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Responses of 20 lake-watersheds in the Adirondack region of New York to historical and potential future acidic deposition

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HIGHLIGHTS

- We calculated CLs and DCLs of sulfate (SO_4^{2-}) + nitrate (NO_3^-) for 20 lake-watersheds from the Adirondack region of New York.
- We evaluated lake water chemistry and biological species richness in response to historical and future acidic deposition scenarios.
- Fish and total zooplankton species richness is projected to increases under hypothetical decrease in future deposition.
- Model simulation also suggests that lake ecosystems will not achieve complete chemical and biological recovery in the future.

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ABSTRACT

Critical loads (CLs) and dynamic critical loads (DCLs) are important tools to guide the protection of ecosystems from air pollution. In order to quantify decreases in acidic deposition necessary to protect sensitive aquatic species, we calculated CLs and DCLs of sulfate (SO_4^{2-}) + nitrate (NO_3^-) for 20 lake-watersheds from the Adirondack region of New York using the dynamic model, PnET-BGC. We evaluated lake water chemistry and fish and total zooplankton species richness in response to historical acidic deposition and under future deposition scenarios. The model performed well in simulating measured chemistry of Adirondack lakes. Current deposition of SO_4^{2-} + NO_3^-, calcium (Ca^{2+}) weathering rate and lake acid neutralizing capacity (ANC) in 1850 were related to the extent of historical acidification (1850–2008). Changes in lake Al^{3+} concentrations since the onset of acidic deposition were also related to Ca^{2+} weathering rate and ANC in 1850. Lake ANC and fish and total zooplankton species richness were projected to increase under hypothetical decreases in future deposition. However, model projections suggest that lake ecosystems will not achieve complete chemical and biological recovery in the future.

1. Introduction

The soil and surface waters in the Adirondack region of New York have been impacted by high rates of acidic deposition due to inherently low supply of basic cations from soil, surficial deposits and bedrock (Driscoll et al., 1991). Recently ecosystems in the Adirondacks have started to recover in response to decreases in acidic deposition associated with the Clean Air Act and associated rules (Driscoll et al., 2007; Waller et al., 2012). However, the mobilization of sulfur (S) or nitrogen (N) previously retained in soil during elevated inputs of atmospheric deposition, and the loss of exchangeable base cations from soil have delayed recovery (Warby et al., 2009; Driscoll et al., 2001). It is important to evaluate the effectiveness of current emission control programs and provide quantitative information to policy makers to guide the additional decreases in NO_3^- and SO_4^{2-} deposition needed for complete recovery from acidification.

A critical load (CL) is a quantitative estimate of an exposure to one or more pollutants, such as sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+), below which significant harmful effects on specified sensitive elements of the ecosystem do not occur according to present knowledge (Nilsson and Grennfelt, 1988; Burns et al., 2008). Dynamic critical load (DCL) has been defined as "the level of exposure based on policy, economic, or temporal considerations" (Porter et al., 2005). CLs depict a steady-state condition, whereas DCLs represent dynamic conditions and reflect a system that is not at steady-state with respect to acidic deposition, but is changing over time.

The concept of CLs was developed through the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutant (LTAP) in Europe to improve understanding and dialog between European scientists and policymakers on ecosystem effects of

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air pollution (Driscoll et al., 2011). In response to the success of this dialog, CLs became an important element in the revision of the NO_x Protocol in December 1988. The first methods used to derive CLs were simple and largely based on (semi) empirical data. Following these efforts steady-state models such as the steady-state water chemistry method were used in the development of CLs (Kennedy et al., 2001). Recently, with interest in time-dependent processes and the effects of multiple pollutants, dynamic models such as the model of acidification and groundwater in catchments (MAGIC; Cosby et al., 1985) and photosynthesis net evapotranspiration–biogeochemical model (PnET-BGC; Wu and Driscoll, 2009) have been applied to calculate CLs. The dynamic biogeochemical model PnET-BGC has been successfully tested and widely applied in the northeastern U.S. (e.g., Zhai et al., 2008). It has been used to calculate CLs and DCLs for Hubbard Brook Experimental Forest, NH (Wu and Driscoll, 2009). However, CLs of NO_3^- and SO_4^{2-} deposition have not been calculated for the Adirondack region using PnET-BGC.

Acid deposition can affect fish, zooplankton and other biotic communities of lake ecosystems (Schindler et al., 1985; Bulger et al., 1999; Sullivan et al., 2006b; Lovett et al., 2009). Acid neutralizing capacity (ANC) is a commonly used chemical indicator of surface water acidification (Wu and Driscoll, 2009) for the calculation of CLs and DCLs because it is a chemically and biologically relevant robust measure of the acid–base status of waters, and models have been able to effectively simulate measured ANC values. Several critical values of ANC have been used for the calculation of CLs and DCLs, including 0, 20 and 50 μeq/L (USEPA, 2009; Blett et al., 2014). Biological indicators reflect the acid–base status of ecosystems through their response to chemical indicators. More importantly, biological indicators represent resources that resonate with the public. Fish and total zooplankton species richness decrease with decreases in ANC on the basis of spatial surveys (Sullivan et al., 2006a; Lovett et al., 2009). These empirical relations could be used to inform management decisions regarding changes in chemistry and biology of surface waters that occur in response to future changes in $SO_4^{2-} + NO_3^-$ deposition.

We used the dynamic model PnET-BGC to quantify historical acidification and project the future response of 20 lake-watersheds in the Adirondack region of New York due to changes in $SO_4^{2-} + NO_3^-$ deposition. Moreover, we determined the CLs and DCLs of $NO_3^- + SO_4^{2-}$ deposition needed to achieve target ANC values of Adirondack lakes; and we evaluated the application of biological indicators as a proxy to assess historical effects of acidic deposition and hypothetical future recovery.

2. Methods

2.1. Site description

We selected 20 lake watersheds from the Adirondack region of New York for analysis based on chemical and physical characteristics (Table 1). These sites were chosen as a subset of lakes from Adirondacks Long Term Monitoring Program (ALTM) (Driscoll et al., 2007). The 20 selected sites represented chronically acidic (ANC < 0 μeq/L; n = 5), episodically acidic (0 < ANC < 50 μeq/L; n = 11) and relative acid-insensitive lakes (ANC > 50 μeq/L; n = 4) based on lake sensitivity to acidification (Driscoll et al., 2001; USEPA, 2009). The 20 sites are also characteristic of a range of acid sensitivity based on lake-watershed classification derived from surficial geology — 11 drainage lakes are situated in watershed with thin deposits of glacial till, seven are medium till drainage lakes, one thick till drainage lake, and one seepage lake (Driscoll et al., 2003). The study sites encompass a range of watershed areas (1.5–186.9 ha), and elevation (421–743 m).

Lake water chemistry data are available through the Adirondack Long Term Monitoring Program (ALTM) (http://www.adirondacklakes.survey.org/). The ALTM provides monthly concentrations of major solutes (e.g., SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+}, ANC, pH). The program was initiated in 1983 with 17 lakes and expanded with the addition of 35 additional lakes in 1992. Two of the 20 sites selected for modeling (Arbutus Lake, Constable Pond) are from the original suite of lakes. Soil chemistry data are available for the modeling sites from a detailed survey of Adirondack watersheds (Sullivan et al., 2006a) and the measured soil base saturation data for the 20 sites was used for calibration. We prepared all required data for inputs, parameters and model testing.

2.2. PnET-BGC model

We used the dynamic biogeochemical model PnET-BGC to calculate CLs and DCLs of acidic deposition and assess historical and project potential future response of Adirondack lake ecosystems to changes in atmospheric deposition. PnET-BGC is a dynamic biogeochemical model that links a C, N and water cycling model PnET-CN (Aber et al., 1997) with a biogeochemical model BGC (Gbondo-Tugbawa and Driscoll, 2001). PnET-CN (Aber et al., 1997) is a lumped-parameter model that simulates net primary productivity and hydrology of forest ecosystems and the cycling and interactions of C and N. The BGC algorithm depicts

Table 1
Characteristics of 20 lakes in the Adirondack region of New York for which simulations were conducted.

Lake	Latitude	Longitude	Elevation (m)	Lake area (ha)	Mean ANC (meq/l)	ALSC lake class
Arbutus Lake	43.9877	74.2416	538	47.93	68.3	Medium till
Brook Trout Lake	43.5999	74.6624	725	28.70	2.5	Thin till
Bubb Lake	43.7708	74.8542	596	18	46.5	Thin till
Carry Pond	43.6816	74.4891	651	2.80	−5.9	Seepage
Clear Pond	44.4869	74.1603	520	40.01	102.6	Thick till
Constable Pond	43.8332	74.7958	693	21.30	−6.2	Thin till
Grass Pond	43.6903	75.0650	548	5.30	27.2	Medium till
Indian Lake	43.6163	74.7533	719	34.83	−4.4	Thin till
Jockeybush Lake	43.3022	74.5858	610	17.30	2.7	Thin till
Limekiln Lake	43.7133	74.8130	629	186.90	26.4	Medium till
Middle Branch Lake	43.6978	75.1022	517	17	52.9	Thin till
Middle Settlement Lake	43.6839	75.1000	547	15.80	9.6	Thin till
North Lake	43.5381	74.9269	674	178.01	3.2	Thin till
Queer Lake	43.8136	74.8069	610	54.50	11.4	Thin till
Raquette Lake	43.7950	74.6514	595	1.50	30.9	Medium till
Squash Pond	43.8263	74.8897	680	1.70	−25.0	Thin till
Sagamore Lake	43.7658	74.6286	743	68	38.9	Medium till
West Pond	43.8111	74.8792	592	8.90	8.0	Thin till
Willis Lake	43.3714	74.2463	421	14.60	65.6	Medium till
Willys Lake	43.9693	74.9547	640	22.93	−10.0	Thin till

Note: ALSC is the abbreviation for Adirondack Lakes Survey Corporation. DOC represented for dissolved organic carbon.

the dynamics of major elements in vegetation, soil and surface water. Together they provide a comprehensive model that simulates energy, water and major element balances, including both biotic and abiotic processes, in forest watershed ecosystems (Gbondo-Tugbawa et al., 2001). The model is capable of simulating N processes, although it is a challenge to depict the year-to-year dynamics due to the complexity of the transformation of this element and the sensitivity of N processes to variations in meteorological conditions (Pourmokhtarian et al., 2012). Intensive measures of N biogeochemical cycles such as net N mineralization, nitrification, foliar concentration and annual N leaching losses have been validated at the Hubbard Brook Experimental Forest (NH) and Harvard Forest (MA) (Aber et al., 1997).

Model input data include meteorological, atmospheric deposition, and land disturbance inputs and a variety of soil and vegetation parameters. Model output includes stores and monthly fluxes of water and fluxes for major elements in ecosystem compartments, and volume-weighted concentrations of major chemical species (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, NO_3^-, SO_4^{2-}, Cl^- dissolved organic carbon [DOC]) and ANC in lake water. More detailed information of the model structure can be found in Gbondo-Tugbawa et al. (2001) and Fakhraei et al. (2014).

2.3. Model data development and evaluation

The model was run on a monthly time step from 1000 AD to 2200 AD. Monthly values of atmospheric deposition of all major elements and meteorological data (minimum and maximum temperature, precipitation, solar radiation) were input for the entire simulation period. Reconstruction of historical conditions was conducted as described below.

Wet deposition has been monitored at Huntington Forest (HF) in the central Adirondacks (43° 58′ N, 74° 13′ W) since 1978 through the National Atmospheric Deposition Program (NADP; site NY20). Dry deposition has been estimated since 2002 through the Clean Air Status and Trends Network (CASTNet). Daily meteorological data (e.g., maximum, minimum air temperature and precipitation) are also available at this site since 1940, provided by State University of New York College of Environmental Science and Forestry (SUNY-ESF). Huntington Forest was chosen as a benchmark to estimate wet deposition for the Adirondack lake-watersheds to which we applied PnET-BGC.

Pre-industrial conditions (i.e., before 1850) were estimated from precipitation chemistry in remote areas (Galloway et al., 1983). The reconstruction of atmospheric wet deposition assumed a linear ramp from pre-industrial values in 1850 to estimated values in 1900. Estimates of wet deposition of major solutes for the historical period were based on historical emissions estimates. Linear regression models were developed between national emissions and measured concentrations in wet deposition at the NADP site for the years 1979–2008. These regression models were utilized to reconstruct historical (1900–1978) wet deposition for all the modeling sites based on historical U.S. emissions (Nizich et al., 1996; USEPA, 2012).

PnET-BGC estimates dry deposition of chemical constituents based on user inputs of dry to wet deposition ratios. Dry to wet deposition ratios for base cations, NH_4^+ and Cl^- were estimated from through fall studies at HF (Shepard et al., 1989). Since a consistent temporal trend was not observed in dry to wet S and N deposition ratios among CASTNET and nearby NADP sites in the northeastern US (http://epa.gov/castnet/javaweb/index.html), a constant dry to wet deposition ratio over time was assumed. Spatial patterns in dry to wet deposition for the SO_4^{2-} and NO_3^- were calculated based on spatial models developed by Ollinger et al. (1993) and modified by Chen and Driscoll (2004) to incorporate effects of forest composition (Cronan, 1985).

To extrapolate climatic drivers (i.e., temperature, precipitation) and wet deposition measured at HF to other study sites in the Adirondacks, the spatial regression models of Ito et al. (2002) and Ollinger et al. (1993) were used, based on meteorological data from the National Climatic Data Center (NCDC) and wet deposition data from the NADP (http://nadp.sws.uiuc.edu/) and NYSDEC (http://www.dec.ny.gov/chemical/8422.html) monitoring sites inside and near the Adirondack Park. Monthly solar radiation data were derived from a spatial model developed by Aber and Freuder (2000).

Land disturbance history was developed for each watershed from historical records of disturbance, including fire and logging prior to 1916, blow down events in 1950 and 1995 and an extensive ice storm in 1998. These data were obtained through Adirondack Park Agency geographical information system (GIS) data layers, ALSC website (http://www.adirondacklakessurvey.org/) and a written history by McMartin (1994).

To evaluate the agreement of simulations with measurements of stream chemistry, we used normalized mean error (NME) and normalized mean absolute error (NMAE) methods (Janssen and Heuberger, 1995). These metrics can be calculated as follows:

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

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. NME represents the error between simulation results and observations. NMAE represents the absolute error between simulation results and observations. Negative values for NME mean that the prediction values are less than observation values. Positive values for NME indicate that the prediction values are more than the observation values.

2.4. Projected future deposition scenarios for Adirondack lake-watersheds

We applied a series of scenarios to evaluate the response of Adirondack lake watersheds to hypothetical future decreases in acidic deposition. Using an acid-sensitive lake watershed, Jockeybush Lake, as an example (lake ANC = 2.7 μeq/L), we illustrate the hindcast and suite of forecast projections of atmospheric SO_4^{2-} + NO_3^- deposition, similar to the approach applied to all sites studied (Fig. 1(a)). The hindcast time series of SO_4^{2-} + NO_3^- deposition was developed using the approach described above (Section 2.2). The mean of SO_4^{2-} + NO_3^- deposition for 2004–2008 was used as an estimate of current deposition (Fig. 1(a)). From current deposition, we projected a suite of hypothetical future deposition scenarios that included a 12-year linear decrease from ambient deposition starting in 2008 to the level of deposition of interest in 2020. This deposition level was continued in the simulations until 2200. These deposition scenarios (0, 20, 40, 60, 80, 100% reductions) reflect 20% increments of the difference between ambient deposition of SO_4^{2-} + NO_3^- in 2008 and pre-industrial deposition (1850).

2.5. Estimates of CLs and DCLs of SO_4^{2-} + NO_3^- for Adirondack lake-watersheds

We chose the critical chemical values for ANC of 0, 20 and 50 μeq/L as targets for DCLs and CLs. These values have been used in prior calculation of CLs (Lien et al., 1996; USEPA, 2009). Initially the model was run for all scenarios of SO_4^{2-} + NO_3^- deposition for each of the study sites. Simulations showed that lake ANC increases as future SO_4^{2-} + NO_3^- deposition is decreased. Then, based on the six model projections for individual sites, lake ANC values were interpolated for a given year of interest to determine the load of SO_4^{2-} + NO_3^- necessary to achieve a target ANC of interest (i.e., 0, 20, 50 μeq/L). In some cases model calculations suggested that even under preindustrial deposition values the target ANC could not be achieved (discussed below). Using these extrapolated data for the 20 sites for a given year, linear regression analysis was conducted to establish relationships between current lake ANC and the deposition of SO_4^{2-} + NO_3^- to achieve a target ANC.

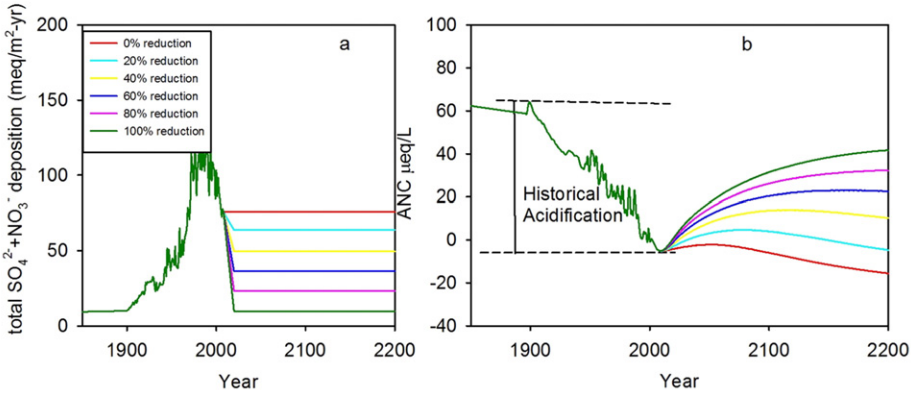

Fig. 1. Time series of (a) historical and hypothetical future deposition scenarios of $SO_4^{2-} + NO_3^-$ for Jockeybush Lake and (b) simulated ANC of Jockeybush Lake in response to changes in $SO_4^{2-} + NO_3^-$ deposition. For future projections, linear decreases are assumed between 2008 and 2020 from the present deposition to the deposition of interest (0, 20, 40, 60, 80, 100% decrease of current value). These future deposition scenarios range from the present deposition to historical deposition at 20% intervals. Deposition of $SO_4^{2-} + NO_3^-$ before 1850 or after 2020 is held constant for the model runs. The term — historical acidification is illustrated based on ANC change from pre-industrial conditions to the minimum ANC for the historical period.

2.6. Regression analysis

We define historical acidification (HA) as the change in simulated ANC from the pre-industrial value of 1850 to the lowest ANC value that occurred over the recent period (1990–2008). Historical acidification is illustrated in Fig. 1(b) for the hindcast for Jockeybush Lake. We examined changes in different lake-watershed classes of ANC and percent soil base saturation (%BS) as a result of historical acid deposition. We used linear regression analysis to explore the relationships for historical acidification with site specific factors including current $SO_4^{2-} + NO_3^-$ deposition, Ca^{2+} weathering rate, historical ANC, elevation, watershed area, and DOC.

2.7. Fish species and total zooplankton species richness

Projections of the chemical indicator ANC were used to evaluate the application of biological indicators (fish species and total zooplankton species richness) of acidification stress and to estimate the response of fish and total zooplankton species richness to changes in the past and future acidic deposition. A logistic relationship between fish species richness and ANC was developed based on the Adirondack Lakes Survey water chemistry and fish surveys conducted during the mid-1980s (Eq. (2); Lovett et al., 2009). A linear relationship between total zooplankton species richness and ANC was also developed based on datasets from three surveys: the U.S. EPA's Eastern Lakes Survey in 1986; EMAP during the period of 1991–1994; EPA Science to Achieve Results (STAR) during the period of 1999–2001 (Eq. (3)) (Sullivan et al., 2006b). These empirical relationships, together with simulated ANC values, were used to depict temporal responses of fish and zooplankton species richness to changes in atmospheric $SO_4^{2-} + NO_3^-$ deposition in the study lakes.

$$\text{Fish Species Richness} = 0.18 + \left[\frac{5.7}{1+\left(\frac{ANC}{28}\right)^{-1.63}}\right]\left(r^2 = 0.9\right) \quad (2)$$

$$\text{Zooplankton Species Richness} = 15.65 + 0.089ANC\left(r^2 = 0.46\right). \quad (3)$$

2.8. Sensitivity analysis

Sensitivity analyses have been previously conducted for PnET-BGC to quantify the relative response of model output variables to uncertainty in inputs or parameters of interest for applications of the model to watersheds in the Northeast (Aber et al., 1997; Gondo-Tugbawa et al., 2001; Pourmokhtarian et al., 2012; Fakhraei et al., 2014). These studies showed that biological processes depicted in the model are sensitive to meteorological inputs such as temperature, precipitation and solar radiation (Pourmokhtarian et al., 2012). Gondo-Tugbawa et al. (2001) conducted a detailed sensitivity analysis of projections of surface water ANC and soil base saturation to abiotic processes. They found that the model is particularly sensitive to soil partial pressure of CO_2, cation exchange capacity, soil mass and soil selectivity coefficients for Ca^{2+} and Al^{3+}.

3. Results

3.1. Model performance

Generally PnET-BGC was able to effectively simulate Adirondack lake chemistry data. The mean of simulated SO_4^{2-}, NO_3^-, divalent base cations (Ca^{2+}+Mg^{2+}), and ANC matched well with the mean of observed values for the 20 lakes for the period 1992 to 2008 (Fig. 2). The mean simulated SO_4^{2-} (94.0 ± 14.0 µeq/L) is similar to the mean observed SO_4^{2-} (95.7 ± 14.1 µeq/L; mean NME: −0.02) for the 20 sites. Simulated NO_3^- is somewhat overpredicted compared with observed values (Fig. 2). The discrepancy between measured NO_3^- (14.6 ± 7.9 µeq/L) and model-simulated NO_3^- (23.2 ± 8.7 µeq/L; mean NME: 0.36) is greater than other solutes due to the challenges in simulation of lake-watershed N dynamics (van Grinsven et al., 1995; Pourmokhtarian et al., 2012). In particular,

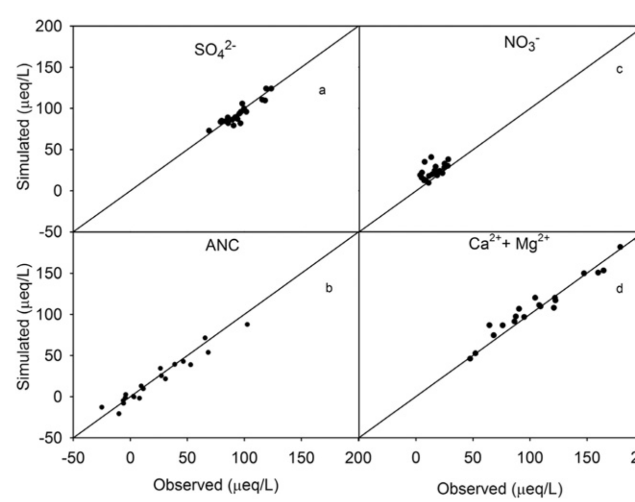

Fig. 2. Comparison of observed and simulated average of SO_4^{2-} (a), NO_3^- (b), ANC (c) and sum divalent base cations (Ca^{2+}+Mg^{2+}) (d) for 20 study lakes. The observed values are average of the measured annual data from ALTM from 1993 to the present. The simulated values are average of the annual simulation data. A 1:1 line is shown.

projections of NO_3^- are sensitive to meteorological conditions and historical land disturbance. Uncertainty in these inputs for individual sites likely contributes to errors in simulations of lake NO_3^-. The mean simulated sum of divalent base cations (112.4 ± 57.2 μeq/L) for the 20 lakes matched well with the mean observed value (110.0 ± 40.7 μeq/L; mean NME: 0.03). Mean simulated ANC (19.5 ± 28.4 μeq/L) also agreed well with the mean observed value (21.9 ± 31.5 μeq/L; mean NME: −0.15). The mean simulated base saturation (11.3% ± 9.3%) was somewhat overestimated compared with the observed value (7.9% ± 3.3%; mean NME: 0.03).

3.2. Long-term simulations of the response of lake-watersheds to historical and potential future acidic deposition

Simulations of historical and hypothetical future deposition scenarios were made for the 20 Adirondack lake watersheds. Jockeybush Lake is used as an example to illustrate the time-series of lake ANC responses to historical acid deposition (1850–2008) and following hypothetical future deposition scenarios from 2008 to 2200 (Fig. 1). Around 1850, the ANC of Jockeybush Lake was estimated to be approximately 60 μeq/L. After about 1900, the ANC was simulated to decrease markedly with increases in atmospheric $SO_4^{2-} + NO_3^-$ deposition until 2008. The historical acidification for Jockeybush Lake was 61.2 μeq/L (i.e., ANC_{1850}–ANC_{2008}). After 2008, the suite of hypothetical scenarios of decreases in acidic deposition was invoked, ranging from 0 to 100%. Simulations of scenarios of marked decreases in deposition exhibited patterns of relatively rapid ANC increase shortly after the decrease in deposition was realized (2020), with the rate of ANC increase decreasing over time. The simulations reached steady-state with respect to the new lower deposition approximately by 2200. Under the scenario of a 100% decrease in $SO_4^{2-} + NO_3^-$ deposition, the maximum ANC of 41.5 μeq/L was attained for Jockeybush Lake, a value considerably lower than the estimate of preindustrial ANC. This apparent hysteresis in the lake-watershed response to increases then decreases in $SO_4^{2-} + NO_3^-$ deposition is attributed to the loss of exchangeable Ca^{2+} and Mg^{2+} from soil during the historical period of elevated deposition. Note, soil base saturation is projected to increase somewhat (Fig. 3) in response to the decreases in $SO_4^{2-} + NO_3^-$ deposition. Under the lower deposition reduction scenarios (0, 20% decreases) following a period (several decades) of increases in ANC, a long-term decline in ANC was simulated due to the maturation of forest stands and simulated long-term declines in lake-watershed retention of atmospheric N inputs due to approaching a condition of N saturation. Note that currently watersheds in the northeastern U.S. are generally not experiencing a condition of N saturation (Driscoll et al., 2003).

We evaluated the acid–base status of the 20 lake-watersheds under preindustrial conditions. Simulations of mean lake chemistry prior to 1850 were 14.8 ± 5.3 μeq/L for SO_4^{2-} and 3.8 ± 1.2 μeq/L for NO_3^- (Fig. 3). These values are considerably less than the current concentrations and illustrate the effect of historical atmospheric deposition on lake chemistry. Model hindcasts of the pre-industrial conditions suggested that none of the 20 study lakes were chronically acidic (ANC < 0 μeq/L). The mean pre-industrial ANC of the study sites was 77.0 ± 45.1 μeq/L (Fig. 3). All the lake-watersheds simulated decreases in ANC from pre-industrial to the current conditions, indicative of acidification associated with historical increases in acidic deposition. The mean of simulated ANC in 2200 increased from 27.8 ± 42.6 μeq/L under 0% reduction scenario to 71.9 ± 43.4 μeq/L under 100% reduction scenario. Soil base saturation exhibited a temporal pattern similar to that of lake ANC. The mean simulated base saturation under pre-industrial conditions was 23.0% ± 11.1% compared to the current simulated values of 11.3% ± 9.3% (Fig. 3). The mean of the simulated base saturation for the 0% reduction scenario and for the 100% reduction scenario in 2200 were 9.5% ± 6.7% and 18.7% ± 10.0%, respectively.

3.3. Historical acidification

There was variation among sites in the calculated values of historical acidification, ranging from 26.0 μeq/L to 100.4 μeq/L. We observed that higher ambient $SO_4^{2-} + NO_3^-$ deposition (2008; $r^2 = 0.30$), Ca^{2+} weathering rate ($r^2 = 0.42$), and pre-industrial ANC ($r^2 = 0.44$) (Fig. 4) leads to higher simulated historical acidification for lake-

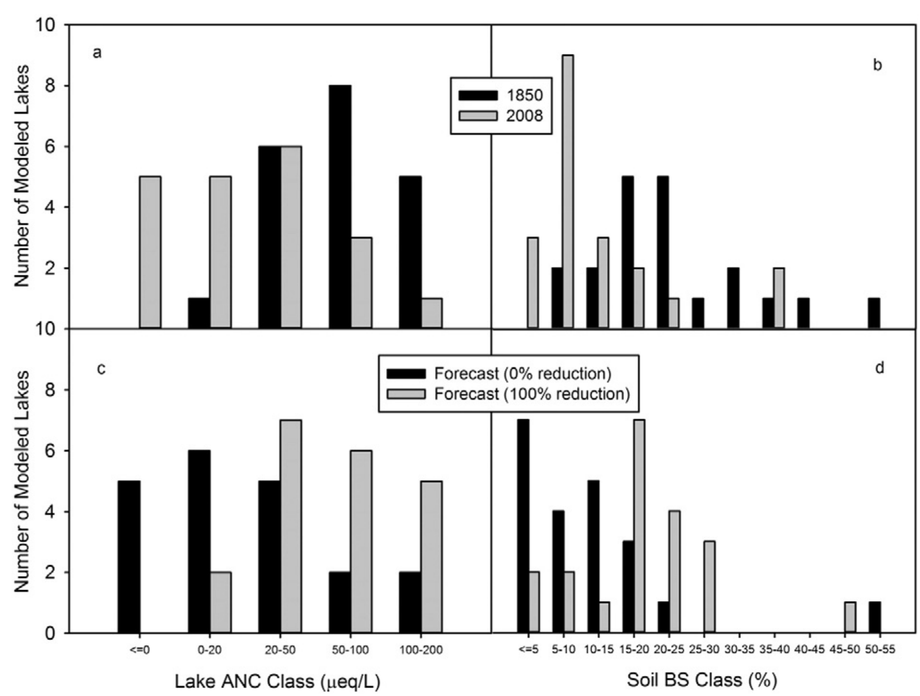

Fig. 3. Comparison of the distribution of simulated ANC (a) and percent base saturation (b) classes in 1850 and 2008; comparison of simulated ANC and base saturation for the 0% reduction scenario (c) and the 100% reduction scenario (d) in 2200 for the 20 study lakes. The x-axis is ANC class or percent soil base saturation class at 5% intervals. The y-axis is the number of lakes within ANC and BS% classes.

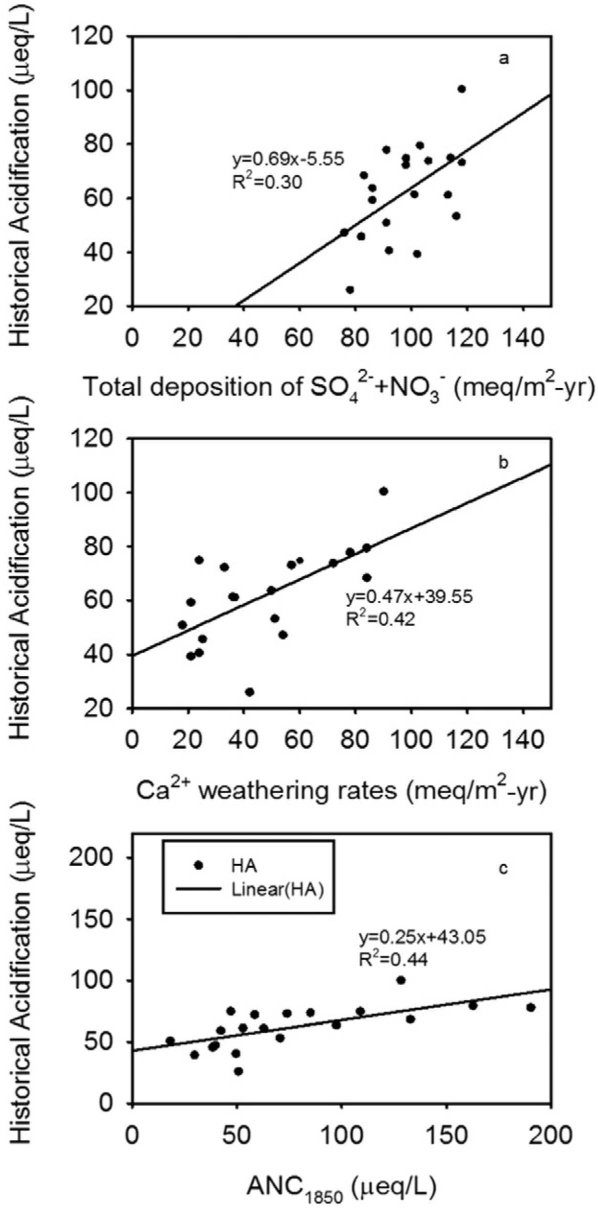

Fig. 4. Relationships between historical acidification and (a) current total deposition of (SO_4^{2-} + NO_3^-), (b) Ca weathering rate, and (c) historical ANC (1850) for simulated sites. Note that historical acidification is lake ANC loss between ANC in 1850 and the lowest ANC that occurred over the recent period (1990–2008).

watersheds. Ca^{2+} weathering rate can compensate for inputs of SO_4^{2-} or NO_3^- and mitigate acidification. Sites with higher preindustrial ANC can more effectively neutralize acidic deposition than sites with inherently lower ANC. The apparently counterintuitive response of historical acidification with Ca^{2+} weathering rate and pre-industrial ANC is due to increases in concentrations Al^{3+} with acidification of the most sensitive watersheds Aluminum is an important pH buffer. We found negative relationships between the increase in surface water Al^{3+} from the current period and preindustrial conditions (i.e., historical Al^{3+} mobilization) and Ca^{2+} weathering rates (ΔAl^{3+}(μeq/L) = −0.62[Ca^{2+} weathering rates](meq/m² - yr) + 45.50; r^2 = 0.18) and pre-industrial ANC (ΔAl^{3+}(μeq/L) = −0.31[preindustrail ANC](μeq/L) + 39.91; r^2 = 0.18). So enhanced mobilization of Al^{3+} from soil to surface waters is an important mechanism neutralizing acidic deposition in the most acid-sensitive watersheds.

3.4. DCLs and CLs of SO_4^{2-} and NO_3^- deposition

We calculated the load of SO_4^{2-} + NO_3^- needed to achieve target ANC values of 0, 20 and 50 μeq/L for 2 years: 2040, representing a DCL (over the shorter term) and 2200, representing the CL, or an approximate steady-state condition. We observed that in general higher inputs of SO_4^{2-} + NO_3^- deposition are required for less sensitive ecosystems to achieve the same target ANC values by a future date (Fig. 5).

We are particularly interested in lakes with current ANC less than target ANC values. The DCLs of SO_4^{2-} + NO_3^- deposition for 2040 ranged from 0 to 42 meq/m²-yr to achieve ANC of 0 μeq/L for five sites with current ANC < 0 μeq/L (Fig. 5). Two lakes are projected to achieve ANC > 0 μeq/L, while three lakes are projected to not reach the target. The DCLs of SO_4^{2-} + NO_3^- deposition ranged from 0 to 51 meq/m²-yr to achieve ANC of 20 μeq/L for 11 sites with current ANC < 20 μeq/L. Two lakes are projected to achieve ANC > 20 μeq/L, while nine lakes will not reach the target. Finally, the DCLs of SO_4^{2-} + NO_3^- deposition ranged from 0 to 35 meq/m²-yr to achieve ANC of 50 μeq/L for 16 sites with current ANC < 50 μeq/L. Two lakes are projected to achieve ANC > 50 μeq/L and 14 lakes will not reach the target by 2040.

The CLs of SO_4^{2-} + NO_3^- deposition ranged from 41 to 62 meq/m²-yr for the five sites with current ANC < 0 μeq/L to achieve ANC of 0 μeq/L (all these lakes will achieve ANC > 0 μeq/L); 0–83 meq/m²-yr for the 11 sites with current ANC < 20 μeq/L to achieve ANC of 20 μeq/L (ten lakes will achieve ANC > 20 μeq/L), and 0–93 meq/m²-yr for the 16 sites with current ANC < 50 μeq/L to achieve ANC of 50 μeq/L (ten lakes will achieve the target ANC > 50 μeq/L) by 2200. Most of the sites are projected to achieve target ANCs (0, 20, or 50 μeq/L) by 2200.

Simulations indicate that lower DCL or CL will be needed to achieve higher target ANC (Fig. 5). Note, simulations indicate that some sites will not be able to reach target ANCs of 20 μeq/L or 50 μeq/L, even if

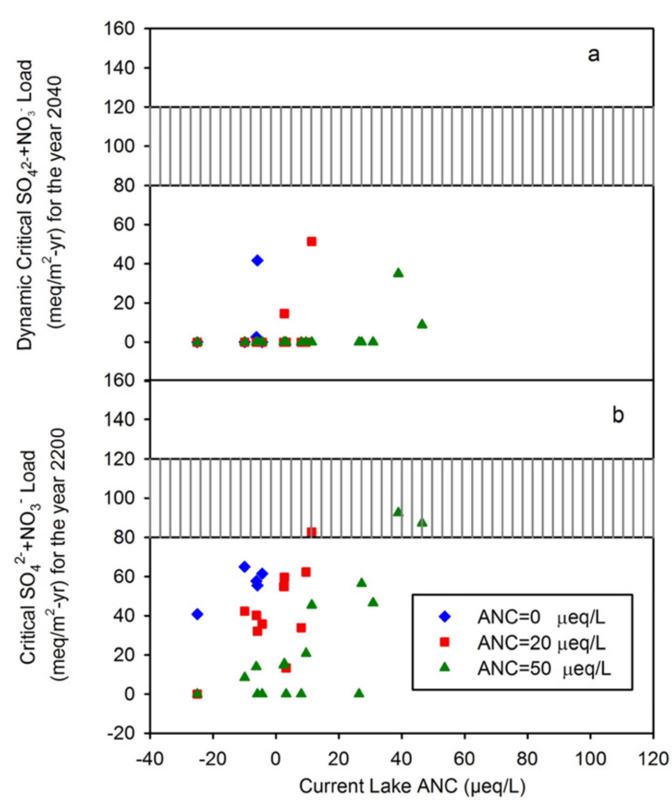

Fig. 5. Relationships between current lake ANC and total deposition of SO_4^{2-} + NO_3^- necessary to achieve target ANC of 0, 20 and 50 μeq/L in 2040 and 2200. Shaded areas represented current total deposition of SO_4^{2-} + NO_3^- for the Adirondacks from 80 meq/m²-yr to 120 meq/m²-yr.

atmospheric deposition decreased to pre-industrial conditions; some sites have DCL or CL values of 0 meq/m^2-yr (see Section 4 below).

3.5. Fish and total zooplankton species richness in response to changes in acidic deposition

Based on the empirical logistic relationship (Eq. (2)) and simulated ANC in 1850, estimated fish species richness in the 20 lakes under pre-industrial conditions ranged from 2.1 to 5.6 (mean 4.5) (ANC: 18 μeq/L to 163 μeq/L) and might have been present in all study lakes (Fig. 6a). From 1850 to the present, (shift from the blue line in Fig. 6 [pre-industrial conditions] to the red line [ambient conditions]) simulations suggest that Adirondack lakes lost fish species (to 0 to 5.3 species, mean 2.2) coincident with increases in acidic deposition (25% of study lakes are projected to be fishless under ambient conditions). Lakes could gain fish species under an aggressive future emissions reduction scenario of a 100% decrease, with a mean species richness of 4.3 by 2200, similar to pre-industrial conditions. In contrast, the scenario of no future change in acidic deposition from 2008 values suggests that there would be no apparent change in fish species richness from ambient conditions.

Analysis of total zooplankton species richness showed similar patterns. The mean of total zooplankton species richness for the study lakes decreased from 23.6 to 19.8 in response to historical increases in acidic deposition from 1850 to current conditions (Fig. 6b). Comparison of future projections for the 0% reduction scenario and the 100% reduction scenario also showed that total zooplankton species richness by 2200 would be 19.0 and 23.9, respectively.

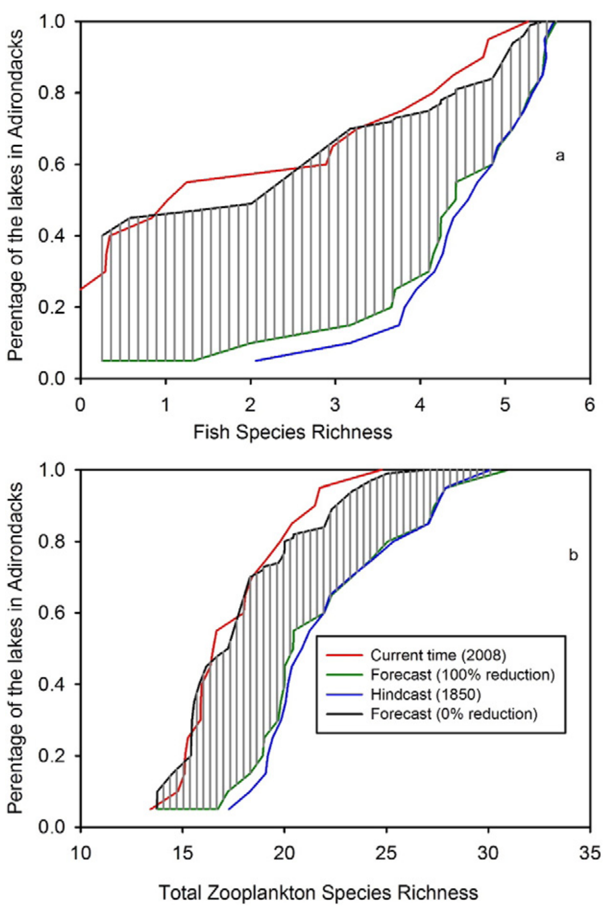

Fig. 6. Projections of cumulative distribution functions of species richness of aquatic biota for the 20 study lakes, including (a) fish species richness and (b) total zooplankton species richness developed from model estimated ANC and empirical relationships between aquatic species richness and lake water ANC. Results for four conditions are shown: pre-industrial (1850; blue), current (2008; red) and a range of future conditions in 2200. Shaded areas represent the range of species richness that could occur under two projected deposition scenarios: 0% reduction and 100% reduction of $SO_4^{2-} + NO_3^-$.

4. Discussion

4.1. DCLs and CLs of $SO_4^{2-} + NO_3^-$ deposition loading for the Adirondacks

Sullivan et al. (2012) calculated DCLs of SO_4^{2-} deposition using the model of acidification of groundwater in catchments (MAGIC) for two future dates (2050 and 2100) and three target ANC values (0, 20 and 50 μeq/L). It was estimated that about 30% of 600 Adirondack lakes having SO_4^{2-} deposition < 50 meq/m^2-yr would achieve an ANC of 50 μeq/L by 2100. Our study is not exactly comparable because we examined decreases in the combination of $SO_4^{2-} + NO_3^-$ deposition. Because NO_3^- is also an important atmospheric pollutant, we calculated CLs for both SO_4^{2-} and NO_3^-. The CLs of $SO_4^{2-} + NO_3^-$ to achieve an ANC of 50 μeq/L by 2200 ranged from 8.4 to 339.0 meq/m^2-yr. Similar to the pattern observed by Sullivan et al. (2012), several of our sites ($n = 5$) could not achieve an ANC of 50 μeq/L under any deposition scenario.

Highly acid sensitive sites (ANC < 0 μeq/L) will have difficulty achieving target ANC values (20, 50 μeq/L) by 2100. Note that some sites have low historical ANC values due to inherently low cation weathering rates and/or elevated inputs of naturally occurring dissolved organic matter which acts as organic acids (Fig. 3). For example, the mean estimated pre-industrial ANC of the thin-till drainage lakes and the seepage study lake is 55.4 μeq/L. Moreover watersheds experienced loss of soil exchangeable base cations as a result of historical acidic deposition, which also challenges acid-sensitive sites to achieve higher targets of ANC in recovery. Given these conditions as well as anticipated hydrochemical changes anticipated under future climate change, it is unlikely that Adirondack lakes will return to their pre-industrial condition.

4.2. Factors that affect historical acidification and recovery

The magnitude of inputs of $SO_4^{2-} + NO_3^-$ deposition drives the extent of ecosystem acidification (Fig. 4a). Acidic deposition increases the leaching of SO_4^{2-} and NO_3^- and depletion of exchangeable base cations, resulting in decreases in ANC. Sites with higher weathering rate and pre-industrial ANC appear to exhibit greater loss of ANC from historical inputs of acidic deposition than the sites with relatively lower weathering rate and pre-industrial ANC. The mobilization of Al^{3+} from soil is an important mechanism to neutralize elevated acidic deposition in acid sensitive watersheds (Driscoll and Postek, 1995). Unfortunately the acid–base chemistry of this process is not adequately depicted in ANC measurements (Sullivan et al., 1989). Moreover, Al^{3+} is highly toxic to aquatic biota (Driscoll et al., 2001).

Calcium weathering rate is difficult to measure but is a critically important process to quantify acidification for modeling studies. To our knowledge, this process has only been quantified for two lake watersheds — Panther Lake and Woods Lake Watershed in the Adirondack region. The average of long-term present-day denudation rates for these two sites was 1679 eq/ha-yr and 198 eq/ha-yr, respectively (April et al., 1986). These values are likely overestimates of actual weathering rates because they include net loss of Ca^{2+} from cation exchange or other ecosystem pools. Because of limitations in the ability to obtain direct measures, we estimated the Ca^{2+} weathering rates for the study sites (180–900 eq/ha/yr) based on model calibration. The calibrated weathering rates for the modeling sites are in the range of measured weathering rates for Panther Lake and Woods Lake Watershed. We hold weathering rates constant for model simulations for a given study site over the entire simulation period (i.e., 1000 to 2200 AD). In reality, Ca^{2+} weathering rate may be variable year by year due to variations in acidic deposition (Hyman et al., 1998) and meteorological conditions.

The magnitude of decreases in $SO_4^{2-} + NO_3^-$ deposition and the time scale of response are important considerations in ecosystem recovery. Under scenarios of limited or no future decrease in acidic deposition, lake-watershed recovery is projected to be short lived. Model simulations suggest that under continued elevated atmospheric N deposition (without forest disturbance), forest watersheds will progress toward a condition of N saturation, exhibit increasing leaching losses of NO_3^-, and resume acidification. In contrast, under scenarios of more aggressive decreases in acidic deposition, lake recovery will continue over the long-term (Fig. 1b). In addition to the effects of decreases in SO_4^{2-} deposition, decreases in NO_3^- deposition were simulated to delay the progression toward a condition of N saturation. Much of the benefit to ecosystems associated with implementing emission controls to decrease acidic deposition will be realized within a few decades, although simulated recovery does proceed slowly for more than a century. This time-dependent response illustrates the advantages in the application of dynamic models for determining DCLs and CLs.

4.3. Application of biological indicators of acidification stress

Acidic deposition is an important factor affecting fish species richness in high elevation lake-watersheds in the northeastern US (Lovett et al., 2009). Comparison of pre-industrial and present distributions of fish and total zooplankton species richness based on empirical relationships from spatial surveys and model simulations of ANC suggest that surface water acidification from acidic deposition has greatly impacted the loss of fish and total zooplankton species. Projected responses to potential decreases in acidic deposition indicate that future emission program could help recover fish and total zooplankton species. There is strong evidence showing that loss of fish populations and decline in fish species richness in the Adirondacks was due to surface water acidification from acidic deposition (Jenkins et al., 2007). Acidification has altered surface water chemistry, causing decreases in pH and increases in concentrations of inorganic monomeric Al, which could adversely impact sensitive species of fish and zooplankton (Rago and Wiener, 1986; Driscoll et al., 2001).

DCL and CL calculations are generally made using chemical indicators of acidification stress. However, there are compelling reasons to use biological relationships in the development of CLs. Based on an evaluation of fish and invertebrate populations in Norwegian surface waters, an ANC of 20 μeq/L was suggested as a CL/DCL target (Lien et al., 1996). We illustrate the potential application of biological indicators of acidification stress in the calculation of CLs through the use of empirical relations of species richness obtained from spatial lake surveys in the Adirondack region. While these relationships relate the extent of acidification and recovery to easily understandable measures, there are a number of limitations in this approach. First, the empirical relationships were obtained from a spatial survey with measured ANC. It is not clear if spatial relationships can be applied to quantify temporal changes. Second, there are many physiochemical and biological factors that influence lake ANC, acidic deposition being only one. Biotic species richness is likely controlled by a number of lake-watershed characteristics (e.g. lake size, availability of spawning and rearing habitat). Last, the empirical spatial relationships do not consider lags in biological recovery that might occur. Organisms are not responding to ANC, but rather some combination of factors that are linked to ANC (e.g., pH, Al). Many explanations have been proposed to explain this apparent hysteresis (e.g., episodic acidification events, time required for species introductions, changes in the food web that have occurred as a result of acidification stress; Driscoll et al., 2001; Monteith et al., 2005; Stockdale et al., 2014), and chemical recovery is no guarantee of biological recovery of acid-impacted ecosystems. There may be additional stressors other than acidification that contribute to loss of species such as shifts in stocking policy, or habitat alteration (Driscoll et al., 1991). The specific mechanisms by which fish and total zooplankton communities respond to decreases in acidic deposition have not yet been defined. More work is needed on the development and application of relationships between aquatic biota responses and recovery from acidification stress.

5. Conclusions

From the application of PnET-BGC to 20 lake-watersheds in the Adirondack region, we conclude:

1) Estimates of pre-industrial ANC for Adirondack lakes range from 18.1 μeq/L to 190.2 μeq/L, suggesting that the magnitude of historical acidification (ANC loss) ranges from about 26.0 to 100 μeq/L. Historical acidification of the lake-watersheds was related to the total current deposition of $SO_4^{2-} + NO_3^-$, Ca weathering rate, and pre-industrial ANC (~1850).
2) Some lakes are projected to reach target ANCs of 0, 20 or 50 μeq/L over the short term (2040) with or without additional emissions controls. However, it appears that some sensitive lakes will not to be able to reach the target ANC over the long term (2200) even under a scenario of complete elimination of anthropogenic acidic deposition. Complete recovery to pre-industrial conditions is not possible for most lake ecosystems.
3) Extrapolation of empirical spatial relationships suggests that Adirondack lake ecosystems have lost fish and total zooplankton species richness starting with the onset of the acidic deposition. Acidified lakes could recover some species under future decreases in deposition. Although biological indicators of acidification provide a compelling approach to document effects and recovery, assumptions concerning their application will require rigorous evaluation.

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