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The application of an integrated biogeochemical model (PnET-BGC) to five forested watersheds in the Adirondack and Catskill regions of New York

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Abstract:

PnET-BGC is an integrated biogeochemical model formulated to simulate the response of soil and surface waters in northern forest ecosystems to changes in atmospheric deposition and land disturbances. In this study, the model was applied to five intensive study sites in the Adirondack and Catskill regions of New York. Four were in the Adirondacks: Constable Pond, an acid-sensitive watershed; Arbutus Pond, a relatively insensitive watershed; West Pond, an acid-sensitive watershed with extensive wetland coverage; and Willy's Pond, an acid-sensitive watershed with a mature forest. The fifth was Catskills: Biscuit Brook, an acid-sensitive watershed. Results indicated model-simulated surface water chemistry generally agreed with the measured data at all five sites. Model-simulated internal fluxes of major elements at the Arbutus watershed compared well with previously published measured values. In addition, based on the simulated fluxes, element and acid neutralizing capacity (ANC) budgets were developed for each site. Sulphur budgets at each site indicated little retention of inputs of sulphur. The sites also showed considerable variability in retention of NO_3^-. Land-disturbance history and in-lake processes were found to be important in regulating the output of NO_3^- via surface waters. Deposition inputs of base cations were generally similar at these sites. Various rates of base cation outputs reflected differences in rates of base cation supply at these sites. Atmospheric deposition was found to be the largest source of acidity, and cation exchange, mineral weathering and in-lake processes served as sources of ANC.

KEY WORDS acidic deposition; modelling; Adirondacks; Catskills; acid neutralizing capacity

INTRODUCTION

Over the past several decades, acidic deposition has altered the structure and function of sensitive forest and aquatic ecosystems across North America, Europe and Asia (Visser, 1995; Driscoll *et al.*, 2001). Acidic deposition has accelerated the leaching of available plant nutrient cations (i.e. Ca^{2+}, Mg^{2+}, K^+) and enhanced dissolution of potentially toxic aluminium from soil. Deposition of strong acids to base-poor soils also resulted in decreases in surface water pH and acid neutralizing capacity (ANC) and increases in surface water concentrations of inorganic monomeric aluminium.

The Adirondack and Catskill regions of New York receive among the highest rates of sulphur and nitrogen deposition in the USA (Driscoll *et al.*, 1991; Stoddard and Murdoch, 1991). Large numbers of surface waters in these two regions are acidic (ANC < 0 μeq l^{-1}). Although these regions experience high levels of acidic deposition, surface waters draining watersheds show considerable variability in acid–base status,

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resulting from differences in acidic deposition, soil characteristics, bedrock geology, vegetation composition, hydrologic flow paths and land use/disturbance history. The response of ecosystems in these two regions to changes in atmospheric deposition is of considerable interest. In this study, an integrated biogeochemical model (PnET-BGC) was used to investigate the element cycling and ANC generation/consumption processes at five intensive study sites from these regions with contrasting patterns of acid–base chemistry. These sites include: (1) Constable Pond, an acid-sensitive watershed (ANC ≈ -8 μeq l^{-1}); (2) Arbutus Lake, a relatively insensitive watershed (ANC ≈ 67 μeq l^{-1}); (3) West Pond, a watershed with elevated concentrations of dissolved organic carbon (DOC) (DOC ≈ 625 μmol l^{-1}, ANC ≈ 0 μeq l^{-1}); (4) Willy's Pond, a watershed within a mature forest (ANC ≈ -10 μeq l^{-1}); and (5) Biscuit Brook, an acid-sensitive watershed (ANC $=$ 20 μeq l^{-1}). Differences across these sites in acidic deposition, soil characteristics, surficial geology and land disturbance history enabled us to examine the roles of these factors in regulating element cycling and acid–base status of soil and surface waters. The application of the model to these diverse sites also enabled further evaluation of the performance of PnET-BGC.

METHODS

Model description

The PnET-BGC model was expanded from PnET-CN (Aber and Federer, 1992; Aber *et al*., 1996, 1997) to include cycling of major elements (e.g. Ca, Mg, K, Na, S, P) through biogeochemical processes. These processes include atmospheric deposition, canopy interaction, hydrology, soil organic matter dynamics, mineral weathering, chemical reactions involving solid and solution phases, and surface water processes (Gbondo-Tugbawa *et al*., 2001). The model operates on a monthly time step and is applied at the stand to small-watershed scales. The model uses the Gaines–Thomas formulation (White and Zelanzy, 1986) to describe cation exchange reactions within the soil. The exchangeable cations considered in the model include Ca^{2+}, Mg^{2+}, Na^{+}, H^{+}, Al^{3+}, K^{+} and NH_4^{+}. A pH-dependent adsorption isotherm is used to describe the SO_4^{2-} adsorption process. The speciation of monomeric aluminium is calculated in the model, including both organic and inorganic forms. Organic acids are described using a triprotic analogue (H_3Org; Driscoll *et al*., 1994) and total amount of organic acids is estimated as a certain fraction (site density) of DOC. The model simulates ANC in surface waters as an analogue to ANC measurement by Gran plot analysis, by considering the contributions of dissolved inorganic carbon (DIC), organic anions and aluminium complexes (Driscoll *et al*., 1994).

Internal lakes processes (e.g. algal uptake and denitrification) can remove large quantities of NO_3^{-} in lakes with relatively long hydraulic retention times (Kelly *et al*., 1987; Mitchell *et al*., 2001a). To simulate the in-lake removal of NO_3^{-}, a simple formulation developed by Kelly *et al*. (1987) was used:

$$R_N = \frac{S_N}{(\overline{Z}/\tau_W) + S_N}$$

where R_N is the NO_3^{-} removal coefficient, $\overline{Z}$ (m) is the mean depth of lake, τ_W (years) is the water residence time and S_N (m year^{-1}) is the mass transfer coefficient for NO_3^{-}. In the study by Kelly *et al*. (1987), S_N averaged at 9·2 m year^{-1} for eight lakes with detectable summer NO_3^{-}. Thus, this value was used in the model simulations. PnET-BGC has been tested against vegetation, soil and water chemistry data from the Hubbard Brook Experiment Forest (HBEF; Gbondo-Tugbawa *et al*., 2001) and has also been used to evaluate the effects of current and future atmospheric deposition scenarios (Gbondo-Tugbawa and Driscoll, 2002). A more detailed description of the model, including a detailed uncertainty analysis of parameter values, is available in Gbondo-Tugbawa *et al*. (2001).

Site description

The locations of the five study sites in New York State are shown in Figure 1.

Figure 1. Locations of the five sites in New York State at which PnET-BGC was applied in this study

Adirondack sites. The Adirondack region of New York is a large forested area (2 400 000 ha) with about 2800 lakes (>2000 m^2 surface area) and many streams (Driscoll *et al.*, 1991). The area receives high rates of acidic deposition (wet SO_4^{2-} deposition of ~8 kg ha^{-1} $year^{-1}$ (as sulphur); wet NO_3^- deposition of ~5 kg ha^{-1} $year^{-1}$ (as nitrogen)) with a spatial pattern of decreasing deposition from the southwest to northeast (Driscoll *et al.*, 1991; Ito *et al.*, 2002). About 27% of the lakes in the region were found to be acidic (ANC < 0 μeq l^{-1}; Driscoll *et al.*, 1998). Bedrock materials of the region are primarily gneisses and metasedimentary rocks. Soils are typically Spodosols derived from glacial till. Vegetation of the region is dominated by northern hardwoods (50%), with some amount of conifers (10%) and mixed forests (25%). Wetlands occupy about 5% of the vegetative cover types and are generally found at lower elevations. Many areas of the region have undergone cutting, and/or experienced catastrophic blowdowns, severe fires and various pests (Driscoll *et al.*, 1991).

The Arbutus watershed of the Huntington Forest (HF) is located in the central Adirondacks. The watershed was heavily cut about 84 years ago and the maximum age of overstory trees is about 100 years (Mitchell *et al.*, 2001a). Minerals within the HF are found to have very high weathering potential and provide large amounts of ANC to the watershed (Foster *et al.*, 1992; Johnson and Lindberg, 1992). As a result, the lake draining this watershed (Arbutus Lake) is insensitive to acidic deposition and has a relatively high ANC. Both Constable Pond and West Pond are located in the western Adirondacks in the North Branch of the Moose River, where atmospheric deposition of SO_4^{2-} and NO_3^- is among the highest in the region. The surficial geology of these watersheds is characterized by shallow deposits of glacial till. As a result, both Constable Pond and West Pond have low values of ANC. Moreover, owing to the large contribution of wetland cover in the watershed, West Pond has relatively high DOC concentrations. Willy's Pond is another acidic lake located in the western Adirondacks. This watershed has a mature forest without any known history of land disturbances by humans. Surface water chemistry of these lakes is monitored monthly by the Adirondack

Table I. A summary for location,[a] physical characteristics,[a] vegetation,[a] geological[a] and chemical characteristics and deposition level for the study sites

	Arbutus Lake	Constable Pond	West Pond	Willy's Pond	Biscuit Brook
Location[a]	43°59′N 74°15′W	43°50′N 74°48′W	43°49′N 74°53′W	43°58′N 74°57′W	41°59′N 74°30′W
Elevation (m)[a]	513	582	585	630	634
Drainage area (ha)[a]	317	1383	184	158	984
Mean depth (m)[a]	3	2·1	1·5	4·9	N/A
Surface area (ha)[a]	50	20·6	10·4	23·9	N/A
Lake retention time (years)[a]	0·6	0·06	0·19	1·00	N/A
Vegetation (%)					
Hardwood	18	21	35	18	100
Conifer	25	6	3	25	0
Mixed	57	72	39	46	0
Wetland	0	1	23	10	0
Forest age (years)	~100	~100	~100	Mature	Mature
Geology	Calcareous-silicate	Granitic gneiss	Granitic gneiss	Granite gneiss	Sandstone, conglomerate
Surficial geology	Medium till	Thin till	Sphagnum bog/thin till	Thin till	Medium/ thick till
Surface water ANC (μeq l^{-1})	67	−8	0	−10	20
Surface water DOC (μmol l^{-1})	404	400	630	215	178
Wet SO_4^{2-} deposition (kg ha^{-1} $year^{-1}$ as sulphur)	6·5[b]	8·4[b]	8·5[b]	8·9[b]	8·1[c]
Wet NO_3^- deposition (kg ha^{-1} $year^{-1}$ as nitrogen)	3·6[b]	4·3[b]	4·4[b]	4·4[b]	4·4[c]

N/A: not applicable.
[a] After Driscoll and Van Dreason (1993), Wigington *et al.* (1996) and Murdoch *et al.* (1998).
[b] Derived from Ito *et al.* (2002); represent values between 1988 and 1999.
[c] Obtained from NADP, http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=NY68, average values of 1988–99.

Lake Survey Corporation (ALSC; Driscoll *et al.*, 1998, 2003a). The characteristics of these study sites are summarized in Table I.

Catskill site. The Catskill region of New York receives among the highest rates of acidic deposition in the USA (e.g. total nitrogen deposition of ~11 kg ha^{-1} $year^{-1}$; (Stoddard and Murdoch, 1991). Many surface waters within the region have low ANC values. Streams in the Catskill region are the major supply of drinking water for the New York City metropolitan area and are famous for trout fishing. The bedrock of the region consists of nearly flat-lying sandstone, shale and conglomerate. Soils are primarily thin Inceptisols with moderate to high acidity and low SO_4^{2-} adsorption capacity (Murdoch and Stoddard, 1992). Vegetation in the Catskill Mountains is primarily northern hardwood forest, including mostly American beech, sugar maple and yellow birch. Biscuit Brook is a tributary to the West Branch Neversink River in the Catskills. Since the 1920s, the watershed has not been logged (Murdoch *et al.*, 1998). Stream water samples of Biscuit Brook have been collected and analysed weekly by the US Geological Survey (USGS) since 1983.

Data sets and inputs

Deposition data. Current wet-deposition data for the major ions (Na^+, Mg^{2+}, K^+, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-} and NH_4^+) for Arbutus Lake (over the period 1978–2000) and Biscuit Brook (over the period 1983–2000) were obtained from the National Acidic Deposition Program (NADP; http://nadp.sws.uiuc.edu/, NY20, HF and NY68, Biscuit Brook). PnET-BGC is run over a period of approximately 300 years and requires estimates of deposition inputs (both wet and dry) for this period. For the period 1700 to 1850, the background deposition was assumed to be 10% of the current deposition. Deposition inputs after 1850 were assumed to increase linearly until 1900. Deposition of SO_4^{2-} and NO_3^- from 1900 to 1978 (for HF or 1983 for Biscuit Brook) was estimated from the empirical relationships between current estimates of SO_2 and NO_x emissions for the airshed of the northeastern USA and the measured precipitation chemistry (Driscoll *et al*., 2001, 2003b). Since no linear relationship was found between NO_x emissions and NO_3^- deposition, deposition of NO_3^- was assumed to be proportional to the emissions. A similar strategy was used to estimate the historical deposition of Na^+, Mg^{2+}, K^+, Ca^{2+} and Cl^-, using empirical relationships between particulate matter (PM-10) emissions and precipitation chemistry. Historical emission data for SO_2, NO_x and PM were obtained from US Environmental Protection Agency (EPA) compilation of emissions of Criteria Air Pollutants (Nizich *et al*., 1996).

Ito *et al*. (2002) examined wet deposition of base cations at two NADP sites (HF and White Face Mountain (WFM)) in the Adirondacks and found no significant differences. Deposition values derived from regression models by Ollinger *et al*. (1993) also suggested similar base cation deposition across these sites. Thus, the same base cation deposition concentrations for Arbutus watershed were used for all the Adirondack sites. Wet depositions of SO_4^{2-}, NO_3^- and NH_4^+ for Constable Pond, West Pond and Willy's Pond were scaled from deposition values measured at Arbutus watershed, using the ratios derived from the regression models by Ito *et al*. (2002).

PnET-BGC estimates dry deposition based on user inputs of dry-to-wet deposition ratios. A dry-to-wet deposition ratio was assumed to be constant for each element at each site throughout the simulation period. Dry deposition measurements for NO_3^- and NH_4^+ for the Adirondack sites were obtained from Mitchell *et al*. (2001b). The dry-to-wet deposition ratio of sulphur could be estimated from the regional regression model developed by Ollinger *et al*. (1993). However, the estimated dry-to-wet deposition ratios (0·34–0·36) were too low to balance the leaching of SO_4^{2-} measured in the surface waters, especially for the Arbutus watershed. Mollitor and Raynal (1982) showed the enhanced collection of dry sulphur deposition under the coniferous canopy at Arbutus watershed. SO_4^{2-} concentrations in throughfall under the conifer canopy were found to be 1·5 times greater than concentrations in precipitation. All the four watersheds in the Adirondacks have substantial amounts of conifer and mixed forest coverage (Table I). Thus, higher dry-to-wet deposition ratios than 0·34–0·36 were expected for these watersheds. For these watersheds, ratios of 0·95, 0·60, 0·45 and 0·50 respectively were used for Arbutus watershed, Constable Pond, West Pond and Willy's Pond in order to simulate the leaching of SO_4^{2-} in surface waters. The magnitude of these values is consistent with the relative values of conifer and mixed vegetation area in these watersheds.

Dry-deposition sulphur and nitrogen measurements for 1995 and 1998–2000 at Biscuit Brook were available from the Clean Air Status and Trends Network (CASTNet; http://www.epa/gov/castnet/sites/cat175.html). However, the estimated dry-to-wet sulphur deposition ratio (0·4) was again too low to simulate SO_4^{2-} loss in streamwater. Watersheds in the Catskills typically have a large elevation range. Interception of cloud and dry deposition of sulphur increase with elevation. Lovett *et al*. (1999) observed that net throughfall of SO_4^{2-} (an estimate of dry deposition) increased by a factor of 13 along the elevation range of 800 to 1275 m at Slide Mountain in the Catskills. Biscuit Brook watershed has an elevation range of 628–1120 m. The measurement of dry deposition by CASTNet is made at 765 m. Thus, higher rates of dry deposition should be expected for the whole watershed. For model simulations, a dry-to-wet ratio of 0·85 was used in order to simulate the output of SO_4^{2-} to the stream water.

Dry deposition measurements of base cations at Arbutus Lake watershed were obtained from the measurements at HF by Shepard *et al*. (1989): Na^+, 0·32; Mg^{2+}, 0·75; K^+, 0·28; Ca^{2+}, 1·37. These values are similar to values reported by Johannes *et al*. (1985) for the western Adirondacks. Thus, ratios derived from Shepard *et al*. (1989) were used for all sites.

Climate data. Climate data needed to run PnET-BGC (monthly precipitation, minimum and maximum temperatures) for the Arbutus watershed are available from measurements at the HF from 1940 to 2000. For years before 1940, average values of 1940–2000 were used. Climate data for Constable Pond, West Pond and

Willy's Pond were scaled from the records at the HF, using the ratios derived from the regression models of Ito *et al*. (2002). Climate data for Biscuit Brook were obtained from a national weather service station located on Slide Mountain for 1962–2000 (http://lwf.ncdc.noaa.gov/oa/ncdc.html, accessed 20 April 2001).

Land disturbance history. Compared with other regions in the northeastern USA, forests in the Adirondacks have generally experienced limited human disturbance. However, many forests in the region have undergone severe logging in the past. The introduction of railroads in the Adirondacks in the mid-1880s enabled the logging of areas that could not be reached before and the logging of hardwoods (Kudish, 1996). The close proximity of West Pond and Constable Pond to the railroad suggested early logging of these watersheds. Although an Adirondack Park Agency (APA) map indicated that both watersheds were covered by green timber (first growth or second growth) in 1916, it is possible that these sites were logged prior to 1916 and had regenerated. Thus, for West Pond and Constable Pond, 80% and 60% of the watershed area respectively was assumed to have been cut in 1900. Apart from human disturbances, natural disturbances (e.g. hurricane, pests, fire) have also affected these forests. Willy's Lake watershed is a mature forest without any history of human disturbances. However, an APA map suggests that 50–100% of the trees in the entire watershed experienced blow down following a 1950 hurricane. Likewise, 40% of Constable Pond watershed experienced 50–100% blow down. The hurricane events are thought to have little impact on nitrogen cycling over the long term, except when followed by salvage harvest (Aber *et al*., 2002). Records of the Adirondacks indicated possible salvage harvests following the 1950 hurricane (McMartin, 1994). Thus, we accounted for this incident in the simulations by assuming 50% and 20% biomass mortality at Willy's Pond and Constable Pond respectively in 1950 with 40% dead biomass removal. To account for the cutting at Arbutus watershed about 84 years ago, we assumed 80% mortality of live biomass and 80% removal of biomass. After 1917, the Arbutus watershed has undergone some small harvests, most significantly in 1960 (18%) and 1967 (12%; M. Mitchell personal communication).

Forests at the lower elevation of the Catskill Mountains have undergone severe disturbances by European settlers (Kudish, 2000). However, forests at higher elevations are generally intact. The belt of tree harvesting is bounded by pastures below and first-growth forests above. For Biscuit Brook watershed, a large portion of the watershed is mature forest (elevation >870 m, about 80% of area). The lower portion of the watershed (about 20% in area) contains second-growth forest (elevation between 710 and 870 m) and agriculture lands (Kudish, 2000). A small fire of hectare scale (<5% of the watershed area) occurred at an elevation of 700 m in 1969 (Kudish, 2000). Thus, for Biscuit Brook, only a small harvest of 20% was assumed for year 1920 and a small fire affecting 5% of the watershed was assumed to occur in 1969.

Vegetation, hydrologic and soil parameters. General vegetation parameters (e.g. photosynthesis and carbon allocation parameters) and hydrologic parameters (e.g. water holding capacity) used to run PnET-CN were reported earlier by Aber and co-workers (Aber and Federer, 1992; Aber *et al*., 1996, 1997). For site-specific parameters, values for northern hardwood reported earlier by Aber and co-workers (Aber and Federer, 1992; Aber *et al*., 1996, 1997) were used. Besides the parameters used to run PnET-CN, PnET-BGC also requires information on element content in vegetation and soil organic matter. For Arbutus watershed, these parameters were derived from the measurements at the HF during the Integrated Forest Study (Johnson and Lindberg, 1992), and for Biscuit Brook they were obtained from the measurements by Yorks (2001). No measurements of the element content of vegetation and soil organic matter are available for the other three Adirondack sites. Note that the element content of vegetation could be greatly influenced by species and element supply at that specific site. For these three sites, the element content values from the HBEF (Whittaker *et al*., 1979) were used, assuming that similar vegetation composition and acidic soils will result in similar element content in vegetation.

Little information on weathering rates is available for these sites; thus, weathering inputs in this analysis were obtained through model calibration. Calibration of weathering inputs was conducted using the observed surface,-water base-cation concentrations in 1983. Weathering rates for 1983 were obtained by adjusting

Table II. Estimated weathering inputs of base cations for each site (g m^{-2} $month^{-1}$)

Site	W_{Na}	W_{Mg}	W_K	W_{Ca}
Arbutus watershed				
Model[a]	0·030	0·020	0·012	0·115
Mass balance[b]	0·026	0·012	0·030	0·127
Constable Pond	0·020	0·008	0·018	0·040
West Pond	0·027	0·012	0·015	0·031
Willy's Lake	0·015	0·003	0·012	0·012
Biscuit Brook	0·010	0·018	0·006	0·108

[a] Values used in the model.
[b] Values derived using sodium mass balance approach.

weathering inputs until predicted surface water outputs for 1983 matched observed values (normalized mean error, NME $< 0·1$; see below). The calibrated weathering inputs were used as constant inputs for the rest of the simulation period, allowing us to assess the model performance by comparing model simulation to observed surface water concentrations after 1983. The estimated weathering rates of base cations used in the model (0·89 keq ha^{-1} $year^{-1}$ for Arbutus watershed to 0·14 keq ha^{-1} $year^{-1}$ for Willy's Pond watershed) were roughly in the same range with the estimates of long-term weathering rates at two other Adirondack sites by April *et al*. (1986): $0·62 \pm 0·21$ keq ha^{-1} $year^{-1}$ for Woods Lake, an acid-sensitive lake/watershed; and $0·50 \pm 0·25$ keq ha^{-1} $year^{-1}$ for Panther Lake, an acid-insensitive lake/watershed. A summary of the estimated weathering rates for each site is given in Table II.

Weathering rates at Arbutus watershed could also be obtained using sodium as indicator element, as described by Gbondo-Tugbawa *et al*. (2001). The weathering inputs of the indicator element (sodium) could be derived using a mass balance approach, and the derived sodium weathering rate was used in conjunction with base cation weathering ratios reported by Johnson and Lindberg (1992) for the HF to derive weathering rates of other base cations. Using this method, the weathering rates of sodium and calcium derived for Arbutus watershed are very similar to values derived through calibration, whereas rates of magnesium and potassium derived using these two methods showed some discrepancies (Table II).

The Gaines–Thomas exchange coefficients were derived from soil solution concentrations and exchangeable base-cation pools measured at the Adirondack sites (Bates, 1999). Exchange coefficients for Biscuit Brook were derived from the measured soil data from the nearby Winnisook watershed (Johnson *et al*., 2000; G. Lawrence, unpublished data). The estimated Gaines–Thomas exchange coefficients used for all the sites are summarized in Table III. Soil SO_4^{2-} adsorption capacity and equilibrium constants for Arbutus watershed were derived from laboratory experiment data (Driscoll, unpublished data). The same SO_4^{2-} adsorption capacity and equilibrium constants were assumed for all the other sites. The fraction of total organic acids to DOC (site density) was derived by dividing the estimated organic acid concentration (i.e. difference between the

Table III. Estimated Gaines–Thomas cation-exchange coefficients used for each study site in model calculations

Cation-exchange reaction	log *K*				
	Arbutus watershed	Constable Pond	West Pond	Willy's Pond	Biscuit Brook
$XH + Na^+ = XNa + H^+$	−1·837	−1·682	−1·707	−1·024	−1·320
$2XH + Mg^{2+} = X_2Mg + 2H^+$	−5·172	−4·927	−4·916	−3·763	−5·117
$XH + K^+ = XK + H^+$	−0·980	−1·058	−0·963	−0·451	−0·439
$2XH + Ca^{2+} = X_2Ca + 2H^+$	−4·978	−4·402	−4·336	−3·289	−5·344
$3XH + Al^{3+} = X_3Al + 3H^+$	−5·262	−6·389	−5·650	−5·108	−5·427

sum of all measured cations and the sum of measured anions in the solution, anion deficit method; Driscoll *et al.*, 1994) by the measured DOC concentrations. Equilibrium constants for other reactions used in model simulations (e.g. the organic acids triprotic analogue) have been reported previously by Gbondo-Tugbawa *et al.* (2001).

Model evaluation criteria

The model-simulated monthly and annual volume-weighted concentrations of the major surface water solutes (e.g. Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^{2-}, Al_m), pH and ANC were compared with data obtained from the Adirondack Long-Term Monitoring Program and the USGS. Surface water chemistry was measured since 1983 for all sites but Willy's Pond, which has been monitored since 1993. The model performance was evaluated using statistical criteria of NME and normalized mean absolute error (NMAE; Jansen and Heuberger, 1995; Alewell and Manderscheid, 1998). NME provides a comparison of predictions and observations on an average basis, and expresses the relative bias of mean predictions. The NMAE indicates the absolute error between model prediction and observation scaled relative to mean observations. An NMAE value of zero indicates full agreement of predicted value with measured data. NME and NMAE are defined as follows:

$$\text{NME} = \frac{\overline{p} - \overline{o}}{\overline{o}} \qquad \text{NMAE} = \frac{\sum_{t=1}^{n} (|p_t - o_t|)}{n\overline{o}}$$

where p_t is the predicted value at time t, o_t is the observed value at time t, $\overline{o}$ and $\overline{p}$ are the average observed and predicted values over time t, and n is the number of observations.

RESULTS

Model performance

Surface water chemistry. The model-simulated surface water SO_4^{2-} concentrations agreed reasonably well with measured values across all the sites (NME = −0·03 to 0·00; Table IV) and indicated the trend of decreasing SO_4^{2-} concentrations in response to decreases in atmospheric deposition (Figure 2). However, the model underpredicted surface water SO_4^{2-} concentrations after 1992 at Arbutus watershed.

The model-simulated annual volume-weighted NO_3^- concentrations also generally agreed with the measured data (NME = −0·19 to 0·14; Table IV), but with larger departures from the measured data than observed for SO_4^{2-} (Figure 3). Simulated NO_3^- concentrations indicated different interannual variations from the observed patterns. The model-simulated interannual variations in NO_3^- were generally driven by climate variations. Thus, for the four Adirondacks sites, simulated NO_3^- concentrations all peaked at the same time around 1987 and again during 1996–2000 (Figure 3). However, the observed NO_3^- concentrations that indicated a different pattern. The model failed to capture the observed peak in NO_3^- concentrations that occurred in 1990 at Constable Pond, Arbutus watershed and Biscuit Brook. A peak in surface water NO_3^- observed in 1990 across the northeastern USA has been attributed to a soil-freezing event in the winter of 1989 (Mitchell *et al.*, 1996) and usually high nitrogen deposition during the winter (Murdoch *et al.*, 1998). Experiments conducted at the HBEF have shown enhanced leaching of NO_3^- from soil in response to induced soil freezing (Fitzhugh *et al.*, 2001). Thus, the lack of soil-freezing effect algorithm in the model might help explain this discrepancy (Aber *et al.*, 2002; Gbondo-Tugbawa and Driscoll, 2002). The model overpredicted NO_3^- concentrations during 1996–2000 at most of the sites. Recent studies have shown the increase in atmospheric CO_2 could facilitate plant uptake of nitrogen (Ollinger *et al.*, 2002; Oren *et al.*, 2001) and result in lower NO_3^- leaching to the surface water (Vitousek *et al.*, 2001). Incorporating the CO_2 effect in the model simulations should lower the predictions in NO_3^- concentrations. However, it is still not clear whether the model is overly sensitive to the climate conditions or whether other important nitrogen retention mechanisms are missing from the model.

Table IV. Summary of simulated and observed surface water constituents and results of model performance for Arbutus watershed, Constable Pond, West Pond, Willy's Pond and Biscuit Brook[a]

Stream constituent	Simulated		Observed		Model performance[b]		
	Mean	SD	Mean	SD	ME	NME	NMAE
Arbutus Lake							
Ca^{2+} (μmol l^{-1})	76·7	6·3	77·4	7·6	−0·8	−0·01	0·07
NO_3^- (μmol l^{-1})	12·0	4·3	11·3	3·9	0·7	0·06	0·32
SO_4^{2-} (μmol l^{-1})	63·7	10·1	64·9	5·6	−1·2	−0·02	0·08
ANC (μeq l^{-1})	67·8	7·5	67·9	7·8	−0·1	0·00	0·12
Constable Pond							
Ca^{2+} (μmol l^{-1})	43·5	3·5	44·9	5·5	−1·3	0·03	0·09
NO_3^- (μmol l^{-1})	34·1	11·9	32·4	10·6	−0·8	0·03	0·31
SO_4^{2-} (μmol l^{-1})	63·5	5·7	64·6	8·1	−1·1	−0·02	0·05
ANC (μeq l^{-1})	−6·3	1·2	−7·7	7·2	1·4	−0·18	−0·74
West Pond							
Ca^{2+} (μmol l^{-1})	43·0	2·6	42·8	7·2	0·2	0·02	0·12
NO_3^- (μmol l^{-1})	16·0	6·2	14·0	3·5	2·0	0·14	0·41
SO_4^{2-} (μmol l^{-1})	52·4	4·0	52·5	7·6	−0·2	0·00	0·06
ANC (μeq l^{-1})	2·2	5·0	2·5	8·2	−0·4	−0·14	3·11
Willy's Pond							
Ca^{2+} (μmol l^{-1})	29·0	2·7	29·0	2·4	0·0	0·00	0·09
NO_3^- (μmol l^{-1})	27·1	6·1	33·6	10·1	−6·5	−0·19	0·35
SO_4^{2-} (μmol l^{-1})	54·2	2·1	55·1	4·9	−0·8	−0·02	0·04
ANC (μeq l^{-1})	−15·7	5·2	−15·3	6·7	−0·4	0·02	−0·41
Biscuit Brook							
Ca^{2+} (μmol l^{-1})	59·9	6·0	59·9	8·1	0·0	0·00	0·05
NO_3^- (μmol l^{-1})	26·1	7·5	25·5	9·8	0·6	0·02	0·32
SO_4^{2-} (μmol l^{-1})	57·6	7·7	59·2	7·6	−1·6	−0·03	0·05
ANC (μeq l^{-1})	19·2	2·0	19·7	4·9	−0·5	−0·02	0·64

[a] Values represent mean and standard deviation (SD) of annual volume-weighted concentrations for the period 1983–2000, except for Willy's Pond (1993–2000).
[b] ME, mean error; NME, normalized mean error; NMAE, normalized mean absolute error.

Using the mineral weathering rates estimated through calibration, the model-simulated surface water concentrations of base cations (i.e. Ca^{2+}) generally compared well to the measured data for all the sites (NME = −0·03 to 0·00; Table IV) and captured the trend of decreases in concentrations over time (Figure 4). For Constable Pond and West Pond, the overprediction in NO_3^- during 1997–2000 caused the elevated leaching of Ca^{2+}. Thus, at these two sites, the model overpredicted Ca^{2+} during this period.

The simulated annual volume-weighted ANC values compared well to the observed values (mean error of −1·5 to 1·4 μeq l^{-1}; Table IV). Consistent with the observed data, the simulations showed little or no long-term trends in surface water ANC (Figure 5). The model overpredicted ANC between 1996 and 2000 at Arbutus watershed, which was probably the combined effect of underprediction in SO_4^{2-} concentration and overprediction in Ca^{2+} concentration during those years. The model also overpredicted ANC at West Pond between 1996 and 2000 as a result of the overprediction in Ca^{2+} in excess of NO_3^-, caused by in-lake attenuation of NO_3^-. Although the model did capture the slight increase in lake-water ANC at Willy's Pond during the monitoring period of 1993–2000, the model-simulated increase in ANC was less than the observed increase. Note that Willy's Pond only has 8 years of record, which is likely insufficient for determining long-term trends.

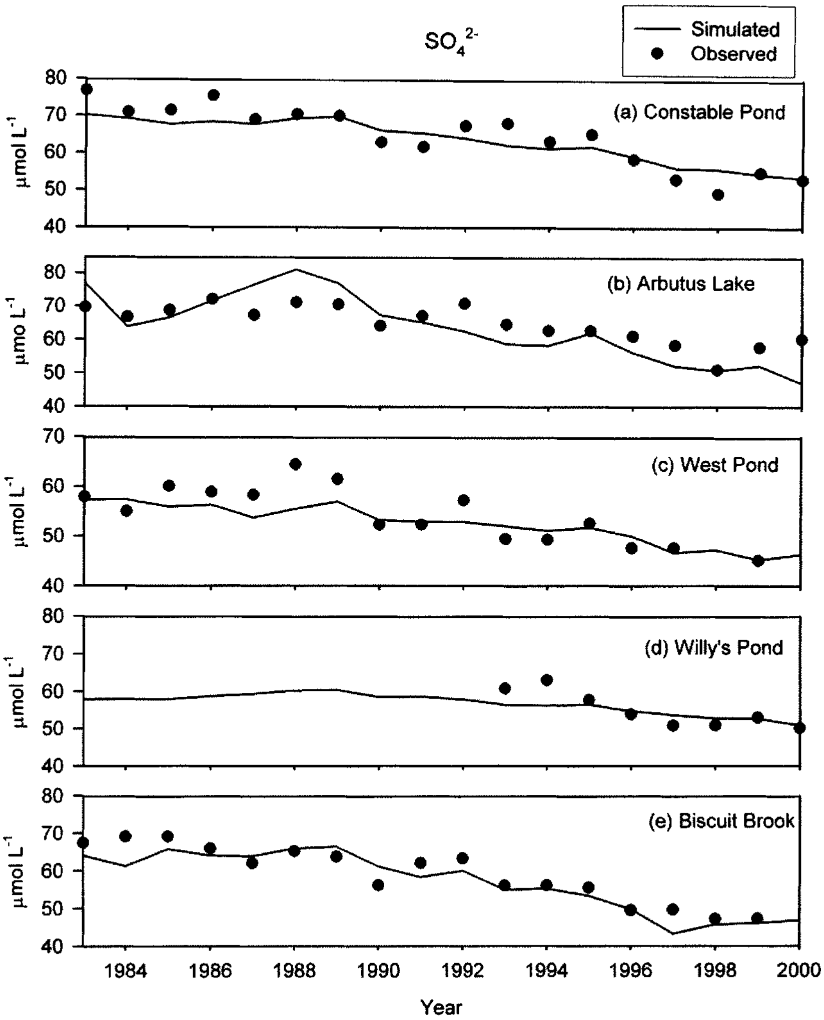

Figure 2. A comparison of measured and model-simulated values of annual volume-weighted concentrations of SO_4^{2-} at (a) Constable Pond, (b) Arbutus watershed, (c) West Pond, (d) Willy's Pond and (e) Biscuit Brook

The model performed well in simulating the base cation concentrations during the winter season, but it underpredicted values during the summer season (Figure 6a). The model overpredicted NO_3^- during the winter season and underpredicted NO_3^- during the summer growing season (Figure 6b). The underprediction of both NO_3^- and Ca^{2+} concentrations during the summer season suggests that the model might overpredict nutrient uptake during the growing season or there might be groundwater sources of NO_3^- and Ca^{2+} discharging into the drainage water. Consistent with the observed data, model-simulated surface water SO_4^{2-} concentrations showed little seasonal variation (Figure 6c). The overall effects of underprediction in Ca^{2+} and NO_3^- concentrations during the summer season resulted in underprediction of ANC during the summer season (Figure 6d), while the model-predicted ANC values during the winter season compared well to the measured data.

Simulated fluxes and pools. The model-simulated fluxes for Arbutus watershed were compared with measured values from previous process studies (Table V). The model-simulated nitrogen mineralization and nitrification rates at Arbutus watershed during 1995–96 were lower than estimates by Ohrui *et al.*

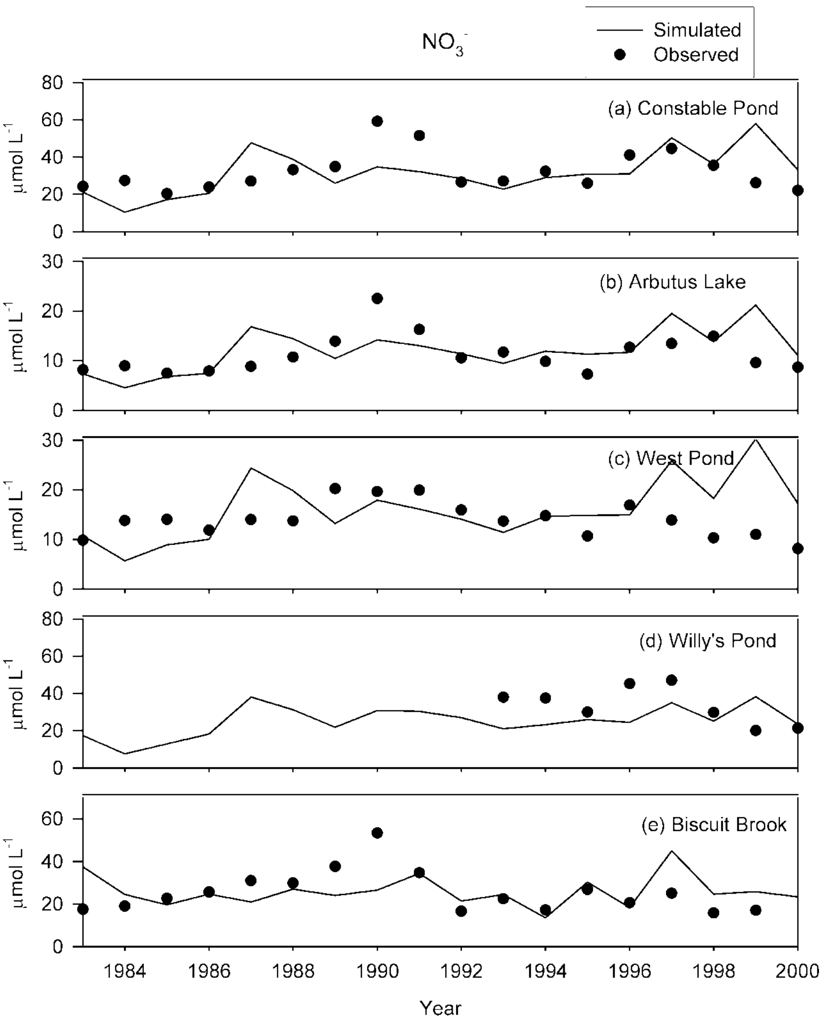

Figure 3. A comparison of measured and model-simulated values of annual volume-weighted concentrations of NO_3^- at (a) Constable Pond, (b) Arbutus watershed, (c) West Pond, (d) Willy's Pond and (e) Biscuit Brook

(1999) at an upland hardwood plot during the same period (Table V). The model-simulated nitrogen foliar and woody litter fall fluxes were in close agreement with the measured values reported by Johnson and Lindberg (1992) during 1985–86 (Table V). However, the model-predicted root litter was greater than the measured values. At a hardwood plot adjacent to the Arbutus watershed, Mitchell *et al.* (1991) estimated nitrogen litter fall (foliar plus woody) and net uptake (increment in bole and wood plus litter fall) to be 44·8 kg ha^{-1} year^{-1} and 44·7 kg ha^{-1} year^{-1} respectively. The estimates by Mitchell *et al.* (1991) did not include the root litter, whereas the modelled litter fall and uptake fluxes of nitrogen (77·3 kg ha^{-1} year^{-1} and 81·9 kg ha^{-1} year^{-1} respectively) included the root litter and thus were higher than values reported by Mitchell *et al.* (1991). For the same reason, the modelled litter fall and uptake fluxes of sulphur (9·6 kg ha^{-1} year^{-1} and 7·2 kg ha^{-1} year^{-1} respectively) were greater than the values of 4·0 kg ha^{-1} year^{-1} and 5·3 kg ha^{-1} year^{-1} respectively obtained by Mitchell *et al.* (1991). Also for the same reason, the modelled values of the mineralization rates of nitrogen and sulphur were greater than those inferred from the element budgets reported by Mitchell *et al.* (1991) (33·9 versus $<$8·8 kg ha^{-1} yr^{-1} for nitrogen;

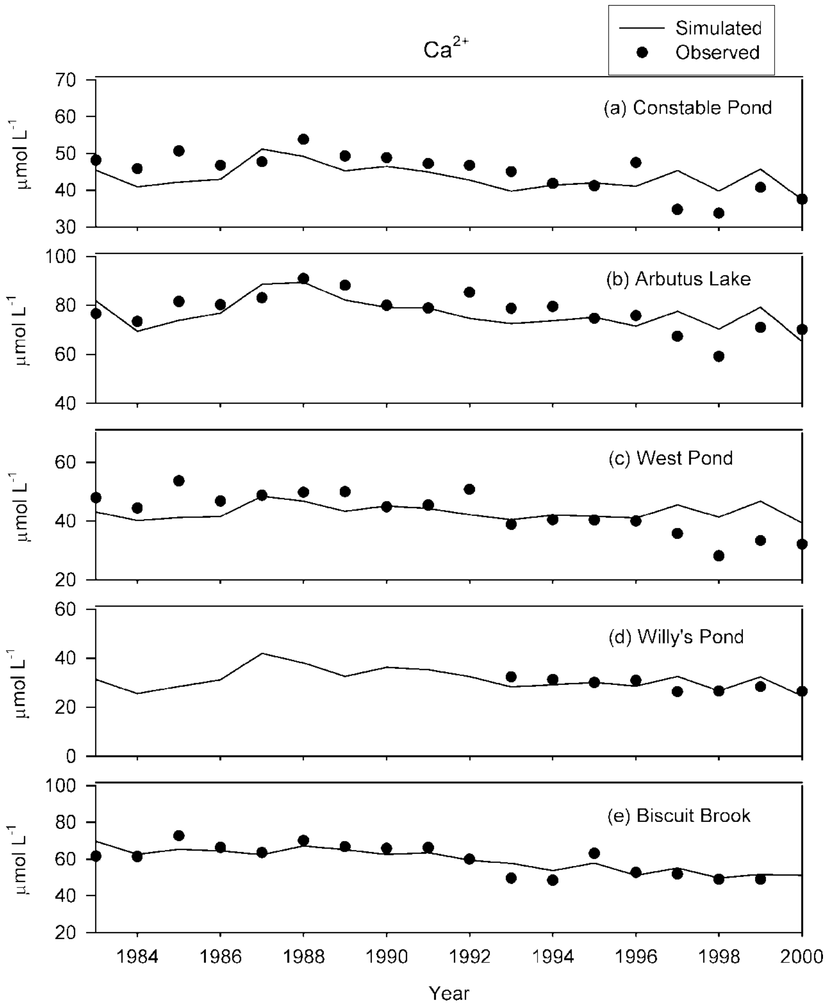

Figure 4. A comparison of measured and model-simulated values of annual volume-weighted concentrations of Ca^{2+} at (a) Constable Pond, (b) Arbutus watershed, (c) West Pond, (d) Willy's Pond and (e) Biscuit Brook

78·9 versus 10·0 kg ha^{-1} $year^{-1}$ for sulphur) during 1985–86. The simulated sulphur mineralization rate was lower than the mineralization rate of the forest floor estimated by David *et al.* (1987). The model suggested a higher rate of mineralization of organic sulphur (10 kg ha^{-1} $year^{-1}$) than desorption of adsorbed $SO_4{}^{2-}$ (0·6 kg ha^{-1} $year^{-1}$). This result is consistent with the findings from a column study with ^{35}S in Arbutus watershed (Dhamala *et al.*, 1990). Dhamala *et al.* (1990) found that, for mineral soils, organic sulphur mineralization–immobilization processes were more important than $SO_4{}^{2-}$ adsorption–desorption processes in the release of sulphur. The importance of organic sulphur as a source of $SO_4{}^{2-}$ has been shown for other sites in the northeastern USA (Mitchell *et al.*, 2001b). The model-estimated litter fall flux and uptake rates for Ca^{2+}, Mg^{2+} and K^+ were similar to the values measured by Foster *et al.* (1992); (see Table V). The model-estimated exchangeable pools for Na^+, Mg^{2+}, K^+ and Ca^{2+} for Arbutus watershed were also similar to the measured data during the Integrated Forest Study (Johnson and Lindberg, 1992).

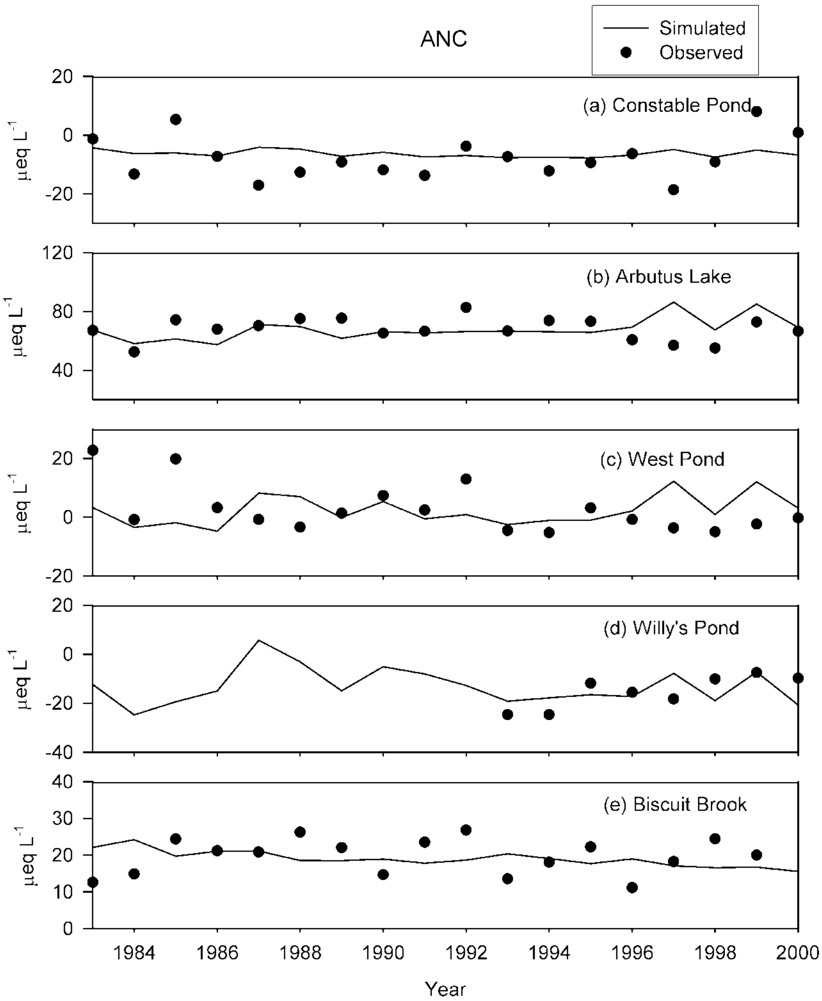

Figure 5. A comparison of measured and model-simulated values of annual volume-weighted values of ANC at (a) Constable Pond, (b) Arbutus watershed, (c) West Pond, (d) Willy's Pond and (e) Biscuit Brook

Element budgets

Element budgets for each site indicated some general patterns in element cycling within these watersheds (Table VI). All these five watersheds showed little retention of sulphur inputs. For most of the sites, drainage outputs of SO_4^{2-} exceeded inputs from total deposition because desorption of SO_4^{2-} and mineralization of sulphur exceeded net plant retention. However, this net release of SO_4^{2-} from the internal pools was small compared with total deposition. Most of these watersheds showed relatively large NO_3^- retention. For most of the sites, plant uptake of NO_3^- exceeded nitrification, and in-lake processes retained substantial amounts of NO_3^-. The drainage loss of NO_3^- was relatively small compared with total deposition inputs. Drainage losses of base cations greatly exceeded deposition and were supplied by various sources, including deposition, canopy exchange, mineralization, mineral weathering, and cation exchange.

Drainage outputs of SO_4^{2-} from these sites generally reflected atmospheric sulphur deposition. The drainage loss of NO_3^-, however, varied across sites, even for sites with similar deposition. Among these five sites, Biscuit Brook of Catskills receives the highest NO_3^- deposition. The drainage loss of NO_3^- at this site was also among the highest of all the sites studied. Although the forest at Biscuit Brook has experienced

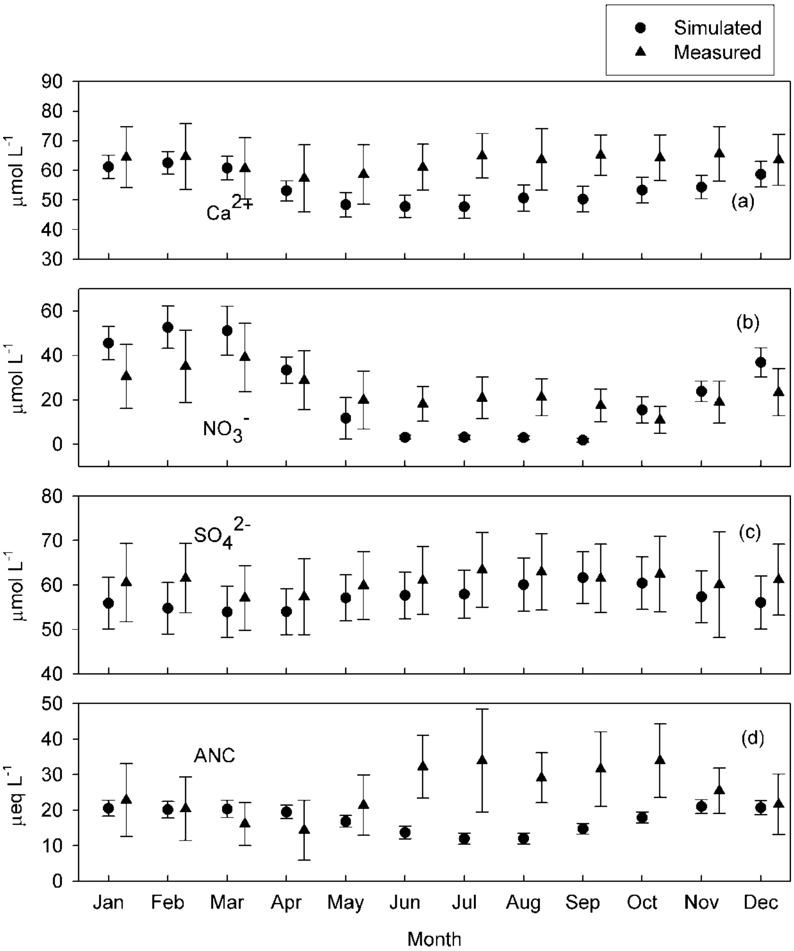

Figure 6. A comparison of measured and model-simulated monthly stream concentrations of (a) Ca^{2+}, (b) NO_3^-, (c) SO_4^{2-} and (d) ANC at Biscuit Brook. Means and standard deviations of values are shown for the period 1983–98

limited land disturbance, it strongly retained inputs of NO_3^- through plant uptake and had relatively low nitrification rates. Total NO_3^- deposition was uniform at the four Adirondack sites and generally lower than the Catskills. However, these sites exhibited considerable variability in drainage loss of NO_3^- due to different land-disturbance history and in-lake processes. The mature forest watershed (Willy's Lake) showed an elevated nitrification rate that was almost three times that of the other sites, and the nitrification exceeded net plant uptake of NO_3^-. Although in-lake processes retained more than 60% of the NO_3^- at Willy's Pond, the NO_3^- flux at the lake outlet was still among the highest of the sites studied. The elevated nitrification rate indicated that the watershed is close to a condition of nitrogen saturation. Differences in land-disturbance history, and maybe slight differences in climate among the Adirondacks sites, appear to have resulted in different rates of nitrification. The Arbutus watershed experienced the most severe and recent disturbances and cooler climate, and thus the nitrification rate at this site was relatively low. However, differences in drainage loss of NO_3^- at Constable Pond, West Pond and Arbutus Lake generally reflected the differences in in-lake retention among these sites. West Pond and Arbutus Lake have longer hydraulic retention times than Constable Pond, and thus retained larger quantities of NO_3^- inputs. As a result, Arbutus Lake and West Pond have relatively low NO_3^- outputs. In contrast to Willy's Pond, plant uptake at the other Adirondack sites exceeded nitrification.

Table V. A comparison of model-simulated fluxes and pools with literature values for the Arbutus watershed

Fluxes	Modelled value[a]	Measured value[a]	Reference
N mineralization rate	89.2	106.9 ± 20.9	Ohrui *et al*. (1999)
N net nitrification	10.3	29.0 ± 6.0	Ohrui *et al*. (1999)
N litter			
Foliar	33.7	35	Johnson and Lindberg (1992); Mitchell *et al*. (1991)
Woody	9.9	9.8	Johnson and Lindberg (1992); Mitchell *et al*. (1991)
Root	32.0	14.8	Johnson and Lindberg (1992)
Total	75.6	59.6	
S net mineralization	10.0	14.2 (forest floor)	David *et al*. (1987)
Litter fall for Ca^{2+}, Mg^{2+} and K^+	49.0, 7.7 and 12.0	36.2, 4.3 and 7.0	Foster *et al*. (1992)
Uptake rate for Ca^{2+}, Mg^{2+} and K^+	58.0, 10.4 and 14.2	45.4, 5.8 and 17.6	Foster *et al*. (1992)
Exchangeable pools for Ca, Mg, K and Na	619, 62, 125 and 33	606, 38, 73 and 48	Johnson and Lindberg (1992)

[a] Units are kg ha^{-1} $year^{-1}$ for the fluxes and kg ha^{-1} for the pools.

Table VI. Simulated fluxes of major element budgets for Constable Pond, Arbutus watershed, West Pond, Willy's Pond and Biscuit Brook[a]

	Flux (kg ha^{-1} $year^{-1}$)				
	Constable Pond	Arbutus Lake	West Pond	Willy's Pond	Biscuit Brook
NO_3-N					
Total deposition[b]	5·7	5·6	5·7	5·7	7·2
Nitrification[c]	11·0	7·5	9·1	26·2	7·3
Uptake[c]	−12·8	−10·3	−11·4	−24·9	−11·4
In-lake processes[c]	−0·9	−1·8	−1·9	−4·6	—
Drainage losses[c]	−3·0	−1·0	−1·5	−2·4	−3·1
SO_4-S					
Total deposition[b]	12·7	11·5	11·9	11·9	15·8
Mineralization[c]	11·1	9·8	10·9	11·4	12·6
Uptake[c]	−11·0	−9·7	−10·8	−11·4	−12·9
Net adsorption[c]	1·0	0·5	−0·5	0·6	0·3
Drainage losses[c]	−13·7	−12·2	−11·5	−12·4	−15·8
Calcium					
Total deposition[b]	2·2	2·1	2·3	2·3	2·2
Canopy exchange[c]	1·8	0·8	1·7	1·7	2·5
Weathering[c]	4·3	12·1	3·3	1·3	12·2
Mineralization/immobilization[c]	36·0	66·8	34·6	30·1	59·2
Uptake[c]	−37·3	−67·8	−36·4	−30·7	−58·4
Net sorption[c]	4·7	4·4	6·0	3·9	3·1
Drainage losses[c]	−11·8	−18·4	−11·5	−8·6	−20·6

[a] Values are averages for the 1983–2000 period. Positive values indicate increases of fluxes in soil solutions.
[b] Measured or estimated flux.
[c] Model-simulated flux.

Drainage outputs of base cations also varied across sites. With relatively uniform base cation deposition across these sites, the differences in base cation leaching reflected differences in the net depletion of base cations from cation-exchange sites, mineral weathering and mineralization. Arbutus watershed and Biscuit Brook watershed have higher mineral weathering rates and, as a result, drainage losses of base cations were significantly higher at these two sites.

ANC budgets

ANC budgets can be used to evaluate the relative importance of biogeochemical processes controlling the acid–base status of surface waters (Cook *et al.*, 1992). For the purposes of this analysis we developed watershed ANC budgets using a charge balance approach:

$$\mathrm{ANC} = 2[\mathrm{Ca}^{2+}] + 2[\mathrm{Mg}^{2+}] + [\mathrm{Na}^{+}] + [\mathrm{K}^{+}] + [\mathrm{NH_4}^{+}] + 3[\mathrm{Al}^{3+}] - [\mathrm{Cl}^{-}] - [\mathrm{NO_3}^{-}] - 2[\mathrm{SO_4}^{2-}] - [\mathrm{F}^{-}] - [\mathrm{A}^{-}]$$

where $[A^-]$ is the equivalent concentration of naturally occurring organic anions.

ANC budgets derived from the model simulations indicated that atmospheric deposition was the largest sink of ANC to the watersheds (Table VII). Net $SO_4{}^{2-}$ desorption from soil was also a small sink of ANC. Cation-exchange reactions generally release base cations to the soil water, consuming Al^{3+} and H^+, and are generally sources of ANC. For the acid-insensitive watershed (i.e. Arbutus watershed), ANC was largely supplied by base cations; in contrast, for the acid-sensitive sites (i.e. Constable Pond, West Pond, Willy's Pond), a large portion of ANC production was derived from aluminium mobilization. As a result, surface waters at these sites were characterized by elevated leaching of aluminium (0·20 keq ha^{-1} $year^{-1}$, 0·13 keq ha^{-1} $year^{-1}$ and 0·31 keq ha^{-1} $year^{-1}$ for Constable Pond, West Pond and Willy's Pond respectively).

After Gbondo-Tugbawa and Driscoll (2002), we use the term 'net mineralization' to represent the net effect of mineralization, microbial immobilization and plant assimilation. For Constable Pond and Biscuit Brook, net mineralization resulted in a small production of ANC, due largely to the net consumption of $NO_3{}^-$. In contrast, at Willy's Pond, nitrification exceeded $NO_3{}^-$ plant uptake; thus, the overall effect of net mineralization was loss of ANC. For the watershed with extensive wetland coverage (i.e. West Pond), decomposition of organic matter produces organic acids (0·21 keq ha^{-1} $year^{-1}$) and the overall effect of net mineralization is loss of ANC. For West Pond, the flux of organic anions was comparable to $NO_3{}^-$ loss. For Arbutus Lake, West Pond and Willy's Pond, in-lake retention of $NO_3{}^-$ served as an important source of ANC (Table VII). At acid-sensitive Willy's Pond, in-lake $NO_3{}^-$ retention was the second largest source of ANC, after net loss of cations from soil exchange sites. Rates of mineral weathering were important sources of ANC in watersheds

Table VII. Components of ANC budgets for the study sites[a]

Component	ANC (keq ha^{-1} $year^{-1}$)				
	Constable Pond	Arbutus Lake	West Pond	Willy's Pond	Biscuit Brook
Atmospheric deposition	−0·99	−0·89	−0·88	−0·88	−1·23
Cation exchange	0·32	0·01	0·29	0·41	0·24
Anion adsorption	−0·07	−0·03	0·02	−0·05	−0·02
Mineral weathering	0·59	1·24	0·56	0·23	0·89
Net mineralization	0·06	−0·05	−0·09	−0·11	0·30
In-lake processes	0·06	0·11	0·13	0·32	—
Drainage output	−0·03	0·41	0·03	−0·06	0·17

[a] Values are averages for the 1983–2000 period. Positive values indicate sources of ANC and negative values indicate ANC sinks to the lake/watershed systems. The values for drainage outputs represent ANC fluxes in drainage water.

with higher ANC values (e.g. Arbutus). Although mineral weathering rates at Constable Pond and West Pond were generally lower than Arbutus watershed, mineral weathering was still an important source of ANC at these sites. The results of our study are similar to the results of Cook *et al*. (1992), who found that terrestrial weathering was the major source of ANC in two watersheds in the northeastern USA.

DISCUSSION (MODEL LIMITATIONS AND UNCERTAINTIES)

Application of PnET-BGC at these five sites demonstrates the critical need for better information on sulphur inputs to the watershed. Studies have shown large variations in deposition resulting from landscape features (elevation and aspect) and vegetation composition (Mollitor and Raynal, 1982; Lovett *et al*., 1998; Weathers *et al*., 2000). Estimates of deposition inputs to the watershed might be biased using only measurements at a single location without considering the landscape and vegetation composition of the entire watershed. For Biscuit Brook, the deposition measurements at lower elevation of the watershed (629 m for wet deposition and 765 m for dry deposition) might not be representative of the entire watershed. For Adirondack sites, deposition might be enhanced due to the presence of coniferous species. These uncertainties in atmospheric deposition undoubtedly affect model predictions of the acid–base status of soil and surface waters.

Effects of landscape features and vegetation composition extend beyond effects on deposition. Various studies have shown that landscape position and vegetation influence element cycling within forested ecosystems (Lovett and Reuth, 1999; Ohrui *et al*., 1999; Goodale and Aber, 2000; Lawrence *et al*., 2000; Lovett *et al*., 2000; Bischoff *et al*., 2001). Nitrogen dynamics are very different within hardwood and conifer forests (Aber and Driscoll, 1997). Even within hardwood forests, significant differences in nitrogen cycling and surface water NO_3^- concentrations have been found in watersheds with different species composition (Lovett and Reuth, 1999; Lawrence *et al*., 2000; Lovett *et al*., 2000; Goodale and Aber, 2001). Our model simulations were conducted by assuming 100% hardwood composition and using the same vegetation parameters for all watersheds. Thus, model calculations failed to account for the possible variations in NO_3^- controlled by species composition. Differences in nitrogen dynamics are also evident between wetlands and upland landscapes. Wetlands of Arbutus watershed were found to be a net sink of nitrogen, storing a large proportion of the nitrogen retained in the catchment (15%) in relation to the small surface area (Bischoff *et al*., 2001). It is possible that wetlands may play an important role in retention of nitrogen in some of the Adirondack sites (especially West Pond). Although the model currently simulates the effects of in-lake retention, role of wetlands in nitrogen and sulphur retention is not depicted by the model.

Land-use history (including changes in species composition) is thought to drive the large spatial variations in nitrogen loss observed in surface waters (Aber and Driscoll, 1997; Lovett and Reuth, 1999; Goodale and Aber, 2001). Model simulations of nitrogen dynamics are greatly influenced by the land-disturbance history specified. However, these land-disturbance histories are subject to large uncertainty. The exact timing and intensity of land disturbances at a particular site is difficult to obtain and quantify. Historical land-use practice and natural disturbances occurring more than a century ago can affect current nitrogen loss to the surface waters (Aber and Driscoll, 1997; Goodale *et al*., 2000; Goodale and Aber, 2001). Accurate quantification of the disturbance history is critical to the successful application of the model. Uncertainty in land-disturbance history will undoubtedly limit the accuracy in model predictions of nitrogen dynamics, particularly regional applications.

As indicated both by the model simulations (Table VI) and field data, there is substantial cycling of elements (base cations, nitrogen and sulphur) through the vegetation and microbial processes. A strength of PnET-BGC over other acidification models is its ability to simulate these biotic processes. However, this representation can also be a limitation. The model depicts large element pools in soil and large fluxes through biotic processes. Any change in these pools and fluxes will greatly influence the element budgets. If these simulated fluxes are not accurate, then model predictions will misrepresent element dynamics. For example, previous studies have indicated that the net mineralization of organic sulphur balances the sulphur outputs from northeastern watersheds (Alewell *et al*., 1999; Mitchell *et al*., 2001b; Gbondo-Tugbawa *et al*., 2002). Model simulations for our study sites, however, suggested that net mineralization only releases limited amounts of sulphur. Unfortunately, we cannot determine whether field measurements overestimate true rates of sulphur mineralization or whether the model underpredicts sulphur mineralization. There are few measurements of sulphur mineralization available to validate model results. In the model, mineralization of sulphur was affected partially by specified inputs of sulphur contents in the vegetation and organic matter. However, the element content of vegetation and organic matter could vary across sites due to different species and element supply rates. Thus, model results are subject to the uncertainties associated with these parameters.

Model simulations on base-cation cycling are also subject to large uncertainty associated with mineral weathering inputs. Mineral weathering is believed to control loss of base cations to the surface waters. However, for most study sites, mineral weathering rates are difficult to quantify and there are no direct measurements to constrain these inputs. Thus, for modelling purposes, weathering inputs were derived through calibration. Quantifying weathering is another limitation for future use of the model at other sites, and particularly for regional applications.

CONCLUSIONS

Application of PnET-BGC to these sites suggested model-simulated surface water SO_4^{2-}, base cations and ANC generally agreed well with the measured data. Model-simulated NO_3^- was also in good agreement with the measured values; however, interannual variations were different from the observed patterns. The model-simulated internal fluxes of major elements at the Arbutus watershed generally agreed with previously published measured values. Element budgets indicated little retention of sulphur inputs within these watersheds, whereas atmospheric deposition of NO_3^- was strongly retained. Land-disturbance history and in-lake processes play important roles in regulating the nitrogen retention within these forest watersheds. With general uniform inputs of base cations from the atmospheric deposition, different levels of base-cation outputs generally reflected differences in the supply of base cations to the watersheds. ANC budgets showed that cation exchange, mineral weathering, net mineralization and in-lake processes could all serve as sources of ANC. In contrast, at the lake/watershed with a mature forest, i.e. Willy's Pond, biotic processes serve as a sink of ANC and mineral weathering provides only a limited source of ANC. Although model results generally compared well to the observed data, the model simulations are subject to uncertainties, and limitations exist for the future application of the model to other sites.

ACKNOWLEDGEMENTS

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