WATER RESOURCES RESEARCH, VOL. 48, W01547, doi:10.1029/2011WR011171, 2012

Target loads of atmospheric sulfur and nitrogen deposition for protection of acid sensitive aquatic resources in the Adirondack Mountains, New York

T. J. Sullivan,[1] B. J. Cosby,[2] C. T. Driscoll,[3] T. C. McDonnell,[1] A. T. Herlihy,[4] and D. A. Burns[5]

Received 19 July 2011; revised 14 December 2011; accepted 23 December 2011; published 31 January 2012.

[1] The dynamic watershed acid-base chemistry model of acidification of groundwater in catchments (MAGIC) was used to calculate target loads (TLs) of atmospheric sulfur and nitrogen deposition expected to be protective of aquatic health in lakes in the Adirondack ecoregion of New York. The TLs were calculated for two future dates (2050 and 2100) and three levels of protection against lake acidification (acid neutralizing capacity (ANC) of 0, 20, and 50 μeq L^{-1}). Regional sulfur and nitrogen deposition estimates were combined with TLs to calculate exceedances. Target load results, and associated exceedances, were extrapolated to the regional population of Adirondack lakes. About 30% of Adirondack lakes had simulated TL of sulfur deposition less than 50 meq m^{-2} yr to protect lake ANC to 50 μeq L^{-1}. About 600 Adirondack lakes receive ambient sulfur deposition that is above this TL, in some cases by more than a factor of 2. Some critical criteria threshold values were simulated to be unobtainable in some lakes even if sulfur deposition was to be decreased to zero and held at zero until the specified endpoint year. We also summarize important lessons for the use of target loads in the management of acid-impacted aquatic ecosystems, such as those in North America, Europe, and Asia.

Citation: Sullivan, T. J., B. J. Cosby, C. T. Driscoll, T. C. McDonnell, A. T. Herlihy, and D. A. Burns (2012), Target loads of atmospheric sulfur and nitrogen deposition for protection of acid sensitive aquatic resources in the Adirondack Mountains, New York, *Water Resour. Res.*, *48*, W01547, doi:10.1029/2011WR011171.

1. Introduction

[2] Atmospheric deposition of sulfur (S) and nitrogen (N), derived from utility, industrial, and area air pollution sources has caused acidification of drainage waters across broad areas of the eastern United States [*U.S. EPA*, 2008], eastern Canada, Europe, and Asia [*Driscoll et al.*, 2010]. Such acidification has been associated with enhanced leaching of sulfate (SO_4^{2-}) and nitrate (NO_3^-), depletion of available calcium (Ca^{2+}) and other nutrient cations from soil, decreased pH and acid neutralizing capacity (ANC) of surface waters, and increased mobilization of potentially toxic dissolved inorganic aluminum from soil [Al_i; *Charles*, 1991; *Sullivan*, 2000]. The effects of acidification are evident throughout aquatic food webs, including reduced species richness and the elimination of the most acid sensitive species of fish, benthic invertebrates, and zooplankton from acidified waters [*Driscoll et al.*, 2001]. In the United States these effects have been especially pronounced in surface waters of the Adirondack Mountains of New York [*U.S. EPA*, 2009], but impacts are broadly evident in the Appalachian Mountains [*Bulger et al.*, 1995], Canada, and Europe [*Havas and Rosseland*, 1995].

[3] Much of the research on the aquatic effects of acidic deposition in the Adirondacks has focused on individual lakes and their watersheds. There is a great deal of information available for a relatively small number of watersheds [cf. *Driscoll et al.*, 1991; *Nierzwicki-Bauer et al.*, 2010], including intensive chemical, and in many cases biological, monitoring data collected during the past one to three decades. However, knowledge of acidification and recovery processes for a small number of watersheds is of limited value as a basis for natural resource management and public policy. Management decisions require information regarding numbers and percentages of the population of lakes for a region that have responded, or are expected to respond in the future, to changes in atmospheric emissions and deposition. Acidic deposition in the Adirondack Mountains region has decreased substantially since the 1980s, and many lakes have shown signs of chemical recovery [*Driscoll et al.*, 2007]. We now need to know the magnitude of additional decreases in atmospheric deposition that will be required for more complete or even full recovery.

[4] The critical load (CL) is the level of sustained atmospheric deposition of S, N, or acidity below which harmful effects to sensitive ecosystems do not occur according to

[1] E&S Environmental Chemistry, Inc., Corvallis, Oregon, USA.
[2] Department of Environmental Sciences, University of Virginia, Charlottesville, Virginia, USA.
[3] Department of Civil and Environmental Engineering, Syracuse University, Syracuse, New York, USA.
[4] Department of Fisheries and Wildlife, Oregon State University, Corvallis, Oregon, USA.
[5] U.S. Geological Survey, Troy, New York, USA.

0043-1397/12/2011WR011171

current scientific understanding [*Nilsson and Grennfelt*, 1988]. The CL is typically calculated as a long-term steady state condition [*Posch et al.*, 2001]. Under constant atmospheric deposition at the determined CL, however, many decades or longer may be needed for a sensitive chemical indicator to reach the designated critical criterion value [*Sullivan et al.*, 2004, 2008]. A dynamic variation of the CL can also be calculated for a certain time period. For example, one might calculate the deposition load that would allow recovery of ANC to a level of 50 μeq L^{-1} by the year 2050 for a particular lake or stream under constant loading. Such a time-variant load is generally called a target load [TL; *Posch et al.*, 2001; *Henriksen and Posch*, 2001].

[5] The CL or TL is typically estimated using one or more process-based or empirical models. Databases developed by seven major assessment or monitoring programs, coupled with dynamic model simulations, offer an opportunity to evaluate the CL or TL of acidic deposition to acid-sensitive Adirondack watersheds: the Eastern Lakes Survey [ELS; *Linthurst et al.*, 1986], Direct/Delayed Response Project [DDRP; *Church et al.*, 1989], Environmental Monitoring and Assessment Program [EMAP; *Larsen et al.*, 1994], Adirondack Long-Term Monitoring Project [ALTM; *Driscoll et al.*, 2003], Adirondack Effects Assessment Program [AEAP; *Nierzwicki-Bauer et al.*, 2010], Adirondack Lakes Survey [ALS; *Kretser et al.*, 1989], and the model-based assessment of *Sullivan et al.* [2007]. The ELS, DDRP, EMAP, and *Sullivan et al.* [2007] studies were all statistically based, thereby allowing population estimates to be developed. ALTM and AEAP involve ongoing long-term lake monitoring efforts, but are not statistically based. DDRP contained a soils sampling component, but the soils data were regionally aggregated and not specific to the watersheds under study. *Sullivan et al.* [2006] developed a database of soil chemistry for the EMAP, ALTM, and AEAP lake-watersheds selected for study here. Such soil data are needed for estimating CLs or TLs using a process-based modeling approach. The best statistical frame for assessing acidification and recovery responses of Adirondack lakes was developed by the U.S. EPA's EMAP, which was designed to provide unbiased regional characterization of the population of Adirondack lakes larger than 1 ha [*Larsen et al.*, 1994].

[6] The most extensive survey of lake water chemistry in the Adirondack Mountains was the ALS [*Kretser et al.*, 1989; *Baker et al.*, 1990]. Over a 4 year period, the ALS assessed the chemistry and fisheries of 1469 lakes. The large number of lakes, however, were not drawn from a statistical frame, and therefore the results cannot be used directly for population estimates. Also, some ALS lakes were smaller than 1 ha, which was the lower size cutoff for the EMAP survey.

[7] The research reported here was undertaken to determine the TL (also called dynamic CL) values that will promote recovery in Adirondack lake ecosystems. Our focus is on the Adirondack ecoregion, and in particular the intensively monitored watersheds, many of which are located in the southwestern Adirondacks. The latter group of watersheds includes many that contain shallow surficial deposits (thin-till) resulting in high sensitivity to acidification, and are expected to be responsive to decreases in atmospheric S and N emissions and acidic deposition. Although we focus on evaluating factors that control TL values for a specific region (i.e., Adirondacks), results of this work are broadly applicable to understanding and applying TLs to the many regions in North America, Europe, and Asia where air pollutants have impacted aquatic ecosystems.

[8] In this study we integrate existing data from the AEAP, ALTM, EMAP, ALS, and DDRP programs to more fully utilize available information and conduct a statistically representative assessment of the TLs of S and N deposition for Adirondack lakes. There are three sets of Adirondack lakes available for TL modeling, each of which has previously been modeled using the model of acidification of groundwater in catchments (MAGIC). *Sullivan et al.* [2007] applied MAGIC to 44 statistically selected EMAP lakes and 32 ALTM lakes, with a 6-lake overlap. MAGIC was previously applied to 35 Adirondack lakes within the USEPA's DDRP project [*Church et al.*, 1989]. Population estimates of modeled CL or TL values for the Adirondack region can be generated using just the 44 EMAP lakes. However, the development of CL or TL maps, based on modeled sensitivity classes and their relationship to mappable water chemistry and/or landscape features, benefit from access to dynamic model output for a larger number of lakes. Thus, there is value in modeling lakes from all three groups.

[9] An important goal of this study is to establish TLs for S and N deposition to acid-sensitive Adirondack lake watersheds that are necessary to promote the continuation of ongoing aquatic recovery. Major objectives include to:

[10] 1. develop approaches to regionalize TL estimates, both numerically and spatially, using available survey frames and a process-based model to constrain weathering estimates;

[11] 2. quantify, classify, and map lakes and their watersheds according to their TL to allow for resource recovery and to protect against further acidification;

[12] 3. determine the extent to which Adirondack lakes are, based on TL and estimated ambient S and N deposition, in exceedance of their TLs; and

[13] 4. provide "lessons learned" on the selection of chemical criterion indicators and their specific critical threshold values for future research and application of TLs to the Adirondacks and other impacted regions.

2. Methods

2.1. Site Selection

[14] The primary sites selected for simulation of TLs were those modeled by *Sullivan et al.* [2007]. In that study, watersheds were selected based on the EMAP statistical design and also from among those that are included in long-term chemical and biological monitoring efforts. The principal data sources used in this study are summarized in Table 1. The regional EMAP probability sample included 115 Adirondack lakes and their watersheds. The total number of target Adirondack lakes included in the EMAP frame is 1829 (SE = 244). These include lakes depicted on 1:100,000-scale USGS maps that are larger than 1 ha, deeper than 1 m, and contain more than 1000 m^2 of open water. Of those target lakes, an estimated 509 had summer index ANC > 200 μeq L^{-1}. These lakes were considered insensitive to acidic deposition and were not specifically

Table 1. Principal Data Sources Used in This Study

Database	Major Information Provided	Relationship to Regional Condition
DDRP	MAGIC calibrations for 27 watersheds	Statistical sampling, but limited to larger lakes
ALS	Lake chemistry on 1136 lakes; lake biology, providing part of basis for specifying critical limit of ANC to protect biota	Not statistically based, but included large percentage of Adirondack lakes
ALTM	Lake chemistry over multiple years for 30 lakes	Not statistically based
AEAP	Lake biology, providing part of basis for specifying critical limit of ANC to protect biota	Not statistically based
EMAP	Basis for numeric extrapolation of site-specific TL estimates for 44 lakes	Statistical sampling of lakes larger than 1 ha
NADP	Wet atmospheric deposition	Interpolated to region
CMAQ	Model estimate of dry:wet deposition ratios	Modeled to region
Adirondack soil survey	Soil chemistry data for 70 watersheds	Included 44 statistically selected watersheds

modeled for the study reported here. The remaining 1320 (SE = 102) low-ANC lakes constituted the principal frame for extrapolation of TL results. Details of the EMAP design were given by *Larsen et al.* [1994]. *Whittier et al.* [2002] presented an overall assessment of the relative effects of various environmental stressors across northeastern lakes using EMAP probability survey data. Based on field measurements, 42% of the lakes in the EMAP statistical frame for the Adirondack region had summer index ANC $\leq$ 50 μeq L^{-1} and another 30% had ANC between 50 and 200 μeq L^{-1}. We focused this study on watersheds containing these two strata of low ANC lakes as they are thought to be most responsive to changes in air pollution. Lake water ANC provides an integrating acid-base chemistry indicator that reflects biotic, edaphic, geologic, and hydrologic conditions of the watershed. Analyses reported here are based on summer index ANC. These approximately correspond to annual average values; ANC measurements during spring, especially in conjunction with snowmelt, would be expected to be lower.

[15] *Sullivan et al.* [2006, 2007] used a random selection process to choose candidate watersheds for soil sampling and modeling from among the 44 EMAP watersheds containing lakes with ANC $\leq$ 50 μeq L^{-1} and the 39 EMAP watersheds containing lakes with ANC between 50 and 200 μeq L^{-1}. To obtain a spatially balanced subsample, the county was used as a spatial clustering variable in a manner identical to that used in the original EMAP probability design [*Larsen et al.*, 1994]. For lakes with ANC between 50 and 200 μeq L^{-1}, we used a variable probability factor based on lake ANC class (50 to 100, 100 to 150, and 150 to 200 μeq L^{-1}) to obtain more samples in the lower ANC ranges. No variable probability factors were used for the ANC $\leq$ 50 μeq L^{-1} lakes. Results of measurements or model projections for the selected EMAP watersheds can be extrapolated to the entire population of watersheds containing lakes with ANC $\leq$ 50 or $\leq$ 200 μeq L^{-1}, using the original EMAP sample weights adjusted for this random subsampling procedure.

[16] Intensively studied watersheds were drawn from the AEAP and ALTM databases, which included an overlap of 27 lakes. Six of the intensively studied watersheds were also included within the selected EMAP lakes. Atmospheric deposition of S and N is relatively high at the modeled sites, ranging from about 42 to 75 meq S m^{-2} yr and 50 to 85 meq N m^{-2} yr in 2002.

[17] It is advantageous to simulate TL for the maximum number of Adirondack lake watersheds possible in order to provide a robust foundation for empirical extrapolation to the larger population of lake watersheds in the Adirondack ecoregion. For that reason, 27 watersheds were modeled from the DDRP study in addition to the 70 that had been sampled for soils by *Sullivan et al.* [2006] and modeled by *Sullivan et al.* [2007]. To calibrate each of these additional watersheds, soils data were borrowed from among the 70 watersheds sampled by *Sullivan et al.* [2006] using a nearest-neighbor approach.

[18] There was additional uncertainty introduced to the TL calculations for the 27 DDRP watersheds by the soil borrowing procedure. This uncertainty was quantified by comparing simulated S TL values for a group of eight watersheds that were successfully calibrated twice: once based on measured soils data and a second time based on soils data that had been borrowed from the nearest-neighbor watershed that also had recent measured soils data. In general, there was little additional uncertainty contributed by the soils borrowing procedure to the TL estimates to protect lake ANC. The relationship between TL based on measured soil data versus TL based on borrowed soil data was strong (r^2 = 0.98–0.99 for the various critical criteria values). Most TL estimates to protect lake ANC that were based on borrowed soils were within 10–15 meq m^{-2} yr of the TL that was calculated using watershed-specific measured soils data in the model calibration. In essence, the model calibration was successfully able to compensate for any error introduced in the model input soil data used to represent a given watershed.

2.2. Target Loads Modeling

[19] There are increasingly well-recognized uncertainties and limitations associated with the widely used simple steady state critical loads modeling approaches [*Curtis et al.*, 2001; *Watmough et al.*, 2005]. Such concerns have led to use of process-based models that include the dynamics of base cation depletion in CL calculations [cf. *Rapp and Bishop*, 2009]. In particular, the empirical F-factors incorporated into many steady state CL applications are poorly suited to the recovery phase of acidification chronology. The F-factor is the ratio of the change over time in the concentration of base cations divided by the change in SO_4^{2-} concentration relative to the preindustrial steady state water chemistry condition. This ratio often becomes

negative in response to recovery processes in the soil, resulting in underestimation of the CL [*Rapp and Bishop*, 2009].

[20] The TL process typically involves selection of one or more sensitive receptor(s), one or more chemical criterion indicator(s) of biological response for the sensitive receptor(s) of concern, one or more critical threshold values for the chemical criterion indicators that have been shown to be associated with adverse biological impacts, and one or more time periods for evaluation. ANC is commonly selected as a chemical criterion indicator for lake water receptors. A number of critical threshold values of ANC have been used as the basis for CL and TL calculations, the most common of which have been 0, 20, and 50 μeq L^{-1}. These levels are believed to approximately correspond to chronic effects on brook trout (ANC = 0 μeq L^{-1}), episodic effects on brook trout and chronic effects on the more sensitive fish species (ANC = 20 μeq L^{-1}), and general effects on other more sensitive aquatic species across a range of taxonomic groups (ANC = 50 to 100 μeq L^{-1} [cf. *Cosby et al.*, 2006; *U.S. EPA*, 2009]).

[21] The exceedance is calculated by subtracting ambient deposition loads from the CL or TL, reflecting the extent to which the level of ambient deposition exceeds the calculated CL or TL. A TL can be set not only on the basis of recovery response times but also on political or economic considerations [*Porter et al.*, 2005; *Burns et al.*, 2008]. A TL can incorporate various management objectives. For example, if the CL for resource recovery has been estimated (e.g., x meq m^{-2} yr), one may set a TL which incorporates a safety factor (e.g., $1.5x$ meq m^{-2} yr) as an interim target with the intention of reaching the TL within a certain number of years. This interim target, although higher than the CL, might be considerably lower than ambient deposition, thereby allowing for only partial resource recovery within a specified period. Conversely, the TL could be set lower than the CL, for example if managers are unwilling to wait the decades or centuries that it might take to attain the critical criterion under constant loading at the CL level. The CL and the TL concepts have been used extensively in Europe for more than two decades to aid in air pollution abatement policy negotiations [*Posch et al.*, 2001; *Driscoll et al.*, 2010].

2.2.1. Magic Modeling Methods

[22] MAGIC is used here as a TL simulation and integration tool. MAGIC was developed to predict the long-term effects of acidic deposition on surface water chemistry. A critical concept in MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time in response to changes in atmospheric deposition, chemical equilibria between soil and soil solution shifts yielding changes in surface water chemistry. The validity of the model has been confirmed by comparison with estimates of lake acidification inferred from paleolimnological reconstructions of historical changes in lake pH [*Sullivan et al.*, 1996; *Jenkins et al.*, 1990; *Wright et al.*, 1986] and with the results of several catchment-scale experimental acidification and de-acidification experiments [e.g., *Cosby et al.* 1995, 1996; *Moldan et al.*, 1998; *Wright and Cosby*, 1987]. MAGIC has been used to reconstruct the history of acidification and to simulate future response on a regional basis and in a large number of individual catchments in both North America and Europe [e.g., *Lepisto et al.*, 1988; *Whitehead et al.*, 1988; *Cosby et al.*, 1990, 2001; *Hornberger et al.*, 1989; *Jenkins et al.*, 1990; *Wright et al.*, 1986, 1994, 1998; *Norton et al.*, 1992; *Ferrier et al.*, 1995; *Sullivan et al.*, 2004, 2008].

[23] MAGIC is a lumped-parameter model that predicts the long-term response of surface water chemistry to changes in acidic deposition [*Cosby et al.*, 1985]. Soil solution and surface water chemistry are simulated to predict the monthly and annual volume-weighted concentrations of major ions. MAGIC includes: (1) a submodel in which the concentrations of major ions are assumed to be governed by simultaneous mass law reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation-speciation of Al and dissolution-speciation of dissolved inorganic C; and (2) a mass balance submodel in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in forest biomass, and losses to runoff. The degree and rate of change of surface water acidity depend both on mass fluxes and the inherent characteristics of the affected soils.

[24] Cation exchange is modeled using equilibrium (Gaines-Thomas) equations with selectivity coefficients for individual base cations (i.e., Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and Al. Sulfate adsorption is represented by a Langmuir isotherm. Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of gibbsite. Aluminum speciation is calculated from hydrolysis reactions and complexation with SO_4^{2-} and F^{-}. Effects of CO_2 on pH and on the speciation of dissolved inorganic C are computed from equilibrium equations. Organic acids are represented as tri-protic analogs [*Driscoll et al.* 1994]. Element weathering and the uptake rate of N as a fraction of the N input are assumed to be constant, based on model calibration. A set of mass balance equations for base cations and strong acid anions are included. Given a description of the historical deposition at a site, the model equations are solved numerically to give long-term reconstructions of surface water chemistry. For more complete details of the model see *Cosby et al.* [1985, 1989].

[25] The model is calibrated to observed data before it can be used to examine potential lake-watershed response. Calibration is achieved by setting the values of fixed parameters within the model that can be directly measured or observed in the system of interest. The model is then run (using observed and/or assumed atmospheric and hydrologic inputs) and the outputs (stream water and soil chemical criterion variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called "optimized" parameters) are adjusted to improve the fit. After a number of iterations, the simulated minus observed values of the criterion variables usually converge to zero within some specified tolerance. The model is then considered calibrated.

2.2.2. Input Data

[26] Wet atmospheric S and N deposition estimates were derived from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) through the year 2005. Wet deposition measurements by NADP/NTN for each of the years during the 5 year period centered on

2002 were interpolated by Grimm to each study watershed and to the study region [cf. *Grimm and Lynch* 1997]. Dry deposition was estimated using output from the CMAQ model for 2002 (R. Dennis, U.S. EPA, personal communication) to establish dry to wet deposition ratios for S and N. For each study watershed, area-weighted total wet plus dry S and N deposition values were calculated using the interpolated NADP wet deposition and the CMAQ dry to wet ratios.

[27] Empirical relationships between regional emissions and ionic concentrations in precipitation, coupled with historical regional emissions inventories, were used to estimate the time series of historical wet S and N deposition for each study watershed [cf. *Driscoll et al.*, 2001]. For the base cations and chloride, background preindustrial deposition was assumed to be 10% of current deposition [*Sullivan et al.*, 2007; *Zhai et al.*, 2008]. Deposition inputs after 1850 were assumed to increase linearly to estimated values obtained for 1950. Wet deposition estimates during 1950 to 1978 for Na^+, K^+, Mg^{2+}, Ca^{2+}, and Cl^- were derived from empirical relationships between wet deposition and emissions of particulate matter [PM-10; *Nizich et al.*, 1996]. The model calculations assumed a fixed dry to wet deposition ratio of 0.5 for each of the base cations and 0.25 for Cl^-, based on the recommendations of *Johannes et al.* [1984] and *Baker* [1991]. Past, current, and future total deposition amounts of major ions were estimated for each study watershed as a spatially weighted watershed average.

[28] Forest uptake fluxes of the three nutrient base cations (Ca^{2+}, Mg^{2+}, K^+; Bc_{up}) were estimated from literature values summarized by the U.S Forest Service, Forest Inventory Analysis (FIA) project by *McNulty et al.* [2007]. To estimate *Bc* removal from the watershed, estimates of annualized growth rate were used under the assumption that 65% of the tree volume is removed from the site during harvest. These uptake terms reflect uptake into woody materials that are removed from the watershed through timber harvest. Uptake into vegetation that subsequently dies on site represents within-watershed recycling; this is not a net watershed loss. Lands identified as designated wilderness and other protected areas were classified as "no harvest"; Bc_{up} was set to zero in such areas. These included areas identified in the Protected Areas database constructed by the Commission for Environmental Cooperation, corresponding to GAP Analysis Program (GAP) codes 1 and 2 [*Scott et al.*, 1993]. The Bc_{up} parameter was determined for each of the modeled watersheds as a spatially weighted watershed average.

[29] The model was calibrated to the available atmospheric deposition and water chemistry data for the Adirondack ecoregion and then interpolated or extrapolated to yield base year estimates of lake water chemistry in the year 2002, which corresponded with available CMAQ estimates of dry deposition and served as the starting period for specifying the TL values. A suite of simulated TL values was developed, each based on a specific combination of selected criterion indicator, critical threshold value, and endpoint year. These included changes in S and N atmospheric loading. For both sets of simulations, deposition of the strong acid anion not being considered for determination of the TL (i.e., N load for determination of target S load) was set to follow future trajectories anticipated by the U.S. EPA in the Clean Air Interstate Rule (CAIR). We investigate TL differences as a function of time frame and critical ANC threshold level.

[30] The most commonly used combination of sensitive receptor and chemical indicator for acidification CL and TL calculation is surface water ANC. For this analysis, ANC is defined by the charge balance as the difference between the sum of the concentrations of the base cations and the strong acid anions:

$$\begin{aligned} \mathrm{ANC} = {} & (\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+} + \mathrm{K}^{+} + \mathrm{NH}_4^{+}) \\ & - (\mathrm{SO}_4^{2-} + \mathrm{NO}_3^{-} + \mathrm{Cl}^{-}). \end{aligned} \tag{1}$$

ANC calculated in this way is often termed CALK, or calculated ANC, as opposed to laboratory titrated ANC.

2.3. Regional Population Frame

[31] In reporting numbers and percentages of Adirondack lakes above or below various TL or exceedance values from MAGIC simulations, the population of lakes must be considered to which these numbers and percentages pertain. Lakes can be defined in various ways, and the selected definition can have considerable influence on the results reported for a regional aquatic TL assessment.

[32] Of particular importance in describing and defining a lake population is the lower size limit for what constitutes a lake. The EPA's ELS surveyed lakes larger than about 4 ha within the Adirondack subregion of the northeast region, which included some landscape that is beyond the borders of the Adirondack ecoregion. The EPA's EMAP study surveyed lakes larger than 1 ha in the Adirondack ecoregion. The ALS included some lakes that were considerably smaller than 1 ha. Because lake size distributions across the landscape tend to be heavily skewed toward smaller size classes, choice of the minimum lake size included in the population of interest has a large influence on calculations of the number and percentage of acid-sensitive lakes.

[33] The EMAP lake frame for the Adirondack ecoregion was further subsetted by *Sullivan et al.* [2006] to only include those lakes that had ANC < 200 μeq L^{-1}. This was done to focus the modeling effort on the lakes with the greatest sensitivity to acidic deposition. There are an estimated 1320 Adirondack lakes in the EMAP frame that have ANC < 200 μeq L^{-1}.

[34] The ALSC surveyed 1469 Adirondack lakes during the period 1984 to 1990. Of those surveyed lakes, 1136 were larger than 1 ha in area and located within the Adirondack ecoregion. The lakes were not statistically selected from a mapped frame, but the ALS did survey a relatively high percentage of the lakes in the Adirondack ecoregion that are larger than 1 ha.

[35] For this assessment, several population frames and lake sets are considered. Results of model calculations and extrapolations must always be evaluated in light of the population of lakes represented. All analyses reported here pertain only to lakes within the Adirondack ecoregion, and to lakes larger than or equal to 1 ha in surface area.

2.4. Regional Extrapolation of Model Output

[36] Regional extrapolation of MAGIC model results focused on (1) numbers and percentages of lakes and their

watersheds projected by the model to have TL and exceedance values at certain levels; and (2) maps showing the locations of lake watersheds in various TL and exceedance classes. The only statistically rigorous spatial frame available for quantitative extrapolation that covered the geographical extent of the Adirondack ecoregion and included lakes as small as 1 ha was EMAP. By applying modeling results from the 44 statistically selected modeled watersheds to the EMAP frame, we were able to estimate TL levels for all of the watersheds in the region that were represented by the statistical design.

[37] The acid-base chemistry of lakes is reflected in the lake water by ANC and the concentrations of strong acid anions and base cations in solution. Thus, independent water chemistry variables selected for spatial extrapolation in this analysis included ANC, pH, sum of base cations (SBC), SO_4^{2-} and NO_3^-.

[38] Candidate landscape variables for statistical extrapolation of watershed-specific TL results to the full study region included measurements of physiography and soil condition. Physiographic variables included watershed area, the ratio of the watershed area to the lake surface area, average watershed elevation, and average watershed slope. Elevation data at a resolution of one arc-second (approximately 30 m) were extracted from NHDPlus data as prepared for the National Elevation Data set by the U.S. Geological Survey (USGS). Soils data from the Soil Survey Geographic (SSURGO) database were available for the majority of the study area (http://soils.usda.gov/survey/geography/ssurgo/). Where SSURGO data were not available, the coarser-scaled State Soil Geographic (STATSGO2; U.S. General Soils Map, http://soils.usda.gov/survey/geography/statsgo/) data were substituted. Soil parameters that were extracted from these databases for this study included depth to restricting layer, percent clay, and pH. SSURGO and STATSGO are spatially represented using "map units." Each map unit is typically composed of multiple "components." The soils parameters were tabulated and coded to each soil map unit based on a component-weighted average. The resulting tabular data were joined with the spatial polygon data and converted to a 30 m grid using the maximum area cell assignment option in ArcGIS. Soils data that coincided with lake locations according to medium resolution NHD data were set to null values.

[39] STATSGO2 data were used where SSURGO data contained no observations or a value of 0. A limited portion of the study area was classified as open water. The no-data cells (corresponding with open water) were filled with an average of the nearby data cells (30 × 30 cell window) using the focal statistics function in ArcGIS. This step was required in order to maintain continuity during application of the continuous upslope averaging function used to calculate watershed-average parameter values [*McDonnell et al.*, 2012].

[40] Depth to restricting layer was defined as the depth to the first soil layer that prevents root penetration and water movement as represented in the soil databases. These depths were calculated for each component and then weighted and summed to generate a representative depth to restricting layer for each map unit. Soil components in SSURGO and STATSGO2 are attributed with percent clay at multiple soil horizons. Therefore, percent clay was calculated as a soil horizon thickness weighted average for each component. The representative percent clay for each map unit was then calculated as a component weighted average. STATSGO2 data were used where SSURGO data contained no observations or a value of 0. The open water cells were treated as for soil depth calculations. The same methods as described for percent clay were followed for generating a representative soil pH value for each map unit.

[41] Regression techniques were used to establish equations for spatial extrapolation of S TLs using Statistix 8.0 [*Analytical Software*, 2006]. Both landscape and water chemistry variables were used as candidate predictor variables in the regression analyses. Watershed averages for the landscape characteristics were used to represent the spatial variability within each watershed. Analyses focused on mappable factors known or suspected to influence watershed sensitivity to acidification in this region. The predictor equations were used to generate aquatic TL maps for the Adirondacks based on MAGIC simulations for protecting the lake water ANC criteria for the years 2050 and 2100.

[42] We also attempted to develop, using only watershed landscape variables, regression equations to predict the MAGIC-simulated TL of S deposition needed to protect lake ANC from decreasing below critical criteria values. Such equations would be useful for estimating TL values at Adirondack locations where measurements of water chemistry are not available. The resulting predictive relationships, however, were judged to be inadequate. As a consequence, MAGIC model simulations of the TL to protect lake ANC were spatially extrapolated to the population of Adirondack lakes for which water chemistry data are available. We were not able to spatially extrapolate the modeled TLs to watersheds lacking water chemistry data.

2.5. Uncertainty

[43] Because the estimates of the model fixed parameters and deposition inputs are subject to uncertainties, a "fuzzy optimization" procedure is implemented for calibrating the model [*Cosby et al.* 1990]. This approach consists of multiple calibrations using random values of the fixed parameters drawn from the observed possible range of values, and random values of atmospheric deposition from a range including uncertainty about the estimated values. Each of the multiple calibrations begins with (1) a random selection of values of fixed parameters and deposition; and (2) a random selection of the starting values of the optimized parameters. The optimized parameters are then adjusted using the *Rosenbrock* [1960] algorithm to achieve a minimum error fit to the target variables. This procedure is undertaken ten times to yield ten calibrations. The final calibrated model is represented by the ensemble of parameter values and variable values of the ten calibrations.

[44] The major sources of uncertainty in the model simulations of TL include input data quality; temporal variability in water chemistry; variability in biological response to water chemistry; model validity and accuracy; model calibration uncertainty; errors associated with missing model input data; and errors associated with regional extrapolation of modeling results from individual watersheds to the region. In this analysis, we focus on the elements of uncertainty arising from the MAGIC model simulations, including (1) the initial estimate of the adjustable parameters

used in the optimization algorithm (noisy response surface); (2) the values of the fixed parameters; (3) measured variables used to evaluate the squared errors (noisy target variables); and (4) errors in the specified inputs used to drive the model.

[45] The relative magnitude of the effects of each of these sources of uncertainty has been extensively evaluated for regional, long-term MAGIC simulations in a series of uncertainty analyses using Monte Carlo methods [see *Cosby et al.*, 1989, 1990; *Hornberger et al.*, 1989; *Sullivan et al.*, 2003, 2004]. The results of those analyses implied that, while their relative effects may vary from application to application (with data quality and/or quantity), each of the four categories of uncertainty could have important effects on MAGIC simulations. The multiple optimization procedure explicitly accounts for components of each of the four categories of uncertainty listed above, and produces a time-variable measure of overall simulation uncertainty for each state variable. The procedures developed in these previous studies were applied to the MAGIC applications in this project. Results were consistent with those found in the previous studies referenced above.

[46] The uncertainty in simulating the TL to protect Adirondack lake ANC was found to be relatively small across the distribution of TL values. In general, the difference between the maximum and minimum simulated TL values was less than about 10 to 20 meq m^{-2} yr.

3. Results and Discussion

3.1. Model Calibration Results

[47] There was close agreement between simulated and measured values of key constituents at all lakes. For the ANC simulations, the root mean square error (RMSE) for predicted versus observed values, based on the average of all measured ANC values at each lake over a 5 year period, was 1.2 μeq L^{-1} and $r^2 = 0.99$. These results suggest that the model calibrations were unbiased for simulating lake acid-base chemistry across the entire group of modeled sites. Thus, these calibrations provide the foundation for TL simulations.

[48] Target load simulations were based on two acidic deposition drivers (S and N), one chemical criterion indicator (ANC), three critical threshold values, and two endpoint years. Selection of these various TL parameters had important influence on the resulting calculations. Decisions regarding the pollutant of interest, appropriate chemical indicator and associated threshold to protect against biological impact, and the timeframe of desired protection all influence the TL calculation. Thus we present a matrix of TL results.

3.2. Sulfur Target Loads

[49] Lower aquatic S TL values (indicating greater acid sensitivity) were generally found for Adirondack lakes that currently have low ANC (Figure 1). Furthermore, S TL values tended to be lower if the objective was to protect lake water to a higher level (i.e., ANC = 50 μeq L^{-1}) as compared with a lower level of protection, such as protecting to ANC = 0 μeq L^{-1}.

[50] The simulated historical and current lake water chemistry can be helpful in evaluating TL results for protecting lakes against acidification. We consider the simulated distributions of lake ANC in the years 1850 (preindustrial period) and 2002 (calibration period) in Figure 2. MAGIC model simulations suggested that there were no acidic (ANC $\leq$ 0 μeq L^{-1}) lakes in the EMAP lake population in 1850 but about 175 such lakes (13% of the low-ANC EMAP population) in 2002. In addition, the simulated numbers of lakes having ANC $\leq$ 20 μeq L^{-1} and $\leq$ 50 μeq L^{-1} increased markedly from 1850 to 2002.

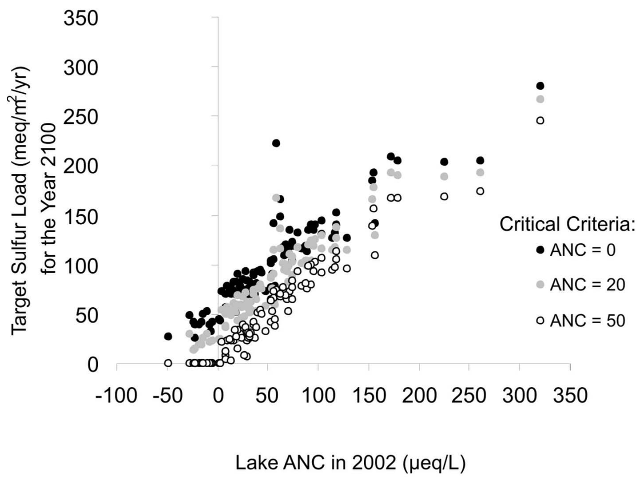

Figure 1. Target load of sulfur deposition for the year 2100 to protect lake ANC from acidifying below various threshold values versus lake ANC in the reference year (2002). The threshold values examined include ANC 0, 20, and 50 μeq L^{-1}; all sites modeled using MAGIC are depicted.

3.3. Nitrogen Target Loads

[51] In general, the TL simulations indicated that most Adirondack lakes are considerably less sensitive to acidification from N deposition, as compared with S deposition. As a consequence, estimated N TL values tended to be relatively high. This pattern is largely because most of the modeled lakes are currently retaining most of the deposited

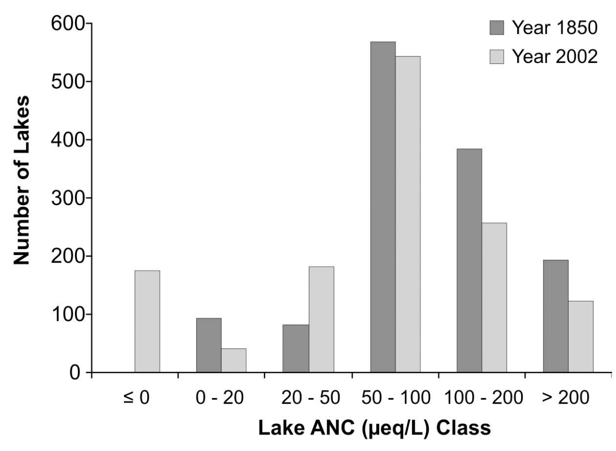

Figure 2. Histogram of extrapolated MAGIC simulations of lake water ANC in 1850 and 2002 to the population of 1320 Adirondack lakes included in the EMAP frame.

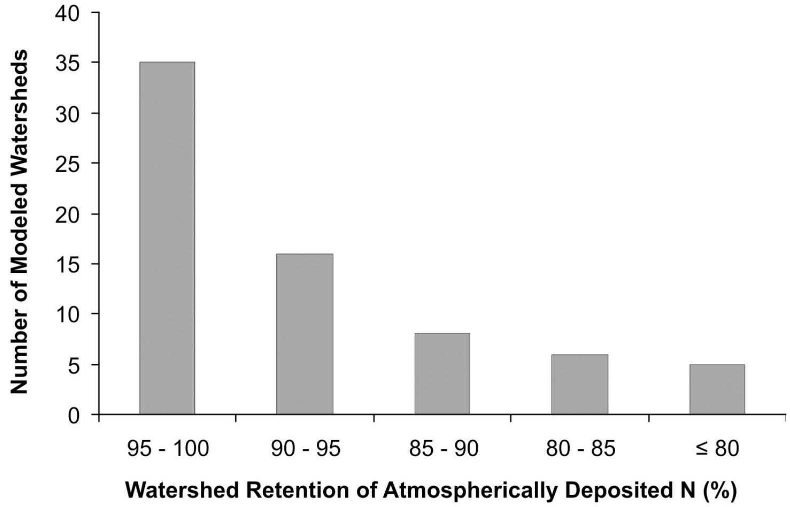

Figure 3. Histogram showing the modeled current percent watershed N retention for 70 Adirondack watersheds.

N within watershed soils (Figure 3). However, some lakes had simulated TL of N deposition equal to zero. There are multiple reasons for this result. First, the N TL simulations were conducted assuming future S deposition as expected in the CAIR emissions control scenario. For some lakes, the TL is exceeded based only on the S deposition level assumed in the simulations to occur in response to existing emissions controls on S. For such lakes, the N TL will be zero, because the ANC target criterion cannot be reached even if there is no added N deposition. There are also some lakes that appear to be currently leaching greater quantities of NH_4^+ than NO_3^- from watershed soil to lake water (e.g., those with a large wetland influence). As N deposition to such watersheds increases in the model scenario, there is a net increase in lake ANC because net NH_4^+ leaching supplies ANC (whereas net NO_3^- leaching consumes ANC). In order to decrease lake ANC in an unacidified lake to a target criterion value, the N deposition to such a lake watershed must decrease, rather than increase. If N deposition cannot be decreased enough to achieve the target ANC for a given lake watershed, the TL for N deposition will be zero.

3.4. Extrapolation to the Adirondack Ecoregion

[52] Model projections of aquatic TLs were numerically extrapolated to two EMAP lake frames (1) 1320 low-ANC ($\leq$200 μeq L^{-1}) lakes, and (2) 1829 lakes that generally span the spectrum of Adirondack lake ANC. In addition, a spatial extrapolation was conducted, based on all lake watersheds (n = 1136) for which water chemistry data were available. Note that each of these regional extrapolations was based on TL calculations performed using MAGIC. These TL calculations were not influenced by the uncertainties inherent in using the F-factor approach to constrain base cation weathering [cf. *Rapp and Bishop*, 2009].

3.4.1. Numeric Extrapolation to EMAP Watersheds Having Lake ANC ≤ 200 μeq L^{-1}

[53] The numbers and percentages of Adirondack lakes having TLs of S deposition in various classes were calculated based on extrapolation of the MAGIC modeling results to the regional EMAP population of Adirondack lakes having ANC $\leq$ 200 μeq L^{-1}. These results are summarized in the upper section of Table 2 by critical threshold value and endpoint year.

[54] The percent of low-ANC Adirondack lakes estimated to have S TLs below 50 meq m^{-2} yr differed by more than a factor of 2 depending on the threshold ANC selected (20 versus 50 μeq L^{-1}). Over 40% of the low-ANC lakes in the EMAP frame had S TL $\leq$ 50 meq m^{-2} yr for protecting lake ANC to 50 μeq L^{-1} in the year 2100. That percentage was only about 17% using the critical ANC threshold of 20 μeq L^{-1}.

[55] To protect lake ANC from negative values (<0 μeq L^{-1}) in the year 2050 or 2100, the S deposition TL for each EMAP lake was above 25 meq m^{-2} yr. If, however, the lake ANC threshold value was set higher, between 12% and 23% of the EMAP lakes had calculated S TL below 25 meq m^{-2} yr, depending on the choice of critical threshold value (20 or 50 μeq L^{-1}) and endpoint year (2050 or 2100). More than half of the 1320 EMAP lakes had relatively high S TL (>100 meq m^{-2} yr) to protect lake ANC to 0 μeq L^{-1} (62% for the endpoint year 2050, 56% for the endpoint year 2100). More than one fourth of the 1320 EMAP lakes had relatively high S TL (>100 meq m^{-2} yr) to protect lake ANC to 50 μeq L^{-1} (31% for the endpoint year 2050, 26% for the endpoint year 2100; Table 2).

[56] Based on MAGIC model outputs extrapolated to the regional lake population, TL population statistics were generated for various endpoint years (Table 3). Results suggested that the median (50th percentile) lake, from among the 1320 Adirondack lakes larger than 1 ha that have ANC < 200 μeq L^{-1}, had S TL equal to 67 meq m^{-2} yr to protect lake ANC to 50 μeq L^{-1} in the year 2100. An estimated 1/4th of those lakes had S TL less than 32 meq m^{-2} yr to achieve that same level of protection (Table 3).

3.4.2. Numeric Extrapolation to All Watersheds in EMAP Frame

[57] Results of TL extrapolation to the entire EMAP lake population frame, irrespective of ANC, are shown in the

Table 2. Estimated Number and Percent of Adirondack Lake Watersheds Having Various Target Load (TL) Values to Protect Against Sulfur-Driven Acidification Within Two EMAP Populations: (1) 1320 Adirondack Lakes That Have ANC Less Than 200 μeq L^{-1} and (2) 1829 Adirondack Lakes Irrespective of ANC, Based on MAGIC Model Simulations for 44 Statistically Selected Lakes

				Number (and Percent) of Lakes in Target Load Class				
				≤25	25–50	50–75	75–100	>100
Receptor	Threshold ANC Value	Endpoint Year	TL(S)	(meq S m^{-2} yr)				
Low ANC Lakes	0 μeq L^{-1}	2050		0 (0)	175 (13.3)	41 (3.1)	289 (21.9)	815 (61.7)
		2100		0 (0)	175 (13.3)	208 (15.8)	197 (14.9)	740 (56.0)
	20 μeq L^{-1}	2050		175 (13.3)	28 (2.1)	313 (23.7)	77 (5.8)	727 (55.1)
		2100		159 (12.0)	58 (4.4)	329 (24.9)	176 (13.3)	599 (45.4)
	50 μeq L^{-1}	2050		301 (22.8)	244 (18.5)	115 (8.7)	252 (19.1)	408 (30.9)
		2100		257 (19.5)	288 (21.8)	293 (22.2)	134 (10.1)	348 (26.4)
All Lakes	0 μeq L^{-1}	2050		0 (0)	175 (9.6)	41 (2.2)	289 (15.8)	1324 (72.4)
		2100		0 (0)	175 (9.6)	208 (11.4)	197 (10.8)	1249 (68.3)
	20 μeq L^{-1}	2050		175 (9.6)	28 (1.5)	313 (17.1)	77 (4.2)	1236 (67.6)
		2100		159 (8.7)	58 (3.2)	329 (18.0)	176 (9.6)	1108 (60.6)
	50 μeq L^{-1}	2050		301 (16.5)	244 (13.3)	115 (6.3)	252 (13.8)	917 (50.1)
		2100		257 (14.1)	288 (15.7)	293 (16.0)	134 (7.3)	857 (46.8)

lower section of Table 2. For this extrapolation, it was assumed that the TL of high-ANC (>200 μeq L^{-1}) lakes, which were not modeled as part of this study, would be high. The number of lakes simulated to be in the lower S TL classes (below 100 meq m^{-2} yr) were the same regardless of which EMAP population frame was selected: the low-ANC frame or the entire frame. However, there were many more lakes estimated to be in the highest S TL class (>100 meq m^{-2} yr) when referenced to all EMAP lakes (Table 2). Percentages of lakes in the various TL classes differed depending on the population frame selected, especially the percentage of lakes estimated to have TL above 100 meq m^{-2} yr.

3.4.3. Spatial Extrapolation to ALS Watersheds

[58] Numeric extrapolations of model-simulated TL values for this project, described above, focused on estimating numbers and percentages of Adirondack lake watersheds predicted to exhibit various TL values. Results varied depending on the statistical lake frame of reference selected. This analysis yielded estimates of numbers and percentages of lakes and watersheds in various TL classes, without any information regarding where within the Adirondack ecoregion those watersheds are located. To satisfy the need to discern the location of acid-sensitive lakes, model results for aquatic TLs were also spatially extrapolated to 1136 lakes included in the ALS.

[59] MAGIC model simulations of the TL of S deposition needed to protect lake ANC from decreasing below designated critical threshold values could successfully be predicted for locations having water chemistry data using only lake water ANC as a predictor variable, with r^2 values ranging from 0.72 (to protect ANC to 0 μeq L^{-1} in the year 2050) to 0.92 (to protect ANC to 50 μeq L^{-1} in the year

Table 3. Target Load (TL) Percentile Values for Three Population Estimates: The EMAP Frame (Numerical Extrapolation From 44 Modeled Lake Watersheds) for All Lakes and for Low-ANC Lakes, and the ALS Data Set (Spatial Extrapolation of TL Based on ALS Survey Lake Chemistry Data for all 1136 Lakes)

			Target Sulfur Load (meq m^{-2} yr) to Protect Against Low Lake ANC					
			ANC = 0 μeq L^{-1}		ANC = 20 μeq L^{-1}		ANC = 50 μeq L^{-1}	
Population Frame	Number	Percentile	2050	2100	2050	2100	2050	2100
EMAP Low ANC Lakes	1320	10th	40	41	13	19	0	0
		25th	79	72	64	59	29	32
		50th	126	113	109	98	72	67
		75th	165	152	149	137	109	104
		90th	212	203	197	189	176	167
EMAP All Lakes	1829	10th	59	55	38	37	0	6
		25th	84	78	66	63	40	38
		50th	155	135	131	120	106	96
		75th	>165	>152	>149	>137	>109	>104
		90th	>212	>203	>197	>189	>176	>167
ALS Surveyed Lakes	1136	10th	47	43	21	21	0	0
		25th	78	71	54	51	23	23
		50th	133	121	113	104	82	77
		75th	211	192	197	179	166	152
		90th	316	287	309	279	279	254

Table 4. Regression Equations to Estimate the Target Load (TL) of Sulfur Deposition to Protect Lake Water ANC From Acidifying Below Designated Threshold Criteria in Designated Future Years[a]

Critical Threshold ANC Value (μeq L^{-1})	Endpoint Year	Equation to Predict Target Load (meq S m^{-2} yr)	r^2
0	2050	TL = 67.9 + 0.790 ANC	0.72
	2100	TL = 61.7 + 0.719 ANC	0.80
20	2050	TL = 43.4 + 0.848 ANC	0.81
	2100	TL = 41.1 + 0.760 ANC	0.86
50	2050	TL = 11.8 + 0.852 ANC	0.90
	2100	TL = 13.7 + 0.765 ANC	0.92

[a]Regressions are based on charge balance ANC determined by the ALS during the 1980s.

2100; Table 4). The most robust predictions were obtained for estimating the S TL to protect lake ANC from acidifying below 50 μeq L^{-1} in the years 2050 and 2100 (r^2 = 0.90 and 0.92, respectively; Figure 4). For sake of simplicity, the final equations applied here only used ANC and a constant to predict each TL. Inclusion of watershed features such as elevation, slope, watershed area, and/or soil characteristics (pH, percent clay, depth) did not appreciably improve TL predictions beyond what was achieved based only on lake ANC.

[60] The spatial patterns in acid sensitivity are readily apparent in map depictions of S TLs extrapolated to the population of ALS lakes. One example is shown in Figure 5, based on protecting the lakes to ANC = 50 μeq L^{-1} in the year 2100. The vast majority of the ALS lakes in the southwestern portion of the Adirondack ecoregion have S TL less than 50 meq m^{-2} yr, as do many lakes in the High Peaks area of the north central Adirondacks.

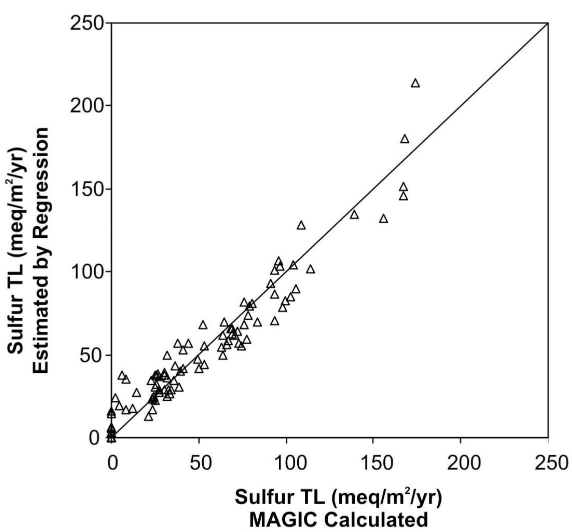

Figure 4. Comparison between target load of sulfur to protect lake ANC, estimated using regression equations, and simulated by the MAGIC model for 97 modeled Adirondack lakes. Results are shown for the year 2100 based on an ANC threshold of 50 μeq L^{-1}. The line indicating 1:1 correspondence is provided for reference.

3.4.4. Comparisons Among Different Extrapolation Approaches

[61] In Table 5, TL results are compared among various groups of Adirondack lake watersheds based on one suite of specifications and assumptions, the estimated TL of S deposition to protect lake water to ANC = 50 μeq L^{-1} in the year 2100. The modeled lakes were generally skewed toward lower S TL values, as compared with the lake population distributions. The EMAP populations (especially the full EMAP population of all lakes, regardless of ANC) and the ALS population were more skewed toward relatively high S TL values.

[62] The population distributions of the S TLs for the low-ANC EMAP population of lakes and for the ALS surveyed lakes were generally similar. Median and quartile S TL values were slightly lower for the ALS lake population than for the EMAP population, although the differences were small.

3.5. Relationship Between Target Load and Watershed Area

[63] Estimated TL values for the 1136 ALS lakes larger than 1 ha varied to some extent with watershed area, although not enough to use watershed area to successfully predict TL. Lakes estimated to have low S TL tended to have smaller (especially <1 km^2) watershed areas. This pattern was evident for the lowest S TL class (<25 meq m^{-2} yr) for TL estimates based on the critical ANC criterion 50 μeq L^{-1} (Figure 6). This was also evident for the two lowest S TL classes (<25, 25–50 meq m^{-2} yr) based on the critical threshold ANC value of 20 μeq L^{-1} (data not shown). It is well known that high sensitivity to acidic deposition is primarily associated with small watersheds, small lakes, and low-order streams [cf. *Sullivan*, 2000, *Sullivan et al.*, 1990]. Small watersheds are more likely to exhibit relatively homogeneous characteristics, including some having low base cation supply from soils and underlying geology. In contrast, larger watersheds are more likely to contain at least limited area of high base cation supply, yielding intermediate water chemistry. Lakes estimated to have relatively high S TL (>100 meq m^{-2} yr) assuming both the 20 and 50 μeq L^{-1} critical ANC criterion threshold values were disproportionately located in larger watersheds.

3.6. Time Frame of Target Load Responses

[64] The modeled S TL values varied with selection of endpoint year (Figure 7). For the most acid-sensitive lake watersheds (i.e., those having S TL less than about 25 to 50 meq m^{-2} yr), the S TL to protect sensitive resources was higher for protection to the year 2100, as compared with 2050. In other words, these most acid-sensitive watersheds were simulated to be able to tolerate slightly higher S loading if one was willing to wait an additional 50 years for the resources to recover from acidification. Lower deposition would be needed to achieve recovery in a shorter time period. For the majority of the modeled watersheds, however, the S TL was higher than 25 to 50 meq m^{-2} yr, and for these less acid-sensitive watersheds the S TL was lower using an endpoint year of 2100. Thus, these watersheds can tolerate lower S loading if the recovery period to achieve resource protection is extended to 2100, as opposed to

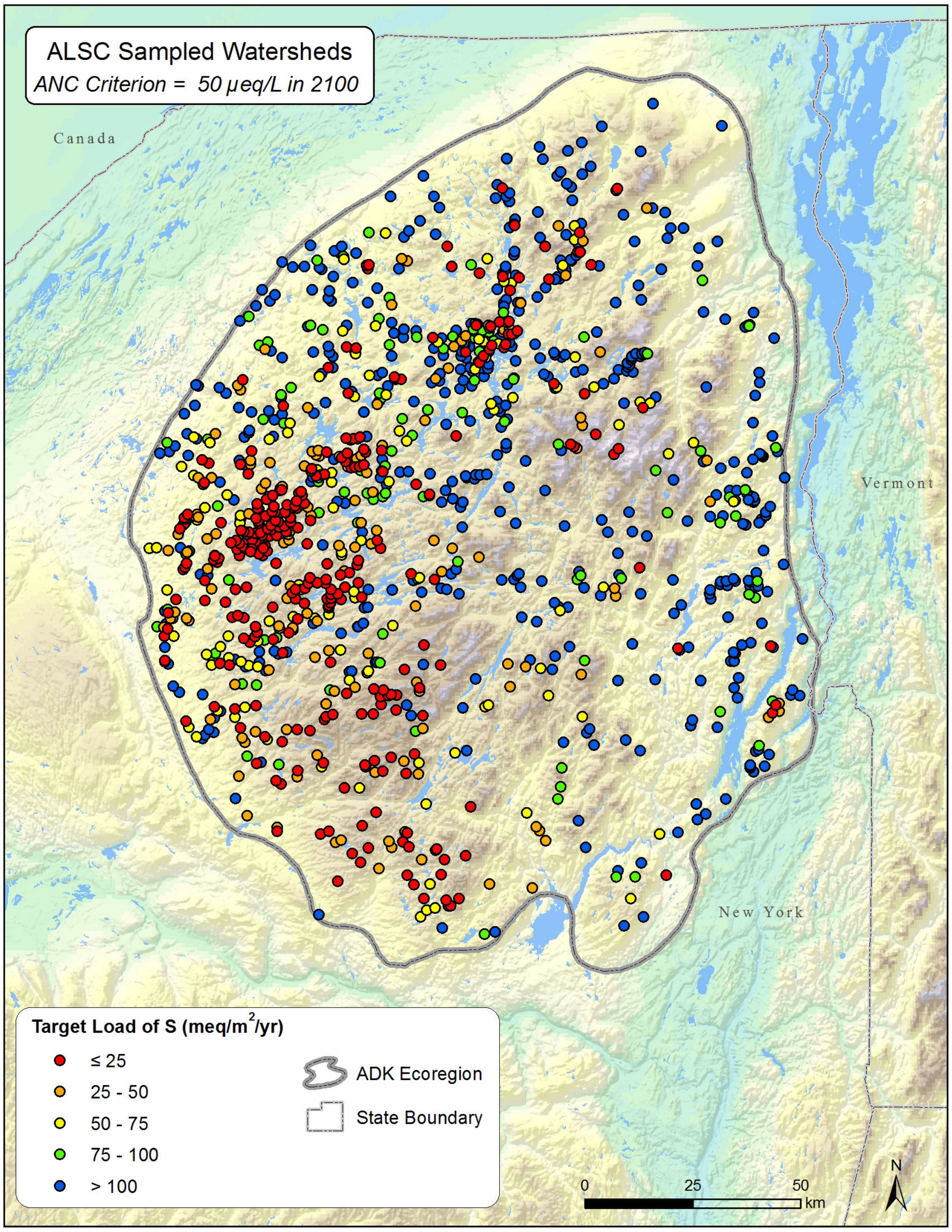

Figure 5. Estimated target load of sulfur deposition to protect lake ANC to 50 μeq L^{-1} in the year 2100, based on extrapolation of MAGIC modeling results to the population of lakes surveyed by the Adirondack Lakes Survey (ALS).

protecting the resources by 2050. The effect of endpoint year designation therefore depends on the current acid-base status of the watershed.

3.7. Target Load Exceedance

[65] Model simulations of TL, and extrapolation of those simulation results to the regional EMAP and/or ALS populations of Adirondack lakes, provide important information regarding the atmospheric deposition of either S or N that various lake watersheds can tolerate without exceeding threshold values believed to be associated with biological harm. These simulated TL values on their own do not reveal whether or not ambient deposition is high enough to exceed those thresholds and actually cause biological harm. That determination is made using the exceedance, which is calculated as the current ambient deposition of S or N minus the respective TL for S or N. Thus, exceedance reflects the extent to which the current loading exceeds the TL based on the critical threshold value of the chemical criterion indicator at which biological harm might be expected.

[66] Regional estimates of ambient (average centered on the year 2002) total wet plus dry S deposition show that S

Table 5. Estimated Percentage of Adirondack Lake Watersheds Having Various Target Load (TL) Values to Protect Against Sulfur-Driven Lake Acidification to ANC = 50 μeq L^{-1} in the Year 2100, Using Different Approaches and Population Frames

Approach	Number of Watersheds	TL(S)	Percentage of Lakes in Target Load Class (meq S m^{-2} yr) ≤25	25–50	50–75	75–100	>100
MAGIC model simulations for all modeled lake watersheds	97		28.9	26.8	17.5	15.5	11.3
MAGIC model simulations for all modeled lake watersheds that were calibrated using watershed-specific soil chemistry data derived from the 2003 soil survey	70		27.1	22.9	21.4	17.1	11.4
Extrapolation of MAGIC model simulation results for 44 EMAP probability survey lakes to the EMAP frame of Adirondack lakes that are larger than 1 ha, deeper than 1 m, and that have ANC ≤ 200 μeq L^{-1}	1320		19.5	21.8	22.2	10.1	26.4
Same as above, except assuming a high TL for all EMAP lakes that were not modeled using MAGIC because they had ANC > 200 μeq L^{-1}	1829		14.1	15.7	16.0	7.3	46.8
Spatial extrapolation of MAGIC model simulation results to all lakes surveyed by the ALS that are larger than 1 ha	1136		25.8	13.1	10.4	8.9	41.8

deposition values are highest in the southwestern portion of the Adirondack ecoregion (~66–75 meq m^{-2} yr) and lowest to the northeast (~42–54 meq m^{-2} yr). These deposition estimates were used together with S TL to calculate S TL exceedance.

[67] The number and percentage of Adirondack lakes that receive ambient S deposition above their respective S TL are reported in Table 6. Results are organized by assumed critical threshold values for the endpoint year 2100 and are referenced to the EMAP population of 1320 low-ANC Adirondack lakes. For protecting lake water ANC, the percent of lakes projected to be in exceedance based on deposition in the year 2002 ranged from 15.5% to protect to ANC = 0 μeq L^{-1} to 46.3% to protect to ANC = 50 μeq L^{-1}; the estimate for protection to ANC = 20 μeq L^{-1} was intermediate (22.7%; Table 6). Comparable calculations for the year 2050 yielded slightly lower estimates of the number and percentage of lakes in exceedance.

[68] The number of low-ANC EMAP lakes estimated to receive S deposition in exceedance of the S TL to protect lake ANC varied with the threshold criterion selected (Table 6). For protecting lake ANC to 0 μeq L^{-1} by the year 2100, 204 lakes (15.5%) are in exceedance based on estimated ambient S deposition in 2002. To protect lake ANC to 20 μeq L^{-1}, 299 lakes (22.7%) are in exceedance. To protect lake ANC to 50 μeq L^{-1}, 611 lakes (46.2%) are in exceedance, and nearly half of those receive current deposition that is greater than two times the S TL. Extrapolated exceedance classes are mapped in Figure 8 for 1136 ALS lakes based on the ANC threshold of 50 μeq L^{-1} for the year 2100. Lakes experiencing atmospheric S deposition more than double their respective S TLs are broadly distributed throughout the southwestern Adirondack Mountains and the High Peaks region in the northcentral portion of the Adirondack ecoregion. Such lakes are rare in the eastern half of the Adirondack ecoregion. This pattern is attributable to previously observed gradients from southwest to northeast of decreasing acidic deposition and precipitation, and variations in surficial and bedrock geology and

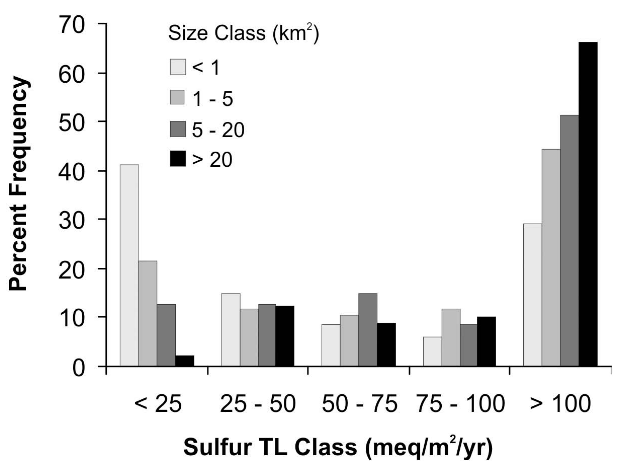

Figure 6. Histogram showing the distribution of ALS lake (n = 1136) watershed areas within target load classes, based on an ANC critical threshold equal to 50 μeq L^{-1} for the year 2100.

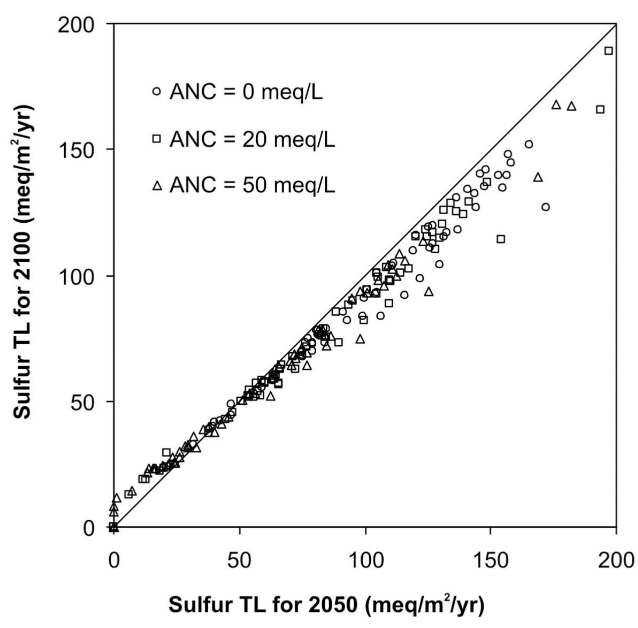

Figure 7. Comparison of sulfur target loads (TL) for 70 lake watersheds to achieve lake ANC protection in 2050 versus 2100.

Table 6. Number and Percent (in Parentheses) of Lake Watersheds Within the Adirondack Study Region in S Deposition Target Load (TL) Exceedance Classes, Based on MAGIC Model Simulations for 44 Statistically Selected Lakes, Using the Endpoint Year 2100

Chemical Indicator (μeq L^{-1})	Critical Threshold Value	Number (and Percent) of Lakes Within Exceedance Class			
		Not in Exceedance	1.0 to 1.5 Times the TL	1.5 to 2.0 Times the TL	>2.0[a] Times the TL
ANC	0 μeq L^{-1}	1116 (84.5)	79 (6.0)	125 (9.5)	0 (0)
	20 μeq L^{-1}	1021 (77.4)	108 (8.2)	16 (1.2)	175 (13.3)
	50 μeq L^{-1}	710 (53.7)	221 (16.7)	103 (7.8)	287 (21.7)

[a]For lakes simulated to have TL = 0, the exceedance class was set to 2.0 times the TL.

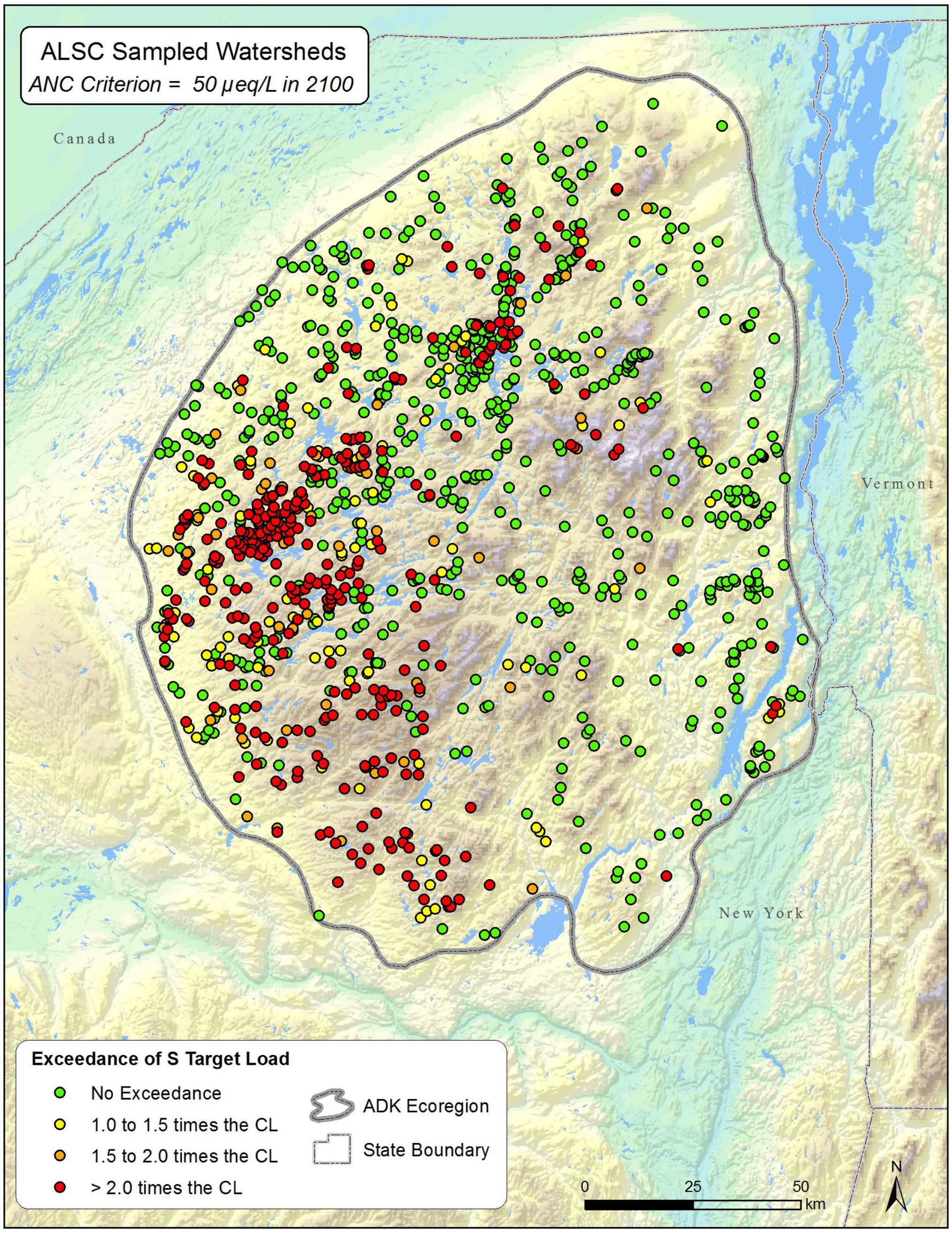

Figure 8. Exceedance classes for 1136 Adirondack lakes based on extrapolation of MAGIC model results of sulfur (S) target loads to the ALS surveyed lakes. Exceedances were calculated for the year 2100 using a critical threshold for ANC of 50 μeq L^{-1}.

associated increasing soil base saturation [*Driscoll et al.*, 1991, 2007; *Sullivan et al.*, 2006, 2007]. To protect lake ANC to 0 μeq L^{-1} by the year 2100, 213 lakes (19%) are estimated to be in exceedance based on S deposition in 2002. To protect lake ANC to 20 μeq L^{-1} by 2100, 340 ALS lakes (30%) are estimated to be in exceedance. To protect lake ANC to 50 μeq L^{-1}, nearly one third (326) of the ALS lakes are estimated to receive ambient S deposition greater than two times the S TL, with a total of 482 (42%) lakes in exceedance.

3.8. "Cannot Get There From Here" Lakes and Watersheds

[69] Depending on the critical threshold value of the chemical criterion indicator and the endpoint year selected for a particular TL analysis, some receptors are unable to attain the threshold value of ANC by the specified endpoint year even if S deposition is decreased to zero and maintained at zero throughout the duration of the simulation (to the endpoint year). These lakes are sometimes called "cannot get there from here" receptors.

[70] There are two major reasons why a specified threshold value for ANC and endpoint year combination is unattainable: (1) the chemical characteristics of the lake or watershed were such that target indicator values were not achieved (i.e., sufficiently high in ANC) during preindustrial times prior to the advent of acidic deposition; or (2) changes to the watershed soils in response to historical acidic deposition have been such that recovery is substantially delayed, for example, due to marked depletion of exchangeable base cations.

[71] All of the EMAP lakes were simulated to be able to achieve ANC = 0 μeq L^{-1}, regardless of endpoint year. Most (93%) EMAP lakes could achieve ANC = 20 μeq L^{-1} by the year 2050 or 2100. Somewhat fewer (84%) could attain ANC = 50 μeq L^{-1} by either of these endpoint years. For the lakes that were judged to be unable to achieve the specified ANC threshold in 2050 and 2100, that inability to achieve the target was attributed primarily to low ANC during preindustrial time, and secondarily to delayed recovery response due to effects of acidic deposition on watershed soils.

3.9. Lessons Learned

[72] The results of this research include important lessons in management of ecosystems in New York, eastern North America, Europe, and Asia that have been highly impacted by acidic deposition. Model simulations indicated the TLs of atmospheric deposition needed to affect resource recovery to a range of chemical indicator values, and at different future time periods. In addition, the estimated aquatic TLs were extrapolated to 1136 lake locations in the Adirondacks that have been surveyed for lake chemistry. Such extrapolations to the broader lake population are important to characterize the regional response and to identify resources at risk for ongoing acidification, locations where acidified lakes and forest soils are most likely to recover, and the long-term sustained deposition loads that would be required to affect such recovery. ANC is a robust chemical indicator of acidification stress because it integrates watershed acid-base chemistry and is relatively easy to simulate. The selection of critical threshold values for chemical criterion indicators and the recovery period are important determinants of TLs and associated management decisions. The most sensitive and/or highly impacted lake watersheds may not achieve indicator threshold values over relevant management periods (i.e., over multiple decades). Although the CL and TL approach provides a useful tool to guide the management of impacted ecosystems, there are clear limitations associated with specifying threshold values for indicators and endpoint years. While this work provides valuable experience to inform future TL analysis, additional research is needed to refine modeling tools and approaches used.

4. Conclusions

[73] Target loads for atmospheric deposition of S and N were calculated for the Adirondack region of New York using the dynamic watershed model MAGIC. A matrix of TL estimates was developed, based on differing air pollutants (e.g., S, N), sensitive resource and associated chemical criterion indicators (e.g., lake water ANC), critical thresholds (e.g., 0, 20, or 50 μeq L^{-1}), and evaluation year (e.g., 2050, 2100). Based on each of the estimated TLs, an exceedance was also calculated to reflect the extent to which the ambient atmospheric deposition loading exceeds the TL that would allow sensitive resources to recover from past damage or to be protected against future damage.

[74] The TL and exceedance estimates simulated by MAGIC were extrapolated to several population frames of Adirondack lakes. These analyses yielded estimates of the numbers and percentages of lakes that exhibit various levels of TL and exceedance. They also allowed aquatic TLs (and associated exceedances) for protecting and restoring lake chemistry to be mapped across the Adirondack ecoregion. Results of these analyses will aid in the management of acid-sensitive Adirondack lakes and watershed soils by revealing the levels of acidic deposition that will allow damaged resources to recover and undamaged resources to remain protected in a sustainable fashion. Moreover, information is provided to improve the future application of TLs to the Adirondacks as well as other acid-impacted regions.

[75] Specific conclusions of this research include the following:

[76] 1. Adirondack lakes that currently have low ANC also tend to have low S TL.

[77] 2. Modeled S TL values are lower if the intention is to protect lakes to a higher threshold for a chemical criterion indicator as opposed to lower levels of protection. Thus, the S TL to protect lake ANC to 50 μeq L^{-1} is lower than the TL to protect to 0 or 20 μeq L^{-1}.

[78] 3. Target loads for N deposition were generally higher than corresponding TLs for S deposition. Most Adirondack watersheds retain the majority of deposited N, with relatively low NO_3^- leaching to surface waters.

[79] 4. Extrapolation of simulated S TLs to the population of Adirondack lakes in EPA's EMAP frame suggested that about 41% of the low-ANC ($\leq$200 μeq L^{-1}) Adirondack lakes larger than 1 ha in area have a S TL that is below 50 meq m^{-2} yr to protect ANC to 50 μeq L^{-1} in the year 2100. The comparable statistic for all Adirondack lakes larger than 1 ha, irrespective of ANC, is about 30%.

[80] 5. MAGIC model simulations of the TL to protect lake ANC were successfully extrapolated to the population

of 1136 ALS lakes using only calculated ANC based on measurements made in the 1980s. The vast majority of the ALS lakes situated in the southwestern Adirondack Mountains had S TL less than 50 meq m^{-2} yr, as did many lakes in the High Peaks area.

[81] 6. Modeled S TL varied with selection of endpoint year and with starting point (above or below the threshold criterion). Lakes having lowest S TLs (most acid-sensitive) could tolerate higher S loading if one was willing to wait longer to achieve chemical recovery. Lakes having higher S TLs (less acid-sensitive) require more stringent controls (lower S loading) if the resource protection is intended to extend further into the future.

[82] 7. Regional S and N deposition estimates were combined with TLs to calculate exceedances. For protecting lake ANC to the year 2100, the percent of the 1320 low-ANC ($\leq$200 μeq L^{-1}) EMAP lakes projected to be in exceedance ranged from about 16% (to protect ANC to 0 μeq L^{-1}) to 46% (to protect ANC to 50 μeq L^{-1}). Some lakes and their watersheds had ambient S deposition that was more than double their respective S TL.

[83] 8. Some threshold criteria for lake ANC were simulated to be unobtainable for given watersheds, even if deposition is decreased to zero and held at zero until the endpoint year. This was largely because the simulated lake ANC was less than the threshold criterion even during preindustrial times in the absence of acidic deposition. In addition, recovery of some lakes has been delayed, largely due to depletion of exchangeable base cations in soil, in response to prolonged historical conditions of elevated acidic deposition.

[84] Calculation of TLs reported here, with extrapolation to the broader population of Adirondack lakes, reveals that about 30% of Adirondack lakes have low atmospheric S deposition TL values (<50 meq m^{-2} yr) to achieve lake ANC = 50 μeq L^{-1} in the year 2100. An estimated 600 Adirondack lakes receive ambient S deposition higher than this TL level, although some ($\sim$175 lakes) probably had lake ANC lower than 50 μeq L^{-1} during preindustrial times, prior to the onset of substantial anthropogenic S deposition.

[85] The TL results presented here provide the technical foundation for air pollution abatement policy and resource management decisions pertaining to lake acidification recovery in the Adirondack Mountains. Furthermore, the approach used here may be modified to address TLs needed for protecting and restoring Adirondack soil, forest, and stream resources and to assess TLs in other acid-impacted regions of the United States.

[86] **Acknowledgments.** This research was supported by a contract from the NY State Energy Research and Development Authority (NYSERDA) to E&S Environmental Chemistry, Inc. (agreement 10567). Wet and dry deposition estimates were provided by J. Grimm and R. Dennis, respectively. Project management support was provided by G. Lampman. Technical assistance was provided by D. Moore, J. Charles, S. Mackey, and T. McPherson.

References

Analytical Software (2006), *Statistix 8.0*, Analytical Software, Tallahassee, Fla.

Baker, J. P., S. A. Gherini, S. W. Christensen, C. T. Driscoll, J. Gallagher, R. K. Munson, R. M. Newton, K. H. Reckhow, and C. L. Schofield (1990), Adirondack lakes survey: An interpretive analysis of fish communities and water chemistry, 1984–1987, report, Adirondack Lakes Surv. Corp., Ray Brook, N. Y.

Baker, L. A. (1991), Regional estimates of dry deposition, Appendix B, in *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, edited by D. F. Charles, pp. 645–652, Springer, New York.

Bulger, A. J., C. A. Dolloff, B. J. Cosby, K. N. Eshleman, J. R. Webb, and J. N. Galloway (1995), The Shenandoah National Park: Fish in sensitive habitats (SNP:Fish) project, An integrated assessment of fish community responses to stream acidification, *Water Air Soil Pollut.*, *85*(2), 309–314.

Burns, D. A., T. Blett, R. Haeuber, and L. Pardo (2008), Critical loads as a policy tool for protecting ecosystems from the effects of air pollutants, *Front. Ecol. Environ.*, *6*(3), 156–159.

Charles, D. F. (Ed.) (1991), *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, 747 pp., Springer, New York.

Church, M. R., et al. (1989), Future effects of long-term sulfur deposition on surface water chemistry in the Northeast and Southern Blue Ridge Province (Results of the Direct/Delayed Response Project), U.S. Environmental Protection Agency, Corvallis, Oreg.

Cosby, B. J., G. M. Hornberger, J. N. Galloway, and R. F. Wright (1985), Modelling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry, *Water Resour. Res.*, *21*(1), 51–63.

Cosby, B. J., G. M. Hornberger, P. F. Ryan, and D. M. Wolock (1989), MAGIC/DDRP final report, U.S. Environ. Prot. Agency, Direct/Delayed Response Proj., Corvallis, Oreg.

Cosby, B. J., A. Jenkins, R. C. Ferrier, J. D. Miller, and T. A. B. Walker (1990), Modelling stream acidification in afforested catchments: Long-term reconstructions at two sites in central Scotland, *J. Hydrol.*, *120*, 143–162.

Cosby, B. J., R. F. Wright, and E. Gjessing (1995), An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway, *J. Hydrol.*, *170*, 101–122.

Cosby, B. J., S. A. Norton, and J. S. Kahl (1996), Using a paired catchment manipulation experiment to evaluate a catchment-scale biogeochemical model, *Sci. Total Environ.*, *183*, 49–66.

Cosby, B. J., R. C. Ferrier, A. Jenkins, and R. F. Wright (2001), Modeling the effects of acid deposition: Refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model, *Hydrol. Earth Syst. Sci.*, *5*(3), 499–517.

Cosby, B. J., J. R. Webb, J. N. Galloway, and F. A. Deviney (2006), Acidic deposition impacts on natural resources in Shenandoah National Park, *Tech. Rep. NPS/NER/NRTR—2006/066*, U. S. Dep. of the Inter., Natl. Park Serv., Northeast Reg., Philadelphia, Pa.

Curtis, C., B. Reynolds, T. E. H. Allott, and R. Harriman (2001), The link between the exceedance of acidity critical loads for freshwaters, current chemical status and biological damage: A re-interpretation, *Water Air Soil Pollut. Focus*, *1*(1–2), 399–413.

Driscoll, C. T., R. M. Newton, C. P. Gubala, J. P. Baker, and S. W. Christensen (1991), Adirondack Mountains, in *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, edited by D. F. Charles, pp. 133–202, Springer, New York.

Driscoll, C. T., M. D. Lehtinen, and T. J. Sullivan (1994), Modeling the acid-base chemistry of organic solutes in Adirondack, NY, lakes, *Water Resour. Res.*, *30*, 297–306.

Driscoll, C. T., G. B. Lawrence, A. J. Bulger, T. J. Butler, C. S. Cronan, C. Eagar, K. F. Lambert, G. E. Likens, J. L. Stoddard, and K. C. Weathers (2001), Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies, *BioScience*, *51*(3), 180–198.

Driscoll, C. T., K. M. Driscoll, K. M. Roy, and M. J. Mitchell (2003), Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition, *Environ. Sci. Technol.*, *37*, 2036–2042.

Driscoll, C. T., K. M. Driscoll, K. M. Roy, and J. Dukett (2007), Changes in the chemistry of lakes in the Adirondack region of New York following declines in acidic deposition, *Water Air Soil Pollut.*, *22*(6), 1181–1188.

Driscoll, C. T., E. B. Cowling, P. Grennfelt, J. Galloway, and R. Dennis (2010), Integrated assessment of ecosystem effects of atmospheric deposition: Lessons available to be learned, *EM*, *2010*, 6–13.

Ferrier, C. A., R. F. Wright, B. J. Cosby, and A. Jenkins (1995), Application of the MAGIC model to the Norway spruce stand at Solling, Germany, *Ecol. Model.*, *83*, 77–84.

Grimm, J. W., and J. A. Lynch (1997), Enhanced wet deposition estimates using modeled precipitation inputs: Final report for the U.S. Forest Service, Northeastern Forest Experiment Station, Northern Global Change Research Program, final report, Environ. Resour. Res. Inst., Pa. State Univ., University Park, Pa.

Havas, M., and B. O. Rosseland (1995), Response of zooplankton, benthos and fish to acidification: An overview, *Water Air Soil Pollut.*, *85*(1), 51–62.
Henriksen, A., and M. Posch (2001), Steady-state models for calculating critical loads of acidity for surface waters, *Water Air Soil Pollut. Focus*, *1*(1–2), 375–398.
Hornberger, G. M., B. J. Cosby, and R. F. Wright (1989), Historical reconstructions and future forecasts of regional surface water acidification in southernmost Norway, *Water Resour. Res.*, *25*, 2009–2018.
Jenkins, A., P. G. Whitehead, B. J. Cosby, R. C. Ferrier, and D. J. Waters (1990), Modelling long term acidification: A comparison with diatom reconstructions and the implications for reversibility, *Philos. Trans. R. Soc. London*, *327*, 435–440.
Johannes, A. H., E. R. Altwicker, and N. L. Clesceri (1984), Atmospheric inputs to the ILWAS watersheds, in *The Integrated Lake-Watershed Acidification Study, Vol. 4: Summary of Major Results*, edited by R. A. Goldstein and S. A. Gherini, Electr. Power Res. Inst., Palo Alto, Calif.
Kretser, W., J. Gallagher, and J. Nicolette (1989), Adirondack lakes study,1984–1987: An evaluation of fish communities and water chemistry, report, Adirondack Lakes Surv. Corp., Ray Brook, N. Y.
Larsen, D. P., K. W. Thornton, N. S. Urquhart, and S. G. Paulsen (1994), The role of sample surveys for monitoring the condition of the nation's lakes, *Environ. Monitor. Assess.*, *32*, 101–134.
Lepistö, A., P. G. Whitehead, C. Neal, and B. J. Cosby (1988), Modelling the effects of acid deposition: Estimation of long term water quality responses in forested catchments in Finland, *Nord. Hydrol.*, *19*, 99–120.
Linthurst, R. A., D. H. Landers, J. M. Eilers, P. E. Kellar, D. F. Brakke, W. S. Overton, R. Crowe, E. P. Meier, P. Kanciruk, and D. S. Jeffries (1986), Regional chemical characteristics of lakes in North America Part II: Eastern United States, *Water Air Soil Pollut.*, *31*, 577–591.
McDonnell, T. C., B. J. Cosby, and T. J. Sullivan (2012), Regionalization of soil base cation weathering for evaluating stream water acidification in the Appalachian Mountains, USA, *Environ. Pollut.*, *162*, 338–344.
McNulty, S. G., E. C. Cohen, J. A. M. Myers, T. J. Sullivan, and H. Li (2007), Estimates of critical acid loads and exceedances for forest soils across the conterminous United States, *Environ. Pollut.*, *149*, 281–292.
Moldan, F., R. F. Wright, R. C. Ferrier, B. I. Andersson, and H. Hultberg (1998), Simulating the Gårdsjön covered catchment experiment with the MAGIC model, in *Experimental Reversal of Acid Rain Effects. The Gårdsjön Roof Project*, edited by H. Hultberg and R. A. Skeffington, pp. 351–362, John Wiley, Chichester, U. K.
Nierzwicki-Bauer, S. A., et al. (2010), Acidification in the Adirondacks: Defining the biota in trophic levels of 30 chemically diverse acid-impacted lakes, *Environ. Sci. Technol.*, *44*, 5721–5727.
Nilsson, J., and P. Grennfelt (Eds.) (1988), Critical loads for sulphur and nitrogen: Report from a workshop held at Skokloster, Sweden, 19–24 March 1988, *NORD Miljo Rapp. 1988: 15*, 418 pp., Nord. Counc. of Minist., Copenhagen.
Nizich, S. V., D. Misenheimer, T. Pierce, A. Pope, and P. Carson (1996), National air pollutant emission trends 1900–1995, *Rep. EPA-454/R-96-007*, U.S. Environ. Prot. Agency, Off. of Air Qual., Research Triangle Park, N. C.
Norton, S. A., R. F. Wright, J. S. Kahl, and J. P. Scofield (1992), The MAGIC simulation of surface water acidification at, and first year results from, the Bear Brook Watershed Manipulation, Maine, USA, *Environ. Pollut.*, *77*, 279–286.
Porter, E., T. Blett, D. U. Potter, and C. Huber (2005), Protecting resources on federal lands: Implications of critical loads for atmospheric deposition of nitrogen and sulfur, *BioScience*, *55*(7), 603–612.
Posch, M., P. A. M. DeSmet, J. P. Hettelingh, and R. J. Downing (2001), Calculation and mapping of critical thresholds in Europe: Status report 2001, report, iv + 188 pp., Coord. Cent. for Eff., Natl. Inst. of Public Health and the Environ., Bilthoven, Netherlands.
Rapp, L., and K. Bishop (2009), Surface water acidification and critical loads: Exploring the F-factor, *Hydrol. Earth Syst. Sci.*, *13*, 2191–2201.
Rosenbrock, H. H. (1960), An automatic method for finding the greatest or least value of a function. *Comput. J.*, *3*, 175–184.
Scott, J. M., et al. (1993), *Gap Analysis: A Geographic Approach to Protection of Biological Diversity*, *Wildl. Monogr. Ser.*, vol. 123, 41 pp., Allen Press, Lawrence, Kans.
Sullivan, T. J. (2000), *Aquatic Effects of Acidic Deposition*., 373 pp., Lewis Publ., Boca Raton, Fla.
Sullivan, T. J., D. L. Kugler, M. J. Small, C. B. Johnson, D. H. Landers, B. J. Rosenbaum, W. S. Overton, W. A. Kretser, and J. Gallagher (1990), Variation in Adirondack, New York, lakewater chemistry as a function of surface area, *Water Resour. Bull. 26*, 167–176.
Sullivan, T. J., B. J. Cosby, C. T. Driscoll, D. F. Charles, and H. F. Hemond (1996), Influence of organic acids on model projections of lake acidification, *Water Air Soil Pollut.*, *91*, 271–282.
Sullivan, T. J., et al. (2003), Assessment of air quality and related values in Shenandoah National Park, *Tech. Rep. NPS/NERCHAL/NRTR-03/090*, U. S. Dep. of the Inter., Natl. Park Serv., Northeast Reg.
Sullivan, T. J., B. J. Cosby, A. T. Herlihy, J. R. Webb, A. J. Bulger, K. U. Snyder, P. Brewer, E. H. Gilbert, and D. L. Moore (2004), Regional model projections of future effects of sulfur and nitrogen deposition on streams in the southern Appalachian Mountains, *Water Resour. Res.*, *40*, W02101, doi:10.1029/2003WR001998.
Sullivan, T. J., I. J. Fernandez, A. T. Herlihy, C. T. Driscoll, T. C. McDonnell, N. A. Nowicki, K. U. Snyder, and J. W. Sutherland (2006), Acid-base characteristics of soils in the Adirondack Mountains, New York, *Soil Sci. Soc. Am. J.*, *70*, 141–152.
Sullivan, T. J., B. J. Cosby, A. T. Herlihy, C. T. Driscoll, I. J. Fernandez, T. C. McDonnell, C. W. Boylen, S. A. Nierzwicki-Bauer, and K. U. Snyder (2007), Assessment of the extent to which intensively-studied lakes are representative of the Adirondack region and response to future changes in acidic deposition, *Water Air Soil Pollut*, *185*, 279–291.
Sullivan, T. J., B. J. Cosby, J. R. Webb, R. L. Dennis, A. J. Bulger, and F. A. Deviney Jr. (2008), Streamwater acid-base chemistry and critical loads of atmospheric sulfur deposition in Shenandoah National Park, Virginia, *Environ. Monit. Assess.*, *137*, 85–99.
U.S. Environmental Protection Agency (2008), Integrated science assessment for oxides of nitrogen and sulfur–ecological criteria, *Rep. EPA/600/R-08/082F*, Natl. Cent. for Environ. Assess., Off. of Res. and Dev., Research Triangle Park, N. C.
U.S. Environmental Protection Agency (2009), Risk and exposure assessment for review of the secondary national ambient air quality standards for oxides of nitrogen and oxides of sulfur, *Rep. EPA-452/R-09-008a*, Off. of Air Qual. Plann. and Stand., Health and Environ. Impacts Div., Research Triangle Park, N. C.
Watmough, S. A., J. Aherne, and P. Dillon (2005), Effect of declining lake base cation concentration on freshwater critical load calculations, *Environ. Sci. Technol.*, *39*, 3255–3260.
Whitehead, P. G., B. Reynolds, G. M. Hornberger, C. Neal, B. J. Cosby, and P. Paricos (1988), Modeling long term stream acidification trends in upland Wales at Plynlimon, *Hydrol. Processes*, *2*, 357–368.
Whittier, T. R., S. B. Paulsen, D. P. Larsen, S. A. Peterson, A. T. Herlihy, and P. R. Kaufmann (2002), Indicators of ecological stress and their extent in the population of northeastern lakes: A regional-scale assessment, *BioScience*, *52*, 235–247.
Wright, R. F., and B. J. Cosby (1987), Use of a process-oriented model to predict acidification at manipulated catchments in Norway, *Atmos. Environ.*, *21*, 727–730.
Wright, R. F., B. J. Cosby, G. M. Hornberger, and J. N. Galloway (1986), Comparison of paleolimnological with MAGIC model reconstructions of water acidification, *Water Air Soil Pollut.*, *30*, 367–380.
Wright, R. F., B. J. Cosby, R. C. Ferrier, A. Jenkins, A. J. Bulger, and R. Harriman (1994), Changes in the acidification of lochs in Galloway, southwestern Scotland, 1979–1988: The MAGIC model used to evaluate the role of afforestation, calculate critical loads, and predict fish status, *J. Hydrol.*, *161*, 257–285.
Wright, R. F., C. Beier, and B. J. Cosby (1998), Effects of nitrogen deposition and climate change on nitrogen runoff at Norwegian boreal forest catchments: The MERLIN model applied to Risdalsheia (RAIN and CLIMEX projects), *Hydrol. Earth Syst. Sci.*, *2*(4), 399–414.
Zhai, J., C. T. Driscoll, T. J. Sullivan, and B. J. Cosby (2008), Regional application of the PnET-BGC model to assess historical acidification of Adirondack lakes, *Water Resour. Res.*, *44*, W01421, doi:10.1029/2006WR005532.

D. A. Burns, U.S. Geological Survey, 425 Jordan Rd., Troy, NY 12180, USA.

B. J. Cosby, Department of Environmental Sciences, University of Virginia, 291 McCormick Rd., Charlottesville, VA 22903, USA.

C. T. Driscoll, Department of Civil and Environmental Engineering, Syracuse University, 151 Link Hall, Syracuse, NY 13244, USA.

A. T. Herlihy, Department of Fisheries and Wildlife, Oregon State University, Nash Hall, Rm. 104, Corvallis, OR 97331, USA.

T. C. McDonnell and T. J. Sullivan, E&S Environmental Chemistry, Inc., PO Box 609, Corvallis, OR 97339, USA. (tim.sullivan@esenvironmental.com)