Transformations of snow chemistry in the boreal forest: accumulation and volatilization

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Abstract:

This paper examines the processes and dynamics of ecologically-important inorganic chemical (primarily NO_3-N) accumulation and loss in boreal forest snow during the cold winter period at a northern and southern location in the boreal forest of western Canada. Field observations from Inuvik, Northwest Territories and Waskesiu, Saskatchewan, Canada were used to link chemical transformations and physical processes in boreal forest snow. Data on the disposition and overwinter transformation of snow water equivalent, NO_3^-, SO_4^{2-} and other major ions were examined. No evidence of enhanced dry deposition of chemical species to intercepted snow was found at either site except where high atmospheric aerosol concentrations prevailed. At Inuvik, concentrations of SO_4^{2-} and Cl^- were five to six times higher in intercepted snow than in surface snow away from the trees. SO_4-S and Cl loads at Inuvik were correspondingly enhanced three-fold within the nearest 0·5 m to individual tree stems. Measurements of snow affected by canopy interception without rapid sublimation provided no evidence of ion volatilization from intercepted snow. Where intercepted snow sublimation rates were significant, ion loads in sub-canopy snow suggested that NO_3^- volatized with an efficiency of about 62% per snow mass sublimated. Extrapolating this measurement from Waskesiu to sublimation losses observed in other southern boreal environments suggests that 19–25% of snow inputs of NO_3^- can be lost during intercepted snow sublimation. The amount of N lost during sublimation may be large in high-snowfall, high N load southern boreal forests (Quebec) where 0·42 kg NO_3-N ha^{-1} is estimated as a possible seasonal NO_3^- volatilization. The sensitivity of the N fluxes to climate and forest canopy variation and implications of the winter N losses for N budgets in the boreal forest are discussed. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS   snow chemistry; nitrogen cycle; sulphate; arctic aerosol; interception; boreal forest; snow accumulation

INTRODUCTION

The productivity of boreal forests is determined by both the physical environment and the availability of nutrient sources. Nutrient sources are extremely wide-ranging in species and elemental composition (C, N, S, K, Ca, P) but nitrogen (N) is the limiting factor for primary productivity of many boreal forests (Boring *et al.*, 1988). Soil moisture, including that contributed by snowmelt, controls evapotranspiration from trees and therefore influences primary production through droughts in the southern boreal forest (Elliott *et al.*, 1998). The N species most readily available for the photosynthesis of organic matter are the inorganic forms NO_3

and NH_4. The rate at which these species are utilized often depends on their concentration whilst the total production (biomass) of the forest is related to the total amount of inorganic N available. In ecosystems where the snow N input dominates annual deposition, the spatial variation of snow therefore controls the spatial distribution of primary productivity (Bowman, 1992). In the case of boreal forests, N to snow is typically less than one-half of the annual input (Stoddard, 1994). S inputs to snow result in high SO_4^{2-} concentrations in snow in the eastern boreal forest of North America (Jones, 1987; Semkin and Jeffries, 1988), where this has been implicated in changes in aquatic chemistry (Jeffries, 1990; Papineau and Haemmerli, 1992). Though anthropogenic SO_4-S in eastern North America is less of a current concern because of improved local emission controls, SO_4-S loads in snow measured in 1992 at the extreme northern edge of the boreal forest (Inuvik region) can exceed the maximum late 1980's winter loads of rural Michigan (Pomeroy *et al.*, 1993).

Transformations of major ions in cold snow have been identified by Delmas and Jones (1987); Pomeroy *et al.* (1991); Laberge and Jones (1991); Jones *et al.* (1993); Pomeroy *et al.* (1995); Cragin and McGilvary (1995) and Pomeroy and Jones (1996) as due to ice crystal sublimation and phoretic scavenging to blowing snow crystals. The results are often contradictory, with field experiments examining wind-blow snow indicating loss of NO_3^- and those examining surface snow suggesting loss of SO_4^{2-}. Some of the contradiction may be attributed to the difficulties of collecting field data that reflect the effects of single processes in extreme, remote environments. In a controlled laboratory experiment, Pomeroy and Jones (1996) found an increase in concentrations of SO_4^{2-} and Cl^- during sublimation from fixed snow suggesting conservative behaviour, but no change in the NO_3^- concentration, suggesting a loss of NO_3^- ion proportional to the sublimation of ice. Conversely, in another cold room experiment, Cragin and McGilvary (1995) found NO_3^- and Cl^- to be conserved whilst SO_4^{2-} was lost during sublimation. The reasons for differences in results are not known but may be due to differing boundary conditions in the cold room, atmospheric and snowpack concentrations of reactive species or sampling error.

The objectives of this paper are to: i) review processes that affect the overwinter accumulation and loss of ecologically-important inorganic ions from boreal forest snow ii) present field measurements of accumulation and loss of these chemical species iii) discuss mechanisms that might control the ion fluxes, their sensitivity to physical snow processes and the influence of forest canopy cover and climate on the processes.

FIELD SITES

Field observations were obtained at two sites representative of southern and northern boreal forest environments in western Canada. The sites include Inuvik, Northwest Territories (NWT) (69°N, 132°W; 20 m.a.s.l.) and Waskesiu, Saskatchewan (54°N, 103°W; 500 m.a.s.l.) as shown in Figure 1. Both sites are remote from local sources of atmospheric emissions of NO_3-N and SO_4-S, though Inuvik is subject to 'arctic haze' and Waskesiu is subject to deposition from industries and agriculture on the nearby Canadian Prairies. Inuvik is representative of the cold, sub-humid, permafrost climate regime of the boreal forest subarctic margin, characterized by long cold winters with low annual snowfall (Table I). North of this site lies the windier, drier and less productive Arctic tundra. In the Inuvik area, sampling was carried out in open black

Table I. Climate characteristics for the boreal forest study sites. Temperature and precipitation data are from the Atmospheric Environment Service. DJF refers to December, January and February, while NMA refers to November, March and April

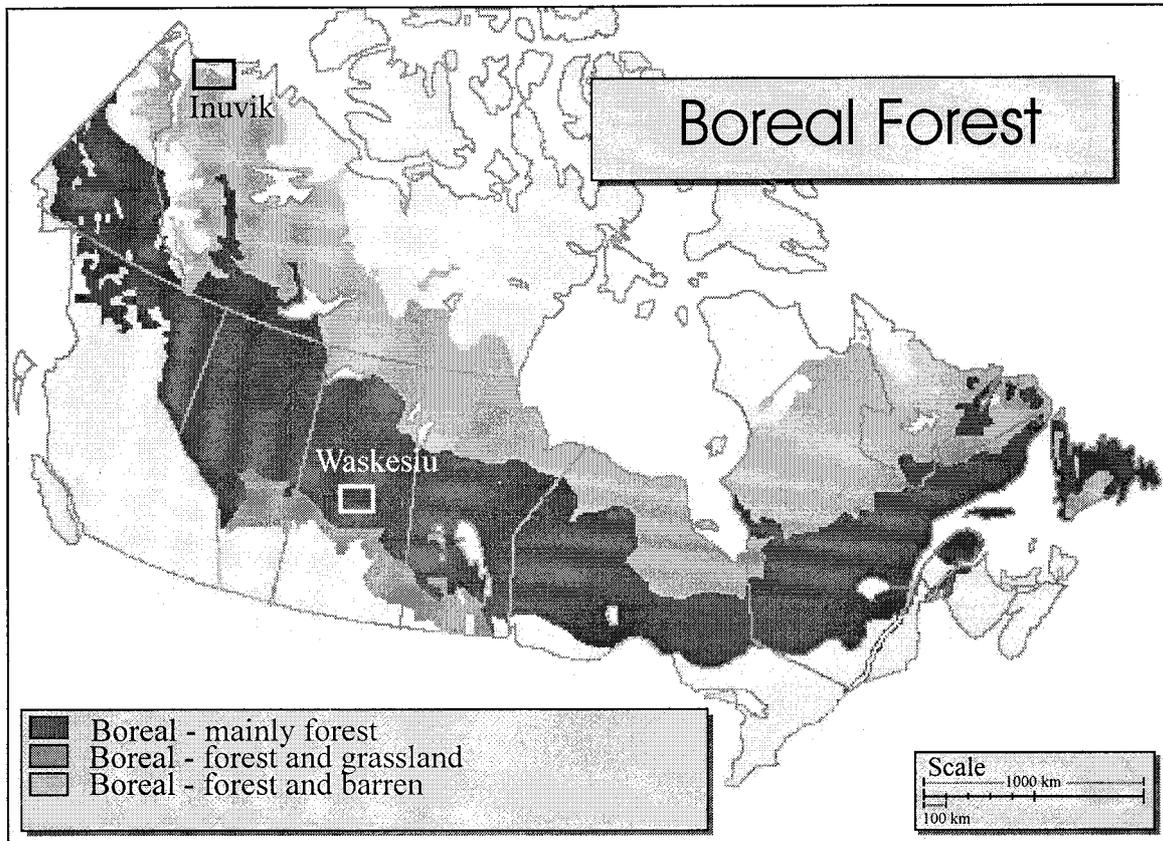|	Inuvik, Northwest Territories	Waskesiu, Saskatchewan
Mean monthly air temp (DJF), °C	−29	−18
Mean monthly air temp (NMA), °C	−20	−5
Air temperature <0 °C (months)	8	6
Annual snowfall (mm)	175	150

Figure 1. Location of sampling sites with respect to the boreal forest of western Canada

spruce forests in both the Havikpak and Trail Valley Creek basins (Pomeroy *et al.*, 1995; Pomeroy and Marsh, 1997). Waskesiu is located in a continental, sub-humid climate regime at the southern fringe of boreal forest, which has similar snowfall as Inuvik, but is warmer, having seasonally frozen soils and an earlier melt period (Table I). South of Waskesiu are the transitional aspen parklands and the semi-arid prairies where precipitation is lower and evaporation and soil nutrient status are higher. Sampling was conducted in the Beartrap Creek basin, within Prince Albert National Park, in dense, mature stands of black spruce, trembling aspen and jack pine.

METHODOLOGY

Field

Snow samples were obtained as follows. At Waskesiu in 1992, snow was sampled from characteristic landscapes (e.g. pine, spruce, aspen, open clearing) and from a vertical profile in a spruce canopy. Five landscapes were sampled along a horizontal canopy density gradient from open clearing (winter leaf area index, LAI = 0) to closed spruce canopy (LAI = 4·1). The stands are small, adjacent and in total extend over less than a 200 m transect. Snow samples and snow physical characteristics were collected from snow strata (up to four per pit), identified in six snow-pits for each landscape. Twenty intercepted snow samples were obtained from black spruce branches in a dense black spruce stand (LAI = 4·5) over a 4-m vertical profile using a portable elevator (Figure 2). The elevator platform was lifted by a hydraulic mechanism driven by storage batteries and hence did not contaminate the local environment. Sampling was carried out

Figure 2. Photograph of portable elevator and sampling method used to obtain intercepted snow samples in a black spruce stand. Note that the elevator is only extended during sampling so that the intercepted snow is otherwise undisturbed

by carefully removing most snow from several branches using a rinsed, Teflon scoop. To collect adequate sample for a particular height, several branch-fulls of snow had to be collected per collection bag. In all cases, samples were placed in HDPE bags, cleaned in dionised water, and then stored at temperatures below 0 °C.

As Inuvik in 1992, snow samples were obtained from snow-pits along four short (several metres) microtransects in various orientations from each of three spruce trees in a sparsely-wooded black spruce stand (LAI = 1·2) using the method described in Pomeroy *et al.* (1995). Snow pits were dug and cleaned with a Teflon scoop that had been rinsed in dionised water. Snow samples were immediately removed from distinctive strata (normally three) that corresponded to depth hoar, partially-metamorphosed snow and fresh snow. Depth, snow density and particle size was measured for each stratum. Bulk concentrations and loads reported here are calculated from averages weighted by the concentration, depth and density of each layer following the methodology of Pomeroy *et al.*

Winter leaf area index (LAI) is the cumulative plan area of stems and leaves (needles) over a unit area of ground. It was measured in winter for all sites using a LICOR LAI-2000 plant canopy analyser. The LAI-2000 uses the optical density of canopy and view angle to determine LAI. LAI is considered the most important measure of canopy cover in predictive models of snow interception (Hedstrom and Pomeroy, 1998).

Laboratory

All chemical analyses were conducted in the Central Chemistry Laboratory of the National Hydrology Research Institute, Saskatoon. Sample preparation, processing and handling were similar for each sampling site. Frozen samples were thawed and filtered the same day using 0·4 μm Nucleopore filters. Inuvik samples were stored in HDPE bottles which had been pre-washed, stored at 4 °C, and shipped in a refrigeration unit from the field sites to the laboratory for analysis. Holding and shipping time before analysis was less than one week. Waskesiu samples were returned to Saskatoon frozen. These samples were thawed, filtered and analysed the same day after storage at −25 °C in a cold room.

NO_3^-, SO_4^{2-} and Cl^- were determined using a Dionex 2010i ion chromatograph, Ca^+ was determined using a Perkin Elmer Models 460, 2380 and 5000 atomic absorption spectrophotometer (Marsh and Pomeroy, 1993; Pomeroy *et al.*, 1995). Quality assurance and quality control were evaluated using numerous blanks on scoops, bags, bottles, filters and analytical equipment. Results from the blank tests were consistently below detection limits (<0.07 mg l^{-1}), indicating that no measurable contamination of samples occurred. The level of precision and analytical limits of detection were at least an order of magnitude less than the concentrations measured in the snow samples. As NH_4^+ was not measured, a formal charge balance could not be conducted, however, the charge residual from the other major anions and cations was generally less than one-half of the magnitude of charge resulting from NO_3^-, with a sign suggesting that it was due to the unmeasured NH_4^+.

DEPOSITION TO SNOW

The processes of accumulation of ions in forest snow are important to this study as affected by forest canopy or micro-meteorological conditions. Dry deposition and wet deposition contribute chemical species to surface snow and to snow intercepted in forest canopies. The delivery of ions in falling snow ('wet' deposition) to snow covers is episodic and varies primarily at large scales but can be locally-affected by orography or open water bodies; such local-scale effects were not present at the relatively level and frozen sites studied. Wet deposition is normally considered the largest single input of atmospheric chemicals to snow in remote regions, though its input can be exceeded by snow relocation processes and associated scavenging in open environments (Pomeroy *et al.*, 1993).

Dry deposition to snow covers occurs continuously. Stoddard (1994) suggests that 40% of annual inputs of N in boreal regions occur as dry deposition. Winter seasonal NO_3^- dry deposition *near* the boreal forest comprised 17% of total deposition in northern Michigan, USA (Cadle and Dasch, 1987) and 5% at Turkey

Lakes in northern Ontario (Semkin and Jeffries, 1988). Sirois and Vet (1988) modelled a 27% seasonal dry deposition contribution for the same region as these two observational studies. There are no studies of dry deposition in the western boreal forest of North America, which is drier and more remote from industry. Dry deposition is affected both by atmospheric sources and surface conditions such as snow liquid water content, surface roughness, temperature, wind speed and snow surface area. The complex interactions between atmospheric chemical species and snow is expected to result in greater spatial variance for dry deposition to boreal forest snow than for wet deposition. Dry deposition is the vertical flux (F) of an atmospheric chemical species to the snow surface. It is operationally calculated as equal to a deposition velocity (v) times the atmospheric concentration (C), where $F = -vC$ (Chamberlain, 1966). The velocity v is composed of an aerodynamic component and a surface component that are added together as inverted 'resistances' (r), where $v = 1/(r_a + r_s)$. Aerodynamic resistance, r_a, varies inversely with the atmospheric friction velocity and aerodynamic surface roughness and resistance therefore varies with wind climatology and roughness of vegetation. Aerodynamic resistances for forests are relatively small, from 33 to 13% of that for open surfaces and at a 4 m/s wind speed range from 17 s/m for stable to 2·5 s/m for unstable atmospheres (Voldner *et al.*, 1986). Consequently, if surface resistance is small, forests are more efficient filters of aerosols and gases by dry deposition than are open sites.

Surface resistance, r_s, is important for gaseous deposition, for which it is often large, and depends upon the uptake of gases by snow. NO_3^- is often transported to and from snow crystals in a gaseous form of HNO_3 vapour. HNO_3 r_s is highest for cold snow, (5 s/m at $-18\,°C$) decreasing as snow wetness increases (1 s/m at $-3\,°C$) (Johansson and Granat, 1986). Wesely's (1989) model confirms that liquid water in snow controls NO_3-N dry deposition, with a decrease in resistance as temperatures increase above $-2\,°C$. Surface resistance for aerosols (containing SO_4^{2-}, Cl^- and/or Ca^+) is also small as they are readily incorporated through impaction and wind pumping into the snowpack (Granat and Johansson, 1983; Waddington *et al.*, 1996).

It is seen that snow wetness can strongly influence dry deposition of gaseous species such as HNO_3. In the boreal forest however, snow location may influence the aerodynamic resistance, r_s, as some snow is intercepted in the canopy throughout the mid-winter. Intercepted snow can remain in the canopy from several hours to several months after a snowfall (Pomeroy and Schmidt, 1993; Hedstrom and Pomeroy, 1998). Interception of snow increases with increasing canopy leaf area, whilst interception as a proportion of snowfall increases with decreasing size of snowfall event (Hedstrom and Pomeroy, 1988). Measurements at Waskesiu show as much as 70% of cumulative seasonal snowfall can be intercepted and stored in dense boreal spruce canopies by mid-winter (Pomeroy *et al.*, 1997). In more open pine and mixed aspen-spruce canopies this value drops to 40% and 6% respectively (Pomeroy and Granger, 1997). As snow becomes wet, its structure becomes weak and unloading occurs, therefore the length of time snow can remain intercepted depends on how consistently cold the climate is (Hedstrom and Pomeroy, 1998). Intercepted snow is subject to enhanced atmospheric exchange compared to surface snow with a surface areas up to 1800 times higher (Pomeroy and Schmidt, 1993) and ventilation velocities an order of magnitude higher than those on the ground (Claasen and Downey, 1995). To examine the potential significance of variable ventilation to dry deposition in cold boreal conditions, experimental data is presented from a boreal forest near Waskesiu from January, 1992 and a boreal forest near Inuvik from April, 1992.

At Waskesiu, snow interception is intermittent with snow remaining in the canopy for up to three or four weeks after a snowfall, depletion is due to rapid sublimation and then unloading when a warm air mass advects sufficient energy into the region (Pomeroy *et al.*, 1997). Waskesiu is south of strong influences from air masses containing arctic aerosols (Barrie, 1995), but is subject to air masses travelling from agricultural and petrochemical industrial zones on the Canadian prairies. A heavy snowfall preceded the measurements presented here, loading black spruce trees with intercepted snow, then consistently cold temperatures ($< -15\,°C$) persisted for ten days until measurements were made. The cold temperatures probably precluded significant biological activity and aqueous chemistry in the canopy. The length of time exposed and temperatures during exposure are typical of mid-winter in the southern boreal forest. Measurements were made from canopy bottom to top, providing a wide range of wind exposure and stability. Canopy tops sustain
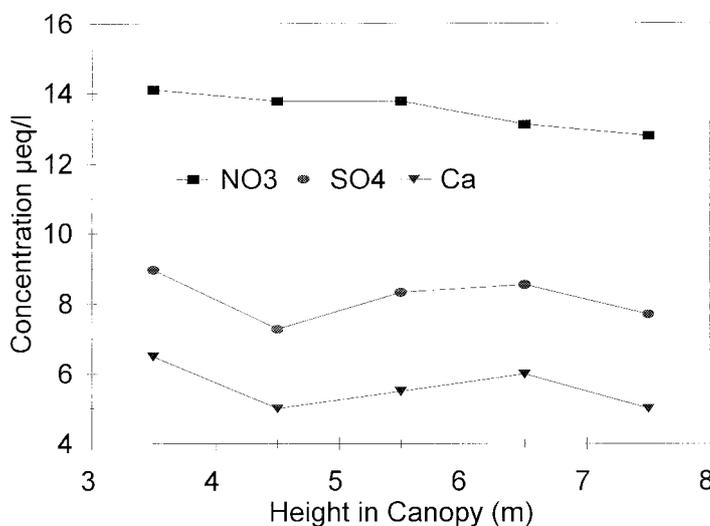
Figure 3. Vertical profiles of major ion concentrations in snow intercepted in a boreal spruce canopy, southern boreal forest (Waskesiu, Sask., January, 1992)

strong turbulent exchanges of sensible and latent heat when snow-covered, whilst there is little turbulent exchange with sub-canopy snow (Harding and Pomeroy, 1996). Concentrations of SO_4^{2-}, Ca^+ were similar throughout the measured vertical profile (Figure 3). NO_3^- concentrations decreased somewhat with height. This decrease is not significant. It is suggested that the low uptake of chemical species by the cold, dry snow caused such high resistances that even dramatically higher ventilation did not result in an appreciably higher rate of dry deposition. The experimental evidence suggests therefore that dry deposition to intercepted snow, as it occurs in the southern boreal forest, is not enhanced by greater ventilation or canopy position.

At Inuvik, there are infrequent mid-winter thaws. In such a cold climate, intercepted snow remains in the canopy for months, covering the branches and sublimating slowly as shown in a photograph of the region in mid-winter (Figure 4a). Under such consistent cold, canopy biological activity and aqueous chemistry are considered inactive. Later in the season, most remaining intercepted snow has unloaded to the surface as shown in an late-winter photograph (Plate 1). An aerosol containing SO_4^{2-} associated with arctic haze (Barrie, 1995) and sea-salt aerosols dominates dry deposition to the region (Pomeroy et al., 1993, 1995). To examine the effect of a long exposure time on deposition to and loss of ions from intercepted snow, Figure 5 shows the premelt concentrations of NO_3^-, SO_4^{2-} and Cl^- in intercepted snow and surface snowpack (Figure 5a, b, c) and the water equivalent (SWE) of surface snow (Figure 5d) measured in micro-transects from the main stem of three similar black spruce trees in an open canopy forest (LAI = 1·2) near Inuvik in late winter (38 samples total; samples collected from layers combined to provide bulk concentrations). The SWE accumulation (Figure 5d) is lowest near to the stem and increases with distance up to 2 m from the stem, beyond which it is no longer diminished by interception. Evidence of unloaded intercepted snow was provided by distinctive hard clumps of snow in surface and depth hoar layers near the trunk.[1] Only small clumps of snow remain intercepted in the canopy at the time of sampling in April (Plate 1), an amount insufficient to account by itself for the reduced SWE near trunks, suggesting sublimation of intercepted snow with a resulting reduction in SWE near trunks. Figure 5a shows NO_3^- concentrations of intercepted snow are approximately three times higher than surface snow directly underneath and three to four times higher than background levels away from the tree. This differs from Cl^- and SO_4^{2-} concentrations in intercepted snow (Figure 5b, c) which are only 40% greater than those in surface snow immediately next to the trunk but quite enriched (five to six fold)

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[1] Intercepted snow is not subject to temperature-gradient metamorphism as surface snow is and therefore retains its fine-crystalline structure and strength at cold temperatures (Hedstrom and Pomeroy, 1998).

Figure 4. Photographs of: a) intercepted snow in a black spruce forest near Inuvik, early February 1992, PLATE 1) the black spruce forest in mid-April 1992 with sampling trenches shown

compared to background levels away from the trunk. Snow near the trunk is enriched to a moderate degree (30%) in NO_3^- compared to background levels (Figure 5a), but a dramatic increase (two to five fold) in SO_4^{2-} and Cl^- concentrations occurs in the nearest metre to the stem (Figure 5b, c). The increased concentrations in intercepted and near-trunk snow may be due to sublimation of snow (Lundberg and Halldin, 1994) and subsequent increase in chemical concentration, or to enhanced dry deposition to intercepted snow. In both cases it is presumed that some remaining intercepted snow is eventually released to the surface. Because both concentrations and SWE increase with distance from the trunk, concentrations alone do not provide sufficient information on what process is operating to enrich intercepted snow prior to unloading.

Figure 6 shows SWE and loads of NO_3-N, SO_4-S and Cl calculated from measured ion concentrations and SWE, plotted against distance from central trunks. NO_3-N loads do not change notably along the transects, indicating no net exchange occurring in the canopy compared to the surface, whereas SO_4-S and Cl loads do increase strongly within 0·5 m of the stem, indicating enhanced dry deposition to intercepted snow or to any exposed branches (less likely to branches because they were exposed for only a short period of late winter). If any NO_3^- is preferentially-deposited to intercepted snow compared to surface snow, then the added NO_3-N must be subsequently consumed or volatilized. Dry deposition of SO_4^{2-} and Cl^- is clearly indicated however by the increase (roughly three-fold) in near-trunk loads over those remote from the trunks. The increase in concentration of ions due to removal of ice mass via sublimation *may* be indicated by the two to three fold increase in NO_3^- concentrations in intercepted snow over surface snow, an amount exceeded two-fold again by SO_4^{2-} and Cl^-. An increase in concentration due to sublimation alone would not result in a change in ion load, as indicated by the behaviour of NO_3-N. The difference in concentration change between NO_3^- and SO_4^{2-} or Cl^- is therefore due to enhanced dry deposition of the latter two ions to intercepted snow, probably

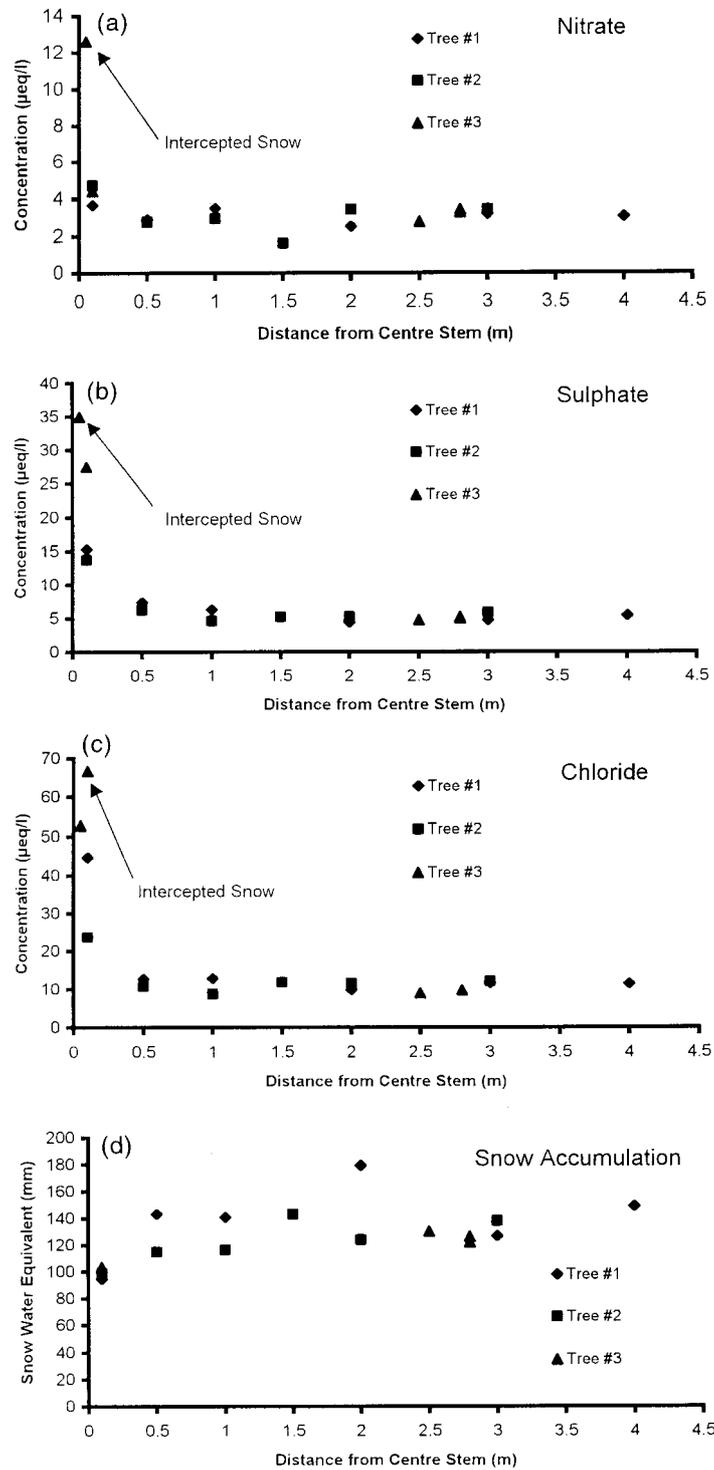Plate 1. The black spruce forest in mid-April 1992 with sampling trenches shown

Figure 5. Transects of ion concentrations in surface and intercepted snow a) NO_3^-, b) SO_4^{2-}, and c) Cl^- and d) SWE with increasing distance from tree stems in a northern boreal forest (Inuvik, NWT April 1992). Mean concentrations for distances on individual transects are shown
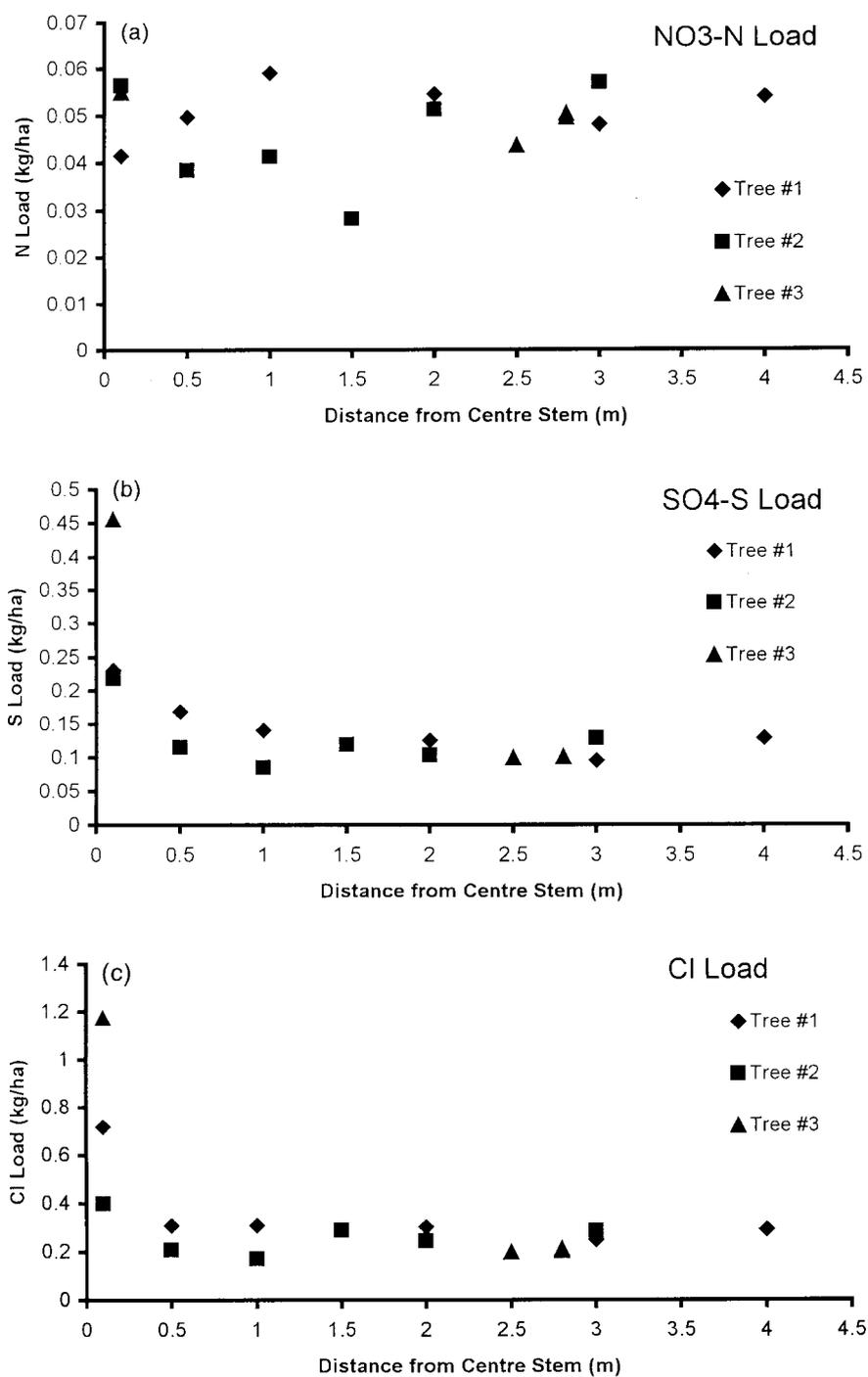
Figure 6. Transects of bulk ion load in surface snow a) NO_3, b) SO_4 and c) Cl with increasing distance from tree stems in a northern boreal forest. Mean loads of distances on individual transects are shown

as arctic aerosol and sea-salt particulates respectively. The climate and atmospheric chemistry of Inuvik appear to promote conservative behaviour for NO_3^-, as the consistently cold dry snow (high resistance to dry deposition of gaseous N species) and incomplete vaporisation of intercepted snow (slow sublimation) are contributing physical factors deriving from the exceptionally cold environment. The exact chemical processes, whoever, that work to retain NO_3-N in slowly sublimating snow at Inuvik are not known. The low basin-scale losses of SWE to intercepted snow sublimation in the region (Pomeroy et al., 1995) imply that even if NO_3^- was not completely conservative during sublimation the impact on basin-wide N budgets in snow would be small.

LOSS OF IONS FROM INTERCEPTED SNOW

The preceding section showed how difficult it can be to distinguish accumulation/deposition from sublimation/volatilization processes in canopy snow. By comparing loads and concentrations in a high sublimation environment with low particulate dry deposition from arctic and oceanic aerosols (Waskesiu), certain processes that lead to ion loss can be more clearly identified. Canopy exchange processes that can affect ion delivery from intercepted to surface snow include ion volatilization whilst intercepted snow is exposed to the atmosphere (here presumably sublimating), and intercepted snow transport via unloading to the surface. The former implies vapour transport whilst the latter can carry ions directly on snow crystals.

Sublimation of intercepted snow can amount to areal losses of approximately 20 mm snow water equivalent (SWE) per month in dry western boreal forests (Schmidt and Troendle, 1992; Pomeroy and Gray, 1995). On an annual basis, depletion of intercepted snow by sublimation increases with increasing leaf area, air temperature and wind speed, and decreases with humidity and time since snowfall (Schmidt, 1991; Pomeroy and Schmidt, 1993; Pomeroy and Gray, 1995; Harding and Pomeroy, 1996).

At Waskesiu more temperate conditions and higher leaf areas lead to greater interception, more rapid sublimation and higher annual losses than found at Inuvik (Pomeroy et al., 1997). Snow ion concentrations, SWE and ion loads were compared from 18 samples under snow-free canopies in stands ranging from (LAI = 0), unleafed trembling aspen (LAI = 0·7), through open jack pine (LAI = 1·5), dense jack pine (LAI = 3), to dense black spruce (LAI = 4·1). The wide range of winter leaf area provided a correspondingly wide range of interception losses. As intercepted snow load, stand-scale wind redistribution and surface snow evaporation were minimal and melt had not yet occurred, it could be assumed that any difference in SWE between stands was due to interception losses caused by sublimation of intercepted snow.

To quantify the effects of snow interception and sublimation on ion concentrations some comparable dimensionless measures need to be defined. Proportional ion concentration (PIC) is found as a function of ion concentration, C, as measured in snow under a forest canopy (subcanopy) and in an adjacent site with no winter canopy (open):

$$PIC = \frac{C_{subcanopy} - C_{open}}{C_{open}} \qquad (1)$$

Similarly, proportional snow interception (PSI) is found as.

$$PSI = \frac{SWE_{subcanopy} - SWE_{open}}{SWE_{open}} \qquad (2)$$

The assumption behind equation (2) is that differences in snow accumulation are due to interception of snow. If the canopy is relatively snowfree at the time of sampling then this difference may be further attributed to sublimation of intercepted snow. Under the correct sampling conditions, equation (1) and (2) permit a
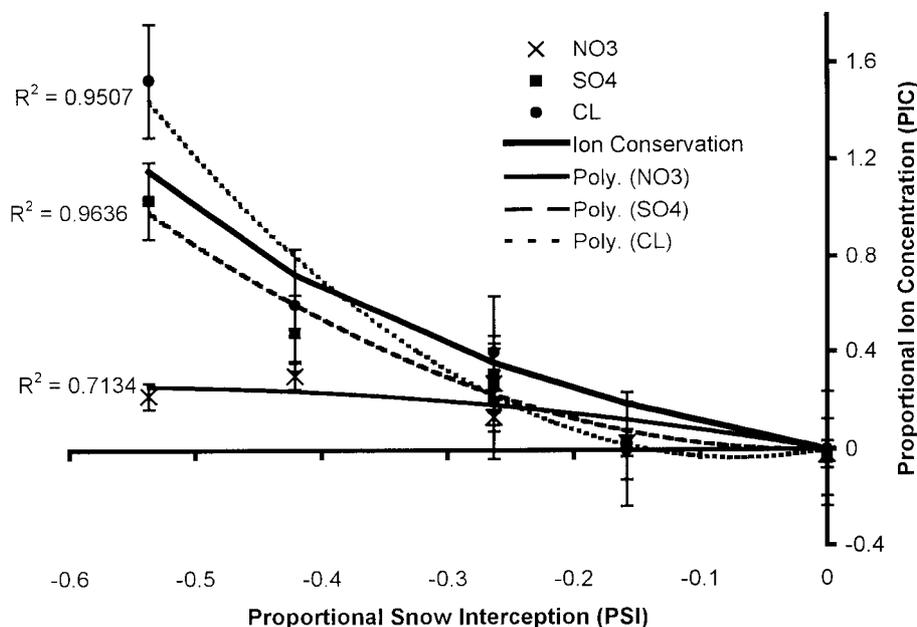
Figure 7. Effect of intercepted snow sublimation on surface show ion concentration in the southern boreal forest, (Waskesiu, Sask., Feb. 1992). Mean data are shown with standard errors of estimate about the mean for proportional ion concentration, PIC (equation (1)). Proportional snow interception, PSI is calculated using equation (2) and reflects sublimation loss. Perfect ion conservation (equation (3)) is shown along with polynomial relationships fitted to measured data (for purposes of visualization) and the correlation coefficients (R^2) for those fits

definition of ion conservation under conditions of sublimated, intercepted snow, where conservative behaviour is governed by a constant ion load (load = concentration × SWE) and is indicated by.

$$PIC = \frac{SWE_{open}}{SWE_{subcanopy}} - 1 \qquad (3)$$

As an example of the calculation, if 50% of cumulative snowfall sublimates, PSI = -0.5, $SWE_{open}/SWE_{subcanopy} = 2$ and if ions are conserved, $PIC = 1$ (doubling of concentration).

Figure 7 shows measured mean PIC (NO_3^-, SO_4^{2-}, Cl^-) and PSI for several forest stand densities with standard errors of estimate of PIC shown to display the range of input data. Lines showing polynomial functions fitted through the measured PIC and PSI for each ion and a theoretical line for sublimation enrichment due to conservative ion behaviour during sublimation (equation (3)) are also shown. Correlation coefficients are shown along with the polynomial lines to indicate goodness of fit of the data to these lines. The polynomial functions have no meaning other than to graphically illustrate trends in the data, the goodness of fit of data to the trends and an indication of whether the trends match conservative, ion behaviour during sublimation. It is evident that SO_4^{2-} and Cl^- concentrations increase with snow sublimation losses, the trends approximately fitting the theoretical increase in PIC calculated from equation (3) (solid line in Figure 5a). The results for NO_3^- however, show relatively little enrichment and suggest that the ion is incompletely conserved during sublimation.

To test the degree of NO_3^- volatilization compared to sublimation of intercepted snow, another dimensionless measure needs to be defined. Proportional ion load (PIL) is found as:

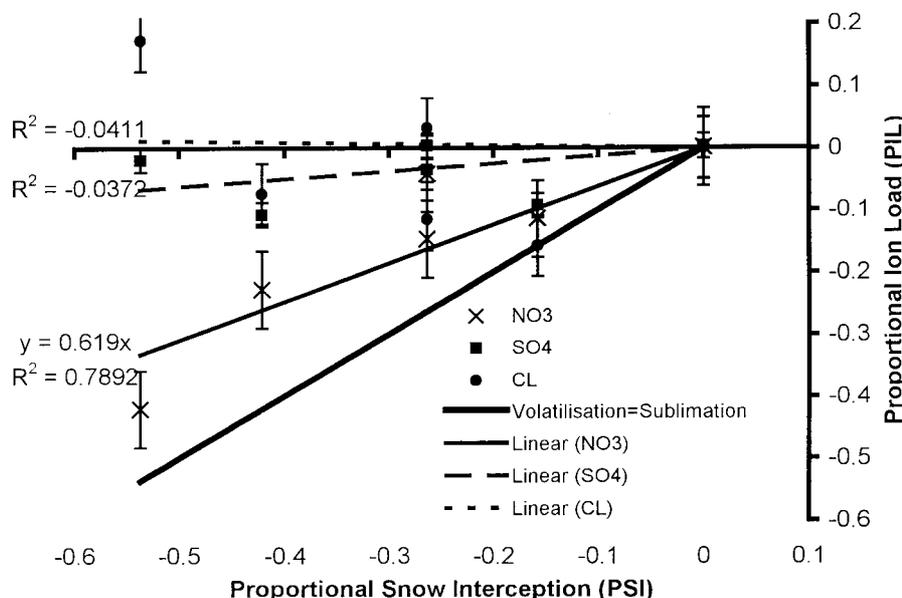$$PIL = \frac{(C\ SWE)_{subcanopy} - (C\ SWE)_{open}}{(C\ SWE)_{open}} \qquad (4)$$

Figure 8. Effect of intercepted snow sublimation on surface snow ion load in the southern boreal forest (Waskesiu, Sask., Feb. 1992). Mean data are shown along with standard errors of estimate of proportional ion load, PIL (equation (4)). A line representing ion volatilization perfectly proportional to snow sublimation (equation (5)) is shown along with linear fitted relationships between measured PIL and PSI and correlation coefficients (R^2) for those relationships

in a similar manner to PSI. For instance, a PIL of -0.5 mean s a 50% loss in ion load from the no-canopy control. PSI was compared to PIL in Figure 8; mean forest stand points along with standard errors in estimate of PIL are shown and linear regression lines fitted through the measured points. The $1:1$ line denotes volatilization equal to sublimation loss. Low slope and R^2 show that the SO_4^{2-} and Cl^- load do not follow the volatilization model. However, NO_3-N load *does* volatilize in proportion to sublimation, the relationship being,

$$PIL(NO_3\text{-}N) = 0.62PSI, \quad R^2 = 0.79 \tag{5}$$

which provides the basis for a simple model of NO_3^- loss from boreal forest snow covers.

The Waskesiu results suggest that NO_3^- is volatilized with 62% efficiency, compared to sublimation of intercepted snow, and that SO_4^{2-} and Cl^- undergo little net exchange associated with snow interception or sublimation. This differs with the conservative net behaviour of NO_3^- and the dry deposition of SO_4^{2-} in the cold boreal forests near Inuvik. The difference in NO_3^- behaviour may be due to differing snow temperatures, and differing rates and completeness of sublimation. The Inuvik winter is consistently cold ($-20°$ to $-50°C$) with consequent extremely slow sublimation that may conserve NO_3^-. By contrast, the Waskesiu winter is more moderate ($-5°$ to $-30°C$), the canopy is warmed by positive net radiation in February and March (Harding and Pomeroy, 1996) and sublimation occurs more rapidly. The difference in SO_4^{2-} and Cl^- deposition between the northern and southern sites is probably due to arctic and sea-salt aerosol presence near Inuvik. However, data from neither site indicates that sublimation plays a role in depleting loads of SO_4^{2-} or Cl^- in snow.

DISCUSSION

The result that NO_3-N volatilization is controlled not by interception alone, but by the rate of intercepted snow sublimation is ecologically interesting as inorganic N is a limiting factor to primary productivity

throughout much of the boreal forest. The snow NO_3-N load is flushed from the pack during a period of rapid spring melt in the boreal forest and is a biologically-available nutrient. Examples of non-linear aquatic responses to inputs of inorganic N from snow have been reported by Peters and Driscoll (1987). Presuming a simple model of snow NO_3^- behaviour that is consistent with observations reported here: that NO_3-N load is lost as a linear function the loss of SWE to intercepted snow sublimation (equation (5)), allows a discussion of the probable sensitivity of NO_3^- loss to canopy and climate.

Climate

Data from two extremes of the boreal forest have been examined suggesting NO_3^- is conservative where sublimation rates are low and volatile where rates are high. Pomeroy and Gray (1995) reviewed forest snow mass balance studies to determine sublimation rates in a wide range of climates across North America and Russia. Their survey showed that from 20 to 45% of annual snowfall (PSI of -0.20 to -0.45) is sublimated from continuous canopy coniferous forests (Ontario, Quebec, Saskatchewan, British Columbia, Yukon, Oregon, Colorado, Siberia). Studies by Pomeroy *et al.* (1995) in the Inuvik area and Satterlund and Haupt (1970) in northern Idaho suggest however that sublimation losses are small ($<5\%$ or PSI < -0.05) in these regions. The Inuvik region is extremely cold and northern Idaho quite humid in winter: apparently these extremes are sufficient to suppress sublimation. With exceptions, a remarkable number of studies showed annual PSI between -0.3 and -0.4, in locations ranging from middle latitude subalpine to high latitude boreal forests with annual snowfall varying from 120 to 600 mm. The similar sublimation losses in varied climates may be due to a counteracting effect of high winter temperatures in accelerating both sublimation rate and probability of unloading.

In high snowfall environments the potential NO_3-N loss can be substantial. Jones and Deblois (1987) measured N loads of up to 2·0 kg N ha^{-1} in Quebec (75% derived from NO_3^-) just before melt began. Presuming that their sub-canopy snow accumulation agreed with PSI $= -0.35$ and that equation (5) can be applied suggests a PIL of -0.22, corresponding to a NO_3^- volatilization loss of 0·42 kg NO_3-N ha^{-1} during sublimation. In contrast maximum NO_3^- loads of 0·18 kg NO_3-H ha^{-1} were measured in deciduous stands at Waskesiu in 1992. If identical PSI and PIL are used, the NO_3^- loss associated with sublimation is only 50 g NO_3-N ha^{-1}. For southern boreal forest environments it would appear that sublimation loss and therefore NO_3^- volatilization from intercepted snow are sensitive primarily to annual snowfall and hence wet deposition with strong gradients from dry mid-continent to the more humid coasts.

Canopy cover

The data from Waskesiu clearly illustrates the sensitivity of sublimation loss and hence NO_3^- volatilization to SWE. Pomeroy and Goodison (1997) and Pomeroy *et al.* (1998) have demonstrated that the strong variation of SWE with canopy cover is due to sublimation of intercepted snow in this environment. Snow mass balance surveys over several years near Waskesiu indicate that sublimation losses increase with increasing canopy density (LAI) and that removal of the canopy cover through clear-cutting or burning causes a corresponding suppression in sublimation loss until the evergreen canopy can be restored. A clearcut 3–5 years old (LAI $= 0.2$) showed no sign of recovery to mature forest interception conditions but one 15 years old (LAI $= 2.1$) intercepted roughly the same amount of snow as a mature pine stand (LAI $= 2.2$), about 35% of annual snowfall (Pomeroy and Granger, 1997). Measurements of annual ion load in snowcovers of clearcuts and spruce stands near Waskesiu in 1995 reported by Pomeroy *et al.* (1997) show the ratio of clearcut (LAI $= 0.2$) to dense spruce (LAI $= 4.1$) NO_3^- loads (1·3 or PIL $= -0.23$) substantially exceed those of SO_4^{2-} (0·98, or PIL $= 0.02$). In this case the increase in NO_3-N with the forest clearing treatment only amounts to between 50 and 100 g NO_3-N ha^{-1}, however the variation in SWE and NO_3-N load in snow with changing canopy cover in these regions may be ecologically important as wet deposition inputs of both snowmelt water and NO_3-N are small and may limit the rate of forest regrowth. An environment with heavier snowfall (eastern Canada) should see a proportionately larger increase in NO_3-N load with forest removal (0·42 kg NO_3-N ha^{-1}). This larger increase in eastern North America may have

implications for acidification of the soil and aquatic environment in regions already considered to be receiving excess N (Jeffries, 1995).

CONCLUSIONS AND IMPLICATIONS

No evidence of enhanced dry deposition of chemical species to intercepted snow was found at either site except where high atmospheric concentrations of SO_4^{2-} and Cl^- prevailed (as 'arctic haze' and sea-salt aerosols). At Inuvik, where these atmospheric conditions and enhanced dry deposition did occur, concentrations of SO_4^{2-} and Cl^- were five to six times higher in intercepted snow than in surface snow away from the trees. This also affected ion loads, with SO_4-S and Cl loads enhanced three-fold within the nearest 0·5 m to individual tree stems, compared to locations away from trees, in a sparsely-wooded area. It is suggested that when surface resistance to deposition is high (as for gaseous forms of N) and/or atmospheric concentrations low (as for aerosols in the southern boreal forest), changes in aerodynamic resistance due to snow interception are irrelevant to dry deposition.

Measurements of snow affected by canopy interception without rapid sublimation provided no evidence of ion volatilization from intercepted snow. However, where intercepted snow sublimation rates were significant (Waskesiu, late winter), ion loads in sub-canopy snow suggested that NO_3^- volatilized with an efficiency of about 62% per snow mass sublimated. Extrapolating this measurement to sublimated losses observed in this and other southern boreal environments suggests that 19–25% of snow inputs of NO_3^- can be lost during intercepted snow sublimation. The N loss is sensitive to the amount of snow intercepted and hence to forest cover; it is therefore suppressed with forest cover removal, as through clear-cutting, with effects remaining until the evergreen canopy cover is restored. The amount of N lost during sublimation may be large in high-snowfall, high N load southern boreal forests (Quebec) where 0·42 kg NO_3-N ha^{-1} is estimated as a possible seasonal NO_3^- volatilization.

The ecological implications of this snow NO_3-N flux are not directly known, however much of the remaining NO_3-N is delivered to the terrestrial and aquatic ecosystems in an inorganic form during spring snowmelt and is available at a time of rapid growth and therefore N demand. For global budgets of N, the variability of snow-N processes with both forest cover and climate is a matter of potential interest, as it is for improved forest and aquatic ecology models of the future. The variation is also of concern for efforts to improve carbon flux estimates for the boreal forest. Further research is needed to identify the chemical mechanism operating during N volatilization and corroborate the process in other environments.

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