Nitrogen mass balances and abiotic controls on N retention and yield in high-elevation catchments of the Sierra Nevada, California, United States

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Abstract. Interannual variations in nitrogen mass balances for the Emerald Lake watershed (ELW) and six additional headwater basins of the Sierra Nevada of California are described and used to investigate the influence of physical (snow regime, runoff, and precipitation) and chemical (N loading) forcings on the observed variability in annual catchment yield and retention of N. At ELW, annual yield of N varied by a factor of 8 (0.4–3.2 kg ha\(^{-1}\) yr\(^{-1}\)) and was a linear function of runoff (\(R^{2} = 0.89\) and 0.74 for dissolved inorganic nitrogen and dissolved organic nitrogen, respectively). Nitrogen yield increased faster than increases in runoff; that is, ecosystem processes enhanced N losses during years with high runoff and retarded losses during dry years. The timing of snowmelt runoff had a large effect on catchment inorganic N dynamics: nitrate pulses were greater and DIN retention was lower in years with deep, late melting snowpacks. We hypothesize that in the Sierra Nevada, labile N pools in soils are increasingly stocked during years with high snowfall amounts. These findings and modeling studies in high-elevation watersheds suggest that if current trends toward warmer air temperatures and earlier snowmelt continue, N retention will increase in the Sierra Nevada.

1. Introduction

Despite considerable effort, accurate modeling of N sources, transformations, and sinks at the catchment scale remains a challenge. Of particular importance is improved understanding of the N retention capacity of watersheds and the response of biological reservoirs to alterations in climate or rates of N deposition, both pressing concerns given growing evidence of changes in climate and the likelihood that emissions of anthropogenic N will increase [Galloway et al., 1994]. Our ability to predict ecosystem responses is predicated on our ability to identify linkages between abiotic variables and biogeochemical cycles [Aber and Driscoll, 1997].

One potential effect of global warming is a change in the extent and duration of snow cover in the arctic and high mountain ranges [Rango and Martinec, 1994; Derksen et al., 2000]. Changes in snow regimes are likely to modify the timing and quantity of water and solute release from melting snowpacks, which in turn will affect the spatial and temporal patterns of soil moisture, temperature, and nutrient availability [Fisk et al., 1998; Baron et al., 2000; Conley et al., 2000]. Little is known regarding the overall impact of these changes on N cycling, but there is increasing evidence that the subnival soil environment is biologically active [Taylor and Jones, 1990; Brooks et al., 1996; Lipson et al., 1999]. Hence there is a strong possibility that changes in snow regimes will have significant effects on biogeochemistry in ecosystems with seasonal snow cover.

Microbial assimilation of nitrate may be an important sink in snow-covered montane and arctic ecosystems where vegetation is dormant for many months [Schimel et al., 1996; Brooks et al., 1997]. At Niwot Ridge in the Rocky Mountains, Williams et al. [1996] and Brooks et al. [1996] suggest microbial N assimilation as a primary control on inorganic N in soil solutions during snow cover, providing a large sink for inorganic N flushed from the seasonal snowpack. The microbial N sink was found to be sensitive to changes in the timing and extent of snow cover. At the Loch Vale watershed in Colorado, dissolved inorganic N (DIN) retention was positively related to snowfall quantity, which was believed to be commensurate with the depth and consistency (i.e., the period of uninterrupted snow cover) of the winter snowpack [Brooks et al., 1999]. This work culminated in a conceptual model of how snow cover controls microbial activity in high-elevation ecosystems [Brooks and Williams, 1999]. The model describes the behavior of the microbial N sink across a gradient of snow cover duration.

Since few long-term biogeochemical studies have been conducted in montane regions, it is unclear whether microbial populations exert similar control on N cycling in other high-elevation ecosystems. More data are needed to test whether alterations in the extent and duration of snow cover induce the same changes in all seasonally snow-covered ecosystems. To date, most studies have focused on inorganic N fluxes despite increasing evidence that organic N may represent a substantial percentage of N inputs and losses from montane ecosystems [Church, 1999; Campbell et al., 2000a, 2000b; McHale et al., 2000; Coats and Goldman, 2001]. To gain a more complete understanding of N biogeochemistry in the context of ecosystem change, all N fractions must be considered.

In this study we describe the interannual variability of N loading to and yield from high-elevation watersheds of the Sierra Nevada of California using a 14 year continuous record from the Emerald Lake watershed (ELW) (1985–1998) and
supporting results from six other intensively studied headwater catchments (1990–1993). With these data we compute annual mass balances for N that include, in addition to inorganic fractions, organic and particulate N. We then examine the relationships between catchment N export and retention and three types of abiotic variables: (1) atmospheric deposition (water and solutes), (2) catchment runoff, and (3) the timing of snowpack formation and melt. Our goal is to quantify the linkages between catchment N cycling and these physiochemical forcings, test hypotheses regarding the effect of snow cover on N biogeochemistry, and discuss the potential impacts of expected climate change on N retention capacity of high-elevation ecosystems in the Sierra Nevada.

2. Site Descriptions

The catchments studied are located in the alpine and subalpine zones of the Sierra Nevada of California and include a wide range of the geographic, geologic, and hydrochemical variation among Sierra Nevada high-elevation headwater catchments [Engle and Melack, 1998]. Geographically, the sites span a majority of the north-south extent of the range; four of the watersheds are located along the eastern slope (Ruby Lake, Crystal Lake, Spuller Lake, and Lost Lake), and the remainder are situated on the western side (ELW, Pear Lake, and Topaz Lake). The Lost and Ruby Lake catchments delimit the range in catchment area (25–441 ha), lake area (0.7–12.6 ha), catchment relief (160–2904 m), and elevation (2475–3390 m) contained among the seven study sites (Table 1). The lakes range in depth from 1.5 m (Topaz) to 16.4 m (Ruby) and in volume from ~35,000 m³ (Spuller) to over 2,000,000 m³ (Ruby).

With the exception of Topaz and Crystal, all of the catchments are glacial cirques underlain by granite and granodiorite rock. The Topaz watershed lacks a distinct cirque topography and is situated on a high-elevation, moderate relief, glaciated plateau. The Crystal Lake cirque is underlain by granite and volcanic bedrock and has thick soils of volcanic tephra. Soil coverage in the catchments ranges from <25% at ELW, Pear, and Ruby to over 40% at Topaz and Crystal (Table 1). Vegetation cover, which consists mainly of grasses, sedges and small shrubs varies over a wide range: 8% at Ruby to over 30% at Crystal, Topaz, and Lost. Trees are sparse in most of the catchments; however, considerable stands are found along the lakeshore in the Lost Lake watershed and scattered throughout the Crystal Lake catchment. These forests consist of western white pine, lodgepole pine, mountain hemlock, and foxtail pine; no mountain alder is found in any of the catchments.

At all sites, precipitation falls predominately as snow during the winter and accumulates with little melt or evaporative losses until spring snowmelt [Leydecker and Melack, 1999]. Rainfall is sparse, comprising ~10% of annual precipitation [Melack and Sickman, 1997]. Snowmelt typically begins in April with peak discharge usually occurring in June. During winters with a large amount of snow, snowmelt onset may be delayed until May with peak runoff occurring in July or August.

Lakes and streams in these catchments are weakly buffered, calcium carbonate–dominated waters. All the lakes are oligotrophic because of low phytoplankton biomass and nutrient concentrations. In terms of N saturation the catchments in this study would be at stage 0 or 1 of Stoddard’s [1994] classification scheme [Sickman et al., 2001]. Currently, the seven catchments neutralize current rates of acidic atmospheric deposition and are not undergoing acidification [Leydecker et al., 1999].

In ELW, ~90% of the basin’s N storage is contained in soils, litter, and soil solution with the balance held in vegetation [Williams et al., 1995]. Internal cycling within the soil N pool is dominated by mineralization of soil organic matter and biological uptake; these fluxes are in approximate balance. Soil N transformations when combined with atmospheric N deposition and N yield suggest that annual catchment N turnover is <5%. Nitrogen fixation and denitrification have not been extensively measured, but Williams et al. [1995] and Brown et al. [1990] suggest that these processes are not a significant source or sink for N in ELW.

3. Methods

All data referenced to year use a hydrologic water year that runs from October 1 through the following September (e.g., water year 1985 runs from October 1, 1984 through September 30, 1985). This reference system closely approximates the annual pattern of precipitation in the Mediterranean climate of California.

3.1. Wet Deposition

Precipitation was divided into two classes. Nonwinter precipitation is rain and snow that fell during the approximate period of April through November. The start of the nonwinter period was determined by the timing of the spring snow survey, which typically took place in early April, and the end of the period was defined by the beginning of snowpack accumulation in the late autumn and early winter.

From May through October, nonwinter precipitation was measured at ELW with an Alter-shield equipped tipping bucket rain gauge and chemical samples were collected in a

Table 1. Watershed and Lake Characteristics of the Sierra Nevada Study Sites

<table>
<thead>
<tr>
<th>Lake/Catchment</th>
<th>Basin Area, ha</th>
<th>Basin Relief, m</th>
<th>Outlet Elevation, m</th>
<th>Soil Cover, %</th>
<th>Vegetation Cover, %</th>
<th>Lake Area, ha</th>
<th>Lake Mean Depth, m</th>
<th>Lake Volume, $\times 10^3$ m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emerald</td>
<td>120</td>
<td>616</td>
<td>2800</td>
<td>22</td>
<td>20</td>
<td>2.7</td>
<td>6.0</td>
<td>162</td>
</tr>
<tr>
<td>Crystal</td>
<td>135</td>
<td>293</td>
<td>2951</td>
<td>53</td>
<td>48</td>
<td>5.0</td>
<td>6.5</td>
<td>324</td>
</tr>
<tr>
<td>Lost</td>
<td>25</td>
<td>160</td>
<td>2475</td>
<td>36</td>
<td>35</td>
<td>0.7</td>
<td>1.9</td>
<td>12.5</td>
</tr>
<tr>
<td>Pear</td>
<td>142</td>
<td>471</td>
<td>2904</td>
<td>22</td>
<td>19</td>
<td>8.0</td>
<td>7.4</td>
<td>591</td>
</tr>
<tr>
<td>Ruby</td>
<td>441</td>
<td>812</td>
<td>3390</td>
<td>18</td>
<td>8</td>
<td>12.6</td>
<td>16.4</td>
<td>2080</td>
</tr>
<tr>
<td>Spuller</td>
<td>97</td>
<td>537</td>
<td>3131</td>
<td>33</td>
<td>19</td>
<td>2.2</td>
<td>1.6</td>
<td>34.7</td>
</tr>
<tr>
<td>Topaz</td>
<td>165</td>
<td>275</td>
<td>3218</td>
<td>41</td>
<td>32</td>
<td>5.2</td>
<td>1.5</td>
<td>76.9</td>
</tr>
</tbody>
</table>

aSoil and vegetation cover are expressed as a percentage of total basin area.
colocated Aerochemetrics sampler. At other catchments, rain gauges and Aerochemetrics samplers were located in the study basins or at nearby weather stations operated by the National Park Service, United States Forest Service, National Atmospheric Deposition Program (NADP), California Air Resources Board, or the University of California, Santa Barbara. Precipitation during periods when rain gauges were inoperable was measured with snowboards or by digging snowpits and sampling the fresh snow.

Winter precipitation was estimated by sampling the catchment snowpack at maximum accumulation. Winter snowfall in these high-elevation basins is conserved because of low evaporation and minimal melt; hence sampling of the spring pack provides an accurate measure of winter precipitation and chemical loading [Williams and Melack, 1991; Leydecker and Melack, 1999]. Throughout the winter the snow surface collects dry deposition so the spring snowpack stores the combined chemical contributions from both wet and dry deposition. Basin-wide, winter snowfall was determined from snow depth surveys (200–300 measurement points per catchment per year) and measurements of snow density collected from snowpits (one to three pits per catchment per year). Snow depths were measured along transects designed to be representative of watershed topography. Average catchment snow-water equivalence (SWE) was calculated by multiplying mean density by mean depth and correcting for the percentage of snow-free area obtained from aerial photographs or satellite imagery.

Chemical samples of the snowpack were obtained in snowpits by collecting duplicate, continuous, vertical sections 1–2 cm in length using a clear PVC tube (5 cm diameter, 50 cm long, with a sharp, beveled cutting edge). Each 40 cm section was placed into a separate polyethylene bag. Field personnel wore powder-free vinyl gloves during sample collection. Bags and sampling apparatus were soaked in deionized water (DIW) for several days before use and kept scrupulously clean. From two to four snowpits were sampled in each catchment each year. All snow samples were kept frozen at $-20^\circ$C until analyzed.

### 3.2. Stream and Lake Chemical Sampling

Dissolved N yield from the catchment was computed from measurements of outflow stream chemistry and discharge. Particulate nitrogen (PN) yield was computed from measurements of lake chemistry and outflow discharge. Catchment outflows were sampled for ammonium, nitrate, and dissolved organic nitrogen (DON) at the outlet stream gauging stations. Stream stage (water depth recorded as transducer voltage) was continuously measured and a stage-discharge relationship established for each outlet stream. For ELW during water years 1985–1989 and for water years 1990–1993 at all other catchments but Spuller the stage-discharge relationships were based on 50–200 tracer determinations of discharge (slug and constant injection of NaCl and rhodamine dye) [Kilpatrick and Cobb, 1985]. From water year 1990 onward, discharge was measured with v-notch weirs at ELW and Spuller.

#### 3.3. Outflow Gauging

Gauging stations were installed in the outlet streams of all catchments. Stream stage (water depth recorded as transducer voltage) was continuously measured and a stage-discharge relationship established for each outlet stream. For ELW during water years 1985–1989 and for water years 1990–1993 at all other catchments but Spuller the stage-discharge relationships were based on 50–200 tracer determinations of discharge (slug and constant injection of NaCl and rhodamine dye) [Kilpatrick and Cobb, 1985]. From water year 1990 onward, discharge was measured with v-notch weirs at ELW and Spuller.

#### 3.4. Chemical Analyses

Rain and stream grab samples were processed within 48 hours of collection; for samples obtained by automated samplers, collection was delayed from 1 to 3 weeks. Snow samples were thawed at 5$^\circ$C under an air/argon atmosphere designed to mimic the partial pressure of carbon dioxide at 3000 m elevation. Ammonium was determined on filtered samples generally within 72 hours by the indophenol blue method [Strickland and Parsons, 1972]. For water years 1986–1998, nitrate was measured on a DIONEX ion chromatograph, employing an AS4A or AS14 separation column and conductivity detection. During water year 1985, nitrate was determined colorimetrically within 1 week of collection using cadmium reduction [Strickland and Parsons, 1972]. Delays for nitrate determination were of the order of days during water years 1985–1987 and of the order of weeks from 1990 onward. Storage tests indicate that filtered, refrigerated samples of Sierra Nevada surface water can be held at least 3 months prior to nitrate analysis [Dickinson and Melack, 1989].

Total dissolved nitrogen (TDN) was determined by the Valderrama [1981] method: filtered water samples were digested with a NaOH-persulfate oxidizing reagent under high heat (260$^\circ$C) and pressure, which converted all N forms to nitrate. Digested samples were adjusted to neutral pH with low-N NaOH and nitrate determined as nitrite after cadmium reduction. The nitrate determinations were done manually from 1985 to 1989 and on a Latchet autoanalyzer from 1990 onward. Dissolved organic N was computed as the difference between TDN and DIN (ammonium plus nitrate). Particulate N was determined by combustion of filters in an elemental analyzer.

#### 3.5. Nonwinter Dry Deposition

No continuous, long-term measurements of nonwinter dry deposition are available for any of the watersheds. Instead, we used deposition rates of N species at a dry deposition station located at Wolverton Meadow, a forest clearing 6 km west of ELW at an elevation of 2250 m. The station is part of the National Oceanic and Atmospheric Administration (NOAA)-
operated Atmospheric Integrated Research Monitoring Network (AIRMoN) dry-deposition network [Hicks et al., 1991; Meyers et al., 1991]. Nitrogen species measured at this station include nitric acid and particulate ammonium and nitrate. The data record begins in July 1986 and ends in September 1998.

The dry-deposition inferential method (DDIM) uses airborne chemical concentrations and the deposition velocity of individual chemical species to compute dry-deposition rates [Meyers et al., 1998]. Ambient air concentrations of nitric acid, particulate nitrate, and ammonium were determined by a filter pack accumulating system that was sampled, on average, every 7 days. Deposition velocities were derived from a semiepiphenal model that used site-specific meteorological data and time-varying information about surface conditions. Input variables included wind speed, wind direction, air temperature, relative humidity, surface wetness, and rainfall.

Quantitative and qualitative differences in surface characteristics between the Wolverton station and the high-elevation study sites likely result in differences in the true rate of nitrogen deposition: the Wolverton DDIM model is parameterized to grass and ponderosa/lodgepole pine while the lake basins have limited vegetation (Table 1). Because of the model’s reliance on leaf area index (LAI), it is likely that dry-deposition rates at the vegetated Wolverton station are higher than actual rates at our study sites. To estimate deposition at ELW, we reduced the Wolverton LAI by 50% (from 3.0 to 1.5) on the basis of estimates of plant surface area and the ratio of catchment surface area to planar area (computed from a 5 m digital elevation model). If all other factors were similar, ELW would receive half of the dry deposition measured at Wolverton. Owing to their close proximity, we assumed that dry deposition at the Pear and Topaz Lakes watersheds was the same as at ELW.

For Ruby, Spuller, Crystal, and Lost Lakes watersheds, we reduced the estimated ELW values by a further 20% on the basis of the long-term ratio of eastern to western slope wet DIN deposition [Melack and Sickman, 1997]. Catchments along the eastern slope of the Sierra Nevada are in the Great Basin Valley air basin, which has better air quality than the San Joaquin Valley air basin [Bytnerowicz and Fenn, 1996; Alexis et al., 1999].

3.6. Volume-Weighted Means, N Fluxes, and Retention

Annual volume-weighted mean (VWM) concentrations were calculated for each N fraction in winter and nonwinter precipitation and outflow. For snow the SWE of individual pit samples was used to weight the samples. Nonwinter and winter loading was calculated by multiplying VWM concentrations by the amount of precipitation and then normalizing the product to watershed area. Nonwinter dry deposition for 1985–1986 and DON for wet deposition in 1985–1986 and 1990–1992 were not quantified. In the case of missing dry deposition we used the average annual dry deposition for 1987–1998. For missing DON we used measured precipitation quantities and the volume-weighted mean concentrations of DON in winter and nonwinter precipitation from existing data from 1987–1989 and 1993–1998.

Annual solute yield was calculated as the product of outflow discharge and the VWM concentration of each species normalized to catchment area. When samples were collected on a daily basis, daily discharge was used to weight the samples; when the sampling interval was >1 day, we used total discharge from one sampling interval midpoint (±1 day) to another.

Herein, the terms export and loss are used synonymously with yield. Annual watershed N retention was computed by subtracting yield from loading and is expressed in kilograms per hectare of catchment area (kg ha⁻¹ yr⁻¹) or as a percentage of loading. Annual retention is the equivalent of deposition-corrected N yield (i.e., yield minus loading) except for the change in sign.

3.7. Error Analysis

Nitrogen fluxes are the product of water volumes and VWM concentrations; thus errors in measuring precipitation or streamflow introduced uncertainty into flux estimates. Other sources of error include analytical error, unsampled precipitation, and low-frequency stream sampling. In Table 2 we summarize the errors in VWM chemistry, water, and elemental flux estimates and N retention at ELW; a complete analysis, including the derivations of these errors, is given by Melack et al. [1998].

4. Results

4.1. Winter Snow

At ELW, winter snowfall represents, on average, 88% of annual precipitation (Table 3). The proportion of annual precipitation contributed by winter snowfall varied within a narrow range: 90% of annual precipitation occurred in the winter during years with high snowfall and little nonwinter precipitation, i.e., 1995 and 1998; in years with low snowfall and more nonwinter precipitation the proportion dropped to 78%. Similar precipitation patterns were observed at the other catchments. The interannual variability in snowfall at ELW was almost fivefold (568–2628 mm) during 1985 to 1998.

Nitrogen concentrations in the settled snowpack at ELW (measured around early April) were slightly over 2 μM for all N species (ammonium, nitrate, and DON) (Table 3). Similar N concentrations were measured for the other catchments (not presented). Interannual variation in N species concentrations was small (range of 1–4 μM), but levels tended to be lower in wet winters (i.e., above normal winter snowfall) than during dry winters (i.e., below normal winter snowfall) [Melack and Sickman, 1997].

4.2. Nonwinter and Annual Precipitation

Nonwinter precipitation, primarily late spring and autumn rainfall, comprised, on average, 12% of annual precipitation at ELW. The volume of nonwinter precipitation varied by a factor of 15 (26–389 mm) during the 14 years of record.

Nitrogen concentrations were higher in nonwinter precipitation than in winter snowfall. Ammonium and nitrate concentrations were >10 times greater (1985–1998 mean of 28 and 23 μM, respectively) than in the spring snowpack (Table 3). The ELW data are representative of nonwinter precipitation in the other catchments (not presented). DON levels were lower relative to snow, (mean of 8.5 μM). Overall, annual VWM ammonium and nitrate concentrations in nonwinter precipitation ranged from –6 to over 90 μM. This large variation is attributable to the mix of storms encountered each year: a paucity of N-rich summer rains resulted in low VWM concentrations, while abundant summer storms and little spring or autumn precipitation, caused VWM N concentrations to be higher. Annually, ammonium VWM concentrations ranged from 2.5 to 8.3 μM, slightly greater than nitrate (2.1–7.6
Table 2. Summary of Expected Errors for Components in the N Budgets at Emerald Lake Watershed

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Percent Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonwinter wet deposition</td>
<td></td>
</tr>
<tr>
<td>Volume error</td>
<td>9</td>
</tr>
<tr>
<td>Sampling error</td>
<td>0–10</td>
</tr>
<tr>
<td>Analytical error</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Winter wet and dry deposition</td>
<td></td>
</tr>
<tr>
<td>Volume error</td>
<td>5</td>
</tr>
<tr>
<td>Sampling error</td>
<td>0–4</td>
</tr>
<tr>
<td>Analytical error</td>
<td>2–7</td>
</tr>
<tr>
<td>Catchment runoff</td>
<td></td>
</tr>
<tr>
<td>Volume error</td>
<td>10–20(^a), 4(^c)</td>
</tr>
<tr>
<td>Sampling error</td>
<td>15–80(^a), 6–23(^c), 10–28(^c), 4–8(^a)</td>
</tr>
<tr>
<td>Analytical error</td>
<td>2–6(^a), 10(^c)</td>
</tr>
<tr>
<td>VWM chemistry</td>
<td></td>
</tr>
<tr>
<td>Nonwinter wet deposition</td>
<td>&lt;5(^i), &lt;3(^i), &lt;6(^i)</td>
</tr>
<tr>
<td>Winter wet and dry deposition</td>
<td>&lt;5(^i), &lt;5(^i), &lt;8(^i)</td>
</tr>
<tr>
<td>Outflow</td>
<td>18–82(^a), 23(^i), 30(^i), 8(^i)</td>
</tr>
<tr>
<td>N loading/N yield</td>
<td></td>
</tr>
<tr>
<td>Nonwinter wet deposition</td>
<td>&lt;18</td>
</tr>
<tr>
<td>Winter wet and dry deposition</td>
<td>&lt;18</td>
</tr>
<tr>
<td>Annual (all forms)</td>
<td>&lt;18</td>
</tr>
<tr>
<td>Outflow (total N)</td>
<td>&lt;30(^k), 15(^l)</td>
</tr>
<tr>
<td>N retention</td>
<td>25(^k), 17(^l)</td>
</tr>
</tbody>
</table>

\(^a\)The total cumulative error for volume-weighted means (VWM), N fluxes, and yields were calculated assuming independence of component variances and standard propagation of error techniques [Taylor, 1990]. Greater detail on the derivation of component errors is given by Melack et al. [1998]. Unless noted, the error stated applies to all dissolved N species. Deposition sampling errors were computed only for years with complete deposition chemistry (dissolved inorganic plus dissolved organic nitrogen (DIN + DON)), i.e., 1985–1987 and 1993–1998. For particulate nitrogen (PN) concentration we estimate the error in VWM chemistry to be less than ±25%, and for PN flux we estimate the error to be less than ±15%. The error for nonwinter dry deposition of N was assumed to be ±25% for computation of N loading. For outflow total N flux the error was computed using the following weightings for N species: 2% NH\(_4\), 49% NO\(_3\), 35% DON, and 14% PN; for total N loading, winter, nonwinter wet-deposition, and nonwinter dry-deposition fluxes were weighted equally. For N yield errors, loading and export were equally weighted. 

\(^b\)1985–1989 (salt dilution derived rating curves).

\(^c\)1990–1998 (V notch weir).


\(^f\)Ammonium, daily to biweekly sampling interval (1993–1998).

\(^g\)Nitrate and DON, daily to biweekly sampling interval (1993–1998).

\(^h\)Nitrate.

\(^i\)DON.

\(^j\)Ammonium.


4.3. N Loading

Annual N loading at ELW ranged from 2.0 to 4.9 kg ha\(^{-1}\) yr\(^{-1}\) from 1985 to 1998 with no long-term trend (Figure 1a). All loading and yield rates are expressed as weight of N rather than N compound weight e.g., kilograms N-NO\(_3\)\(^{-}\) rather than kilograms NO\(_3\). The average loading was 3.0 kg ha\(^{-1}\) yr\(^{-1}\). High winter precipitation, i.e., 1986, 1995, and 1998, resulted in the greatest N deposition; however, relatively dry years like 1987, 1991, and 1997 had only slightly less deposition owing to a surfeit of N-rich nonwinter precipitation. During most years the majority of annual N deposition occurred during nonwinter periods (Figure 1). The ratio of nonwinter to winter N deposition for ELW was 1.5:1. On average, 41% of the loading was nitrate (including nitric acid in dry deposition), 31% was ammonium, and 23% was DON.

Wet deposition of N to the alpine and subalpine zones of the Sierra Nevada was spatially uniform (Figure 1b). For the years of 1990–1993, DIN loading from wet deposition varied from 1.1 to 1.5 kg ha\(^{-1}\) yr\(^{-1}\). Nitrogen deposition at the Ruby and Topaz Lakes catchments tended to be lower, but the differences were within the limits of error in our estimates of N loading.

Dry deposition contributed, on average, 20% of total N loading, but this ratio was variable (4–40%). Nonwinter dry N deposition was inversely related to wet deposition at ELW (Figure 2). The coefficient of determination for the equation (dry N = −0.18(wet N) + 1.06) was 0.6, and the equation was significant at the \(p < 0.01\) level. Data from 1994 are presented in Figure 2 but were not used in the regression; 1994 was an El Niño–Southern Oscillation year with exceptionally clean air conditions.

4.4. N Yield

Annual VWM nitrate showed relatively large variations among the study sites (Table 4). At most locations, ammonium concentrations were at or near the detection limit; only at Pearl Lake were measurable levels commonly encountered. For VWM nitrate, two categories of watersheds were evident: catchments where nitrate was at or near the detection limit for most of the year (i.e., Crystal, Lost, and Topaz) and catchments with relatively large snowmelt nitrate pulses and measurable nitrate concentrations during the remainder of the year (ELW, Pear, Ruby, and Spuller) [Melack et al., 1998]. Within these latter watersheds, VWM nitrate was similar, ranging from 4 to 5 \(\mu\)M. Low nitrate sites tended to have a higher proportion of vegetation cover; for example, vegetation covers 32–48% of the low nitrate catchments but only 8–20% of those with higher nitrate concentrations (Table 1).

Inorganic N was the predominant form of N yield from ELW, comprising, on average, 51% of annual N export (Figure 3a). At ELW, DON contributed, on average, 35% of annual N loss; at the other catchments, DON export comprised from ~20 to 60% of annual N yield (Figure 3b). Particulate N was a minor (<15%) contributor to catchment N yield; mean particulate N concentrations ranged from 1.3 to 3.6 \(\mu\)M and were usually lower than nitrate or DON (Table 4). Ammonium export was negligible at all sites. There was a large variation in
the quantity and form of N yield among the catchments (Figure 3b). For a 2 year period with complete chemistry for all N species at all sites (1990–1991), N losses varied from 0.2 to nearly 1.0 kg ha\(^{-1}\) yr\(^{-1}\). At low N yield sites like Crystal, Lost, and Topaz, DON and PN were the largest component of N losses (Figure 3b).

Annual N yield (DIN + DON + PN) from ELW varied from 0.5 to over 3.0 kg ha\(^{-1}\) yr\(^{-1}\) (Figure 3a). Yield was primarily a function of annual runoff; N yield was greatest during years with high precipitation (1986, 1993, 1995, and 1998) and lowest during drought years (1987–1992). The coefficients of determination in linear regressions between catchment runoff and export were 0.89 for DIN and 0.74 for DON (Figures 4a and 4b). At the other catchments, DIN yield was also highly correlated with runoff: coefficients of variation were >0.90 (not shown), although the available data (1990–1993) are highly leveraged by 1993, a water year with above average runoff.

Yield of DIN and DON were significantly related to total nitrogen (TN) loading \((p < 0.05)\) with higher yields in years with greater loading (Figures 4c and 4d). However, it is likely that statistically significant relationships between loading and yield are an artifact of covariance between TN inputs and runoff: when both TN loading and runoff were used in multiple regressions predicting N yield, only runoff was found to be significant.

Using ELW data, we investigated the relationship between catchment N yield (DIN and DON) and the nitrate pulse and four independent variables related to the seasonal snowpack:

**Figure 1.** (a) Annual N loading to the Emerald Lake watershed, 1985–1998, and (b) mean annual dissolved inorganic nitrogen (DIN) loading to seven high-elevation watersheds in the Sierra Nevada, 1990–1993. Error bars denote standard errors.

**Figure 2.** Relationship between total N deposition in annual wet deposition and the amount of annual dry inorganic N deposition at Emerald Lake watershed. Data for water year 1994 are shown but were not used in the regression.
date of snowpack formation, snowpack water-equivalence, snowpack DIN load, and the timing of snowmelt. Several indices for the timing of snowmelt were considered, including the onset of snowmelt, date of peak discharge, and date of centroid of snowmelt mass (i.e., date when 50% of snowmelt has occurred). The centroid of mass index was chosen for the regression analyses because it is an easily determined and hydrologically robust measure for the timing of snowmelt over an entire catchment [Dunne and Leopold, 1978]. In addition, distributed snowmelt modeling suggests that by the date of 50% snowmelt, almost all portions of ELW have contributed runoff [Colee, 2000]. Dates for snowpack formation and snowmelt timing

<table>
<thead>
<tr>
<th>Catchment</th>
<th>NH₄⁺, μM</th>
<th>NO₃⁻, μM</th>
<th>DON, μM</th>
<th>PN, μM</th>
<th>Runoff, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emerald</td>
<td>0.2</td>
<td>4.9</td>
<td>3.5</td>
<td>1.4</td>
<td>1129</td>
</tr>
<tr>
<td>Crystal</td>
<td>0.0</td>
<td>0.5</td>
<td>3.2</td>
<td>1.5</td>
<td>424</td>
</tr>
<tr>
<td>Lost</td>
<td>0.1</td>
<td>0.6</td>
<td>2.7</td>
<td>1.3</td>
<td>1210</td>
</tr>
<tr>
<td>Pear</td>
<td>0.5</td>
<td>4.0</td>
<td>2.9</td>
<td>3.3</td>
<td>703</td>
</tr>
<tr>
<td>Ruby</td>
<td>0.2</td>
<td>4.7</td>
<td>1.9</td>
<td>3.6</td>
<td>524</td>
</tr>
<tr>
<td>Spuller</td>
<td>0.0</td>
<td>4.6</td>
<td>3.1</td>
<td>1.6</td>
<td>819</td>
</tr>
<tr>
<td>Topaz</td>
<td>0.3</td>
<td>1.9</td>
<td>3.2</td>
<td>1.3</td>
<td>606</td>
</tr>
</tbody>
</table>

*Data are the average of the annual volume-weighted means from 1985 to 1998 at Emerald Lake watershed (ELW) and 1990 to 1993 at the other catchments. DON is dissolved organic nitrogen, and PN is particulate nitrogen. For catchments other than ELW, DON and PN data are solely from 1990 to 1991.

Figure 3. (a) Annual N yield from the Emerald Lake watershed, 1985–1998, and (b) mean annual N yield from seven high-elevation watersheds in the Sierra Nevada, 1990–1991.
were expressed as the day of the water year (DOWY), i.e., the first day of October is day 1.

Given the likelihood that the independent variables covary, regressions were performed between the snowpack parameters to evaluate the degree of covariance (Figure 5). There was no significant relationship between SWE and the timing of snowpack formation (Figure 5a). During most years, continuous snow cover formed during the month of November (DOWY 31–61). SWE was highly correlated with runoff; the relationship is not linear, but logarithmic, caused by carry over of snow from one water year into the next (Figure 5b). SWE was also positively related to the timing of snowmelt, explaining 66% of the variation in the timing of the centroid of runoff mass (Figure 5c). SWE and DIN loading are positively related ($r^2 = 0.5$; Figure 5d) since loading is the product of snowpack concentrations and water equivalence.

Most N export from ELW occurred during the rising limb of the snowmelt hydrograph as nitrate. The magnitude of the nitrate pulse (i.e., the increase in nitrate concentrations from low presnowmelt levels to the highest concentration measured during snowmelt) largely determined the annual catchment N yield. There was no significant relationship between the timing of snowpack formation and the magnitude of the snowmelt nitrate pulse (Figure 6a). Weak, positive relationships were observed between the pulse magnitude and SWE or DIN loading (Figures 6b and 6c); the equations explained only 20–25% of the variation in the nitrate pulse and were not significant at the $p < 0.05$ level. In contrast, the timing of snowmelt explained 90% of the variation in strength of the nitrate pulse (Figure 6d) and demonstrated that outflow nitrate concentrations were greater when snowmelt occurred later in the year.

4.5. Catchment N Retention

No significant relationships were found between catchment ammonium, DON, or total dissolved nitrogen (TDN) retention and any abiotic variable (atmospheric loading, runoff, SWE, or date of snowpack formation) using ELW data. Coefficients of determination were near zero, suggesting that for these N fractions, there was little abiotic forcing of catchment retention rates.

Of the N species examined, only nitrate retention was significantly related to the abiotic variables (Figure 7). We found strong negative correlations between nitrate retention and SWE (Figure 7b; $R^2 = 0.59$, $p < 0.01$) and the timing of snowmelt (Figure 7c; $R^2 = 0.73$, $p < 0.001$). Nitrate retention was also negatively related to runoff (not shown). As with N yield, there was no significant relationship between nitrate retention and the timing of snowpack formation (Figure 7a). The weak, inverse relationship between nitrate retention and DIN loading (Figure 7d; $R^2 = 0.32$) is counterintuitive and probably an artifact of the covariance between loading and SWE.

![Figure 4. Relationships among annual DIN and dissolved organic nitrogen (DON) yield and annual total N (TN) loading and runoff at the Emerald Lake watershed, 1985–1998.](image-url)
There was insufficient data to perform regressions between N retention and the abiotic variables for the other catchments. Instead, we examined the relative DIN retention of these watersheds in two hydrologically different years: a drought year, 1992, and a wet year, 1993. For comparison, at ELW, SWE during 1993 was 3.5 times greater than in 1992 (2185 versus 617 mm), and the centroid of snowmelt mass occurred 37 days later (DOWY 261 versus DOWY 224). Catchment DIN retention, expressed as a percentage of DIN loading, for water years 1992 and 1993 is presented in Table 5. In all cases, retention was lower in 1993 than in 1992. At catchments with relatively high N retention (Crystal, Topaz, and Lost), the wet-year:dry-year differences were relatively small compared to less N retentive catchments (Ruby, Pear, and ELW). These data reinforce the observation that DIN retention is lower in years with deep, late melting snowpacks.

5. Discussion

5.1. Controls on Catchment Nitrogen Yield

At ELW, annual N yield averaged 1.6 kg ha\(^{-1}\), slightly less than the 2 kg ha\(^{-1}\) reported at Loch Vale for 1982–1993 [Baron and Campbell, 1997]. The N fluxes for these two high-elevation catchments are similar despite DIN levels several times greater at Loch Vale; higher runoff at ELW offsets lower N concentrations. Baron and Campbell [1997] reported that nearly all of the N loss from Loch Vale occurs as DIN; particulate N and DON were minor components. In contrast, at ELW and the other Sierra Nevada catchments, organic N losses were similar to or greater than DIN losses. During the autumn of 1999, 130 lakes in the Sierra Nevada and the Rocky Mountains (a subset of the original Environmental Protection Agency Western Lakes Survey) were sampled. All nitrogen fractions were measured, i.e., nitrate, ammonium, DON, PN, TDN, and TN. The mean and standard error were 0.59 ± 0.03 for the ratio of DON to TDN in the sampled lakes and 0.47 ± 0.03 for the ratio of DON to TN [J. O. Sickman and D. W. Clow, unpublished data, 1999]. These synoptic data, along with the detailed DON budgets presented here, suggest that organic N fluxes are dominant pathways for N losses in high-elevation ecosystems of the western United States.

The linear relationship between runoff and the yield of DIN and DON at ELW demonstrates that N losses are largely a transport-dependent process at the catchment scale. Yield increased at a rate ~50% greater than the increase in runoff; DIN export varied by a factor of 9, while runoff varied by a factor of 5.7. DON increased at a rate 20% greater than the increase in runoff. These findings imply that N yield is not a
simple function of runoff or soil flushing; other processes enhance losses during years with high runoff and/or increase retention during dry years. Since the lake is not a major source or sink for DIN [Melack et al., 1989], biological process within the terrestrial portions of the catchment offer the most likely explanation.

In the Sierra Nevada the growing season is strongly influenced by snowpack duration. In years with shallow snow cover, soils become snow-free earlier, which may increase the amount of N sequestered in vegetation. Although the nitrate pulse occurs prior to the runoff centroid (at ELW the mean separation was 24 days), nitrate flux out of the catchment is driven by runoff and typically reaches a maximum near peak outflow (the mean separation between nitrate and runoff centroids was 7.7 days). High-snow years delay runoff and retard the recession of snow-covered area. To test whether the potential for N uptake by vegetation is greater during drier years, we examined the timing of nitrate export, nitrate concentrations and snow recession for two dissimilar years at ELW: 1994 with below normal snow accumulation (830 mm) and 1995 with above normal accumulation (2630 mm). In both years the majority of nitrate export occurred after the peak in nitrate concentrations (Figure 8). Snowmelt occurred earlier in 1994 than in 1995, and ~66% of the nitrate export (March 1 to September 30) took place after the catchment became 50% snow-free (May 22). Because ELW is a northwest facing cirque, most of the late season snowpack is restricted to the higher north facing half which contains a lower proportion of soils and vegetation [Williams et al., 1995; Cline et al., 1998]. In contrast, ~30% of the 1995 nitrate export took place after snow cover decreased to 50% (July 18). Using a wet-year/dry-year time series of DON concentrations from 1998 (2070 mm) and 1999 (870), we observed the same relative pattern for the timing of DON availability and snow recession (not shown). These observations support the hypothesis that the amount of N accessible to actively growing vegetation is influenced by snow regime and that vegetation uptake should be considered as a possible explanation for enhanced DIN and DON retention in dry years.

Alternatively, the observed relationship between DIN/DON yield and runoff could be controlled primarily by microbial population dynamics. Enhanced N loss during years with deep, late melting snowpacks could be the result of labile N pools increasingly stocked during long periods of snow cover; the size of these pools may be proportional to the intervening time between episodes of runoff. The alpine microbial community immobilizes N after plant senescence in the autumn, and community biomass generally increases until snowmelt runoff [Lipson et al., 1999]. Nitrogen is released from the microbial population during the later stages of spring runoff. However, the environmental trigger for this release is not known; probable causes include spring freeze-thaw events, microbial community shifts, or soil moisture conditions. In years with above normal
snowfall the amount of N in the microbial pool may be larger and the timing of its release may be later than in years with normal to below normal snowfall. Earlier studies at ELW suggest that internal sources and transformations of N within the terrestrial environment roughly balance the annual N requirements of vegetation [Williams et al., 1995]; hence variations in microbial N cycling induced by changes in snow regime could alter this balance, producing the observed interannual pattern of DIN/DON yield. However, detailed studies of N sources and sinks over several snowmelt seasons will be required to determine the relative importance of vegetation and microbial populations on annual N budgets in the Sierra Nevada.

In the United States the only other alpine/subalpine where detailed N budgets exist for comparison is Loch Vale. Figure 9a shows annual precipitation versus DIN yield for the Emerald and Loch Vale watersheds (Loch Vale data are from Baron and Campbell [1997] and Brooks et al. [1999]). Two points are worth noting: (1) the Sierra Nevada has a more variable hydrologic cycle, i.e., a greater range in annual precipitation and (2) there is no identifiable relationship between precipitation and DIN yield at Loch Vale. The dissimilar behavior to similar abiotic forcing at Loch Vale may be explained by the relatively narrow variability of precipitation and its effect on hydrological processes, such as soil flushing and moisture, or by the increased importance of, possibly dissimilar, biological controls. We propose that complex interactions between vegetation, microbial N cycling and snow cover in these catchments cause the observed differences, and these interactions will be explored in section 5.2.

### Table 5. Year to Year Changes in DIN Retention for Seven High-Elevation Watersheds in the Sierra Nevada

<table>
<thead>
<tr>
<th>Watershed</th>
<th>DIN Retention 1992, %</th>
<th>DIN Retention 1993, %</th>
<th>Difference, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>99.3</td>
<td>95.7</td>
<td>3.6</td>
</tr>
<tr>
<td>Emerald</td>
<td>85.1</td>
<td>43.6</td>
<td>41.5</td>
</tr>
<tr>
<td>Lost</td>
<td>96.4</td>
<td>90.2</td>
<td>6.2</td>
</tr>
<tr>
<td>Pear</td>
<td>89.4</td>
<td>63.3</td>
<td>26.1</td>
</tr>
<tr>
<td>Ruby</td>
<td>83.2</td>
<td>48.8</td>
<td>34.4</td>
</tr>
<tr>
<td>Spuller</td>
<td>72.7</td>
<td>63.5</td>
<td>9.2</td>
</tr>
<tr>
<td>Topaz</td>
<td>89.2</td>
<td>87.8</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*DIN retention is expressed as a percentage of DIN loading. Water year 1992 had later snowpack formation, less snow accumulation, and earlier snowmelt than 1993.*

**Figure 7.** Relationships between annual catchment nitrate retention and snow regime at ELW, 1985–1998.
cycled and does not come directly from the snowpack. Second, the quantity of N loading to ELW (mean of 3.0 kg ha\(^{-1}\) yr\(^{-1}\)) is small in comparison to the amount of N released in annual net mineralization within catchment soils, \(\sim 15\) kg ha\(^{-1}\) yr\(^{-1}\), and the amount of N in storage, \(\sim 150\) kg ha\(^{-1}\) [Williams et al., 1995]. Thus it seems unlikely that variable uptake of atmospheric DIN is the major factor controlling DIN yield and retention at ELW. Instead, we believe that variations in N yield and retention are primarily controlled by losses from internal N pools and are not due to differential uptake of atmospheric N [cf. Lovett et al., 2000]. We hypothesize that differences in annual nitrate retention are related to the amount of labile nitrate produced in soils prior to and during snowmelt. In the Sierra Nevada, snow regimes may primarily affect N cycling by controlling the timing of snowmelt, which directly determines the time available for microbial mineralization and nitrification in soils prior to spring runoff. Annual N export during wet years with late snowmelt may also be enhanced by lower N availability to growing vegetation and more intensive hydrologic flushing of soils.

At Niwot Ridge, snow cover, through its influence on soil temperature, was found to have a measurable effect on soil microbial populations and heterotrophic N uptake rates in soils [Brooks et al., 1997; Williams et al., 1998]. Early accumulating, consistent snow cover maintained soil temperatures above \(-5^\circ C\) (the freezing point of water in these organic acid-rich soil solutions), thereby increasing microbial biomass and the capacity for N retention and release compared with shallower snowpacks where soils remained frozen for much of the winter. Brooks and Williams [1999] present a conceptual model of snow cover controls on heterotrophic activity in alpine catchments. The model defines four zones of snow cover that bracket a continuum from sites with no snow cover and deeply frozen soils (zone 1) to sites with deep, nearly perennial snow

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**Figure 8.** Time course of daily nitrate flux (solid line), nitrate concentration (circles), and snow cover depletion (dashed line) in the Emerald Lake watershed during the snowmelt periods of 1994 and 1995. During 1994, winter snowfall was 63% of normal, and during 1995 it was 198% of normal. Nitrate flux is expressed as a fraction of total snowmelt flux (i.e., daily flux divided by total flux between March 1 and August 31). Snow cover depletion was estimated from measurements of snow-covered area determined from aerial photographs and field observations.
In general, the hypothesis assumes that heterotrophic activity in subnivean soils is inversely related to the amount of nitrate leachate in soil solutions. The model predicts that in watersheds with soil freeze-thaw cycles (zone 2), nitrate leachate will decline as snow duration increases. In zone 3, soils rarely freeze, and nitrate leachate in soils is low and relatively insensitive to changes in snow cover duration.

The conceptual model was tested with long-term data from Loch Vale; Brooks et al. [1999] found a direct relationship between annual precipitation and catchment DIN retention (precipitation was assumed to be an analogue of snow cover duration) (Figure 9b). Using a subset of the available data, Brooks et al. [1999] found that precipitation explained nearly 80% of the variation in DIN retention (expressed in kg ha\(^{-1}\) yr\(^{-1}\)); this was seen as a confirmation of the model and suggests that the Loch Vale catchment would fall within zone 2. Data from earlier years at Loch Vale generally support the positive DIN retention-precipitation relationship found by Brooks et al. [1999]; however, 1994 and 1985 fall outside the Loch Vale regression line. Water year 1994 was originally excluded from the analysis because of exceptionally high N loading (4.3 kg ha\(^{-1}\) yr\(^{-1}\)); however, N deposition during 1985, (3.8 kg ha\(^{-1}\) yr\(^{-1}\)) was comparable with loading measured in the late 1990s (3-3.3 kg ha\(^{-1}\) yr\(^{-1}\)) and does not seem anomalous.

The strong inverse relationship between DIN retention and precipitation at ELW is opposite to the Loch Vale pattern and does not fit the snow duration:nitrate leachate relationship predicted for either a zone 2 or zone 3 watershed in the model (Figure 9b; retention is expressed as a percentage of DIN loading to facilitate comparisons between the two catchments). Nitrate retention at ELW is similar to the Brooks and Williams [1999] predictions for a zone 4 watershed with nearly permanent snow cover, such as the Martinelli catchment near Niwot Ridge.

The relationship between DIN retention and precipitation...
was also examined in two alpine subcatchments, Icy Brook and Andrews Creek, that comprise ~70% of the Loch Vale watershed [Campbell et al., 2000a]. The analysis showed no relationship between annual precipitation and DIN retention within either subcatchment (expressed as either DIN mass or as a percentage of loading). Campbell et al. [2000a] suggest this disagreement between N cycling in the subbasins and the overall catchment is due to DIN assimilation in the meadows and subalpine forest of the lower Loch subbasin.

The finding that snowpack dynamics control ecosystem N retention in both the Rocky Mountains and Sierra Nevada strongly supports a linkage between snow regimes and microbial N cycling in high-elevation ecosystems. However, the actual direction of these effects were variable: longer snow cover had no effect or increased N retention (Icy Brook and Andrews Creek versus Loch Vale) in the Rocky Mountains but decreased N retention in catchments throughout the Sierra Nevada. The differential response to a common climatic variation, i.e., alterations in snowpack, suggests that N dynamics in the Sierra Nevada may be significantly different from the Colorado Front Range of the Rocky Mountains. More importantly, these observations demonstrate that seasonally snow-covered ecosystems exhibit heterogeneous responses to the same climatic forcing.

Possible explanations for differential responses of N cycling to snow cover include differences in vegetation, soil temperature, moisture, and N deposition (the Rocky Mountains receive approximately twice the loading measured in the Sierra Nevada [Sickman et al., 2001]). Alpine soil temperature may also be different in the Sierra Nevada: Sierra Nevada soils are warmer and rarely freeze during the winter [Brown et al., 1990; Williams et al., 1995, 1998; J. O. Sickman and J. M. Melack, unpublished data, 2000]. At Niwot Ridge, soil temperatures for most of the winter were typically below the freezing point of water, but warmer with deep, consistent snow cover. Available soil temperature data for the Sierra Nevada indicate that solids do not freeze even when snowpack formation is delayed until January. Figure 10 shows soil temperature during the snow accumulation seasons of 1999 and 2000 at the Topaz Lake watershed (elevation of 3218 m). The 2 years represent extremes in the timing of snowpack formation, although air temperatures were similar. In 1999, the snowpack started to form very early, and accumulation proceeded through a series of snowfall-ablation cycles. After each snow event, soil temperature declined with progressively smaller decreases as autumn progressed. During periods of snow cover, soil temperature fluctuations were muted. Prior to large snowfalls in mid-January, there was no snow at the thermistor site in 2000 and soil temperatures were 1–3°C higher than in 1999. Even after snow cover formed, soil temperatures stayed elevated compared with the previous year (mean annual temperature at ELW is 4.8°C). Without frozen soils, alpine microbial activity in the Sierra Nevada is likely to progress uninterrupted during the winter, while it may be limited in the Rocky Mountains by lack of liquid water and lower temperatures [Fisk et al., 1998].

Soil carbon and N are affected by soil temperature and may

Figure 10. (top) Air temperature and (bottom) soil temperature in the Topaz Lake watershed during the autumn and early winter of 1999 and 2000. Soil depth was measured at a depth of 10 cm using a thermistor and solid state data logger; temperatures were recorded hourly. Snow events are denoted by arrows.
provide another explanation as to why N dynamics differ between the two mountain ranges. Freeze/thaw cycles can result in release of substrates by microbial death and cell lysis [Schimel and Clein, 1996]. Research by Mitchell et al. [1996] illustrates the potential of soil freezing to alter catchment-scale N yield. After a particularly severe freeze in 1989, release of labile N in soils and fluxes of nitrate in streams increased markedly in montane watersheds in Maine, New Hampshire, and New York. At Niwot Ridge the rapid expansion of microbial biomass at the onset of snowmelt was attributed to increasing substrate availability (C and N) supplied by the thawing of frozen soils and inputs from the melting snowpack [Brooks et al., 1996]. In the absence of severe freeze/thaw cycles, substrate limitation of microbial N uptake may be more severe in the Sierra Nevada than in the alpine zone of the Rocky Mountains.

5.3. Climate Change and High-Elevation Ecosystems

Long-term records of snow surveys and river discharge provide evidence that hydrologic cycles in the higher elevations of the Sierra Nevada are changing. Winter surface air temperatures have increased an estimated 2°C since a minimum near 1950 and have affected streamflow of major Sierra Nevada rivers [Dettinger and Cayan, 1995]. Further studies suggest that winter and early spring runoff have increased in the northern Sierra Nevada owing to earlier snowmelt [Papacko, 1993]. A recent analysis by Johnson [1998] of a 60 year record of snow survey measurements indicates that accumulation and melt patterns are gradually changing: below 2400 m, less snow is accumulating, and it is melting earlier; at higher elevations, snowfall is increasing, and snowmelt begins earlier in the year and progresses at a more rapid rate.

These observations of changing snow regimes are mirrored by results from hydrological and chemical modeling in high-elevation ecosystems. The Alpine Hydrochemical Model (AHM) predicts that under a double-CO$_2$ scenario, snowmelt in ELW will occur earlier in the spring and proceed at a more rapid rate [Wolford and Bales, 1996]. Early, more rapid flushing of catchment soils resulted in AHM predicting lower solute concentrations in surface waters during snowmelt compared with current conditions. Recently, Baron et al. [2000] reached similar conclusions about the response of the Loch Vale watershed to climate warming using the Regional Hydro-Ecological Simulation System (RHESSys). The RHESSys model predicts that under a +4°C temperature change, snowmelt runoff at Loch Vale will occur earlier and stream nitrate concentrations will decrease, indicating an increase in N retention with temperature. The strong inverse relationship observed between DIN retention and the timing of snowmelt at ELW agrees with these modeling results: years with earlier snowmelt had lower nitrate concentrations and higher DIN retention. On the basis of the modeling studies and our observations at ELW we hypothesize that if atmospheric deposition stays constant and current trends toward warmer air temperatures and earlier snowmelt continue, N retention will increase in montane regions of the Sierra Nevada. Higher N retention will result in smaller nitrate pulses to streams during snowmelt, thereby reducing the level of episodic acid-neutralizing capacity (ANC) depression experienced in these dilute waters and lowering overall sensitivity to N deposition [Leydecker et al., 1999].

6. Summary and Conclusion

Detailed nitrogen mass balances for seven high-elevation Sierra Nevada watersheds were presented and used to examine the linkages between climatic variations and watershed-scale N cycling. Large interannual variations in snowfall and snowmelt runoff occur in the Sierra Nevada of California, and this variation is related to ecosystem yield and retention of N. The timing of snowmelt and the quantity of runoff exerted strong controls on catchment-scale N biogeochemistry: years with deep, late melting snowpacks had larger nitrate pulses and lower DIN retention than years with shallow snowpacks. The timing of snowpack formation, in contrast, had no detectable influence on N yield or retention and was not related to the depth, duration, or consistency of snow cover.

The effect of changing snow regimes in the Sierra Nevada was the opposite of that found at plot-scale studies at Niwot Ridge and at the catchment-scale at Loch Vale watershed; the conceptual model of Brooks and Williams [1999] regarding the influence of snow regime on subnival N biogeochemistry may not apply to regions which do not experience severe soil freezing. We hypothesize that differences in the N biogeochemistry of the Rocky Mountains and Sierra Nevada are primarily related to the effect of snowpacks on soil temperature and the role of heterotrophic microbial populations in subnival environments; that is, do they act primarily as a net source or net sink for DIN during periods of snow cover? In the Rocky Mountains the available data suggest that microbial populations primarily control ecosystem N retention by sequestering DIN inputs from snowmelt when plants are dormant; late forming, shallow, and intermittent snowpacks allow soils to freeze, reducing the microbial N sink. In contrast, we hypothesize that deep, late melting snowpacks in the Sierra Nevada result in increased time for microbially mediated mineralization and nitrification prior to snowmelt; labile N pools are smaller during years with shallow, early melting snowpacks. Also, during low-snow years, more N may have been available to plants during favorable growing conditions than during years with deep, late melting snowpacks, which increased catchment N retention rates relative to high-snow years.

Although we can describe the relationship between catchment snow cover and N yield and retention, we are lacking a detailed, mechanistic understanding of the spring nitrate pulse in the Rocky Mountains and Sierra Nevada. Isotopic analyses of nitrate in high-elevation watersheds suggest that the major source of the pulse is not from the snowpack, but rather from catchment soils. However, preferential elution of nitrate from the snowpack is well documented and the timing of snowpack elution and the stream nitrate pulse nearly coincide [Williams and Melack, 1991]. These observations raise the question, How is snowpack nitrate taken up in these ecosystems at the same time that soil nitrate is being released?

Nitrogen sources to streams in general are incompletely understood and the subject of ongoing research [Creed and Band, 1998; Biron et al., 1999; McGlynn et al., 1999]. Many of these studies stress the heterogeneous nature of N sources and sinks across space and time and demonstrate the complex interactions between abiotic and biotic controls on N cycling at the catchment scale. It is becoming clear that similarly complex processes are controlling the uptake of snowpack N and the release of soil N in alpine environments as well. The finding that high-elevation ecosystems exhibit heterogeneous responses to the same abiotic forcings underscores the complex-
ity of the N cycle and the need for detailed mechanistic studies in a variety of locations.

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