

Modeling the Timeline for Acidification from Excess Nitrogen Deposition for Rocky Mountain National Park

Annual Report, 2003

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1. Introduction

Nitrogen wet deposition of 3-5 kg N/ ha to the east side of the Colorado Front Range in Rocky Mountain National Park (ROMO), in the form of nitrate and ammonium, is among the highest measured in the State. Precipitation pH values are more acidic than is natural (NADP 2000, Baron et al. 2000). Stream chemical records from the Green Lakes south of Rocky Mountain National Park suggest acidification of headwaters during spring snowmelt (Williams and Tonnessen 2000), and we have documented ecological changes from N in aquatic and terrestrial ecosystems (Baron et al. 2000).

Excess N deposition will cause lake and stream acidification in a process similar to that caused by sulfate deposition, with an important difference. Soils control the potential for lake and stream acidification, through loss of soil base cations. Base cations, such as calcium and magnesium, leach from soils with acid anions such as sulfate and nitrate. But because nitrogen is a critical plant nutrient, any realistic projection of nitrogen-caused acidification must include understanding ecosystem nutrient cycling. The objectives of this project are to model how and when acidification will occur under current and potential future nitrogen deposition amounts. We expect to be able to answer the question: How much N deposition is necessary to depress soil base saturation and cause surface waters to acidify?

Our task for the first year of this project (**Phase I** June 2002 to December 31, 2003) was to develop and parameterize DAYCENT and PHREEQC for Icy Brook, Andrews Creek,

and Loch Vale. We describe below our progress in model development and application. We took two widely accepted and tested models, one of ecosystem biogeochemistry (the daily version of CENTURY) and the other of soil and water chemical equilibrium (PHREEQC), and coupled them. The model is being tested against a rich data set available from Loch Vale Watershed that includes wet deposition, meteorology, forest biomass and nutrient ratios, soil microbial activity, soil and soil solution chemistry, stream discharge, and stream chemistry for a 20-year period.

2. Model Descriptions

The point model used for our simulations is a coupled DayCent 5/PHREEQC implementation with an additional geochemical submodel that provides communication between DayCent 5 and PHREEQC models.

The purpose of creating the linked DayCent 5/PHREEQC model was to couple the biogeochemical calculations of DayCent with the geochemical soil solution calculations of the PHREEQC model. With regard to nitrogen, we hoped to increase understanding of how N-deposition amounts affect biological assimilation, soil organic matter composition, change in alkalinity and acid neutralization capacity of surface waters, pH changes, aluminum mobilization, base cation depletion, and base cation flux.

2.1 Description of DayCent 5 Model

Version 5 of the daily Century model (DayCent 5), is a point model that evolved from DayCent 4 (Parton et al., 1998; Kelly et al., 2000; Del Grosso et al., 2001a) and has coevolved with version 5 of the monthly Century (Century 5) soil organic matter model (<http://www.nrel.colostate.edu/projects/century5/reference/index.htm>). Both Century 5 and DayCent 5 represent a major change in the technical aspects of the model implementation, and include new algorithms and structures for the physical soil, erosion, deposition, and depth distribution of organic C. Century 5 and DayCent 5 also include the current cumulative set of bug fixes to their algorithms, easier and quicker access to simulation results, and improved numerical stability and error checking. DayCent 5 and Century 5 have an object oriented architecture, implemented in C++, that provides a common code base for the monthly and daily versions.

DayCent 5 can track the cycling of organic and inorganic C, N, P, and S in forest, grassland, cropland, and savanna systems. Aspects of C, N, P, and S cycling include atmospheric deposition, fertilization, soil organic matter decomposition, leaching thru the soil and release to stream flow, plant uptake and production, symbiotic fixation, litterfall, and biomass removal by harvest, grazing, or fire. DayCent 5 also computes evapotranspiration from plants and soil, and sublimation of the snowpack. For each of up to ten soil layers defined for the site, DayCent 5 calculates daily water flux in and out of a layer, daily soil minimum and maximum temperatures, and daily nitrogen trace gas fluxes.

DayCent 5 implements a layered soil structure and algorithms to manage soil layers (Hilinski, 2001). Soil algorithms include calculations for soil properties and pools across layers (whole or fractional layers.) A site can begin with an initial soil organic layer depth (usually 20cm) and with up to ten soil layers, each layer having a unique initial thickness, texture, bulk density, and water content. In addition, the bulk density and thickness of the soil layers comprising the organic layer depth are adjusted with changes in organic C. Soil algorithms also include erosion, deposition, homogenization and division of layers. During the course of a simulation, the number of layers can be reduced to as few as one, through erosion, or increased to any number of layers, through deposition. Erosion pool amounts can optionally be saved in an erosion output file. Eroded pools can become deposited material in the simulation for an adjacent site. The soil erosion and deposition capabilities of DayCent 5 were not used for the simulations described in this paper, and the number of soil layers remained constant throughout each simulation, although the depth of the organic layer may have changed with soil organic matter addition or removal.

Century 5 and DayCent 5 provide a new algorithm for estimating total organic C in the soil profile. Soil organic C is distributed over depth in the physical soil according to an exponential density distribution of organic C, which decreases with depth.

DayCent 5 requires daily input of precipitation, and minimum and maximum air temperatures. DayCent 5 flux and state variables are summarized in both monthly and daily output files that are written in ASCII CSV (comma separated variable) format to allow direct importation into spreadsheet programs. DayCent also outputs a “site file” that contains values for all important state variables that can be used as an initialization “site file” for subsequent runs, thus providing restart capability.

2.2 Description of PHREEQC Model

PHREEQC version 2 is a computer program written in the C programming language that is designed to perform a wide variety of low-temperature aqueous geochemical calculations. PHREEQC is based on an ion-association aqueous model and has capabilities for (1) speciation and saturation-index calculations; (2) batch-reaction and one-dimensional (1D) transport calculations involving reversible reactions, which include aqueous, mineral, gas, solid-solution, surface-complexation, and ion-exchange equilibria, and irreversible reactions, which include specified mole transfers of reactants, kinetically controlled reactions, mixing of solutions, and temperature changes; and (3) inverse modeling, which finds sets of mineral and gas mole transfers that account for differences in composition between waters, within specified compositional uncertainty limits model (Parkhurst and Appelo 1999).

Version 2.7 of the PHREEQC was used in the coupled model. The types of geochemical reactions we utilized include speciation, ion-exchange equilibria, fixed-pressure gas-phase equilibria, dissolving and precipitating phases to achieve equilibrium, and irreversible aqueous mineral phase reactions. No surface-complexation or kinetically

controlled reactions have yet been defined for our simulations, but may be included in future simulations.

2.3 Description of linked model

2.3.1 Description of linked model and its data flow (Figure 1)

DayCent 5 tracks the cycling of ammonium (NH_4^+), nitrate (NO_3^-), inorganic P, inorganic S (assumed to be SO_4^{2-}), and organic C, N, P, and S. DayCent's processes include atmospheric deposition, fertilization, soil organic matter decomposition, mineralization, symbiotic fixation, plant and microbial assimilation, nitrogen trace gas production, and inorganic and organic leaching. A new geochemical submodel was developed for DayCent to track the cycling and state of additional pools and properties in the soil and water such as base cations, alkalinity species, metals, pH, and soil cation exchange capacity. Like DayCent, the geochemical submodel incorporates wet deposition data and leaches its constituents through the soil. DayCent's geochemical model also provides a the communication mechanism between DayCent 5 and PHREEQC and other processes that are not part of either model, including elution of constituents from the snowpack. Biologically mediated production or release of base cations and alkalinity species is not simulated.

The geochemical submodel contains layered soil pools and properties, and maintains the same number of layers as DayCent's soil model so that there is a one-to-one correspondence between the geochemical model's soil layers and DayCent 5's soil layers. The geochemical submodel tracks pH, and the fate of Al, HCO_3^- , CO_3^{2-} , Ca^{2+} , Cl^- , Fe^{2+} , Fe^{3+} , K^+ , Mg^{2+} , Mn^{2+} , Mn^{3+} , Na^+ , and SiO_2 into and through the soil layers and into streamflow. It also tracks species-specific cation exchange capacities (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) in each soil layer. It accesses, from DayCent's soil class, the quantities of dissolved organic C, N, P, S and inorganic N, P, S in each soil layer and the quantities of these elements released to stream flow. The geochemical submodel communicates with DayCent's soil class, but it otherwise operates independently of DayCent. The geochemical submodel only requires an interface to a soil class that will provide it with necessary information such as soil moisture and soil texture.

Figure 1 shows the flow of water and its constituents in the coupled model. Prior to simulation, the user must provide several types of inputs in addition to those required by the DayCent 5: (1) Daily atmospheric deposition amounts for each constituent and property of precipitation (Ca^{2+} , Cl^- , K^+ , Mg^{2+} , Na^+ , NH_4^+ , NO_3^- , SO_4^{2-} , and pH), (2) Initial snow pack amount and concentrations are required for same species in that are in precipitation. (3) Initial soil solution concentrations of dissolved soil species in each soil layer (Al, CO_3^{2-} , Ca^{2+} , Cl^- , Fe^{2+} , Fe^{3+} , HCO_3^- , K^+ , Mg^{2+} , Mn^{2+} , Mn^{3+} , Na^+ , and SiO_2), (4) Initial species-specific cation exchange capacity in each soil layer (number of moles of CaX_2 , MgX_2 , NaX , KX , NH_4X , HX , FeX_2 , MnX_2 , AlX_3 , AlOHX_2), and (5) potential annual denudation rates for each mineral phase that has potential to be dissolved in the soil solution.

Each daily simulation of the linked model begins with DayCent's computations with a few additions. For one, DayCent does not have the ability to store atmospherically deposited constituents in the snow pack for release as the snow melts. The geochemical model currently has a simple elution model, releasing constituents in proportion to the amount of snow melt. Further updates to this linked model will include a more realistic preferential elution model. After DayCent 5 computed the soil water fluxes between layers, and the leaching of C, N, P, and S, the geochemical submodel computes the leaching of its constituents. Next geochemical submodel prepares to call the PHREEQC model.

PHREEQC was unaltered for this linkage except to change the main program into a function that can be called by DayCent's geochemical submodel. For each daily simulation, DayCent's geochemical submodel writes the state of the solutions and cation exchangers within each soil layer, the deep water storage below the soil profile (aquifer), and the outflow (runoff plus water exiting the deep water storage) to an ASCII PHREEQC input file, soln.pqi. When there are n soil layers, there are up to $n+2$ solutions defined in soln.pqi, plus a SELECTED_OUTPUT block that specifies the information PHREEQC will output. After PHREEQC performs its equilibrium calculation for each solution in soln.pqi, it writes its results to a "selected output file", soln.sel, an ASCII text file in spreadsheet format. The geochemical submodel parses soln.sel, and uses these values to update its soil properties and pools. (DayCent's Soil nitrate, ammonium, P, and S pools are NOT updated after PHREEQC executes. Only the geochemical submodel's pools are updated).

The user has the option of concatenating the content of all daily .pqi files into one large .pqi file to record all solutions that DayCent generated during a simulation. Similarly, the user has an option to concatenate the content of all daily selected output files that PHREEQC generates during the simulation. Both the daily .pqi file and the simulation .pqi file can be used as input to any PHREEQC executable (version 2.7 or higher).

Relying on ASCII files to transfer information between DayCent and PHREEQC slows execution when compared to reading/writing directly to/from PHREEQC's data structures. The benefit is that any updates in the PHREEQC model can be incorporated with little effort, there is less chance of introducing programming error, and all exchanges of information can be easily recorded for future scrutiny and to aid debugging.

DayCent 5 writes a number of output files that include daily values for soil water content by layer, soil temperature by layer, trace gas emissions, water fluxes, plant production, and plant and soil respiration. DayCent 5 also writes a number of files that include monthly values for C,N,P,S in soil organic matter pools, soil N,P,S mineral pools by layer, and plant C,N,P,S amounts. In addition to DayCent 5's output files, the linked model creates a number of geochemical output files that include daily stream chemistry, daily soil layer composition and solution chemistry, a report summarizing monthly and annual import and export totals and VWM concentrations of all constituents, and a final soil composition file (in the same format as the initial soil composition file (so that a

subsequent geochemical simulation can be initialized with the preceding simulation's state).

2.3.2 Biogeochemical model processes description (Figure 2)

Plant, soil, and stream processes simulated by the linked model are summarized in Figure 2, with DayCent's processes to the left of the diagram, and PHREEQC's soil and stream water reactions on the right side.

Plant dynamics. The linked model simulates plant dynamics for forest, crop, grass, and savanna systems. Carbon is dynamically allocated to above and below ground plant parts according to nutrient availability, water stress, and plant type. Plants take up mineral N,P,S from soil as needed to maintain carbon:element ratios in the range specified for the plant. Nitrogen is translocated to plant storage at certain times in the growing season. Dead above ground plant material is dropped onto the soil surface, and along with dead root biomass, is incorporated into soil organic matter.

Soil dynamics. Soil organic matter is incorporated into the soil through litter fall and death of roots. Soil organic matter is decomposed by soil microbes, redistributing among active, passive, and recalcitrant soil organic pools. Mineralization by soil microbes produces nitrate, ammonium, and inorganic P and S. Water containing inorganic species enters the soil thru rainfall and snowmelt. Water flowing downward through the soil leaches organic C, N, P, and S, along with a number of inorganic constituents. Nitrification and denitrification reactions release N_2O and NO_x . Soil water reaches equilibrium with CO_2 produced by heterotrophic and root respiration. Dissolution of primary and secondary minerals, such as calcite, pyrite, feldspars, and clays, consume and release base cations, aluminum hydroxides, bicarbonate, metallic cations, hydrogen ions, silica, sulfate, and other inorganic species into soil solution. Cations in solution are absorbed and desorbed from permanent negatively exchange sites (X^-). Water exiting the soil profile enters a deep storage layer (aquifer); a user-specified fraction of this deep water storage is released to stream flow each day. Geochemical reactions in the deep storage layer include only aqueous reactions and not cation exchange and mineral dissolution. The water in deep storage is in equilibrium with ground water CO_2 . Dissolved organic carbon and nitrogen (DOC and DON) react with other species in soil solution, but at the time of this writing, the specific reactions have not been defined.

Stream dynamics

The fraction of precipitation and snow melt that does not infiltrate the soil surface carries dissolved inorganic species to stream flow. Water exiting the soil profile or deep storage layer carries leached organic and inorganic species that are also added to stream flow. The CO_2 dissolved in soil solution degasses as it encounters the lower partial pressure of

the atmosphere. Geochemical reactions in stream flow include the same aqueous reactions defined for soils, except cation exchange and mineral dissolution.

3.0 Methods

We simulated three representative sites in Loch Vale Watershed: forest, tundra, and rock. Tables 1a-1c summarize their soil and vegetation characteristics. Wet meadows/bogs have not yet been simulated. All runs used the same weather file. Weather in LVWS is recorded at the lower elevations in the watershed, adjacent to the forest. Weather for tundra and rock may be adjusted in future simulations to reflect cooler temperatures and lower effective precipitation for these higher elevation sites that are scoured by wind.

The forest covers a 40-hectare area in the lowest elevations of LVWS. It is composed of spruce and fir trees. Forests contain the deepest, most developed soils in the watershed.

The tundra covers a 70-hectare area in the highest elevations of LVWS. It has moderately deep soils with perennial vegetation.

Rock covers a 500+ hectare area of LVWS. It includes solid granite and gneiss, and talus slopes, with a small amount of perennial vegetation.

Spinup runs. The forest, tundra, and rock simulations each began with a 165-year DayCent spinup run (without geochemical calculations) to equilibrate soil organic matter pools with plant production. The weather used to drive the spinup runs was measured LVWS precipitation and air temperatures from 1985-1999, repeated in eleven 15-year cycles. The state of the model at the end of each spinup run was saved for the subsequent geochemical run. Annual nitrogen deposition rates were prescribed at $0.30 \text{ gN m}^{-2}\text{yr}^{-1}$. DayCent simulated only C and N; we did not set up DayCent to simulate P and S.

Geochemical runs. Runs that include the geochemical calculations (Figure 2) for each of the three sites were simulated for years 1985-1999. Each site used the same daily wet deposition amounts; these were derived from weekly NADP deposition concentrations. Annual nitrogen deposition rates averaged $0.285 \text{ gN m}^{-2}\text{yr}^{-1}$. The source of P and S in the geochemical runs was precipitation and mineral dissolution. P and S were leached through the soil without plant or microbial uptake or release.

Descriptions of N-deposition Scenarios

No nitrogen deposition scenarios have been simulated yet.

4.0 Results

Preliminary results are presented below. Note that they are first runs without any tuning to fit the data. We expect improvements to occur rapidly now that the model runs and produces reasonable output.

4.1 Annual summary (Table 2)

Simulated forest NPP is in the expected range of around 200 gC/m²/yr, although below ground live carbon is underestimated for tundra (Table 2a). Soil Organic Matter (SOM) is underestimated, while N-mineralization is overestimated for tundra (Table 2b). In the simulations, increasing below ground production in tundra tends to increase SOM, but also increases N-mineralization. The annual average outflow per m² for tundra and rock is likely too high, since it is greater than the watershed average annual output (Table 2c). Sublimation is underestimated for tundra and rock, and evapotranspiration (ET) rates are underestimated for forest and tundra (Table 2c).

The range of concentrations of soil solution Ca, Mg, K, Na, NO₃-N, NH₄-N, Fe, and Si simulated in the 10-20cm forest layer were compared to measured concentrations at 15 cm (Table 2d). The simulated maximum concentrations for all these species except NH₄-N were underestimated at this simulation depth. Simulated forest soil solution concentrations of Ca, Mg, and Fe above 10cm tend to be higher (results not shown), indicating that leaching intensity may need to be increased, or that *in situ* mineral dissolution in this layer may need to be increased. Leaching intensity of NO₃-N appears to be too great (results not shown).

4.2 Forest and Tundra soils (Figures 3, 4)

Figures 3 and 4 show the daily dynamics of forest and tundra soil cation exchange capacities (CECs) and soil solution pH. (See [anreportgraphs.ppt for clearer images](#)). Similar graphs for the rock simulation are not presented since rock was not initialized with any cation exchange capacity. All soil CECs at the start of the geochemical runs were initialized from measured CECs in Loch Vale. Generally stable amounts of CaX₂ in all soil layers are simulated for both forest and tundra, though we'd like to improve the stability of CaX₂ in the top soil layers over the 15-year simulation period. AlOHX₂ is more seasonally dynamic, with peak AlOHX₂ amounts in the summer. Simulated soil solution pH for forest and tundra is in the range of what is expected, except for the second soil layer (layer [1]) which is too acidic in both forest and tundra simulations. For these runs, we simulated the dissolution of minerals in the top layer only, but it appears that mineral dissolution needs to be simulated in other soil layers also.

4.3 Forest, tundra, and rock discharge (Figure 5)

The onset of melt in the forest simulations and in the observed flow is generally consistent. Simulated forest outflow shows more response to rain events than observed watershed outflow. The observed outflow shows a recession curve that is due to

staggered contributions of melt from higher elevations of the watershed. We expect the per-square-meter outflow from the forest (in the lowest elevations of the watershed) to peak higher and earlier than the watershed average outflow. Note that the forest outflow graphed in Figure 5 is centimeters of water over 5% of the watershed; one centimeter of outflow from the 40-ha forest is equivalent in volume to 0.06 centimeter of outflow from the 660-ha watershed.

Currently there is little sulfate export in the forest simulation. Concentrations of sulfate from tundra and rock streamflow are in the range (0.0 - 1.6 mg/L) whereas measured watershed sulfate concentrations are (0.5 – 3.0 mg/L). For all three site simulations, PHREEQC calculations lead to a net consumption of sulfate (total exports were less than precipitation inputs) despite simulating the dissolution of pyrite.

5.0 Discussion

To mimic total watershed response, separate representative sites within a watershed need to be simulated and their results combined. The contribution of each site to total discharge quantity and quality can be weighted by the percentage of the watershed occupied by each area represented, and maybe other factors. We have done this successfully before in a previous modeling exercise (Baron et al. 1994).

The stoichiometry of mineral dissolution described by Mast et al. (1990) differs from reactions defined in the current PHREEQC data base file (phreeqc.dat). For example, dissolving 29 (moles ha⁻¹ year⁻¹) biotite, 7 chlorite, 99 feldspar, 18 kaolinite, 6 pyrite, and 106 calcite yields

167 moles SiO₂ (Mast), 443 moles SiO₂ (phreeqc.dat)
56 moles Fe (Mast), 6 moles (phreeqc.dat)
304 moles HCO₃⁻ (Mast), 106 moles HCO₃⁻ (phreeqc.dat)
-82 moles H⁺ (Mast), -512 moles H⁺ (phreeqc.dat)

This may partially explain the higher than expected concentrations of SiO₂ in simulated stream discharge, the lower than expected concentrations of Fe in simulated stream discharge (results not shown).

A summary of future model development that may lead to more realistic results can be found in the next section.

6.0 What's next: Plans for development of the DayCent 5/PHREEQC

- More realistic preferential elution function for release of constituents from the snowpack. Currently, constituents are released in proportion to melt.
- More realistic calculation of daily potential mineral dissolution rates. Currently a potential annual rate (per m²) is defined, and the daily potential rate (per m²) is the annual potential rate divided by 365. In addition, we need to determine where mineral dissolution actually takes place in the soil profile and simulate that more

- realistically. For simplicity we simulated mineral dissolution in the top soil layer and relied on leaching to bring weathering products to lower layers.
- Estimate the amount and composition of dry deposition in LVWS and add a method of incorporating dry deposition data into the model.
 - Update PHREEQC database file (phreeqc.dat):
 - Add reactions for DOC.
 - Develop alternative mineral dissolution reactions for albite, anorthite, kaolinite, and biotite to use for LVWS simulations. The stoichiometry of these dissolution reactions as defined by the default PHREEQC database is somewhat different than those defined by Mast et al. 1990). The largest discrepancies are in the yields of SiO_2 , Fe, HCO_3^- , and consumption of H^+ . Dissolution of oligoclase in Loch Vale (73% Na and 27% Ca) was mimicked with a proportionate dissolution of albite (Na-feldspar) and anorthite (Ca-feldspar).
 - Is an improved leaching function needed for H, Ca, Mg, Na, K, HCO_3^- , CO_3 , Al, Fe, Mn, Cl, etc? Currently all aqueous species leach in proportion to the amount of water draining out of a soil layer. If water moves upward (i.e. evaporation from a layer or difference in potential), solution species do not move upward. In other words, only pure water can move upward in soil.
 - Simulated alkalinity values in the streamflow of all 3 sites are lower than measured streamflow alkalinity for the watershed (What are the expected soil alkalinity values?).
 - Sulfate export for all 3 simulated sites is too low.
 - There may be too much nitrate leaching from soils in DayCent.
 - Look at simulated conductivity values.
 - Look at simulated Eh values.

Research Questions:

- What happens to total base cation saturation over the simulation period with observed N-deposition rates?
- The default PHREEQC database did not have reaction for H^+ absorption/desorption with the exchanger. Why not? For the reaction we added, do we have the correct “log_k” and “delta_h” values?
- What is the NH_4X effect at high ionic concentrations?
- The default PHREEQC database did not have reaction for biotite dissolution. Why not? For the reaction we added, do we have the correct “log k” and “delta h” values?
- What are the sources of alkalinity in LVWS? What are their relative contributions?
- What are the PHREEQC reactions leading to sulfate consumption in forest, tundra, and rock?
- Do we need soil and surface equilibrium with other gases besides CO_2 (such as O_2)?

Work Plan:

August - December 2003:

1. Match observed and simulated surface water chemistry for Loch Vale
2. Create and run N-deposition scenarios for Loch Vale
3. Write paper about the results of the above runs

January-April 2004

1. Develop GUI for DayCent/PHREEQC model
 - a. Options are extending CMI (V-library) or extending Mark Easter's Century interface (Visual Basic) or starting from scratch with Visual Basic.
 - b. Take a Visual Basic Class from Continuing Ed.

May 2004-??

1. Run other LTER site simulations with model
2. Plan for workshop

Individual Simulations for Loch Vale Watershed

(See p. 228, LVWS book)

Terrestrial 99% of 660ha = 653.4 ha

Surface water 1% of watershed (use 6 ha)

Forest: 5% of terrestrial (use 40 ha)

Tundra: 11% of terrestrial (use 70 ha)

Meadows 1% of terrestrial (use 6 ha)

Rock/Talus 82% of terrestrial (use 538 ha)

Table 1a. Forests

Soils: Forest soils (Cryoboralf)

Percent of watershed: 5% of terrestrial (use 40ha)

Percent of contribution to daily stream flow: ?

Location: Valley Floor below Timberline Falls,

Description: ?

Parent material: Granite and gneiss

Parent material source: Glacial Till

Slope: 9%, convex

Topography: Moraine veneer

Organic layer depth: 10 cm

Initial organic layer pH: 4.84

Vegetation: Fir, spruce

Soil depth: 55 cm

Number of soil layers: 5

Number of soil layers available to plants: 5

Other notes: Base saturation < 35%, argillic horizons. Most acidic soils in LVWS: 1) mature weathering state, 2) regular supplies of organic matter from coniferous litterfall, 3) gentle topography results in increased residence time and effective subsoil leaching. Leaching has exhausted calcite supply. Receives N from precipitation (3.25 kg/ha/yr) as well as runoff from bedrock (3.15 kg/ha/yr).

Forest soil layers

Soil 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 stony loamy sand

Forest soil initial soil layer properties:

Soil	pH	Sand	Silt	Clay	Organic	Bulk	Field	Wilting
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Layer					Carbon	Density (g/cm ³)	Capacity	Point
0	4.84	10.0%	85.0%	5.0%	13.1%	0.79	0.49	0.18
1	4.84	10.0%	85.0%	5.0%	13.1%	0.79	0.48	0.17
2	3.78	10.0%	70.5%	19.5%	2.7%	1.14	0.45	0.24
3	3.72	10.0%	61.7%	28.3%	2.5%	1.30	0.44	0.27
4	3.74	10.0%	73.8%	16.2%	1.3%	1.50	0.38	0.22

Forest soil initial cation exchange capacities

Soil Layer	CaX2 (meq/100g)	MgX2 (meq/100g)	KX (meq/100g)	NaX (meq/100g)	AlX3 (meq/100g)	FeX2 (meq/100g)	HX (meq/100g)	MnX2 (meq/100g)	NH4X (meq/100g)
0	18.4	3.2	0.9	0.1	10.5	0	1.8	0	0
1	18.4	3.2	0.9	0.1	10.5	0	1.8	0	0
2	5.0	1.0	0.4	0.1	18.9	0	1.0	0	0
3	3.6	0.8	0.2	0.1	25.2	0	0.7	0	0
4	2.6	0.6	0.1	0.1	16.2	0	0.4	0	0

Table 1b: Tundra

Soils: Alpine ridge soils (Cryochrepts, [Cryohemists])

Percent of watershed: 11% of terrestrial (use 70ha)

Percent of contribution to daily stream flow: Soils may be physically disjunct from valley floor, separated by sheer cliffs, steep slopes, or snow fields. **Is there a contribution to LVWS outlet streamflow?**

Location: Thatchtop Mountain and the ridge above Andrews Creek, with smaller areas above treeline in Sky Pond/Glass Lake basin.

Description: Cryochrepts: Shallow and stony, NE face of the ridge and in saddles

Parent Material: Granite and gneiss

Parent material source: Boulder field

Slope: 7%, concave

Topography: Saddle position on alpine ridge

Organic layer depth: 2 cm

Initial organic layer pH: 5.0

Vegetation: Forbs, [sedges, lichen]

Soil depth: 25 cm

Number of soil layers: 3

Number of soil layers available to plants: 3

Other notes: Effective precipitation much less than actual due to intense wind that causes evaporation, sublimation, or physical removal. Receives N from precipitation (3.25 kg/ha/yr) as well as runoff from bedrock (2.86 kg/ha/yr). The alpine tundra is a permanent sink to N, N is stored in plant tissue and soil organic matter, but gaseous losses are believed to be low (Baron, 1992, p. 229).

Alpine soil layers

Soil Layer	Thickness (cm)	Depths (cm)	Description
0	2	0 - 2	Oe: moderately decomposed organic matter
1	3	2 - 5	A: cobbly sandy loam
2	20	5 - 25	Bw: cobbly sandy loam BC

Alpine initial soil layer properties:

Soil Layer	PH	Sand	Silt	Clay	Organic Carbon	Bulk Density (g/cm ³)	Field Capacity	Wilting Point
0	5.0	10.0%	83.0%	7.0%	11.6%	0.70	0.60	0.28
1	4.95	10.0%	80.5%	9.5%	2.8%	0.70	0.57	0.26
2	4.66	10.0%	77.4%	12.6% 6.1%	0.9% 0.2%	0.75	0.51	0.21

Alpine soil initial cation exchange capacities

Soil Layer	CaX2 (meq/100g)	MgX2 (meq/100g)	KX (meq/100g)	NaX (meq/100g)	AlX3 (meq/100g)	FeX2 (meq/100g)	HX (meq/100g)	MnX2 (meq/100g)	NH4X (meq/100g)
0	36.6	7.2	0.9	0.1	1.5	0	0.5	0	0
1	13.0	3.0	0.2	0.1	5.1	0	0.5	0	0
2	4.8 1.4	2.2 0.2	0.1 0.1	0.1 0.1	12.6 6.9	0 0	0.2 0.6	0 0	0 0

Table 1c. Rock

Soils: Talus/Rock

Percent of watershed: 82% of terrestrial (use 538ha)

Percent of contribution to daily stream flow: ?

Location: Mostly upper-mid elevations of the watershed.

Description: Steep cliffs and talus slopes

Parent material: granite and gneiss

Parent material source: ?

Slope: ?

Topography: ?

Organic layer depth: 1 or 2 cm.

Initial organic layer pH: 6.0

Vegetation: sparse

Soil depth: 2 cm

Number of soil layers: 1

Number of soil layers available to plants: 1

Other notes: Does significant nitrification or denitrification occurs here? These soils reflect a more active physical weathering environment in which calcite from microveins of bedrock is more frequently exposed. Dry deposition inputs may be important.

Rock soil layers

Soil Layer	Thickness (cm)	Depths (cm)	Description
0	0	0 - 2	Coarse texture with high bulk density

Rock initial soil layer properties:

Soil Layer	pH	Sand	Silt	Clay	Organic Carbon	Bulk Density (g/cm ³)	Field Capacity	Wilting Point
0	6.0	50%	25%	25%	0.0%	1.75	0.25	0.22

Rock initial cation exchange capacities

Soil Layer	CaX2 (meq/100g)	MgX2 (meq/100g)	KX (meq/100g)	NaX (meq/100g)	AlX3 (meq/100g)	FeX2 (meq/100g)	HX (meq/100g)	MnX2 (meq/100g)	NH4X (meq/100g)
0	0	0	0	0	0	0	0	0	0

Table 1d. Wet meadows/bogs

Soils: Alluvial/Bog Soils (Cryoquent)

Percent of watershed: 1% of terrestrial (use 6ha)

Percent of contribution to daily stream flow: ?

Location: adjacent to streams

Description: highly organic

Parent material: forbs, sedges

Parent material source: organics, stream sediment

Slope: 1%, plane

Topography: hummocky bog

Organic layer depth: 33 cm

Initial organic layer pH: ?

Vegetation: forbs

Soil depth: 43 cm

Number of soil layers: 5

Number of soil layers available to plants: 2

Other notes: Greyed C horizon, evidence of a highly reduced environment.

Wet meadow soil layers

Soil Layer	Thickness (cm)	Depths (cm)	Description
0	4	0 - 4	Oi: slightly decomposed
1	11	4 - 15	Oe1: decomposed
2	10	15 - 25	Oe2: decomposed
3	8	25 - 33	Oa: highly decomposed
4	10	33 - 43	Cg: loam

Wet meadow initial soil layer properties:

Soil Layer	pH	Sand	Silt	Clay	Organic Carbon	Bulk Density (g/cm ³)	Field Capacity	Wilting Point
0	3.83				16.8%			
1	3.96				22.1%			
2	4.12				22.1%			
3	4.30				17.0%			
4	4.36			17%	3.0%			

Wet meadow soil initial cation exchange capacities

Soil Layer	CaX2 (meq/100g)	MgX2 (meq/100g)	KX (meq/100g)	NaX (meq/100g)	AlX3 (meq/100g)	FeX2 (meq/100g)	HX (meq/100g)	MnX2 (meq/100g)	NH4X (meq/100g)
0	6.6	1.6	0.6	0.3	21.6	0	1.7	0	0
1	3.2	0.4	0.2	0.1	20.4	0	1.1	0	0
2	3.2	0.4	0.2	0.1	20.4	0	1.1	0	0
3	5.6	0.6	0.1	0.1	14.1	0	0.9	0	0
4	5.4	1.2	0.1	0.1	9.3	0	0.7	0	0

Sources and Sinks of each constituent of interest:

Constituent	Sources (in order of importance)	Sinks (in order of importance)	Obs. Ratio Export/Import (1984-1988)	Comments
PH	precipitation, pyrite dissolution	$H^+ + HCO_3^- = H_2CO_3$	0.06	precipitation pH is at least 1.0 units less than outflow pH. Most H ⁺ consumed by weathering and exchange processes.
Ca ²⁺	calcite dissolution, precipitation, oligoclase -> kaolinite	biotite -> smectite-illite (minor)	3.46	
Mg ²⁺	biotite -> smectite-illite, chlorite -> smectite-illite, precipitation,		3.41	
Na ⁺	oligoclase -> kaolinite, precipitation,		2.63	
K ⁺	biotite -> smectite-illite, precipitation,	chlorite -> smectite-illite (minor)	3.88	

Cl ⁻	precipitation,	none	0.74?	
NH ₄ ⁺	precipitation,	microbial and plant uptake	0.14	Net consumption of NH ₄
NO ₃ ⁻	precipitation,	microbial and plant uptake	0.86	Net consumption of NO ₃
SO ₄ ²⁻	precipitation, pyrite oxidation,		1.08	
SiO ₂	oligoclase -> kaolinite, kaolinite -> Al(OH) ₃	biotite -> smectite-illite, chlorite -> smectite-illite (minor)	100% exports	
Alkalinity (HCO ₃ ⁻)	calcite dissolution, oligoclase -> kaolinite, biotite -> smectite-illite, chlorite -> smectite-illite, oligoclase -> kaolinite	H ⁺ + HCO ₃ ⁻ = H ₂ CO ₃ , nitrogen assimilation		
DOC/DON	organic leaching			

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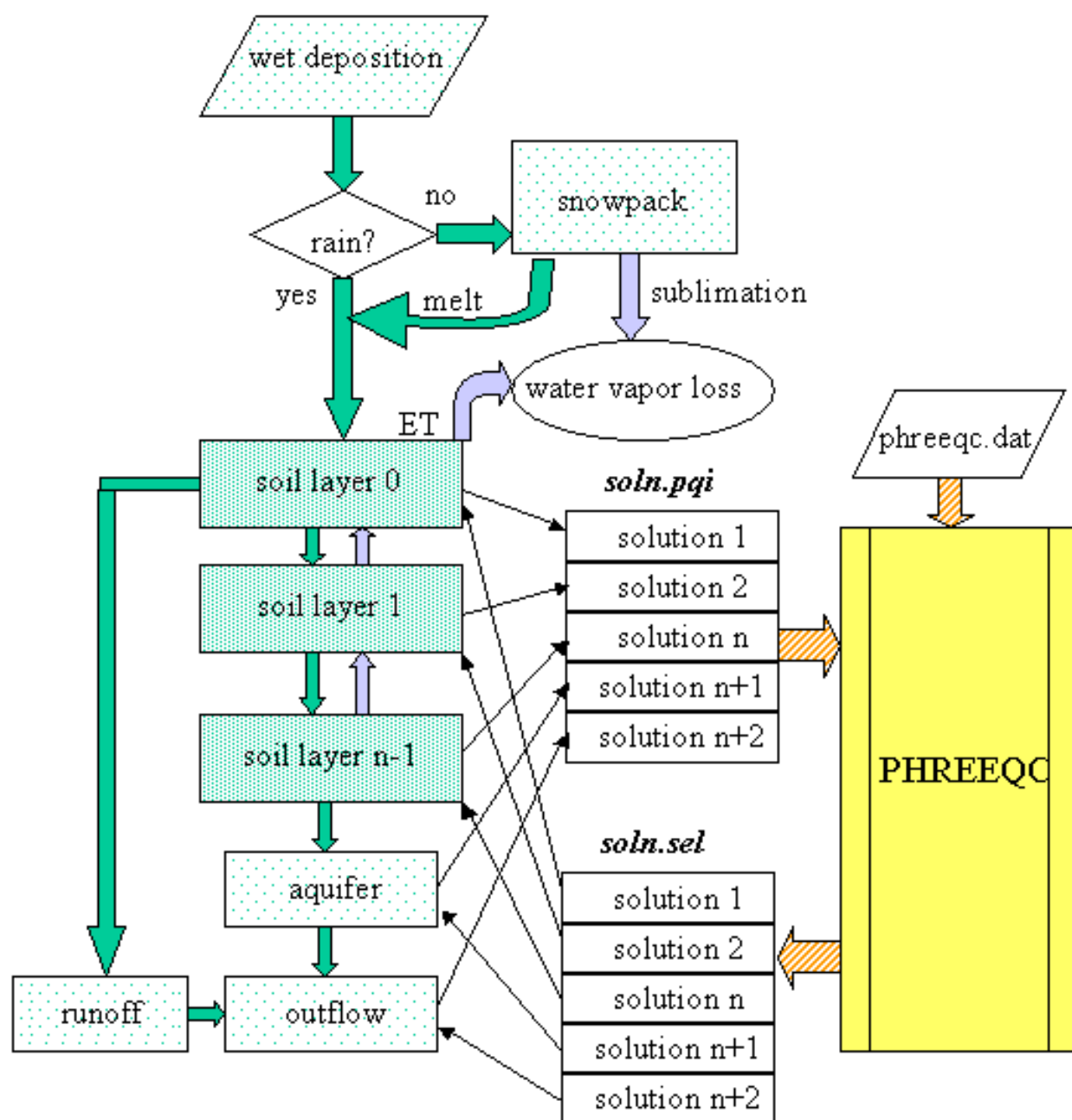
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Coupled DayCent 5 / PHREEQC model

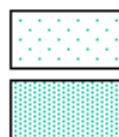
Flow of Data



KEY

→ H₂O + species

→ H₂O only



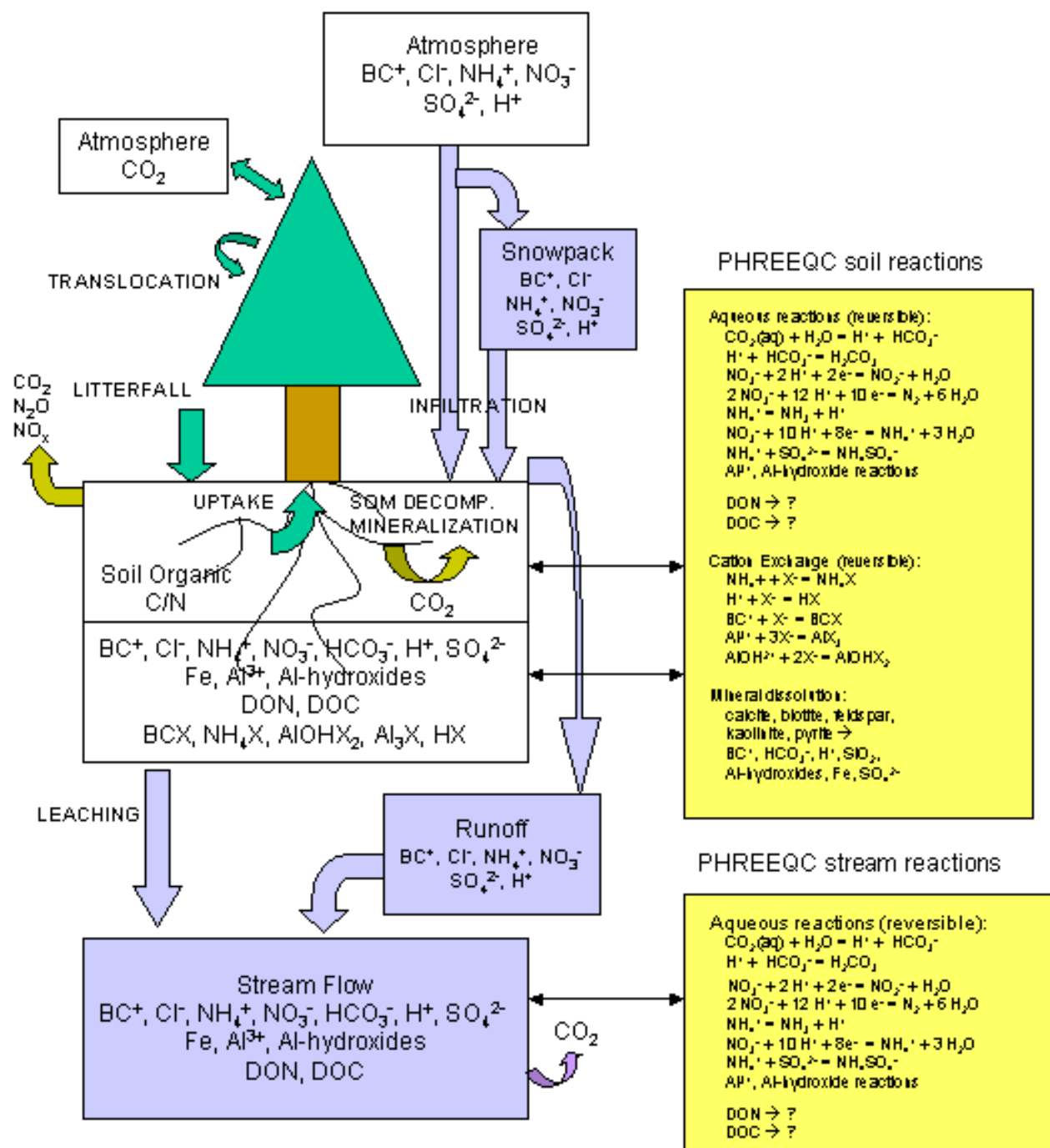
aqueous species only

aqueous species + exchanger

Coupled DayCent 5 / PHREEQC model

Carbon/Nitrogen Processes

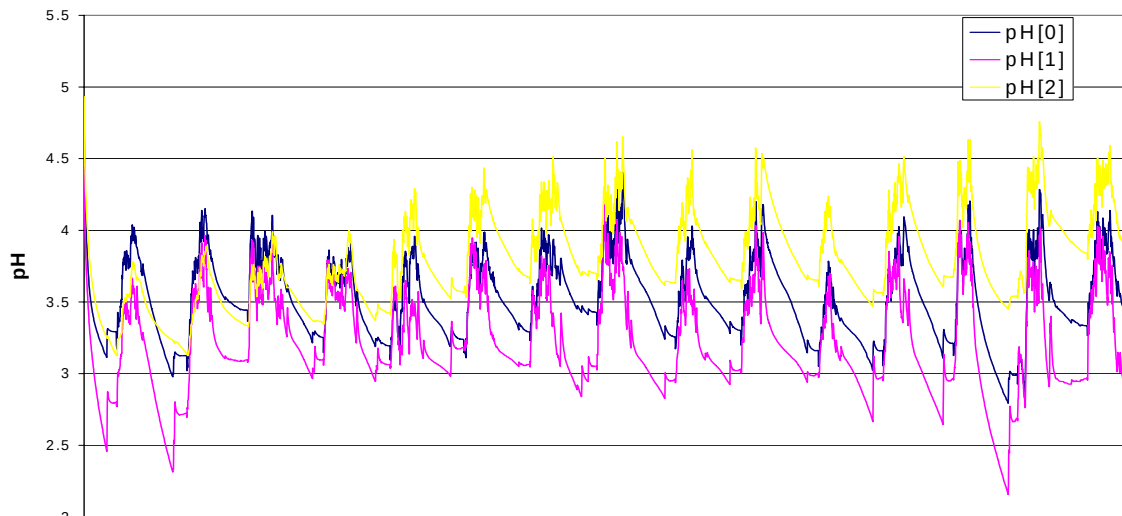
Base Cation, Acid, Alkalinity, Aluminum Reactions



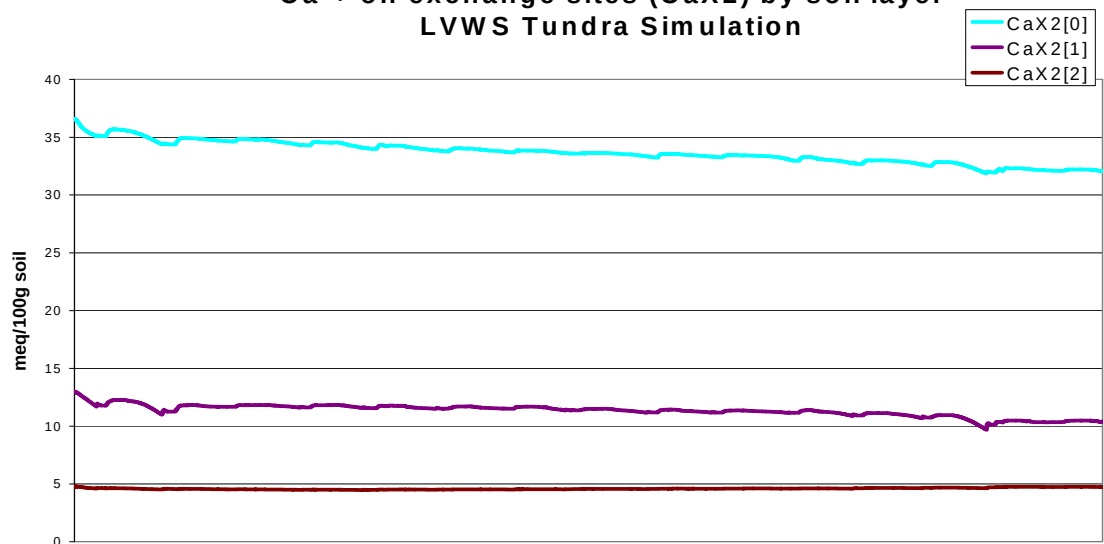
*Complete cycles of Sulfur and Phosphorus not shown
 BC^+ represents monovalent and divalent base cations
 X^- represents permanent cation exchange site

DOC/DON = dissolved organic C/N
 SOM = Soil Organic Matter

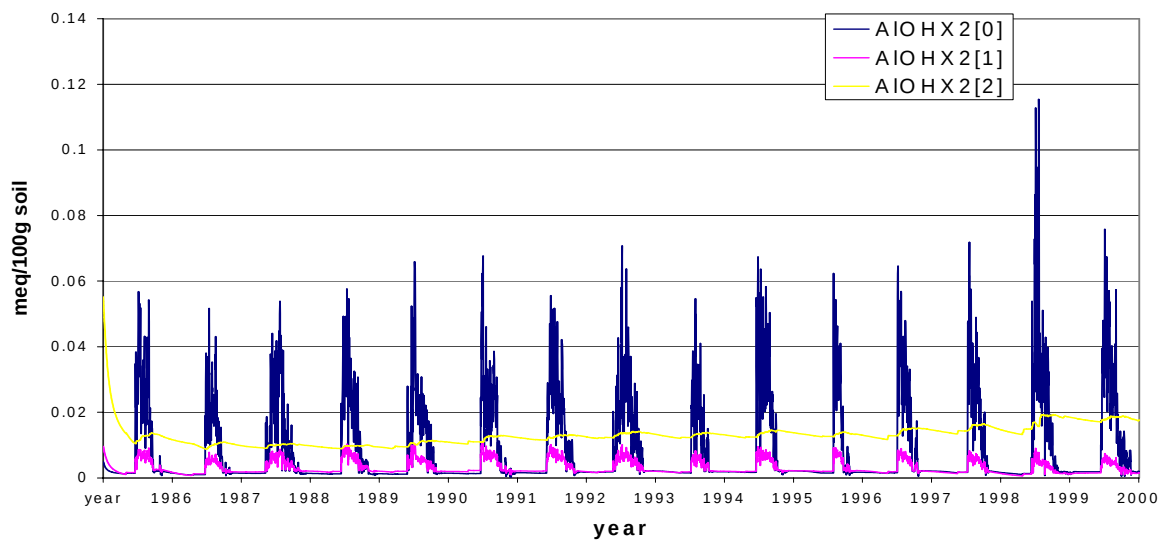
pH in soil solution by layer - LVWS Tundra Simulation



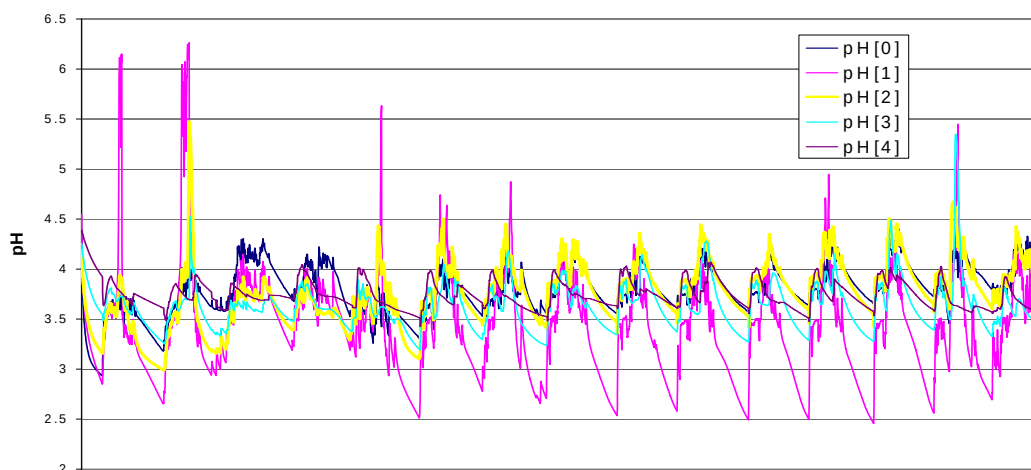
Ca²⁺ on exchange sites (CaX2) by soil layer LVWS Tundra Simulation



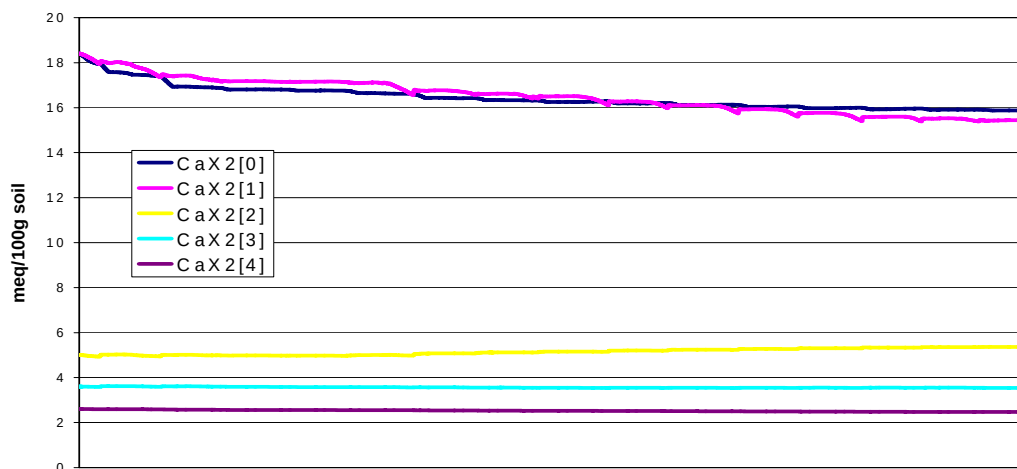
AlOH²⁺ on exchange sites (AlOHX2) by soil layer - LVWS Tundra Simulation



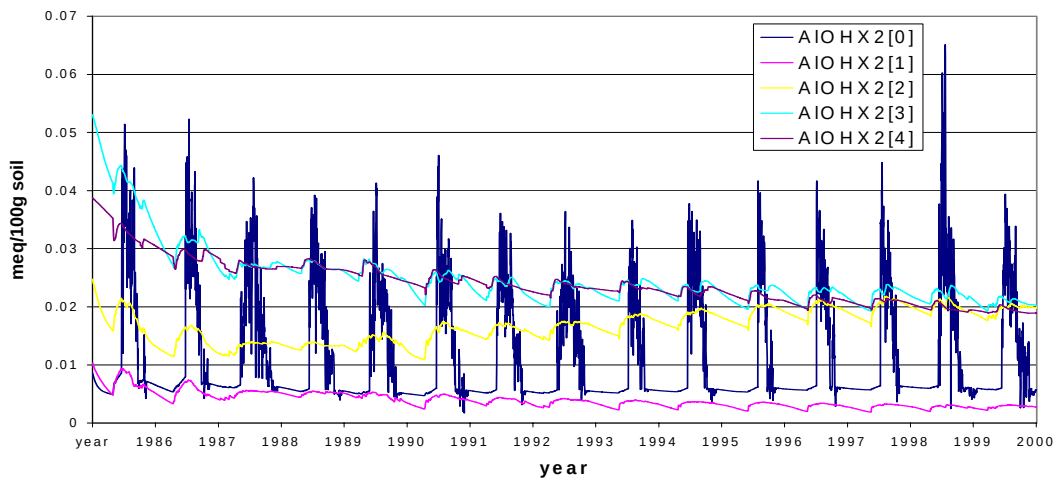
pH in soil solution by layer - LVWS Forest Simulation



Ca²⁺ on exchange sites (CaX2) by soil layer - LVWS Forest Simulation



**AlOH²⁺ on exchange sites (AlOHX2) by soil layer
LVWS Forest Simulation**



Outflow from LVWS Forest Simulation and Observed Outflow from Loch Outlet

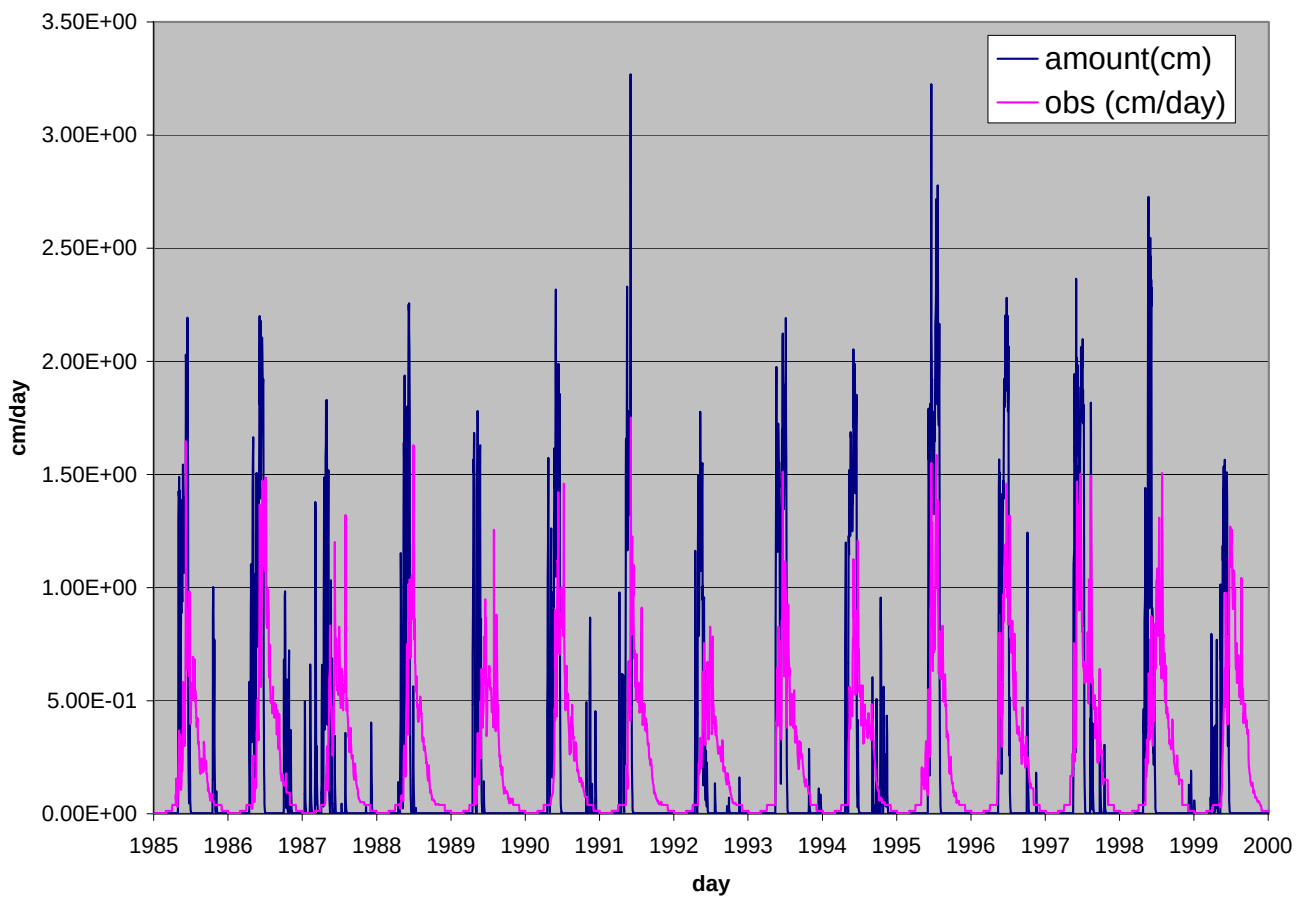


Figure 5

Table 2. LVWS simulated and observed annual averages (1985-1999)

	Table 2a. Simulated and observed above and below ground NPP							
	simulated NPP (above) (gC/m2/yr)	simulated NPP (below) (gC/m2/yr)	NPP (total) (gC/m2/yr)	simulated below ground live carbon (gC/m2)	NPP (above) (gC/m2/yr)	observed NPP (below) (gC/m2/yr)	NPP (total) (gC/m2/yr)	observed below ground live carbon (gC/m2)
Forest	152.30	70.38	222.67	1300.00			200 ^a	
Tundra	51.06	287.01	338.07	450.00	43 - 135 ^a			2250 - 4200 ^a
Rock	1.21	0.62	1.83	0.40				

	Table 2b. Simulated and observed N-mineralization and soil organic matter carbon			
	simulated net N mineralization (gN/m2/yr)	observed net N mineralization (gN/m2/yr)	simulated total soil organic matter carbon (gC/m2)	observed total soil organic matter carbon (gC/m2)
Forest	2.34	0.14 - 5.0 ^a	4651.31	4500 - 7500 ^a
Tundra	6.67	~2.0 ^a	8524.52	13,500 - 39,600 ^a
Rock	0.07		18.65	

	Table 2c. Simulated and observed outflow, ET, and sublimation					
	simulated site 1985-1999 outflow (cm/yr)	observed 1985-1999 LVWS outflow (cm/yr)	simulated 1985-1999 ET (cm/yr)	estimated 1984-1989 ET (cm/yr)^b	simulated 1985-1999 sublimation (cm/yr)	estimated 1984-1988 LVWS sublimation (cm/yr)^b
Forest	69.51	80.69	27.86	52.50	10.61	26 - 88
Tundra	90.38	80.69	6.46	23.40	10.61	26 - 88
Rock	93.49	80.69	3.46		10.61	26 - 88

	Table 2d. May - September simulated and observed forest soil water concentrations at 15 cm					
	1996-1999 simulated range (mg/L)	1996-1999 observed range (mg/L)	5/17-10/10, 1996 observed range (mg/L)	5/22-8/20, 1997 observed range (mg/L)	5/13-9/2, 1998 observed range (mg/L)	6/2-8/4, 1999 observed range (mg/L)
Ca	0.04 - 10.26	0.21 - 30.38	0.21 - 20.71	0.40 - 22.06	0.21 - 30.38	0.27 - 6.33
Mg	0.01 - 2.00	0.09 - 2.47	0.10 - 2.46	0.09 - 1.66	0.14 - 2.47	0.15 - 1.08
K	0.24 - 4.32	0.03 - 4.40	0.04 - 4.40	0.03 - 2.52	0.09 - 3.42	0.07 - 2.38
Na	0.03 - 0.58	0.09 - 5.45	0.23 - 5.45	0.17 - 3.59	0.09 - 1.77	0.09 - 1.06
NO3-N	0.025 - 0.576	0.008 - 3.307			0.008 - 3.307	0.032 - 0.114
NH4-N	0.225 - 3.23	0.002 - 0.202			0.002 - 0.202	0.032 - 0.173
Fe	0.0 - 0.02	0.02 - 4.79	0.07 - 2.77	0.02 - 4.79	0.06 - 2.03	0.06 - 0.92
Si	0.13 - 4.31	0.20 - 17.59	0.51 - 17.59	0.20 - 8.73	0.86 - 9.10	0.92 - 4.06