



## Regional application of the PnET-BGC model to assess historical acidification of Adirondack lakes

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[1] The Adirondack region of New York has high inputs of acidic deposition and large numbers of acidic lakes. The biogeochemical model, PnET-BGC, was applied to 44 statistically representative Environmental Monitoring and Assessment Program (EMAP) lake watersheds in the Adirondacks. Model simulations help provide an understanding of historical effects of acidic deposition on soils and lake waters. Model simulations indicate that median annual concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in the 44 EMAP lakes were 15.9  $\mu\text{eq/L}$  and 3.8  $\mu\text{eq/L}$ , respectively, in 1850, compared to the median current measured values of 88.8  $\mu\text{eq/L}$  and 20.0  $\mu\text{eq/L}$ . Simulated median values of pH, acid-neutralizing capacity (ANC), and soil percent base saturation were 6.63, 67.7  $\mu\text{eq/L}$ , and 12.3%, respectively, in 1850, compared to the median current measured values of 5.95, 27.8  $\mu\text{eq/L}$ , and 7.9%. The estimated historical surface water acidification was greatest in lakes having low ANC below values of 100  $\mu\text{eq/L}$ . This pattern of historical acidification is in agreement with a previous paleolimnological investigation.

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### 1. Introduction

[2] The acidification of soils and surface waters by atmospheric deposition has been recognized as a significant environmental problem since the early 1970s. Acidic deposition causes the accumulation of sulfur and nitrogen in soil, and changes the chemical composition of soils by depleting exchangeable nutrient cations and increasing mobility of aluminum [Driscoll *et al.*, 2001; Reuss and Johnson, 1986]. The loss of critical nutrients may adversely impact sensitive forest vegetation. Research shows that declines of red spruce and sugar maple in the eastern United States may be linked to acidic deposition [DeHayes *et al.*, 1999; Horsley *et al.*, 2000; Juice *et al.*, 2006]. Acidic deposition affects the water quality of streams and lakes by increasing acidity and concentrations of aluminum, both of which contribute to decreases in species diversity of aquatic biota [Driscoll *et al.*, 2001].

[3] The Adirondack region of New York is one of the most extensively studied regions in the United States that exhibits ecological effects from acidic deposition [Driscoll *et al.*, 2003]. This region is particularly sensitive to acidification because of the high precipitation which contains elevated concentrations of strong acids, shallow acidic soils, and low Ca supply from surficial deposits and bedrock.

[4] Historical changes in water chemistry are difficult to assess because of the lack of direct observations prior to the

1980s. Nevertheless, these changes are an important benchmark to evaluate the success of ongoing and future emission control programs. Acid-base chemistry models can be used to quantify changes in acid-base chemistry of soil and surface waters, and to further understand of the response of chemical and biological processes to historical or proposed future changes in atmospheric deposition. Investigators have applied acid-base chemistry models to conduct regional assessments of the effects of acidic deposition in Europe, North America and China [e.g., Aherne *et al.* 2003; Clair *et al.* 2007; Moldan *et al.* 2004], including an analysis of the U.S. Environmental Protection Agency (EPA) Direct/Delayed Response Project (DDRP) lakes in the Adirondack region [Chen and Driscoll 2005b]. In this study, we build on these previous studies by applying the biogeochemical model PnET-BGC (photosynthesis net and evapotranspiration-biogeochemistry) to a probabilistic survey of acid-sensitive Adirondack lakes, the Environmental Monitoring and Assessment Program (EMAP) in order to investigate long-term changes in soil and lake waters in response to historical changes in atmospheric deposition.

### 2. Methods

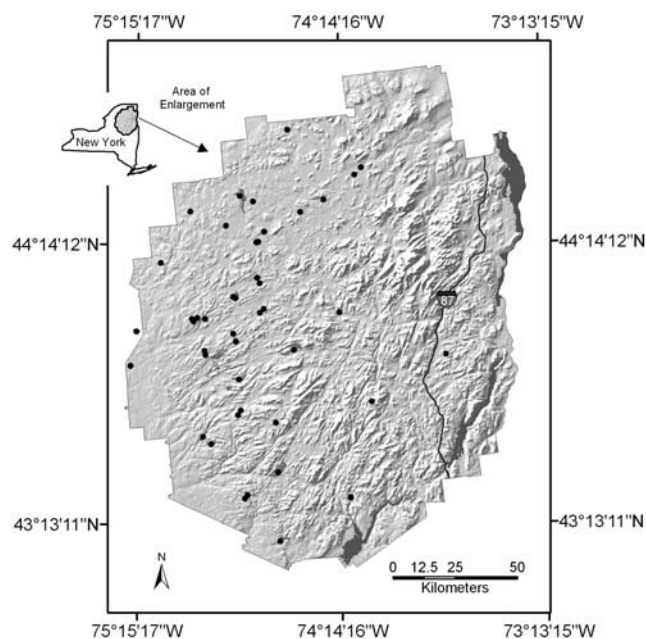
#### 2.1. Model Description

[5] PnET-BGC is an integrated forest-soil-water model that has been used to assess the effects of air pollution and land disturbances on forest and aquatic ecosystems [Gbondo-Tugbawa *et al.*, 2001]. The model was developed by linking two submodels: PnET-CN (PnET-carbon and nitrogen) [Aber *et al.*, 1997] and BGC [Gbondo-Tugbawa *et al.*, 2001]. The main processes in the model include tree photosynthesis, growth and productivity, litter production and decay, mineralization of organic matter, immobilization of nitrogen, nitrification [Aber *et al.*, 1997], vegetation and

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**Figure 1.** Location of the 44 Environmental Monitoring Assessment Program (EMAP) study sites in the Adirondacks. Note that the inset shows the location of the park within New York State.

organic matter interactions of major elements, abiotic soil processes, solution speciation, and surface water processes [Gbondo-Tugbawa *et al.*, 2001]. The hydrologic algorithms used in PnET-BGC are summarized by Aber and Federer [1992] and Chen and Driscoll [2005c]. PnET-BGC has the capability of using multiple soil layers [Chen and Driscoll, 2005c], but for the long-term simulations conducted in this study a single soil layer was utilized. For lake simulations, it is assumed that the water column is completely mixed. The model predicts monthly concentrations and fluxes of major solutes in lake water, monthly concentrations and pools of exchangeable cations and adsorbed sulfate in soil, and monthly fluxes of major solutes from soil and forest vegetation. In this application of the model a monthly time step was utilized. A detailed description of the model and sensitivity analysis of parameters was provided by Gbondo-Tugbawa *et al.* [2001]. They found that soil and surface water predictions were most sensitive to parameter values of soil mass, soil partial pressure of CO<sub>2</sub>, soil cation exchange capacity, and cation exchange selectivity coefficients of Ca<sup>2+</sup> and Al<sup>3+</sup>. The model was applied first at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire [Gbondo-Tugbawa *et al.*, 2001], and then extended successfully to the Adirondack and Catskill regions of New York [Chen *et al.*, 2004] and northern New England [Chen and Driscoll, 2005a]. The model has also been used to predict the response of acid-sensitive forest ecosystems to future controls on atmospheric emissions at the HBEF, the Adirondacks and northern New England [Gbondo-Tugbawa and Driscoll, 2003; Chen and Driscoll, 2005a, 2005b].

## 2.2. Site Description

[6] Lakes selected for modeling in this study were based on U.S. EPA's EMAP. In the Adirondacks, the regional EMAP probability sample consists of 115 lakes representa-

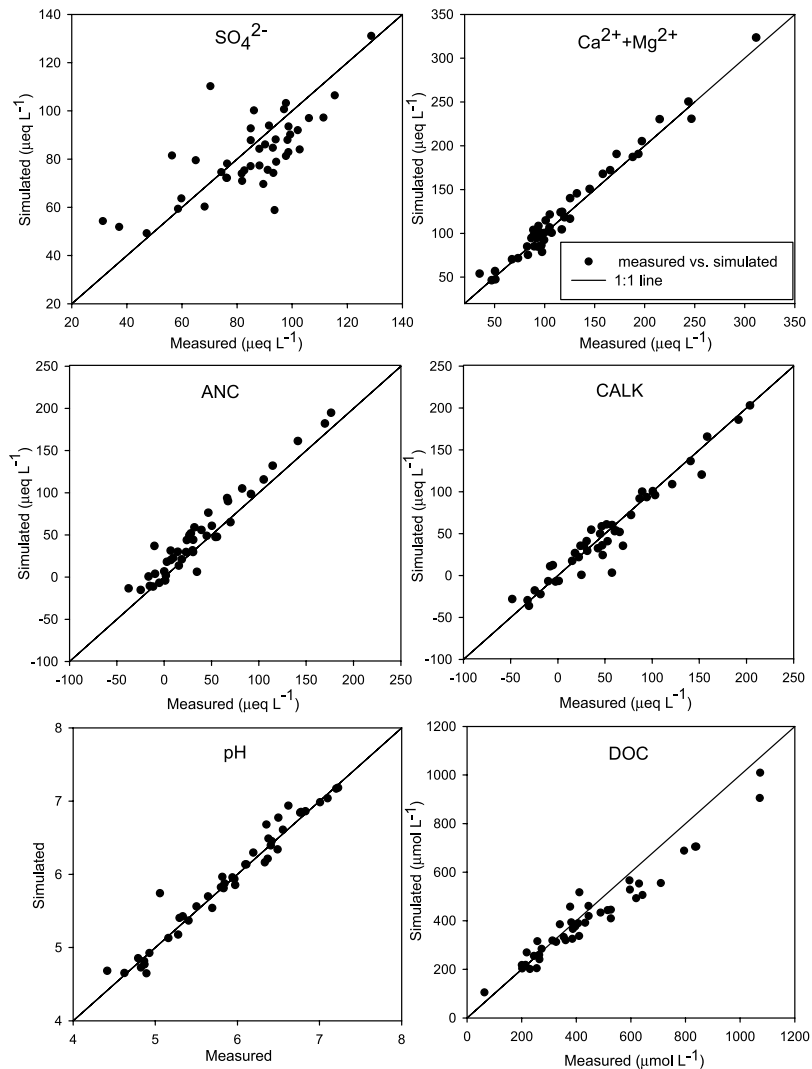
tive of 1817 lakes greater than 1 ha in surface area. Of these 115 lakes, 44 lakes (Figure 1) that had summer acid-neutralizing capacity (ANC) values less than 200  $\mu\text{eq/L}$  were selected for study. This study focused on these lakes as they are most responsive to changes in acidic deposition. The sum of the weighting factors for these lakes is 1320, which is the estimate of the total number of lakes in the target population. Of the 44 lakes modeled, six are also intensively studied monitoring sites of the Adirondack Long-Term Monitoring (ALTM) program, which have monthly water chemistry data over the interval 1982 to 2005 or 1992 to 2005 [Driscoll *et al.*, 2003]. Five of these ALTM sites have average ANC less than 50  $\mu\text{eq/L}$ . The other 38 EMAP sites only have 1 to 8 measurements of water chemistry that were collected during the summer and fall within the period 1984 to 2003. The hydraulic residence times of the lakes were determined by estimated lake volumes divided by model-calculated discharge to the lakes.

[7] The modeling results from the ALTM and EMAP sites complement and inform one another. The detailed time series of ALTM lakes provide a good test and improved understanding of how well the model simulates seasonal and long-term patterns of lake chemistry, and therefore increases confidence in model performance for the other EMAP lakes with limited water chemistry data. Model results from the EMAP can be used to make population-level predictions of the regional response to changes in acidic deposition. These results are valuable because the EMAP population of lakes is more sensitive to acidic deposition than the previous regional study conducted for the DDRP sites because of the smaller size of the target lake population (i.e., minimum lake area of 1 versus 4 ha) [Sullivan *et al.*, 2006b], and therefore should be more indicative of the response of the Adirondack region to air pollution disturbance. Finally, this modeling study was conducted in conjunction with a detailed soil survey [Sullivan *et al.*, 2006a]. Data from this soil survey enabled us to obtain many independent parameter values for the model application.

## 2.3. Model Inputs

### 2.3.1. Wet and Dry Deposition

[8] Estimates of monthly deposition for all major solutes (i.e., Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) are used in the model starting from the year 1000 A.D. The recent monthly wet deposition fluxes of these species were derived from measured precipitation amount and volume-weighted concentrations at the Huntington Forest, which has been a National Acidic Deposition Program monitoring site since 1978. Wet deposition data prior to 1978 were reconstructed based on historical emissions for the Adirondack source region described by Driscoll *et al.* [2001], assuming values for background deposition based on measurements in remote areas [Gbondo-Tugbawa *et al.*, 2002; Gbondo-Tugbawa and Driscoll, 2003]. The amount of precipitation at the center of each modeled watershed was calculated for each site from a spatial model developed by Ito *et al.* [2002]. Two spatial models were used to obtain estimates of annual average atmospheric deposition for each EMAP site. Sulfate, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> annual concentrations in precipitation across the sites were derived from the model developed by Ito *et al.* [2002]; the annual concentrations of other species were obtained from the model developed by Ollinger *et al.* [1993]. These spatial



**Figure 2.** Comparison of measured and simulated average  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+} + \text{Mg}^{2+}$ , ANC, calculated alkalinity (CALK), pH, and dissolved organic carbon (DOC) values for each of the 44 EMAP sites. For a given year, annual volume-weighted concentrations are compared with measured values (generally collected during late summer or early fall). The observations shown are the mean value for years when measured values are available.

data were scaled to values from the Huntington Forest in order to develop a deposition time series for all EMAP sites. It was assumed that the deposition time series for the EMAP sites were proportional to values at the Huntington Forest. By multiplying precipitation quantity estimates times estimates of ion concentrations in precipitation, wet deposition estimates were obtained for each study site.

[9] PnET-BGC utilizes dry deposition data in the form of dry to wet deposition ratios for each element. For the base cations,  $\text{NH}_4^+$  and  $\text{Cl}^-$ , a uniform ratio for each species was obtained from experimental data at the Huntington Forest [Shepard *et al.*, 1989]. The spatial model developed by Ollinger *et al.* [1993] was used to obtain values of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  dry to wet deposition ratios. Downing *et al.* [1995] and Palmer *et al.* [2004] indicated that decreases in dry S deposition in recent years have occurred at a faster rate than decreases in wet deposition in response to declines in  $\text{SO}_2$  emissions. Therefore time-variable dry to wet deposition ratios for S deposition at Huntington Forest were

used in this study [Chen and Driscoll, 2004]. On the basis of these ratios, the model of Ollinger *et al.* [1993] was used to estimate dry deposition of S at the study sites. Coniferous forest cover enhances dry S deposition to a watershed [Cronan, 1985]. Therefore the enhanced collections of dry S deposition under coniferous and mixed forests were also considered [Chen and Driscoll, 2004].

### 2.3.2. Climate Data

[10] Model inputs for climate are also monthly data starting from the year 1000 A.D., including minimum and maximum temperature, PAR (Photosynthesis Active Radiation), and the amount of precipitation. The monthly minimum and maximum temperature and precipitation amounts for each site were derived from the spatial model of Ito *et al.* [2002]. Solar radiation was derived from a regional regression model developed by Aber and Freuder [2000].

### 2.3.3. Soil and Vegetation Parameters

[11] Soil parameters in the model were held constant through the model runs. Soil mass was calculated according

**Table 1.** Summary of Measured (1984–2003) and Simulated Water Concentrations and Model Performance for Lake Concentrations Based on 169 Measurements in 38 Lakes<sup>a</sup>

Lake Constituent	Measured		Simulated		Model Performance	
	Mean	Standard Deviation	Mean	Standard Deviation	NME	NMAE
SO <sub>4</sub> <sup>2-</sup>	81.6	23.1	77.9	16.3	-0.05	0.18
Mg <sup>2+</sup>	30.1	15.8	33.9	17.3	0.13	0.21
Ca <sup>2+</sup>	83.5	43.5	83.3	44.2	-0.002	0.14
ANC	33.7	49.3	45.2	49.0	0.34	0.48
CALK	50.4	56.6	46.4	53.2	-0.08	0.32
pH	5.86	0.78	5.90	0.76	0.007	0.03
DOC	470	282	433	209	-0.08	0.23

<sup>a</sup>Values are expressed as  $\mu\text{eq/L}$ , except pH and DOC ( $\mu\text{mol C/L}$ ). CALK refers to calculated alkalinity ( $\text{CALK} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+} - \text{SO}_4^{2-} - \text{NO}_3^{-} - \text{Cl}^{-}$ , where individual solute concentrations are expressed as  $\mu\text{eq/L}$ ). NME is normalized mean error; NMAE is normalized mean absolute error.

to the equation from Adams [1973], using measurements of percentage loss on ignition and estimated soil depth (0.5 m was used for all sites). The Gaines-Thomas formulation [White and Zelazny, 1986] was used to calculate cation exchange coefficients using measured soil chemistry data and lake water chemistry as a surrogate for soil solutions. Soil SO<sub>4</sub><sup>2-</sup> adsorption was depicted using a pH-dependent isotherm [Gbondon-Tugbawa *et al.*, 2001]. Water holding capacity was set to 12 cm for all sites, following the research of Ollinger *et al.* [1998].

[12] There are four sets of parameters corresponding to four types of vegetation: northern hardwood, spruce-fir, red maple-red oak mixture, and pine [Aber *et al.*, 1997]. The parameters for the dominant vegetation type were used for each site. Land cover data were obtained for each watershed through a geographic information system (GIS) data layer for the region [Sullivan *et al.*, 2006b].

### 2.3.4. Land Disturbance History

[13] Land disturbance history was incorporated into historical simulations. This information was largely obtained from a 1916 land cover map, information on major blow down events, and historical records of disturbance [McNeil *et al.*, 2006]. Although there is considerable uncertainty, a land disturbance history was developed for each watershed. In general, there was widespread forest disturbance from logging and fire around 1900 and forest blowdown from a large storm in 1950 [Sullivan *et al.*, 1999].

### 2.3.5. Model Calibration and Application

[14] The EMAP watersheds were assumed to be homogeneous. The model runs were started in 1000 A.D. and run under constant background deposition and no land disturbance until 1850 to achieve steady state. Changes in atmospheric deposition and land disturbance events were initiated after 1850. PnET-BGC was initially applied to the ALTM sites where detailed time series data were available. This time series of lake chemistry data provided a good opportunity to evaluate model performance. All model inputs, and vegetation, soil and hydrologic parameters were either directly available for model application or could be derived or estimated from field data or values in the literature, with the exception of element mineral weathering rates. Element mineral weathering rates were determined for each site through model calibration and held constant for model simulations.

### 2.3.6. Metric of Model Performance

[15] Two statistical indicators [Janssen and Heuberger, 1995] were used to evaluate model performance:

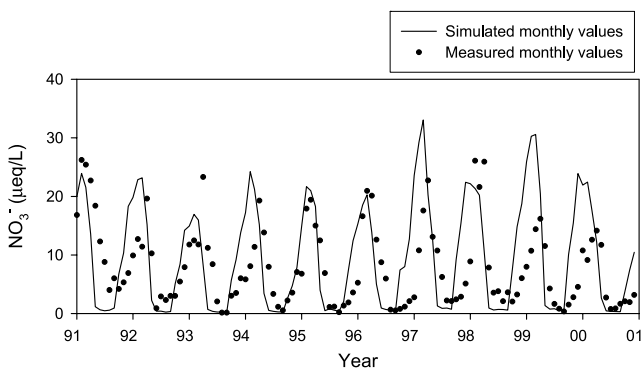
$$\text{NME} = \frac{\bar{P} - \bar{O}}{\bar{O}} \quad \text{NMAE} = \frac{\sum_{i=1}^n (|P_i - O_i|)}{n|\bar{O}|},$$

where NME is the normalized mean error, NMAE is the normalized mean absolute error,  $\bar{P}$  and  $\bar{O}$  are the mean predicted and observed values, respectively,  $P_i$  and  $O_i$  are the predicted and observed values at time  $i$ , respectively. NME provides a comparison of the predictions and observations on an average basis, and gives an indication of overestimation ( $\text{NME} > 0$ ) or underestimation ( $\text{NME} < 0$ ) of simulations. NMAE is an absolute indicator for discrepancy between model predictions and observations. The smaller the value, the closer model simulations are to measured values.

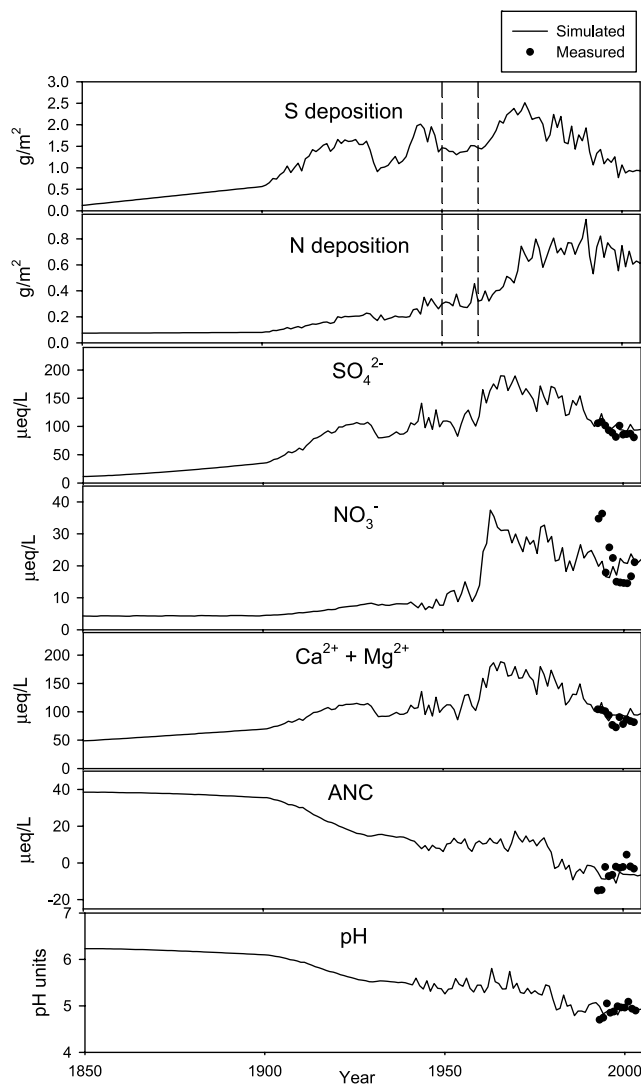
## 3. Results and Discussion

### 3.1. Model Performance

[16] The average concentrations of all measurements for each site were compared with the corresponding simulated concentrations (Figure 2 and Table 1). The measured and



**Figure 3.** Measured and simulated monthly NO<sub>3</sub><sup>-</sup> concentrations for Arbutus Pond from January 1991 to December 2000.



**Figure 4.** Estimates of atmospheric S and N deposition and simulated annual volume-weighted concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+} + \text{Mg}^{2+}$ , ANC, and pH at Indian Lake during 1850–2005. Measured annual volume-weighted values from the Adirondack Long-Term Monitoring (ALTM) program are shown for comparison. Also shown are vertical dashed lines that indicate the timing of land disturbance events, a minor blowdown in 1950 and a heavy selective logging in 1960.

simulated  $\text{SO}_4^{2-}$  concentrations had similar mean values (81.6  $\mu\text{eq/L}$  versus 77.9  $\mu\text{eq/L}$ ). However, there were considerable differences between measured and modeled values for some lakes (i.e., a relatively large departure from the 1:1 line in Figure 2). This deviation may be caused in part by high variability in S deposition. It is difficult to capture actual deposition for an individual site by a simple empirical deposition model. In addition, in-lake S retention, wetland S retention, and soil  $\text{SO}_4^{2-}$  adsorption algorithms in the model likely greatly simplify actual watershed S dynamics. The simulated base cation concentrations, pH and calculated alkalinity (CALK) generally agree well with measured data. We define CALK ( $\mu\text{eq/L}$ ) as the sum of base cations ( $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+$ ) less the sum of strong

acid anions ( $\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-$ ). The model also simulates ANC based on pH, concentrations of dissolved inorganic carbon, and species of naturally occurring organic anions and Al [Gbondo-Tugbawa et al., 2001]. The simulated ANC was slightly overestimated by the model (Table 1). This deviation may be caused by underestimated dissolved organic carbon (DOC) and overestimated monomeric aluminum ( $\text{Al}_m$ ) values. The simulated DOC concentrations agreed well with measured data at lower concentrations (below 600  $\mu\text{mol C/L}$ ), but underestimated DOC at higher values.

[17] Most modeled sites had limited observed data (i.e., a few measurements during summer and fall). The annual volume-weighted concentrations simulated from the model were used to compare with the observed data. In general, measured concentrations of the sum of base cations, pH and ANC values in Adirondack lakes are highest during the low-flow summer and autumn seasons, and lowest during spring snowmelt [Driscoll and van Dreason, 1993]. Using sparse measured concentrations for the summer and autumn seasons as representative of the annual concentrations may bias model results for individual lakes. Measured lake  $\text{SO}_4^{2-}$  concentration show little seasonal variation. In contrast,  $\text{NO}_3^-$  concentrations generally exhibit a distinct seasonal pattern [Driscoll and van Dreason, 1993]. During summer and autumn,  $\text{NO}_3^-$  concentrations are low because of plant uptake and denitrification. Both the measured and the model-simulated monthly  $\text{NO}_3^-$  concentrations for Arbutus Pond, for example, show considerable seasonal variation (Figure 3). The simulated average annual volume-weighted  $\text{NO}_3^-$  concentration for the EMAP sites is 19.7  $\mu\text{eq/L}$ . The annual volume-weighted concentrations of  $\text{NO}_3^-$  for the intensively monitored ALTM sites are comparable to this value, but the observed  $\text{NO}_3^-$  concentrations were much lower in the EMAP lakes which were only sampled during summer and fall (mean  $\text{NO}_3^-$  3  $\mu\text{eq/L}$ ). Therefore the measured  $\text{NO}_3^-$  data for the non-intensively sampled EMAP sites are not a good indication of model performance for annual volume-weighted concentrations.

### 3.2. Historical Acidification

[18] The model-simulated long-term water chemistry for an EMAP site that is also an ALTM lake, Indian Lake, is shown in Figure 4. Model simulations suggest that annual volume-weighted  $\text{SO}_4^{2-}$  concentrations were low during preindustrial times ( $\sim 1850$ ; 11  $\mu\text{eq/L}$ ), then increased markedly in response to increases in emissions and deposition of S. Values peaked near 1970 (184  $\mu\text{eq/L}$ ), approximately 15 times greater than preindustrial values. By the year 2000, annual volume-weighted  $\text{SO}_4^{2-}$  concentrations in lake water had decreased by half (94  $\mu\text{eq/L}$ ) because of decreases in atmospheric S deposition associated with controls on  $\text{SO}_2$  emissions as a result of the Clean Air Act. Note, however, that lake  $\text{SO}_4^{2-}$  concentrations were still relatively high when compared with preindustrial levels. Simulated annual volume-weighted  $\text{NO}_3^-$  concentrations in lake water were also low in 1850 (4  $\mu\text{eq/L}$ ). Values increased slightly by 1950. Because of the blowdown event in 1950 and heavy selective logging during the 1960s, combined with increased  $\text{NO}_x$  emissions and deposition, annual volume-weighted  $\text{NO}_3^-$  concentrations in this lake increased markedly since the 1950s. There was a decrease in lake water  $\text{NO}_3^-$  after 1980, perhaps because of recovery

**Table 2.** Model-Simulated Median Concentrations and the Quartile Values for Lake Chemistry and Soil Percent Base Saturation at the 44 EMAP Sites for Preindustrial Time and Current Measured Values<sup>a</sup>

	Preindustrial Time (1850)			Current Time (Measured)		
	Median	25th Percentile	75th Percentile	Median	25th Percentile	75th Percentile
SO <sub>4</sub> <sup>2-</sup>	15.9	13.4	18.8	88.8	76.2	97.8
NO <sub>3</sub> <sup>-</sup>	3.8	2.6	5.0	20.0 <sup>b</sup>	11.0	27.9
pH	6.63	6.00	6.93	5.95	5.29	6.45
ANC	67.7	51.0	91.4	27.8	2.4	55.1
Soil percent BS	12.3	10.1	14.6	7.9 <sup>c</sup>	6.3	9.9

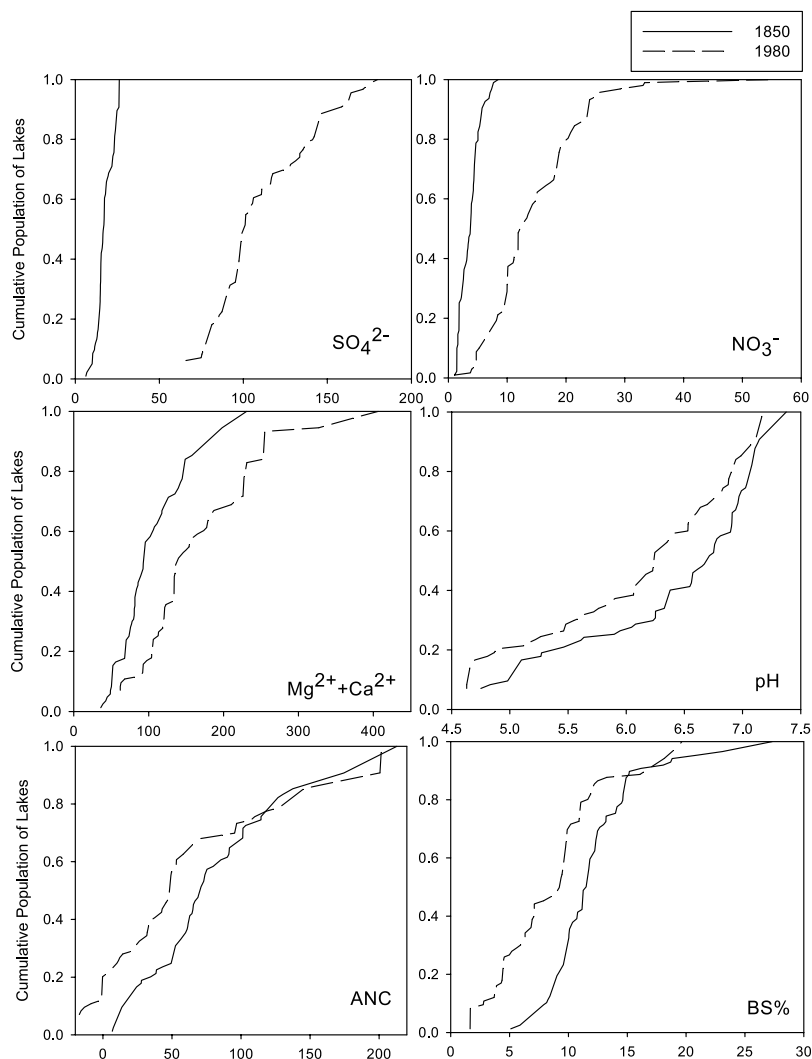
<sup>a</sup>Values are expressed as  $\mu\text{eq/L}$ , except pH and percent BS.

<sup>b</sup>Measurements are for the six ALTM sites.

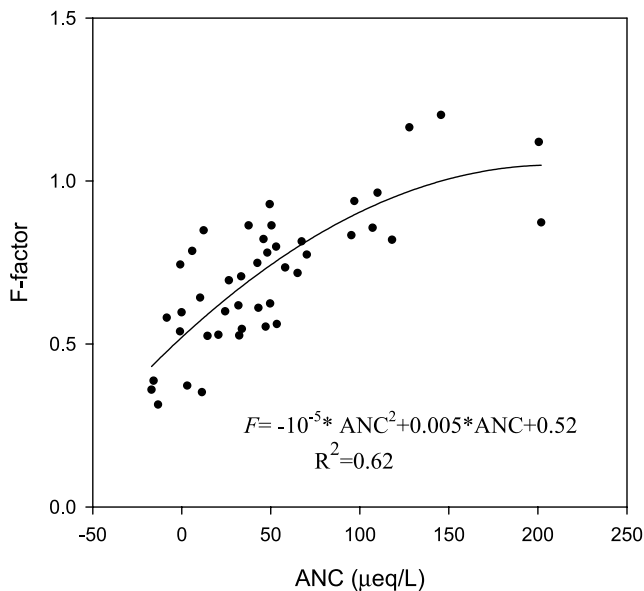
<sup>c</sup>Median and quartile values are presented for measurements during summer 2003; other values for current time are presented as median and quartile values of all measurements for each site.

following the disturbances of the previous decades. Simulated annual volume-weighted concentrations of divalent cations (i.e., Ca<sup>2+</sup> + Mg<sup>2+</sup>) were relatively low in 1850 (50  $\mu\text{eq/L}$ ). With increasing concentrations of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in Indian Lake, there were marked increases in model-simulated values of lake Ca<sup>2+</sup> + Mg<sup>2+</sup>. The annual volume-weighted

ANC and pH values of Indian Lake in 1850 were estimated to be about 38  $\mu\text{eq/L}$  and 6.2, respectively, but decreased throughout most of the 20th century. By 1980, the simulated annual volume-weighted ANC and pH values had declined to about 6  $\mu\text{eq/L}$  and 5.1, respectively. Although the model calculated annual volume-weighted concentrations



**Figure 5.** Comparison of the cumulative distribution of model-simulated lake water chemistry and soil percent BS in 1850 and 1980 for the population of Adirondack lakes. ANC and ion concentrations are expressed in  $\mu\text{eq/L}$ .



**Figure 6.**  $F$  factors calculated from model results for the period 1850–1980 as a function of simulated ANC in 1980 for the 44 EMAP sites in the Adirondack region of New York.

of  $\text{SO}_4^{2-} + \text{NO}_3^-$  decreased between 1980 and 2000,  $\text{Ca}^{2+} + \text{Mg}^{2+}$  coincidentally decreased by nearly an equivalent concentration, resulting in little change in ANC and pH values. In general, model predictions of the time series of water chemistry of Indian Lake followed the measured values. Note, however, that the model greatly underpredicted the first 2 years (a) (i.e., 1993–1994) of observed annual volume-weighted  $\text{NO}_3^-$  concentrations and as a result over-predicted ANC and pH values.

[19] Lake concentrations of strong acid anions were relatively low, and pH, ANC and soil percent base saturation (BS) values were higher in the Adirondacks during preindustrial times as compared with more recent values (Table 2). We made population estimates by extrapolating the results of model simulations for the 44 EMAP lakes to the whole population of low-ANC lakes in the region (1320 lakes greater than 1 ha;  $\text{ANC} \leq 200 \mu\text{eq/L}$ ). Comparison of the cumulative distribution of model-simulated lake water concentrations and soil percent BS in 1850 and 1980 is shown in Figure 5. The results suggest that  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and base cation concentrations in preindustrial times were much lower than current values. In 1850,  $\text{SO}_4^{2-}$  concentrations in all lakes were less than  $25 \mu\text{eq/L}$ , and the median value was about  $15 \mu\text{eq/L}$ . These preindustrial  $\text{SO}_4^{2-}$  concentrations agree with the estimate of  $13 \mu\text{eq/L}$  for lakes in the Adirondacks by Sullivan [2000]. By 1980, the median  $\text{SO}_4^{2-}$  concentration had increased to about  $100 \mu\text{eq/L}$ . Lake  $\text{NO}_3^-$  concentrations also increased markedly, with the median value increasing from about  $4 \mu\text{eq/L}$  in 1850 to  $12 \mu\text{eq/L}$  in 1980. The increases for the sum of divalent base cation concentrations were less than the increases for  $\text{SO}_4^{2-}$  concentrations, with the median value increasing from  $93 \mu\text{eq/L}$  in 1850 to  $140 \mu\text{eq/L}$  in 1980. This large change in  $\text{SO}_4^{2-} + \text{NO}_3^-$  relative to the sum of base cation concentrations is the major mechanism driving the decrease of ANC and pH associated with acidic deposition.

[20] Simulated lake water ANC and pH, and soil percent BS, decreased from preindustrial conditions to present. The median value for ANC decreased from about  $70 \mu\text{eq/L}$  in 1850 to  $50 \mu\text{eq/L}$  in 1980. Note, however, there were more lakes in 1980 with simulated ANC values greater than  $120 \mu\text{eq/L}$  than there were in 1850. This counterintuitive pattern was realized through model simulations for sites with relatively high ANC values. Some of these lakes were apparently not acidified by increased acidic deposition, but rather ANC values increased from preindustrial conditions. For these sites (three lakes that represent 175 lakes in the population), the base cation concentrations were all high. The simulated  $\text{Ca}^{2+}$  concentrations for these lakes in 1980 were all greater than  $180 \mu\text{eq/L}$ , with the highest value greater than  $300 \mu\text{eq/L}$ . This simulated alkalization phenomenon is consistent with the theory proposed by Kilham [1982]. These three lakes all have relatively large hydraulic retention times (i.e.,  $> 0.5 \text{ y}$ ). Inputs of acidic deposition to these relatively base-rich watersheds likely result in a stoichiometric increase in the sum of basic cation concentrations. The subsequent retention of some of the deposited  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in the lakes results in net production of ANC associated with historical inputs of acidic deposition.

[21] The population median value for pH decreased from 6.7 in 1850 to 6.2 in 1980. About 27% of the population of lakes had pH less than 6.0 in 1850, and 38% had pH less than 6.0 in 1980. The median value for B horizon soil percent BS of the study watersheds decreased from 11.5% to 9.2%. About 25% of the population of lake watersheds had soil percent BS less than 10% in 1850, and 70% had soil percent BS less than 10% in 1980. These data suggest that the acidic deposition following the Industrial Revolution caused widespread acidification of both soil and surface waters in the Adirondack region.

### 3.3. Comparison With a Paleolimnological Study

[22] It is difficult to quantify historical changes in water chemistry in response to acidic deposition because direct long-term observations only extend back to the 1970s and 1980s, while the acidic deposition originated more than a century earlier. Fortunately, paleoecological techniques provide a reliable method to estimate historical chemical changes [Charles and Norton, 1986]. Paleolimnological reconstructions of past lake water chemistry are based on transfer functions derived from relationships between current chemistry and diatom or chrysophyte remains in lake surface sediments [Charles and Norton, 1986]. Paleoecological studies in the Adirondack region have shown that most lakes that are currently acidic have been acidified since preindustrial times [Del Prete and Schofield, 1981; Charles and Norton, 1986; Cumming et al., 1994].

[23] The  $F$  factor is defined as the proportional change in the sum of base cations relative to the change in the sum of strong acid anions in surface waters impacted by acidic deposition [Sullivan et al., 1990]:

$$F = \frac{\Delta C_B / \Delta C_A}{(\Delta [\text{Na}^+ + \text{Mg}^{2+} + \text{K}^+ + \text{Ca}^{2+}]) / (\Delta [\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-])}$$

where ion concentrations are expressed in  $\mu\text{eq/L}$ . An  $F$  factor equal to 1 indicates that there is an equivalent change in concentration of the sum of base cations ( $\Delta C_B$ ) with a

unit change in the concentration of the sum of strong acid anions ( $\Delta C_A$ ), resulting in no change in ANC. A  $F$  factor less than 1 shows that a unit increase in the concentration of strong acid anions will result in some decrease in ANC, with the largest ANC reductions occurring in lake watersheds with the lowest  $F$  factors. The  $F$  factors were calculated from the model results for preindustrial time [1850] and the year 1980 for the 44 EMAP lakes (Figure 6). Earlier research has suggested that  $F$  factors should be less than 0.4 for acid-sensitive lake watersheds [Sullivan *et al.*, 1990]. However, on the basis of model results,  $F$  factors for the EMAP lakes were calculated to be in the range of 0.3 to 1.2, with a mean value of 0.7. Our analysis suggests that the  $F$  factors across the EMAP lakes generally increase with lake ANC values.  $F$  factors above 1.0 occurred in the three EMAP lakes experiencing the alkalization phenomenon. The relatively high values of  $F$  factor reported here are similar to results obtained from a paleolimnological analysis of 48 Adirondack lakes by Sullivan *et al.* [1990], which had values ranging from 0.5 to above 1.0. These relatively high  $F$  factors indicate that watershed and in-lake processes play important roles in neutralizing acidic atmospheric deposition [Sullivan *et al.*, 1990]. The high  $F$  factors and the close correspondence between changes of lake water base cation and strong acid anion concentrations suggest that the base cation supply is critical in neutralizing the inputs of strong acids, and the elevated inputs of strong acids could deplete exchangeable soil pools of nutrient cations over time, ultimately limiting recovery following reductions in acid emissions and deposition [Driscoll *et al.*, 1998, 2001].

#### 4. Conclusions

[24] 1. In this study, the PnET-BGC model was applied to 44 EMAP sites in the Adirondack region of New York, including both intensively monitored sites (six ALTM sites) and sparsely monitored sites (38 other EMAP sites). The model simulations generally captured the trends of annual solute concentrations in lake water for the ALTM sites. The model also generally calibrated well for the sites with sparse monitoring data.

[25] 2. Simulation results showed that lake water concentrations of strong acid anions (i.e.,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ), and base cations were relatively low, and pH and ANC values were higher during preindustrial times ( $\sim 1850$ ) compared to current conditions. The B horizon soil base saturation of the lake watersheds also decreased considerably over the past 150 a. These results indicate that acidic deposition has greatly altered soils and surface waters in the Adirondack region.

[26] 3.  $F$  factors for these sites were calculated based on the simulated data for preindustrial conditions and current time. Regional patterns of  $F$  factors agree with a previous paleolimnological study. The relatively high  $F$  factors suggest that the watershed and in-lake processes play important roles in neutralizing acidic atmospheric deposition inputs. The base cation supply is critical in neutralizing the inputs of strong acids, and the elevated inputs of strong acids could deplete soil pools of exchangeable nutrient cations.

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