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Hydrochemical modeling of coupled C and N cycling in high-elevation catchments: Importance of snow cover

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Abstract. Several ecosystems in the western US are already undergoing nitrogen (N) saturation, a condition where previously N limited ecosystems are no longer N limited. This state of N saturation leads to adverse impacts on terrestrial ecology and water quality. Due to the complexities of terrestrial carbon-nitrogen cycling, integrated hydrologic-biogeochemical modeling provides a tool to improve our understanding and discern between the impacts of changes in N deposition from changes in other ecosystem processes. A model of biogeochemical processing in alpine watersheds was developed and applied to the Emerald Lake watershed. Simulations of major terrestrial carbon and nitrogen pools and fluxes were adequate. The use of snow cover information to estimate soil temperatures improved model simulations indicating that snow cover processes need to be incorporated into biogeochemical models of seasonally snow covered areas. The model simulated mineral nitrogen processes well but significant changes in denitrification and dissolved organic nitrogen export processes appear to be necessary. Our results also showed that variations in snow cover duration have more of an impact on mineral N export, plant uptake and mineralization than appears possible due to changes in atmospheric deposition.

Introduction

Over the last several decades there has been increasing concern about the damage that human perturbations to the nitrogen cycle may be causing (Galloway et al. 1995). A particular focus for research in the forested and wildland catchments of the world has been the increase in atmospheric deposition of reactive nitrogen to remote watersheds. Increases in atmospheric deposition appear to have caused an increase in nitrate export from forested, chaparral, subalpine and alpine catchments. Many investigators have hypothesized that long term increases in atmospheric nitrogen deposition have resulted in a decreased ability of terrestrial ecosystems to retain additional inputs of nitrogen (Fenn et al. 1998; Henriksen and Brakke 1988; Aber et al. 1989; Stoddard 1994). In the urbanizing western US, the Front Range of the Rocky Mountains and the chaparral and coniferous zones around Los Angeles are currently undergoing nitrogen saturation (Baron et al. 1994; Williams et al. 1996a; Fenn et al. 1998). The alpine zone of the Sierra Nevada Range could be impacted by increases in atmospheric nitrogen deposition from the ongoing urbanization of the Central Valley, California (Sickman et al. 2001).

While increases in atmospheric deposition to terrestrial ecosystems have been implicated in the rise in nitrate concentrations in aquatic ecosystems, the link is difficult to prove due to the complexities of the terrestrial carbon-nitrogen cycle (Parton et al. 1993; Baron et al. 1994). Large pools of nitrogen already on the landscape prevent simple cause and effect assumptions about the correlation between increased atmospheric deposition and increases in nitrate export from terrestrial ecosystems. In fact, a diverse array of causes may result in increasing nitrogen export, including: changes in climate, history of disturbance, fire history, soil freezing, wintertime snowpack, and drought (Sickman and Melack 1998; Brooks et al. 1996; Fenn et al. 1998; Aber et al. 1998).

Because of this diverse set of causes it is important to use coupled hydrologic biogeochemical models to investigate the effects of changes in atmospheric deposition and climate variability on watershed biogeochemical processes. We developed a biogeochemical model for snow-covered catchments that could be easily adapted to work in conjunction with the Alpine Hydrochemical Model (AHM). We relied on the existing literature of other biogeochemical models, particularly the CENTURY model, in developing our model (Parton et al. 1987; Running and Gower 1991; Jenkins et al. 1997).

After development of this model we applied it to the Emerald Lake watershed to answer several questions. First, what processes can a complex biogeochemical model properly represent and which ones does it fail to represent? Second, what do the process level failure's indicate about the model and the watershed being investigated? Third, how important is snow-covered area (SCA) in determining the biogeochemistry of alpine watersheds?

Model description

The existing models of catchment and plot scale nitrogen cycling (e.g. CENTURY and PNET for example) (Parton et al. 1987; Aber and Federer 1992) depend on a simplified representation of the nitrogen cycle for determining the processes controlling carbon and nitrogen cycling in a watershed. The CENTURY model is one of the more widely used carbon-nitrogen cycling models and it has been applied to alpine ecosystems previously with some success (Baron et al. 1994). The AHM was specifically built for working in alpine watersheds and incorporates the effects of snow cover into its hydrology and geochemistry. We used the biogeochemical equations related to carbon and nitrogen from the CENTURY model with the hydrology driven by the AHM.

The carbon-nitrogen model, consists of three parts: a soil carbon cycling model, a nitrogen cycling model linked to the carbon model and a plant growth model linked to the other two components, all of which were based on the CENTURY model (Parton et al. (1987, 1988, 1993)).

Soil carbon model

The soil carbon model consists of 8 compartments, the fluxes in and out of which are controlled by properties of each pool as well as empirically determined rate constants for soil organic matter decay (Parton et al. 1987). The 8 pools are: surface litter structural material, soil structural material, surface litter metabolic material, root litter structural material and root litter metabolic, surface microbes, soil microbes, slow soil carbon and passive soil carbon. A flow chart description of the soil carbon model taken from Parton et al. (1993) is included as Figure 1. The decomposition rate for each of the pools (in order listed as above) is as follows:

$$\frac{dC_I}{dt} = K_I L_C A C_I \qquad I = 1,2 \tag{1}$$

$$\frac{dC_I}{dt} = K_I A T_m C_I \qquad I = 3 \tag{2}$$

$$\frac{dC_I}{dt} = K_I A C_I \qquad I = 4,5,6,7,8 \tag{3}$$

$$T_m = (1 - 0.75T) \tag{4}$$

$$L_C = e^{(-3L_s)} \tag{5}$$

where C_I = the carbon in pool listed above; K_I is the maximum decomposition rate (day^{-1}) for each of the above pools (K_I = 0.010685, 0.01315, 0.02, 0.16438, 0.40548, 0.050685, 0.000548, 0.0000123 respectively); A is the combined effect of soil moisture and soil temperature on decomposition, T_m is the effect of soil texture on active SOM turnover; T is silt plus clay content (fraction); and L_c is the impact of lignin content of structural material (L_s) on structural decomposition. The maximum decomposition rates used are those reported by Parton et al. (1993). The C fluxes between pools and the corresponding fraction lost to respiration are included in Figure 1.

Two adjustments to the model structure of Parton et al. (1993) were necessary. First, the non-linear equation describing the effect of soil temperature on soil organic matter decomposition (Baron et al. 1994) was extended down to −5 °C, which is the temperature at which (Brooks et al. 1993) observed no soil respiration in the alpine tundra of Niwot Ridge, Colorado. Second, the effect of soil moisture on soil organic matter decomposition was computed using soil moisture status from the AHM which has a more robust hydrologic model than Parton et al. (1993). The equation used was:

$$M_e = (\theta_t - \theta_w)/(\theta_s - \theta_w) \tag{6}$$

where M_e is the effect of soil moisture on organic matter decomposition, θ_t is the

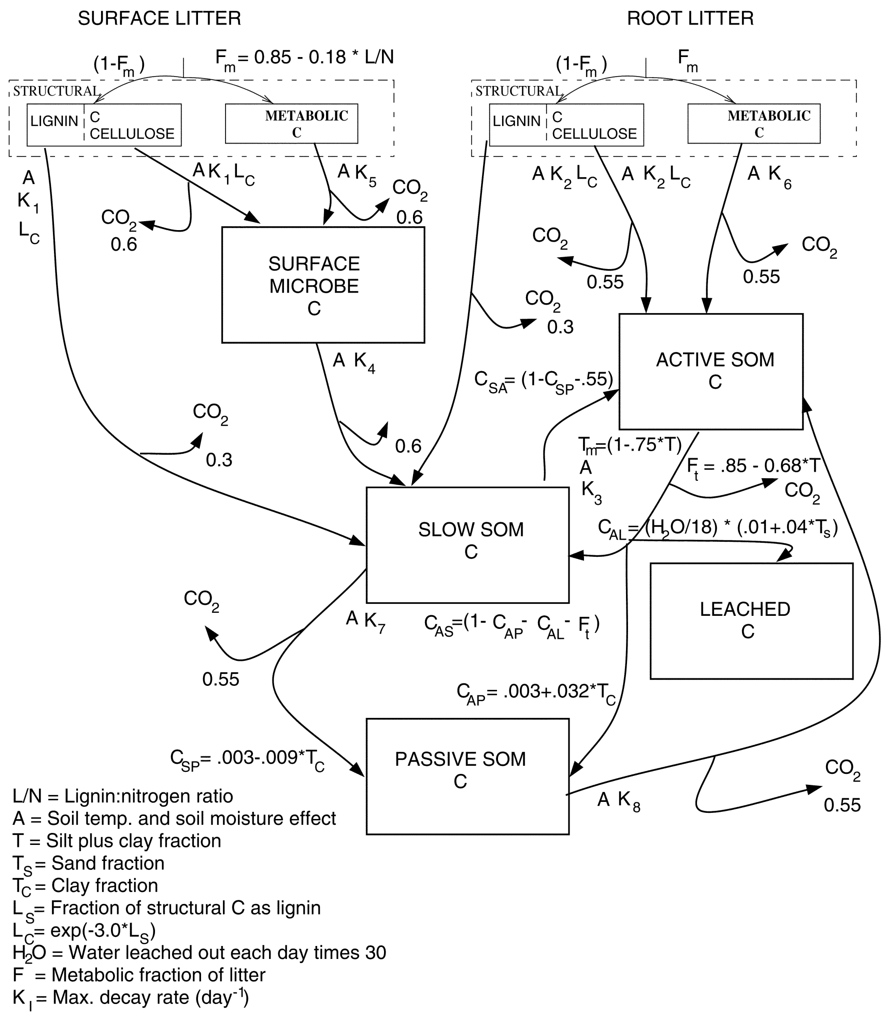

Figure 1. Carbon box diagram (Parton et al. 1993)

soil water content at timestep t, θ_w is the water content at which plants wilt, θ_s is the saturated soil water content. M_e is equivalent to the fraction of pores filled with water in the soil.

Soil nitrogen model

The soil nitrogen model mirrors that of the soil carbon model (Figure 2). Organic nitrogen fluxes follow those of carbon at the C:N ratio of the pool receiving the flow of C and N. The C:N ratios of the pools are 150, 150, 3–15, 10–20, 12–20, and 7–10 respectively for surface and soil structural material, active SOM, surface

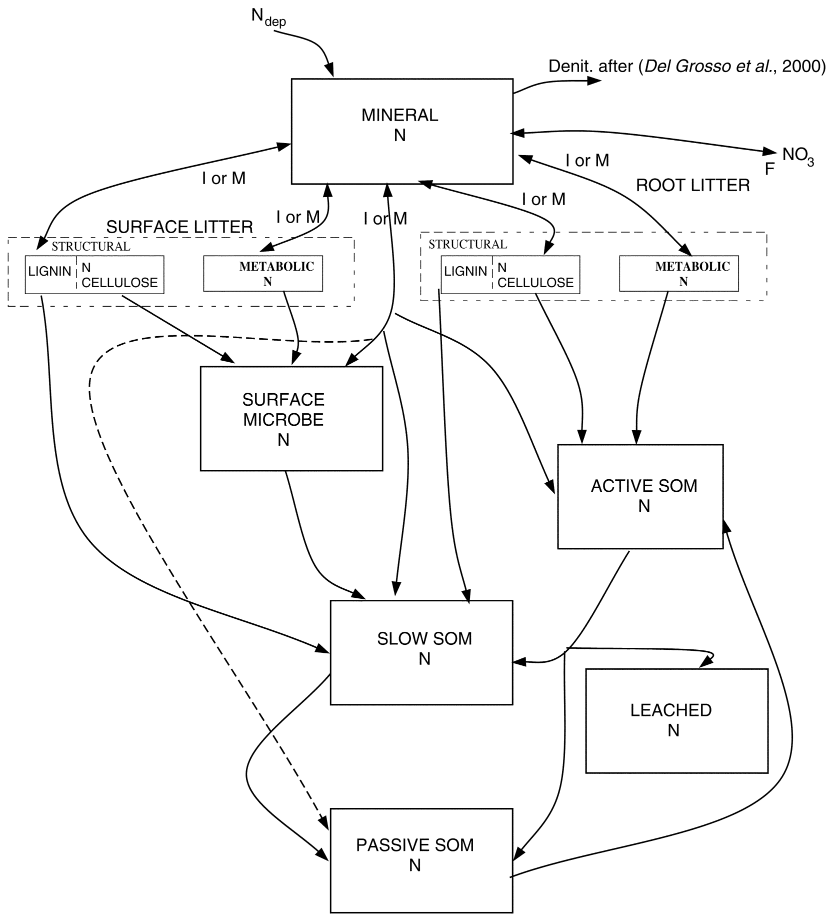

Figure 2. N soil organic matter flows (Parton et al. 1993). N fluxes follow those of carbon with nitrogen moving from one box to the next having the C:N ratio of the receiving compartment.

microbes, slow and passive SOM fractions. The C:N ratio of surface microbes varies with the N content of plants. The C:N ratio of the three soil organic matter pools varies according to the mineral N concentration of the soil. Mineral nitrogen in the soil was not differentiated into pools of nitrate and ammonium. The C:N ratio of the surface and subsurface metabolic pools depends on the C:N ratio of the incoming litter and its lignin (Parton et al. (1987, 1988, 1993)). Nitrogen fixation was set to an available literature value for alpine tundra of 4.9 kg ha^{-1} yr^{-1}. (Bowman et al. 1996).

A previous version of our model with a simple fraction based algorithm for denitrification (Parton et al. 1993) was inadequate for describing biogeochemistry for the Emerald Lake watershed (Meixner et al. 1999). For alpine watersheds denitrification might be a much more important process than previously expected since soils are saturated for long periods of time. We decided to improve the process level representation of denitrification in our model by incorporating a denitrification model developed by (Del Grosso et al. 2000). We omitted the effects of soil respiration found in their experiments since alpine soils are typically coarse textured, and Del Grosso et al. (2000) showed that there was no significant difference between high and low respiration denitrification rates in coarse textured soils. The equations used to define our denitrification algorithm were:

$$\text{Dentrification} \quad \text{loss} = 1.15(\text{Mineral} \quad \text{N})^{0.57} \tag{7}$$

Mineral N is the concentration of mineral N in the soil (g m^{-2}) and denitrification loss is loss of mineral N (g m^{-2} day^{-1}) via denitrification. Water limitation is a fractional quantity that is multiplied by denitrification potential to arrive at the actual denitrification rate used by the model.

$$\text{Water} \quad \text{Limitation} = 0.5 + (\arctan(0.6\pi(0.1M_e - 0.8)))/\pi \tag{8}$$

where M_e is the relative saturation of the soil calculated as shown in Equation (6).

We also changed the rate of mineral N (inorganic N) leaching in our model. Due to the daily time step we allowed leaching of mineral nitrogen to occur freely with soil solution. Thus leaching was determined by simply taking the ratio of water draining the soil to the total soil water content. The mineral N soil concentration was then multiplied by this fraction to determine the amount of mineral N to be leached on that day. This change was possible due to the daily time step of our model as well as the detailed hydrological output from the AHM.

Plant growth model

Only a grassland plant growth submodel is currently incorporated into the algorithm (Figure 3). Following Parton et al. (1993), the maximum production each day was calculated as:

$$P_p = P_{\max} T_p M_P S_P \tag{9}$$

where P_p is potential plant production rate (g m^{-2} day^{-1}), P_{max} is maximum potential aboveground plant production rate (8.3 g m^{-2} day^{-1}), T_p is the effect of soil temperature on plant production rate, M_p is the effect of soil moisture on plant production rate, and S_p is the effect of self shading on plant production rate. Root and shoot death and root to shoot ratios were treated in Parton et al. (1993) but for the exceptions noted below.

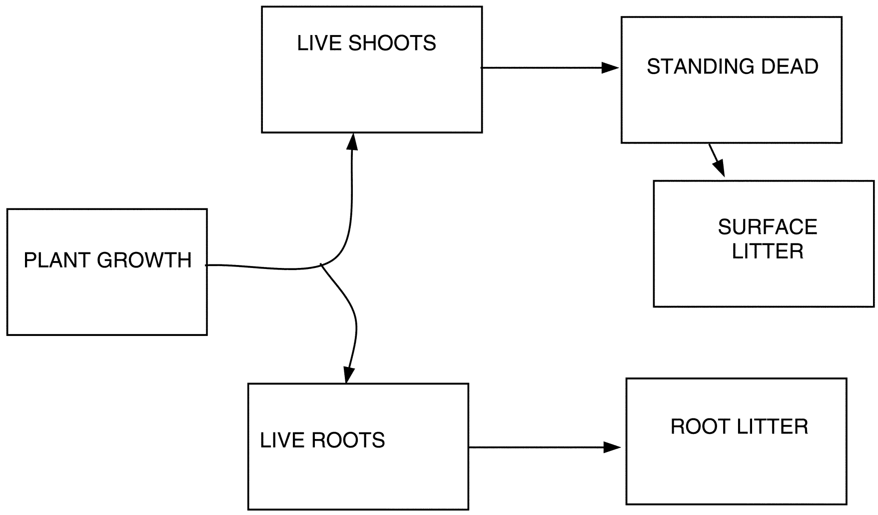

Figure 3. Grass growth model diagram (Parton et al. 1993). Plant growth rate depends on soil temperature, soil moisture and a self-shading factor. Root and shoot death depends on soil moisture function and for live shoots on plant senescence at the end of the growing season.

Several changes relative to Parton et al. (1993) were necessary to couple the carbon-nitrogen model with AHM. The maximum potential plant production and root and shoot death rates were divided by 30 to achieve a daily value. The effect of soil temperature on plant growth was assumed to be for C_3 plants due to the alpine ecosystem being simulated. Finally, the effect of soil moisture on plant growth was simplified to a single function as:

$$M_p = \theta_a \times 1.24 - 0.060 \tag{10}$$

where M_p is the effect of soil moisture on plant production rate, θ_a is the fraction of soil pores filled with water, and the two constants were calculated from Figure 6a in Parton et al. (1993).

Methods and data

We applied our model to the Emerald Lake watershed in Sequoia National Park, California as a test of the algorithm and its applicability to alpine watersheds. The Emerald Lake watershed is a 120 ha headwater catchment located in the Sierra Nevada (36°35′ N, 118°40′ W), with elevation ranging from 2800 m at the lake to 3417 m at the summit of Alta Peak (Figure 4). The watershed is 48% covered by exposed granite and granodiorite, 23% by soil and 23% by talus and includes a 2 ha lake (Tonnessen 1991; Wolford et al. 1996). Emerald was selected for four reasons: a long time-series of stream chemistry measurements (Melack et al. 1998),

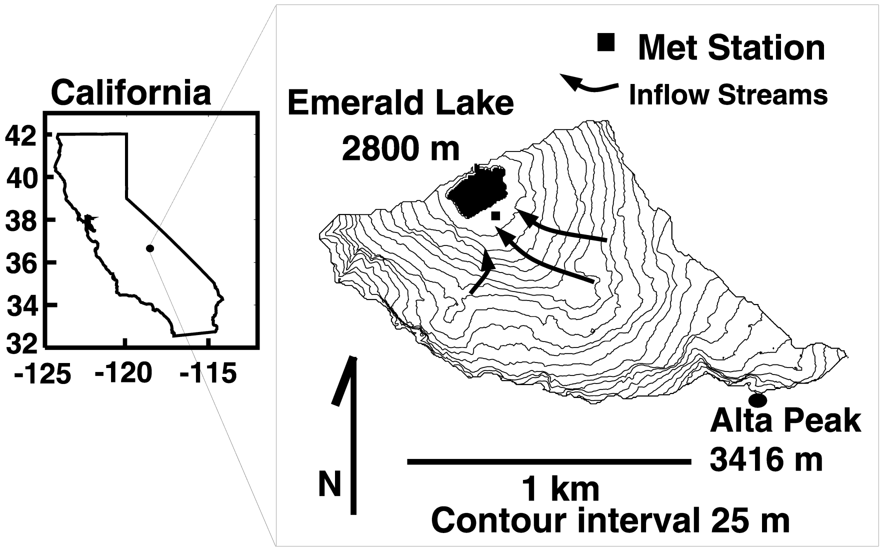

Figure 4. Location and topographic map of the Emerald lake watershed.

more than a decade of data on atmospheric deposition (Melack et al. 1997), good measurements of soil and vegetation processes (Rundel et al. 1988; Brown et al. 1990), and familiarity with the watershed (Wolford et al. 1996; Meixner et al. 1999).

Estimation of four time series inputs was necessary: soil temperature, atmospheric N deposition, water draining the soil, and soil water content. Soil temperature was estimated in two ways. The first method used a 30-day average of air temperature in the Emerald Lake watershed. Moving averages over a 30-day time period give a reasonable estimate of soil temperature. Daily mean air temperature was reconstructed using the 52-year record of minimum and maximum-recorded air temperature at the Grant Grove Ranger Station in Sequoia National Park (A. Esperanza, personal communication). The overlapping period between these long term records and the much shorter meteorologic measurements at Emerald Lake (Leydecker and Melack 2000) were compared using a linear regression (r^2 of 0.86). A graph of the reconstructed time series with the available Emerald Lake data from the 1980's and 1990's shows that the reconstructed values are effective at capturing the major variability of air temperature at Emerald Lake (Figure 5). The reconstructed air temperatures were only used when no observations were available for the Emerald Lake watershed. The second method assumed that when the soil was snow-covered, the effective air temperature was –0.1 °C. The purpose of this second methodology was to investigate the effect that snow cover would have on modeled biogeochemical processes. The main difference between the two soil temperature time series is the colder soils for a longer period of time for the snow covered area temperature record and the lack of freezing soils under snow cover.

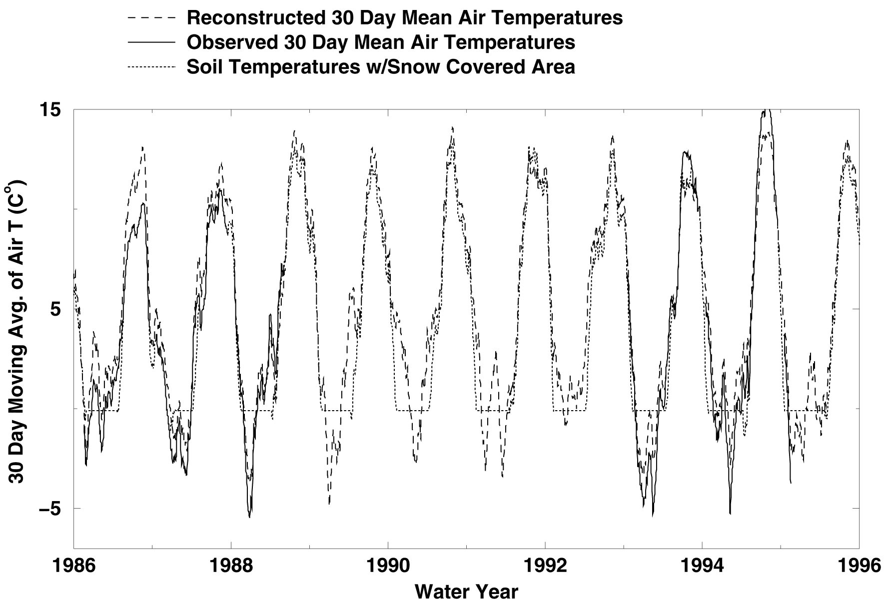

Figure 5. Measured and reconstructed 30 day mean air temperature for Emerald Lake. Figure shows how incorporation of snow cover effects on soil temperatures shortens the growing season and eliminates severe soil freezing events.

Few soil temperature records exist for the Emerald Lake watershed, but existing data indicate that the soils rarely freeze (Sickman et al. 2001). The rare freezing of soils indicates that the snow covered area time series is the more realistic time series for soil temperatures in the Emerald Lake watershed.

Three levels of atmospheric deposition (wet and dry combined) were used as inputs to the model. Two of the deposition amounts were the lowest (1 kg ha^{-1} yr^{-1}) and highest (3.6 kg ha^{-1} yr^{-1}) observed annual mineral N deposition rates for the Emerald Lake watershed (Melack et al. 1997). An additional simulation was done with twice the highest N deposition rate (7.2 kg ha^{-1} yr^{-1}).

Output from a 47 year AHM simulation using reconstructed discharge data (Gutmann 2000) provided soil drainage and soil water state. The 47 year input time series was used to simulate plant growth and soil organic matter processes with our model. A total of six different simulations were conducted, three with 30-day mean air temperature as the predicted soil temperature (one each for the three deposition levels) and three with the soil temperatures fixed under the snow covered area (SCA) and using the 30 day mean air temperature when snow free. For each simulation a total of 1880 years were simulated. Only the last 47 years of each simulation were analyzed. The long runs were necessary to permit equilibration of ecosystem dynamics, including plant and soil processes (Baron et al. 1994).

After completing our simulations we compared the results to available estimates of ecosystems components and fluxes. Previous studies at Emerald have focused on vegetation processes (Rundel et al. 1988), soil processes (Brown et al. 1990)

Table 1. Simulated and observed ecosystem components for the Emerald Lake watershed.

	No snow cover			Snow cover			Field
Deposition level	Low[1]	High[1]	Double[1]	Low[1]	High[1]	Double[1]	Obs. [2,3]
Live shoots (g m^{-2})	33	37	41	15	21	26.1	n/a
Live roots (g m^{-2})	1640	1884	2112	767	1090	1380	685 (230)
Live N (g m^{-2})	26	30.4	34	12.2	17	22	n/a
Total soil C (g m^{-2})	8340	9300	10200	4800	6000	7200	17500
Total soil N (g m^{-2})	500	545	590	322	382	440	1195
Active soil C (g m^{-2})	190	220	250	91	130	160	n/a
Active soil N (g m^{-2})	13	15	17	6	9	11	n/a

[1] Simulated values are mean for last 15 years of an 1880 year simulation.
[2] Observed values multiplied by 0.45 to convert biomass to g carbon. Where possible standard deviation is provided within the brackets.
[3] Rundel et al. (1988)

and watershed fluxes of nitrogen (Williams et al. 1995). Mineral N fluxes in stream water are almost entirely NO_3^- since ammonium concentrations are generally below detection limits (Williams et al. 1995).

Results

The long runs permitted the ecosystem equilibration as expected with only minor differences in model output noted for the final period of 47 years simulated as opposed to the preceding 47 years. Four major results can be seen looking at the modeling results for individual ecosystem components (Table 1). First, increased atmospheric deposition resulted in more biomass and more soil organic matter. Second, using soil temperatures of –0.1 °C under snow-cover resulted in less live biomass and smaller soil organic matter pools for carbon and nitrogen. Third, the predicted below ground biomass for the low deposition with snow-cover scenario actually overlaps the observed below ground biomass when the error in the measurements is taken into account. Fourth, neither the results using average 30-day air temperature or the SCA soil temperature time series come close to the observed soil organic carbon. The results for both soil temperature time series are well below the observed 17,500 g m^{-2}, the results using 30 day mean air temperature are closer but are still a factor of 2 less than the observed values.

From our modeling results of ecosystem processes (Table 2), five points stand out. First, using the SCA soil temperature time series resulted in smaller annual production and smaller N fluxes per year. Second, increasing N deposition resulted in greater biomass production and larger fluxes of N per year. Third, both soil temperature inputs underpredict observed above ground biomass production. Fourth, the SCA soil temperature time series does a better job of simulating below ground biomass production, net N mineralization and plant uptake, with the simulated val-

Table 2. Simulated and observed ecosystem processes for Emerald Lake

	No snow cover			Snow cover			Field
Deposition level	Low[1]	High[1]	Double[1]	Low[1]	High[1]	Double[1]	Obs.[2]
Above ground C prod. (g m^{-2} yr^{-1})	95	100	113	39	55	71	174 (72)[3]
Below ground C prod. (g m^{-2} yr^{-1})	86	110	124	43	61	78	57 (35)[3]
Net Mineralization (g m^{-2} yr^{-1})	3.4	3.9	4.3	1.6	2.2	2.8	1.3 (1.0)[4]
Plant uptake (g m^{-2} yr^{-1})	2.9	3.3	3.7	1.3	1.9	2.3	1.3 (0.9)[4]
Denitrification (g m^{-2} yr^{-1})	0.71	1.00	1.39	0.52	0.89	1.33	0.014[5]
Mineral N Leaching (g m^{-2} yr^{-1})	0.18	0.21	0.24	0.08	0.12	0.16	0.11[5]
DON Leaching (g m^{-2} yr^{-1})	0.005	0.006	0.007	0.003	0.004	0.005	0.168[5]

[1] Simulated values are mean for last 15 years of an 1880 year simulation.
[2] Observed values multiplied by 0.45 to convert biomass to g carbon. Where possible standard deviation is provided within the brackets.
[3] Rundel et al. (1988)
[4] Brown et al. (1990)
[5] Williams et al. (1995)

ues falling within the range of observed values of these fluxes. Finally, the magnitude of denitrification is overpredicted, while the magnitude of dissolved organic nitrogen export is underpredicted by the model.

Comparing model predicted N fluxes and the observed N fluxes for the Emerald Lake watershed reveals a number of interesting facts about the model and about the carbon and nitrogen cycling of the watershed (Figures 6 and 7). In making these comparisons it is important to note that the model is simulating the ten percent of the watershed covered by tundra-like vegetation. Therefore comparisons of measurements of stream N flux and our model should be understood to be a comparison of similarity and not that the fluxes should be identical. Comparing average mineral N flux (average of high deposition and low deposition simulations) for the snow-cover and no snow-cover cases against all of the available stream flux observations (adjusted from concentration to mass flux using measurements of streamflow) indicates that the snow-covered series is superior to that using average air temperatures (Figure 6). A closer look at a four-year time period (1993–1996 water years) indicates that the snow-covered temperature time-series captures the temporal variability of watershed N flux better than the air temperature series (Figure 7).

Our model simulations were able to capture inter-annual variation in mineral N export caused by climatic variations, but were less successful in predicting the timing of intra-annual changes in catchment N losses. During the drought of the late 1980s, stream mineral N export declined in the Emerald Lake watershed. This decline was followed by an increase in mineral N export during the wet years of the 1990's (Sickman et al. 2001); our simulations capture this trend. However, during the drought years of the late 1980's and early 1990's the model simulates large spikes of mineral nitrogen in the soils of the watershed in late summer and early fall but these large fall spikes of mineral N were not observed in the discharge time

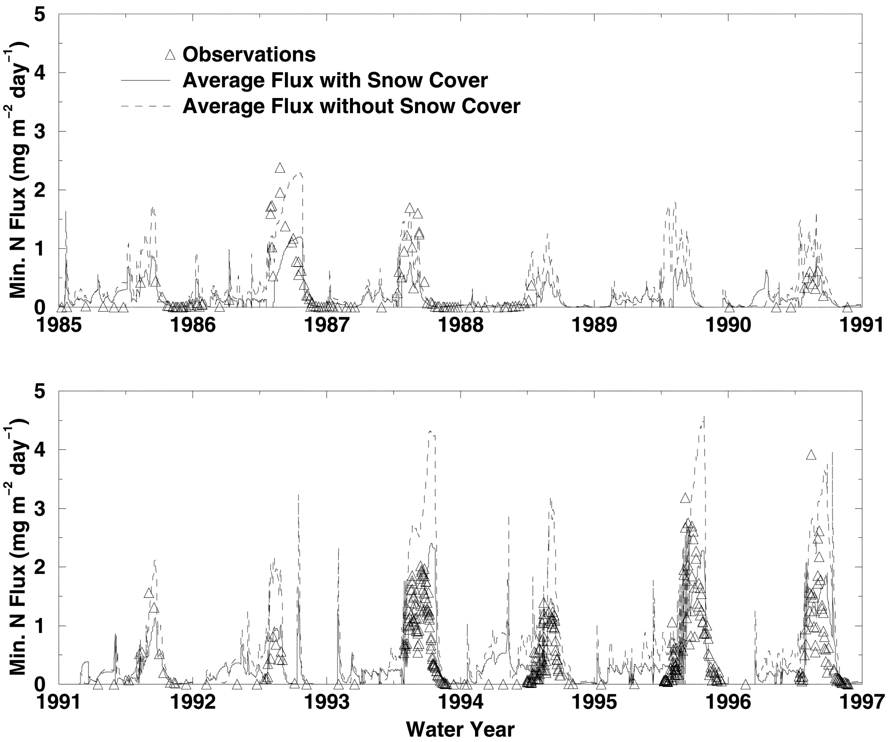

Figure 6. N flux results for soil temperature scenarios with snow cover and without snow cover. Results indicate that model is matching general trend of observed N flux for the Emerald Lake watershed. Decline in mineral N flux is captured during the late 1980's and increase in mineral N flux during 1990's is also captured.

series from Emerald Lake. In addition the annual spring-peak for mineral N flux observed in the model simulations was delayed from the observed peak in mineral N flux; the SCA temperature scenario did a better job than 30-day mean air temperature at simulating the observed pulse of NO_3^-. All scenarios indicate that there should be mineral N available for leaching throughout the winter, however very little mineral N is observed in the streams of the Emerald Lake watershed during the winter. Finally, doubling deposition increased mineral N export by $\sim 35\%$ for the snow covered soil temperature scenario for both the change in peak mineral N export and the change in annual export (Table 3 and Figure 8).

Discussion

The carbon and nitrogen cycle simulations for Emerald Lake provide information about both the natural processes governing nitrogen cycling in alpine watersheds and the simulation model: i) the conversion of the CENTURY algorithm to a daily

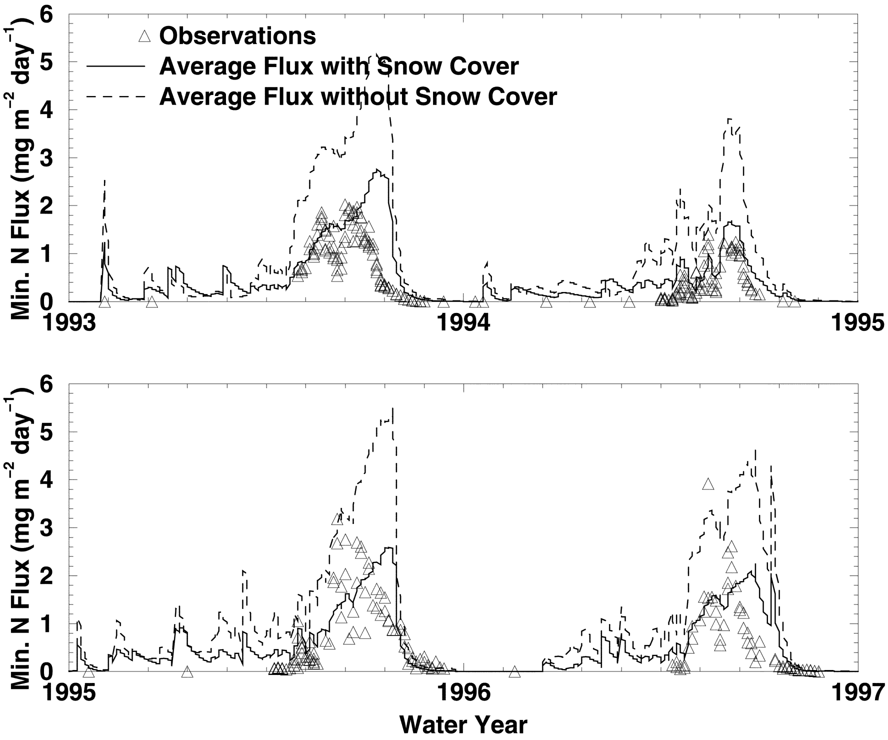

Figure 7. Measured and modeled mineral N flux shown for 1993 through 1996 both the case using snow cover and no snow cover to control soil temperatures. Simulations incorporating snow cover capture timing and magnitude of mineral N flux from the Emerald Lake watershed.

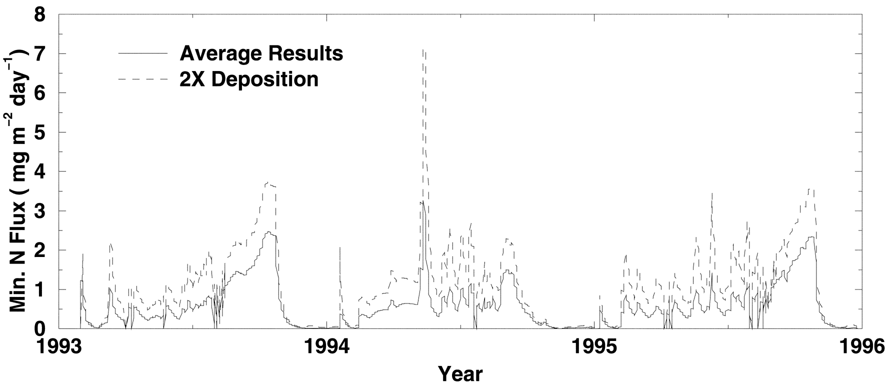

Figure 8. Effect of doubling N deposition on N flux out of the bottom of the soil profile. Results are shown for the modeling cases using soil temperatures incorporating the effects of snow cover case.

format receiving four time-series inputs was successful, ii) denitrification and dissolved organic nitrogen processes are currently inadequately represented, iii) snow covered area improves simulations of N cycling, and iv) the model was generally capable of capturing inter-annual variation in mineral N export but was less successful in predicting the timing of the spring export pulse.

The CENTURY model was originally built to simulate soil organic matter processes in the Great Plains, USA (Parton et al. 1987). Transferring the model and changing it to represent the alpine meadows of the Sierra Nevada is a stretch for the underlying representation of terrestrial carbon-nitrogen cycling. The results from our modeling exercise indicate that the modeled processes are able to adequately simulate carbon-nitrogen cycling in alpine ecosystems confirming the results of Baron et al. (1994). However, their application of the CENTURY model was in the Rocky Mountains, which are significantly colder, have a less variable precipitation regime, less extensive snow-cover and more commonly frozen soils in winter than the Sierra Nevada. Also, their simulations used a monthly time step, while our simulations used a daily time step.

These simulations do indicate some problems with the current model representation of carbon-nitrogen cycling in alpine watersheds. The algorithm was unable to adequately model total soil carbon, which is a similar result as Baron et al. (1994). The results overpredicted live subsurface biomass except in the case of the low deposition scenario with snow cover. The algorithm was also unable to properly predict the amount of above ground biomass production on an annual basis. However, the model was fairly successful in simulating N mineralization and plant N uptake. As a whole, our results indicate that the current algorithm is a good starting point for further research into carbon-nitrogen cycling in alpine watersheds.

One advance made in this model application over the results of Baron et al. (1994) is that their results predicted a significant flux of mineral nitrogen before the real watershed had its flush of mineral nitrogen. Our model does not have this difficulty but instead indicates that there is a delayed peak. The reason for this improvement in biogeochemical modeling performance may be due to the incorporation of the denitrification model of (Del Grosso et al. 2000). Prior to the incorporation of the denitrification model our simulations showed a similarly early mineral nitrogen pulse. The reason for the delay relative to field observations may be that denitrification is currently over-estimated in the model. This result points to denitrification as a significant mineral nitrogen loss process in alpine watersheds, and one that is very poorly characterized for most seasonally snow covered systems.

The fluxes for denitrification in the model are about 100 times those estimated from measurements. However, the measured values are for summer and are likely low; the generally wet soils under snowpacks encourage wintertime denitrification (Williams et al. 1995). Still the wide divergence between measured and modeled denitrification rates indicates that the model as currently constructed is overestimating denitrification. On the other hand the model significantly underestimates dissolved organic nitrogen (DON) fluxes (by several orders of magnitude) from the soil as compared to observed DON fluxes out of the watershed (Williams et al. 1995). Again these differences indicate problems with the model related to DON fluxes, possibly because the equations governing dissolved organic matter flux in

CENTURY depend on data for tropical climates (McDowell and Asbury 1994). The poor simulations of DON processes by our model indicate that DON processes in alpine soils and watersheds should be investigated further.

Importance of snow cover – quantity and extent

The use of SCA to adjust the soil temperature was successful in improving model simulations. The SCA time-series resulted in better simulations of NO_3^- flux, plant N uptake, N mineralization, and below ground live biomass. The 30-day mean air temperature results were significantly different from the results using SCA; almost all biomass or soil organic matter pools are nearly double or even triple those simulated with the SCA time series. The fluxes of mineral N are also much larger for the 30-day mean air temperature time series.

The importance of snow covered area in properly simulating biogeochemical processes in alpine watersheds can also be seen by looking at the temporal accuracy of the mineral nitrogen fluxes that we predict for the Emerald Lake watershed. Our simulations indicate a decline in mineral N export during the drought and a latter resurgence in mineral N export during the wet years of the 1990's. This simulated trend matched well with the observed N fluxes in the watershed (Figure 6). The implication of these results is that drought led to declines in mineral N export while wet years lead to an increase in N export. Others have shown that late lying snowpack at the Emerald Lake watershed appears to have an impact on nitrogen export from the watershed (Sickman et al. 2001). The contribution here is to offer a possible causal link between snow cover and the increase in mineral N export. Looking at the soil temperature inputs we used (Figure 5) it is easy to observe that soil temperatures are most impacted by snow cover by a shortening of the growing season, most particularly in a delay in the commencement of the growing season due to cool soils.

Brooks and Williams (1999) developed a conceptual model of snow cover controls on mineral N export in alpine watersheds. In their model nitrate leaching (mineral N export) increases when there is either too little snow or large deep long lasting snowpacks. When there is little snow cover, soil freezing causes more nitrate leaching, while extremely deep snowpacks can cause the same circumstance due to less carbon substrate available for soil microbial communities. At Emerald Lake the only cause for increasing mineral N export appears to be increases in snow cover duration that delay spring plant uptake of mineral nitrogen and possibly limit carbon substrate for soil microbial communities. Increases in leaching due to limited snow cover and soil freezing do not appear to exist. The nonexistence of shorter snow cover duration leading to increased mineral N export at the Emerald Lake watershed may be due to the relatively mild winters in the Sierra Nevada that results in limited soil freezing. Also, Emerald appears to move very readily from the high mineral N export of extended snow cover of the Brooks and Williams (1999) model into conditions which limit mineral N export when there is moderate snow

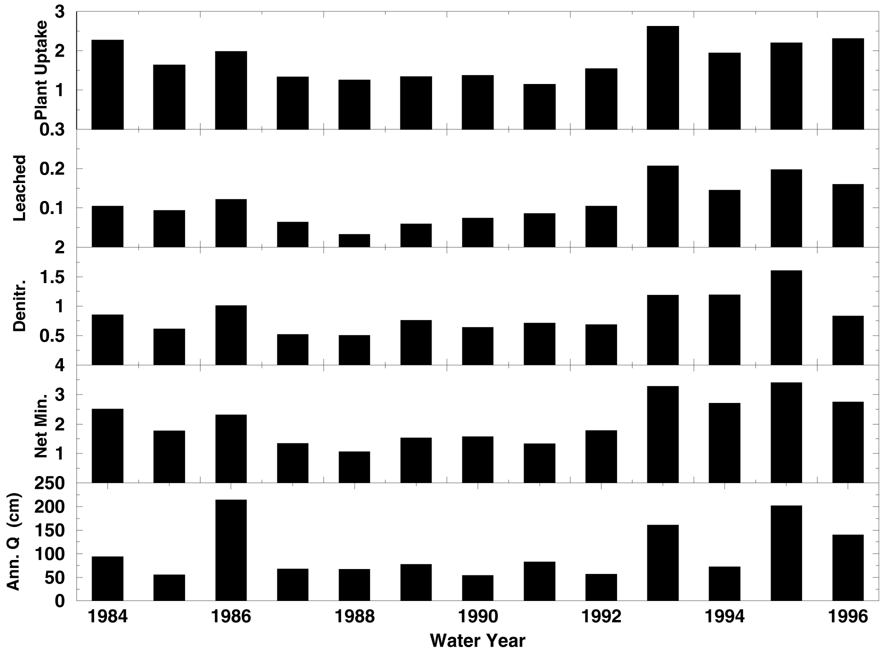

Figure 9. Annual nitrogen fluxes from the snow covered area high deposition simulations for 1984–1996. All of the N fluxes (plant uptake, leached N, denitrified N and net mineralization) are in g m^{-2} $year^{-1}$. Note general decrease in N process intensity during the late 1980's early 1990's drought and later resurgence in N process intensity during the wetter period from 1993 to 1996.

cover. In fact N leaching increasing in long duration snow cover years occurs despite noted increases in plant growth and carbon availability in these snowy wet years in the Emerald Lake watershed (J. Sickman, personal communication).

This increase in productivity seems to belie the Brooks and Williams (1999) model in that they indicate that the lack of carbon substrate is the cause for increased mineral N export during long duration snow cover seasons. Our simulation results indicate that it is changes in plant uptake and N mineralization that cause these differences (Figure 9). In a suit of three wet years (1986, 1993 and 1995) our results show that gross mineralization (sum of daily net mineralization) was 3.0 g m^{-2} $year^{-1}$, a significant increase over the gross mineralization, 1.4 g m^{-2} $year^{-1}$, for three comparable dry years (1988, 1989, 1990). Meanwhile simulated plant uptake for the wet years was 2.3 g m^{-2} $year^{-1}$, which also was an increase over the dry year uptake of 1.3 g m^{-2} $year^{-1}$. The increase in plant uptake was not as large as the increase in mineralization indicating that the remainder of the mineralized N must go to either denitrification (1.3 g m^{-2} $year^{-1}$ in wet years vs. 0.6 g m^{-2} $year^{-1}$ in dry years) or leaching of mineral N (0.18 g m^{-2} $year^{-1}$ in wet years vs. 0.06 g m^{-2} $year^{-1}$ in dry years) from the soils and into the streams. This increase in leaching of mineral N is also larger than the changes observed for a doubling of atmospheric N deposition.

Our results show that long-duration snow-cover limits plant uptake, which in concert with increased mineralization rates leads to more mineral N available for export from alpine basins. More broadly, our results indicate that snow-cover information should be incorporated into simulations of biogeochemistry in alpine and arctic landscapes since snow-cover has a demonstrable impact on model output and is known to cause changes in terrestrial biogeochemistry (Williams et al. 1996b; Sickman and Melack 1998; Williams et al. 1998; Brooks et al. 1999; Brooks and Williams 1999; Sickman et al. (2000, 2001)).

Changes in deposition

The model simulations indicate that with a doubling of current N deposition rates, stream mineral N export is likely to increase about 35% at Emerald Lake. This increase comes mainly in the form of an increase in spring mineral N export, with base flow levels remaining at or near zero (Figure 8). This finding indicates that the Emerald Lake watershed would remain somewhere between Stage 0 and Stage 1 of N saturation as defined by Stoddard (1994) under doubled N loading. However, an increase in mineral N export of this magnitude may lead to some adverse impacts on water quality. Leydecker et al. (1999) showed that the impact of a 50% increase in stream NO_3^- and SO_4^{2-} export would make 6% of the lakes surveyed during the Western Lakes Survey (Landers et al. 1985) episodically acidified. Our results indicate that a doubling of N deposition would likely lead to smaller impacts on alpine lake water quality since it would only increase mineral N export by 35%.

Care should be taken in setting critical loads for alpine areas in California however, since our results indicate that wet versus dry years led to larger changes in mineralization and mineral N leaching rates than a change in deposition would cause. While the Sierra Nevada currently receives some of the lowest atmospheric deposition rates in the world, climate variability may play a larger role in determining future changes in mineral N export than changes in atmospheric deposition rates. Increases in atmospheric deposition and the deleterious effects that this might have on surface water quality might be counteracted by changes in climate that are encouraging smaller and earlier melting snowpacks in the Sierra Nevada (Dettinger and Cayan 1995). Thus future increase in atmospheric N deposition and its effects on surface water quality may be counteracted by the effects on surface water quality induced by expected climate warming in California from a doubling of CO_2 (Lettenmaier and Gan 1990; Sickman et al. 2001)

Hydrologic controls

The lack of correspondence between the modeled fall spike of mineral N export and the constant baseflow fluxes of mineral N during the winter may indicate a hydrologic disconnect between the soils and surface waters of the Emerald Lake watershed. The NO_3^- concentrations in Emerald Lake soils may indeed spike in the late summer of drought years but this spike may either not reach the streams or the signal may be mixed out by more dilute waters from talus areas or from rock fractures. When there are fall rains pulses of NO_3^- have been observed in the outflow of Emerald Lake (Melack et al. 1998; Sickman et al. 2000). This asynchrony may also be due to a flushing episode that the AHM hydrologic input to the algorithm does not currently capture. The N flushing hypothesis put forth by Creed et al. (1996) states that as soils saturate they release NO_3^- that has been hydrologically disconnected from the stream during a seasonal or longer period drought. A flushing release of mineral N in addition to the spring pulse as simulated by our model may combine to create the observed mineral nitrogen pulse that we see in the Emerald Lake watershed. These results indicate that a mechanism for the delay of these NO_3^- pulses needs to be incorporated into our model as well as the AHM. In order to investigate this flushing mechanism in the field monitoring of soil chemical conditions should be conducted to see if there are higher levels of NO_3^- present in soil waters during the winter and if these levels decline during spring snowmelt.

Conclusions

The incorporation of AHM output as input into a simplified version of the CENTURY algorithm was a variable success, which should be improved upon through validation of the modeling results using further field measurements and experiments. Special focus needs to be paid to denitrification and dissolved organic nitrogen processes during future fieldwork since these two processes do not appear to be well represented by the current model. The incorporation of SCA as an input to biogeochemical models for alpine watersheds has an important impact on model processes and appears to be necessary to achieve good simulations of watershed carbon-nitrogen cycling. Our results also confirm the conclusions of Sickman et al. (2001) that long snow cover duration seasons lead to increases in mineral N export and that these changes are due to decreased plant uptake relative to N mineralization in these wet years. These results also indicate that increases in N deposition could increase NO_3^- export from the watershed but not as much as climate variability and change might be expected to. Finally, improvements in the hydrology of AHM appear to be necessary to adequately time the pulse of NO_3^- from the Emerald Lake watershed during spring.

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