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# Snowpack controls on nitrogen cycling and export in seasonally snow-covered catchments

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## Abstract:

Here we provide an overview of current research activities on nitrogen (N) cycling in high-elevation catchments of the Colorado Front Range. We then use this information to develop a conceptual model of how snow cover controls subnivial (below snowpack) microbial processes and N leachate from the snow-soil interface to surface waters. This model is based on research that identifies subnivial processes as a major control on the leaching loss of N from soil during snowmelt. These subnivial soil processes are controlled by the development of the seasonal snow pack that insulates soil from cold air temperatures and allows heterotrophic microbial activity in the soil to immobilize N. In this model the duration of snow-cover is divided into four snowpack regimes; zone I is characterized by shallow-short duration snowpacks, zone II is characterized by high interannual variability in snow depth and duration, zone III is characterized by early developing, continuous snow cover, and zone IV is characterized by deep, long-duration snow cover verging on perennial snowpacks. In zone I, soils remain frozen and there is little microbial activity and N leachate is high. In zone II, total microbial activity is highly variable and the amount of N leachate is highly variable. In zone III, total microbial activity is high and there is little N leachate. In zone IV, microbial activity is reduced because of carbon limitation and N leachate is high. This model suggests that a portion of the spatial and temporal variability observed in N export from these seasonally snow-covered systems is due to variability in winter snow cover across landscape types and inter-annually within a landscape type. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS snow; nitrogen; biogeochemistry; climate; water chemistry

## INTRODUCTION

Increased atmospheric deposition of anthropogenic N in high elevation ecosystems of the western United States has focused research on the controls on N export from these systems (Lewis and Grant, 1980; Grant and Lewis, 1982; Sievering *et al.*, 1992; Williams *et al.*, 1996a; Fenn *et al.*, 1998; Baron and Campbell, 1997). These catchments are a major source of water for both urban and agricultural uses, as well as protected wilderness and park lands. Several researchers have associated changes in surface water chemistry with increased N deposition in the western United States (Baron, 1991; Baron *et al.*, 1994; Williams *et al.*, 1996b),

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suggesting that these areas are highly sensitive to N deposition and may be experiencing the early stages of N saturation.

Snow melt dominates the annual hydrologic cycle in these high-elevation catchments, potentially making the effects of this N deposition on both terrestrial and aquatic systems qualitatively and quantitatively different than in most catchments impacted by high levels of N deposition. In direct contrast to increases in N export in surface water of these high-elevation catchments (Williams *et al*., 1996b), studies of terrestrial N cycling in these catchments indicate that vegetation remains N limited during the growing season (Bowman *et al*., 1993). Similarly, net N mineralization during the growing season is much lower than vegetation N demand (Fisk and Schmidt, 1995), suggesting that little or no inorganic N should be available for export from the catchment. These apparent contradictions between our results and the models of N saturation (Aber *et al*., 1989; Stoddard, 1994) warrant additional research.

The combination of dormant vegetation, cold temperatures, and extensive snow cover in alpine areas suggests little or no biological activity occurs outside of the summer growing season. However, Salisbury (1985) observed a surprising amount of biological activity beneath deep snow packs in the Bear River Range, Utah, that he attributed primarily to relatively warm soil conditions below the insulating snow cover. Significant levels of heterotrophic microbial activity in snow covered soils have been suggested by previous researchers (Skoagland *et al*., 1988; Taylor and Jones, 1990), yet few studies have quantified the importance of this activity to carbon and N cycles. In general, microbial activity can continue as long as free water is available, typically down to $-5\,^{\circ}C$ (Schimel *et al*., 1996), although microbial activity has been reported at temperatures as low as $-6{\cdot}5\,^{\circ}C$ (Coxon and Parkinson, 1987).

Here we provide an overview of current research activities on N cycling in high-elevation catchments of the Colorado Front Range. Our focus is on microbial controls, and our analysis does not include the potential influence of invertebrates and other animals that may be active during the snow season (Addington and Seastedt, 1999). We then use this information to develop a conceptual model of how snow cover may control subnivial (below snowpack) microbial processes and N leachate from the snow-soil interface to surface waters. The primary value of this conceptual model is to suggest additional hypotheses in an attempt to explain spatial and temporal differences in the nitrate ($NO_3^-$) concentrations of surface waters in seasonally snow-covered catchments at high-elevations.

## SITES DESCRIPTION

The majority of the research was conducted in the Green Lakes Valley (40°03′N, 105°35′W) of the Colorado Front Range. The Green Lakes Valley is an east-facing headwater catchment that abuts the continental divide, 700 ha in area and ranging in elevation from 3250 m to about 4000 m. The catchment appears typical of the high-elevation environment of the Colorado Front Range, and includes Niwot Ridge, where research has been conducted since the early 1950's (Caine and Thurman, 1990). Bedrock is crystalline, with about 80% of the basin composed of exposed bedrock and talus. About 80% of the annual precipitation in the Green Lakes Valley occurs as snow. Streamflows are markedly seasonal, varying from less than $0{\cdot}1\ m^3\ s^{-1}$ during the winter months to greater than $1{\cdot}5\ m^3\ s^{-1}$ at maximum discharge during snow melt just below Lake Albion at the lower end of the valley (Caine, 1996). Surface waters are dilute, with acid neutralizing capacities (ANC) generally less than 200 μeq $L^{-1}$ at all sampling sites (Caine and Thurman, 1990). Here we present results from the outflow of Green Lake 4, which drains an area of 220 ha at an elevation of 3550 m.

Niwot Ridge forms the northern boundary of Green Lakes Valley and is a UNESCO Biosphere Reserve and a Long-Term Ecological Research (LTER) network site. The LTER network site is a participant in the National Atmospheric Deposition Program (NADP) and has maintained an NADP wet deposition site since 1985 on the Niwot Ridge saddle at an elevation of 3500 m. The Saddle site on Niwot Ridge is characterized by well-developed alpine tundra and deep soils. Surface water samples were collected from the ephemeral Saddle stream which drains Niwot Ridge; the catchment area is about 8 ha. Additional surface water

 

samples were collected from a seasonal stream draining the 8-ha Martinelli catchment about 400 m from the Saddle site in Niwot Ridge. The Martinelli catchment has a poorly developed soil structure with little vegetation and is dominated by a late-melting snow patch (Caine, 1989).

## METHODS

Research focusing on the sources, sinks, and transformations of N in high elevation systems in the Colorado Front Range has been conducted since the early 1990's. These various research efforts have followed N from atmospheric deposition (Sievering *et al*., 1992, 1996; Williams *et al*., 1998a), within-snowpack transformations (Brooks *et al*., 1993; Williams *et al*., 1996c), cycling in soil (Fisk and Schmidt, 1996; Brooks *et al*., 1996, 1998; Lipson *et al*., 1998), gaseous losses (Brooks *et al*., 1997; Fisk *et al*., 1998) and export in surface water (Caine and Thurman, 1990; Brooks *et al*., 1996; Williams *et al*., 1996a,b,c). This work has led us to focus on the interactions between snowmelt and soil N pools as a major control on N loss in surface waters from these high-elevation ecosystems.

Physical and chemical properties of the snowpack are sampled about weekly at the Niwot Ridge saddle site following the protocol of Williams *et al*. (1996a). Snow water equivalence (SWE) measurements are made using a 1-L stainless steel cutter in vertical increments of 10 cm (Williams and Melack, 1991a). Temperature of the snowpack is measured every 10 cm with 20-cm long dial stem thermometers, calibrated to 0·2 °C using a one-point calibration at 0 °C. Grain type, size, and snowpack stratigraphy are also recorded. Depth-weighted values are then calculated for snowpack density, temperature, and water equivalent. Raw and calculated values, along with additional information on methods, are available at the Niwot Ridge LTER site (http://culter.Colorado.EDU:1030/Subnivean/) (Williams *et al*., 1999 (in press)).

Snow samples were collected for chemical content following the protocol of Williams and Melack (1991a). Snowpits were dug weekly to biweekly from the snow surface to the ground. Snow samples were collected using bevelled PVC tubes (50-mm diameter, 500-mm long), which had been soaked in 10% HCl and then rinsed at least five times with deionized water. Vertical, contiguous cores were collected in increments of 200 to 400 mm, from the snow-air interface to the snow-ground interface. Snow was transferred from the cores into new polyethylene bags and transported 4 km to our analytical facilities the same day as collection. Snowpits were refilled after each sampling episode to minimize changes in melt rates and meltwater flow through snow. Within snowpack transformations of N were investigated using a variety of techniques, including bacterial and fungal cultures (Brooks *et al*., 1993) and the addition of isotopically-labeled $^{15}NH_4^+$ and $^{15}NO_3^-$ (Williams *et al*., 1996c).

Release of $NH_4^+$ and $NO_3^-$ from the snowpack was investigated in 1994 and 1995 by collecting snowpack meltwater in 1-$m^2$ snow lysimeters before contact with the ground following the protocol of Bales *et al*. (1993). Meltwater flowed by gravity from the snow lysimeters about 5 m into a subnivian laboratory. Meltwater discharge was measured continuously in tipping buckets, conductance was measured continuously using an inline conductance meter, and grab samples were collected about daily and analyzed for $NO_3^-$ and $NH_4^+$ concentrations.

Immobilization of inorganic N in microbial biomass was measured using the following technique so that our results would be comparable to similar measurements made by other studies that have investigated microbial controls on N-cycling (Fisk and Schmidt, 1995, 1996; Fisk *et al*., 1998; Lipson and Monson, 1998; Lipson *et al*., in press). Microbial biomass N was determined using a chloroform fumigation — direct extraction procedure (Brookes *et al*., 1985). For each sample, a subsample weighing 15 g was shaken for 30 min in 100 mL of 0·5 *M* $K_2SO_4$ at 125 rpm on a rotary shaker followed by immediate filtration through Whatman no. 1 filter paper. A second subsample was fumigated with chloroform for 5 days in a vacuum desiccator and then extracted in the same manner. Extracts were digested by persulfate oxidation and analyzed for total N. The difference in extractable N content of the fumigated and unfumigated soils represented the chloroform-labile N in soil microbial biomass. A correction factor of 0·54 was then applied to estimate microbial N (Brookes *et al*., 1985).

 

Mobile inorganic N moving through the O and A horizons of snow-covered soil was measured with paired ion-exchange resin bags, following the protocol of Brooks *et al.* (1996). The paired resin bags were installed at the soil surface and at a depth of 50 to 80 mm at 24 sites that ranged from shallow to deep snowpack conditions. Resin bags were installed in the autumn when snow began accumulating and collected as sites became snow free. Net production of mobile, inorganic N in snow-covered soils was calculated as the difference between surface and buried resin bags at each of the 24 sites. Resin bags (16-50 mesh) contained 20 mL (wet volume) of mixed cation and anion exchange resins loaded with $H^+$ or $OH^-$ with a total exchange capacity of 0·57 meq $mL^{-1}$, following the protocol of Binkley and Matson (1983).

Snow depth and duration were manipulated using a $2{\cdot}6 \times 60$ m snow fence which was installed during October 1993, made of a composite Centaur® polymer (Walker *et al.*, 1993). The snow fence is removed at the start of the growing season and re-installed each subsequent October. The presence of the snow fence results in a gradient of snow depth and duration, from deeper and earlier snow accumulation to shallower and later snow accumulation. Snow depth was measured manually at grid points located every 10 m on a $60 \times 70$ m grid. Soil temperatures were measured with permanent thermistors having leads extending above the seasonal snowpack, at 0 and 0·15 m soil depths every 10 m along a central transect through and beyond the snow drift and lee areas caused by the snow fence.

Samples of nitrous oxide ($N_2O$) under the snowpack were collected using the method of Sommerfeld *et al.* (1993), which consists of 10-mm thick stainless steel disks covered with 50 μm stainless steel mesh, placed at the snow-ground interface and within the snowpack, and connected to the snow surface with 1·6-mm (id) Teflon tubing. Gas samples were then collected at the snow-ground interface, at various heights within the snowpack, and in the atmosphere just above the snowpack, providing boundary conditions for a steady state diffusion model designed to account for snowpack porosity as detailed in Brooks *et al.* (1996). All samples were collected in glass syringes and analyzed within 24 hours by gas chromatography (Hewlett-Packard 5880A) at the University of Colorado's Mountain Research Station.

Surface waters were collected as grab samples at daily to weekly sampling frequency, following the protocol of Williams and Melack (1991b). Water samples were collected in polyethylene bottles soaked with DI water overnight and then rinsed copiously five times; bottles were further rinsed three times with sample water at the time of collection. Samples were transported the same day as collection to our wet chemistry laboratory and treated the same as melted snow samples.

Ammonium was determined colorimetrically within 24 hours of melting for snow samples and after collection of water samples, on a Lachat flow injection analyzer using a phenolate reaction enhanced by nitroprusside; detection limit was 9·8 μg N $L^{-1}$ (0·7 μeq $L^{-1}$) and precision 2·7%. Subsamples were immediately filtered through pre-rinsed (300 ml), 47-mm Gelman A/E glass fiber filters with *ca.* 1-micron pore size. Filtered samples were stored in the dark at 4 °C for subsequent analyses within one to four weeks. Anions were measured using ion chromatography (Dionex DX 500) employing chemical ion suppression and conductivity detection. The detection limit for $NO_3^-$ was 1·4 μg N $L^{-1}$ (0·1 μeq $L^{-1}$) and precision was 1·5%.

Resin bags were processed within 12 hours of returning from the field for $NH_4^+$ and $NO_3^-$. Inorganic N was extracted with 2N KCl (1 : 5, weight : volume) by shaking at 250 rpm for 60 minutes and allowed to sit at room temperature for 18 hours. These extracts were filtered through pre-rinsed (300 ml distilled water) Whatman no. 1 filter paper and aliquots were analyzed on the Lachat autoanalyzer. Ammonium was analyzed as in snow and water samples; $NO_3^-$ was analyzed using a sulfanilamide reaction following reduction to nitrite on a cadmium column.

## RESULTS

Analysis of the long-term NADP record from Niwot Ridge shows that about 70% of annual inorganic N in wetfall occurs as snow from September through May (Williams *et al.*, 1998a). Nitrate concentrations and loading are presented for the winter and spring of 1994 from our index snowpit (Figure 1). Volume-weighted

 

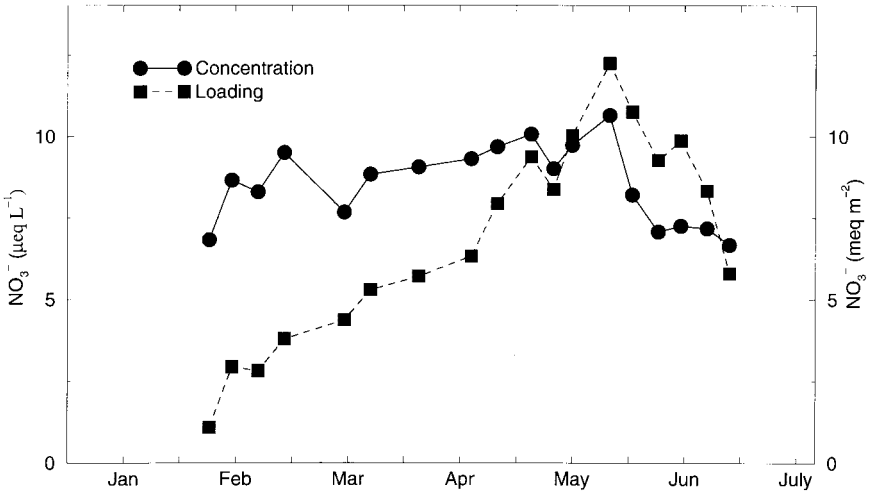


Figure 1. Time series of $NO_3^-$ concentrations ($\mu$eq $L^{-1}$) and loading (meq $m^{-2}$) in the seasonal snowpack from 1994

mean concentrations of $NO_3^-$ were about 7 μeq $L^{-1}$ near 1 January and then gradually increased to maximum concentrations of about 10 μeq $L^{-1}$ at the initiation of snowmelt runoff near 1 May. Nitrate loading in the snowpack was about 1 meq $m^{-2}$ near 1 January and then gradually increased with increasing snow water equivalence to a maximum of about 12 meq $m^{-2}$ at the initiation of snowmelt runoff.

There appeared to be little microbial activity within the snowpack prior to the initiation of snow melt. Snowpacks were sampled on 15 dates for total microbial biomass, ratio of bacteria to fungi, and major inorganic ions (Brooks *et al.*, 1993). Snowpacks were sampled in April, before appreciable snow melt had occurred. Levels of viable microbial biomass remained low throughout the period, peaking at 0·05 C μg $mL^{-1}$ or about $10^{-4}$ cells $mL^{-1}$. Microscopic analyses showed that this biomass was composed primarily of bacteria. Fungi were not detected in samples collected above treeline. Based on observed population sizes and growth rates it is unlikely these organisms were capable of significantly altering the chemical composition of snowmelt. The increases in both concentration and loading of $NO_3^-$ in the seasonal snowpack with time (Figure 1) were consistent with little modification of N content by microbial activity within the snowpack.

Additions of isotopically-labelled N to the snowpack also suggest that there is little modification of either ammonium ($NH_4^+$) or $NO_3^-$ concentrations in the seasonal snowpack at Niwot Ridge prior to and during the early stages of snow melt. Ammonium and $NO_3^-$ labelled with $^{15}N$ applied as non-conservative tracers to the snow showed no evidence of nitrification in the snowpack (Williams *et al.*, 1996c). Furthermore, $NH_4^+$ movement through the amended snowpack was highly correlated with a conservative chloride tracer ($r^2 = 0{\cdot}99$). In an unamended snowpack, $NH_4^+$ concentrations in meltwater before contact with the ground were highly correlated with $NO_3^-$ concentrations ($r^2 = 0{\cdot}98$), consistent with no nitrification in the snowpack.

*Ionic pulse*

Solutes were released from the seasonal snowpack in the form of an ionic pulse. Maximum concentrations of $NO_3^-$ in snow meltwater before contact with the ground ($C_i$) ranged from about four times bulk snowpack concentrations ($C_a$) in 1994 to about 20 times bulk snowpack concentrations in 1995 (Figure 2). In both years, the $C_i/C_a$ ratio then declined in an exponential fashion with time (Figure 2). Bulk snowpack concentrations of $NO_3^-$ in both years were similar, about 10 μeq $L^{-1}$. The difference in the magnitude of the ionic pulse between 1994 and 1995 was caused by differences in climate. The 1994 snow melt season was characterized by a short, rapid and continuous snow melt period while the 1995 snow melt season was

 

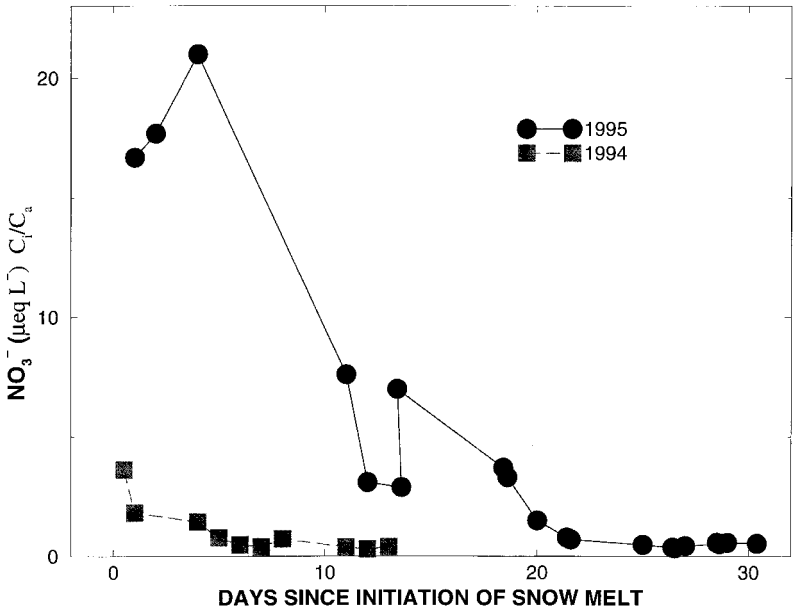


Figure 2. Time series from 1994 and 1995 of the ratio of $NO_3^-$ concentration in meltwater before contact with the ground ($C_i$) to bulk snowpack concentrations at the initiation of snow melt ($C_i$)

characterized by numerous snow events, many melt-freeze cycles within the snowpack, and a much slower and drawn-out melt period (Williams *et al.*, 1996a). The release of solutes in the form of an ionic pulse at Niwot Ridge is consistent with results from the Snowy Range of Wyoming (Bales *et al.*, 1990), the Sierra Nevada in California (Williams *et al.*, 1991b), and European countries (Johannessen and Henriksen, 1978).

*Snow-soil interactions*

Much of the inorganic N released from the snowpack appears to infiltrate the underlying substrate and undergo biogeochemical modifications. An experimental addition of isotopically-labelled $NH_4^+$ and $NO_3^-$ applied to the snowpack showed that greater than 80% of the $^{15}NH_4^+$ was found in underlying soils, indicating that $NH_4^+$ released from snow can be rapidly immobilized by underlying soils (Williams *et al.*, 1996a). A lesser amount of $^{15}NO_3^-$ applied to the snowpack was found in underlying soils, demonstrating the potential for the immobilization of $NO_3^-$ released from the snowpack in underlying soils (Williams *et al.*, 1996a).

The depth and duration of the overlying snowpack appeared to control soil temperature and in turn the ability of soils to sequester inorganic N released from storage in the seasonal snow-pack. Snow depth behind the snowfence in 1994 increased 100 to 200% compared to prefence snow depths at the same measurement locations in 1993 (Williams *et al.*, 1998b). To illustrate, maximum snow depth increased from 0·77 m in 1993 to 1·60 m in 1994 at the same location after installation of the snow fence (Figure 3), even though precipitation measurements showed there was more snowfall in 1993 than in 1994. Snow duration behind the snowfence increased an average of 90 days, from December through May in 1993 to October through June in 1994. The increase in snow depth and duration behind the snowfence caused an increase in soil temperatures during the winter months. Minimum soil surface temperatures in 1993 were −14 °C and occurred at the first measurement in January when snow depth was relatively shallow at 0·32 m (Figure 3). As snow depth increased and persisted in 1993, soil temperatures warmed at the rate of about 0·13 °C $d^{-1}$, becoming near 0 °C in April. In contrast, the deeper and earlier snowpack in 1994 resulted in much warmer soil temperatures than in 1993. Minimum soil temperature in January of 1994 was −5 °C and soils gradually warmed towards

 

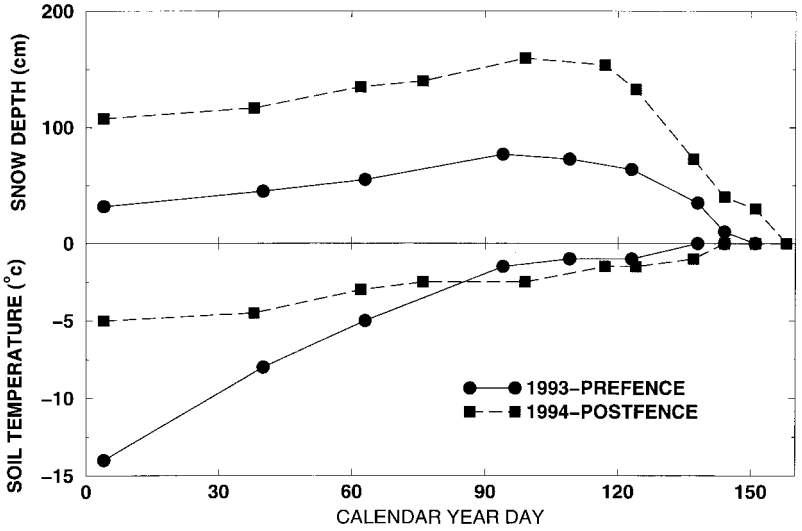


Figure 3. Time series of soil temperature and snow depth before (1993) and after (1994) installation of a snowfence ($n = 3$)

0 °C at the rate of 0·025 °C $d^{-1}$ (Figure 3). In both years, soil temperature was near 9 °C at the end of April and snowmelt began in the first to second week of May. These results suggest that a snow depth of about 40 cm effectively insulated the soil from the atmosphere and allowed soils to warm under the winter snowpack. This experimental observation is consistent with energy balance measurements that demonstrated the soil-atmosphere boundary became de-coupled with snow depths of 30–40 cm (Cline, 1995).

The incorporation of isotopically-labelled inorganic N released from storage in the seasonal snowpack into underlying soils suggests that microbial activity may affect source-sink relationships for N during snow melt runoff. Nitrous oxide ($N_2O$) flux provides a good, non-destructive index of N cycling by biological processes in subnivial or snow-covered soils, because its production requires several microbially-mediated processes. On Niwot Ridge, over-winter $N_2O$-N loss was sensitive to changes in snow cover, ranging from less than 0·2 mg N $m^{-2}$ from a shallow, late-developing snowpack to 23·3 mg N $m^{-2}$ from sites with early, deeper, and longer-duration snowpacks (Brooks *et al.*, 1997). Manipulation of snow cover depth and duration with the snow fence showed similar results, with subnivial $N_2O$ flux increasing about three-fold under the augmented snowpack in the lee of the snow fence compared to the control site (Williams *et al.*, 1998b). Demonstrating the importance of subnivial processes to annual N cycling in high-elevation catchments, daily $N_2O$ fluxes during snow melt were three to five times greater than daily fluxes during summer (Brooks *et al.*, 1997). These patterns in $N_2O$ emissions from snow-covered soils were consistent with the hypothesis that snowpack depth, extent, and duration are important controls on N-cycling in high-elevation catchments.

Consistent with our measurements of gaseous N fluxes from microbial processes in snow-covered soil, the depth and timing of seasonal snow cover also appear to control the size of the microbial biomass N pool and the amount of N leachate from soils during melt (Brooks *et al.*, 1998). At sites with similar vegetation and soils but differing amounts of snow cover, microbial biomass under snow immobilized 4·3 mg N $m^{-2}$ at sites with deep, consistent snow cover and only 1·7 mg N $m^{-2}$ at sites with shallow, inconsistent snow cover (Figure 4). Nitrogen leachate showed the opposite pattern of microbial biomass, with mobile N leachate recovered in resin bags ranging from 0·27 mg N $m^{-2}$ at sites with deep, consistent snow cover to 1·14 mg N $m^{-2}$ at sites with shallow, inconsistent snow cover. This inverse relationship between microbial N immobilization under snow and N leachate during melt appears to hold true across a range of soil and vegetation types, with N leachate decreasing significantly ($p < 0{\cdot}001$) as an exponential function of increasing microbial biomass underneath the snowpack ($r^2 = 0{\cdot}92$) (Figure 4). The leachate values from

 

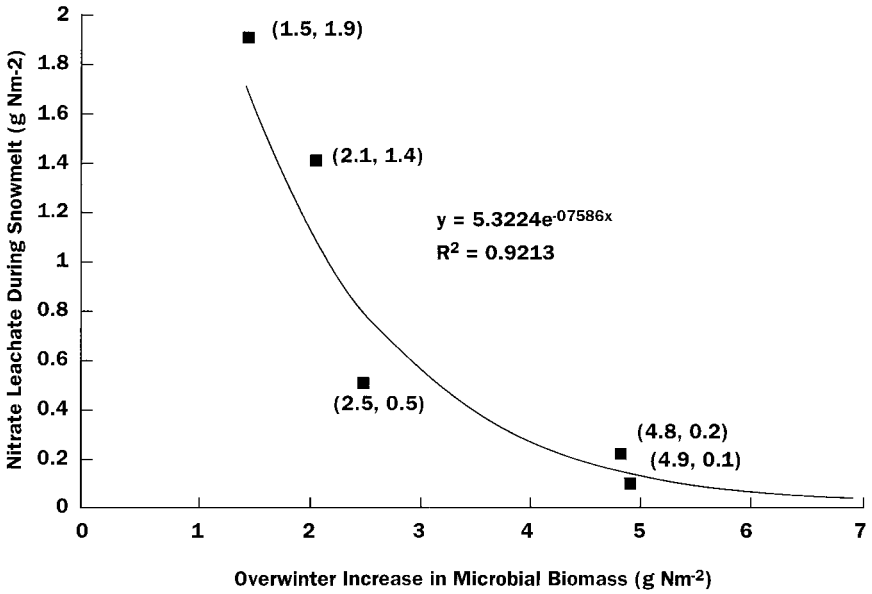


Figure 4. Nitrate leachate collected in resin bags buried in soils underneath the seasonal snowpack as a function of microbial biomass

resin bags were for all mobile sources of $NO_3^-$, including $NO_3^-$ released from storage in the overlying snowpack and $NO_3^-$ produced by nitrification processes in the underlying soils.

The observed control of snow cover on microbial activity appears to have two components. Insulation provided by snow cover with low thermal conductivity allows soils to be warmer than the atmosphere and makes free water available which can support heterotrophic activity (Brooks *et al.*, 1996). The second component is control over the amount of substrate available for heterotrophic activity in subnivial soils by the timing of snow cover early in the winter season. In the absence of early season snow cover, as soils freeze there is lysis of both plant and microbial cells. When soil subsequently thaws, this freeze-thaw lysis of cells increases available, labile carbon sources for heterotrophic activity (Schimel and Clein, 1996; Brooks *et al.*, 1997; Brooks *et al.*, 1998).

*Stream water*

Nitrate concentrations in stream flow from the outlet of Green Lakes 4 show a characteristic annual pattern (Figure 5). The annual maxima in $NO_3^-$ concentrations occurs at the initiation of snow melt runoff with values around 30 μeq $L^{-1}$s, consistent with both the release of $NO_3^-$ from the snowpack in the form of an ionic pulse and infiltrating snow melt flushing out soil $NO_3^-$. Annual minimum values of $NO_3^-$ occur during the growing season. The low values of $NO_3^-$ are consistent with retention of inorganic N through biological assimilation during the growing season.

The annual minima in $NO_3^-$ concentrations appears to be sensitive to increases in annual deposition of inorganic N in wetfall. Inorganic N in wetfall has increased at the rate of about 0·25 kg $ha^{-1}$ since the beginning of the NADP record in 1985 (Figure 5). In apparent response to large increases of atmospheric deposition of inorganic N in wetfall in 1989 and 1990, annual minimum concentrations of $NO_3^-$ from Green Lake 4 increased from below detection limits to about 10 μeq $L^{-1}$ (Figure 5). Since 1990, annual minimum concentrations of $NO_3^-$ at Green Lakes 4 have varied widely, from below detection limits of 0·1 μeq $L^{-1}$ to about 8 μeq $L^{-1}$.

In addition to these temporal variations in $NO_3^-$ concentrations of surface waters, there are also spatial variations in the concentrations of $NO_3^-$ in surface waters. Nitrate concentrations from the 8-ha ephemeral stream draining the Niwot Saddle were always near or below detection limits (Figure 6). In contrast, $NO_3^-$

 

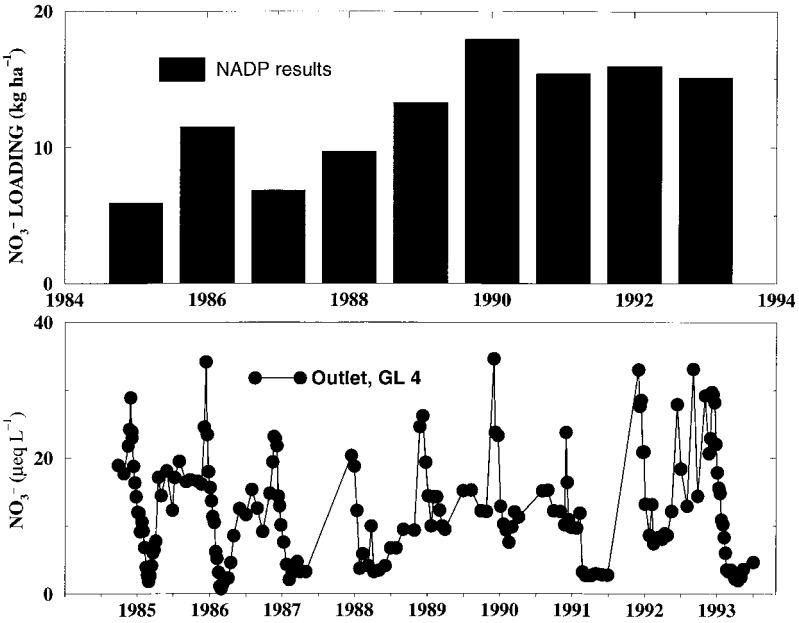


Figure 5. A time series of $NO_3^-$ export from the 220-ha Green Lakes 4 and annual inorganic N deposition in wetfall from the nearby NADP collector

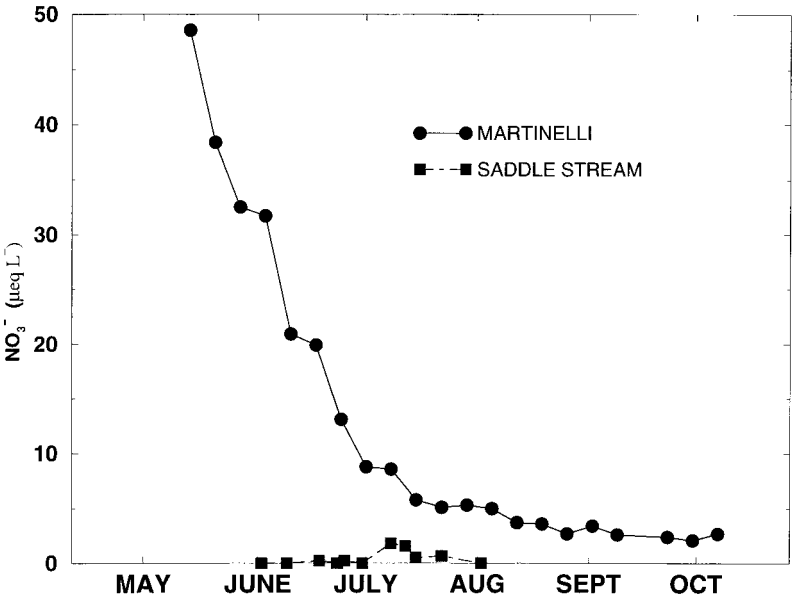


Figure 6. Nitrate concentrations during snow melt runoff in two paired catchments each 8-ha in area. The Martinelli catchment is dominated by a late-lying snow patch over 10 m in depth with poorly developed soils while the Saddle site has well-developed soils and consistent snow cover that averages about 3 m in depth

 

concentrations from the stream draining the 8-ha Martinelli catchment about 400 m SW of the Niwot Saddle stream had a maximum concentration of almost 60 μeq $L^{-1}$ at the initiation of snow melt runoff and then decreased over time. Differences in the amount and duration of snow cover may partially explain the differences in $NO_3^-$ concentrations of streams draining these co-located catchments.

## DISCUSSION

The large proportion of annual N deposition stored in the seasonal snowpack, together with evidence that N within the snow is preferentially eluted in the first portion of melt without undergoing significant transformations or immobilization, suggest that much of the N-cycling in high-elevation catchments occurs during the snow-covered season. The recovery of isotopically-labelled N in the soil under the snow cover, together with direct evidence of microbial N immobilization within the soil, suggests that heterotrophic immobilization of N in soil is an important control on the retention of N in the terrestrial environment. The amount of heterotrophic immobilization in turn, appears to be controlled by the development of the seasonal snow cover. Consistent snowpacks insulate the soil from the cold air temperatures above the snow surface and allow soils to thaw before snowmelt (Sommerfeld *et al*., 1991, 1993; Brooks *et al*., 1995, 1996). The timing of snowpack development appears to determine how severely soils may freeze before being insulated by snow, and how long soils remain thawed before the initiation of snowmelt.

The two most important factors controlling the biogeochemical environment under high-elevation snowpacks is the severity of soil frost and the duration of thawed soil. Freeze-thaw events are known to release labile, readily utilizable, organic carbon compounds that promote heterotrophic microbial activity (*e.g*. Schimel and Clein, 1996). The effects of this increase in carbon substrate have been observed in the field when fluxes of $CO_2$ and $N_2O$ from seasonal snowpacks increased exponentially following a severe, early winter freeze before the development of a consistent snowpack on Niwot Ridge (Brooks *et al*., 1997). Long-duration, early developing snowpacks do not result in a pulse of available carbon substrate (Brooks *et al*., 1997), but allow soil to remain thawed throughout the snow-covered season (Sommerfeld *et al*., 1993, 1996) providing an environment where lower levels of heterotrophic activity may occur all winter. In both of these situations, a stable active heterotrophic biomass was present in soil at the initiation of melt. In contrast, the absence of consistent snow cover results in soils that may remain frozen throughout most, or all of the winter, precluding the development of an active heterotrophic microbial biomass. The effect of the presence or absence of active heterotrophic biomass on N cycling during snowmelt can be seen in the difference in N leachate measurements between snowpacks that were deep with consistent coverage compared to ones that were shallow in depth with inconsistent coverage (Figure 4). This relationship is opposite of what would be expected if the amount of N leached from the soil was directly related to the amount of water in the seasonal snowpack available to infiltrate soil at these sites.

Based on these results, we propose a conceptual model to describe N cycling in seasonally snow-covered alpine catchments during the snow-covered season. In this model, the duration of winter snow cover increases along the X axis and total over-winter heterotrophic activity and N leachate increase along the Y axes (Figure 7). The duration of snow-cover is divided into four snowpack regimes; zone I is characterized by shallow short-duration snowpacks, zone II is characterized by high interannual variability in snow depth and duration, zone III is characterized by early developing, continuous snow cover, and zone IV is characterized by deep, long-duration snow cover verging on perennial snowpacks.

At sites with a very short duration snow cover (zone I) the soil remains frozen through much of the winter, there is very little free water available, and over-winter heterotrophic activity is very low. Consequently, there is a very weak N sink and N leachate is high. Both N from atmospheric deposition and soil inorganic N will contribute to N-leaching losses from these areas. In zone II, the snowpack develops later in the season and sites may experience a freeze event that increases labile carbon substrate. This increased substrate increases heterotrophic activity and promotes the growth of microbial biomass once soils thaw under the snowpack. Total microbial activity and the amount of N retention in the soils is highly variable, with an interaction

 

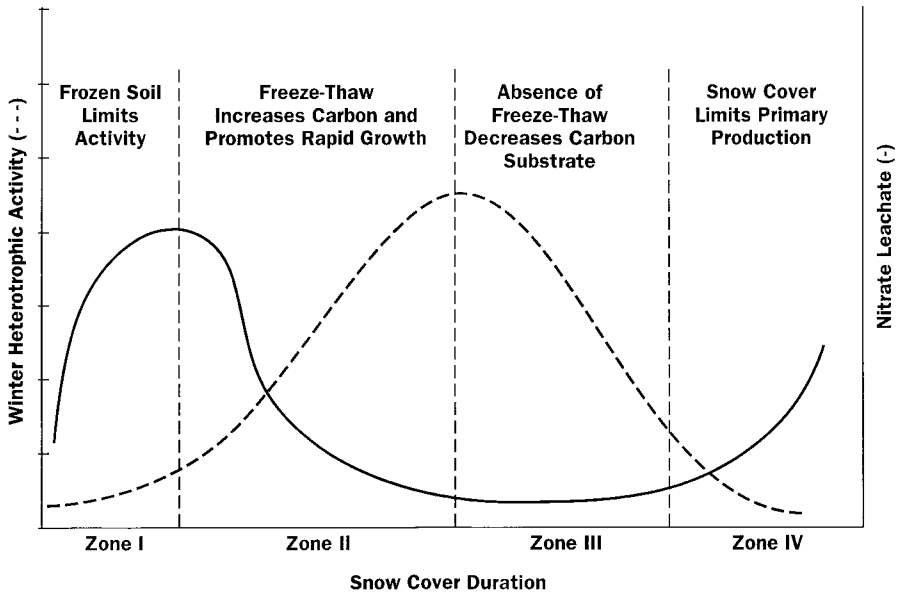


Figure 7. A conceptual model of how snow cover controls subnivial heterotrophic activity in alpine catchments at mid-latitudes. The duration of winter snow cover increases along the X axis and total over-winter heterotrophic activity and N leachate increase along the Y axes. The snow-pack controls on subnivial microbial activity in turn exert control on the assimilation of inorganic N released from the snowpack and the export of $NO_3^-$ to surface waters

effect that depends on the severity of the freeze event and the duration of thawed soil under snow for heterotrophic processing of the carbon substrates. Soils in this zone can be expected to be a net N sink during heavy snow years and an N source during low snow years. In zone III the snow cover develops early in the winter and soils typically do not experience severe freeze-thaw events. Free water is available throughout the winter and heterotrophic activity continues through the winter and N retention is relatively high. In zone IV snow cover is present for much of the year, perhaps never melting in heavy snow years. Microbial activity under snow in zone IV is reduced because there is very little primary production during the growing season to provide carbon substrate. In these areas there is a weak N sink during snow melt and $NO_3^-$ stored in the seasonal snowpack contributes directly to snow melt runoff.

The Martinelli catchment is characteristic of zone IV. The late-lying snow patch results in little net primary production during the growing season. Microbial activity is carbon limited with little growth of microbial biomass under these deep and extensive snowpacks. There is also a limited ability to assimilate inorganic N released from the snowpack. Consequently, much of the $NO_3^-$ released from storage in the snowpack goes directly to streamflow.

Most of the Saddle site is characteristic of zone III. The snowpack has sufficient depth and duration to insulate soils from the atmosphere, resulting in high levels of heterotrophic activity and a strong microbial sink for inorganic N released from storage in the snowpack during snow melt. While there may be high mineralization of organic matter (Williams *et al.*, 1998b) and over-winter production of inorganic N (Brooks *et al.*, 1996), both snowpack and soil sources of inorganic N are immobilized in microbial biomass. Therefore, little $NO_3^-$ is available for export in surface waters.

The area most sensitive to changes in winter snow cover is Zone II, where small changes in either the timing or amount of snow cover can have very large effects on soil biogeochemical processes before and during snow melt. We suggest that the large temporal variability during the growing season in $NO_3^-$ concentrations from Green Lake 4 can be explained by interannual differences in snow accumulation. The Green Lake 4 catchment consists of a mosaic of landscape types, where the amount of snow cover varies

 

from year to year. Years with early and consistent snow accumulation result in little $NO_3^-$ export during the growing season and years with late and light snowfall result in higher amounts of $NO_3^-$ in surface waters during the growing season. Consequently, $NO_3^-$ export in surface waters will be a non-linear function in response to increases in atmospheric deposition of inorganic N because of temporal and spatial differences in snow cover controls on subnivean N cycling. This model suggests that a portion of the spatial and temporal variability observed in N export from these seasonally snow-covered systems is due to variability in winter snow cover both across the landscape and inter-annually.

We recently applied this conceptual model to a ten-year record of stream water export of $NO_3^-$ in the Loch Vale catchment of Rocky Mountain National Park (Brooks *et al.*, in press). Loch Vale is located approximately 90 km north of Niwot Ridge/Green Lakes Valley and contains a similar mixture of vegetation and talus environments. Average annual inorganic N in wet depositions at this site was 2·61 kg $ha^{-1}$ $yr^{-1}$ (CV 0·21), while average annual export was 1·84 kg $ha^{-1}$ $yr^{-1}$ (CV 0·13). While the variability in both deposition and export were relatively low, net N retention of 0·74 kg $ha^{-1}$ $yr^{-1}$ was much more variable with a CV of 0·55. Furthermore, basin retention of inorganic N in wetfall was not significantly related to deposition of inorganic N. Annual snowfall amount, however, was significantly ($p = 0{\cdot}006$) related to net N retention and explained 68% of the inter-annual variability in N export.

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