NICE – Abstract

Measurements of atmospheric and snow mixing ratios of nitrates and nitrites and their fluxes above the snow surface were made during two intensive campaigns during spring time 2001 at Ny-Ålesund, Svalbard as part of the EU project "The **NI**trogen **C**ycle and **E**ffects on the oxidation of atmospheric trace species at high latitudes" (NICE). During the spring of 2001 the Kongsfjord next to our sampling site remained unseasonably unfrozen.

Recent findings of NO_x and HONO production in snow interstitial air showed that photochemical production of NO_x in or above snow surfaces is sufficient to alter the composition of the overlying atmosphere. The possible effects of this reaction cycle are fivefold. First, the reactivation of nitrate extends the influence of NO_x emissions, both spatially and temporally, as NO_x may be re-emitted after it has been oxidized to HNO_3 and deposited. Second, the resulting emissions of NO_x may alter the net rate of tropospheric O_3 production in some region. Third, if some of the released NO_x is exported, nitrate deposition to snowpacks may be less than previously believed. Fourth, in remote regions, the production of OH radicals within the snowpack (directly produced from NO_3^- photolysis) or from photolysis of released HONO may surpass OH production from O_3 photolysis. Finally, the reactivation of NO_3^- is apparently coupled with oxidation of snowpack organic matter, apparently resulting in release of oxidized compounds such as aldehydes.

At Ny-Ålesund of the measured nitrogen species only HNO_3 showed a significant flux above the snow surface, a mean deposition of -8.7 nmol $h^{-1}m^{-2}$ was observed in late April / early May 2001. During snowfall periods dry deposition of HNO_3 may contribute up to 10% of the N budget in the snow; however, the main source for N is wet deposition in falling snow. Other measured nitrogen species showed no significant fluxes which may be in part due to the measurement uncertainties and long integration times of the used denuder technique, and atmospheric turbulence and mixing. These HNO_3 fluxes may be due to the reaction of HNO_3 with NaCl, or may be simply uptake of HNO_3 by ice, which is alkaline because of the sea salt in our marine environment.

The surface snow at Ny-Ålesund showed very complex stratigraphy; the NO_3^- mixing ratio in snow varied between 65 and 520 ng g^{-1}, the total NO_3^- content of the snowpack was on the order of 2700 ng cm^{-2}. In comparison the atmospheric boundary layer column showed a NO_3^- content of only 8 ng cm^{-2}. The limited exchange, however, between the snow and the atmosphere was attributed to low mobility of NO_3^- in the observed snow. NO_3^- was mostly connected to Ca^{2+} in alkaline snow, and thus immobile.

HNO_3 is not a major contributor to the NO_3^- signal in snow. This is not surprising, as NO_3^- arrives to the snow surface as $Ca(NO_3)_2$, and is immobile. Thus exchanges are limited.

Also photolysis will also have only limited effects, since reaction products may be immobilized inside a solid. This is unlike Alert, Nunavut or Summit, Greenland, where NO_3^- was in the absence of NaCl, (in acidic ice) in more mobile forms. Exchanges were easier, and air-snow exchanges of NO_3^- followed different mechanisms. In particular, photolysis products could be released more easily.

The results of NICE, together with earlier results of the Polar Sunrise Experiment ALERT 2000 and ISCAT in Antarctica show that the reactivation of NO_x from snow nitrate is an important source of NO_x over snow surfaces. We were to confirm suggested reaction mechanisms for these exchanges. These results are very important in formulating possible scenarios in more polluted mid latitude snow-covered European environments (e.g. Alpine regions).

NICE, as well as similar efforts in this fairly new scientific discipline (PSE, Summit, ISCAT), investigated a new fundamental chemical mechanism; a property of snow interstitial air, that was formerly not recognized. With the data collected to date in the various experiments, it would be premature to assess possible European or even global pollution scenarios. Focused modeling efforts incorporating these newly characterized fundamental mechanisms are necessary at least on a European scale.

The NItrogen Cycle and Effects on the oxidation of atmospheric trace species at high latitudes (NICE)

H. J. Beine, A. Ianniello, I. Allegrini
C.N.R. – IIA, Roma, Italy

F. Dominé, L. Legagneux
CNRS – LGGE, Grenoble, France

M. Nardino, T. Georgiadis
C.N.R. – ISAC, Bologna, Italy.

K. Teinilä, V.-M. Kerminen, R. Hillamo
FMI – Air Quality Research, Helsinki, Finland

S. Nyeki
Lab. Atmospheric Chemistry, Paul Scherrer Institute, Villigen PSI, Switzerland

G. Coulson, I. Colbeck
Institute for Environmental Research, Univ. Essex, Colchester, Essex, England

K. Eleftheriadis
Environ. Radioactivity Lab., NCSR Demokritos, Athens, Greece

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Introduction

During 1998 two discoveries of the interaction of NOx with snow surfaces/ aerosols have revolutionized the current understanding of Nitrogen chemistry. Participating in an attempt to characterize the incorporation of nitrogen species in glacier ice *Honrath et al.* [1999] discovered that NOx was emitted into snow interstitial air at Summit, Greenland. This release was photochemically driven. At Alert, Nunavut (formerly North West Territories), Canada, *Ridley et al.* [1999] found during the Polar Sunrise Experiment 1998 NOx mixing ratios ≤ 5 pmol/mol during the dark season. After polar sunrise NOx was significantly enhanced, and displayed a diurnal cycle with magnitudes of 8 - 35 pmol/mol. They concluded that a sunlight-dependent surface source must be dependent for this cycle.

Interactions of the atmosphere with surfaces - snow or aerosol surfaces – were virtually unknown until recently. *Li* [1994] was the first to suggest that HNO_3 was re-activated upon aerosols to produce HONO, which was observed at mixing ratios of ≥20 pmol/mol in the presence of sunlight at Alert. He found apparent near-equilibrium between aerosol NO_2^- and HONO. The necessity for an *in-situ* source of HONO was addressed by *Beine and Allegrini* [1998]; at typical spring noontime photolysis rates of $J_{HONO} \approx 1.8\times10^{-4}$ s^{-1} HONO has a lifetime of only 9 min. At Summit *Dibb et al.* [1998] found that NOy was being absorbed by snow surfaces. The most abundant soluble anion in snow was found to be NO_3^- [*Dibb and Jaffrezo*, 1997].

Together with the discoveries of NOx being produced in surfaces, these separate measurements of chemical trace species in the gas and aerosol phase point to a chemical mechanism that involves some liquid or solid phase transfer in turning HNO_3 or aerosol NO_3^- into NOx and HONO. HONO in the sunlit atmosphere is subsequently photolyzed to produce NOx and OH radicals.

These recent findings of NO_x and HONO production in snow interstitial air show that photochemical production of NO_x in or above snow surfaces is sufficient to alter the composition of the overlying atmosphere [*Honrath et al.*, 1999; *Ridley et al.*, 2000]. The current understanding of this process points towards the absorption of some NO_y species by snow surfaces, the presence and subsequent reduction of NO_3^- in a surface phase followed by photochemical release of NO, NO_2, and HONO [*Honrath et al.*, 2000; *Dubowski et al.*, 2001]. The release of NO_x and HONO was quantified during springtime at Alert 2000 on the order of 40 nmol m^{-2} h^{-1} each [*Beine et al.*, 2002a, *Zhou et al.*, 2001].

The current understanding of the reaction mechanism can be summarized in the following cartoon:

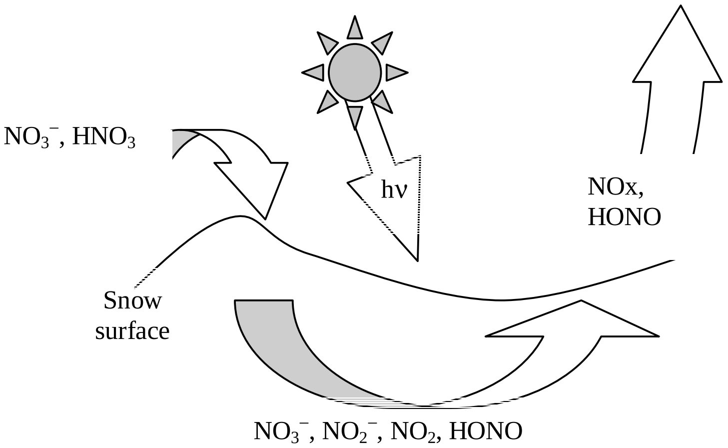


Figure 1. Cartoon of the reaction mechanism of NO_x / HONO production and atmosphere – snow interactions

The possible effects of this reaction cycle are fivefold. First, the reactivation of nitrate extends the influence of NO_x emissions, both spatially and temporally, as NO_x may be re-emitted after it has been oxidized to HNO_3 and deposited. Second, the resulting emissions of NO_x may alter the net rate of tropospheric O_3 production in some region. Third, if some of the released NO_x is exported, nitrate deposition to snowpacks may be less than previously believed. Fourth, in remote regions, the production of OH radicals within the snowpack (directly produced from NO_3^- photolysis) or from photolysis of released HONO may surpass OH production from O_3 photolysis. Finally, the reactivation of NO_3^- is apparently coupled with oxidation of snowpack organic matter, apparently resulting in release of oxidized compounds such as aldehydes.

While the release of active N has been investigated and quantified, little is known about the sources of snow nitrate and other interactions of this NO_3^- with the snow layer and the atmosphere. At Alert 2000 it was found that the predominant source for snow NO_3^- was wet deposition during snowfall [*Ianniello et al.*, 2002]. Snow experiments have been performed at Alert, showing that the mobility and thus availability for photochemical reactions of snow NO_3^- depend on snow temperature and snow type and its acidity [*Beine et al.*, 2002b].

We use the Arctic environment as a clean 'reactor'; in most midlatitude locations close-by anthropogenic contamination makes the sampling and analysis of aerosol chemistry extremely difficult and confusing. The results of our Arctic work, however, are applicable to at least all of Europe's snow covered regions.

HNO_3 was generally understood to be the final sink of N-species in the atmosphere. It is deposited via dry and wet mechanisms to underlying surfaces. In flux models this is a sink term that needs to be considered with respect to acid rain or arctic haze, i.e. HNO_3 as an aggressive contaminant. The role of HNO_3 in boundary layer photochemistry was thought to be of little importance. This view changes quickly. Nitric acid is apparently recycled into the atmosphere. Through the production of NOx and HONO it can enter a catalytic cycle, in which O_3 can be produced – in quantities yet unknown.

In addition to possible aerosol driven reactions, which convert NOy to HONO, heterogeneous formation of nitrous acid on snow and ice by NO_2 may also be postulated. Such reaction was clearly identified as possible source of nitrous acid in urban environments. The reaction provides both HONO and HNO_3. The former is released into the atmosphere, while the latter remains in the surface. This reaction may also occur on snow and ice surfaces where HONO may be retained and desorbed into the atmosphere.

This process is of central importance for Europe, as > 50% of the land surface north of 20ºN is snow covered during winter. Additionally, it is likely that similar processes also occur in the upper troposphere.Some controversy exists about the possibility that these reactions occur in cirrus clouds. Recent laboratory studies indicate that HNO_3 efficiently adsorbs on ice surfaces [*Abbatt, 1997*; *Zondlo et al.*, 1997], and recent field measurements suggest that such HNO_3 uptake does occur in the troposphere [*Weinheimer et al.*, 1998]. If our hypothesis that NO_3^- absorption on aerosols/snow crystals leads to photochemical NOx release is correct, similar NOx release from NO_3^- is expected on cirrus cloud particles. This process may provide an effective mechanism for the release of NOx from upper tropospheric HNO_3. This could explain the inability of current photochemical models to adequately simulate NOx/HNO_3 ratios in the upper troposphere [*Liu et al.*, 1992; *Chatfield*, 1994; *Davis et al.*, 1996; *Jacob et al.*, 1996; *Wang et al.*, 1998; *Lawrence and Crutzen*, 1998; *Hauglustaine et al.*, 1998]. NOx release from adsorbed HNO_3 would effectively increase the lifetime of NOx, both on the ground and in the upper troposphere. It is therefore essential that the chemistry for these observations be better understood, as such release would increase O_3 production rates and would need to be incorporated into global atmospheric chemistry models to accurately estimate anthropogenic impacts on tropospheric ozone.

Scientific Questions and Objectives of NICE

NICE was proposed and funded for the following specific **scientific questions** in order to explore and understand this process:

- Which species are involved in the conversion of NO_3^- to NOx?

- Is HNO_3 a direct source of HONO and NOx?
- Which NOy specie supplies NO_3^- to the aerosol / snow surface?
  Does HNO_3 / particulate NO_3^- on aerosols provide the major source of nitrogen in the remote regions of the Northern hemisphere?
  Are there any mechanisms that can bring PAN into the liquid or aerosol phase to account for the observed NO_3^-?

- What is the reactive medium?

- Where do these reactions occur? Is it on ‘free’ aerosols ‘everywhere’, or is a snow surface necessary?

- How are aerosol properties changed with their composition during the chemical conversions.

- How do aerosol properties and composition (size distribution, ionic distribution, water content, acidity, etc.) influence the process of conversion?

- What is the contribution from HONO to the OH radical concentration?

- What is the effect of this mechanism on the transport of NOy species and global O_3 production?

The **scientific objectives** of this work are:

- To resolve on which active medium in which phase these reactions occur.

- The work by *Honrath et al.* [1999] and *Ridley et al.* [1998] shows unambiguously that NOx is produced in or close to surfaces. Through combined aerosol and chemistry gradient measurements above a snow surface, reaching into the snow surface, we will identify the location and character of the reactive medium.

- To identify the role of aerosol composition and properties on the re-activation of nitrate in snow-covered tropospheric surfaces.

- Through gradient field measurements of physical and chemical aerosol properties we will quantify the change of properties above surfaces. Thus we will identify how the re-activation occurs mechanistically.

- To identify the source terms of NOx and HONO above snow surfaces.

- Through gradient gas-phase measurements of nitric acid and nitrous acid, together with photolytic rate constants, we will identify the source terms and quantify the budget of nitric acid, nitrous acid, and NOx.

Experiment

The Fieldsite at Ny-Ålesund

The fieldsite was chosen ca. 2 km up-fjord of the *Ny-Ålesund International Arctic Research and Monitoring Facility* (78º54'N, 11º53'E) at Svalbard:

The sampling location was at sea level, ca. 20 m next to the unseasonably unfrozen fjord. The local wind field is documented for this specific location through SODAR measurements; during springtime the majority of the local flow arrived from easterly directions [*Beine et al.*, 2001a]. Thus local pollution was naturally kept to a minimum. In order to keep the upwind snow surface as pristine as possible, a large restricted region was established around the measurement site.

Measurements were made during two intensive campaigns; a 'dark intensive', Feb. 21 – March 8 (DOY 52 – 67), when the sun was below the horizon, and a 'light intensive' during 24 h sunlight from April 24 – May 19 (DOY 114 – 139).

We used a wind-vane and anemometer connected to shut off valves to discontinue sampling when the air flow arrived from a 120º sector around the town of Ny-Ålesund or under certain low-flow conditions. This shut-off system protected the denuder/filter measurements, as well as the impactor, and some of the physical aerosol measurements.

Denuder/Filter measurements

Measurements of atmospheric nitrogen species were made with the C.N.R. – IIA denuder/filter system (and ion chromatographic (IC) analysis) at two sampling altitudes above the snow surface: 2 cm (L) and 180 cm (H). 12 h and 24 h long samples were collected at both heights, and analyses were subsequently carried out usually within 12 h at the Italian research station "Base Artica CNR Dirigibile Italia" in Ny-Ålesund.

The annular denuder/filter pack sampling method and the analytical procedures were described in detail [*Possanzini et al.*, 1983; *Allegrini et al.*, 1987, *Beine et al.*, 2001b]. A brief account is given here for sampling of NO_3^- and NO_2^- species; other species such as HCl, HBr, SO_4^{2-} etc. were measured simultaneously with this method. Nitrous acid (HONO) and nitric acid (HNO_3) in the gas phase were sampled with a combination of sodium fluoride (NaF), sodium carbonate (Na_2CO_3) and alkaline carbon coated denuders (two of each). This denuder line is followed by a cyclone (2.5 μm aerodynamic diameter cut point) and a filter pack for the collection of atmospheric aerosols, such as nitrate (NO_3^-) and nitrite (NO_2^-) in the coarse and fine fractions, respectively. The filter pack included a 47-mm Teflon filter (Gelman Teflon, 1-μm pore size) for the collection of particles, a Nylon filter (Nylosorb Gelman, 47 mm, 1-μm pore size) and two Na_2CO_3-glycerol impregnated paper filters (Whatman 41) for the collection of evaporated species from the front Teflon filter. The samples were analyzed by ion chromatography (Dionex IC mod. DX120) using Dionex AS12 column for anions and Dionex CS12 column for cations.

For chromatographic analyses, control samples, consisting of 100 ng/ml calibration solution of anions (Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, $Ca2^+$), were analyzed every seven samples in order to re-calibrate the ion chromatograph. The variation in the concentration of the control samples was generally of the order 0.5-1 %. Calibration solutions are prepared every week from 1000 mg/l standard solutions (MERCK).

Field blanks were measured every 3 days, these blank values are shown in Table 1. To optimize blank values and detection limits of the analytical method and the sampling technique, special care was taken in the field and in the laboratory to the quality control/assurance procedures [*Perrino et al.*, 1990; *Ianniello et al.*, 1999]. The detection limits (L.O.D.) of the analytical technique (Table 1) are calculated as the analyte signal which is three times the standard deviation (3σ) of a very low concentration measurement. The L.O.D. for denuder measurements of various particulate and gaseous species (Table 1) are evaluated on the basis of the L.O.D. of the analytical method and of the standard deviations of field blanks. The precision is given here as relative standard deviation (RSD). In the case where field blanks were below the analytical detection limit, the detection limits of species were calculated as the 3σ variation of IC baseline noise. Data below the 3σ detection limits are shown with their numerical value.

Table 1. Measurement of nitrite and nitrate with denuder/filters and IC analysis (a)

Species	Field blank (b) measured by IC during the dark intensive (c) [pmol mol^{-1}]	Field blank (b) measured by IC during the light intensive (d) [pmol mol^{-1}]	Precision [%] (e)	3σ detection limit [pmol mol^{-1}]
HONO (gas)	0.18	0.19	1.5	0.55
NO_2^- (particle)			1.2	0.57
HNO_3 (gas)	0.34	0.39	2.57	0.27
NO_3^- (particle)			3.0	1.05

(a) These values were calculated using the procedures shown in detail by *Perrino et al.* [2001] and *Beine et al.*, [2001b]. The field blank has the highest contribution to the overall blank. The laboratory and glass blanks are up to ca. 75% and 40% of the field blanks for NO_2^- and NO_3^-, respectively.
(b) 24-h samples
(c) 12-h samples
(d) at ca. 10 pmol mol^{-1}

Snow sampling

Snow was sampled regularly for ionic analyses during the spring campaign, with an emphasis on surface snow. The snow stratigraphy was very complex in the spring because of frequent snowfalls that deposited small amounts of snow, and of extensive erosion, remobilization, and (more rarely) accumulation by wind. Moreover, surface melting was also observed twice in the spring, which added further heterogeneity to the snowpack. Because of these features, it was often difficult to identify and monitor a given snow layer. To overcome this difficulty, the snowpack was very carefully observed twice a day or more near the atmospheric sampling site. Layer identification was made on the spot, by observing the crystals with a magnifying glass. When in doubt, crystals were sampled and observed with a photomacrographic equipment in the cold room (maintained at –20°C) of the Japanese research station 'Rabben' near the airport at Ny-Ålesund, ca. 5 km down-fjord from the sampling site. For ionic analyses, triplicate samples were taken using polyethylene gloves, with the usual precautions to avoid sample contamination, and were analyzed within 12 hrs using the IC system described above.

3D Meteorology and Derivation of Fluxes

To derive the characteristics of the surface-atmosphere interaction and to determine the turbulent fluxes we used at Ny-Ålesund a sonic anemometer (Metek USAT 1). Additionally, profile measurements of air temperature and wind speed were performed, to be able to compute fluxes of chemical species. The instrument was set up ca. 5 m distance from the denuder measurements. The anemometric data were stored in a PC after electronic processing (two axis rotations and the computation of 15 min. averages of the main physical quantities and standard deviations along with the momentum and sensible heat flux determination).

Results

Nitrogen species

Figure 2 shows the measurement results for gaseous HONO and HNO_3 and total particulate NO_2^- and NO_3^- as box-and-whisker plots at both inlets for both intensives. The median values for HONO, NO_2^-, and HNO_3 were below 5 pmol mol^{-1} during the dark intensive at both inlets, NO_3^- showed a median mixing ratio of 21 and 22 pmol mol^{-1} at the lower and upper inlet, respectively. HONO and NO_2^- increased only slightly until the light intensive, their mixing ratios were still below 5 pmol mol^{-1} at either inlet. NO_3^- increased by about 1/3 to median values of 28 and 30 pmol mol^{-1}. The most pronounced change between the two intensives can be observed in HNO_3; the median mixing ratio increased 5 – 6 fold to 11 and 18 pmol mol^{-1} at the lower and upper inlet, respectively. As seen in Figure 2, the scatter of each measured species did not vary significantly with either sampling location or time.

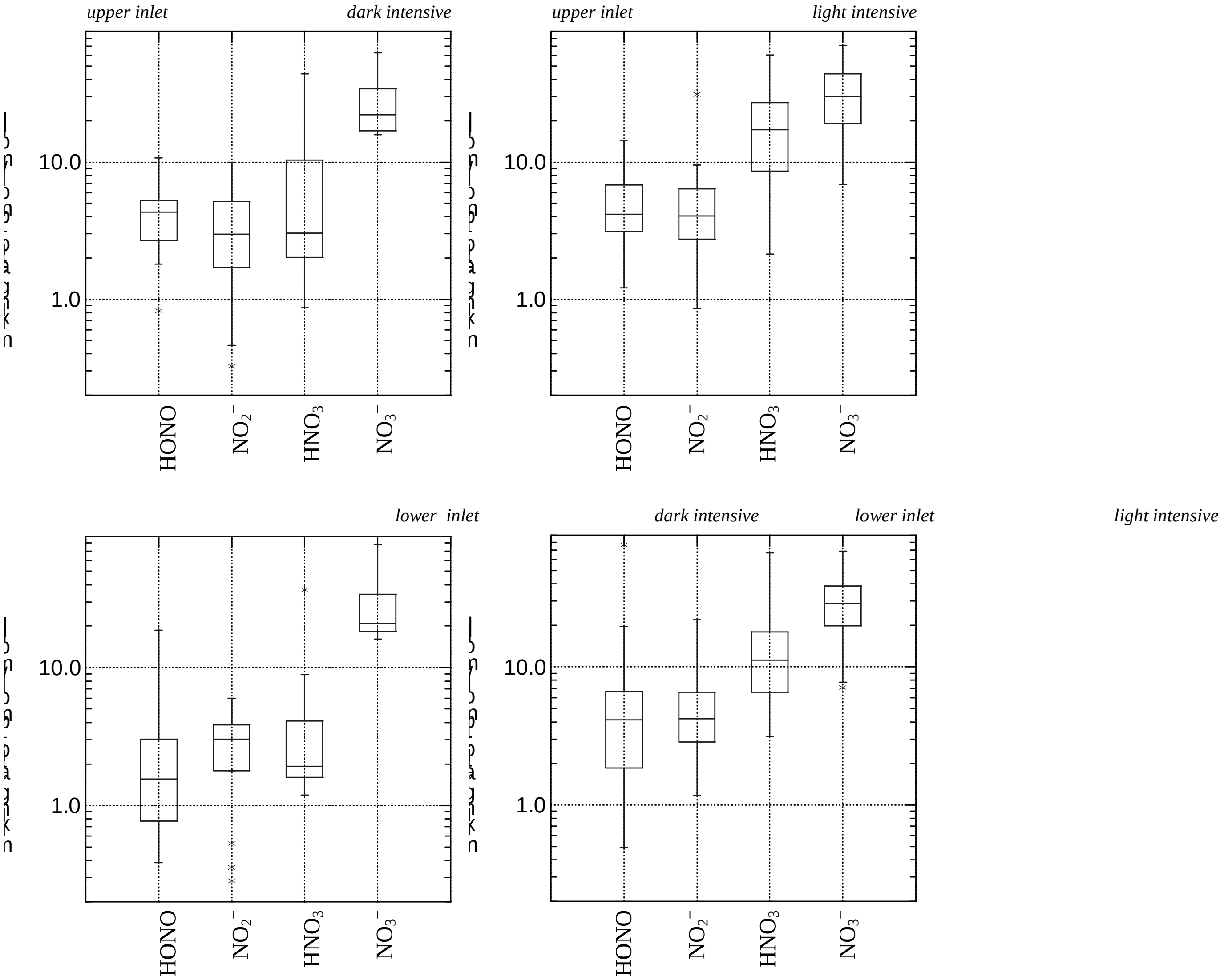


Figure 2. Box-and-whisker plots of the nitrogen measurements at the lower and upper inlet (lower and upper row, respectively) during the dark and light intensive (left and right column, respectively). In the box the middle line shows the median, the box includes 50% of the distribution, and the whiskers extend to 95% of the distribution [*Systat 9*, 1999].

Previous measurements made with a similar method at the Zeppelin monitoring station near Ny-Ålesund during March and April 1999 (comparable in time to the NICE light intensive) showed similar mean low mixing ratios for HONO and NO_2^- of 2.7 and 3.1 pmol mol^{-1}, respectively. Also NO_3^- is in the same range (29.7 pmol mol^{-1} in 1999). HNO_3, however, did not show increased mixing ratios during the spring of 1999; the mean mixing ratio stayed at 4.3 pmol mol^{-1}, only slightly higher than our values from the dark intensive.

Nitrates were also measured with the same method during the Polar Sunrise Experiment at Alert 2000 [*Ianniello et al.*, 2002]; During the dark February 2000 intensive median HNO_3 and NO_3^- mixing ratios were 2.0 and 24.6 pmol mol^{-1}, during the light April/May 2000 intensive these mixing ratios increased to 8.5 and 48.1 pmol mol^{-1}, respectively. The values for both nitrates were similar during our dark intensive. During daylight at Ny-Ålesund, however, the increase in HNO_3 was a little more, while the increase in NO_3^- was much less than at Alert. While the light conditions at Alert were similar to those during our intensives at Ny-Ålesund, Alert was much colder, drier, and there was much less air movement.

The specific composition of aerosols and the ratios of HNO_3/NO_3^- are a function of temperature, aerosol acidity, as well as the kinetic production/destruction/deposition rates of both HNO_3 and NO_3^-. Since this system is very complex, we limit ourselves to qualitative considerations. We assessed an ionic balance (($Cl^- + NO_2^- + Br^- + NO_3^- + SO_4^{2-}$) – ($Na^+ + NH_4^+ + K^+ + Mg^{2+} + Ca^{2+}$) in units of [neq m^{-3}]) of the fine and coarse aerosols (Figure 3), however, without measurements of the liquid water content, we can not derive the pH value.

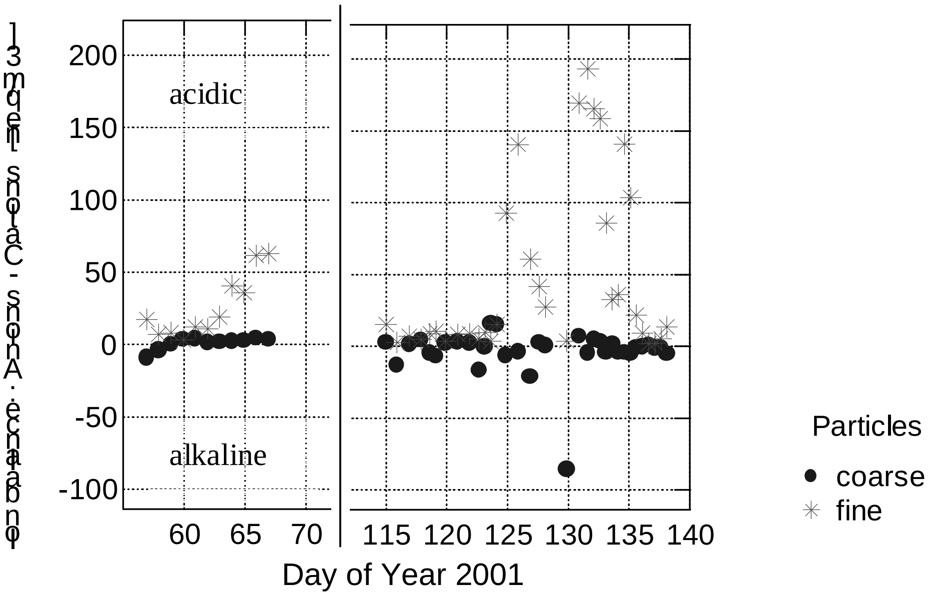


Figure 3. Ion balance for the high line during both intensives at Ny-Ålesund: ($Cl^- + NO_2^- + Br^- + NO_3^- + SO_4^{2-}$) – ($Na^+ + NH_4^+ + K^+ + Mg^{2+} + Ca^{2+}$) [neq m^{-3}] for coarse (> 2.5 µm aerodynamic diameter) (blue circles) and fine (< 2.5 µm) particles (red stars).

During the light intensive fine particles in Ny-Ålesund were mostly acidic, while the coarse particles were practically neutral. As was partly already shown by *Teinilä et al.* [2002], particles around 1µm in spring may contain NO_3^- either on sea-salt or crustal aerosols. On these smaller particles most of the fractionation is due to sulfate ($H_2SO_4 + NaCl \rightarrow NaHSO_4 + HCl$), covering any effect of nitrate. Starting at 2 µm, a good correlation between NO_3^- and Ca^{2+} is observed. NO_3^- in the form of crustal (Ca^{2+}) aerosols are well known [e.g. *Prospero et al.*, 1981]. We do not see any meaningful correlation between NO_3^- and Na^+, however. The majority of nitrate during spring time is located on aerosols >1.5 µm, which is thus mostly crustal dust. At Ny-Ålesund higher temperatures favor volatilization of HNO_3 from the aerosol; additionally, higher NO_x mixing ratios [*Beine et al.*, 1997; 2002a] will lead to increased HNO_3 formation. Due to the higher wind dry deposition of NO_3^- may be favored. Hence the HNO_3/NO_3^- ratio is higher than at Alert; possible alkaline aerosol (due to the presence of sea-salt) is not sufficient to counter balance the above mentioned factors.

ΔHNO_3

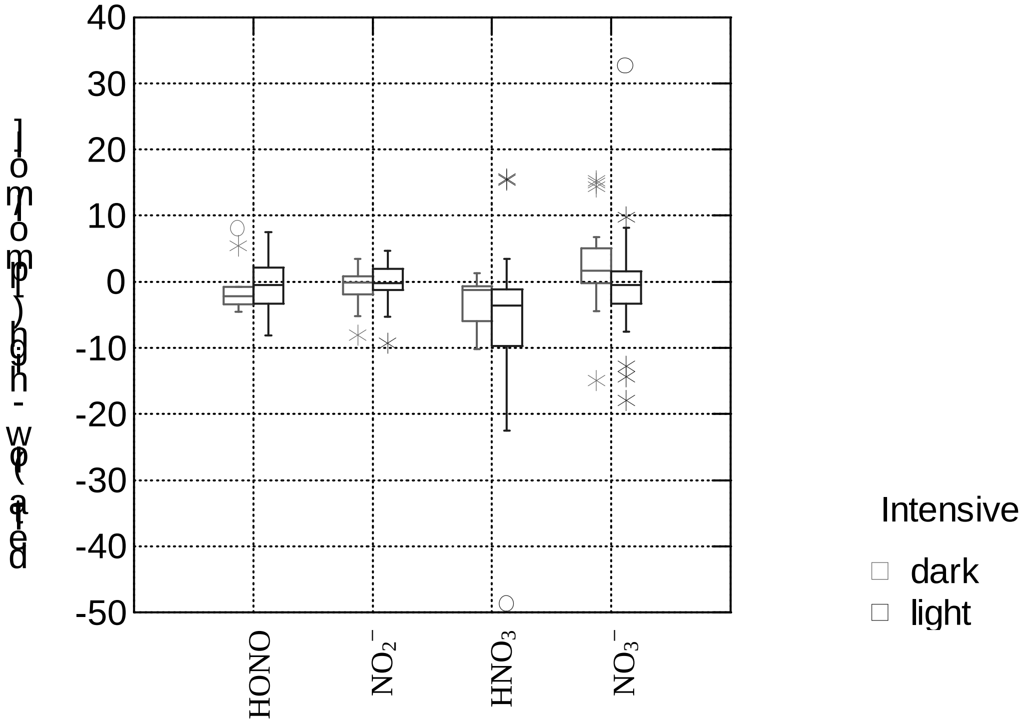


Figure 4. Δ (low – high) of nitrogen species during the two intensives. Only Δ_{HNO_3} was statistically significantly different from zero. During the dark intensive the mean Δ_{HNO_3} was –2.90 pmol mol^{-1} (95% confidence interval from –5.56 to –0.24, p=0.0356), during the light intensive Δ_{HNO_3} was –5.49 pmol mol^{-1} (95% confidence interval from –9.39 to –1.59, p=0.0072).

The difference in mixing ratios Δ between the two sampling heights (Δ = L – H) was statistically significant only for HNO_3 (Figure 4). During the light intensive the median Δ_{HNO_3} was –5.5 pmol mol^{-1}, which implies deposition to the surface. This, again, is in contrast to the findings at Alert, where snow was found to be a source of HONO [*Zhou et al.*, 2001], and a sink for particulate NO_3^-, but at most times not HNO_3 [*Ianniello et al.*, 2002]. During the summer 2000 at Summit, HNO_3 fluxes were mostly downward [*Honrath et al.*, 2002]. A significant difference between Alert and Ny-Ålesund is the sea salt content of the snow. At Ny-Ålesund, the median Cl^- was about 1500 ng/g. At Alert, it was about 250 ng/g before a storm event on April 25-29, 2000. That storm brought in marine air, increasing Cl^- to about 1500 ng/g. It can then be hypothesized that the reaction

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl \qquad (2)$$

lead to HNO_3 deposition to the snow [*Fenter et al.*, 1994]. The rate obviously depends on the concentration of NaCl, and thus would be much more efficient at Ny-Ålesund, relative to pre-storm Alert. Indeed, for the 3 days prior to the storm, the snow at Alert was a small source of HNO_3; during the storm it was a sink of about equal strength (up to 30 nmol m^{-2} h^{-1}). After the storm no HNO_3 fluxes were detected anymore.

Fresh snow usually contains little sea salt, and is slightly acidic (~ pH 5.5). Wind deposition of NaCl turns to snow alkaline (~ pH 10.0). Therefore surface snow that has been exposed to sea salt is a good sink for HNO_3. Deeper snow layers may remain acidic and release HNO_3, which immediately gets trapped in the alkaline surface layer.

The difference in Δ_{NO3-} may be attributed to meteorology. The higher windspeeds at Ny-Ålesund may prevent particle settling, especially since NO_3^- in the Arctic is found almost exclusively on large particles [*Teinilä et al.*, 2002]. At the same time, however, snow acts as a filter, and may do so more efficiently when there is more air flowing through it, i.e. at higher windspeeds. This filtering effect of snow has been observed in both the Alert 2000 and Ny-Ålesund 2001 data sets [F. Dominé, unpublished results]. However, within the time resolution of the denuder/filter method no significant Δ_{NO3-} was observed at Ny-Ålesund. The same complexity of multiple opposing influences applied to NaCl deposition, where at the fieldsite next to the open ocean particle settling is reduced by increasing turbulence, while at the same time snowpack ventilation has the potential to filter out particles.

Atmospheric stability and fluxes of HNO_3

No diurnal pattern was significant for u_* over the duration of the light intensive, except that the variability was slightly increased in the morning hours. While the majority of the u_* values fall below 0.1 ms^{-1}, corresponding to days with higher windspeeds, values up to 0.3 ms^{-1} were observed. This is higher than at Alert 2000, where the median u_* was 0.075, and the maximum did not exceed 0.16 ms^{-1} [*Beine et al.*, 2002].

Using both the measured Δ_{HNO_3} and the measured eddy diffusivity for the same time period, the atmospheric surface fluxes for HNO_3 were derived. The average value for the deposition flux was –8.7 nmol h^{-1} m^{-2} (and was statistically significant, p = 0.0229, t = -2.3908, 95%CI = ±7.46). This is only a third of the deposition of particle NO_3^- that was observed at Alert 2000 [*Ianniello et al.*, 2002]. There deposition of particulate NO_3^- was a significant source of snow nitrate, while after the deposition of NaCl (see above) no significant fluxes of HNO_3 were observed. Two extreme values of –60 and –80 nmol m^{-2} h^{-1} HNO_3 deposition were observed during the largest observed snowfall during our campaign (DOY 119). The winds were calm (< 3 ms^{-1}), temperatures and relative humidities very high. The observed HNO_3 concentrations on this day, however, were the highest observed. The measurement at the upper line was 116 pmol/mol. This suggests that the airmass brought HNO_3 with the snow, and HNO_3 was scavenged by that snowfall and deposited to the surface.

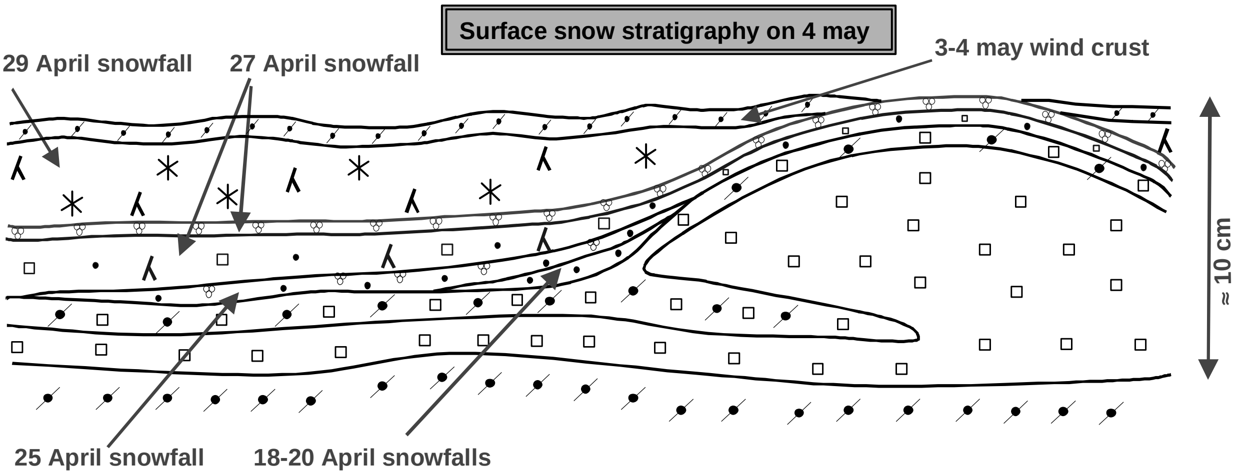
Since windy conditions at Ny-Ålesund likely prevented particle settling, and hence the fluxes of particle NO_3^- at Ny-Ålesund were not significant, the deposition of HNO_3 is the only direct source of NO_3^- on to the snowpack. This is not counting the wet and dry HNO_3 / NO_3^- incorporation during snow formation, nor possible, as yet undocumented chemical transformations of NOy reservoir species such as peroxyacetyl nitrate (PAN) or alkyl nitrates to NO_3^- in the snow phase [*Ford et al.*, 2000]. *Beine and Krognes* [2000] showed an anticorrelation of PAN mixing ratios with the relative atmospheric humidity at Ny-Ålesund, but no further evidence is available that PAN, or alkyl nitrates, lead to a nitrate signal in snow, either directly or indirectly.

Under the crude assumption that our observed mean fluxes hold true for an entire winter season (September to May), the accumulation of snow NO_3^- from atmospheric HNO_3 would be on the order of 50 µmol m^{-2}. If this affected the surface layer (top 5 cm) of the snow, of mean density of 0.2 gcm^{-3}, the increase was 310 ppbw (ng/g) over the entire season. This translates to about 1 ppb per day, which is a change virtually impossible to detect in the snow.

The largest observed source of HNO_3 was deposition during the major snowfall on DOY 119. During that snowfall 5 cm/m^{-2} snow of density 0.124 gcm^{-3} fell with a NO_3^- content of 200 ng/g. Assuming that the high HNO_3 deposition of –60 to –80 nmol m^{-2} h^{-1} lasted for 24 h, the contribution of gaseous HNO_3 to the NO_3^- content in the fresh snow is only ca. 10%. Thus dry particle NO_3^- deposition was not significant at Ny-Ålesund, so that the main NO_3^- source for snow seems to be wet deposition in falling snow. A similar conclusion was reached for Alert 2000 [*Ianniello et al.*, 2002].

Snow Stratigraphy and NO_3^- concentration in snow

The snow stratigraphy was very complex. Most of the stratigraphic observations were made near the Amundsen mast (ca. 100 m to the South inland from the atmospheric sampling location). The accumulation at these coastal sites is less than on locations further inland because of strong wing erosion. Nine snowfall events were observed between April 18 and May 9. Many of them were blown away by wind and did not contribute to accumulation. The April 25 and 27 snowfalls were stabilized by the formation of a thin melt-freeze crust and were monitored in detail. The April 29 snowfall was over 5 cm thick and was not eroded until May 8, and then only partially so, so it could also be studied over an extended period. The surface snow stratigraphy on May 4 is shown in Figure 6, to illustrate its complexity.



✳ **Fresh-looking snow crystals**

ʎ **Recognizable particles**

⁄ **Wind packed small particles**

• **Small rounded grains**

ꝏ **Melt-freeze layer**

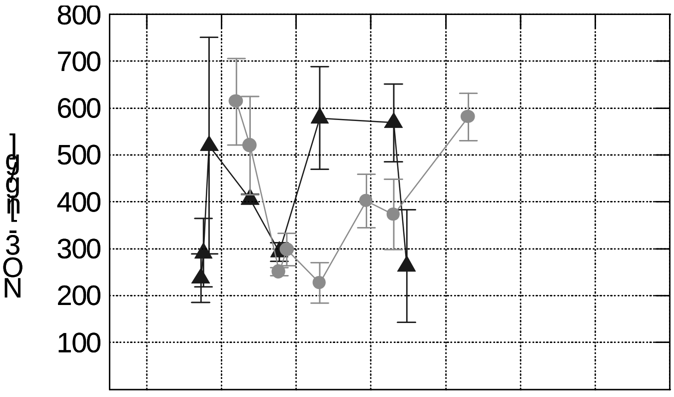
□ **Faceted crystals**

Figure 6 Surface stratigraphy of the snowpack near the Amundsen mast. The total thickness of the snowpack is about 40 cm.

In general, the snow composition was found to be very variable within a given layer, both vertically and horizontally. This is not due to contamination problems, as sampling in unperturbed areas yielded little variation (<5% between triplicate samples). (Moreover, the sampling and analysis procedures were similar to those used at Alert, where there was little wind, and where variations amongst triplicates were also <5 %. The vertical variation can simply be attributed to varying atmospheric composition during precipitation. The horizontal variation is more difficult to explain, and several reasons can be suggested. First of all, many different layers were outcropping at any time, so that a new snowfall was in contact with layers that varied with location. Interactions between layers may lead to exchanges of solutes, and this may have resulted in horizontal variations. Second, wind was often blowing during precipitation, resulting in mixing between fresh snow and already deposited snow. Since snow chemistry varied during precipitation, and since wind results in irregular snow mixing, horizontal variations can be expected from these effects. These variations added noise to the data, even though we attempted to sample one given snowbank, and progressed within this snowbank with every sampling in an effort to minimize the effects of horizontal variations.

Figure 7 shows the variation of the NO_3^- concentration in the snow that was brought in during snowfalls on April 27 (Fig 7a.) and April 29 (Fig. 7b). The April 27 layer was covered by the April 29 snowfall and was not exposed again until May 8, when only parts of it outcropped again. The analyses after May 8 show snow that was still covered. Of the 5 cm-thick April 29 snowfall both the middle and the top layer were sampled. The bottom part was not sampled to avoid contamination of the underlying April 27 layer that was richer in NO_3^-. The sum of the two April 27 layers in Fig. 7a seems to remain constant, which suggests that exchange amongst layers may have taken place, without a net emission. The windpacked sublayer that formed on top of this layer on May 4 was sampled after its formation. This wind-pack was composed of April 29 snow only as in general wind-blown snow does not accumulate on the wind-swept area near the Amundsen mast. The first samplings were done near the Italian station, rather than at the Amundsen mast. However, no significant difference appeared between samples taken at both sites, and other samplings did not suggest contamination of snow within the town of Ny-Ålesund, thus, the data were combined in Figure 7. We observe no significant trend in the snow NO_3^- in these layers, which is consistent with the role of sea-salt in the surface layer to prevent loss of NO_3^-. This is in contrast to our observations at Alert, where a significant reduction of surface NO_3^- occurred [*Beine et al.*, 2002; *Ianniello et al.*, 2002]. However, at Ny-Ålesund the frequently large horizontal and vertical variations in snow composition, that manifested themselves in variations in the triplicate samples, made the detection of subtle trends impossible.

a.



b.

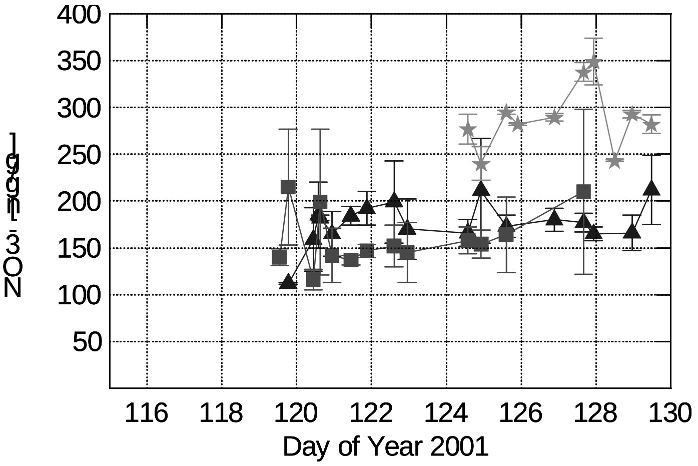


Figure 7. a. Time series of the NO_3^- content of the April 27, 01 snowfall. The top (blue triangles) and bottom (orange circles) parts of the layer were sampled separately. **b.** Time series of the NO_3^- content of the April 29, 01 snowfall. The top (blue triangles) and middle (red squares) layers were sampled separately. The very top of the layer became windpacked on May 4, 01, and was subsequently sampled separately (green stars). Error bars are standard deviations in triplicate samples.

The one significant observation is that the formation of the windpacked sub-layer was accompanied by an increase in the NO_3^- concentration. At this point we have no definite explanation for this increase in NO_3^- in the wind-crust layer of the April 29 snow fall. Deposition of NO_3^- by wind may be a possible explanation. The snow would then have filtered particles. Such wind deposition has been observed for NaCl. We found that at Ny-Ålesund NaCl deposition in the surface layers relative to the non-exposed snow did increase. A correlation of Ca^{2+} with NO_3^- is visible in the snow chemistry, which support filtering of (crustal) particles (Figure 8). However, no atmospheric NO_3^- flux is significant. An alternative explanation, however, may be simply more snow sublimation by wind. Nitrate would have remained constant in mass, while H_2O decreased, and thus caused the increase in concentration.

Additionally, in the snow at Ny-Ålesund a correlation between NO_3^- and Cl^- was observed, the slope of the correlation depends on the sampled snow layer. It is likely that chemical or physical reactions occur that affect both species simultaneously. Similar unexplained correlations of NO_3^- and Cl^- were also observed at Summit, Greenland (J. L. Jaffrezo, personal communication). We cannot resolve either question here, but merely add them to underscore the complexity of the observed snow layers.

Summary of Chemical Aerosol Properties

Nss-sulfate (nss-SO_4^{2-}) was the most abundant ionic compound, having an average concentrations slightly grater than 1000 ng m^{-3} throughout the measurements. During the light campaign two episodes with high nss-SO_4^{2-} concentrations (> 3500 ng m^{-3}) were observed, which is an indication of a strong photochemical production of sulfate in the Arctic troposphere after the Polar sunrise. The concentration time series of ammonium (NH_4^+) followed typically that of nss-SO_4^{2-}, especially during the dark campaign. The overall concentration ratio between NH_4^+ and nss-SO_4^{2-} was rather low, which demonstrates that the bulk aerosol was usually quite acidic. The concentration of another sulfur-containing ion, methanesulfonate

(MSA^-), remained below the detection limit during the dark campaign. During the light campaign the MSA^- concentration averaged 50 ng m^{-3}, which indicates that the biogenic activity in the nearby oceans had been started. The calculated MSA^- to nss-SO_4^{2-} ratios (1.3-26 %) suggest that some (on average <15 %) of the measured sulfate was of biogenic origin during the light campaign.

Sodium (Na^+) and chloride (Cl^-), originating both from the sea-salt, were the most abundant ions after nss-SO_4^{2-}. The average sea-salt particle concentration decreased slightly towards the light campaign. The concentration of nss-calcium (nss-Ca^{2+}), a crustal tracer, increased by a factor four from the dark to the light campaign, but the concentration of the other crustal tracer, nss-magnesium (nss-Mg^{2+}) was nearly the same during both the campaigns. The concentration of nitrate (NO_3^-) was rather low throughout the measurements, averaging roughly one tenth of the concentration of nss-SO_4^{2-}. From the analysed dicarboxylates, oxalate was the only one showing concentrations above the detection limit.

The calculated correlation coefficients between different ionic components showed that the sea-salt tracers Na^+ and Cl^- correlated very strongly with each other but not with any other ion. During the dark campaign the anthropogenic tracers nss-SO_4^{2-}, NH_4^+, NO_3^-, oxalate and nss-K^+ were quite clearly correlated with each other, as were also the crustal tracers nss-Ca^{2+} and nss-Mg^{2+}. During the light campaign the correlation between the anthropogenic tracers was not as clear as during the dark campaign. The low correlation between nss-SO_4^{2-} and NH_4^+ during the light campaign compared with the dark campaign indicates that the production of nss-SO_4^{2-} was more complex after the Polar sunrise. The poor correlation between the crustal tracers nss-Ca^{2+} and nss-Mg^{2+} during the light campaign, together with the fact that the concentrations of nss-Ca^{2+} were elevated during the light campaign, may be an indication that the measurement site was affected by more than one crustal source. One such a source is apparently long-range transport Asian dust, the other one being locally-emitted soil particles.

Oxalate did not correlate with any other ion during the light campaign, so it can be assumed that oxalate was produced photochemically from organic precursors, transported into the Arctic, after the Polar sunrise. One interesting feature was that NO_3^- did not correlated with nss-SO_4^{2-} during the light campaign, but correlated instead with nss-Ca^{2+}. One explanation for this is that both these ions had a local source during the light campaign.

The measured size distributions demonstrated that nss-SO_4^{2-}, NH_4^+ and MSA^- were found predominantly in the submicron size range, whereas Na^+, Cl^-, NO_3^-, nss-Ca^{2+} and nss-Mg^{2+} were predominantly in the supermicron size range. The ions nss-SO_4^{2-}, NH_4^+ and MSA^- showed typically three modes in the submicron size range: a mode close to 0.1 µm and two modes between 0.1 and 1 µm. The modal structures of these ions were very similar, indicating that they were internally mixed in submicron particles. The ions Na^+, nss-Ca^{2+} and nss-Mg^{2+} showed a tail in the submicron size range, containing on average 10% of the found Na^+ and nss-Ca^{2+} and over 20 % of the found nss-Mg^{2+}. The very small fraction of NO_3^- found in the submicron size range was probably associated with either sea-salt or crustal particles.

Supermicron particles contained mainly sea-salt ions Na^+ and Cl^-. Typically two modes for Na^+ in the supermicron size range could be seen. Supermicron sea-salt particles showed a clear chloride depletion being on average around 20%. The chloride that was evaporated from sea-salt particles was replaced with sulfate, nitrate and during the light campaign also with methanesulfonate. Nss-Ca^{2+} was the most abundant ion from soil derived particles. The dominant mode of nss-Ca^{2+} peaked between 2 and 4 µm and showed sometimes also a mode between 7 and 9 µm, indicating that at least some fraction of the soil particles were of local origin.

Fluxes of Nitrates Between Snow Surfaces and the Atmosphere in the European High Arctic

Introduction

The aim of this section is to help identify the atmospheric sources of snow-NO_3^-, and to help understand the mechanism of the exchange reactions. Here we assess the importance of the snow surface on the atmospheric NO_3^- budget. (and vice versa).

NO_3^- Exchange with and within Snow

Exchange reactions with the atmosphere will preferentially affect surface snow layers. Both the snow stratigraphy and chemistry at Ny-Ålesund were very complex. The atmosphere was interacting with several different outcropping snow surface layers at any one time; quantifying the exchanges is then very difficult.

The specific surface area (SSA) [*Cabanes et al.*, 2002] of the April 29 snowfall decreased by a factor greater than 2 over a time period of 3 days. This allows us to test whether species responsible for the NO_3^- signal in snow were adsorbed on the surface of snow crystals. Recent studies [*Abbatt*, 1997, *Zondlo et al.*, 1997] indicate that HNO_3 readily adsorbs onto snow crystals while its solubility into the ice crystalline lattice is low [*Thibert and Dominé*, 1998]. Thus, if HNO_3 is a major contributor to the NO_3^- signal, a SSA decrease of a factor of 2 should result in a NO_3^- decrease of a factor of 2 in three days, coupled to an HNO_3 flux to the atmosphere of about 1.8 μmol m^{-2} h^{-1}. Neither the expected decrease in snow NO_3^- nor the NO_3^- flux to the atmosphere were observed, from which we deduce that HNO_3 is not a major contributor to the NO_3^- signal in snow. Particulate NO_3^- or the NO_3^- ion associated with counter cations other than H^+, which will reduce NO_3^- mobility [*Thibert and Dominé*, 1998] are then probably responsible for the NO_3^- signal in snow.

The NO_3^- concentration in the snow at Ny-Ålesund was 65 to 520 ppbw, with a total NO_3^- content of the snowpack on the order of 2700 ng/cm^2 (or 435 μmol m^{-2}) near the Amundsen mast. This value was up to 5 times higher in areas that were not wind-swept, and where snow accumulation reached up to 2 meters. This is 10 times more than the value from atmospheric HNO_3 deposition alone. Atmospheric NO_3^- concentrations of ca. 200 ng/m^3 (ca. 70 pmol mol^{-1}; as HNO_3 and particulate NO_3^-) add up to a column boundary layer (300 m) content of only 8 ng/cm^2. Thus even an undetectable release of NO_3^- by the snowpack has the potential to considerably increase boundary layer NO_3^- concentrations.

However, for such a release or exchange to occur, the snow NO_3^- has to be mobile. NH_4NO_3 is mobile whereas NO_3^- tied to Na^+, Ca^{2+} or Mg^{2+} would be immobile. The median snow NH_4^+ concentrations from different layers of various snowfalls at Ny-Ålesund was only 31 ng/g; this amounted to 2.5% of all available equivalent cations. Additionally, no correlation existed between NH_4^+ and NO_3^- in the atmospheric aerosol, but that NH_4^+ was associated with SO_4^{2-}, and NO_3^- with Ca^{2+}. Hence the majority of NO_3^- was likely fairly immobile. Moreover, with metamorphism, particles may become imbedded inside ice grains and thus fossilized (this has been observed inside ice crystals in ice cores [*Fuji et al.*, 1999]). Alternatively, ionic species may interact with ice to form ionic mixtures that could even be liquid, and that would spread on the ice crystal surfaces. [*Koop et al.*, 2000]. In that case, NO_3^- would probably be potentially mobile. Through the acidification of the surface layer NO_3^- could be released as HNO_3. Sulfate is high in Ny-Ålesund snow, ammonium and other cations are in comparison low, so that the resulting pH should be quite low in fresh snow. If all the ions were in liquid brine on the snow surface, then most of the NO_3^- would be released as HNO_3. This, however, was not observed. Through the deposition of NaCl the snow surface turns alkaline (Figure 18); thus it is likely that NO_3^- is tied up in immobile particles. The potential for exchanges may thus not be as high as suggested by the mass balance of nitrate between the atmosphere and the snow.

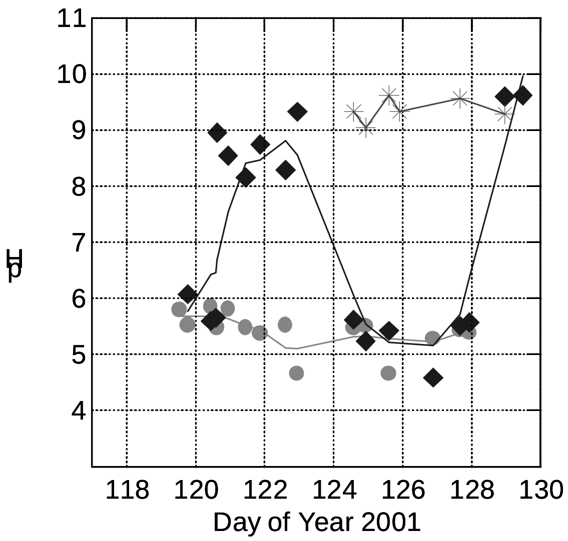


Figure 18. pH of the observed snow layers; Green circles show the mid layer, which stayed covered throughout the entire observation period, and remained acidic. The top layer (blue diamonds) turned alkaline within 2 days of snow deposition. When the wind crust formed, the former 'top layer' became covered. The wind crust (red stars) was alkaline.

Because of coarse aerosol chemistry, NO_3^- can expected to be fairly immobile. Ca^{2+} is well soluble in water, so the $Ca(NO_3)_2$ aerosol may disintegrate on the ice and become soluble. If this is the case, the high pH of surface snow will prevent diffusion and mobility, as NO_3^- will interact with immobile cations [*Thibert and Domine*, 1998]. Thus in either case NO_3^- will remain immobile.

As far as the photochemical reactivation of snow NO_3^- is concerned; this photolysis is fast enough to affect atmospheric NO_x levels, but it is too slow to affect snow chemistry [*Honrath et al.*, 2002; *Jones et al.*, 2000]. Even on the timescale of a month, changes would be hard to detect, but with the horizontal and vertical chemistry variations that we observe in snow surfaces, any change would simply be undetectable.

Scientific Conclusions

At Ny-Ålesund during the spring of 2001 at a coastal site close to the unseasonably unfrozen fjord only deposition fluxes of HNO_3 were detected. Other measured nitrogen species showed no significant fluxes which may be in part due to the measurement uncertainties and long integration times of the used denuder technique, and atmospheric turbulence and mixing. These HNO_3 fluxes may be due to the reaction of HNO_3 with NaCl, or may be simply uptake of HNO_3 by ice, which is alkaline because of the sea salt in our marine environment.

HNO_3 is not a major contributor to the NO_3^- signal in snow. This is not surprising, as NO_3^- arrives to the snow surface as $Ca(NO_3)_2$, and is immobile. Thus exchanges are limited.

Also photolysis will also have only limited effects, since reaction products may be immobilized inside a solid. This is unlike Alert, Nunavut or Summit, Greenland, where NO_3^- was in the absence of NaCl, (in acidic ice) in more mobile forms.

Exchanges were easier, and air-snow exchanges of NO_3^- followed different mechanisms. In particular, photolysis products could be released more easily.

In conclusion we can say that understanding NO_3^- exchanges between the snow and the atmosphere will require more efforts in determining NOy speciation in the snow, and particularly what contributes to the NO_3^- signal in snow. We also need to understand nitrate localization and reactivity in snow. Our results suggest that on the timescale of a month, nitrate as such is not easy to mobilize in snow. Destruction by photolysis and release of NO_x was not detectable with our analytical systems. Our HONO measurements nevertheless suggest that NO_x fluxes may have been a lot smaller than at Alert or Summit. The sampling site near the open Kongsfjord near Ny-Ålesund was decidedly marine, hence the snow shows a marked marine character of the snow.

Importance of Results

Results from the experimental campaigns were presented at the EGS meeting in NICE on March 26, 2001, at the Torino Symposium in September 2001, and at the AGU meetings in San Francisco in Dec. 2001 and 2002.

One result of this work concerns international collaboration, and the competitiveness of European science. We were able to interest a number of European scientists in a collaboration with our experimental efforts. Also, due to C.N.R.- IIA's contribution to PSE, and the international (American) interest in NICE, we will be involved in the planning of future large international experiments to investigate snow and air chemistry and interactions. A new Polar Sunrise Experiment is planned for 2005/2006, and Ny-Ålesund is discussed as a possible location for this effort. C.N.R. – IIA hosted data meetings both for the Polar Sunrise Experiment Alert 2000 and NICE in Rome, bringing together scientists from North America and Europe.

The results of NICE, together with earlier results of the Polar Sunrise Experiment ALERT 2000 and ISCAT in Antarctica show that the reactivation of NO_x from snow nitrate is an important source of NO_x over snow surfaces. These results are very important in formulating possible scenarios in more polluted mid latitude snow-covered European environments (e.g. Alpine regions).

NICE, as well as similar efforts in this fairly new scientific discipline (PSE, Summit, ISCAT), investigated a new fundamental chemical mechanism; a property of snow interstitial air, that was formerly not recognized. With the data collected to date in the various experiments, it would be premature to assess possible European or even global pollution scenarios. Focused modeling efforts incorporating these newly characterized fundamental mechanisms are necessary at least on a European scale.

The results allow us to formulate two important questions, that are highly relevant for climate change, atmospheric composition change, atmospheric oxidative capacity, and thus global change.

First – pertaining specifically to the Polar regions; does Re-NO_xification occur on snow surfaces above sea ice on the Arctic (and Antarctic) ocean? Recently saline frost flowers were identified as potential sources for halogen species in Polar regions; they provide immense surface areas, and thus provide the interface for chemical reactions and phase transitions. However, NICE has shown that acidic snow is necessary for the effective transport of NO_3^- in the form of HNO_3 to the reactive snow surface for photolytic reaction. Thus a saline (alkaline) frost flower may not be a proper snow surface for this reaction.

Second – and more important from a socio-economic perspective for Europe; since in midlatitude Europe atmospheric and snow concentrations of NO_3^- and HNO_3 are significantly higher than in the remote background Arctic environment of Ny-Ålesund, snow temperatures are likely higher, snow surfaces are in the absence of sea-salt acidic, and UV light is also available sufficiently in midlatitude winter, Re-NO_xification **must** be a common feature of snow anywhere in Europe. Thus this mechanism is universal to snow and must be investigated further with focused attention to issues such as trans-boundary pollution transport, ozone production, nitrogen deposition, etc.

This multiphase interaction of the boundary layer with the snow surface may provide an important feedback mechanism for global change; as temperatures change and snow pattern change (e.g. in Alpine regions), the distribution of NO_3^- and NO_x will certainly change, too. In consequence OH and the climate gas O_3 will change their spatial distribution as well, which, in turn, may have an influence on weather pattern and the climate.

The interaction and chemistry between phases (snow-air) were recognized as an important scientific topic at the recent IGAC meeting (in Crete, Greece); such that a new IGAC activity “Air-Ice Interactions” (AICI) is being founded.

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