0.04	0.22
1995 mean	3.60	0.66	0.75	0.18	1.00	0.07	0.08	0.46
Median	3.25	0.61	0.59	0.14	0.67	0.05	0.06	0.41

Season-long summaries for the 2 years are compared to the 2 month long period of overlap. Concentrations are in nanomoles per gram.

samples collected in the 1992-1996 seasons is in progress [*Slater et al.*, 1996]. The focus of the present paper will be restricted to NO3- in several intervals where air-snow comparisons are valid.

A key feature of the seasonal overview presented in Table 2 is that NO3- is clearly the dominant soluble ionic species in summer snow. Mean and median concentrations of NO3- exceed those of the next most abundant ions (NH4+ and SO4=) by more than a factor of 3.6. On average, NO3- concentrations were more than twofold higher than the sum of NH4+ and SO4= and exceeded the sum of all other measured ions. It should also be noted that the mean and median concentrations of NO3- differed only of the order of 10% between the two seasons (Table 2).

3.3 Carboxylic Acids in the Atmosphere

Both acetic (CH3COOH) and formic (HCOOH) acids are present in surface-level air at Summit in much higher concentrations than HNO3 (Table 1; also compare Figure 3 with Figures 1b and 2b). Temporal variations of the two carboxylic acids are tightly linked during both background periods and passage of plumes (Figure 3). Correlation coefficients between CH3COOH and HCOOH were 0.81 and 0.92 for all samples collected 1.5 m above the surface in 1994 and 1995, respectively. The sources of carboxylic acids over the Greenland ice sheet are poorly understood, but this important question cannot be addressed herein. For the present purposes it is noteworthy that the concentrations of HCOOH and CH3COOH were comparable between the summers of 1994 and 1995 (Table 1).

3.4 NOy Concentrations

As a result of the problems noted above, NOy data are available only for the 1995 season. The similar concentrations of HNO3, carboxylic acids, and NO3- in snow between the two seasons suggest that 1995 was not an anomalous summer, so we assume the observations discussed below are representative of recent summers. The limited NOy concentration and flux data from 1994 are within the ranges observed in 1995, lending support to this assertion.

During 1995 the concentration of NOy decreased by about a factor of 5 from early May to early July (Figure 2c). Decreasing NOy concentrations through the season drove an increase of the HNO3/NOy ratio from values well below 0.5% in early May to sustained values of about 1% in early July, with occasional short peaks in the range of 7-9 % (Figure 4). Mean and median values for the HNO3/NOy ratio at Summit in summer 1995 were 1.3% and 0.8%, respectively.

Measurements of NOy and the individual species comprising the reactive N family at high northern latitudes are
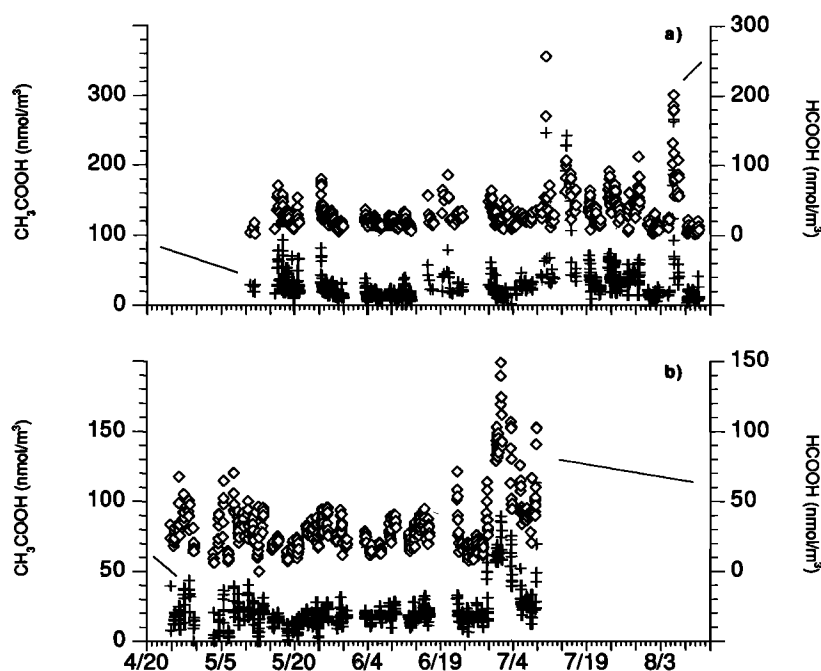
Figure 3. Concentrations of acetic and formic acids 1.5 m above the snow at Summit in the (a) 1994 and (b) 1995 seasons. Note the offset of the two y axes to separate the curves.
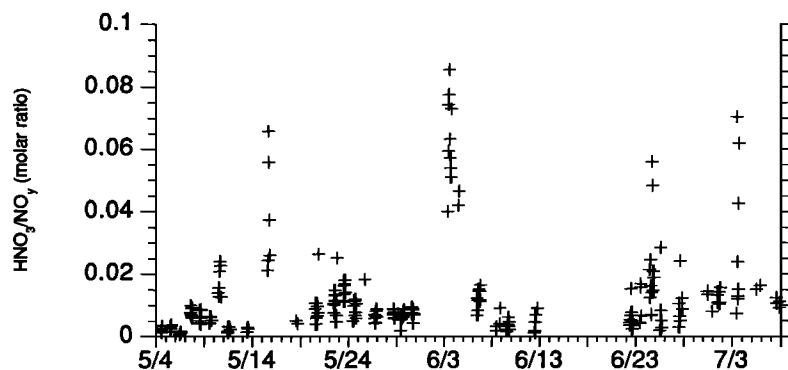
Figure 4. Time series of HNO_3/NO_y at Summit in 1995.

very limited, but a compilation of these results does highlight some important characterstics of N chemistry at high northern latitudes (Table 3). Peroxyacetylnitrate (PAN) represents a major fraction of reactive N except when higher temperatures facilitate its thermal decomposition (e.g., in the boundary layer during summer). Nitric acid concentrations tend to

Table 3. Mean Concentrations of Reactive Nitrogen Species Measured in High Northern Latitudes

	NO_x	HNO_3	PAN	NO_y	Ref. *
Surface-Based Sampling					
Summit					
June-August, 1991		0.6			1
June-July, 1993		0.9			2
May-August, 1994		0.5			3
April-July, 1995		0.5		47.6	3
Alert					
March-April, 1985	1.5	1.6	8.9		4
March-April, 1988		0.4-	8.9-		5
		4.0	22.3		
Barrow					
March, 1989	<3.0			12.0-	6
				33.0	
March-April, 1990	0.4			24.9	7
May-November, 1990	<0.1			3.1	
Airborne Sampling					
ABLE 3A, July-August, 1988					8
0-1.5 km	1.3	3.5	0.9	16.5	
1.5-3 km	1.3	3.2	3.8	21.4	
3-4.5 km	1.2	2.3	8.5	28.6	
4.5-6.1 km	1.3	2.4	12.5	31.2	
ABLE 3B, July-August, 1990					9
North Bay					
0-2 km	2.8	6.2	4.0	16.2	
2-4 km	3.5	7.6	15.2	36.8	
4-6 km	1.9	3.2	13.6	38.4	
Goose Bay					
0-2 km	1.6	5.0	2.5	9.1	
2-4 km	1.6	3.2	9.8	14.9	
4-6 km	2.0	2.0	13.6	23.4	

All concentrations in nanomoles per cubic meter at standard temperature and pressure.

*References: 1, *Silvente* [1993]; 2, *Dibb et al.* [1994]; 3, *this work*; 4, *Bottenheim et al.* [1986]; 5, *Bottenheim et al.* [1993]; 6, *Jaffe et al.* [1991]; 7, *Honrath and Jaffe* [1992]; 8, *Sandholm et al.* [1992]; 9, *Singh et al.* [1994]

decrease with altitude, but the levels at Summit are considerably lower than free tropospheric measurements made near the 3 km elevation of the ice sheet. As a result the ratio HNO_3/NO_y at Summit is also notably low, such that HNO_3 accounts for a smaller fraction of reactive N at Summit than at other investigated locations. When measured, NO_x has been a minor fraction of reactive N at all high northern sites (Table 3), so we assume the same is true at Summit. Low concentrations of NO_x, HNO_3, and $p\text{-}NO_3^-$ and relatively high concentrations of NO_y at Summit suggest that PAN and other organic nitrates may represent a very large fraction (>>90%) of reactive N over the Greenland ice sheet in summer.

We recognize that the NO_y measurements made during the NASA Arctic Boundary Layer Expedition (ABLE) 3 campaigns are now felt to overestimate the concentrations of reactive N oxides due to conversion of some nonreactive N species (J. Bradshaw et al., An update on reactive odd-nitrogen measurements made during NASA's GTE programs, submitted to *Journal of Geophysical Research*, 1997) and that laboratory studies by the Harvard group indicate that their systems can also suffer from such positive artifacts *[Kliner et al., 1997]*. JWM, [1998] discuss the likely severity of such artifacts in the Summit NO_y data set and conclude that 150 pptv (6.7 nmol m⁻³ STP) is an upper limit estimate of the possible offset between NO_y measurements and the concentration of reactive N oxides at Summit. The conclusions we will draw in this paper would not be negated even if the NO_y data overestimated reactive N concentrations by several hundred parts per trillion by volume throughout the season.

4. Discussion

It has long been supposed that deposition of HNO_3, by the processes of scavenging in snow and ice fog falling onto the surface and direct dry deposition to the snow surface, accounts for the majority of NO_3^- measured in polar snow and ice, with only minor contributions from $p\text{-}NO_3^-$ [e.g., *Legrand and Delmas*, 1986, 1988; *Steffensen*, 1988; *Laj et al.*, 1993; *Wolff*, 1995]. This hypothesis was supported by recent aerosol sampling campaigns at Summit during the summer, which generally found that concentrations of $p\text{-}NO_3^-$ were extremely low while concentration of other ions, particularly $SO_4^=$, were much higher, yet NO_3^- was overwhelmingly dominant among soluble ions in the snow [e.g., *Bergin et al.*, 1995]. Determination of HNO_3 concentrations at Summit by several techniques has confirmed that HNO_3 is usually the dominant fraction of TIN (TIN = $HNO_3 + p\text{-}NO_3^-$) during

summer, but the concentrations of TIN are quite low (Table 3). *Dibb et al.* [1994] pointed out that the ratio TIN/p-SO₄= in the atmosphere just above the snow at Summit is generally ≤1, while the NO₃⁻/SO₄= ratio in fresh summer snow often exceeds 10.

An intuitively attractive explanation for the simultaneous observation of relatively high NO₃⁻ concentrations in surface snow and low concentrations of TIN in air just above the snow would be depletion of HNO₃ in near-surface air through dry deposition to the surface. However, at least two lines of evidence suggest caution before embracing this hypothesis. First, the maximum NO₃⁻ concentrations in buried summer snow layers sampled in pits at Summit almost never exceed, and only rarely even reach, 5 nmol g⁻¹ [e.g., *Mayewski et al.*, 1990b; *Whitlow et al.*, 1992], yet surface snow NO₃⁻ concentrations during summer near 10 nmol g⁻¹ or higher are common (Figures 1 and 2) [*Slater et al.*, 1996]. The apparent loss of NO₃⁻ from summer snow within the first year after deposition suggests that snow may be a source of TIN at times rather than a continuous strong sink [*Dibb et al.*, 1994]. Second, *Bergin et al.* [1995] found that deposition of snow and ice fog could account for 99% of the NO₃⁻ that accumulated in surface snow during summer 1993, leaving little room for a large contribution from dry deposition of HNO₃. Further, modeling of the deposition of soluble species by ice fog suggested that PAN and related species could be making contributions to the flux of NO₃⁻ in fog that rivaled the incorporation of HNO₃ [*Bergin et al.*, 1996]. While *Bergin et al.* [1996] admit that their calculations are illustrative rather than quantitative, largely because of the complete lack of any direct measurements of PAN at Summit, they point out that similar processes in clouds forming snow could make PAN an even larger player in the snow NO₃⁻ budget.

4.1 The 1994 Season

The extensive sampling conducted in 1994 provided more insights into the magnitude and interrelationships of short-term variations in the concentrations of HNO₃ and NO₃⁻ in air and snow, respectively, at Summit. On many days there was a marked diurnal variation in HNO₃, with peaks most common in early afternoon and minima during the late evening and early morning hours. Binning all data by time of day shows a subdued, but statistically significant, midafternoon peak (Figure 5a). The nighttime minima may reflect depletion of HNO₃ beneath the strong, surface-based inversion that characterizes the Summit site during summer when winds are light [*Dibb et al.*, 1992; *Bergin et al.*, 1996]. Recovery of HNO₃ concentrations during daytime could reflect downward mixing of free tropospheric air that had not lost HNO₃, as the inversion lifts and weakens. However, the concentrations of carboxylic acids just above the snow show a similar diurnal pattern, with the potentially critical difference that their peak concentrations, and initial increase from nighttime minima, occur several hours before those of HNO₃ (Figure 5b). Such an offset in timing would not be expected if downward mixing of air from aloft was the primary process responsible for daytime peaks of all three gases.

We have previously shown that the carboxylic acids can be rapidly lost from surface snow at Summit and have suggested that degassing of these acids could be an important proximate source for air just above the snow [*Dibb et al.*, 1994]. Thus it appears that we must consider degassing of carboxylic acids from the snow as a potential contributor to their daytime peak concentrations and cannot immediately rule out a similar surface source of HNO₃ on timescales of hours.
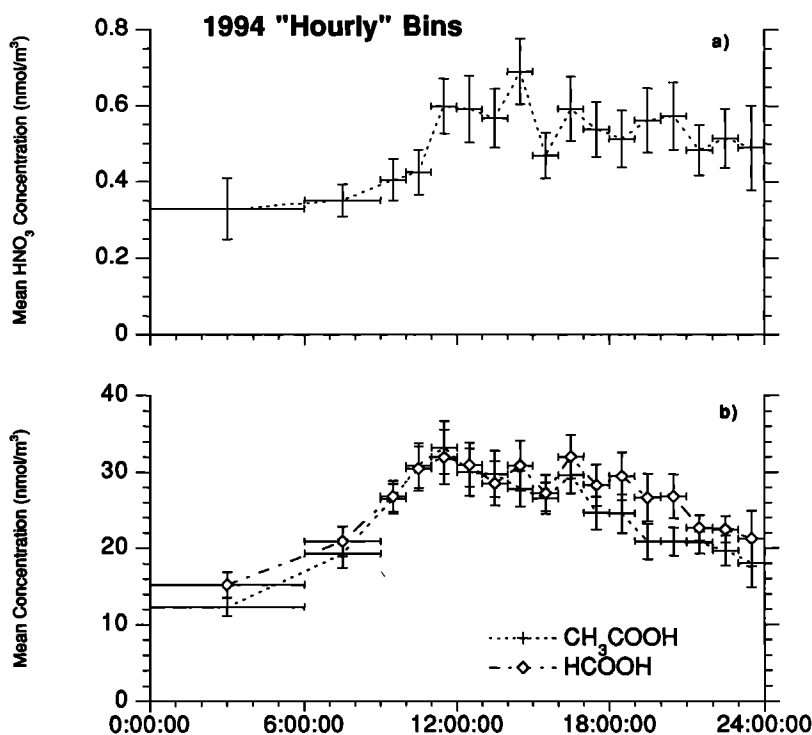
Figure 5. Mean concentrations of (a) HNO₃ and (b) carboxylic acids binned by time of day during the 1995 season. The bin widths were chosen to give approximately equal numbers of data points in each bin. The vertical error bars represent the standard error of the means, and the horizontal bars represent bin width.
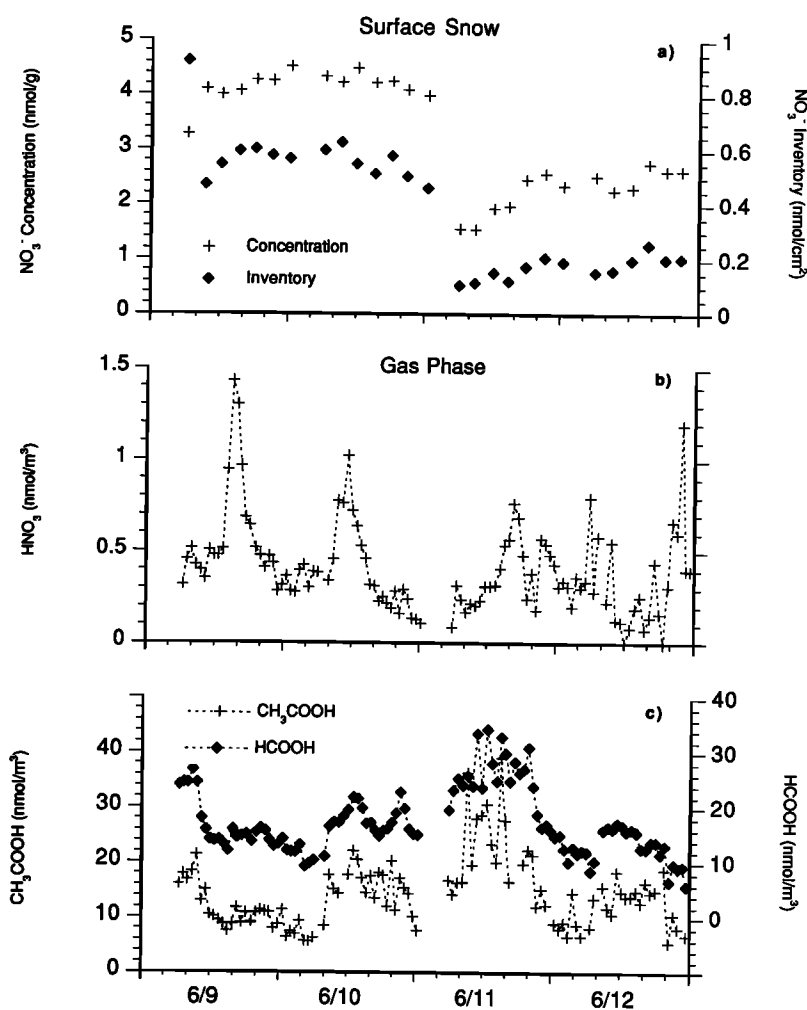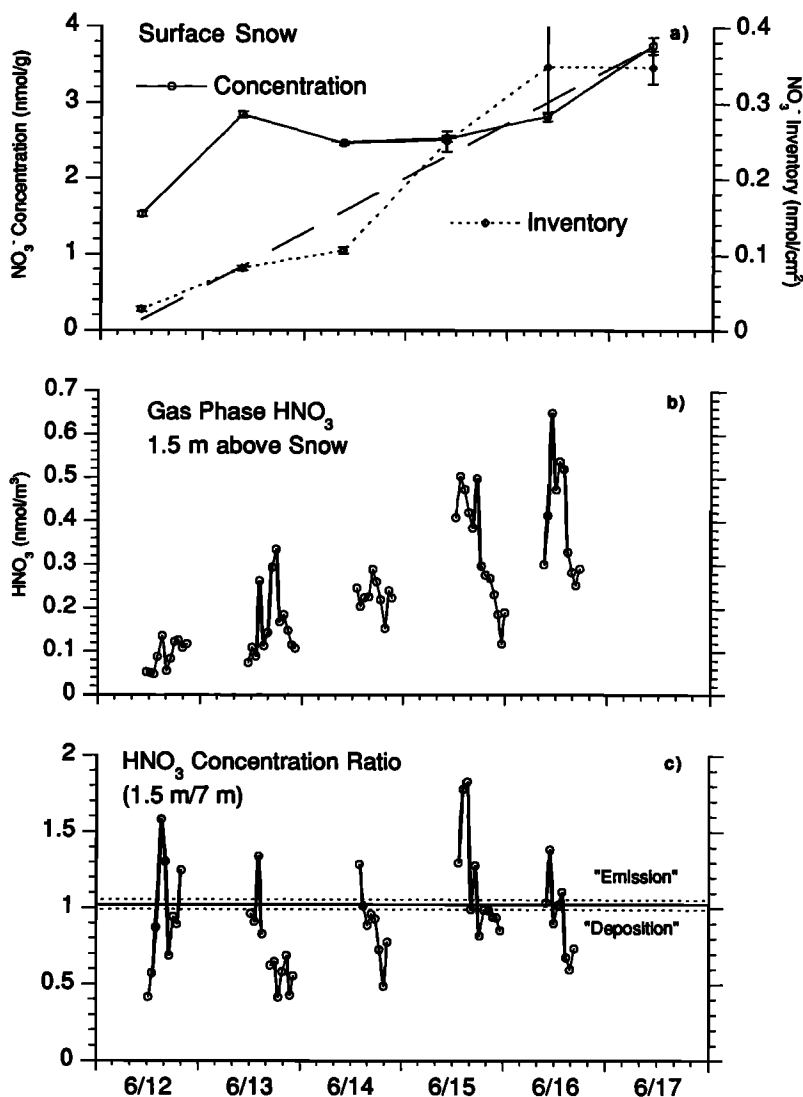
Figure 6. A 1994 case study of relationships between (a) NO_3^- in surface snow, (b) HNO_3 and (c) carboxylic acids in the air above the snow. A snowfall event late June 10 into early June 11 created a new layer of surface snow with lower concentrations and inventories of NO_3^-. Note the offset of the two y axes in Figure 6c.

Simultaneous sampling of air and snow was expected to provide some constraints on the magnitude of HNO_3 flux into or out of the snow. During the first 2 days of an intensive sampling period June 9-12, very clear daytime HNO_3 peaks with amplitudes of about 1 nmol m⁻³ were observed (Figure 6b). If we assume that all of this HNO_3 came out of, then redeposited to, the surface layer of snow, there should be changes in the NO_3^- inventory of the surface layer that are antiphase with those in the gas phase, yet little or no change was seen in NO_3^- inventory during this period (Figure 6a). However, a 1 nmol m⁻³ increase of HNO_3 in a well-mixed 100 m column below the inversion would require a loss of only 0.01 nmol NO_3^- cm⁻² from the snow over a period of a few hours. Inventory changes this small are nearly impossible to detect given the inherent small-scale spatial variability of surface snow [*Dibb*, 1996], as reflected in the standard deviation of adjacent replicates in Figure 6a. A more realistic scenario might relax the assumption of a well-mixed column (allowing for decreasing concentrations higher above the presumed surface source), which would require an even weaker source, such that losses could never be identified by repeated sampling of the surface snow layer. We conclude that even high-resolution (every 3 hours) sampling of surface snow does not help to discriminate between the snow and downward

mixing of air aloft as the source of daytime HNO_3 increases at Summit.

4.2   The 1995 Season

Another case study examining air-snow relations during a 6 day period in 1995 when the same layer of snow remained at the surface (no new snow, ice fog, or drifting of the surface layer) is presented in Figure 7. In this case the NO_3^- inventory was measured only once each day, but it steadily increased at an average rate of 0.07 nmol cm⁻² d⁻¹ (0.029 μmol m⁻² h⁻¹) (Figure 7a). The concentrations of HNO_3 1.5 m above the snow were relatively low during this period (compare Figure 7b with Figure 2b) but would be consistent with dry deposition velocities (V_d, flux/atmospheric concentration) of HNO_3 in the range of 2-8 cm s⁻¹. This range of V_d is already on the high side of previous estimates for HNO_3 deposition to various surfaces [e.g., *Cadle et al.*, 1985; *Huebert and Robert*, 1985; *Walcek et al.*, 1986] but may be underestimated since we have assumed that the flux was downward at a constant rate throughout the period (see below). Untenably high estimates of V_d for HNO_3 would provide indirect evidence for the deposition of additional reactive N species to the snow.

Figure 7. A 1995 case study of relationships between (a) NO_3^- in surface snow, (b) HNO_3 in air above the snow, and (c) HNO_3 gradients above the snow (see text). The same layer of snow remained at the surface throughout the period. The dashed line in Figure 7a is a linear least squares fit to the increase of inventory over time (0.07 nmol cm^{-2} d^{-1}).

Estimates for V_d at Summit can be obtained independently from the flux measurements made with the Harvard system [JWM, 1998]. We estimate the aerodynamic resistance (R_a) from measured wind speed and momentum flux and use this to approximate dry deposition velocities ($V_d = 1/R$, where $R = R_a + R_b + R_c$, R_b = boundary layer resistance and R_c = surface resistance). By neglecting the resistances other than aerodynamic we calculate an upper limit for V_d. Unfortunately, few data are available from the sonic anemometer during the mid June period of interest. However, throughout the season such upper limit estimates for V_d at Summit were generally below 1 cm s⁻¹ and never exceeded 1.5 cm s⁻¹. Furthermore, *Johansson and Granat* [1986] suggested that the other resistances can not be neglected when considering deposition of HNO_3 to cold snow, since they found that R_c controlled V_d at 0.4 cm s⁻¹ for temperatures as warm as -8°C. Aerodynamic resistance became the controlling factor only when the snow approached the freezing point. It

thus appears difficult to attribute the increasing NO_3^- inventory in snow (Figure 7a) to deposition of HNO_3.

Clear midday peaks in HNO_3 on June 13, 15, and 16 (Figure 7b) could reflect an upward flux during part of these days (see discussion of the 1994 case study above). We measured HNO_3 vertical gradients by operating mist chamber samplers at 1.5 and 7 m above the snow surface for much of 1995, including the mid-June interval in Figure 7. For part of each day the concentrations of HNO_3 were significantly higher at 1.5 than 7 m (Figure 7c), consistent with an upward flux. Intervals of apparent downward flux were also seen each day. It thus appears that HNO_3 can be rapidly exchanged from air-to-snow and snow-to-air. We acknowledge that these gradient measurements do not provide insight into the magnitude of HNO_3 flux into or out of the snow, but we are confident that they do reflect the direction of exchange. Accounting for the facts that HNO_3 deposition was not continuous for the entire 6 days, and that there were periods of loss, would require V_d
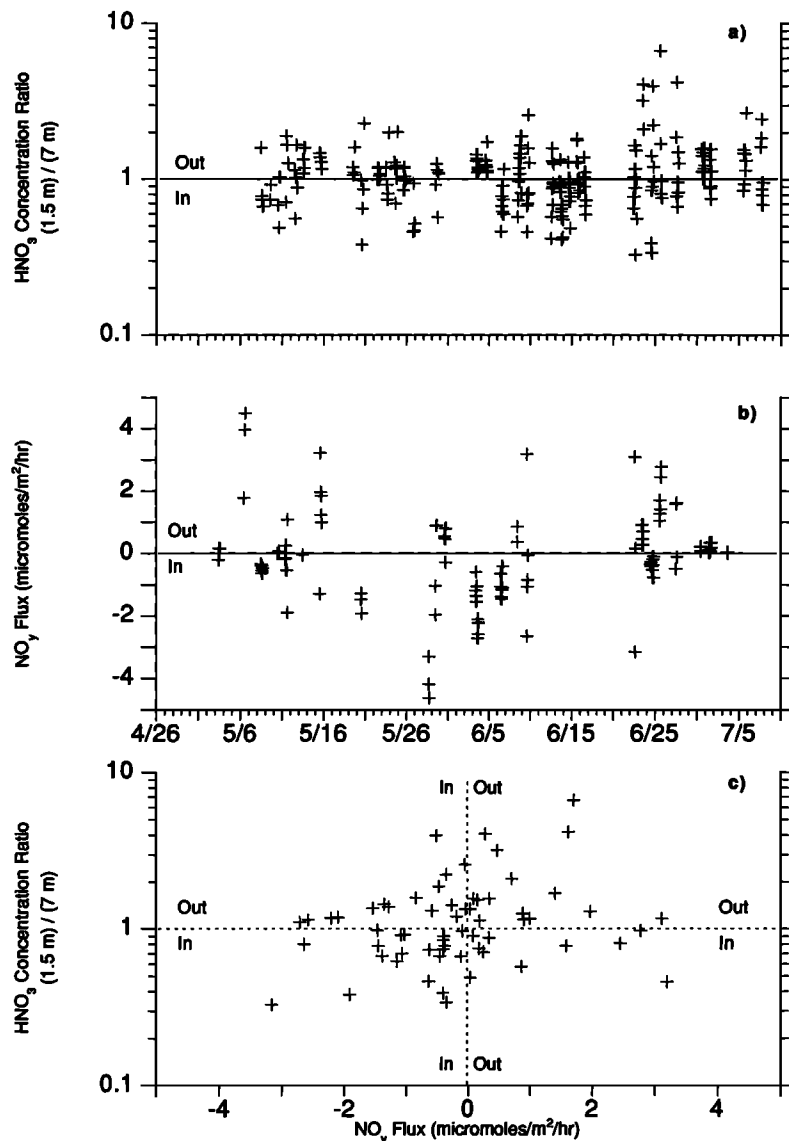
Figure 8. Time series of (a) HNO₃ gradients and (b) NOᵧ fluxes during the 1995 season with (c) a scatterplot for all intervals when both parameters were measured at the same time.

during periods of deposition to be quite a bit larger than the 2-8 cm s⁻¹ range estimated above, and we have seen that these values are already problematically high. Nitric acid cannot be the only reactive N species contributing to the increasing NO₃⁻ inventory in the snow.

Unfortunately, instrument problems resulted in no NOᵧ concentration or flux measurements during this short period of interest. However, apparent deposition of NOᵧ at rates greatly in excess of the 0.03 μmol m⁻² h⁻¹ required by the increase in snow NO₃⁻ inventory June 12-16 was quite common throughout the 1995 season (Figure 8b). In fact, downward fluxes of NOᵧ in excess of 1 μmol m⁻² h⁻¹ were seen to persist through the entire 8-10 hour sampling period on several days. If these fluxes were entirely due to deposition of HNO₃, they would have swamped the NO₃⁻ inventories measured in surface snow (Figures 6 and 7). Similarly, fluxes of NOᵧ out of the snow at comparable rates were also common (Figure 8b) and should have been reflected in very large decreases in snow NO₃⁻ inventory if HNO₃ was the reactive N species "causing"

the measured NOᵧ flux. This mismatch between the magnitudes of NOᵧ flux and NO₃⁻ inventory suggests that air-snow exchange of HNO₃ alone cannot explain the NOᵧ fluxes.

Of course, sparseness of the NOᵧ flux record and other influences on the surface snow composition (i.e., fog, drifting, and new snow) limit the number of direct comparisons possible, thereby weakening any arguments based on failure to observe expected changes in the snow NO₃⁻ inventory. Additional support for the hypothesis that downward fluxes of NOᵧ must include more than deposition of HNO₃ is provided by calculating V_d for HNO₃ under the assumption that the standard hypothesis is correct (i.e., HNO₃ is the only depositing reactive N species, such that $V_d = NO_y$ flux/HNO₃ concentration). For the 60 intervals when NOᵧ flux was into the snow (of 112 intervals with measured NOᵧ flux (Figure 8b)), the mean V_d was 96 cm s⁻¹, with extremes reaching nearly 600 cm s⁻¹. Earlier we noted that values near 10 cm s⁻¹ would be above upper limits suggested by several previous studies of HNO₃ deposition to various surfaces and

that estimates of aerodynamic resistance at Summit suggest an upper limit below 1.5 cm s⁻¹. Finally, and conclusively, we point out that during the 64 intervals when HNO_3 gradients and NO_y flux were both measured, the direction of exchange (air-to-snow versus snow-to-air) were opposite slightly more than 40% of the time (Figure 8c). It is especially significant that during 16 of these intervals, HNO_3 was leaving the snow against significant downward fluxes of NO_y.

It is clear that HNO_3 is not the only, nor even the dominant, reactive N species contributing to NO_y flux into and out of the snow at Summit. Information available at this time does not allow us to identify the reactive N species that are supporting these fluxes, but PAN and other organic nitrates would seem to be the most likely candidates, since previous studies have shown PAN to be a major fraction of the reactive N oxide pool in the Arctic atmosphere (Table 3).

It is also not yet possible to determine whether there is any net exchange of NO_y between air and snow during the summer, since this would be the small difference between two very large numbers and we cannot estimate the integrated flux in either direction with any confidence from our discontinuous record. It may be that we are simply observing NO_y streaming into the pore spaces of the firn at some periods and then leaving shortly (a few hours) thereafter without interacting with the ice crystals. Such a scenario would be consistent with our observation that changes in NO_3^- inventory in the snow are orders of magnitude smaller than would be expected from the NO_y fluxes. However, the fact that NO_3^- inventories were observed to increase at rates that are too high to be accounted for by deposition of HNO_3 suggests that some small fraction of one or more of the other reactive N species fluxing into the snow is retained (and converted to a form that yields NO_3^- in aqueous solution) when most of it fluxes back out. We suspect that PAN may be sparingly soluble in the quasi-liquid layer *Conklin and Bales* [1993] suggest should be present on polar firn grains, especially if this layer is acidic [Holdren et al., 1984]. Hydrolysis of PAN would then yield NO_3^- and CH_3COO^-, which would partition between the bulk ice, surface layer and the air filling pore spaces in the firn. It is also possible that N_2O_5 (if present at significant concentrations in the air entering the firn at Summit in summer) could be hydrolyzed to HNO_3 in the postulated surface film on the grains. *Ravishankara and Hanson* [1996] indicate that this heterogeneous reaction, known to be a significant pathway removing NO_x from the polar stratosphere, is accelerated when the condensed phase is supercooled liquid rather than ice.

Such sources of NO_3^- could easily exceed the available supply of HNO_3 and p-NO_3^- in near-surface air (recall that HNO_3 rarely accounted for as much as 1% of measured NO_y (Figure 4)). This hypothesis would probably be difficult to test by seeking antiphase variations between NO_y concentrations and snow NO_3^- inventories, since, as we noted in our discussion of the daytime HNO_3 peaks, changes in NO_3^- inventory as large as 0.05 nmol cm⁻² would only require changes of a few nmol m⁻³ in NO_y concentration (well below 10% of surface level concentrations). However, this approach might be fruitful if continuous, high-resolution measurements were made of the individual reactive N species that are actually interacting with the snow, since differences of several nanomole per cubic meter would represent a larger fraction of ambient concentrations and hence should be easier to identify and quantify.

5. Conclusions

Our investigations of air-snow exchange of reactive N at Summit during summer has not yet opened the way to reconstruction of reactive N in past times from NO_3^- records in polar ice core. We have shown that very low concentrations of HNO_3 just above the snow surface cannot be attributed simply to efficient dry deposition of HNO_3 to the snow; rather we found rapid alternation between deposition and emission of HNO_3. Fluxes of HNO_3 out of the snow during the daytime contribute to observed early afternoon peaks in HNO_3 in the air just above the snow, but the mass exchange is too small to have detectable effects on the NO_3^- inventory in the surface layer of snow over the timescales of a few hours examined in this study. However, degassing of HNO_3 from surface and near-surface snow over longer timescales could account for the failure of the snowpack to preserve the very high NO_3^- concentrations measured in summer snow.

Concentrations and fluxes of NO_y were several orders of magnitude larger than those of HNO_3. Relatively large fluxes of NO_y into and out of the snow seemed to be in rough balance (small net exchange), a finding that could be taken to mean that N species other than TIN can be ignored in interpretations of NO_3^- records in snow and ice. However, our NO_y flux record is too discontinuous for us to assert that the large fluxes into the snow are in fact balanced by those out of the snow. We presented one case study where the NO_3^- inventory in snow increased too much over a period of 6 days to be ascribed to the very low concentrations of HNO_3 in the atmosphere at the time and suspect this situation may occur often. In such cases the possibility that other N species are depositing to snow, and being partially converted to NO_3^-, must be considered a strong one. The magnitudes of the NO_y pool and short-term upward and downward NO_y fluxes immediately above the snow surface are so large in relation to the NO_3^- inventory in surface snow that retention of as little as 1% of the reactive nitrogen oxides fluxing through the snow could be a large term in the snow N budget, rivaling or exceeding the contribution by HNO_3.

Further progress on these issues will require improved understanding of the N species contributing to the NO_y signal. At Summit it seems that PAN and other organic nitrates must be the dominant components of reactive N, but these compounds are not believed to be readily deposited to the surface of snow [Bottenheim et al., 1986]. On the other hand, N_2O_5 might readily deposit to snow, but its photolysis in the continuous light of polar summer would be expected to keep concentrations quite low. To date, no measurements of NO, NO_2, N_2O_5, PAN, or any other organic nitrates have been made at Summit. Ideally, fluxes of these reactive nitrogen species should be measured along with simultaneous measurements of HNO_3 flux and NO_3^- concentrations in snow. At a minimum, detailed concentration time series of all these species for several weeks during summer would provide major insights into atmospheric N chemistry over the Greenland ice sheet and how well NO_3^- in snow is reflecting it. Such measurements are also likely to indicate which of the other reactive N species appears to be depositing to, or degassing from, the snow. Once candidate species have been identified, controlled laboratory and field experiments will be required to determine the environmental parameters that control the partitioning of reactive nitrogen between snow and air. Until

improved understanding of these relationships is obtained, the potential wealth of the unprecedented NO_3^- records from the deep Summit ice cores will remain largely untapped.

References

Bakwin, P. W., et al., Reactive nitrogen oxides and ozone above a taiga woodland, *J. Geophys. Res.*, 99, 1927-1936, 1994.

Bergin, M. H., J.-L. Jaffrezo, C. I. Davidson, J. E. Dibb, S. N. Pandis, R. Hillamo, W. Maenhaut, H. D. Kuhns, and T. Makela, The contributions of snow, fog and dry deposition to the summer fluxes of major anions and cations at Summit, Greenland, *J. Geophys. Res.*, 100, 16,275-16,288, 1995.

Bergin, M. H., S. N. Pandis, C. I. Davidson, J.-L. Jaffrezo, J. E. Dibb, A. G. Russell, and H. D. Kuhns, Modeling of the processing and removal of trace gas and aerosol species by Arctic radiation fogs and comparisons with measurements, *J. Geophys. Res.*, 101, 14,465-14,478, 1996.

Bottenheim, J. W., A. G. Gallant, and K. A. Brice, Measurements of NO_y species and O_3 at 82° N latitude, *Geophys. Res. Lett.*, 13, 113-116, 1986.

Bottenheim, J. W., L. A. Barrie, and E. Atlas, The partitioning of nitrogen oxides in the lower Arctic troposphere during spring 1988, *J. Atmos. Chem.*, 17, 15-27, 1993.

Cadle, S. H., J. M. Dasch, and P. A. Mulawa, Atmospheric concentrations and the deposition velocity to snow of nitric acid, sulfur dioxide, and various particulate species, *Atmos. Environ.*, 19, 1819-1827, 1985.

Conklin, M. H., and R. C. Bales, SO_2 uptake on ice sphere: Liquid nature of the ice-air interface, *J. Geophys. Res.*, 98, 16,851-16,855, 1993.

Davidson, C. I., Mechanisms of wet and dry deposition of atmospheric contaminants to snow surfaces, in *The Environmental Record in Glaciers and Ice Sheets*, edited by H. Oeschger and C. Langway, pp. 29-51, John Wiley, New York, 1989.

Dibb, J. E., J.-L. Jaffrezo, and M. Legrand, Initial findings of recent investigations of air-snow relationships in the Summit region of Greenland, *J. Atmos. Chem.*, 14, 167-180, 1992.

Dibb, J. E., R. W. Talbot, and M. H. Bergin, Soluble acidic species in air and snow at Summit, Greenland, *Geophys. Res. Lett.*, 21, 1627-1630, 1994.

Dibb, J. E., R. W. Talbot, S. I. Whitlow, M. C. Shipham, J. Winterle, J. McConnell, and R. Bales, Biomass burning signatures in the atmosphere and snow at Summit, Greenland: An event on 5 August 1994, *Atmos. Environ.*, 30, 553-561, 1996.

Holdren, M. W., C. W. Spicer, and J. M. Hales, Peroxyacetyl nitrate solubility and decomposition rate in acidic water, *Atmos. Environ.*, 18, 1171-1173, 1984.

Honrath, R. E., and D. A. Jaffe, The seasonal cycle of nitrogen oxides in the Arctic troposphere at Barrow, Alaska, *J. Geophys. Res.*, 97, 20,615-20,630, 1992.

Huebert, B. J., and C. H. Robert, The dry deposition of nitric acid to grass, *J. Geophys. Res.*, 90, 2085-2090, 1985.

Jaffe, D. A., R. E. Honrath, J. A. Herring, S.-M. Li, and J. D. Kahl, Measurements of nitrogen oxides at Barrow, Alaska during spring: Evidence for regional and northern hemispheric sources of pollution, *J. Geophys. Res.*, 96, 7395-7405, 1991.

Johansson, C., and L. Granat, An experimental study of the dry deposition of gaseous nitric acid to snow, *Atmos. Environ.*, 20, 1165-1170, 1986.

Klemm, O., R. W. Talbot, D. R. Fitsjarrald, K. I. Klemm, and B. L. Lefer, Low to middle tropospheric profiles and biosphere/troposphere fluxes of acidic gases in the summertime Canadian taiga, *J. Geophys. Res.*, 99, 1687-1698, 1994.

Kliner, D. A. V., B. C. Daube, J. D. Burley, and S. C. Wofsy, Laboratory investigation of the catalytic technique for measurement of atmospheric NO_y, *J. Geophys. Res.*, 102, 10,759-10,776, 1997.

Kuhns, H. D., Variability of air and snow chemical species concentrations in central Greenland, Ph.D. thesis, 87 pp., Carnegie Mellon Univ. Pittsburgh, Pa, 1997.

Laj, P., J. M. Palais, J. E. Gardner, and H. Sigurdsson, Modified HNO_3 seasonality in volcanic layers of a polar ice core: Snow-pack effect or photochemical perturbation, *J. Atmos. Chem.*, 16, 219-230, 1993.

Lefer, B. L., et al., Enhancement of acidic gases in biomass-burning impacted air masses over Canada, *J. Geophys. Res.*, 99, 1721-1737, 1994.

Legrand, M. R., and R. J. Delmas, Relative contributions of tropospheric and stratospheric sources to nitrate in Antarctic snow, *Tellus, Ser. B*, 38, 236-249, 1986.

Legrand, M. R., and R. J. Delmas, Soluble impurities in four Antarctic ice cores over the last 30,000 years, *Ann. Glaciol.*, 10, 116-120, 1988.

Logan, J. A., Nitrogen oxides in the troposphere: Global and regional budgets, *J. Geophys. Res.*, 88, 10,785-10,807, 1983.

Mayewski, P. A., M. J. Spencer, M. S. Twickler, and S. Whitlow, A glaciochemical survey of the Summit region, Greenland, *Ann. Glaciol.*, 14, 186-190, 1990.

Munger, J. W., S. C. Wofsy, P. S. Bakwin, S.-M. Fan, M. L. Goulden, B. C. Daube, A. H. Goldsteing, K. E. Moore, and D. R. Fitzjarrald, Atmospheric deposition of reactive nitrogen oxides and ozone in a temperate deciduous forest and a subarctic woodland, 1, Measurements and mechanisms, *J. Geophys. Res.*, 101, 12,639-12,657, 1996.

Platt, U., The origin of nitrous and nitric acid in the atmosphere, in *Chemistry of Multiphase Atmospheric Systems*, edited by W. Jaeschke, Springer-Verlag, New York, 1986.

Ravishankara, A. R., and D. R. Hanson, Differences in the reactivity of Type I polar stratospheric clouds depending on their phase, *J. Geophys. Res.*, 101, 3885-3890, 1996.

Sandholm, S. T., et al., Summertime tropospheric observations related to N_xO_y distributions and partitioning over Alaska: Arctic Boundary Layer Expedition 3A, *J. Geophys. Res.*, 97, 16,481-16,509, 1992.

Silvente, E., Contribution à l'étude de la fonction de transfert air neige en régions polaires, these de doctorat, Univ. Joseph Fourier-Grenoble I, Grenoble, France, 1993.

Singh, H. B., et al., Summertime distribution of PAN and other reactive nitrogen species in the northern high latitude of eastern Canada, *J. Geophys. Res.*, 99, 1821-1835, 1994.

Slater, J. F., J. E. Dibb, and I. I. Pittalwala, Interannual variability in the soluble ionic composition of summer snow at Summit, Greenland, (abstract) *Eos Trans. AGU*, 77(46), Fall Meet. Suppl., F428, 1996.

Steffensen, J. P., Analysis of the seasonal variation in dust, Cl^-, NO_3^- and SO_4^{2-} in two central Greenland firn cores, *Ann. Glaciol.*, 10, 171-177, 1988.

Walcek, C. J., R. A. Brost, J. S. Chang, and M. L. Wesely, SO_2, sulfate, and HNO_3 deposition velocities computed using regional land use and meteorological data, *Atmos. Environ.*, 20, 949-964, 1986.

Whitlow, S. I., P. A. Mayewski and J. E. Dibb, A comparison of major chemical species seasonal concentration and accumulation at South Pole and Summit, Greenland, *Atmos. Environ., Part A*, 26, 2045-2054, 1992.

Wolff, E. W., Nitrate in polar ice, in *Ice Core Studies of Global Biogeochemical Cycles, NATO ASI Ser.*, vol. 30, edited by R. J. Delmas, pp. 195-224, Springer-Verlag, New York, N.Y., 1995.

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