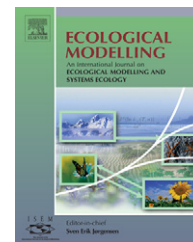


available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/ecolmodel

Application of a coupled ecosystem-chemical equilibrium model, DayCent-Chem, to stream and soil chemistry in a Rocky Mountain watershed

Melannie D. Hartman^{a,*}, Jill S. Baron^{b,1}, Dennis S. Ojima^{a,2}

^a Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO 80523-1499, USA

^b U.S. Geological Survey, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO 80523-1499, USA

ARTICLE INFO

Article history:

Received 17 February 2005

Received in revised form

17 August 2006

Accepted 5 September 2006

Published on line 16 October 2006

Keywords:

Ecosystem modelling

Alpine

Subalpine

Stream chemistry

Nitrogen

Acid neutralizing capacity

ABSTRACT

Atmospheric deposition of sulfur and nitrogen species have the potential to acidify terrestrial and aquatic ecosystems, but nitrate and ammonium are also critical nutrients for plant and microbial productivity. Both the ecological response and the hydrochemical response to atmospheric deposition are of interest to regulatory and land management agencies. We developed a non-spatial biogeochemical model to simulate soil and surface water chemistry by linking the daily version of the CENTURY ecosystem model (DayCent) with a low temperature aqueous geochemical model, PHREEQC. The coupled model, DayCent-Chem, simulates the daily dynamics of plant production, soil organic matter, cation exchange, mineral weathering, elution, stream discharge, and solute concentrations in soil water and stream flow. By aerially weighting the contributions of separate bedrock/talus and tundra simulations, the model was able to replicate the measured seasonal and annual stream chemistry for most solutes for Andrews Creek in Loch Vale watershed, Rocky Mountain National Park. Simulated soil chemistry, net primary production, live biomass, and soil organic matter for forest and tundra matched well with measurements. This model is appropriate for accurately describing ecosystem and surface water chemical response to atmospheric deposition and climate change.

© 2006 Elsevier B.V. All rights reserved.

1. Introduction

Watershed response models to atmospheric deposition have long focused on geochemical processes that lead to surface water acidification. As US sulfur dioxide emissions have sharply decreased in response to the US Clean air Act Amendments, the importance of atmospheric nitrogen species in wet and dry deposition has become apparent. Nitrogen deposition, from both nitrogen oxide and ammonia emissions, is elevated

above background throughout the US (NADP/NTN, 2005). Excess N deposition will cause lake and stream acidification in a process similar to that caused by sulfate deposition, with an important difference. Because nitrogen is a critical nutrient for plants and microbes, any realistic projection of nitrogen-caused acidification must include understanding of ecosystem nutrient cycling. Nitrogen export is a function of deposition, climate, and internal nitrogen-cycling processes, including plant uptake and nitrogen immobilization in soil

* Corresponding author. Tel.: +1 970 491 1609; fax: +1 970 491 1965.

E-mail addresses: melannie@nrel.colostate.edu (M.D. Hartman), jill@nrel.colostate.edu (J.S. Baron), dennis@nrel.colostate.edu (D.S. Ojima).

¹ Tel.: +1 970 491 1968; fax: +1 970 491 1965.

² Tel.: +1 970 491 1976; fax: +1 970 491 1965.

0304-3800/\$ – see front matter © 2006 Elsevier B.V. All rights reserved.

doi:10.1016/j.ecolmodel.2006.09.001

organic matter (Matson et al., 2002). Further, the addition of nitrogen to nearly all ecosystems stimulates biological activity, leading to increases in plant productivity, microbial activity, trace gas emissions, and alteration of species assemblages (Matson et al., 2002). Models that ignore the ecological aspects of atmospheric nitrogen deposition are missing processes that are important in their own right, and can inform decision makers of environmental changes well in advance of acidification.

We coupled two widely accepted and tested models, one of daily biogeochemistry for forest, grassland, cropland, and savanna systems, DayCent (Parton et al., 1998), and the other of soil and water geochemical equilibrium, PHREEQC (Parkhurst and Appelo, 1999). The purposes of creating the linked DayCent/PHREEQC model, hereafter referred to as DayCent-Chem, were to capture the biogeochemical responses to atmospheric deposition and to explicitly consider those biogeochemical influences on soil and surface water chemistry. The linked model expands on DayCent's ability to simulate N, P, S, and C ecosystem dynamics by incorporating the reactions of many other chemical species in surface water. We use DayCent-Chem to investigate how wet and dry deposition affect biological assimilation, soil organic matter composition, acid neutralization capacity (ANC) and pH of surface waters, aluminum mobilization, soil base cation depletion, and base cation flux. Because DayCent-Chem operates on a daily timestep, it has the potential to simulate episodic acidification.

Many computer models have been used to evaluate and predict the effects of atmospheric deposition and global change on ecosystems (Tiktak and van Grinsven, 1995; Kickert et al., 1999). DayCent-Chem, a model of intermediate complexity, differs from several other non-spatial, non-empirical hydrochemical models in its process detail, types of processes simulated, and timestep. Some models, like Model of Acidification in Catchments (MAGIC) and Alpine Hydrochemical Model (AHM), are useful tools for forecasting and hindcasting acidification trends (Cosby et al., 1985, 2001; Wolford et al., 1996; Meixner et al., 2000). PnET-BGC and NuCM represent ecosystem processes, but the former operates on a monthly time step and the latter requires extensive parameterization (Johnson et al., 1993; Gbondo-Tugbawa et al., 2001). SOILVEG and the combined FORGRO/NUCSAM models, with detailed descriptions of biogeochemical and canopy processes that include direct effects of pollution, have been used to evaluate the short- and long-term effects of multiple stressors on forest stands, but do not simulate stream discharge and chemistry (van Heerden et al., 1995; Mohren and van de Veen, 1995). There is no one model to fit all applications, and the diversity of hydrochemical models gives researchers many comparative tools for investigating such problems as episodic or chronic acidification and metal toxicity in surface waters, ecosystem responses to deposition, and determining critical loads on ecosystems.

We tested DayCent-Chem against a long-term data set available from Andrews Creek in Loch Vale Watershed (LVWS), Rocky Mountain National Park, Colorado. The long-term data set has attracted other modelers: AHM and MAGIC have been applied to Andrews Creek, and two ecosystem models, RHESSys and CENTURY have been applied to the larger Loch Vale Watershed (Baron et al., 1994, 2000; Hartman et al.,

1999; Meixner et al., 2000; Sullivan et al., 2005). We addressed the following questions. (1) How well can the model simulate ecosystem processes and chemistry of alpine tundra and sub-alpine forest? (2) Can the separate site-level runs be combined successfully to describe stream chemistry in spatially heterogeneous watersheds? (3) Do the biological processes within DayCent-Chem contribute to the model's ability to simulate stream chemistry?

2. Model descriptions

2.1. DayCent 5 model

CENTURY is a non-spatial, lumped parameter model that simulates C, N, P, S, and water dynamics in the soil-plant system at a monthly timestep over time scales of centuries and millennia (Parton et al., 1987, 1994). CENTURY can represent a grassland, crop, forest, or savanna system with parameters that describe the site-specific plant community and soil properties. DayCent, the daily timestep version of CENTURY, adds layered soil temperature, a trace gas submodel, a more detailed soil hydrology submodel, and explicitly represents inorganic N as either NO_3^- or NH_4^+ (Parton et al., 1998; Kelly et al., 2000; Del Grosso et al., 2001). DayCent 5 is an object oriented model written in the C++ programming language, that implements a layered soil structure and algorithms to manage soil layers (Hilinski, T.E., 2001. Implementation of an Algorithm for a Layered Soil Submodel with Application to the CENTURY Model, <http://www.nrel.colostate.edu/projects/century5/reference/index.htm>). The model is initialized with an organic soil depth and up to 10 soil layers where each layer has a specified thickness, texture, bulk density, field capacity, wilting point, and saturated hydraulic conductivity. Climate drivers required for DayCent 5 are daily precipitation, and minimum and maximum air temperatures. DayCent 5 output includes daily evapotranspiration; soil water content; outflow; inorganic and organic C, N, P, and S stream fluxes; C, N, P, and S contents in soil and plant pools; net primary production (NPP); nutrient uptake; trace gas flux; and heterotrophic respiration (<http://www.nrel.colostate.edu/projects/century5/reference/index.htm>).

2.2. PHREEQC model

PHREEQC (Parkhurst and Appelo, 1999) is a model based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, exchangers, and sorption surfaces. The model is written in the C programming language and has an extensible chemical data base. We used version 2.7 of PHREEQC in the linked model to compute aqueous speciation, ion-exchange equilibria, fixed-pressure gas-phase equilibria, dissolution and precipitation of mineral phases to achieve equilibrium, and irreversible aqueous mineral phase reactions. The aqueous model uses ion-association and Debye Hückel expressions. Ion-exchange reactions are modeled with the Gaines-Thomas convention and equilibrium constants derived from Appelo and Postma (1993). Except for changing PHREEQC's main program to a subroutine, we did not alter the PHREEQC model.

2.3. Data flow in the linked model

In addition to DayCent 5's required inputs (described in Section 2.1), the user must provide: (1) daily atmospheric wet deposition concentrations for precipitation species Ca^{2+} , Cl^- , K^+ , Mg^{2+} , Na^+ , NH_4^+ , NO_3^- , SO_4^{2-} , and H^+ ; (2) daily dry deposition amounts or dry:wet ratios for all precipitation species; (3) initial snow pack water content and chemical composition; (4) initial soil solution concentrations; (5) exchangeable cations in each soil layer; (6) potential annual denudation rates for each mineral phase that could be dissolved in the soil, groundwater, or stream solutions.

DayCent-Chem implements a geochemical submodel of layered pools and properties that provides information exchange, such as of water fluxes and solute concentrations, between the coupled models, and performs daily geochemical output (Fig. 1). The geochemical submodel defines soil layers and a groundwater pool that correspond to those in DayCent 5's original soil class. DayCent-Chem calculates daily wet deposition amounts from precipitation concentrations and dry deposition amounts from dry:wet ratios if dry amounts are not input explicitly. Surface water concentrations are computed in a two step process where solutes are first transported, then PHREEQC undertakes solution reactions. At each timestep the model updates exchangeable cation pools (CaX_2 , MgX_2 , NaX , KX , NH_4X , HX , FeX_2 , MnX_2 , AlX_3 , AlOHX_2 , where X^- is a permanent negatively charged exchange site) and soil solutions in each soil layer, along with groundwater and stream solutions. In addition to standard DayCent 5 output files (Section 2.1), at each daily timestep the model writes the solution chemistry for soil layers, groundwater, and stream.

DayCent-Chem invokes the PHREEQC model through a subroutine call, but the transfer of information to and from

PHREEQC occurs through its standard ASCII input and output files. For each daily timestep, the model writes the initial compositions of the soil layers, groundwater, and stream solutions to the PHREEQC input file, soln.pqi (Fig. 1). When there are n soil layers, there are $n + 2$ solutions defined in soln.pqi, plus a SELECTED.OUTPUT block that tells PHREEQC what information to put out. PHREEQC performs its calculations on each initial solution in soln.pqi, it writes its reacted solution results to a "selected output file", soln.sel. The model parses soln.sel, and updates its soil, groundwater, and stream pools with these values.

2.4. DayCent-Chem model processes

DayCent-Chem (Fig. 2) simulates atmospheric deposition, plus snowpack, plant, soil, and stream dynamics (left side of figure) while utilizing PHREEQC's soil and stream water reactions (right side of figure).

2.4.1. Atmospheric deposition and fertilization

Atmospheric deposition occurs in wet and dry forms. If the air temperature is cold enough, deposition will be routed to the snowpack, otherwise it will be routed to the soil surface where it can infiltrate the soil, seep into groundwater, or run off directly to stream flow. Additional N, P, and S may be incorporated into the top soil layer through inorganic fertilizer or organic matter additions.

2.4.2. Plant dynamics

Carbon is dynamically allocated to above and below ground plant parts according to nutrient availability, water stress, and vegetation type. Plants take up nutrients (NO_3^- , NH_4^+ , P, and S) from soil as needed to maintain carbon:nutrient ratios in the

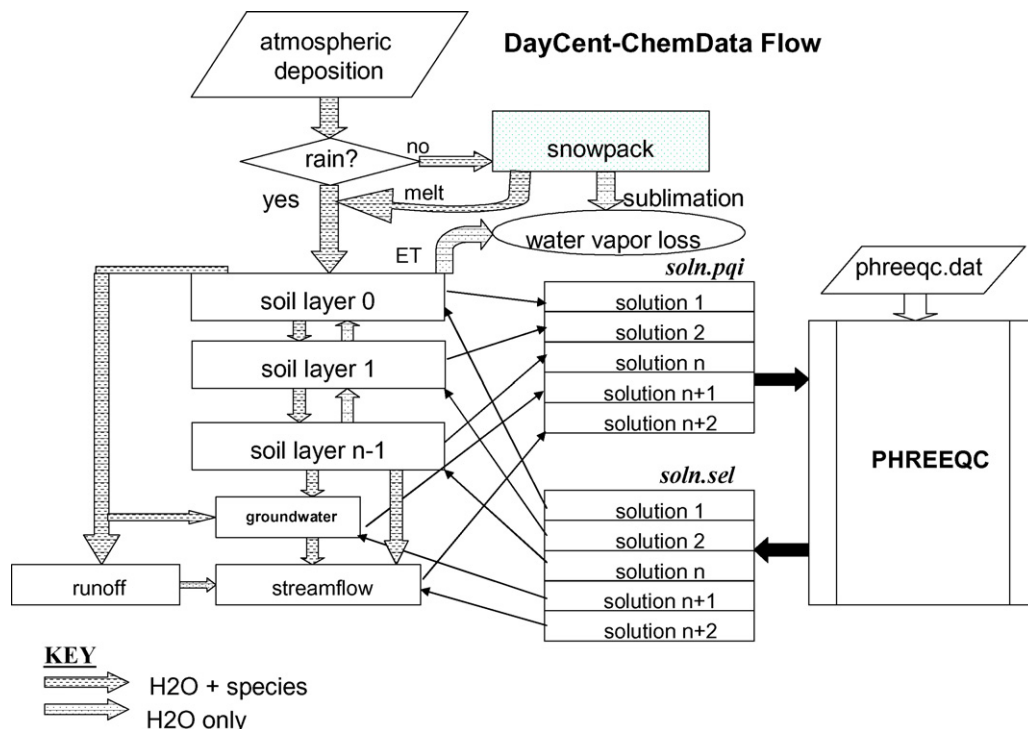


Fig. 1 – Data flow within the DayCent-Chem model.

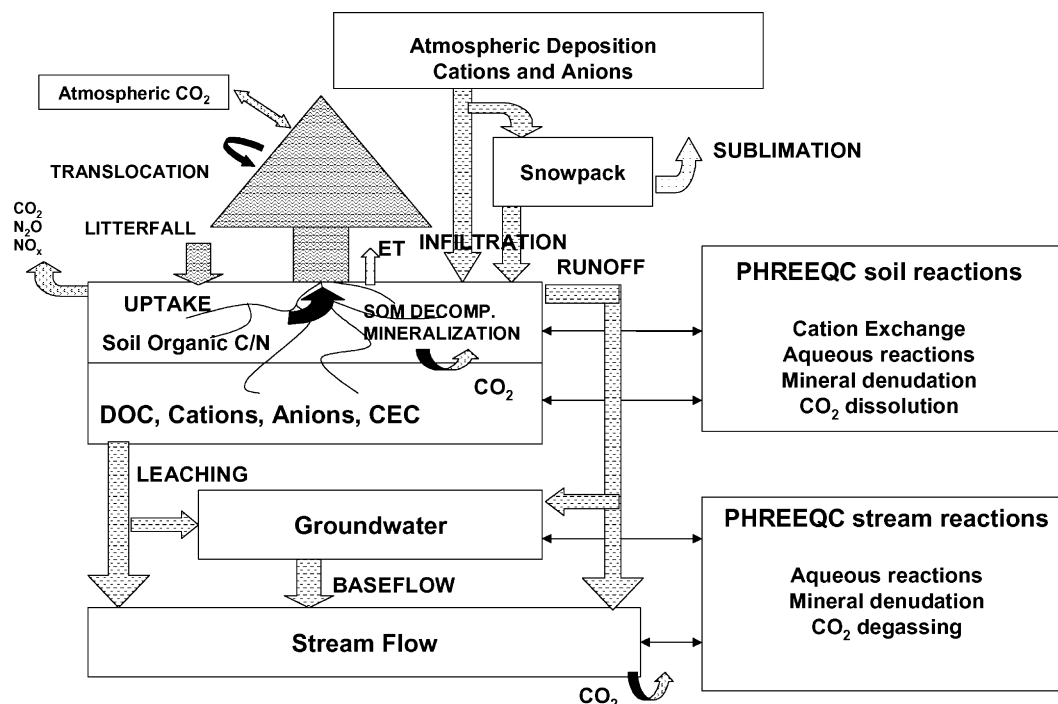


Fig. 2 – DayCent-Chem model processes.

range specified for the plant. Nutrients from senescing leaves are translocated to plant storage at the end of the growing season. Dead plant material remains standing or is dropped onto the soil surface. Some plant types are able to reduce their mineral N demand by symbiotically fixing nitrogen.

Because the DayCent model simulates only C, N, P, and S dynamics, there is no assimilation of base cations (Ca^{2+} , Mg^{2+} , K^+) by plants in the linked model; we assume that annual plant uptake of these three nutrients equals the amount released through decomposition of plant material. This assumption may hold for undisturbed ecosystems, but not for recently disturbed areas or relatively young forests. Net cation assimilation is small ($25 \text{ meq m}^{-2} \text{ year}^{-1}$) in the old-growth forest of LVWS, but there may be spatial variation within the soil profile between the uptake of base cations and their release through decomposition of fine roots and litter (Arthur, 1990).

2.4.3. Soil and weathering dynamics

Organic matter is incorporated into the soil through litter fall and death of roots. Decomposing organic matter is redistributed among active, passive, and slow pools while N, P, and S is either mineralized or immobilized. CO_2 produced by heterotrophic respiration is dissolved in soil solutions. Rainfall and snowmelt infiltrating the litter leach dissolved organic C, N, P, and S (DOC, DON, DOP, and DOS, respectively). Both inorganic and organic species are transported downward with water that further leaches organic and mineral soil. Nitrification and denitrification produce N_2 , N_2O , and NO_x through oxidation and reduction of NH_4^+ and NO_3^- , respectively. Cations in solution are adsorbed and desorbed from permanent negatively-charged exchange sites (X^-). Dissolu-

tion of primary and secondary minerals releases base cations, aluminum hydroxides, bicarbonate, metallic cations, hydrogen ions, silica, sulfate, and other inorganic species into soil layer, groundwater, and stream solutions. A portion of DOC is organic acid that reacts with other species in soil and stream solutions. Water exiting the soil profile enters either the stream or groundwater; a user-specified fraction of this groundwater storage is released to stream flow each day.

Annual denudation rates of common primary and secondary minerals are model inputs, and each mineral can be dictated to dissolve only, to precipitate only, or to do either. The maximum amount of any mineral that can be dissolved within a solution on a given day is calculated by dividing its annual denudation rate by 365. The user specifies the distribution of minerals among the soil layers, groundwater, and stream. For solutions where mineral dissolution occurs, the daily potential denudation rates of each mineral are listed in a PHREEQC EQUILIBRIUM.PHASES reaction. This means minerals can dissolve until they reach equilibrium with the solution, or until the maximum daily amount has been dissolved, whichever comes first. No kinetically limited mineral dissolution reactions are considered. Minerals precipitate when their components are oversaturated in solution.

The production and flushing of DOC in soils influences stream chemistry. In particular, DOC has the capacity to complex with free heavy metal cations, reducing their toxicity (Drever, 1982). In the model, DOC concentrates in soil over the winter when soil water flux is low, and is flushed from the soil when water flow increases. Naturally occurring organic acids are modeled using a triprotic analog (H_3Org) (Driscoll et al., 1994; Gbondo-Tugbawa et al., 2001). The total amount of

organic analog present is estimated as

$$[\text{Org}^{n-}]_{\text{Total}} = \text{SiteDenDOC}, \quad (1)$$

where SiteDenDOC (Table 1) is site density, which is the moles of organic anion sites per moles of DOC, and Org^{n-} is the organic analog anion in soil solution.

Acid neutralizing capacity (ANC) is calculated as the concentration ($\mu\text{eq L}^{-1}$) of H^+ acceptors minus concentrations of H^+ donors and allows for the contribution of dissolved inorganic carbon as well as organic solutes that bind H^+ and certain hydroxy-Al and organo-Al complexes (Driscoll et al., 1994; Gbondo-Tugbawa et al., 2001).

$$\begin{aligned} \text{ANC} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + [\text{Al}(\text{OH})_2^+] \\ & + 3[\text{Al}(\text{OH})_4^-] + [\text{HOrg}^{2-}] + 2[\text{Org}^{3-}] + [\text{AlOrg}] \end{aligned} \quad (2)$$

2.4.4. Surface water and snow dynamics

Stream flow is controlled by a number of model parameters to obtain a watershed response (Table 1). Rain and snow melt that do not infiltrate the soil surface carry precipitation solutes to stream flow along with dissolved organics leached from surface litter, although a fraction of surface runoff (RO2DEEP) can be routed to groundwater for deferred release into the stream. Water that infiltrates the soil profile leaches organic and inorganic species. DayCent directs a constant fraction (STORMF) of soil drainage to stream flow and (1-STORMF) to groundwater; a constant fraction (BASEF) of groundwater is routed to stream flow. Some of the CO_2 carried from soil solutions and groundwater degasses as it encounters the lower partial pressure of the atmosphere. Geochemical reactions in stream flow and groundwater include the same aqueous reactions defined for soils, except for cation exchange.

Three parameters regulate snowpack accumulation, melt, and sublimation (Table 1). Precipitation is added to the snowpack when maximum daily air temperature is below $\text{TMELT}(1)$, and snow melts above this temperature. The rate of melt is a function of $\text{TMELT}(2)$ and the difference between maximum daily air temperature and $\text{TMELT}(1)$. When a snowpack is present, the maximum amount of sublimation is the product of parameter FSUBLIM and a potential evapotranspiration rate calculated by the model as a function of air temperature. $\text{FSUBLIM} > 1$ is used to account for sublimation by wind that can substantially increase snowpack loss from windy, high elevation environments (Hartman et al., 1999).

Elution causes early melt water to be the most chemically concentrated of the season. Even when ionic concentrations in precipitation are low, snowpacks may accumulate large quantities of ionic species and release these species in a strong ionic pulse (Campbell et al., 1995). The magnitude of the ionic pulse depends on snow depth, rate of melt, and number of melt/freeze cycles in the snowpack (Williams and Melack, 1991; Bales, 1992), and therefore may vary regionally, spatially within a watershed, and/or from year to year at the same site (Williams and Caine, 2001). To simulate elution, the model allows the user to increase the rate of ionic release from the snowpack for a specified duration at the commencement of snowmelt.

2.4.5. Dissolved gases

The total amount of dissolved inorganic carbon in soil, groundwater, and stream solutions is regulated in part by equilibrating solutions with $\text{CO}_2(\text{g})$. The partial pressure of $\text{CO}_2(\text{g})$ in soil and groundwater solutions, $p\text{CO}_2$ soil (Table 1) was set to $10^{-2.5}$ atm (Lindsay, 2001). The stream water solution and the top soil layer are brought to equilibrium with $p\text{CO}_2(z)$, where z (m) is the site elevation. The barometric formula multiplied by an adjustment factor (Table 1) defines the value of $p\text{CO}_2(z)$ used by the model,

$$p\text{CO}_2(z) = p\text{CO}_2(0) \times e^{-gz/RT} \times 10^{\log_{10} p\text{CO}_{2\text{adj}}}, \quad (5)$$

where $p\text{CO}_2(0)$ is the $p\text{CO}_2$ at mean sea level ($10^{-3.5}$ atm), g the gravitational constant (9.81 m s^{-2}), R the specific gas constant of air ($287.0 \text{ J kg}^{-1} \text{ K}^{-1}$), and T is the air temperature (K).

3. Methods

3.1. Study area

The 183 ha Andrews Creek watershed is located within the larger Loch Vale watershed, Rocky Mountain National Park, CO. It ranges in elevation from 3200 to 4000 m and is dominated by bedrock (57%) and talus (31%) with alpine tundra soils comprising 11%. Andrews Glacier (10 ha) and a small tarn comprise the remaining land cover fractions of the Andrews Creek watershed (Meixner et al., 2000). The tarn was not included in the modeling effort. The hydrology is dominated by annual winter snow that melts during the spring and summer. Discharge appeared to be augmented by glacier and permafrost

Table 1 – Fitted parameter values for the bedrock/talus, tundra, and forest simulations

Parameter	Bedrock/talus	Tundra	Forest	Description
siteDenDOC	0.023	0.023	0.046	≥ 0.0 , moles of H^+ binding sites per moles organic C
$\log_{10} p\text{CO}_{2\text{adj}}$	0.3	0.5	0.25	Fixed change in $\log_{10}(p\text{CO}_2)$ of surface water ($0.5 = \sqrt{10}$ -fold increase)
$\log_{10} p\text{CO}_{2\text{soil}}$	-2.5	-2.5	-2.5	$\log_{10}(p\text{CO}_2)$ (atm) in soil solutions
doNredox	1	0	0	1 (true) or (0) false—allow $\text{N}(-3)/\text{N}(+5)$ redox
$\text{TMELT}(1)$	-4.0	-4.0	0.0	Temperature above which snow melts ($^{\circ}\text{C}$)
$\text{TMELT}(2)$	0.05	0.05	0.05	Centimeter snow melted per $^{\circ}\text{C}$ per day
FSUBLIM	1.0	2.0	1.0	Potential sublimation rate multiplier
BASEF	0.05	0.05	0.05	Base flow fraction (0–1)
STORMF	0.0	0.0	0.0	Storm flow fraction (0–1)
RO2DEEP	0.5	1.0	1.0	Fraction of runoff routed to groundwater (0–1)

Table 2a – Forest soil layer properties and initial exchangeable cations (meq 100 g⁻¹) as measured for a Cryoboralf (Baron et al., 1992b)

Layer	Thickness (cm)		Depths (cm)		Description				
0	5		0–5		Oi: slightly decomposed organic matter				
1	5		5–10		Oe: decomposed organic matter				
2	10		10–20		E: very cobbly silt loam				
3	15		20–35		Bt: extremely cobbly sandy loam				
4	20		35–55		Bc: extremely stoney loamy sand				
	pH	Organic carbon (%)	Clay (%)	CaX ₂	MgX ₂	KX	NaX	AlX ₃	HX
0	4.84	13.1		18.4	3.2	0.9	0.1	10.5	1.8
1	4.84	13.1		18.4	3.2	0.9	0.1	10.5	1.8
2	3.78	2.7	19.5	5.0	1.0	0.4	0.1	18.9	1.0
3	3.72	2.5	28.3	3.6	0.8	0.2	0.1	25.2	0.7
4	3.74	1.3	16.2	2.6	0.6	0.1	0.1	16.2	0.4

melt water after year 1997 (Clow et al., 2003). Stream discharge is monitored continuously at a gaging station at the base of the watershed during the ice-free season. Stream water samples are collected weekly for chemical analysis at the same location.

An old-growth Englemann spruce-subalpine fir forest is located just below the Andrews Creek stream gage. The forest is characterized as cool, sheltered, well-drained, with relatively deep soils. Soils are coarse-textured with an overlying organic layer averaging 5 cm (Rueth et al., 2003).

Talus slopes in LVWS are the primary ground water reservoir, with a maximum storage capacity equal to or greater than annual discharge (Clow et al., 2003). Groundwater flowing from talus can account for $\geq 75\%$ of streamflow in Andrews Creek during storms and the winter baseflow period. Ice stored as permafrost (including rock glaciers) is the second largest ground water reservoir in LVWS (Clow et al., 2003).

Average annual precipitation from 1984 to 2003 measured at the Loch Vale weather station was 106 cm (S.D. 18), approximately 65% of which was snow (NADP/NTN, 2005). The climate is cold and windy, with a mean annual temperature of 1.5 °C (Baron, 2002).

3.2. Simulated land cover types

Separate bedrock/talus and tundra sites were simulated and their results combined to derive total watershed response for

Andrews Creek. The contribution of each site to total discharge quantity and quality was weighted by the percentage of the watershed occupied by each area represented. The combined bedrock/talus and tundra simulation, hereafter referred to as the combined alpine run, had a 89% contribution from bedrock/talus and 11% from tundra (Meixner et al., 2000). The bedrock/talus simulation represents solid metamorphic and igneous bedrock surfaces and cliffs, talus slopes, and block slopes with a small amount of perennial vegetation. The tundra of Andrews Creek Watershed has moderately deep soils with dry to moist perennial sedge meadows. Tundra vegetation and soil organic matter parameters for DayCent were obtained from a nearby alpine research site, Niwot Ridge (Conley et al., 2000).

Although subalpine forest within LVWS lies primarily below the Andrews Creek outlet, we simulated forest dynamics to further test the biological and soil processes of the model against a rich data set available for this forest. We did not model the entire Loch Vale watershed, nor did we include the forest simulation in Andrews Creek results.

3.3. Parameter estimation and initial conditions

Soil layer thickness, pH, clay content, organic matter percentage, and exchangeable cations for tundra and forest soils were initialized with data for a Cryochrept and Cryoboralf, respectively (Tables 2a, 2b and 2c; Baron et al., 1992b). For the

Table 2b – Tundra soil layer properties and initial exchangeable cations (meq 100 g⁻¹) as measured for a Cryochrept (Baron et al., 1992b)

Layer	Thickness (cm)		Depths (cm)		Description				
0	2		0–2		Oe: moderately decomposed organic matter				
1	3		2–5		A: black cobbly sandy loam, 20% coarse				
2	12		5–17		Bw: brown cobbly sandy loam, 30% coarse				
3	15		17–32		Bw: brown cobbly sandy loam, 30% coarse				
	pH	Organic carbon (%)	Clay (%)	CaX ₂	MgX ₂	KX	NaX	AlX ₃	HX
0	5.0	11.6	7.0	36.6	7.2	0.9	0.1	1.5	0.5
1	4.95	2.8	9.5	13.0	3.0	0.2	0.1	5.1	0.5
2	4.66	0.9	12.6	4.8	2.2	0.1	0.1	12.6	0.2
3	4.66	0.9	6.1	4.8	2.2	0.1	0.1	12.6	0.2

Table 2c – Bedrock/talus soil layer properties and initial exchangeable cations (meq 100 g⁻¹)

Layer	Thickness (cm)			Depths (cm)			Description			
0	2			0–2			Coarse texture with high bulk density			
	pH	Organic carbon (%)	Clay (%)	Bulk density (g cm ⁻³)	CaX ₂	MgX ₂	KX	NaX	AlX ₃	HX
0	5.0	0.0	25	2.0	0.3	0.04	0.02	0.01	0.3	0.02
All numbers were estimated.										

Table 3 – Annual potential mineral denudation rates for Loch Vale watershed (LVWS) and their distribution over bedrock/talus, tundra, and forest

Mineral	(Mast, 1992) LVWS average (mol ha ⁻¹ year ⁻¹)	Bedrock/talus (mol ha ⁻¹ year ⁻¹)	Tundra (mol ha ⁻¹ year ⁻¹)	Forest (mol ha ⁻¹ year ⁻¹)
Calcite	106	129	0	0
Albite (73% of 99 moles oligoclase)	72.3	47	217	289
Anorthite (27% of 99 moles oligoclase)	26.7	17	80	107
Biotite	29	19	87	116
Kaolinite	18	0 ^a	0 ^a	0 ^a
Chlorite	7	5	21	28
Pyrite	6	4	18	24
Smectite	0	0 ^a	0 ^a	0 ^a
SiO ₂ (a)	0	153	153	n/a

Tundra (11% of LVWS) had the potential to dissolve minerals at three times the watershed rate. Forest (6% of LVWS) had the potential to dissolve minerals at four times the watershed rate. The remaining mineral dissolution was allocated to bedrock/talus. SiO₂(a), amorphous silica, was added to calibrate stream silica, alkalinity, and pH.

^a Mineral allowed to precipitate only.

bedrock/talus simulation, we created a single shallow dense soil layer with very low cation exchange capacity (Table 2c). Because measured sulfate adsorption in LVWS was less than 1.2 mmol kg⁻¹ and soil PO₄³⁻ concentrations are low (Baron et al., 1992b), sulfate and other anion adsorption reactions were not included in Andrews Creek simulations.

We prescribed different weathering rates to bedrock/talus, tundra, and forest simulations (Table 3). Primary mineral weathering reactions in LVWS have been quantified using a combination of traditional mass-balance calculation methods and strontium isotope mixing calculations (Mast et al., 1990; Clow, 1992; Mast, 1992; Clow et al., 1997). Calcite weathering occurs in fresh talus surfaces, but is not likely in older more weathered soils (Walthall, 1985; Clow and Sueker, 2000). Silicate mineral weathering has a strong influence on tundra waters (Clow and Sueker, 2000), and the influence of sulfide-bearing minerals is significant in Andrews Creek (Campbell et al., 1995). The kinetically limited dissolution of crystalline minerals can not account for the regulation of SiO₂ in LVWS stream waters, and faster reacting amorphous aluminosilicates may play an important role in regulating SiO₂ concentrations in alpine soils (Clow, 1992; Campbell et al., 1995). Walthall (1985) reported that minerals in LVWS forest soils dissolve at four times the watershed average rate. We assumed that silicates and pyrite in tundra soils dissolve at three times the watershed rate, and assigned 100% of calcite weathering to the bedrock/talus site. The 99 moles of oligoclase (Na:Ca = 73:27) are represented as 72.3 moles of albite and 26.7 moles of anorthite. We prescribed amorphous silica dissolution in tundra and bedrock/talus soils to better estimate stream silica concentrations.

3.4. Weather data

Precipitation, and daily minimum and maximum air temperatures data were taken from the LVWS weather station (3159 m; www.nrel.colostate.edu/projects/lvws/pages/homepage.htm). The median elevation of Andrews Creek basin is ~400 m higher than the weather station, so we applied an environmental lapse rate of 6 °C per 1000 m (Daly et al., 2002) to account not only for the higher elevation of Andrews Creek basin, but also the shadowing effect of cliff faces and northerly aspect of the catchment that limits solar heating during much of the year (Campbell et al., 1995).

Both weekly and daily precipitation amounts were measured at NADP/NTN site CO98 (NADP/NTN, 2005). Weekly measurements were often available when daily precipitation values were missing, particularly during the snow season. In this case, we adjusted daily precipitation uniformly for each missing value during the week, so that the weekly sum was equal to the measured weekly amount. When neither daily nor weekly values were recorded, daily precipitation was set to 0.0. A second weather station in Andrews Creek basin was used to fill in missing temperature data using linear regression equations.

3.5. Daily wet and dry deposition estimates

Daily wet deposition concentrations were derived from weekly concentrations by assuming individual precipitation events had the same concentrations as the week-long sample. Field pH values were used when possible, otherwise lab pH values were substituted. Missing concentrations of any solute for a

particular day of year were assigned the multi-year average concentration for that same day of year.

The composition and proportion of dry deposition varied seasonally and spatially in LVWS (Table 4). Quarters 1, 2, 3, and 4 were January–March (winter), April–June (spring), July–September (summer), and October–December (autumn), respectively. To calculate seasonal dry:wet deposition ratios of NO_3^- , NH_4^+ , and S (SO_2 plus SO_4^{2-}), we used the 1995–2002 quarterly dry deposition measurements for site ROM406 of the Clean Air Status and Trends Network (CASTNet, U.S. Environmental Protection Agency, Washington, D.C., 2003, <http://www.epa.gov/castnet/>), and the corresponding quarterly wet deposition measurements from NADP/NTN site CO98 in LVWS. The ROM406 site is located within forest at an elevation of 2743 m, approximately 10 km SE of and 400 m lower than NADP/NTN site CO98. According to the CASTNet derived dry:wet ratios (Table 4), the highest proportions of NO_3^- dry-fall occurred in the summer (0.65) and spring (0.52) quarters, whereas the highest proportions of S dryfall occurred in the winter (0.29) and autumn (0.28) quarters. The dry:wet NH_4^+ ratio was greatest in the winter quarter (0.17). For forest simulations we used these SO_4^{2-} , NO_3^- , and NH_4^+ dry:wet ratios. For tundra and bedrock/talus we used one-half these NO_3^- and NH_4^+ dry:wet ratios. Because N deposition is affected by upslope conditions (Baron et al., 1992a), we assumed the treeless high elevation areas of LVWS do not capture as much dryfall nitrogen as forests due to their smaller LAI and relative position upslope of forests. Additionally, the dry:wet ratios for NO_3^- and NH_4^+ , derived from Clow and Mast (1995) for a treeless area in the summer, were much lower than CASTNET/NADP derived ratios while dry:wet SO_4^{2-} ratios were similar (Table 4).

We estimated dry:wet ratios for base cations and Cl^- using bulk deposition measurements from two sources (Table 4). For each constituent i , the dry:wet ratio was calculated as,

$$\frac{\text{bulk deposition}_i - \text{wet deposition}_i}{\text{wet deposition}_i}, \quad (6)$$

where wet deposition_i was measured at the nearest NADP/NTN collector. We used measurements of bulk deposi-

tion in the LVWS snowpack (Campbell et al., 1995) to estimate the dry:wet ratios of Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and Cl^- from October to March. For April–September base cation and Cl^- dry:wet ratios we used measurements of bulk deposition on a granite surface in LVWS, taken at 3300 m, above treeline (Clow and Mast, 1995). For most of the year, dry deposition estimates for Ca^{2+} , Mg^{2+} , and K^+ were greater or equal to the amount of wet deposition of these cations. Dry deposition of Na^+ and Cl^- were insignificant in the winter.

3.6. Calibration

DayCent-Chem was calibrated using Andrews Creek stream chemistry and discharge data for years 1992–1999; years 2000–2003 we used for evaluation.

Model calibration required several steps: (1) match simulated net primary production, soil organic matter content, and nitrogen mineralization rates with corresponding observed values, (2) match daily and annual total discharge with measured amounts, (3) match daily stream chemistry with measured concentrations, and (4) match simulated annual volume-weighted mean soil and stream concentrations with measured means.

Since the geochemical calculations are computationally intensive, DayCent was brought to an equilibrium state without utilizing PHREEQC. First, we ran the model for 400 years using background (pre-industrial) inputs of nitrogen ($0.04 \text{ gN m}^{-2} \text{ year}^{-1}$) (Galloway et al., 1996). Next, we ran the model for 30 years with current average deposition rates ($0.35 \text{ gN m}^{-2} \text{ year}^{-1}$) that varied from year to year as a linear function of precipitation. Finally, we ran the model for years 1984–2003 with the geochemical model calculations. All runs used daily 1984–2003 weather, repeated over and over if necessary.

We tuned the model on uncertain values such as the fraction of mineral denudation in each soil layer, parameters that control watershed average discharge, and pCO_2 of stream water and soil water (Table 1) to represent measured 1992–1999 daily stream discharge and stream chemistry. Stream concentration calibrations were made by visually comparing daily and annual simulated and measured stream discharge and

Table 4 – Estimated dry:wet deposition ratios for LVWS

	Quarterly ^a (1, 2, 3, 4)	October–March ^b	April–September ^c
NO_3^-	0.29, 0.52, 0.65, 0.39	0.25	0.13
NH_4^+	0.17, 0.13, 0.14, 0.13	0.5	Consumption in bulk collector
SO_4^{2-}	0.29, 0.23, 0.27, 0.28	0.29	0.23
Ca^{2+}		2.5	1.71
Mg^{2+}		1.0	3.89
Na^+		Insignificant	0.40
K^+		Very small	3.33
Cl^-		Insignificant	0.21

Quarters 1, 2, 3, and 4 are winter (January–March), spring (April–June), summer (July–September), and autumn (October–December), respectively. The ratios in boldface were used for the forest simulation. The same wet:dry ratios were used for the alpine and bedrock/talus simulations except that NO_3^- and NH_4^+ dry:wet ratios were halved.

^a Computed from CASTNET ROM406 and NADP CO98 data.

^b Campbell et al., 1995 (WY1992): dry:wet computed as $(\text{snowpack}_{\text{max}} - \text{NADP}_{\text{Oct-Mar}}) / \text{NADP}_{\text{Oct-Mar}}$.

^c Clow and Mast, 1995 (July 5–August 19, 1994): dry:wet computed as $(\text{bulk dep} - \text{NADP}) / \text{NADP}$.

species concentrations. Our goals were to constrain the simulated concentrations within the range of measured concentrations and capture the timing and patterns of flow dilution and flow concentration for each solute. Elution parameters were adjusted to better fit stream Cl^- , SO_4^{2-} , and NO_3^- . The pH of soil and stream solutions was computed as a charge balance in solution.

We computed three separate performance measures for discharge and all solutes to evaluate the model. These included the normalized root mean square error (NRMSE), the normalized mean absolute error (NMAE) (Janssen and Heuberger, 1995) and the Nash-Sutcliffe value (Nash and Sutcliffe, 1970). A Nash-Sutcliffe value less than zero indicates that the mean of the observation is a better predictor of observed data than the model prediction; values close to 1.0 indicate good agreement.

3.7. $N(-3)/N(+5)$ Redox reactions

DayCent-Chem can be run with or without PHREEQC's $N(-3)/N(+5)$ redox reactions, where $N(-3)$ and $N(+5)$ are the N oxidation states of NH_4^+ and NO_3^- , respectively. Nitrification and denitrification are a part of DayCent's soil processes, and allowing PHREEQC to duplicate these reactions may be redundant or even incorrect. PHREEQC's $N(-3)/N(+5)$ redox was turned off for the tundra and forest simulations with multiple soil layers, but was allowed for the bedrock/talus simulation that describes only a single shallow and dense soil layer.

4. Results

4.1. Stream discharge and chemistry

The model performed slightly better for calibration years 1992–1999 than for evaluation years 2000–2003 (Table 5). Nash-Sutcliffe values, computed for daily discharge and stream concentrations, were closer to 1.0 for 1992–1999 for all values except discharge. Evaluation years corresponded to some of the driest years in Andrews Creek. Overall, model results compared better to measurements for wetter-than-average years than for drier years. Precipitation was above the 1984–2003 106 cm average during 1993–1997. Precipitation was below the average in 1992 and 1998–2003.

Daily stream concentrations were close to measured for Andrews Creek during spring and summer, but the model was less able to reproduce stream chemistry during winter when flow was very low. On the days simulated discharge was less than 0.01 cm (0.02 cfs), modeled stream concentrations were filtered from the graphs (Fig. 3b–j). Error terms (NRMSE and NMAE) were smaller and Nash-Sutcliffe values were closer to 1.0 for the majority of solutes when the 16% of the values representing very low flow were not included (Table 5).

The model captured total annual flow best through 1997, and after 1997 the model underpredicted annual totals (Fig. 4a). This underestimate of annual total discharge is reflected in the daily hydrographs on the falling limb of years 1998 and 2000–2003 when simulated flow is below measured flow (Fig. 3a). Daily simulated discharge followed the hydro-

Table 5 – Nash-Sutcliffe (Nash-Sut) and normalized mean absolute mean (NMAE) values for daily stream concentrations and discharge

	Combine run: calibrated vs. evaluation years				Combined run 1992–2003: non-filtered vs. filtered				1992–2003 Runs: combined run vs. individual tundra and bedrock/talus runs			
	1992–1999 (Nash-Sut)		2000–2003 (Nash-Sut)		Non-filtered (Nash-Sut)		Filtered (Nash-Sut)		Non-filtered (NMAE)		Filtered (NMAE)	
pH	-1.84	-3.34	-1.76	-1.65	0.03	0.03	0.03	0.03	-1.76	-3.38	-1.79	0.03
NO_3	-2.94	-14.88	-4.01	-3.05	0.57	0.48	0.48	0.48	-4.01	-4.79	-5.34	0.62
ANC	-2.40	-9.44	-3.88	-5.72	0.47	0.46	0.46	0.46	-3.88	-2.28	-6.02	0.57
SO_4	-1.04	-3.59	-1.39	-1.57	0.36	0.36	0.36	0.36	-1.39	-0.63	-3.44	0.50
Cl	-2.82	-3.05	-2.77	-3.10	0.62	0.62	0.68	0.68	-2.77	-1.87	-4.05	0.74
Ca	-3.87	-8.59	-4.15	-1.70	0.44	0.44	0.31	0.31	-4.15	-11.25	-4.31	0.45
Mg	-3.35	-9.27	-4.05	-2.39	0.50	0.50	0.38	0.38	-4.05	-7.82	-4.80	0.53
K	-1.91	-5.94	-2.29	-2.98	0.51	0.51	0.52	0.52	-2.29	-6.26	-3.40	0.56
Na+	-1.86	-5.96	-2.29	-1.91	0.35	0.35	0.30	0.30	-2.29	-9.03	-5.14	0.51
BC	-2.95	-7.66	-3.34	-1.46	0.39	0.39	0.27	0.27	-3.34	-5.57	-4.12	0.42
Si	-4.33	-7.45	-4.77	-4.85	0.38	0.38	0.33	0.33	-4.77	-5.26	-8.76	0.50
Q	0.58	0.63	0.60	0.52	0.49	0.49	0.47	0.47	0.60	0.65	0.58	0.50
NH_4	-1.15	-15.64	-1.93	-0.71	1.81	1.40	1.40	1.40	-1.93	-65.80	n/a	n/a

The leftmost column of numbers represent calibrated and evaluation years, respectively. The next four columns represent non-filtered and filtered values. Non-filtered values include all days measurements were available, and filtered include only days simulated discharge was ≥ 0.01 cm. The rightmost six columns represent combined run vs. tundra vs. bedrock/talus runs. Normalized relative mean squared errors (NRMSE) showed the same trends as NMAE and are not included here.

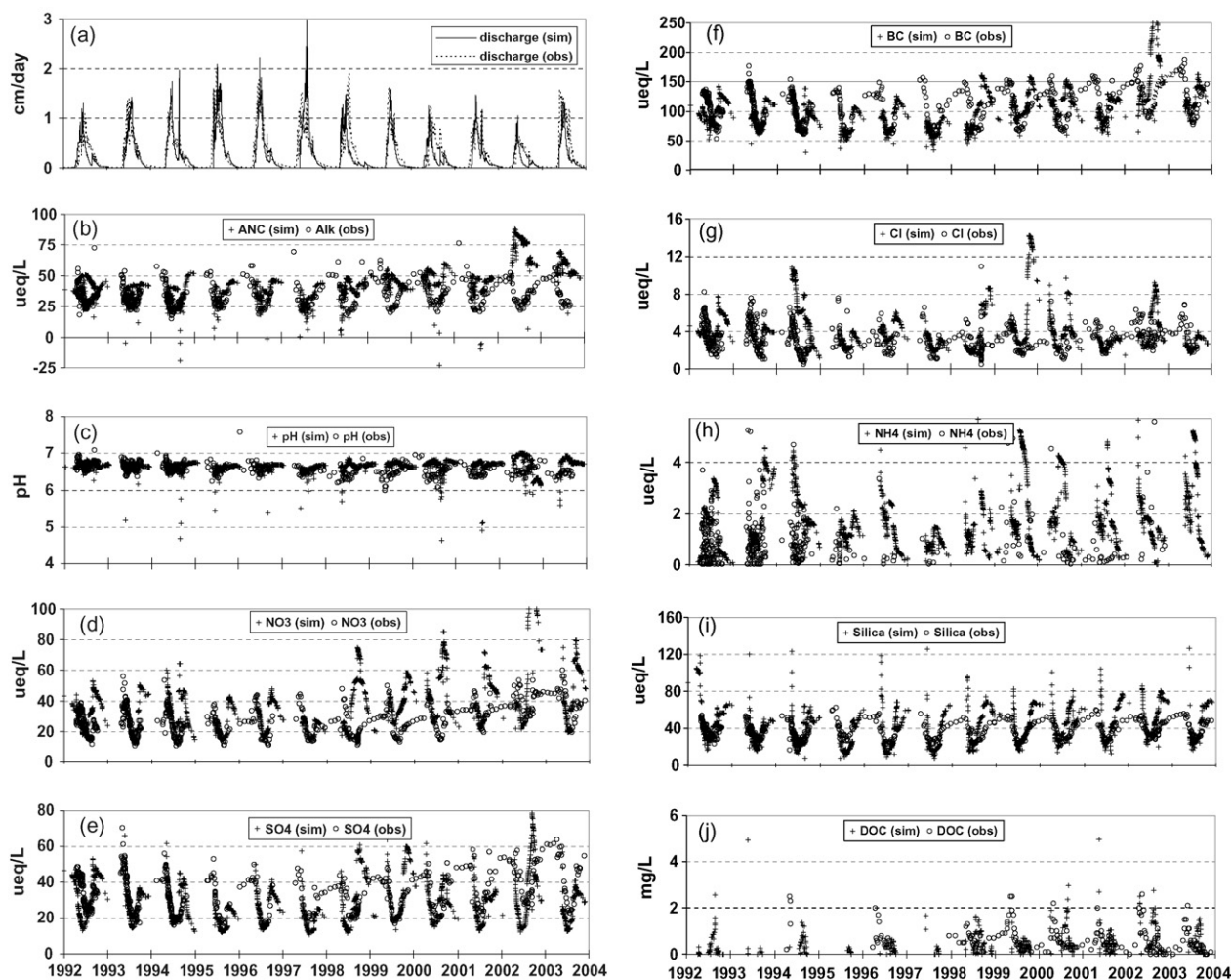


Fig. 3 – Daily discharge and solute concentrations as simulated for the combined alpine run (solid lines or plus signs) and observed in Andrews Creek (dashed lines or open circles): (a) discharge; (b) ANC; (c) pH; (d) NO_3^- ; (e) SO_4^{2-} ; (f) base cations (Ca + Mg + K + Na); (g) Cl^- ; (h) NH_4^+ ; (i) silica; (j) DOC. Observed NH_4^+ concentrations (h) were not available for 1998 and 2003.

graphs of measured discharge for Andrews Creek with an R^2 of 0.64 (Fig. 3a). For most years, the simulated onset of snow melt and the amount and timing of peak flow were close to measured values. The model overpredicted some runoff events in 1994, 1996, 1997, and 2002, and there was a large spike in simulated discharge for late August of 1994.

With the exception of a few outliers, simulated daily ANC was within the range of observed concentrations (Fig. 3b). For most years through 1997, the model captured the observed increase in stream ANC going into winter, and its subsequent dip during snowmelt. Simulated daily ANC concentrations were particularly sensitive to daily discharge estimates, and were underestimated when discharge was overestimated, and visa versa. Outliers ($\text{ANC} < 10 \mu\text{eq L}^{-1}$) always occurred when there was an abrupt increase in simulated discharge that simultaneously diluted simulated stream base cation (BC) concentrations. Simulated annual volume-weighted mean ANC concentrations were within $12 \mu\text{eq L}^{-1}$ of measured values for 1992–1997, but were overestimated by $8\text{--}36 \mu\text{eq L}^{-1}$ the other years (Fig. 4b).

Simulated pH tracked simulated ANC (Fig. 3c) and was within the range of observed values, though a few outliers occurred on days when ANC was also underestimated. Simulated annual volume-weighted mean pH was within 0.2 units of measured except for years 1994 and 2003 when it was 0.4 and 0.3 units greater, respectively, than measured (Fig. 4c).

Measured NO_3^- was concentrated during initial snowmelt due to elution and soil and ground water flushing, dipped to its minimum concentration during the summer when plants and microbes take up nitrogen, and gradually increased as discharge decreased into autumn. The model captured this pattern of observed NO_3^- concentrations, but sometimes underestimated maximum concentrations or overestimated minimum concentrations (Fig. 3d). From 1998 to 2003, simulated daily NO_3^- concentrations were higher than observations beginning in August or September until December (Fig. 3d). Simulated annual volume-weighted mean concentrations of NO_3^- fluctuated around observed concentrations, and were within $8 \mu\text{eq L}^{-1}$ of observed concentrations all years (Fig. 4d). Simulated NH_4^+ concentrations, like measured

Table 6 – Simulated and observed annual water fluxes, annual nitrogen fluxes, annual NPP, annual range of live biomass, and average soil organic matter

Average annual values (1984–1999 except where indicated)	Simulated tundra	Observed tundra	Simulated bedrock–talus	Observed bedrock–talus	Simulated combined run	Observed Andrews Creek	Simulated forest	Observed forest
Discharge (cm year ⁻¹), 1992–1999	83.8 (13.9)	n/a	91.5 (18.4)	n/a	90.6 (17.9)	96.0 (13.4)	59.8 (16.8)	n/a
ET (cm year ⁻¹)	6.1 (1.9)	23.4 ^a	11.7 (3.9)	17.0 ^a , 15% summer precip ^b (~8 cm)	11.0 (3.6)	n/a	27.0 (6.1)	52.5 ^a
Sublimation (cm year ⁻¹)	26.5 (7.1)	26–88 ^a	15.0 (4.2)	26–88 ^a	16.3 (4.5)	n/a	20.8 (5.4)	26–88 ^a
Stream N (gN m ⁻² year ⁻¹), 1992–1997	0.29 (0.08)	n/a	0.34 (0.06)	n/a	0.33 (0.06)	0.32 ^c	0.32 (0.1)	n/a
Net mineralization (gN m ⁻² year ⁻¹)	2.1 (0.7)	~2.0 ^d	0.02 (0.01)	n/a	x	n/a	2.1 (0.3)	2.0–3.0 ^e
NPP above ground	43.0 (9.3)	44–135 ^f	8.8 (0.2)	n/a	x	n/a	111 (24)	163 ^{e*}
NPP total (gC m ⁻² year ⁻¹) [*]	95.1 (24.3)	149–219 ^f	1.3 (0.4)	n/a	x	n/a	186 (43)	136–340 ^{e*}
Above ground live biomass (gC m ⁻²) [*]	0–63.8	60–117 ^f	x	n/a	x	n/a	4270–4408	5511 ^{e*}
Below ground live biomass (gC m ⁻²) [*]	425–515	225–929 ^f	x	n/a	x	n/a	1170–1266	1200 ^{e*}
Soil organic matter (gC m ⁻²)	9,550	6700 ^g , 13,000 ^h	17.7	n/a	x	n/a	6910	6800 ^e

Standard deviations are shown in parentheses. Mean annual precipitation from 1984–1999 was 109.8 cm, and from 1992–1999 was 117.5 cm. Years prior to 2000 are summarized since data were measured before then. Asterisk (*) denotes the observed values published in grams of biomass were divided by 2.25 to convert to grams of carbon (gC). Observed NPP and biomass for tundra include both dry and moist meadows; n/a (not available); x (not reported).

^a Baron and Denning (1992).

^b Clow and Mast (1995).

^c Campbell et al. (2000).

^d Bowman (1992).

^e Arthur and Fahey (1992).

^f Bowman and Fisk (2001).

^g Seastedt (2001).

^h Conley et al. (2000).

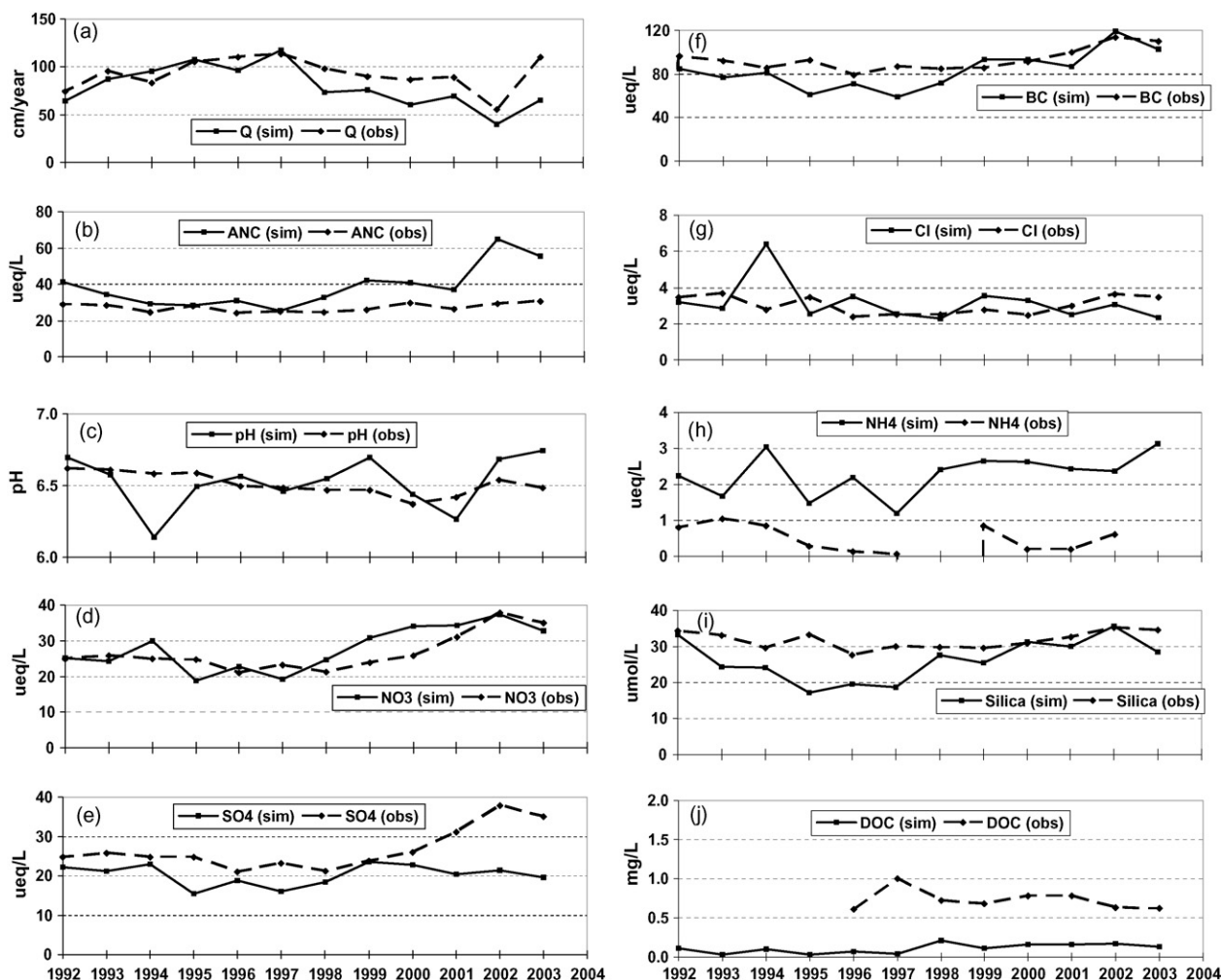


Fig. 4 – Annual mean discharge and annual volume-weighted mean solute concentrations as simulated for the combined alpine run (solid lines) and observed in Andrews Creek (dashed lines): (a) discharge; (b) ANC; (c) pH; (d) NO_3^- ; (e) SO_4^{2-} ; (f) base cations ($\text{Ca} + \text{Mg} + \text{K} + \text{Na}$); (g) Cl^- ; (h) NH_4^+ ; (i) silica; (j) DOC. Observed NH_4^+ concentrations (h) were not available for 1998.

concentrations, lacked a strong seasonal pattern but were in the range of measured concentrations (Fig. 3h). Both simulated and measured annual volume-weighted mean NH_4^+ concentrations were very low and within $2 \mu\text{eq L}^{-1}$ of each other (Fig. 4h). Predicted mean annual 1992–1997 inorganic nitrogen export ($0.33 \text{ gN m}^{-2} \text{ year}^{-1}$) was very close to the measured flux for Andrews Creek ($0.32 \text{ gN m}^{-2} \text{ year}^{-1}$) (Campbell et al., 2000) (Table 6).

The model did especially well at capturing observed daily trends in sulfate concentrations (Fig. 3e). Like NO_3^- , simulated and measured SO_4^{2-} concentrations were highest during snowmelt, and were at a minimum during the summer. Simulated SO_4^{2-} concentrations for the final third of years 1998, 1999, and 2002 were greater than measured; discharge was underestimated during this time of year in 1998 and 2002. Simulated annual volume-weighted mean concentrations of SO_4^{2-} that did not become more concentrated for drier years as was observed, and were underestimated by $11\text{--}16 \mu\text{eq L}^{-1}$ in 1995, 2001–2003 (Fig. 4e).

Measured Cl^- and BC concentrations followed seasonal patterns similar to NO_3^- and SO_4^{2-} , concentrating during ini-

tial snowmelt, diluting through June or July, and gradually concentrating the remaining months of the year (Fig. 3f and g). Simulated daily concentrations of Cl^- followed this pattern reasonably well except during 1994 and in the autumn of years 1998, 1999, 2000, and 2002 when simulated concentrations were much higher than observed (Fig. 3g). Simulated and observed annual volume-weighted mean concentrations of Cl^- were within $1 \mu\text{eq L}^{-1}$ of each other all years except 1994 (Fig. 4g).

The model underestimated maximum BC concentrations in spring, and overestimated them some years in autumn, but prior to 1998 generally captured the observed pattern of flow dilution during snowmelt and flow concentration during the lower flow periods (Fig. 3f). Both simulated and observed patterns of silica showed flow dilution during snowmelt and flow concentration during low flow (Fig. 3i). Simulated daily concentrations of silica tended to have a wider range of values than were measured, and were particularly higher than observed for a one to two week period at the onset of snow melt, and in autumn of most years after 1997. Simulated annual volume-weighted mean concentrations of base cations

(BC) and silica were close to observed values after 1997 (Fig. 4f and i).

Simulated and measured daily DOC concentrations had the same range of values (Fig. 3j). Simulated annual volume-weighted mean DOC concentrations were lower than measured DOC (Fig. 4j). Infrequent measurements of DOC in Andrews Creek may have made this gap between simulated and measured annual DOC appear larger than it actually was.

4.2. Combined runs versus separate runs

Stream chemistry from the combined alpine run approximated measurements better than individual tundra and bedrock/talus runs (Table 5). The combined run results had the smallest error terms for pH, NO_3^- , base cations, Si, and NH_4^+ . The tundra simulation had the smallest error terms for ANC, SO_4^{2-} , Cl, and discharge, and tundra had a slightly higher R^2 for discharge. The bedrock/talus runs did not have the smallest error term for any solute. Though some biological processes were simulated for bedrock/talus that contributed 89% to stream discharge and chemistry, the greater plant growth, soil organic matter leaching, and soil depth represented by the tundra simulation improved overall results. The 100% bedrock/talus simulation overpredicted the magnitude of daily runoff more often than the combined run did. The contribution of DOC to stream flow (Figs. 3j and 4j) was almost exclusively from the tundra simulation. Because the bedrock/talus run included calcite dissolution (from rock surfaces) and the tundra did not, daily stream BC and ANC concentrations for this simulation were generally higher and further from measurements than those of the combined simulation.

4.3. Evapotranspiration, sublimation, NPP, biomass, mineralization, and soil organic matter

4.3.1. Tundra

Model estimates of net primary production (NPP) and live biomass for tundra were lower than, but close to, measured values from nearby Niwot Ridge ($40^\circ 03' \text{N}$ $105^\circ 35' \text{W}$, ~30 km southwest of LVWS) (Table 6). Actual average annual production rates for LVWS tundra are probably lower than those at Niwot Ridge due to shallower soils and steeper slopes at LVWS (Arthur, 1992). Simulated above ground NPP for tundra ($43 \text{ gC m}^{-2} \text{ year}^{-1}$) was at the low end of that measured at Niwot Ridge ($44\text{--}135 \text{ gC m}^{-2} \text{ year}^{-1}$) (Bowman and Fisk, 2001), while total NPP (95 gC m^{-2}) was less than measured ($149\text{--}219 \text{ gC m}^{-2}$) (Bowman and Fisk, 2001). Year-long simulated aboveground live biomass ($0\text{--}63.8 \text{ gC m}^{-2}$) was at the low end of Niwot measurements ($60\text{--}117 \text{ gC m}^{-2}$) (Bowman and Fisk, 2001) while belowground live biomass ($425\text{--}515 \text{ gC m}^{-2}$) was in the middle of the measured range ($225\text{--}929 \text{ gC m}^{-2}$) (Bowman and Fisk, 2001). The model's above-to-belowground biomass ratio at the peak of the growing season was about 1:8, while measured above-to-below ground biomass ratios ranged from 1:3.7 to 1:12 (Bowman and Fisk, 2001).

The model did well at estimating N-mineralization and total soil organic matter, but underpredicted total evapotranspiration for tundra (Table 6). Simulated N-mineralization rates ($2.1 \text{ gN m}^{-2} \text{ year}^{-1}$) were very close to those observed

on Niwot Ridge ($\sim 2.0 \text{ gN m}^{-2} \text{ year}^{-1}$) (Bowman, 1992) and soil organic matter (9550 gC m^{-2}) was within the range observed: 6700 gC m^{-2} for dry alpine sedge meadows at Niwot Ridge (Seastedt, 2001) and $13,000 \text{ gC m}^{-2}$ (Conley et al., 2000). Simulated tundra evapotranspiration (ET) (6.1 cm year^{-1}) was about 26% of a previously approximated amount ($23.4 \text{ cm year}^{-1}$), and sublimation ($26.5 \text{ cm year}^{-1}$) was at the low end of the expected range ($26\text{--}88 \text{ cm year}^{-1}$) (Baron and Denning, 1992).

4.3.2. Bedrock/talus

The bedrock/talus simulation represented a variety of rock surfaces with minimal plant production where runoff and evaporation are dominant processes. Simulated discharge from the rock surface ($91.5 \text{ cm year}^{-1}$ (S.D. 18.4)) was higher than simulated tundra discharge ($83.8 \text{ cm year}^{-1}$ (S.D. 13.9)) (Table 6). Average annual simulated ET for bedrock/talus ($11.7 \text{ cm year}^{-1}$) was between two previous approximations. Clow and Mast (1995) estimated that ET from a rock surface is approximately 15% of summer precipitation (or approximately 8 cm year^{-1}), and Baron and Denning (1992) estimated that ET was approximately $17.0 \text{ cm year}^{-1}$. Simulated sublimation for bedrock/talus (15 cm year^{-1}) was below the expected range ($26\text{--}88 \text{ cm year}^{-1}$) (Baron and Denning, 1992).

4.3.3. Forest

Simulated net primary production (NPP) and live biomass for forest were lower than, but close to, measured values (Arthur and Fahey, 1992) (Table 6). Simulated above ground NPP for forest ($111 \text{ gC m}^{-2} \text{ year}^{-1}$) was lower than was measured ($163 \text{ gC m}^{-2} \text{ year}^{-1}$), while total simulated NPP (186 gC m^{-2}) was within the measured range ($136\text{--}340 \text{ gC m}^{-2}$). The range of simulated belowground live biomass ($1170\text{--}1266 \text{ gC m}^{-2}$) included a measured value (1200 gC m^{-2}), while simulated aboveground live biomass ($4270\text{--}4408 \text{ gC m}^{-2}$) was lower than measured (5511 gC m^{-2}).

As with tundra, the model did well at estimating N-mineralization and total soil organic matter but underpredicted total evapotranspiration for forest (Table 6). The simulated N-mineralization rate for forest ($2.1 \text{ gN m}^{-2} \text{ year}^{-1}$) was at the low end of measured values ($2.0\text{--}3.0 \text{ gN m}^{-2} \text{ year}^{-1}$) (Arthur, 1990; Arthur and Fahey, 1992) and soil organic matter (6910 gC m^{-2}) was close to the mean measured value (6800 gC m^{-2}) (Arthur and Fahey, 1992). Simulated forest evapotranspiration (ET) ($27.0 \text{ cm year}^{-1}$) was about 50% of a previously approximated amount ($52.5 \text{ cm year}^{-1}$), while sublimation ($20.8 \text{ cm year}^{-1}$) was also lower than previous estimates ($26\text{--}88 \text{ cm year}^{-1}$) (Baron and Denning, 1992).

4.4. Simulations without biologic calculations

To test model sensitivity to its biological processes, we ran tundra and bedrock/talus simulations that bypassed calculations of SOM decomposition, mineralization, nitrification, denitrification, and plant production. We compared simulated stream chemistry for the tundra simulations with and without biology, and for the combined alpine simulations with and without biology.

Modeled stream NO_3^- , ANC, pH, discharge, and DOC for tundra were sensitive to the model's biological calculations.

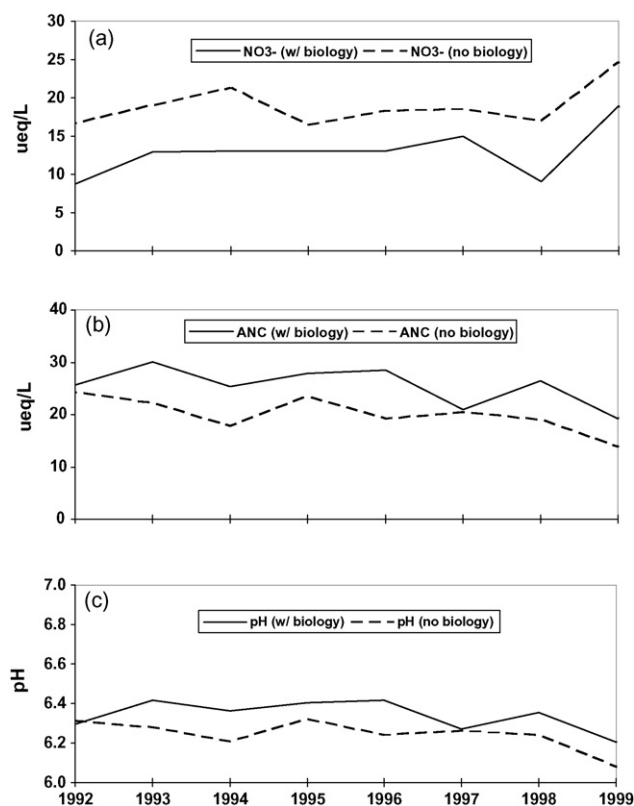


Fig. 5 – Annual volume-weighted mean concentrations for tundra runs with (solid lines) and without (dashed lines) biological calculations: (a) NO_3^- ; (b) ANC; (c) pH.

Results showed that tundra biological processes reduced stream NO_3^- concentrations, and increased stream ANC concentrations, pH, and evapotranspiration. Compared to results for tundra without biology, the tundra run with biology had annual (volume-weighted) mean stream nitrate concentrations that were $3\text{--}8\ \mu\text{eq L}^{-1}$ (average $6\ \mu\text{eq L}^{-1}$) less (Fig. 5a), annual mean ANC concentrations that were up to $10\ \mu\text{eq L}^{-1}$ (average $5\ \mu\text{eq L}^{-1}$) greater (Fig. 5b), annual stream pH that was as much as 0.2 units higher (Fig. 5c), and discharge that was $2\text{--}7\ \text{cm year}^{-1}$ less.

Differences in stream chemistry were less noticeable between the combined runs (11% tundra, 89% bedrock/talus) with and without biology. The combined run without biology had annual mean stream nitrate concentrations that were $0\text{--}3\ \mu\text{eq L}^{-1}$ more, annual mean ANC that was up to $1.4\ \mu\text{eq L}^{-1}$ less, and discharge that was $0.3\text{--}1.0\ \text{cm year}^{-1}$ more, than the combined run with biology. The higher annual mean NO_3^- concentrations for the combined runs without biology were attributed primarily to late summer and early autumn nitrate concentrations that were up to $20\ \mu\text{eq L}^{-1}$ greater than were shown by combined run with biology. Since the combined run with biology overestimated NO_3^- concentrations in the late summer and early fall, runs without biology depart further from observations. The lower annual mean ANC concentrations for the combined run without biology were attributed primarily to the lower late summer and early fall ANC concentrations.

4.5. Soil solution chemistry

Measurements of interstitial solute concentrations were not available for the tundra soils in LVWS, so we compared simulated tundra soil chemistry to soil chemistry data from Niwot Ridge. Soil water pH values from our tundra simulations were comparable to, but generally higher than, some pH measurements at Niwot Ridge. The Inceptisols on Niwot Ridge were moderately acidic, with average pH ranging from 4.7 to 5.0 in moist meadow and about 5.5 in dry meadow (Seastedt, 2001). The simulated volume-weighted mean of soil water pH for the soil profile varied seasonally and ranged from 5.4 to 6.1. Other measurements of soil water pH at Niwot Ridge from June through August (Litaor, 1988) averaged 5.7 and were very close to our simulated volume-weighted mean pH for tundra soils (5.8) for these same months.

Average June through August soil water concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and alkalinity at Niwot Ridge (Litaor, 1988) were much higher than the concentrations that we simu-

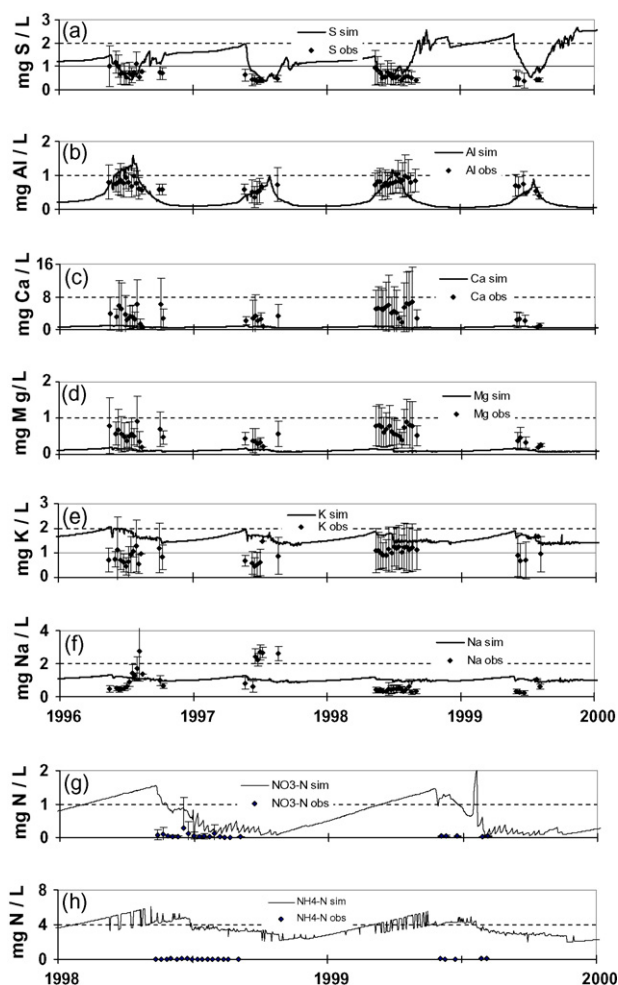


Fig. 6 – Simulated forest soil solution concentrations integrated for the top 20 cm (solid lines), and mean of measured values for the top 15 cm (black dots): (a) S; (b) Al; (c) Ca; (d) Mg; (e) K; (f) Na; (g) $\text{NO}_3\text{-N}$; (h) $\text{NH}_4\text{-N}$. Note graphs for $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ show years 1998–2000, while all the others show 1996–2000. Error bars on measured values show \pm one standard deviation.

lated for the tundra soils. For these same months, measured volume-weighted mean SO_4^{2-} concentrations (Litaor, 1988) were equivalent to those we simulated for tundra ($26 \mu\text{eq L}^{-1}$). Simulated summer NO_3^- concentrations for tundra soils ($14 \mu\text{eq L}^{-1}$) were on average 64% of those measured at Niwot Ridge ($22 \mu\text{eq L}^{-1}$) (Litaor, 1988) that receives greater N deposition (NADP/NTN, 2005), but estimated NO_3^- concentrations were not significantly different from measured concentrations.

Simulated forest soil chemistry compared well to measurements for some constituents. Multiple lysimeter measurements from the top 15 cm of soil of three forest plots were available over a 2–4 year period, approximately once a week from mid May to September (Rueth et al., 2003; Williams et al., in preparation). The average of all lysimeter measurements for each day, along with their standard deviations, were plotted against model results averaged for the top 20 cm of soil (Fig. 6). Simulated S and Al soil solution concentrations were close to measurements most days (Fig. 6a and b). Modeled Ca and Mg concentrations were generally lower than observations, but for many days were within one standard deviation of measurements (Fig. 6c and d). Modeled K and Na concentrations were generally higher than those measured but were within one standard deviation some days (Fig. 6e and f). Simulated NO_3^- -N concentrations were generally higher than measured, but were within one standard deviation some days whereas simulated NH_4 -N concentrations were a magnitude larger than measurements (Fig. 6g and h).

5. Discussion

5.1. Model performance

DayCent-Chem replicated seasonal and annual stream chemistry and discharge for Andrews Creek in years with abundant precipitation. In warm, dry years, especially those after 1997, the simulated discharge was lower than actual discharge and solutes were more concentrated than measured values. The discrepancy appears to have more to do with melting of permanent ice in Loch Vale, a function the model does not perform, than model performance. Streamflow in Andrews Creek is generally 70–80% of measured annual precipitation, with the remainder lost via evapotranspiration and sublimation (Clow et al., 2003). From 1997 to 2001 the measured discharge:precipitation ranged 87–101%, and was 114% in 2003. Summer air temperatures in Loch Vale have been the warmest on record since 1997, so while these were years of low precipitation inputs, they were also years with temperatures high enough to raise the permafrost line and melt ice in rock and ice glaciers and permafrost (Clow et al., 2003).

The 1994 spikes in simulated daily and annual Cl^- stream concentrations (Figs. 3g and 4g) resulted from a suspiciously high concentration (and deposition) of Cl^- in the 11/30/1993–12/7/1993 NADP weekly record. This high input of Cl^- to the model was stored in its snowpack and did not show up in simulated streamflow until the onset of snowmelt in 1994. Simulated annual pH dropped in 1994 (Fig. 4c), reflecting a negative charge imbalance from the high Cl^- concentration (Fig. 4g). We do not know why measured stream chemistry did

not reflect the high Cl^- input that was measured in wet deposition in late 1993.

The simulated discharge spike in late August of simulation year 1994 (Fig. 3a) has been problematic for at least two other hydrologic models applied to LVWS (Hartman et al., 1999; Meixner et al., 2000). The overprediction of this summer rainfall discharge peak has been attributed to either incorrect precipitation measurements as input to the models or insufficient soil zone storage within the models. The high simulated discharge peak simultaneously caused stream ANC to become negative and pH to drop (Fig. 3b and c).

Modeling stream ANC and pH was challenging in part because they were very sensitive to complex silica reactions and to stream $p\text{CO}_2$. While Mast (1992) quantified mineral weathering reactions with incomplete mineral dissolution (i.e. biotite and chlorite to smectite-illite, and oligoclase to kaolinite) it was not possible to describe the stoichiometry of these incomplete reactions to the PHREEQC model. To mimic the incomplete dissolution of silicates, smectite and kaolinite were allowed to precipitate or dissolve (Dave Parkhurst, personal communication). Prescribing the dissolution of amorphous silica was also required. We increased stream $p\text{CO}_2$ above expected ambient $p\text{CO}_2$ at the elevation of Andrews Creek ($10^{-3.68}$ atm) to improve pH estimates. Increasing stream $p\text{CO}_2$ also improved estimates of annual mean SO_4^{2-} , NO_3^- , NH_4^+ , and Si concentrations but elevated simulated stream ANC above observations. Using the AHM model, Meixner et al. (2000) also found that calibrated $p\text{CO}_2$ for Andrews Creek ($10^{-3.4}$ atm) was greater than ambient $p\text{CO}_2$. An analysis of a large number of lakes worldwide showed that boreal, temperate, and tropical lakes were typically supersaturated with CO_2 at concentrations that were often multi-fold greater than atmospheric CO_2 (Cole et al., 1994).

The model did especially well predicting spring and summer sulfate and aluminum soil water concentrations for forests. The simulated summer sulfate concentrations for tundra soil were close to those measured at Niwot Ridge. DayCent-Chem slightly underpredicted base cation concentrations for forest and tundra soils, but this could be due to uncertainties in estimating dry deposition and mineral denudation rates.

Soil and ground water processes are important to describing the stream chemistry of the watershed even though bedrock and talus cover 89% of Andrews Creek. The combined runs produced better results than bedrock-talus simulations alone. The greater water storage capacity of soils and evapotranspiration in tundra tempered the magnitude of daily runoff events, and tundra contributed the primary biological influence on stream chemistry.

5.2. Model comparisons

Different approaches to modeling reflect differences in modeling philosophy, differences in hypotheses being tested, and the anticipated model outcomes. Additionally models have computational and data input requirements. “Quantitative models allow the investigator to observe patterns embedded in the data, to synthesize data on disparate components into an integrated view of ecosystem function, and ultimately to predict the future behavior of some aspects of the ecosystem under given scenarios of future external drivers (Canham et

al., 2003, p. 1).” DayCent-Chem is mechanistically rich and reflects our desire to capture daily biological, biogeochemical, and geochemical responses to changes in nitrogen availability. It was used for the purposes of this paper to observe and synthesize data; we plan to use it predictively in future efforts.

Four other models have been applied to Andrews Creek or Loch Vale. The Alpine Hydrochemical Mode (AHM) and the Regional Hydro-Ecologic Simulation System (RHESSys) were used to observe, synthesize, and predict (Hartman et al., 1999; Baron et al., 2000; Meixner et al., 2000). CENTURY and MAGIC were used to predict future stream chemistry conditions only (Baron et al., 1994; Sullivan et al., 2005). DayCent-Chem differs from these four models. DayCent-Chem includes explicit biogeochemical processes and computationally intensive geochemical calculations, but does not require complex spatial data processing for initialization and analysis and executes on personal computers well under an hour.

AHM, a lumped conceptual model that was designed specifically to represent daily hydrochemistry of alpine watersheds, was used to predict stream chemical response to doubling of N deposition. Nitrogen equations in the model are fitted to measured stream values, and cannot reflect terrestrial nutrient cycling or ecosystem processes below treeline (Meixner et al., 2000). DayCent-Chem and AHM produced very similar results for Andrews Creek, with AHM capturing discharge slightly better, but seasonal change in ANC slightly worse.

RHESSys is a spatial data process and simulation system that computes daily water and carbon budgets of terrestrial ecosystems but does not include geochemical equations. It was applied to Loch Vale, including Andrews Creek, to project changes in watershed hydrology and tundra and forest productivity under climate change (Hartman et al., 1999; Baron et al., 2000). The underlying model structures and data requirements are different than DayCent-Chem, and the purpose completely different, but RHESSys was able to reproduce measured discharge values within 8% of annual flow for 2 years (1993–1994), compared with 14% for DayCent-Chem for those same years (Hartman et al., 1999).

Two monthly models, CENTURY and MAGIC, have been applied to Andrews Creek and/or Loch Vale (Baron et al., 1994; Sullivan et al., 2005). CENTURY, the parent model of DayCent-Chem, was used to ask questions about ecosystem responses to nitrogen deposition (Baron et al., 1994). As with DayCent-Chem, separate forest and tundra landscape units were simulated. Time series comparisons were not made, but forest and tundra ecosystem C and N pools and N mineralization rates were within the range of measured values. For simulation years 1984–1992, DayCent-Chem and CENTURY estimated similar stream N flux for tundra, but DayCent-Chem had higher stream N flux for forest. MAGIC is a lumped parameter model that has been used extensively to predict the long-term effects of acid deposition on stream water chemistry (Cosby et al., 1985). The dynamics of exchangeable base cations in response to strong acid anion inputs drive soil and stream chemistry; and ecological nitrogen cycling is parameterized with first order rate equations. MAGIC was used as a diagnostic tool to evaluate the sensitivity of Andrews Creek to increases in atmospheric strong acid anion deposition, and measured data were used only for calibration (Sullivan et al., 2005). While

it was impossible to compare DayCent-Chem model output to MAGIC model output at this stage, acidification forecasts with DayCent-Chem are forthcoming.

5.3. The importance of including biological processes in atmospheric deposition effects models

Simulated stream chemistry was sensitive to soil organic matter turnover, mineralization, nitrification, denitrification, plant production, and transpiration. Tundra simulations that bypassed these biological calculations showed large increases in annual mean stream NO_3^- , large decreases in annual mean ANC, a slight decrease in annual stream pH, and discharge that was increased because of reduced evapotranspiration. Soil organic matter leaching from tundra provided the only input of DOC to simulated streamflow.

Our comparison of simulations with and without N cycling provides an extreme example of the importance of biological processes, illustrating that even in this Rocky Mountain catchment soils and vegetation influence stream chemistry. Comparisons of DayCent-Chem results for forested catchments with models that take a simpler approach toward N cycling are yet to be made. Those comparisons will yield insight into the role of soils and vegetation in influencing acidification potential from atmospheric deposition. That is an important question of interest to regulatory agencies and resource managers, but it reflects only part of the effects caused by atmospheric deposition. Nitrogen, being an essential nutrient for all living organisms, changes terrestrial ecosystems through eutrophication before acidification occurs. Although the largely unvegetated Andrews Creek basin was not the best place to illustrate how the model represents terrestrial nutrient cycling, DayCent-Chem provides this important information to allow model users and their audiences to evaluate the full spectrum of environmental effects caused by atmospheric deposition.

6. Conclusion

DayCent-Chem, a non-spatial biogeochemical model of intermediate complexity, was able to replicate the seasonal and annual stream chemistry of an alpine catchment, Andrews Creek in Rocky Mountain National Park. The contributions of separate bedrock/talus and tundra simulations were aurally weighted. Simulated stream concentrations of many solutes matched well with observations when the model accurately predicted daily and annual discharge. The model had some difficulty accurately portraying some stream solutes during winter low flow. Parameters that regulated runoff, baseflow, melt, and elution helped to calibrate the model's response to the spatially variable processes.

The model matched spring and summer sulfate and aluminum soil water concentrations for forests, and simulated summer sulfate concentrations for tundra soil. Additionally, model estimates of net primary production, biomass, soil organic matter, and net mineralization rates for alpine tundra and subalpine forest were close to measurements.

Soil and ground water processes are important to describing the stream chemistry of the watershed even though bedrock and talus cover 89% of Andrews Creek. The com-

bined runs produced better results than bedrock-talus or tundra simulations alone. Simulated stream chemistry was sensitive to the model's plant and biological soil processes. Although the tundra simulation contributed only 11% to the combined alpine run, modeling plant and soil processes of tundra improved the model's ability to estimate daily runoff and seasonal stream nitrate concentrations. We expect the importance of including biological processes in the model to increase for simulations of more vegetated systems.

DayCent-Chem is a daily time-step, process-based model that computes a number of biologic and abiotic processes that respond automatically to climate and deposition inputs. The value of this model beyond the application described here will be to test how strongly terrestrial N cycling influences surface water chemistry. Nitrogen cycling processes that are explicitly described by the model, will be important to evaluating potential ecosystem response to alternative scenarios of deposition and climate change.

Acknowledgements

We thank D. Parkhurst for his consultation, and D. Campbell, D. Clow, D. Manthorne, and D. Hultstrand of the U.S. Geological Survey, Loch Vale Water Energy and Biogeochemical Budgets (WEBB) project for data; S. Del Grosso and R. Conant reviewed an earlier version of this manuscript. Funding was provided by the U.S. Environmental Protection Agency Clean Air Markets Division, EPA STAR Grant R829640, National Park Service Air Resource Division, and by the U.S. Geological Survey Western Mountain Initiative.

REFERENCES

- Arthur, M.A., 1990. The Effects of Vegetation on Watershed Biogeochemistry at Loch Vale Watershed, Rocky Mountain National Park, Colorado. Ph.D. Dissertation, Cornell University, Ithaca, NY, 179 pp.
- Arthur, M.A., Fahey, T.J., 1992. Biomass and nutrients in an Englemann spruce—subalpine fir forest in north central Colorado: pools, annual production, and internal cycling. *Can. J. For. Res.* 22, 315–325.
- Arthur, M.A., 1992. Vegetation. In: Baron, J. (Ed.), *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed*. Ecol. Studies, vol. 90. Springer-Verlag, New York, pp. 76–92.
- Appelo, C.A.J., Postma, D., 1993. *Geochemistry, Groundwater and Pollution*. A.A. Balkema, Rotterdam, p. 536.
- Bales, R.C., 1992. Snowmelt and the ionic pulse. In: *The Encyclopedia of Earth Science*, vol. 1. Academic Press, Orlando, FL, pp. 199–207.
- Baron, J., Denning, A.S., 1992. Hydrologic budget estimates. In: Baron, J. (Ed.), *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed*. Ecol. Studies, vol. 90. Springer-Verlag, New York, pp. 28–47.
- Baron, J., Denning, A.S., McLaughlin, P., 1992a. Deposition. In: Baron, J. (Ed.), *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed*. Ecol. Studies, vol. 90. Springer-Verlag, New York, pp. 48–75.
- Baron, J., Walthall, P.M., Mast, M.A., Arthur, M.A., 1992b. Soils. In: Baron, J. (Ed.), *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed*. Ecol. Studies, vol. 90. Springer-Verlag, New York, pp. 108–141.
- Baron, J., Ojima, D.S., Holland, E.A., Parton, W.J., 1994. Nitrogen consumption in high elevation Rocky Mountain tundra and forest and implications for aquatic systems. *Biogeochemistry* 27, 61–82.
- Baron, J.S., Hartman, M., Band, L.E., Lammers, R., 2000. Sensitivity of a high elevation Rocky Mountain watershed to altered climate and CO₂. *Water Resour. Res.* 36, 89–99.
- Baron, J.S. (Ed.), 2002. *Rocky Mountain Futures: An Ecological Perspective*. Island Press, Washington, p. 325.
- Bowman, W.D., 1992. Inputs and storage of nitrogen in winter snowpack in an alpine ecosystem. *Arctic Alpine Res.* 24, 211–215.
- Bowman, W.D., Fisk, M.C., 2001. Primary production. In: Bowman, W.D., Seastedt, T.R. (Eds.), *Structure and Function of an Alpine Ecosystem: Niwot Ridge, Colorado*. Oxford University Press, New York, NY, pp. 177–197.
- Campbell, D.H., Clow, D.W., Ingersoll, G.P., Mast, M.A., Spahr, N.E., Turk, J.T., 1995. Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains. *Water Resour. Res.* 31, 2811–2822.
- Campbell, D.H., Baron, J.S., Tonnessen, K., Brooks, P., Schuster, P., 2000. Controls on nitrogen flux in alpine/subalpine watersheds. *Water Resour. Res.* 36, 37–48.
- Canham, C.D., Cole, J.J., Lauenroth, W.K., 2003. *Models in Ecosystem Science*. Princeton University Press.
- Clow, D.W., 1992. *Weathering Rates from Field and Laboratory Experiments on Naturally Weathered Soils*. University of Wyoming, Laramie, Ph.D. Dissertation, 116 pp.
- Clow, D.W., Mast, M.A., 1995. Composition of precipitation, bulk deposition, and runoff at a granitic bedrock catchment in the Loch Vale Watershed, Colorado, USA, in Tonnessen, K.A., Williams, M.W., Tranter, M., eds., *Biogeochemistry of seasonally snow-covered catchments*, Boulder, Colorado, International Association of Hydrological Sciences, p. 235–242.
- Clow, D.W., Mast, M.A., Bullen, T.D., Turk, J.T., 1997. ⁸⁷Sr/⁸⁶Sr as a tracer of mineral weathering reactions and calcium sources in an alpine/subalpine watershed, Loch Vale, Colorado. *Water Resour. Res.* 33, 1335–1351.
- Clow, D.W., Sueker, J.K., 2000. Relations between basin characteristics and stream-water chemistry in alpine/subalpine basins in Rocky Mountain National Park, Colorado. *Water Resour. Res.* 36, 49–62.
- Clow, D.W., Schrott, L., Webb, R., Campbell, D.H., Torizzo, A., Dornblaser, M., 2003. Ground Water Occurrence and Contributions to Streamflow in an Alpine Catchment, Colorado Front Range. *Ground Water* 41, 937–950.
- Cole, J.J., Caraco, N.F., Kling, G.W., Kratz, T.K., 1994. Carbon dioxide supersaturation in surface waters of lakes. *Science* 265, 1568–1570.
- Conley, A.H., Holland, E.A., Seastedt, T.R., Parton, W.J., 2000. Simulation of carbon and nitrogen cycling in an Alpine Tundra. *Arct. Antarct. Alp. Res.* 32, 147–154.
- Cosby, B.J., Hornberger, G.M., Galloway, J.N., Wright, B.F., 1985. Modeling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resour. Res.* 21, 51–63.
- Cosby, B.J., Ferrier, R.C., Jenkins, A., Wright, R.F., 2001. Modeling the effects of acid deposition: refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model. *Hydrol. Earth Syst. Sci.* 5, 499–517.
- Daly, C., Gibson, W.P., Taylor, G.H., Johnson, G.L., Pasteris, P., 2002. A knowledge-based approach to the statistical mapping of climate. *Climate Res.* 22, 99–113.
- Del Grosso, S.J., Parton, W.J., Mosier, A.R., Hartman, M.D., Brenner, J., Ojima, D.S., Schimel, D.S., 2001. Simulated interaction of carbon dynamics and nitrogen trace gas fluxes using the DAYCENT model. In: Shaffer, M.J., Ma, L., Hansen, S. (Eds.), *Modeling Carbon and Nitrogen Dynamics for Soil*

- Management. Lewis Publishers, Boca Raton, Florida, pp. 303–332.
- Drever, J.I., 1982. *The Geochemistry of Natural Waters*. Prentice-Hall, Inc., Englewood Cliffs, NJ, p. 388.
- Driscoll, C.T., Lehtinen, M.D., Sullivan, T.J., 1994. Modeling the acid–base chemistry of organic solutes in Adirondack, New York, lakes. *Water Resour. Res.* 30, 297–306.
- Galloway, J.N., Keene, W.C., Likens, G.E., 1996. Processes controlling the composition of precipitation at a remote southern hemispheric location: Torres del Paine National Park, Chile. *J. Geophys. Res.* 101, 6883–6897.
- Gbondo-Tugbawa, S.S., Driscoll, C.T., Aber, J.D., Likens, G.E., 2001. Evaluation of an integrated biogeochemical model (PnET-BGC) at a northern hardwood forest. *Water Resour. Res.* 37, 1057–1070.
- Hartman, M.D., Baron, J.S., Lammers, R.B., Cline, D., Band, L.E., Liston, G.L., Tague, C., 1999. Simulations of snow distribution and hydrology in a mountain basin. *Water Resour. Res.* 35, 1587–1603.
- Janssen, P.H.M., Heuberger, P.S.C., 1995. Calibration of process-oriented models. *Ecol. Mod.* 83, 55–66.
- Johnson, D.W., Swank, W.T., Vose, J.M., 1993. Simulated effects of atmospheric sulfur deposition on nutrient cycling in a mixed deciduous forest. *Biogeochemistry* 23, 169–196.
- Kelly, R.H., Parton, W.J., Hartman, M.D., Stretch, L.K., Ojima, D.S., Schimel, D.S., 2000. Intra- and interannual variability of ecosystem processes in shortgrass steppe. *J. Geophys. Res.* 105 (D15), 20093–20100.
- Kickert, R.N., Tonella, G., Simonov, A., Krupa, S.V., 1999. Predictive modeling of effects under global change. *Environ. Pollut.* 100, 87–132.
- Lindsay, W.L., 2001. *Chemical Equilibria in Soils*. The Blackburn Press, Caldwell, NJ, p. 449.
- Litaor, M.I., 1988. Soil solution chemistry in an alpine watershed, Front Range, Colorado, USA. *Arctic Alpine Res.* 20, 485–491.
- Mast, M.A., Drever, J.I., Baron, J., 1990. Chemical weathering in The Loch Vale Watershed, Rocky Mountain National Park, Colorado. *Water Resour. Res.* 26, 2871–2978.
- Mast, M.A., 1992. Geochemical characteristics. In: Baron, J. (Ed.), *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed*. *Ecol. Studies*, vol. 90. Springer-Verlag, New York, pp. 93–107.
- Matson, P., Lohse, K.A., Hall, S.J., 2002. The globalization of nitrogen deposition: consequences for terrestrial ecosystems. *Ambio* 31, 113–119.
- Meixner, T., Bales, R.C., Williams, M.W., Campbell, D.H., Baron, J.S., 2000. Stream chemistry modeling of two watersheds in the Front Range, Colorado. *Water Resour. Res.* 36, 77–88.
- Mohren, G.M.J., van de Veen, J.R., 1995. Forest growth in relation to site conditions: application of the model FORGRO to the Solling spruce site. *Ecol. Model.* 83, 173–183.
- Nash, J.E., Sutcliffe, J.V., 1970. River flow forecasting through conceptual models, I. A discussion of principles. *J. Hydrol.* 10, 282–290.
- National Atmospheric Deposition Program/National Trends Network (NADP/NTN), 2005. Illinois State Water Survey, Urbana, IL. <http://nadp.sws.uiuc.edu/>.
- Parkhurst, D.L., Appelo, C.A.J., 1999. User's Guide to PHREEQC (Version 2)—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations, U.S. Geological Survey Water-Resources Investigations Report 99-4259, Denver, CO, 312 pp.
- Parton, W.J., Schimel, D.S., Cole, C.V., Ojima, D.S., 1987. Analysis of factors controlling soil organic matter levels in Great Plains grasslands. *Soil Sci. Soc. Am. J.* 51, 1173–1179.
- Parton, W.J., Schimel, D.S., Ojima, D.S., Cole, C.V., 1994. A general model for soil organic matter dynamics: sensitivity to litter chemistry, texture and management. In: Bryant, R.B., Arnold, R.W. (Eds.), *Quantitative Modeling of Soil Forming Processes*. Soil Science Society of America, Madison, WI, pp. 147–167.
- Parton, W.J., Hartman, M., Ojima, D., Schimel, D., 1998. DAYCENT and its land surface submodel: description and testing. *Global Planet. Change* 19, 35–48.
- Rueth, H.M., Baron, J.S., Allstott, E.J., 2003. Responses of old-growth Engelmann spruce forests to nitrogen fertilization. *Ecol. Appl.* 13, 664–673.
- Seastedt, T.R., 2001. Soils. In: Bowman, W.D., Seastedt, T.R. (Eds.), *Structure and Function of an Alpine Ecosystem: Niwot Ridge, Colorado*. Oxford University Press, New York, NY, pp. 157–173.
- Sullivan, T.J., Cosby, B.J., Tonnessen, K.A., Clow, D.W., 2005. Surface water acidification responses and critical loads of sulfur and nitrogen deposition in Loch Vale watershed, Colorado. *Water Resour. Res.* 41, W01021, doi:10.1029/2004WR003414.
- Tiktak, A., van Grinsven, H.J.M., 1995. Review of sixteen forest–soil–atmosphere models. *Ecol. Model.* 83, 35–53.
- van Heerden, K., van Grinsven, H.J.M., Tiktak, A., 1995. Simulation of forest stress for the Solling spruce site with SOILVEG. *Ecol. Model.* 83, 185–195.
- Walthall, P.M., 1985. *Acidic Deposition and the Soil Environment of Loch Vale Watershed in Rocky Mountain National Park*. Ph.D. Dissertation. Colorado State University, Fort Collins, CO, 148 pp.
- Williams, K.E., Baron, J.S., Advani, S., Rueth, H.M., Krcmarik, A., Geick, S., Botte, J. Interaction of nitrogen and base cations in subalpine forest soils east and west of the continental divide in Colorado's Rocky Mountains, in preparation, for submission to *Biogeochemistry*.
- Williams, M.W., Melack, J.M., 1991. Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada. *Water Resour. Res.* 27, 1575–1588.
- Williams, M.W., Caine, N., 2001. Hydrology and hydrochemistry. In: Bowman, W.D., Seastedt, T.R. (Eds.), *Structure and Function of an Alpine Ecosystem: Niwot Ridge, Colorado*. Oxford University Press, New York, NY, pp. 75–96.
- Wolford, R.A., Bales, R.C., Sorooshian, S., 1996. Development of a hydrochemical model for seasonally snow-covered alpine watersheds: application to Emerald Lake Watershed, Sierra Nevada, California. *Water Resour. Res.* 25, 829–837.