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Enhancement of snowpack inorganic nitrogen by aerosol debris

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ABSTRACT

The NO_3^-, Cl^- and Ca^{2+} loading and provenance of the lower wetted-refrozen part of an Arctic snowpack sampled in spring 1999 is analysed. This wetted-refrozen layer (WRL) formed during rain-on-snow events in early winter 1998, being subsequently buried by later snowfall. It is a unique environment within which to study NO_3^- provenance, since it is effectively sealed off from the atmosphere, and solute is mostly stored in superimposed ice, ice lenses and wetted-refrozen snow. Post-depositional losses/gains of NO_3^- by volatilization/dry deposition are, therefore, minimized. Partitioning of WRL Ca^{2+} and NO_3^- loads into their respective sea salt/atmospheric components and an excess component indicates significant contributions of excess Ca^{2+} (~80% of total) and NO_3^- (11–64% of total). These excess loads are thought to arise from a combination of preferential elution during lateral meltwater drainage and the release of Ca^+ and N (as NO_3^- and NH_4^+) from snowpack debris during wetting. Dissolution experiments on local snowpack debris provide envelopes of Ca^{2+} and NO_3^- release that are in line with the excess loads of these species at most sampling sites and are supportive of the latter hypothesis. This is the first study to date to indicate debris as a possible source of non-atmospheric nitrogen to snow. It has implications for nitrogen cycling in other catchments where snow contains significant aerosol sourced from N-containing lithologies and organic matter.

1. Introduction

Snowpack NO_3^- and NH_4^+ are important nutrients within the soil/snow system in Arctic regions (Jones, 1999). Here, most N is present in soil organic matter as humic substances and the release of high NO_3^- and NH_4^+ concentrations from snow at the start of the melt season may stimulate microbial activity in soils (Jones, 1999). These inorganic N species in snow derive mainly from atmospheric sources such as NO_x, principally via the wet and dry deposition of long distance transported industrial pollutants, with a smaller proportion as naturally produced N through biomass burning and lightning (Holland et al., 1999). This contribution to snowpack N is well studied in Arctic environments (Semb et al., 1984; Mayewski et al., 1987; Beer et al., 1991; Fischer et al., 1998). Less well studied are the more minor N contributions to the snowpack from biological, volcanic and particulate sources. These potentially sustainable non-atmospheric sources of N may become more important if reduced industrial emissions in temperate latitudes lower Arctic atmospheric N deposition in the future (Fischer et al., 1998; Kekonen et al., 2002; Matoba et al., 2002). In this paper we focus on the dissolution of debris in generating NO_3^- within the snowpack upon wetting.

Layers of dust and coarser lithogenic material are commonly reported in Alpine and polar snowpacks, being derived either from local rock and soil outcrops, or transported from remote locations over thousands of kilometres (Hinkley, 1994; Maupetit and Delmas, 1994; Schwikowski et al., 1995; Delmas et al., 1996). There are two main mechanisms by which airborne material may influence the NO_3^- loading of a snowpack. First, crustal aerosol particles may react with HNO_3 and NO_2 whilst in the atmosphere or snowpack (eq. 1), forming NO_3^- salts on the particle surface (Wolff, 1984; Wu and Okada, 1994; Shrestha et al., 1997; Beine et al., 2003).

$$2HNO_3 + CaCO_3 \Leftrightarrow Ca(NO_3^-)_2 + CO_2 + H_2O. \quad (1)$$

This process has been demonstrated at several locations, including Nagoya, Japan (Wu and Okada, 1994), South Dakota, United States (Wolff, 1984), the Himalayas (Shrestha et al., 1997) and Svalbard (Beine et al., 2003). Although this mechanism may raise rates of N deposition to the snowcover significantly, the ultimate source of the N is atmospheric and significant concentrations of HNO_3, NO_2 and crustal aerosol are required concurrently in the atmosphere. At present associations found between

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Ca^{2+} and NO_3^- in the Vostok, NorthGRIP and Dome C ice cores have been attributed to this mechanism (Legrand et al., 1999; Röthlisberger et al., 2002; Ruth et al., 2002).

The second means by which debris may influence the N loading of a snowpack has no direct link to the atmosphere and has yet to be fully demonstrated. Many rock types and soil contain organic or inorganic forms of nitrogen, either as recalcitrant organic nitrogen (e.g. kerogen), nitride minerals in meteorites and mantle rocks, salts of ammonium or nitrate or as fixed NH_4^+ in silicate minerals (Holloway and Dahlgren, 2002). Concentrations range from trace levels ($<$200 mg N kg^{-1}) in granites to levels of ecological significance ($>$1000 mg N kg^{-1}) in some sedimentary and metasedimentary rocks (Holloway and Dahlgren, 2002). These rock types are now known to be important in contributing N to surface and groundwaters in temperate regions under certain conditions (Hendry et al., 1984; Holloway and Dahlgren, 2001). Hodson et al. (2005) recently demonstrated a surplus of dissolved organic nitrogen and particulate nitrogen in runoff at Midre Lovenbreen, which they suggest may be partially derived from young organic material associated with cryoconite biota at the glacier surface or older organic material associated with soils and/or bedrock. The importance of debris as a source of nitrogen, however, has not been fully demonstrated in nival environments. During snowmelt, rock and soil particles undergo hydrolysis and release considerable concentrations of crustal ions such as Ca^{2+}, Mg^{2+} and Na^+ (Maupetit and Delmas, 1994; Delmas et al., 1996), but the release of NO_3^- and NH_4^+ has not been assessed. The significance of this process for generating NO_3^- in situ will depend largely on the mineralogy and provenance of the snowpack debris aerosol. Attempts to establish relationships between concentrations of debris and NO_3^- in snow have been made in a limited number of studies. Some have shown no significant relationship between the two variables (Hinkley, 1994; Sun et al., 1998). Others show some association (Legrand et al., 1999; Röthlisberger et al., 2000; Ruth et al., 2002; Teinilä et al., 2003). Since NO_3^- derives also from atmospheric sources and is highly prone to post-depositional loss (Honrath et al., 1999; Pomeroy et al., 1999; Jones et al., 2000; 2001; Dubowski et al., 2001) or biological consumption (Jones, 1991), correlations may be naturally difficult to identify in fallen snow. There has been no attempt to isolate snowpack debris and perform dissolution experiments that would indicate any N release over time.

This paper examines the solute loading of a high Arctic snowpack during spring 1999 in an area that receives considerable debris inputs from local sources during winter (Teinilä et al., 2003). During the early accumulation period of this snowpack (first snowfall in early October), several rain-on-snow events caused widespread melting and re-freezing (Wadham and Nuttall, 2002). There was no melting during the remainder of the accumulation period. This created a snowpack that comprised a lower layer of wetted-refrozen snow (WRS), ice lenses and superimposed ice and an upper layer of non-wetted refrozen snow. The lower wetted-refrozen layer (WRL) provides a unique environment within which to search for and detect debris-derived NO_3^-. In this semi-closed system, post-depositional losses/gains of NO_3^- (e.g. by volatilization, photochemical decay and dry deposition) that would normally mask any NO_3^- acquisition from debris are minimized. We focus on the loading of three solutes in the WRL, each of contrasting provenance; Cl^- (atmospheric origin), Ca^{2+} (predominantly crustal origin) and NO_3^- (mixed origin). No NH_4^+ was measured in snow samples. We aim to detect and measure any component of the snowpack NO_3^- load that cannot be explained by atmospheric deposition and that may derive from debris sources. Low temperature laboratory dissolution experiments are performed on local snowpack debris in order to quantify the amount of NO_3^- and other solutes released by weathering, for comparison with snowpack records.

2. Methods

2.1. Field sampling

2.1.1. Field site. Fieldwork was conducted on Midre Lovènbreen (78° 53′ N), a 6 km^2 glacier located in northwest Spitsbergen (Fig. 1a). The snow in this region contains significant debris, derived largely from local rock outcrops and exposed soils (Teinilä et al., 2003). The lithology of the upper catchment comprises Lower–Mid Proterozoic mica schist with carbonate and quartzite beds, and that of the lower catchment is Upper Proterozoic phyllite with carbonate and quartzite beds. The regional geology is similar but also includes some Carboniferous and Permian sandstones and shales. Snow sampling was conducted in spring 1999 (April 30 to May 11; Day of year (DOY) 121–132) at 5 sites (ML2–ML10; 160–420 m asl.) along the central stake line used by the Norsk Polarinstitutt for mass balance monitoring (Fig. 1b).

2.1.2. Meteorological monitoring. Air temperature and snow depth were monitored continuously between 1 September 1998 and 1 June 1999 (DOY 244–151) at sites, ML2 and 500 m downglacier of ML10 (Fig. 1b). Full details of meteorological monitoring are given in Wadham and Nuttall (2002). The snow depth record was used to derive a record of snow precipitation at the glacier.

2.1.3. Snow sampling. Snow pits, 2 m^2 at the base, were excavated to the end of summer 1998 glacier surface at sites, ML2, ML5 and ML7. A core was also retrieved from the snowpack at ML10 using a PICO manual ice auger. Snow depth was measured and the physical stratigraphy of the snowpack was recorded in detail at each pit and in the core. Samples were collected for snow density determination at 5–20 cm intervals down the snow pit profile using a metal cylinder of known volume. Since this did not give a continuous record of snow density at every site, measured values have been interpolated using the local snow pit stratigraphic record. The error on these density determinations is estimated to be $\pm$20 kg m^{-3} where no interpolation was necessary (ML2) and $\pm$50 kg m^{-3} where interpolation was required

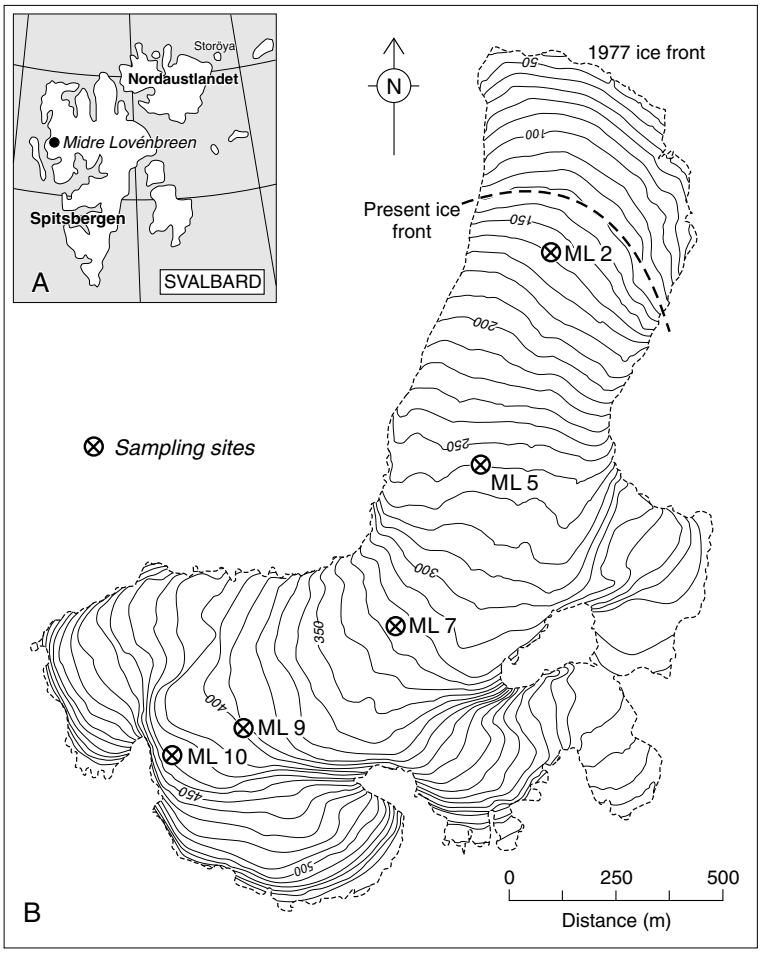

Fig. 1. (a) Location of field site, Midre Lovènbreen, Svalbard (b) Map of Midre Lovènbreen, showing location of glacier sampling sites.

(ML5 and ML7). Densities at ML10 were not measured directly but inferred from the snow stratigraphy at this site and measured density values at the other four sites. The accuracy of inferred densities at ML10 is estimated to be ± 50 kg m^{-3}.

Two metre squares of plastic mesh laid on the glacier surface in autumn 1998 at sampling sites served as artificial marker horizons for the glacier summer surface. The distribution, thickness, air bubble and sediment content of any superimposed ice formed above the mesh during winter 1998/1999 was measured in spring 1999. Superimposed ice density was determined from shallow ice cores, 0.1–0.5 m in length, taken from the base of each snowpit. Cores were sectioned and the dimensions and weight of each section measured to give ice density (accuracy $= \pm 20$ kg m^{-3}). Sampling of all sites, except ML7, was conducted when air temperatures were $<0\,^{\circ}$C. Air temperatures during sample collection at ML7 were $>0\,^{\circ}$C and snow on the outer pit face was wet.

Samples for chemical analysis were taken from a pre-cleaned pristine face of snow pits at ML2–ML7, and from the pre-cleaned snow core at ML10. Snow samples were vertically continuous, collected to coincide with the major stratigraphic layers. Ten to fifteen samples were taken from the full depth of the superimposed ice layer, where present, using a clean ice axe. Additional superimposed ice samples were taken from the shallow ice cores collected for density and superimposed ice thickness determination. The chemical composition of these core and excavation samples has been used to compute a mean chemical composition of the superimposed ice layer at each site.

Snow samples were sealed in two clean plastic bags immediately after collection. Ice cores were placed in clean plastic tubing. They were stored at $-20\,^{\circ}$C in a cold room prior to processing. All ice and snow samples were handled using clean plastic gloves throughout. Ice cores were cut into 0.025–0.05 m sections using a clean band saw and sealed in two plastic bags. These, together with snowpit ice and snow samples, were melted in a microwave. Temperature during melting was close to $0\,^{\circ}$C. Once melted, samples were filtered through 47 mm Whatman 45 μm cellulose nitrate filters using standard techniques and stored in clean, pre-rinsed polyethylene bottles. Samples were stored for up to 2 months prior to chemical analysis.

2.2. Dissolution experimental methods

Dissolution experiments were performed on debris, collected from superimposed ice samples (re-frozen snowmelt: Wadham

and Nuttall, 2002) and WRS at sites ML2 and ML5 during a previous sampling period (spring 1998). The aim of the experiments was to determine any N release from debris during wetting.

Prior to experimentation, aerosol particles were filtered out of melted snow and ice samples using 47 mm Whatman 45 μm cellulose nitrate filters. Filters were left to dry slowly at room temperature ($\sim$25 °C). Once dry, they were stored in aluminium foil prior to the experiments. Three experiments were run, each using different sediment removal techniques from the filters. In Experiment 1, the upper veneer of aerosol was brushed carefully off the filter. In Experiment 2, several particles derived from filtration of 400 ml of snow sample were crushed using an agate pestle and mortar. In this experiment, the particles were simply picked off the filter. Experiment 3 used debris derived from filtration of 1500 ml of snow/superimposed ice sample. The aerosol was removed from the filter by rinsing with deionized water. In all experiments, there was no physical abrasion of the filter surface during aerosol removal and NO_3^- contamination from the filter is believed to be negligible. This is supported by two independent lines of evidence. First, a control experiment was performed where a cellulose nitrate filter was immersed in deionized water for 10 minutes, emulating aerosol removal techniques in Experiment 3. Here, no NO_3^- was detected in the water after immersion. Second, a re-wetting experiment (O'Connor, 2004) was run, in which aerosol previously used in a dissolution experiment was rinsed with deionized water (removing any potential contaminants) and subsequently immersed in deionized water for several days. The concentrations of NO_3^- present in this control solution were not significantly different from non-rewetted aerosol, suggesting that there was no filter effect (O'Connor, 2004).

The three experiments described give approximate maximum (Experiment 2; pre-wetted and reactivated material) and minimum (Experiment 1 and 3; pre-wetted but not reactivated material) estimates of solute release from snowpack debris. In reality, solute release from snowpack aerosol would be expected to lie somewhere in between the results from Experiment 2 and Experiments 1 and 3, since aerosol would not be pre-wetted, a factor which is known to reduce solute release (Brown et al., 1996) and would not have been crushed, which increases solute release (Brown et al., 1996). In both experiments, the aerosol was placed in a 70 ml polyethylene bottle along with 60 ml of deionized water and left in a refrigerator at 3 °C for 5 d. The mass of the aerosol in each experiment was calculated, and gave minimum sediment concentrations of 530, 630 and 130 mg l^{-1} for Experiments 3, 2 and 1, respectively. The bottles were shaken at 6–12 hourly intervals. Samples were removed from the bottles using a sterile plastic syringe at 1, 6, 24, 48 and 120 hr after the start of the experiment. Samples were filtered through Whatman 45 μm cellulose nitrate filters and analysed for major cations and anions by ion chromatography.

2.3. Chemical analysis

Concentrations of cations: Ca^{2+}, Mg^{2+}, K^+, Na^+, and anions: Cl^-, NO_3^- and SO_4^{2-} in ice, snow and experimental samples were determined by ion chromatography on a Dionex DX500 System. NH_4^+ concentrations were also determined for samples derived from dissolution experiments using a Bran and Luebbe Autoanalyser 3. Anion analysis was conducted using a AG11 guard column and a AS11 analytical column with chemical suppression (sulphuric acid). Eluant used for anion analysis was 30 mM NaOH solution. Cations were analysed using a CG12A guard column and a CS12A analytical column with electrochemical suppression. Eluant used was 20 mM methanesulphonic acid. Injection of samples was done automatically and the sample loop was 100 μl for cations and anions. The precision of Ca^{2+}, K^+, Na^+, Mg^{2+}, NO_3^-, NH_4^+, Cl^- and SO_4^{2-} analyses was $\pm$1%, $\pm$ 5%, $\pm$10%, $\pm$3%, $\pm$5%, $\pm$15%, $\pm$4% and $\pm$2%, respectively. Accuracy was $-$12%, 30%, 20%, $-$15%, +12%, +15%, $-$1% and +2%, respectively.

2.4. Sedimentological analysis

An Environmental Scanning Electron Microscope (ESEM), ElectroScan 2020 fitted with a Princeton Gamma-Tech (PGT) Prism EDX detector, was used to determine the physical appearance and elemental composition of the aerosol particles. Images/spectra/maps were acquired using PGT IMIX acquisition/analysis software. Two samples were analysed (Sample 1 and 2), both comprising aerosol derived from superimposed ice samples. These samples were not the same as those used for dissolution experiments, but derived from the same snow sample batch in the field. A small amount of each sample was sprinkled on to adhesive carbon pads stuck on 12 mm diameter pin stubs and mounted on a stage in the analysis chamber. The chamber was evacuated in 'wet' mode and 'flooded' three times to introduce water vapour. The accelerating voltage was 20 keV, the working distance 19 mm, the stage tilt 40°, the chamber pressure 5 Torr and the area of sample analysed was $\sim$0.5 $\times$ $\sim$0.5 mm (200$\times$ magnification).

X-ray photoelectron spectroscopy was used to acquire a wide scan survey spectrum (to generate EDX spectra) and regional scans for the elements, C, O, Na, Mg, Al, Si, S, K, Ca, Ti and Fe in Sample 1. A portion of the sample was pressed onto adhesive-backed copper tape mounted on a stainless steel sample holder and inserted into the vacuum chamber for analysis. A Thermo VG Scientific (East Grinstead, England) Escascope x-ray photoelectron spectrometer was used to acquire the data using an aluminium Kα (hν = 1486.6 eV) X-ray source operating at 300 W (15 kV; 20 mA). The largest analytical area, $\sim$4 mm $\times$ $\sim$3 mm, was used to maximize the data acquisition rate.

The total carbon and nitrogen content of the bulk debris was determined using a Carlo Erba Elemental analyser 1106, where

accuracy of determinations was ~5%. Due to the small mass of material, the total carbon and nitrogen content could not be separated into its organic and inorganic components.

2.5. Data analysis

The thickness of the WRL ranged from 0.37 m at ML2 to 0.7 m at ML10. The product of the thickness of each stratigraphic layer (m) and layer density (kg m^{-3}) gives water equivalents (w.e.) of accumulation in each sampled layer of the snowpack (in m^3). These have been summed to give total w.e. of accumulation (in m^3) and w.e. in the WRL.

The loads of the three solutes, Cl^-, NO_3^- and Ca^{2+} (μeq m^{-2}) in the major stratigraphic layers of the WRL were calculated as a product of layer thickness (m), layer density (kg m^{-3}) and measured solute concentration (μeq l^{-1}). These loads were summed to give the total solute load in the WRL.

WRL Ca^{2+} loads have been partitioned into a sea salt derived and an excess component and NO_3^- loads into an atmospheric derived and an excess component as follows (excess contributions are indicated by *). The sea salt component of Ca^{2+} has been computed using standard ratios of Cl^-:Ca^{2+} in sea water, $(Ca^+:Cl^-)_{SEAWATER}$, and the Cl^- load in each sample, LOAD-Cl^-_{TOTAL}, (Holland, 1978). The excess component, LOAD*Ca^+, is calculated as the difference between this calculated sea salt component and the total Ca^{2+} load, LOAD-Ca^+_{TOTAL} (eq. 2).

$$\mathrm{LOAD^*Ca^+} = \mathrm{LOAD} - \mathrm{Ca^+_{TOTAL}} - \left[\mathrm{LOAD} - \mathrm{Cl^-_{TOTAL}} \times (\mathrm{Ca^+ : Cl^-})_{\mathrm{SEAWATER}}\right]. \quad (2)$$

Atmospheric NO_3^- derives predominantly from acidic nitrogen species in the atmosphere. The atmospheric NO_3^- load was calculated using a bulk atmospheric NO_3^- concentration (BULK-NO_3^-) for the WRL and WRL water equivalents (WRL w.e.) at each site. As for Cl^-, the excess NO_3^- load, LOAD*NO_3^-, was computed by difference.

$$\mathrm{LOAD^*NO_3^-} = \mathrm{LOAD} - \mathrm{NO_{3\,TOTAL}^-} - \left[\mathrm{BULK} - \mathrm{NO_3^-} \times \mathrm{WRL\ w.e.}\right]. \quad (3)$$

By calculating a bulk NO_3^- concentration for the WRL, variability in NO_3^- concentrations between deposition events (Tranter et al., 1986; Maupetit and Delmas, 1994) is eliminated. Bulk concentrations of NO_3^- are derived using time series of precipitation (in w.e.) generated from snow depth records 400 m downglacier from ML10 and at ML2 (Wadham and Nuttall, 2002) and NO_3^- concentrations of freshly deposited snow recorded in Ny Ålesund by Det Norske Meteorologiske Institutt (Fig. 2). The product of

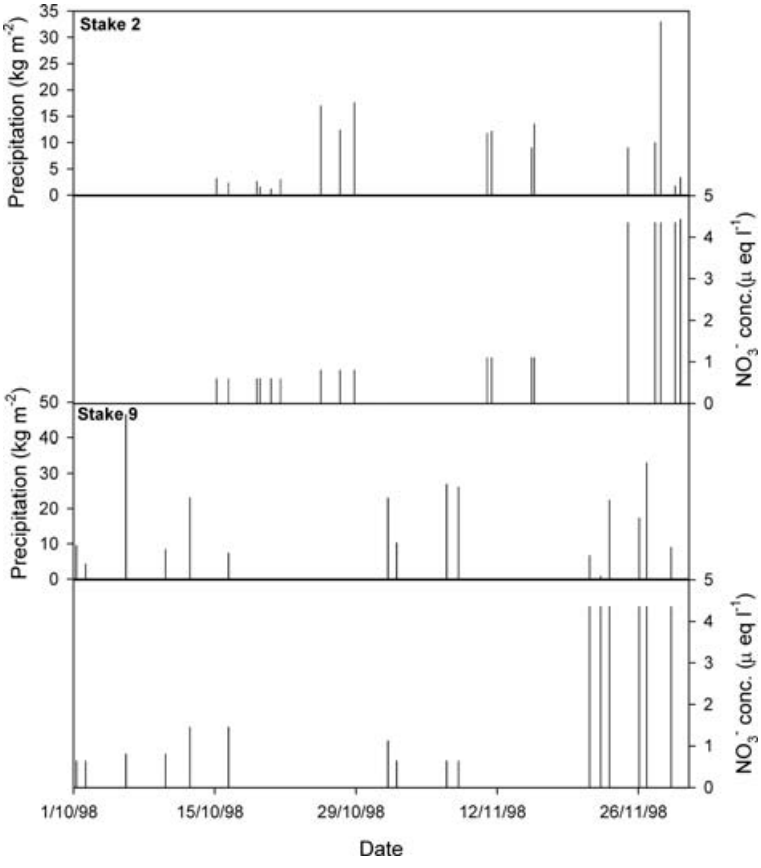

Fig. 2. Temporal variation in water equivalents of precipitation recorded at ML2 and 400 m downglacier from ML10 prior to the November rain-on-snow events and the corresponding NO_3^- concentrations in precipitation measured at Ny Ålesund (Norsk Meteorologisk Instututt, Tørseth et al., 1999).

the NO_3^- concentration and w.e. of a precipitation event, equal to NO_3^- load, was divided by the total w.e. of precipitation prior to the early winter rain-on-snow events, to give the bulk NO_3^- concentration. These calculations generated bulk concentrations for NO_3^- of 2.1 and 2.0 for ML2 and near-ML10, respectively.

It is appreciated that a number of factors may introduce error to calculated bulk NO_3^- concentrations. First, spatial variation in atmospheric deposition may produce variable NO_3^- inputs to each site (Tranter et al., 1987). Since NO_3^- is derived predominantly from remote non-marine sources, the spatial variability in its depositional flux varies less than sea salt (e.g. Cl^-, and Na^+) and predominantly crustal derived species (e.g. Ca^{2+}) (Tranter et al., 1987; Bales et al., 1989; Williams and Melack, 1991; Williams et al., 1992; Rohrbough et al., 2003). The difference between bulk NO_3^- concentrations for ML2 and 500 m downglacier of ML10 (2.1 and 2.0 μeq l^{-1}, respectively) values gives horizontal coefficients of variation of 5% for NO_3^-. This value is smaller than coefficients of variation reported elsewhere in catchment scale studies (range = 9–30%; mean = 15.5%; Rohrbough et al., 2003) and is lower than former estimates made at the field site of ~25% (Hodson, personal communication 2004). In order to better account for spatial variation in NO_3^- input to the glacier, we impose a 25% variation on the value of ~2 μeq l^{-1}, giving maximum and minimum atmospheric NO_3^- concentrations at each site of 2.5 and 1.5 μeq l^{-1}. These values are used to generate a range of potential atmospheric/excess NO_3^- loads for each site.

Second, sublimation may have affected NO_3^- concentrations in the WRL. NO_3^-, found in some studies to be volatilized during sublimation (Hogan et al., 1985; Mulvaney et al., 1998; Pomeroy et al., 1999), would have decreased in concentration in the WRL. Hence, bulk concentrations of NO_3^- may be slightly overestimated, since they were calculated from fresh precipitation. Research elsewhere has shown the effect of sublimation to be $30 \pm 15\%$ at accumulation rates of 62 kg m yr^{-1} and to become less significant with increasing accumulation rates (Weller et al., 2004). Since accumulation rates reported here are an order of magnitude higher than those documented by Weller et al. and a large proportion of solute in the WRL is contained within ice layers and superimposed ice, we consider the effect of sublimation on NO_3^- concentrations to be minimal.

Third, dry deposition of NO_3^- is not accounted for in this partitioning scheme and may also alter NO_3^- concentrations in freshly deposited snow. The NO_3^- input due to dry deposition can be estimated using eq. 4.

$$F = (v_d C) \times \text{no. PPT FREE DAYS}, \quad (4)$$

where F is depositional flux of the solute species (μmol m^{-2}), v_d is the depositional velocity of the species (in m s^{-1}) and C is its atmospheric concentration (in μg N m^{-3}). These variables are multiplied by the number of precipitation-free days (no. PPT-FREEDAYS) between 1 October 1998 (DOY 274), when accumulation began and 29 November (DOY 333), when the last rain-on-snow event was recorded in winter 1998/1999. We employ concentrations of ($NO_3^- + HNO_3$) in air measured by the Norwegian Institute for Air Research at Zepellin Station (485 m asl) 2 km away. The v_d of HNO_3 (gives maximum estimate, since v_d for NO, NO_2, NO_3^- and peroxyacyl nitrates or PAN are generally smaller; Cadle et al., 1985) is prescribed an approximate mean value of 1 m s^{-1}, compiled from a range of experimental values under different snow temperature and wetness conditions (Cadle et al., 1985; Dasch and Cadle, 1986; Johansson and Granat, 1986). The depositional flux of NO_3^- is also estimated using minimum and maximum values for v_d of 0.4 and 5.7 m s^{-1}, respectively (Johansson and Granat, 1986). These are based on experimental values for dry snow at -5 °C (= mean glacier air temperature on precipitation-free days) and for a mixture of snow and water. The v_d of Cl^- is 4.3 m s^{-1} (Dasch and Cadle, 1986). These calculations indicate that 3–17 μeq NO_3^- m^{-2} were dry deposited on the glacier during the WRL accumulation period. These quantities represent 1–3% of the mean NO_3^- load in the WRL at ML2–ML10. This very small magnitude of NO_3^- dry deposition suggests that neglecting this component of the WRL NO_3^- load will have a negligible effect on the partitioning of NO_3^- into atmospheric and excess components.

3. Results

3.1. Snow pack processes

The WRL accumulated between DOY 272 (29 September) and DOY 334 (30 November), 1998. The rain-on-snow events that caused the WRL to develop in 1998 have already been documented in Wadham and Nuttall (2002). In summary, these episodes comprised three discrete events on 22–23, 25–27 and 29 November. Complete warming of the snowpack to 0 °C was observed at ML2 and the top 0.3 m of the snowpack attained 0 °C close to ML10. Ice lenses and WRS were common in the lower 0.6 m of all sampling sites, with superimposed ice also being formed at ML2, ML5 and ML7. No melt was generated by subsequent warm events in winter 1998/1999 (Wadham and Nuttall, 2002).

Dust horizons were evident in the stratigraphy of all snow pits, where maximum concentrations of ~13 mg l^{-1} were derived by weighing the mass of aerosol acquired by filtration of a known volume of melted snow sample. Significant debris concentrations were also observed in superimposed ice, particularly at ML2. ESEM images of aerosol in superimposed ice samples (Fig. 3a) show particles sizes of 50–200 μm, although several of these particles appear to be clumps of smaller (<25 μm) particles. This demonstrates that snow debris was mainly local in origin, since a diameter of <2–4 μm is required for long-range transport (Kuhn, 2001). EDX spectra show that the mineralogical composition of debris in the same samples comprises mainly Al and Si. Smaller quantities of K, Mg, Na and Ca also exist (Fig. 3b). The peak in carbon is an artefact of the SEM sample preparation process, during which samples are carbon coated.

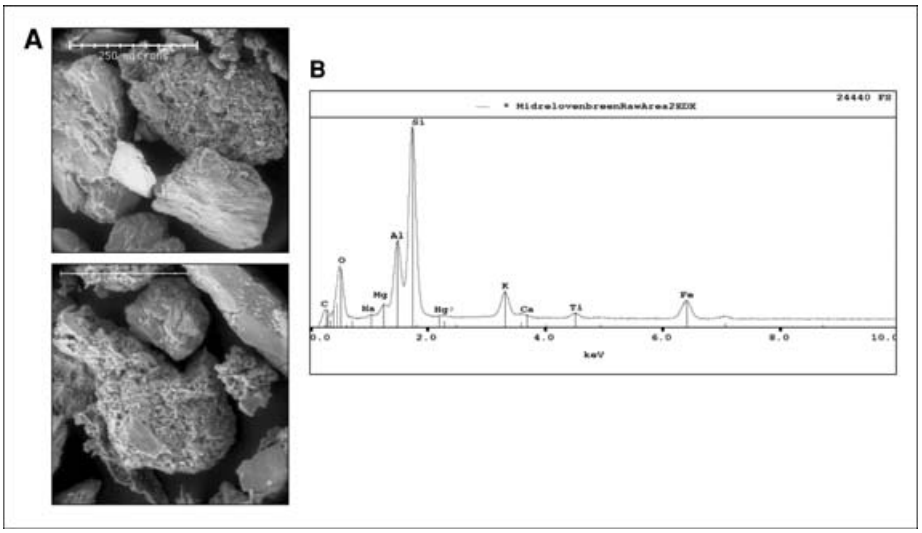

Fig. 3. (a) ESEM micrographs of the Midre Lovènbreen aerosol contained in superimposed ice Samples 1 and 2 (b) EDX spectrum derived from the Midre Lovènbreen superimposed ice Sample 1.

Examination of the EDX elemental distribution maps (not presented) for Sample 1 indicates the presence of several different mineral types, namely, quartz, plagioclase (Na–Ca) feldspars and phyllite. The presence of secondary calcite is confirmed by results of dissolution experiments, in which significant concentrations of Ca^{2+} are released and matched by similar concentrations of HCO_3^- (Table 1). This inference is consistent with the local catchment lithology (see earlier). Although no nitrogen was detected by SEM in aerosol samples, elemental analysis indicated a N content of 0.22% (∼2200 ppm) and a C content of 2.61% (giving a C:N ratio of ∼10:1). This N content is higher than the typical percentage N content of limestone, mica schist and phyllite (all components of the Midre Lovènbreen lithology), which fall within the ranges 0.002–0.03, 0.001–0.05 and 0.02–0.09%, respectively (Holloway and Dahlgren, 2002). The most likely reason for this discrepancy is the inclusion of organic material from soils in the aerosol. The similarity of the C:N ratio of debris to typical C:N ratios of organic particulate matter at the earth's surface is consistent with this interpretation (Guildford and Hecky, 2000).

3.2. Solute processes

The down-pit variation in the concentrations of NO_3^- and Cl^- at sampling sites is displayed alongside the snowpack stratigraphy in Fig. 4. Snowpack w.e. are also displayed. The down-profile variation in Ca^{2+} is not displayed, but shows similar trends to Cl^-. Both NO_3^- and Cl^- display the same general trends in load with snow depth. Elevated concentrations of solutes are evident at the base of the pack at ML2, ML5 and ML7 corresponding to the superimposed ice layer and WRS. Peak solute concentrations at ML10 occur above the snowpack base, corresponding to the position of ice lenses.

The total and atmospheric WRL Cl^-, NO_3^- and Ca^{2+} loads are shown in Fig. 5. Error bars indicate uncertainty in load calculations associated with chemical analysis and density measurements. For NO_3^-, spatial variation in the atmospheric NO_3^- input is also included in the uncertainty. Excess loads are presented in Fig. 6. Total loads of Cl^- and Ca^+ generally increase with w.e. (Fig. 5), suggesting their main origin is wet as opposed to dry deposition. Total loads of NO_3^- only display an increase

Table 1. Concentrations of solutes (in μeql$^-$1) released during dissolution experiments after 1 hr and 120 hr (* denotes that species have been corrected for the sea salt input)

	$*SO_4^{2-}$ Time (hr)		Cl^- Time (hr)		$*NO_3^-$ Time (hr)		$*NH_4^+$ Time (hr)		$*Na^+$ Time (hr)		$*K^+$ Time (hr)		$*Mg^{2+}$ Time (hr)		$*Ca^{2+}$ Time (hr)		HCO_3^- Time (hr)	
	1	120	1	120	1	120	1	120	1	120	1	120	1	120	1	120	1	120
Experiment 1	5.1	6.0	9	9	3.5	4.8	2.2	1.9	0.1	0.4	3	3.9	1.2	3.3	20	14	18	10
Experiment 2	5.1	11.5	5	10	4.7	6.8	3.1	3.4	3	1	3.3	4.4	1.1	4.8	105	230	105	230
Experiment 3	4.9	7.0	19	17	2.4	3.2	2.7	3.1	0	0.8	7.2	7.7	1.4	4.8	11	18	11	23

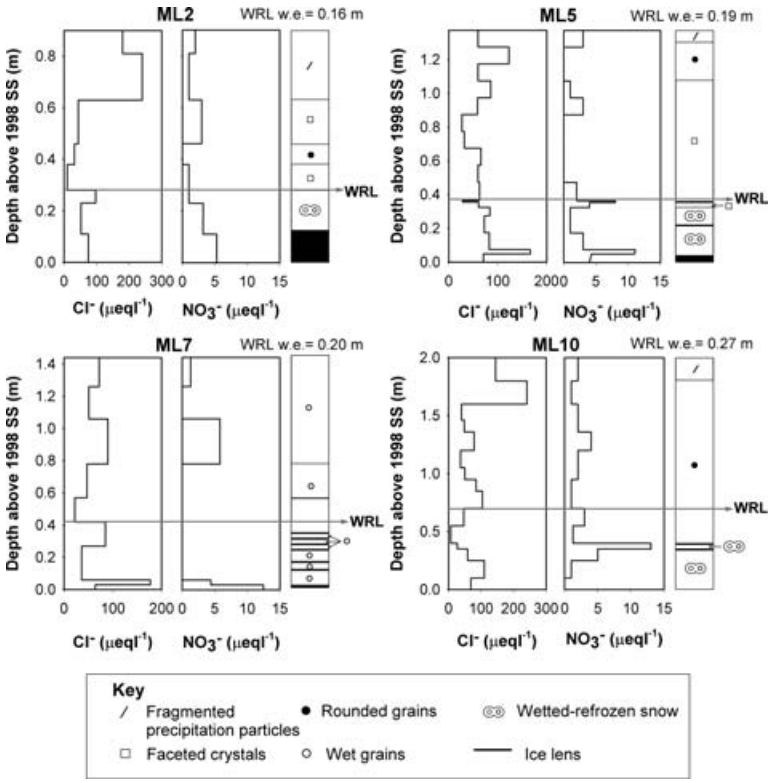

Fig. 4. Profiles of snowpack Cl^- and NO_3^- concentration and physical stratigraphy at each sampling site.

Table 2. Percentage contribution of excess WRL loads of NO_3^- and Ca^{2+} to the total NO_3^- and Ca^{2+} loads in the WRL

	% Contribution			
	ML2	ML5	ML7	ML10
NO_3^-	39–64	29–58	51–18	11–56
Ca^{2+}	77–78	78–79	78	78–90

between ML7 and ML10. The excess component dominates loads of Ca^{2+} at all sites (Table 2). A significant, albeit variable proportion of NO_3^- at all sites, (e.g. 253–410 μeq m^{-2}/∼39–64% of total NO_3^- at ML2; Table 2), cannot be accounted for by atmospheric deposition. The uncertainty in NO_3^- loads make it difficult to establish a trend in the two components with altitude.

Initial (after 1 hr) and final (120 hr) concentrations of SO_4^{2-}, Cl^-, NO_3^-, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+} released from debris in Experiments 1–3 are presented in Table 1. Concentrations of Na^+, K^+, Mg^{2+} and Ca^{2+} have been corrected for the sea salt derived component using standard ratios of each ion to Cl^- in seawater (Holland, 1978). Concentrations of NO_3^-, NH_4^+ and SO_4^{2-} have been corrected for the atmospheric component using the ratio of the ion to Cl^- in snow collected during the same field period (∼0.09 for N:Cl^-, 0.05 for SO_4^{2-}:Cl^-). HCO_3^- concentrations are calculated from the charge balance for each experiment.

The release of cations K^+, Mg^{2+} and Na^+ is consistent with the predominantly alluminosilicate lithology of much of the catchment. The significant concentrations of Ca^{2+} and HCO_3^- released in all experiments, however, also point to the dissolution of calcite in the aerosol. A key feature of the dissolution results is the release of significant concentrations of both NO_3^- and NH_4^+ (up to 6.8 and 3.1 μeq l^{-1}, respectively) from debris (Table 1). Quantities of NO_3^- and NH_4^+ presented in Table 1 give theoretical percentage N contents in the aerosol dissolved in Experiments 1, 2 and 3 of 0.013, 0.012 and 0.015%, respectively. These values are considerably lower than the measured N content of the material at 0.22%, and indicate that only ∼5% of the nitrogen present in the debris was dissolved in experiments.

4. Discussion—sources of excess NO_3^- and Ca

The most probable source of excess Ca^{2+} in the WRL (∼78% at all sites; Table 2) is the dissolution of debris in snow. This is in line with previous studies (Maupetit and Delmas, 1994; Delmas et al., 1996) and is consistent with results from the dissolution experiments on snowpack debris, in which Ca^{2+} was the dominant ion released in all three experiments. The balance of Ca^{2+} and HCO_3^- indicates the preferential dissolution of calcite, present in trace quantities in the predominantly silicate snowpack aerosol (Fig. 3b) (White et al., 1999). Maximum and minimum estimates of Ca^{2+} release in μeq Ca^{2+} m^{-2} are calculated. These are derived using the product of the final concentration of Ca^{2+}

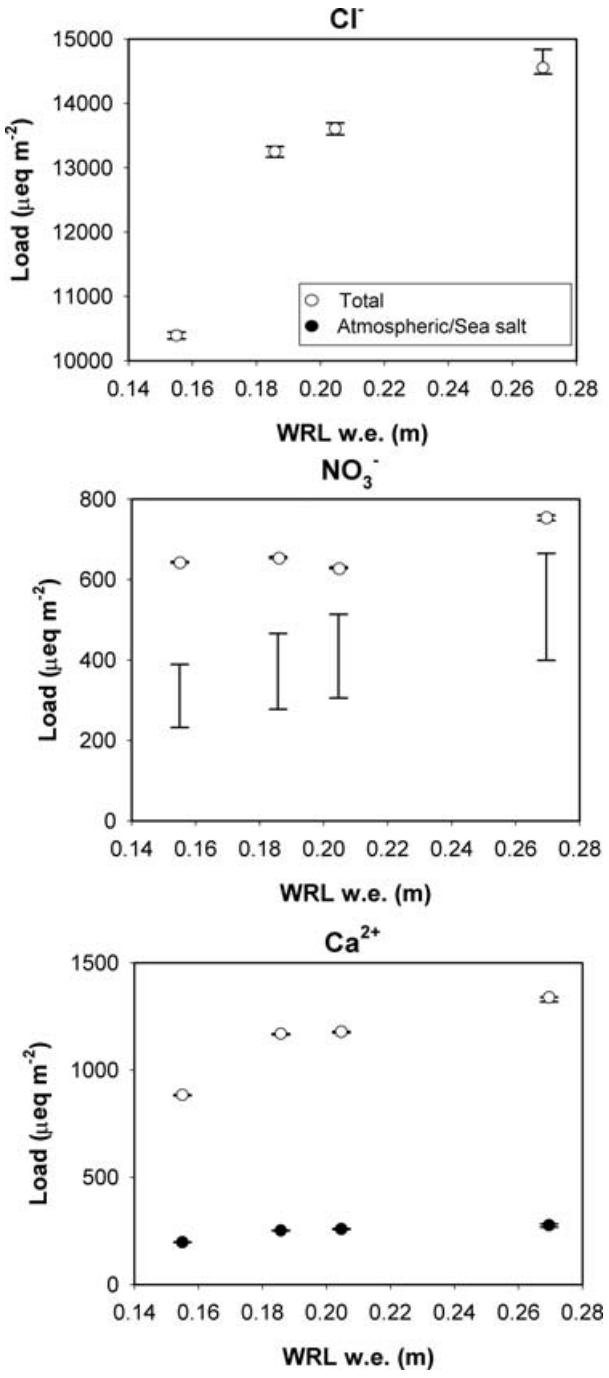

Fig. 5. Variation of total and atmospheric/sea salt Cl^-, NO_3^- and Ca^{2+} loads with site WRL water equivalents.

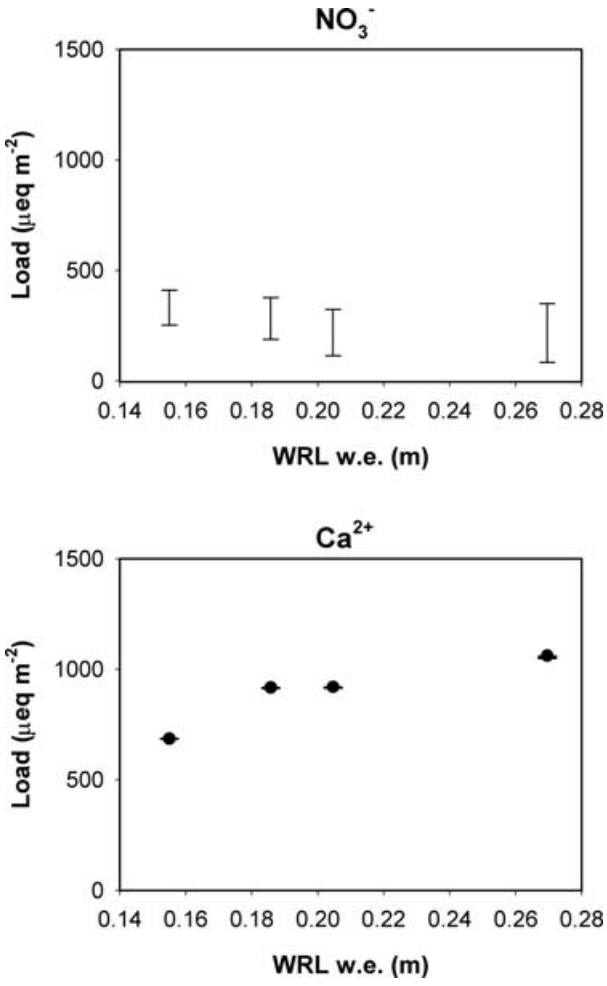

Fig. 6. Variation of excess Cl^-, NO_3^- and Ca^{2+} loads with site WRL water equivalents.

released in Experiments 2 and 1, respectively, and the w.e. in the WRL at each sampling site. These estimates were subsequently adjusted to take account of the higher concentrations of aerosol used in the experiments (530 and 630 mg l^{-1}, respectively, in Experiments 1 and 2) compared to those observed in snow in the field (13 mg l^{-1}). These calculations give Ca^{2+} yields that approximately span the range of excess Ca^{2+} loads observed at sites ML2–ML10 (Fig. 7). The slight increase in excess Ca^{2+} loads with WRL w.e. also suggests that the dissolution of snowpack debris is somehow related to accumulation. Since the loads of acid nitrate and sulphate species also relate directly to w.e., this association may relate to the proton loading of the snowpack and potential for acid hydrolysis of crustal aerosol.

NO_3^- loads in the WRL are dominated by the atmospheric component at all sites apart from ML2 (Figs 5, 6 and Table 2). This is consistent with the results of other studies and reflects the deposition of acidic nitrogen pollutants, HNO, NO_2, NO_3^-, etc. over Svalbard during the snow accumulation period (Semb et al., 1984; Simoes and Zagorodnov, 2001).

The generally smaller loads of excess NO_3^- (Fig. 6) have not been reported elsewhere. There are a number of possible explanations for these trends.

(1) **Underestimation of atmospheric nitrate due to preferential elution**: Preferential elution of solute during snowmelt is

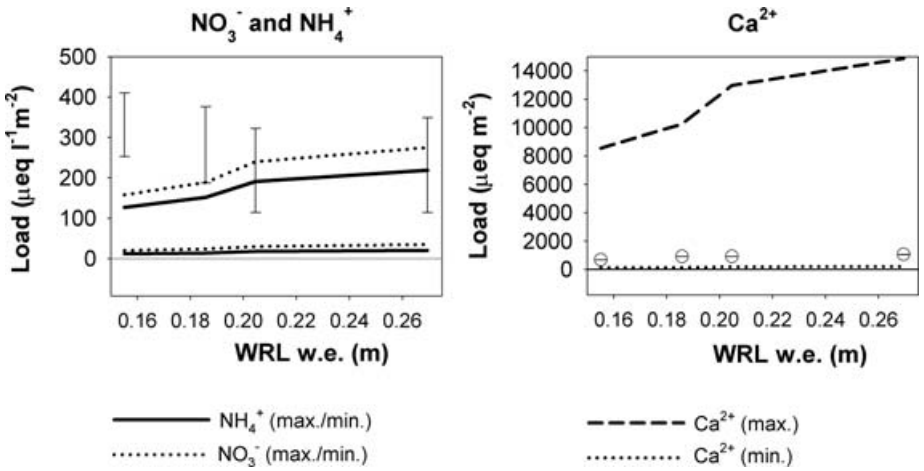

Fig. 7. Comparison of excess NO_3^- and Ca^{2+} loads (see Fig. 4) with potential (a) NO_3^-, NH_4^+ and (b) Ca^{2+} release from snowpack aerosol, as estimated from dissolution experiments.

a widely documented phenomenon (Brimblecombe et al., 1985; Tsiouris et al., 1985; Tranter et al., 1992), and results in solutes being eluted from the snowpack with varying degrees of efficiency. Preferential elution as a consequence of vertical meltwater flow during the rain-on-snow events can be disregarded as a mechanism for altering NO_3^- concentrations in the WRL, since the entire thickness of this layer was sampled at all sites. Preferential elution of NO_3^- during lateral meltwater flow, however, could have caused a change in solute concentrations in the WRL. The variable thicknesses of superimposed ice present at ML2–ML7 (0.05–0.9 m) indicate that a water layer formed at the base of the snowpack at all these sites during the rain-on-snow events. Drainage at the snowpack base could, therefore, have enabled the elution of more mobile solutes. In all studies to date, Cl^- has been identified as the least mobile of all major ions in snow, with original concentrations being preserved in semi-melted snow profiles (Eichler et al., 2001). In this study, concentrations of Ca^{2+} follow a similar trend to Cl^-, suggesting that preferential elution of this ion is likewise of minor importance. Preferential elution of NO_3^- from neighbouring snow to the sampled profile by water flow at the snowpack base might explain the unusually high total NO_3^- loads at ML2 and ML5, and why these do not follow the trend of increase with altitude displayed by Ca^+ and Cl^-. The steady increase displayed by the latter two ions between ML2 and ML10 is consistent with their being relatively unaffected by preferential elution in this study. Only between ML7 and ML10 do trends in total NO_3^- follow those in total Ca^+, suggesting that NO_3^- enhancement by preferential elution no longer masks the expected increase in total solute loads with altitude between these two sites. Stratigraphic profiles from ML10 indicate less extensive melting at this site; no superimposed ice was formed and only small ice layers were present in the snow profile (Fig. 4). Under these conditions, NO_3^- elution during lateral meltwater drainage would be expected to exceed that at ML2–7, due to the increased efficiency of elution coincident with a decrease in melting (Davies et al., 1987). Instead, there is no significant difference between the amount of excess NO_3^- present at ML7 and ML10. This suggests that the excess NO_3^- component at ML10 and potentially other sites may not be solely accounted for by preferential elution and that there may be a source of non-atmospheric NO_3^- present.

(2) **Heterotrophic organisms**: Although excretion by heterotrophic organisms grazing on organic N-substrates may enhance snowpack inorganic N loads (Jones, 1991), the low level of animal activity on the glacier makes this unlikely to be a major supplier of inorganic N to the snowpack.

(3) **Release from debris**: It has already been established from excess Ca^+ loads that debris is present in the snowpack and weathers chemically during melting. The dissolution of snowpack debris and release of exchangeable N from debris surfaces, including soil particles, is a possible explanation for some of the excess NO_3^- present at sampling sites. What is unclear, however, is the mechanism by which this NO_3^- is added to snow. Aeolian crustal aerosol is already known to enhance rates of atmospheric NO_3^- deposition by absorbing atmospheric HNO_3 and NO_2 (Wolff, 1984; Wu and Okada, 1994; Shrestha et al., 1997; Beine et al., 2003). This process, however, is already accounted for in our atmospheric/excess partitioning scheme, which uses NO_3^- in freshly deposited snow samples to correct total NO_3^- for the atmospheric component. It cannot, therefore, explain the presence of excess NO_3^- in snow. An alternative explanation is that upon wetting, the dissolution of snowpack debris and exchange of adsorbed species releases some nitrogen, in addition to Ca^{2+} and other solutes. Support for this hypothesis derives from dissolution experiments described earlier, which indicate the release of 2–7 μeq l^{-1} of NO_3^- and 2.5–4 μeq l^{-1} of NH_4^+ from crushed and non-crushed snowpack debris from Midre Lovènbreen (Table 1). While the NH_4^+ is believed to derive from the dissolution of NH_4^+-containing minerals (e.g. micas, K-feldspars, present in the catchment lithology) and/or

mineralization of organic matter (Holloway and Dahlgren, 2002) in the aerosol, the source of the NO_3^- is uncertain. NO_3^- is not released from either of these two sources and NO_3^--containing minerals are not present in the catchment lithology. One possibility is that the NO_3^- in both field and experimental samples is produced by oxidation of NH_4^+ during nitrification (eq. 5).

$$2NH_4^+ + 3O_2 \Leftrightarrow 2NO_2^- + 2H_2O + 4H^+$$
$$2NO_2^- + O_2 \Leftrightarrow 2NO_3^-. \quad (5)$$

Several studies report the conversion of NH_4^+ to NO_3^- by nitrifying bacteria in snow (Baron et al., 1995; Campbell et al., 2000). Others have used this process to explain NO_3^- surplus in runoff from snow-covered catchments (Sueker et al., 2001; Tockner et al., 2002; Hodson et al., 2005). Some studies, however, fail to report nitrifying bacteria in snow (Brooks et al., 1993; Williams et al., 1996). This suggests that nitrification may not be universal, but dependant on input to the snowpack of proglacial/sub-nival soil particles, where nitrifying bacteria are common (Williams et al., 1996; Bieber et al., 1998). Debris at the glacier site is known to contain a component of local proglacial cryosols (Teinilä et al., 2003), explaining the relatively high percentage N contents, and it is likely that nitrifying bacteria are transferred to the experimental solution via the debris. If these bacteria remain active during sediment storage or are reactivated upon wetting during the experiments, some NH_4^+ released from silicate minerals/organic matter would be oxidized to NO_3^- (eq. 5). Since debris used in these experiments released some $^*NH_4^+$, there is a plausible source of $^*NO_3^-$ via nitrification.

As for Ca^{2+}, estimates of NO_3^- release in μeq NO_3^- m^{-2} can be made using experimental data. Maximum and minimum estimates of NO_3^- release are derived from NO_3^- concentrations released in Experiments 2 (6.8 μeq l^{-1}) and 3 (3.2 μeq l^{-1}), respectively (Fig. 7). Calculations of minimum and maximum NH_4^+ release from snowpack aerosol are also shown in Fig. 7. The envelope of NO_3^- release is roughly in line with estimates of excess NO_3^- at ML7 and ML10, with higher excess NO_3^- at ML2–5 reflecting possible preferential elution of NO_3^- at these sites. Further oxidation of NH_4^+ released from the aerosol to NO_3^- would effectively double this yield.

These findings have considerable significance for studies of nutrient cycling in Arctic catchments, where dry deposition of debris to the snowpack is significant. Since most rock types do contain a small proportion of nitrogen and soil may also be a component of the aerosol, some degree of enhancement would be expected in most catchments. The soil-derived material effectively inoculates the glacier with bacteria (e.g. nitrifiers) and exchangeable forms of N. This fertilization may be vital for the glacier surface ecosystem, e.g. cryoconite holes, that thrive on the glacier (e.g. Sawström et al., 2002; Hodson et al., 2005). In this study the N-containing material is probably a combination of NH_4^+-containing silicates such as mica schist and phyllite, together with organic material present in carbonates and soil. Similar N enhancement processes may occur in different supraglacial environments where debris is present, for example cryoconite holes and glacial ice. There are implications in the latter instance for the interpretation of N-based paleo-environmental records in deep ice cores where dust layers are present (Legrand et al., 1999; Röthlisberger et al., 2000; Ruth et al., 2002), since this material may weather chemically to yield NO_3^- and NH_4^+. In the dissolution experiments performed here, only ~5% of the nitrogen present in the debris was dissolved, indicating that further release is possible. Hence, snowpack debris may under certain conditions constitute a semi-sustainable nutrient source for micro-organisms.

5. Conclusions

The provenance of three solutes (Cl^-, Ca^{2+} and NO_3^-) in the lower wetted-refrozen part of an Arctic snowpack at four contrasting sites is examined in detail. Cl^- is assumed to derive entirely from the atmosphere, in the form of sea salt. Ca^{2+} and NO_3^- loads are partitioned into their respective sea salt/atmospheric components and an excess component. Excess Ca^+ accounts for ~80% of total Ca^{2+} loads, acquired by chemical weathering of locally derived snowpack crustal aerosol. NO_3^- loads also have a significant excess component (up to 64% of total loads). Some of this NO_3^- enhancement may derive from preferential elution processes during lateral meltwater drainage at sampling sites and is of atmospheric origin. This is particularly true of the lower altitude sites, where a water layer formed at the base of the snowpack during the rain-on-snow events. A component of excess NO_3^- is also believed to be released alongside Ca^{2+} from snowpack debris, an inference strongly supported by dissolution experiments that show NO_3^- and NH_4^+ yields from snowpack aerosol in line with field excess NO_3^- loads. The mechanism by which NO_3^- is acquired from the debris, however, is unclear. One possibility is that NH_4^+ is released from organic matter and NH_4^+-containing minerals in snow debris, some of which is subsequently converted to NO_3^- by nitrifying bacteria present on soil material in the aerosol. This is the first study to date to indicate snowpack debris as a possible source of nitrogen in some Arctic snow-covered catchments. It has significance given the low levels of bio-available N species in these environments.

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