ASSESSMENT OF THE EXTENT TO WHICH INTENSIVELY STUDIED LAKES ARE REPRESENTATIVE OF THE ADIRONDACK MOUNTAIN REGION

FINAL REPORT 06-17
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ASSESSMENT OF THE EXTENT TO WHICH INTENSIVELY-STUDIED LAKES ARE REPRESENTATIVE OF THE ADIRONDACK MOUNTAIN REGION

FINAL REPORT

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PREFACE

The New York State Energy Research and Development Authority (NYSERDA) is pleased to publish "Assessment of the Extent to Which Intensively-Studied Lakes are Representative of the Adirondack Mountain Region" This report was prepared by E&S Environmental Chemistry, Inc. This project was funded as part of the **New York Energy $mart^{SM}** Environmental Monitoring, Evaluation and Protection (EMEP) program and represents one of several studies focusing on ecosystem response to pollutants associated with the generation of electricity. More information on the EMEP program may be found on NYSERDA's website at: www.nyserda.org/programs/environment/emep/ .

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Abstract

This research represents a multi-disciplinary and multi-institutional effort to extrapolate research, monitoring, and modeling results, including physical, chemical, and biological findings from intensively-studied lakes to the regional population of acid-sensitive Adirondack lakes. Extrapolation was based on the statistical frame of EPA's Environmental Monitoring and Assessment Program (EMAP). Intensively-studied sites were drawn from RPI's Adirondack Effects Assessment Program (AEAP) and the New York State Department of Environmental Conservation's Adirondack Long-term Monitoring Project (ALTM). A total of 70 watersheds were included in this effort, which involved field sampling to develop a statistically-representative soils database and model projections using the MAGIC and PnET-BGC models to classify lakes according to their sensitivity to change in atmospheric sulfur (S) and nitrogen (N) deposition.

We studied edaphic characteristics at 199 locations within 44 statistically-selected Adirondack lake-watersheds, plus 26 additional watersheds that are included in long-term lakewater monitoring programs. The statistically-selected watersheds were chosen to be representative of Adirondack watersheds containing lakes larger than 1 ha and deeper than 1 m that have lakewater acid neutralizing capacity (ANC) less than or equal to 200 µeq/L. Results of soil analyses and model projections of lakewater chemistry were extrapolated to the watersheds of 1,320 low-ANC lakes. In general, the concentrations of exchangeable base cations, base saturation, and soil pH were low. More than 75% of the target lakes received drainage from watersheds having average soil B horizon exchangeable Ca concentrations less than 0.52 cmol_c/kg, base saturation (BS) less than 10.3%, and pH (H_2O) less than 4.5. Variations in the effective cation exchange capacity in both O and B horizons were closely correlated with soil organic matter content. These data provide a baseline against which to compare future changes in regional soil chemistry. In addition, the soil data provided input for aquatic effects models used to project future changes in surface water chemistry and biological conditions.

Lake water chemical recovery responses have been indicated in ongoing lakewater monitoring databases and in modeling results reported here. However, our modeling results

further suggested that, for many Adirondack lakes, chemical recovery might fail to continue in the future. We simulated that low-ANC lakes would actually reacidify under emissions control regulations in place at the time of development of this modeling effort. Both models suggested that most of the Adirondack lakes that are currently lowest in ANC ($\leq$ 20 μeq/L) would begin to reacidify within approximately the next two decades under the Base Case scenario. This reacidification was attributable to projected continued declines in mineral soil % BS within the lake watersheds. Continued chemical recovery was suggested, however, under additional emissions controls.

We developed empirical relationships between lakewater ANC and the species richness of zooplankton and fish, based on available data. These relationships were then applied to PnET-BGC model hindcast and forecast projections to generate estimates of the extent to which changes in species richness might accompany projected chemical changes. Using the empirical relationships between zooplankton species richness and lake ANC, the median inferred loss of zooplankton species from 1850 to 1990 was 2, with some lakes inferred to have lost up to 6 species.

Ignoring other factors that might influence habitat quality, we estimated that the median EMAP study lake had lakewater acid-base chemistry consistent with the presence of five fish species in 1850, prior to the onset of air pollution. Twenty percent of the lake population was estimated to have pre-industrial lakewater ANC consistent with supporting fewer than 4.1 fish species. By 1990, these median and 20th percentile values for estimated fish species richness had been reduced to 4.6 and 2.0 species, respectively. None of the emissions control scenarios suggested that the median Adirondack lake would gain more than 0.4 fish species by 2100, based on application of this empirical relationship to the PnET-BGC projections of future lakewater chemistry. However, 20% of the lakes (those most acid-sensitive) were estimated to change ANC to an extent consistent with a further loss of 1.3 fish species by 2100 under the Base Case, and a gain of 0.9 and 1.5 species under the Moderate and Aggressive Additional Emissions Control scenarios, respectively.

Model output comparison between MAGIC and PnET-BGC focused on site-by-site comparisons of simulation outputs, regional comparisons using cumulative distribution functions, and patterns of historical and future simulated ANC in comparison with variations in sulfur deposition and baseline (1990) values for ANC and mineral soil % BS. In general, PnET-BGC estimated less historical acidification and less future chemical recovery as compared with MAGIC. This inter-model difference was most pronounced for lakes having ANC between about 50 and 150 µeq/L.

The MAGIC and PnET-BGC models differed somewhat in their assessment of how representative are each of the modeled ALTM lakes compared with the overall population of Adirondack lakes. For each modeled long-term monitoring lake, we estimated the percentage of lakes in the overall population that were simulated by each model to be more acid-sensitive than the subject lake. Both models estimated that the modeled ALTM lakes were largely among the lakes in the population that had acidified most between 1850 and 1990. Both models estimated that virtually all of the modeled ALTM lakes were in the top 50% of acid sensitivity compared with the 1,829 Adirondack lakes in the EMAP statistical frame, irrespective of lake ANC. This result was found for projections of both past acidification and future recovery. It is important to note, however, that the Adirondack Lakes Survey sampled a large fraction (~ 75%) of the lakes in the region during the mid-1980s. Thus, the statistical sampling by EMAP is not the only way to evaluate regional patterns.

The results of this research will allow fuller utilization of data from on-going chemical and biological monitoring and process-level studies. A mechanism is provided for regionalization of findings. This approach was accomplished by developing/refining relationships among watershed characteristics, chemical change, and biological responses to changing levels of acid deposition. Such information is important for the management of the ecosystems in New York that are most responsive to changes in acid deposition.

In this project, we determined types of Adirondack watersheds in which acidified lakes might be expected to chemically recover, and by how much, in response to varying levels of future S and N emissions controls. We also identified types of watersheds in which recovery is unlikely or will be substantially delayed. This information will be useful for determining watersheds that may require the most intensive research or remediation efforts.

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List of Acronyms

AEAP	Aquatic Effects Assessment Program
AIC	Aikake's Information Criteria
AirMon	Atmospheric Integrated Research Monitoring Network
ALSC	Adirondack Lakes Survey Corporation
ALTM	Adirondack Long-term Monitoring Program
ANC	Acid neutralizing capacity
BS	Base saturation
CAIR	Clean Air Interstate Rule
CALK	Calculated ANC
CASTNet	Clean Air Status and Trends Network
CEC	Cation exchange capacity
CEC_e	Effection cation exchange capacity
DDRP	Direct Delayed Response Project
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
EGU	Electricity generating units
ELS	Eastern Lake Survey
ELS-II	Phase II of the Eastern Lake Survey
EMAP	Environmental Monitoring and Assessment Program
EPA	Environmental Protection Agency
GIS	Geographic information system
GPS	global positioning system
HDDE	Heavy duty diesel engines
IAQR	Interstate Air Quality Rule
LNDE	Land-based non-road diesel engines
LOI	Loss on ignition
LTM	Long-term Monitoring program
MACT	Maximum achievable control technology
MAGIC	Model of Acidification of Groundwater in Catchments
NADP	National Atmospheric Deposition Program
NAPAP	National Acid Precipitation Assessment Program
NY-GAP	New York State Gap Analysis Program
NYSDEC	New York State Department of Environmental Conservation
NYSERDA	New York State Energy Research and Development Authority
PCA	Principal components analysis
PM	Particulate matter
PnET-BGC	Photosynthesis and evapotranspiration biogeochemistry model
QA/QC	Quality assurance/Quality Control
RACT	Reasonably available control technology
RMSE	Root mean square error
SAA	Sum of acid anions
SBC	Sum of base cations
SIP	State Implementation Plan
STAR	Science to Achieve Results
USDA	U.S. Department of Agriculture
UV-B	Ultraviolet radiation

Glossary

Acid anion - negatively charged ion that does not react with hydrogen ion in the pH range of most natural waters.

Acid-base chemistry - the reaction of acids (proton donors) with bases (proton acceptors). In the context of this report, this means the reactions of natural and anthropogenic acids and bases, the result of which is described in terms of **pH** and **acid neutralizing capacity** of the system.

Acid cation - hydrogen ion or metal ion that can hydrolyze water to produce hydrogen ions, e.g., ionic forms of aluminum, manganese, and iron.

Acid neutralizing capacity (ANC) - the equivalent capacity of a solution to neutralize strong acids. The components of ANC include weak bases (carbonate species, dissociated organic acids, alumino-hydroxides, borates, and silicates) and strong bases (primarily, OH^-). ANC can be measured in the laboratory by the Gran titration procedure or defined as the difference in the equivalent concentrations of the base cations and the mineral acid anions.

Acidic deposition - transfer of acids and acidifying compounds from the atmosphere to terrestrial and aquatic environments via rain, snow, sleet, hail, cloud droplets, particles, and gas exchange.

Acidic episode - an **episode** in a water body in which **acidification** of surface water to an **acid neutralizing capacity** less than or equal to 0 occurs.

Acidic lake or stream - a lake or stream in which the **acid neutralizing capacity** is less than or equal to 0.

Acidification - the decrease of **acid neutralizing capacity** in water or **base saturation** in soil caused by natural or anthropogenic processes.

Acidified - pertaining to a natural water that has experienced a decrease in **acid neutralizing capacity** or a soil that has experienced a reduction in **base saturation.**

Acidophilic - describing organisms that thrive in an acidic environment.

Analyte - a chemical species that is measured in a water sample.

Anion - a negatively charged ion.

Anthropogenic - of, relating to, derived from, or caused by humans or related to human activities or actions.

Base cation - an alkali or alkaline earth metal cation (Ca^{2+}, Mg^{2+}, K^+, Na^+).

Base cation buffering - the capacity of a watershed soil or a sediment to supply base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) to receiving surface waters in exchange for acid cations (H^+, Al^{3+}); may occur through cation exchange in soils or weathering of soil or bedrock minerals.

Base cation supply - The rate at which base cations can be supplied to buffer incoming acid cations; this rate is determined by the relative rate of mineral weathering, the availability of base cations on exchange sites, and the rate of mobile anion leaching.

Base saturation - the proportion of total soil **cation exchange capacity** that is occupied by exchangeable **base cations**, i.e., by Ca^{2+}, Mg^{2+}, K^+, and Na^+.

Bias - a systematic difference (error) between a measured (or predicted) value and its true value.

Biological effects - changes in biological (organismal, populational, community-level) structure and/or function in response to some causal agent; also referred to as biological response.

Calibration - process of checking, adjusting, or standardizing operating characteristics of instruments or coefficients in a mathematical model with empirical data of known quality. The process of evaluating the scale readings of an instrument with a known standard in terms of the physical quantity to be measured.

Catchment - see **watershed**.

Cation - a positively charged ion.

Cation exchange - the interchange between a cation in solution and another cation on the surface of any surface-active material such as clay or organic matter.

Cation exchange capacity - the sum total of exchangeable cations that a soil can adsorb.

Cation leaching - movement of cations out of soil, in conjunction with mobile anions in soil solution.

Cation retention - the physical, biological, and geochemical processes by which cations in watersheds are held, retained, or prevented from reaching receiving surface waters.

Chronic acidification - see **long-term acidification**.

Circumneutral - close to neutrality with respect to **pH** (neutral pH = 7); in natural waters, pH 6-8.

Conductance - (See **specific conductance**.)

Confidence limits - a statistical expression, based on a specified probability, that estimates the upper and/or lower value (limit) or the interval expected to contain the true population mean.

Decomposition - the microbially mediated reaction that converts solid or dissolved organic matter into its constituents (also called decay or mineralization).

Denitrification - biologically mediated conversion of nitrate to gaseous forms of nitrogen (N_2, NO, N_2O); denitrification occurs during decomposition of organic matter.

Dissolved inorganic carbon - the sum of dissolved (measured after filtration) carbonic acid, bicarbonate, and carbonate in a water sample.

Dissolved organic carbon - organic carbon that is dissolved or unfilterable in a water sample (0.45-µm pore size)

Drainage basin - see **watershed**.

Drainage lake - a lake that has a permanent surface water inlet and outlet.

Dry deposition - transfer of substances from the atmosphere to terrestrial and aquatic environments via gravitational settling of large particles and turbulent transfer of trace gases and small particles.

Dynamic model - a mathematical model in which time is included as an independent variable.

Empirical model - representation of a real system by a mathematical description based on experimental or observational data.

Episodes - a subset of hydrological phenomena known as events. Episodes, driven by rainfall or snowmelt, occur when **acidification** takes place during a **hydrologic event**. Changes in other chemical **parameters**, such as aluminum and calcium, are frequently associated with episodes.

Episodic acidification - the short-term decrease of **acid neutralizing capacity** from a lake or stream. This process has a time scale of hours to weeks and is usually associated with **hydrological events**.

Equivalent - unit of ionic concentration, a mole of charge; the quantity of a substance that either gains or loses one mole of protons or electrons.

Evapotranspiration - the process by which water is returned to the air through direct evaporation or transpiration by vegetation.

Forecast - to estimate the probability of some future event or condition as a result of rational study and analysis of available data.

Frame - a structural representation of a population providing a sampling capability.

Gran analysis - a mathematical procedure used to determine the equivalence points of a titration curve for **acid neutralizing capacity**.

Ground water - water in a saturated zone within soil or rock.

Hindcast - to estimate the probability of some past event or condition as a result of rational study and analysis of available data.

Hydraulic residence time - a measure of the average amount of time water is retained in a lake basin. It can be defined on the basis of inflow/lake volume, represented as "RT," or on the basis of outflow (outflow/lake volume) and represented as T_W. The two definitions yield similar values for fast-flushing lakes, but diverge substantially for long-residence time seepage lakes.

Hydrologic(al) event - pertaining to increased water flow or discharge resulting from rainfall or snowmelt.

Hydrologic(al) flow paths - surface and subsurface routes by which water travels from where it is deposited by precipitation to where it drains from a **watershed**.

Hydrology - the science that treats the waters of the earth--their occurrence, circulation, and distribution; their chemical and physical properties; and their reaction with their environment, including their relationship to living things.

Inorganic aluminum - the sum of free aluminum ions (Al^{3+}) and dissolved aluminum bound to inorganic ligands; operationally defined by **labile monomeric aluminum**.

Labile monomeric aluminum - operationally defined as aluminum that can be retained on a cation exchange column and measured by one of the two extraction procedures used to measure **monomeric aluminum**. Labile monomeric aluminum is assumed to represent inorganic monomeric aluminum (Al_i).

Liming - the addition of any base materials to neutralize surface water or sediment or to increase **acid neutralizing capacity**.

Littoral zone - the shallow, near-shore region of a body of water; often defined as the band from the shoreline to the outer edge of the occurrence of rooted vegetation.

Long-term acidification - the decrease of **acid neutralizing capacity** in a lake or stream over a period of hundreds to thousands of years, generally in response to gradual leaching of ionic constituents.

Mineral acids - inorganic acids, e.g., H_2SO_4, HNO_3, HCl, H_2CO_3.

Mineralization - process of converting organic nitrogen in the soil into ammonium, which is then available for biological uptake.

Mineral weathering - dissolution of rocks and minerals by chemical and physical processes.

Mitigation - generally described as amelioration of adverse impacts caused by acidic deposition at the source (e.g., emissions reductions) or the receptor (e.g., lake liming).

Mobile anions - anions that flow in solutions through watershed soils, wetlands, streams, or lakes without being adsorbed or retained through physical, biological, or geochemical processes.

Model - an abstraction or representation of a **prototype** or system, generally on a smaller scale.

Monomeric aluminum - aluminum that occurs as a free ion (Al^{3+}), simple inorganic complexes (e.g., $Al(OH)_n^{3-n}$, AlF_n^{3-n}), or simple organic complexes, but not in polymeric forms; operationally, extractable aluminum measured by the pyrocatechol violet method or the methyl-isobutyl ketone method (also referred to as the "oxine" method) is assumed to represent **total monomeric aluminum**. Monomeric aluminum can be divided into labile and non-labile components using cation exchange columns.

Monte Carlo method - technique of stochastic sampling or selection of random numbers to generate synthetic data.

Natural acids - acids produced within terrestrial or aquatic systems through natural, biological, and geochemical processes; i.e., not a result of acidic deposition or deposition of acid precursors.

Nitrification - oxidation of ammonium to nitrite or nitrate by microorganisms. A by-product of this reaction is H^+.

Nitrogen fixation - biological conversion of elemental nitrogen (N_2) to organic N.

Nitrogen saturation - condition whereby nitrogen inputs to an alpine or forested ecosystem exceed plant uptake requirements.

Non-labile monomeric aluminum - operationally defined as aluminum that passes through a cation exchange column and is measured by one of the two extraction procedures used to measure **monomeric aluminum**; assumed to represent organic monomeric aluminum (Al_o).

Organic acids - heterogeneous group of acids generally possessing a carboxyl (-COOH) group or phenolic (C-OH) group; includes fulvic and humic acids.

Organic aluminum - aluminum bound to organic matter, operationally defined as that fraction of aluminum determined by colorimetry after sample is passed through a strong cation exchange column.

Parameter - (1) a characteristic factor that remains at a constant value during the analysis, or (2) a quantity that describes a statistical population attribute.

pH - the negative logarithm of the hydrogen ion activity. The **pH** scale is generally presented from 1 (most acidic) to 14 (most alkaline); a difference of one **pH** unit indicates a tenfold change in hydrogen ion activity.

Physiography - the study of the genesis and evolution of land forms; a description of the elevation, slope, and aspect of a study area.

Plankton - plant or animal species that spend part or all of their lives in open water.

Pool - in ecological systems, the supply of an element or compound, such as exchangeable or weatherable cations or adsorbed sulfate, in a defined component of the ecosystem.

Population - for the purpose of this report, (1) the total number of lakes within a given geographical region or the total number of lakes with a given set of defined chemical, physical, or biological characteristics; or (2) an assemblage of organisms of the same species inhabiting a given ecosystem.

Precision - a measure of the capacity of a method to provide reproducible measurements of a particular **analyte** (often represented by variance).

Probability sample - a sample in which each unit has a known probability of being selected.

Project - to estimate future possibilities based on rational study and current conditions or trends.

Quality assurance - a system of activities for which the purpose is to provide assurance that a product (e.g., data base) meets a defined standard of quality with a stated level of confidence.

Quality control - steps taken during sample collection and analysis to ensure that data quality meets the minimum standards established in a **quality assurance** plan.

Regionalization - describing or estimating a characteristic of interest on a regional basis.

Retention time - the estimated mean time (usually expressed in years) that water resides in a lake prior to leaving the system. (See **hydraulic residence time**.)

Scenario - one possible deposition sequence following implementation of a control or **mitigation** strategy and the subsequent effects associated with this deposition sequence.

Short-term acidification - see **episode**.

Simulation - description of a **prototype** or system response to different conditions or inputs using a **model** rather than actually observing the response to the conditions or inputs.

Simulation model - **mathematical model** that is used with actual or synthetic input data, or both, to produce long-term time series or predictions.

Species richness - the number of species occurring in a given aquatic ecosystem, generally estimated by the number of species caught using a standard sampling regime.

Specific conductance - the conductivity between two plates with an area of 1 cm^2 across a distance of 1 cm at 25°C.

Steady state - the condition that occurs when the sources and sinks of a property (e.g., mass, volume, concentration) of a system are in balance (e.g., inputs equal outputs; production equals consumption).

Stratified design - a statistical design in which the population is divided into strata, and a sample selected from each stratum.

Strong acid anion sum (SAA or C_A) - refers to the equivalent sum of SO_4^{2-}, NO_3^-, Cl^-, and F^-. The term specifically excludes organic acid anions.

Strong acids - acids with a high tendency to donate protons or to completely dissociate in natural waters, e.g., H_2SO_4, HNO_3, HCl^-, and some **organic acids**. (See **acid anions**.)

Strong bases - bases with a high tendency to accept protons or to completely dissociate in natural waters, e.g., NaOH.

Subpopulation - any defined subset of the target **population**.

Sulfate adsorption - the process by which sulfate is chemically exchanged (e.g., for OH^-) or adsorbed onto positively charged sites on the soil matrix; under some conditions this process is reversible, and the sulfate may be desorbed.

Sulfate reduction - (1) the conversion of sulfate to sulfide during the decomposition of organic matter under anaerobic conditions (dissimilatory sulfate reduction) and (2) the formation of organic compounds containing reduced sulfur compounds (assimilatory sulfate reduction).

Sulfate retention - the physical, biological, and geochemical processes by which sulfate in **watersheds** is held, retained, or prevented from reaching receiving surface waters.

Sum of base cations (SBC or C_B) - refers to the equivalent sum of Ca^{2+}, Mg^{2+}, Na^+, and K^+. The term specifically excludes cationic Al^{n+} and Mn^{2+}.

Surficial geology - characteristics of the earth's surface, especially consisting of unconsolidated residual, colluvial, alluvial, or glacial deposits lying on the bedrock.

Target population - a subset of a **population** explicitly defined by a given set of exclusion criteria to which inferences are to be drawn from the sample attributes.

Total monomeric aluminum - operationally defined simple unpolymerized form of aluminum present in inorganic or organic complexes.

Turnover - the interval of time in which the density stratification of a lake is disrupted by seasonal temperature variation, resulting in entire water mass becoming mixed.

Variable - a quantity that may assume any one of a set of values during analysis.

Watershed - the geographic area from which surface water drains into a particular lake or point along a stream.

Weak acids - acids with a low proton-donating tendency that tend to dissociate only partially in natural waters, e.g., H_2CO_3, H_4SiO_4, and most **organic acids**. (See **acid anions**.)

Weak bases - bases with a low proton-accepting tendency that tend to dissociate only partially in natural waters, e.g., HCO_3^-, $Al(OH)_4^-$.

Wet deposition - transfer of substances from the atmosphere to terrestrial and aquatic environments via precipitation, e.g., rain, snow, sleet, hail, and cloud droplets. Droplet deposition is sometimes referred to as occult deposition.

1.0 INTRODUCTION

Ecosystem damage from air pollution in the Adirondack Mountains, New York, is believed to have been substantial, mainly from atmospheric deposition of sulfur (S; Driscoll et al. 1991, Sullivan 2000, Driscoll et al. 2003). Most efforts to quantify damages, and to examine more recent ecosystem recovery, have focused on lakewater chemistry. However, relatively large decreases in regional upwind S emissions and generally similar decreases in S deposition in the Adirondack Mountains over the past two decades have resulted in limited recovery of lakewater acid-base chemistry (Stoddard et al. 1998, 2003; Driscoll et al. 2003). Sulfate (SO_4^{2-}) concentrations in lakewater have decreased markedly, but so have the concentrations of base cations. Therefore, measured increases in lakewater pH and acid neutralizing capacity (ANC) have generally been small. This limited chemical recovery of surface waters in the Adirondack Mountains and elsewhere in the northeastern United States has been attributed in large part to base cation depletion, especially Ca^{2+}, of watershed soils (Lawrence et al., 1995; Likens et al., 1996) in response to long-term elevated levels of S deposition. Changes in atmospheric deposition of base cations have also likely contributed (Gbondo-Tugbawa and Driscoll 2003). The relatively small recent increases in lakewater pH and ANC in response to substantial reductions (> 40%) in S deposition (Stoddard et al., 2003) might be attributable to remaining base cation exchange buffering in these watershed soils. There is evidence that historic increases in S deposition resulted in large increases in base cation concentrations of many Adirondack lakes, resulting in only small reductions in ANC during that period (c.f., Sullivan et al., 1990; Cumming et al., 1992). Thus, it might be reasonable to expect that subsequent decreases in solution SO_4^{2-} concentrations and mobility would result in decreased base cation concentrations in runoff. Unfortunately, data that characterize the acid-base chemistry of Adirondack soils are scarce, particularly data that define changes in soil conditions over time.

Much of the acidic deposition effects research 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 (c.f., Driscoll et al. 1991, Sullivan 2000), including intensive chemical, and in many cases biological, monitoring data collected during the past one to two decades. Despite substantial variability, there are recognizable patterns with respect to watershed characteristics associated with various acidification processes (c.f., Driscoll and Newton 1985, Driscoll et al. 1991, Sullivan et al. 1999). However, knowledge of acidification and recovery processes for individual watersheds is of limited value as a basis for public policy.

It is necessary to determine the extent to which these well-studied watersheds represent larger units. Management decisions require information regarding numbers and percentages of lakes that have behaved, or in the future will be expected to behave, in various ways. Clearly, chemical, and likely biological, recovery is now occurring in some Adirondack lakes. We need to know how many, what kind, and the extent to which such recovery will continue and/or accelerate in response to current or further decreased S and nitrogen (N) deposition.

Databases developed by six major research programs offer an opportunity to evaluate the chronic effects of acidic deposition on 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. 2003a), Adirondack Effects Assessment Program (AEAP), and the Adirondack Lakes Survey Corporation's (ALSC) survey (Kretser et al. 1989). The ELS, DDRP, and EMAP studies were all statistically based, thereby allowing population estimates to be developed. ALTM and AEAP involve on-going long-term lake monitoring efforts, but are not statistically based. Only DDRP contained a soils sampling component, but the soils data were aggregated to the entire northeastern United States, rather than the Adirondack Mountain region.

Long-term monitoring programs have been collecting chemical and biological data for the past one to two decades from Adirondack lakes, some of which show evidence of recent resource recovery. The ALTM project has been conducting monthly monitoring of the water chemistry of 17 lakes, mostly in the southwestern Adirondack Mountains, since 1982 (Driscoll et al. 2003). In 1992, the program was expanded by the addition of 35 lakes to the monitoring effort. The AEAP has been sampling the water chemistry, zooplankton, and fisheries of 30 lakes approximately twice per summer since 1994. Most of those lakes are also included within ALTM. Because the ALTM and AEAP study lakes were not statistically selected, they can be considered judgment samples.

The most extensive survey of lakewater chemistry in the Adirondack Mountains was that of the ALSC (Kretser et al. 1989, Baker et al. 1990). Over a four-year period, ALSC surveyed the chemistry and fisheries of 1,469 lakes. Despite the large number of lakes included, however, they were not drawn from a statistical frame, and therefore the results cannot be used for population estimates.

The best statistical frame for assessing acidification and recovery responses of Adirondack lakes was developed by the U.S. EPA's EMAP (Larsen et al. 1994). The EMAP included lakes as small as 1 ha, involved both chemical and more limited biological characterization, and it was based on more accurate maps than the DDRP. The EMAP was designed to provide unbiased regional characterization of the entire population of Adirondack Mountain lakes.

There is currently not a mechanism available with which to extrapolate results of either of the chemical and long-term biological monitoring studies to the regional population of Adirondack lakes, and this seriously curtails the ultimate utility of these important data. Resource managers and policymakers need to know the extent to which current and projected future emissions reductions will lead to regional ecosystem recovery, both chemical and biological. Such recovery is being quantified at the ALTM and AEAP monitoring site locations, but could not be directly extrapolated to the larger population of lakes in the region. The ALTM and AEAP were designed to study lake-specific trends and seasonality. The focus has mainly been on lakes that are highly responsive to changes in acidic deposition. Site selection for the ALTM and AEAP programs was driven in part by such considerations as the existence of historical and/or ongoing data collection, sampling logistics, and the expectation that lakes in the southwestern portion of the Adirondack Mountains region had been most impacted by acidic deposition. Questions of representativeness of the study lakes as compared with the region were not considered.

Stoddard et al. (1998) found that long-term monitoring (LTM) sites in the northeastern U.S., including those in the Adirondacks, covered the range of current ANC and base cation concentrations of the most sensitive subpopulations of lakes in the Northeast region. Thus, the intensive monitoring studies and EMAP apparently do not represent the same population of lakes. Information has not been available with which to determine the extent to which these generally low-ANC ALTM lakes are representative of the overall population with respect to acidification and recovery responses.

Rates of ongoing and future ANC increase in Adirondack lakes in response to decreases in acidic deposition are of considerable policy interest. However, making regional assessments from sites such as the long-term monitoring sites that were not statistically selected can lead to incorrect evaluations. Paulsen et al. (1998) reported on a number of inaccurate assessments made as a result of extrapolating such data. In all cases, a statistically-based probability survey showed markedly different regional conditions than did an evaluation that assumed that available data adequately represented the regional population of interest. The data record for the EMAP probability lakes is insufficient for measurement of recovery responses. Although these lakes can be used as a basis for model forecasts of recovery, they provide limited ability to determine whether or not predicted responses actually occur. Similarly, the scarcity of seasonal water chemistry data and biological response data for the probability lakes limit their utility for assessment purposes. Nevertheless, the probability lakes are essential in order to place results and conclusions from the intensively-monitored lakes into the regional context.

Future changes in the structure and function of aquatic communities will be required to restore ecosystem health. Biological response data, especially for zooplankton and to a lesser extent for fish, phytoplankton, and bacteria, are available for Adirondack lakes from the AEAP, EMAP, ALTM, and ALSC programs. Data recently collected within these programs can provide important information regarding the biological resources at greatest risk of adverse impacts from acidic deposition, and the spatial and temporal patterns of biological recovery as deposition continues to decline.

There is great interest in techniques, such as liming, to accelerate the recovery of aquatic and terrestrial organisms in acid-sensitive regions of New York as acidic deposition continues to be reduced. If the rate of chemical recovery can be increased, it may be possible to more rapidly restore biological community structure and function. However, much can be gained by examining the rate at which aquatic ecosystems are recovering now in response to recent emissions reductions, and to forecast the rate of near-term future recovery under already promulgated air pollution controls. Knowledge of the rate of ongoing responses and of the characteristics associated with those lakes that are actually recovering is critical to development of sound management policies. Such information will provide the basis for evaluating the efficacy of current and possibly expanded accelerated-recovery programs.

Prior to initiation of this study, there were no soil chemistry data available for most of the EMAP watersheds in the Adirondack Mountains. Furthermore, there were no soil databases for the Adirondack Mountain region that were well-suited for evaluating the effects of acidic deposition on soils, or for providing the basis for model projections of aquatic and terrestrial resource recovery. This critical data deficiency regarding Adirondack soils also precluded effective and comprehensive regional modeling to (a) predict future responses of Adirondack watersheds to varying emissions control scenarios, (b) determine critical loads of atmospheric deposition required to protect against further acidification, or (c) define atmospheric deposition goals to allow resource recovery.

The U.S. Environmental Protection Agency's (EPA) DDRP database (Church et al. 1989) has been used for several past modeling studies to project the response of Adirondack lakes to varying scenarios of future acidic deposition (e.g., NAPAP 1991, Turner et al. 1992, Van Sickle and Church 1995). However, there are several limitations of the DDRP soils database for conducting an assessment of the responses of Adirondack lakes to various atmospheric deposition scenarios today because:

1. Soil aggregation for the DDRP was based on mapped soils information for the entire Northeast, rather than the Adirondack sub-region specifically (a consequence of the broader regional objectives of the DDRP study). As a result, soil data for a particular Adirondack watershed were not necessarily derived from soil pits actually excavated within that watershed or even within the Adirondack sub-region.

2. The data are about two decades old and may not be compatible with data collected for current assessment purposes, including data for intensively-studied watersheds.

3. Although the DDRP watersheds were statistically selected, they are representative only of watersheds containing lakes larger than 4 ha (a consequence of the regional maps available for Eastern Lakes Survey lake selection in 1985). It has subsequently been shown that a high proportion of smaller Adirondack lakes (1-4 ha) are acidic or highly acid-sensitive (Kretser et al. 1989, Baker et al. 1990, Sullivan 1990, Sullivan et al. 1990), but were not included in the DDRP design.

The degree to which regional Adirondack soil conditions exert controls on drainage water chemistry is not well understood, but may be substantial. For example, recent research in Shenandoah National Park, Virginia, has shown a consistent pattern of lower streamwater ANC in watersheds (n=14) having lower soil base saturation (BS). All Shenandoah watersheds that had BS < 15% also had average streamwater ANC < 100 μeq/L. None of the watersheds that had ANC < 20 μeq/L showed BS greater than about 12% (Sullivan et al. 2003).

Here we integrate existing data from the AEAP, ALTM, EMAP, and ALSC programs to more fully utilize available data and provide the foundation for statistically representative assessments of watershed responses to changing levels of S and N deposition. The primary objective was to develop an approach for extrapolating spatially-limited but temporally-intensive knowledge regarding changes in the chemistry and biology of acid-sensitive lakes and their watersheds in order to conduct regional assessments of ecosystem condition in the Adirondacks. In the process, lakes were classified according to their responsiveness to future changes in S and N deposition. This research also developed a mechanism for further utilization of critical biological response data that are available for a relatively small number of lakes.

This research was undertaken to provide the foundation for determining the extent to which impacted Adirondack lakes and their watershed soils can, and will, recover, both chemically and biologically, following reductions in acidic deposition. The focus is on the Adirondack Mountain region as a whole, and in particular the intensively-monitored watersheds, many of which are in the southwestern portion of Adirondack Park. The latter group of watersheds include many that contain shallow surficial deposits (thin-till) that are highly acid-sensitive and that have been expected to be most responsive to reductions in acidic deposition.

Our primary objective was to develop approaches for extrapolating spatially-limited knowledge regarding changes in the chemistry and biology of acid-sensitive lakes and their watersheds in order to conduct regional assessments of ecosystem condition and recovery in the Adirondacks. Secondary objectives included to develop a statistically-representative soils database, provide a mechanism for further utilization of critical biological response data that are available for a relatively small number of lakes, classify lakes according to their responsiveness to future changes in S and/or N deposition, and provide the technical foundation for establishment of critical and target loads of acid deposition. An additional aim was to obtain a clear picture of the temporal and spatial evolution of chemical and biological recovery processes, as lakes improve in acid-base chemistry in response to reductions in acidic deposition.

2.0 METHODS

2.1 Site Selection

2.1.1 Study Watersheds

A group of watersheds was selected for soil sampling based on the EMAP statistical design. An additional set of watersheds was selected for sampling from among those that are subjects of long-term chemical and biological monitoring efforts. In the Adirondacks, the regional EMAP probability sample consisted of 115 lakes and their watersheds. The total number of target Adirondack lakes included in the EMAP frame was 1,829 (SE = 244). These include the lakes depicted on 1:100,000-scale USGS maps that were larger than 1 ha, deeper than 1 m, and that contained more than 1,000 m^2 of open water. Of those target lakes, an estimated 509 had summer index lakewater ANC > 200 μeq/L; these were considered insensitive to acidic deposition effects and were not included in the study reported here. The remaining 1,320 (SE = 102) low-ANC lakes constituted the frame for extrapolation of soil results. An estimated 58% of these low-ANC target lakes had ANC < 50 μeq/L at the time of EMAP sampling (1991-1994). 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 had summer index ANC ≤ 50 μeq/L and another 30% had ANC between 50 and 200 μeq/L. We focused this study on watersheds containing these two strata of low ANC lakes (≤ 50 and between 50 and 200 μeq/L) as they are thought to be most responsive to changes in air pollution. Lakewater ANC provides an integrating watershed acid-base chemistry variable that reflects biotic, edaphic, geologic, and hydrologic conditions from throughout the watershed. Throughout this report, we present summer index ANC values. These approximately correspond to annual average values; ANC measurements during spring, especially in conjunction with snowmelt, would be expected to be lower.

We used a random selection process to choose candidate watersheds for soil sampling from among the 44 EMAP watersheds containing lakes with ANC ≤ 50 μeq/L and the 39 EMAP watersheds containing lakes with ANC between 50 and 200 μeq/L. Both primary and alternate sampling candidates were selected in the order they were to be included, in anticipation of the problem that we would be unable to sample some of the selected watersheds (e.g. access difficulty or permission denied). The goal was to sample as least 30 EMAP watersheds containing lakes having ANC ≤ 50 μeq/L and 10 EMAP watersheds containing lakes having ANC between 50 and 200 μeq/L. To obtain a spatially balanced subsample, we used county 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, we used a variable probability factor based on lake ANC class (50 to 100, 100 to 150, and 150 to 200 μeq/L) to obtain more samples in the lower ANC ranges. No variable probability factors were used for the ANC ≤ 50 μeq/L lakes. Results of data or model projections for the selected EMAP watersheds can be easily extrapolated to the entire population of watersheds containing lakes with ANC ≤ 50 or ≤ 200 μeq/L, using the original EMAP sample weights adjusted for this random subsampling procedure.

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. We included in this study 29 of the 30 AEAP watersheds which have extensive databases for both chemical and biological lake monitoring. Selected EMAP and ALTM/AEAP study watersheds are listed in Table 2-1.

2.1.2 Soil Sampling Locations

Candidate sampling locations within the study watersheds were selected within general landscape units, as defined by the intersection of soil and vegetative data for the Adirondack Park. The soil spatial database used in site selection was derived from the meso soil data of the Adirondack Park Agency, which were judged to provide the best spatial soil coverage available for the entire study area. The soil geographic information system (GIS) coverage was produced in 1975 from general county soil maps prepared by the USDA Soil Conservation Service in cooperation with Cornell University Agricultural Station (USDA 1975). The base map was developed at 1:62,500 scale by the State of New York Office of Planning Coordination (Roy et al. 1997). Soil types from this database were designated for our study to represent three drainage classes defined as "excessively drained" = excessively and somewhat excessively drained, "well drained" = well and moderately well drained, and "poorly drained" = somewhat poorly, poorly and very poorly drained. Six parent material classes were defined as "organic" = organic soils, "alluvial and lacustrine" = alluvium and lacustrine, "glacial outwash" = glacial outwash, "glacial till" = glacial till with circum- neutral pH, "ablation and basal till" = till derived primarily from non-calcareous minerals, and "shallow over bedrock" = shallow soils.

Table 2-1. Study watersheds.

Probability (EMAP) Sites				Intensively-Monitored Sites		
Lake Name	EMAP ID	ALSC ID	Watershed Area (km^2)	Lake Name	ALSC ID	Watershed Area (km^2)
Low ANC (<50 μeq/L)				***Low ANC (<50 μeq/L)***		
Antediluvian Pond	NY287L	060126	1.5	Big Moose Lake	040752	92.7
Bennett Lake	NY256L	050182	2.7	Brook Trout Lake	040874	1.8
Bickford Pond	NY297L	030273	0.7	Bubb Lake	040748	179.0
Big Alderbed	NY017L	070790	15.9	Carry Pond	050669	0.2
Boottree Pond	NY284L	030374	0.1	Constable Pond	040777	9.7
Canada Lake	NY292L	070717	101.5	Dart Lake	040750	14.8
Dismal Pond	NY791L	040515	2.1	G Lake	070859	4.3
Dry Channel Pond	NY033L	030128	1.8	Grass Pond	040706	2.4
Effley Falls Pond	NY277L	040426	640.8	Helldiver Pond	040877	0.3
Hope Pond	NY012L	020059	0.5	Indian Lake[a]	040852	10.8
Horseshoe Pond	NY285L	030373	0.9	Jockeybush Lake	050259	1.5
Indian Lake[a]	NY015L	040852	10.8	Lake Rondaxe	040739	139.4
Little Lilly Pond	NY029L	040566	2.2	Limekiln Lake	040826	10.4
Long Lake	NY018L	070823	0.7	Long Pond	050649	0.1
Lower Beech Ridge Pond	NY790L	040203	0.3	Middle Branch Lake	040707	3.6
Mccuen Pond	NY782L	060039	0.6	Middle Settlement Lake	040704	1.0
North Lake[a]	NY279L	041007	75.4	North Lake[a]	041007	75.4
Parmeter Pond	NY278L	030331	0.5	Queer Lake	060329	3.5
Payne Lake	NY794L	040620	1.7	Round Pond	040731A	0.1
Razorback Pond	NY280L	040573	0.2	Sagamore Lake	060313	48.4
Rock Pond	NY286L	060129	35.9	South Lake[a]	041004	14.5
Rocky Lake	NY527L	040137	1.1	Squash Pond	040754	0.5
Second Pond	NY013L	050298	4.4	Squaw Lake[a]	040850	1.2
Seven Sisters Pond	NY288L	060074	0.7	West Pond	040753	1.2
Snake Pond	NY281L	040579	0.5	Wheeler Lake	040731	0.2
South Lake[a]	NY282L	041004	14.5	Willis Lake	050215	1.4
Squaw Lake[a]	NY014L	040850	1.2	Willys Lake[a]	040210	1.3
Trout Pond	NY767L	060146	2.5			
Upper Sister Lake	NY030L	040769	13.9			
Whitney Lake	NY797L	070936	2.3			
Willys Lake[a]	NY789L	040210	1.3			
Witchhopple Lake	NY788L	040528	19.7			
Wolf Pond	NY515L	030360	0.2			
Intermediate ANC (50-200 μeq/L)				***Intermediate ANC (50-200 μeq/L)***		
Arbutus Pond[a]	NY786L	050684	3.2	Arbutus Pond[a]	050684	3.2
Blue Mountain Lake	NY520L	060307	51.7	Cascade Lake	040747	4.8
Bog Pond	NY528L	060175	27.3	Moss Lake	040746	12.5
Carry Falls Reservoir	NY522L	060035C	2265.1	Raquette Lake Reservoir	060315A	1.9
Clear Pond	NY529L	020070	0.9	Windfall Pond	040750A	4.0
Clear Pond	NY005L	060176	1.6			
Gull Pond	NY020L	050418	0.2			
Hitchins Pond	NY768L	060144	133.3			
Long Pond	NY010L	030170	0.6			
Piseco Lake	NY775L	050234	143.7			
Seventh Lake	NY533L	050631A	43.1			

[a] Occurs in both probability and intensively-monitored groups.

The forest cover types spatial database used in site selection was derived from the New York State Gap Analysis Project (NY-GAP), which was completed in 1998 based on Landsat-5 thematic mapper satellite imagery data acquired between 1991 and 1993. Thirty-one land cover types were identified by NY-GAP using the National Vegetation Classification System (Grossman et al. 1998, Anderson et al. 1998). These were classified for this project into coniferous, mixed, and deciduous forest and wetland types.

In most cases, three target site locations were selected for soil sampling per watershed, with each site being randomly located within the identified predominant landscape units located for practical reasons within 200 m of the lakeshore or inlet stream(s) in the lower 60% of each watershed. Some larger EMAP watersheds contained other study watersheds nested within them. Therefore, these larger watersheds contained more than three target sites for soil sampling. Within each of the three most dominant mapped landscape units in each watershed, we identified a target sampling position using random numbering, a map of hydrography, and the identified vegetation and soils classes.

2.2 Data Compilation

Several water chemistry databases were acquired for use in model calibration. Data were derived primarily from the EMAP, ALTM, and Adirondack Lakes Survey Corporation (ALSC) survey and monitoring efforts. The required lake water and soil composition data for the modeling efforts included the following measurements:

- stream water composition: pH, ANC, Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, NO_3^-, and Cl^-
- soil properties: thickness and total cation exchange capacity, exchangeable bases (Ca^{2+}, Mg^{2+}, K^+, and Na^+), bulk density, porosity, and pH

Where available, the stream water chemistry database also included dissolved organic (DOC) and inorganic (DIC) carbon, H_4SiO_4, and inorganic monomeric Al (Al_i).

ANC ranges defined for acidification modeling in this study were similar to those proposed by Bulger et al. (1999):

- ANC $\leq$ 0 μeq/L - acidic;
- ANC > 0 to $\leq$ 20 μeq/L - highly sensitive to episodic acidification to ANC below zero;

- ANC > 20 to ≤ 50 μeq/L - potentially sensitive to episodic acidification to ANC below zero;
- ANC > 50 to ≤ 100 μeq/L - may be sensitive to episodic acidification to low ANC values;
- ANC > 100 μeq/L - not likely to be sensitive to acidification.

Availability of lake water composition data for at least one sample occasion was a prerequisite for all candidate sites for model application. Typically, multiple lake water composition records were available. For most of the lakes included in the ALTM and/or AEAP studies, about 10 to 20 years of monthly monitoring data were available. For most other study lakes, data from approximately 3 to 10 water samples were available. For 13 study lakes, additional water samples were collected and analyzed at Syracuse University in 2003, following methods comparable to those of ALTM. All available water chemistry data were used for the PnET-BGC model calibration at most sites. However, for 5 of the lakes having 20 years of monitoring data, calibration was based on the first 10 years of data, and the balance was used for model performance evaluation. The Model of Acidification of Groundwater in Catchments (MAGIC) was calibrated to each study watershed using available data collected over a five-year period; the balance was used for model performance evaluation.

2.3 Field Sampling

2.3.1 Soils

Soils were sampled during the summer of 2003. At each soil-sampling site, an initial evaluation was made to determine whether the selected site was representative of the surrounding soil/vegetation unit, and whether the unit matched the mapped soil drainage and forest type classification. An alternate location was chosen if the initial pre-selected location was heavily disturbed, located on or very close to a road, under water, or not representative of the surrounding topography. If the initial site was unacceptable, the location of the sampling site was moved 50 m parallel to the stream drainage and a new site was evaluated. If the site failed to correspond with the mapped vegetation type, it was only moved if the targeted site conditions were available close by; otherwise, the landscape conditions were accepted as they occurred in the field and recorded, irrespective of the mapped information. The site was then qualitatively evaluated to determine if it was representative of the sampling unit in terms of canopy cover, slope, and vegetation. If it was not, then a more representative site was selected in the immediate vicinity. Site locations were documented using a global positioning system.

For each pedon, we sampled the O and uppermost 10 cm of the mineral B horizon. Where an E horizon was present, it was typically thin and was assumed to be less reactive than the O and B horizons and was not included in the sampling. With limited resources, we chose to focus on the O and B horizons for our chemical analyses. This focus provided the data needed for future modeling efforts. Because of the relatively abrupt horizon boundaries in the upper solum of these Spodosols, and the likelihood of acidification effects from air pollution occurring from the top down, we were able to spatially anchor and standardize the mineral soil sampling increment among pedons to a constant and morphologically consistent profile segment. Thus, we sampled all mineral soils as B horizons only, and consistently sampled the upper 10 cm increment of this horizon. In no instance was soil sampled across major horizon boundaries. In a few instances, mineral soil was not present at the selected site.

At each sampling location, we gently brushed off the fresh surface litter without disturbing the O horizon. The entire O horizon, from the surface to the underlying mineral soil boundary, was quantitatively excavated from beneath a 15 X 15 cm template. For sample size considerations, where the O horizon was over 20 cm deep, it was divided in half vertically for sampling; where it was shallow, multiple units were sampled and combined. The E horizon, if present, was gently scraped away and the upper 10 cm of the B horizon was collected. The B horizon was not excavated quantitatively from within the frame, but was sampled using hand digging implements to remove a representative sample from the face of the pedon proportionally across the uppermost 10 cm depth increment of the B horizon.

Samples were labeled according to watershed number (1-100), soil pedon number (1-3), horizon, date of sampling, and name of sampler. Replicate soil samples were identified as such. Samples were placed in plastic bags in the field and transported in coolers back to the field laboratory, where the air-drying process was begun prior to shipment to the analytical laboratory. Samples of the O horizon and the mineral soil were shipped in coolers to the analytical laboratory at the University of Maine, Orono for processing and analyses.

2.3.2 Lakewater

Thirteen lakes were sampled for water chemistry during the months of August and September, 2003. These were generally the study lakes that had not been sampled within the past decade within the EMAP, ALTM, or AEAP sampling programs. Water samples were collected at a depth of 1 m in the deepest portion of the lake. Samples were stored on ice and shipped to Syracuse University for laboratory analyses.

2.4 Laboratory Analysis

2.4.1 Soils

Upon arrival at the laboratory, soil samples were unpacked and continued to be air-dried. Air-dried samples were then sieved (6 mm for O horizon, 2 mm for mineral soil) and homogenized by riffle-splitter before being subsampled for analysis. Percent air-dry moisture content was calculated to allow for the expression of all data on an oven-dried basis. Soils were oven-dried in a forced draft oven at 70° C for O horizons and 105° C for B horizons. Soil chemical analyses utilized methods widely accepted as appropriate for surface chemical characterization of forest soils. Soil pH was measured in $CaCl_2$ (0.01 M) and deionized water according to Hendershot et al. (1993) using 2 g of organic or 5 g of mineral soil material in 10 ml of solution. Exchangeable base cations and Al were extracted with 1 M NH_4Cl at a ratio of 2 g of organic soil or 5 g of mineral soil to 100 mL extraction solution and shaken for 1 h (Blume et al. 1990, Fernandez et al. 2003). All extracts were vacuum filtered through Whatman 42 filter paper (Whatman Inc., Clifton, NJ) and analyzed by flame emission (K and Na) or plasma emission spectroscopy (Ca, Mg, and exchangeable Al). Exchangeable acidity was determined by extraction with 1 M KCl (Blume et al. 1990) followed by titration to the phenolphthalein endpoint. Total C and N were determined by LECO™ combustion. As described in Fernandez et al. (2003), soil organic matter content was estimated on oven-dried samples by loss-on-ignition (LOI) at 450°C. Effective cation-exchange capacity (CEC_e) was calculated as the sum of the exchangeable base cations (Ca, Mg, K, and Na) plus exchangeable acidity. Base saturation was calculated as the percentage of the CEC_e occupied by exchangeable bases, whereas Ca, Mg, or Al saturation was calculated as the percentage of the CEC_e occupied by these individual exchangeable cations. The methods used in this study were similar to those used previously in the University of Maine at Orono laboratory and defined in the quality assurance (QA) Plans and methods of the U.S. EPA Watershed Manipulation Project (Erickson et al. 1987), USDA Forest Service Forest Response Project (Robarge and Fernandez 1986), and the DDRP of the U.S. EPA (Blume et al. 1990).

2.4.2 Lakewater

Upon receipt at Syracuse University, samples were analyzed for dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, and monomeric Al fractions as shortly after collection as possible (generally less than 72 hrs). Samples were stored at 4°C until the remainder of the analytical measurements were made. The analytical measurements used in this study are standard methods, except for the determination of Al fractions (Table 2-2). Because of concerns over the ecological effects of elevated concentrations of inorganic Al, concentrations of monomeric Al fractions were measured. Labile (or inorganic) monomeric Al is determined as the difference between monomeric and non-labile (or organic) monomeric Al. Although these fractions are operationally defined, labile monomeric Al is thought to represent inorganic forms of monomeric Al, while non-labile monomeric Al is thought to depict organic complexes of Al.

2.5 Soil Data Aggregation

Soil data were aggregated for each study watershed by computing a spatially-weighted average of all soil characteristics in landscape units that occurred within that watershed. This aggregation was done for each of the primary soil variables. Exceptions included such calculated variables as base saturation, which were recalculated subsequent to performing the spatial aggregation for each of the primary variables used in the calculation.

Typically, soil data were available for two or three landscape units within each watershed (i.e., landscape units in which soil pits had been excavated within that particular watershed). In the case of nested study watersheds, the larger watersheds often contained soil data for many more than three landscape units.

For landscape units that had not been sampled for soils within a given study watershed, data were derived from the nearest study watershed that included sampling of that landscape type. Thus, based on soil data collected within a particular study watershed, combined with data borrowed from neighboring watersheds, soil data were derived for each of the landscape units

Table 2-2. Analytical methods for lakewater chemistry used in this study.

Analyte	Method	Reference
SO_4^{2-}, NO_3^-, Cl^-, F^-	Ion chromatography	EPA 1987
NH_4^+	Phenate colorimetry; autoanalyzer	EPA 1987
Ca^{2+}, Mg^{2+}, Na^+, K^+	Atomic absorption spectrometry	EPA 1987
PH	Potentiometry with glass electrode	EPA 1987
Acid neutralizing capacity (ANC)	Strong acid titration and Gran plot analysis	EPA 1987
Dissolved inorganic carbon (DIC)	CO_2 detection by infrared (IR) spectrometry	EPA 1987
Dissolved organic carbon (DOC)	UV-enhanced persulfate oxidation, detection of CO_2 by IR spectrometry	EPA 1987
Dissolved silica	Heteropoly blue complex colorimetry; autoanalyzer	EPA 1987
Monomeric Al	Pyrocatechacol violet colormetry; autoanalyzer	McAvoy et al. 1992
Non-labile monomeric Al	Fractionation by cation exchange column, analysis for monomeric Al	McAvoy et al. 1992
Specific conductance	Conductivity bridge	EPA 1987

found within that study watershed. These data then formed the basis for spatially averaging each primary variable to derive watershed average soil characteristics for each watershed.

2.6 Modeling

2.6.1 Modeling Approach

2.6.1.1 <u>MAGIC Model</u>

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry (Cosby et al. 1985a,b). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of: 1) a submodel in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation- speciation of Al and dissolution-speciation of 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 biomass and losses to runoff. At the heart of 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 owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

Cation exchange is modeled using equilibrium (Gaines-Thomas) equations with selectivity coefficients for each base cation 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 $Al(OH)_3$. Aluminum speciation is calculated by considering hydrolysis reactions as well as complexation with SO_4^{2-} and F-. Effects of CO_2 on pH and on the speciation of inorganic C are computed from equilibrium equations. Organic acids are represented in the model as tri-protic analogues. Weathering and the uptake rate of N are assumed to be constant. 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 complete details of the model see Cosby et al. 1985 a,b; 1989). MAGIC has been used to reconstruct the history of acidification and to simulate the future trends 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. 1989, 1990, 1996; Hornberger et al. 1989; Jenkins et al. 1990a-c; Wright et al. 1990, 1994; Norton et al. 1992; Sullivan and Cosby 1998; Sullivan et al. 2004).

The aggregated nature of the model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model that can be directly measured or observed in the system of interest (called “fixed” parameters). The model is then run (using observed and/or assumed atmospheric and hydrologic inputs) and the outputs (stream water and soil chemical variables, called “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.

The estimates of the fixed parameters and deposition inputs are subject to uncertainties so a "fuzzy optimization" procedure is implemented for calibrating the model. The optimization procedure consists of multiple calibrations using random values of the fixed parameters drawn from the observed possible range of values, and random values of 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. The final calibrated model is represented by the ensemble of parameter values and variable values of the ten calibrations.

2.6.1.2 PnET-BGC Model

PnET-BGC (Figure 2-1) is an integrated dynamic biogeochemical model that simulates chemical transformations of vegetation, soil and drainage water. It was formulated by adding the sub-model BGC (biogeochemistry) to PnET-CN, a model of carbon, water and nitrogen balances (Aber and Federer 1992, Aber and Driscoll 1997, Aber et al. 1997), in order to expand the model to include vegetation and organic matter interactions of major elements (i.e., Ca^{2+}, Mg^{2+}, K^+, Na^+, Si, S, P, Al^{3+}, Cl^-, F^-), abiotic soil processes, solution speciation, and surface water processes (Gbondo-Tugbawa et al. 2001). Calibration is based on empirical relationships and observations. The model was initially developed for and applied to the northern hardwood forest ecosystems. It was tested extensively at the Hubbard Brook Experimental Forest, New Hampshire, including a detailed sensitivity analysis of parameter values. The model has subsequently been applied to intensively-studied watersheds in the Adirondack and Catskill regions of New York and applied regionally to the Adirondacks (Chen and Driscoll 2005a) and northern New England (Chen and Driscoll 2005b,c).

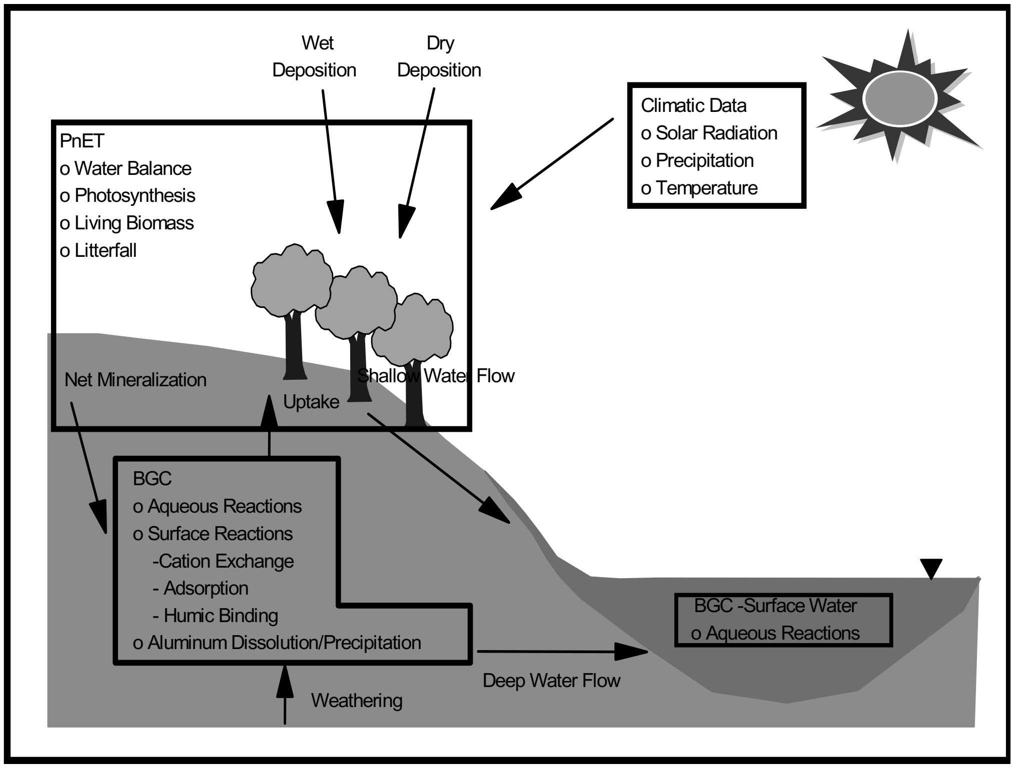


Figure 2-1. Schematic overview of the biogeochemical model PnET-BGC.

The model PnET-BGC runs on a monthly time step and requires inputs of climate, wet and dry deposition chemistry and weathering data. Climate inputs consist of minimum and maximum air temperature, solar radiation and precipitation. The model uses a constant dry-to-wet deposition ratio by default, but a variable ratio can also be applied (Chen and Driscoll 2004). Variable dry-to-wet deposition ratios were used in this investigation. Atmospheric deposition is higher under coniferous trees than deciduous trees. As a result, the model inputs utilize canopy enhancement factors to depict the increased deposition observed in coniferous and mixed forest stands compared to hardwood forests. Deposition data for all major elements are required as model inputs. Weathering rates are assumed to remain constant over time.

PnET-BGC simulates major biogeochemical processes, such as forest canopy element transformations, hydrology, soil organic matter dynamics, nitrogen cycling, geochemical weathering and chemical equilibrium reactions in solid and solution phases. and allows for simulations of land disturbance. The model uses mass transfer relations to describe weathering, canopy interactions and surface water processes. Chemical equilibrium relations describe anion adsorption, cation exchange and soil solution and surface water speciation. Adsorption of sulfate, a major contributor to acidification of soils and streams, is modeled using a pH-dependent isotherm. Cations considered in the model are Ca^{2+}, Mg^{2+}, Na^{+}, H^{+}, Al^{3+}, K^{+} and NH_4^{+} and their exchange is described using a Gaines-Thomas formulation. Soil solution equilibrium reactions are described using the tableau approach (Morel and Hering 1993). A more detailed description of the model can be found in Gbondo-Tugbawa et al. (2001).

The model uses historical reconstructions of climatic, atmospheric deposition and land disturbance in order to make hindcasts of the response of forests to past acidic deposition. The model can also been used to predict the response of acid-sensitive forest ecosystems to future changes in acidic deposition, for example in response to controls on atmospheric emissions.

2.6.2 Input Data

2.6.2.1 Baseline Emissions

The acid-base chemistry modeling for this project was conducted using 2001 as the Base Year. The effects models were calibrated to the available atmospheric deposition and water chemistry data and then interpolated or extrapolated to yield Base Year estimates of lakewater chemistry in the year 2001, which served as the starting point for specifying future emissions control scenarios, and for modeling future water chemistry. Base Year emissions for NO_x, SO_2, and NH_3 are given in Table 2-3. They were taken from EPA's average annual emissions inventory for the year 2001, developed in conjunction with modeling analyses in support of the Interstate Air Quality Rule (IAQR; U.S. EPA 2004).

Table 2-3. EPA emissions inventory (in million tons) for the Base Year (2001).

	EGU	Non-EGU[a]	Total
NO_x	4.82	18.16	22.98
SO_2	10.71	5.87	16.58
NH_3	0.011	4.871	4.882

[a] Includes on-road, non-road, and area sources.
Source: U.S. EPA (2004)

2.6.2.2 Future Emissions

Three scenarios of future emissions reductions were selected as the basis for projecting future chemical recovery of lakes. These included a Base Case scenario which assumed that emissions levels will be capped on the basis of existing regulatory controls as of January, 2004, a scenario which assumed moderate additional emissions controls above and beyond the Base Case, and a scenario which assumed more aggressive additional emissions controls. Each was implemented as percent reductions in NO_x and SO_2 emissions from 2001 levels. It was assumed that future emissions and deposition of base cations will stay constant at 2001 levels.

The Base Case emissions scenario represents emissions predicted by the U.S. EPA in the absence of further controls beyond those already promulgated or expected to be promulgated as of January 2004 (U.S. EPA 2004). Additional local controls that may be required in order to meet ozone and/or particulate matter standards were not included. Specific rules and measures included within the emissions estimates were as follows:

- Land-based Non-road Diesel Engines (LNDE; U.S. EPA 2003; www.epa.gov/nonroad/454r03009.pdf)
- Heavy Duty Diesel Engines (HDDE; U.S. EPA 2000a; www.epa.gov/otaq/models/hd2007/r00020.pdf)
- Tier 2 tailpipe standards
- NO_x State Implementation Plan (SIP) call
- Reasonably Available Control Technology (RACT) for NO_x in 1-hour ozone nonattainment areas.

Adjustments were also made by U.S. EPA to the non-road sector inventories to include the effects of the Large Spark Ignition and Recreational Vehicle rules, and to the non-EGU sector inventories to include the SO_2 and particulate matter co-benefit effects of the proposed Maximum Achievable Control Technology (MACT) standard for industrial boilers and process heaters (U.S. EPA 2004).

Future emissions under each scenario for each future year were specified as follows. Linear ramps were constructed of emissions change from 2001 (Table 2-3) to reach EPA's estimates of emissions in 2010 (Table 2-4), and similarly from 2010 to 2015 (Table 2-4). Thereafter, emissions were held constant at 2015 levels for the remainder of each scenario.

Table 2-4. Future emissions in 2010 and 2015 of NO_x, SO_2, and NH_3 specified for the three emissions control scenarios.

Scenario	2010				2015			
	EGU (Million Tons)	Non-EGU[a] (Million Tons)	Total (Million Tons)	Percent Reduction from 2001 (%)	EGU (Million Tons)	Non-EGU (Million Tons)	Total (Million Tons)	Percent Reduction from 2001 (%)
1) Base Case (existing rules)								
NO_x	3.94	13.78	17.73	-22.85	4.01	11.93	15.94	-30.64
SO_2	9.86	5.43	15.29	-7.78	9.22	5.55	14.77	-10.92
NH_3	0.002	5.000	5.002	+2.46	0.002	5.113	5.115	+4.77
2) Moderate Additional Controls								
NO_x	3.94	13.78	17.73	-22.85	1.70	11.93	13.63	-40.69
SO_2	9.86	5.43	15.29	-7.78	2.25	5.55	7.80	-52.96
NH_3	0.002	5.000	5.002	+2.46	0.002	5.113	5.115	+4.77
3) Aggressive Additional Controls								
NO_x	3.94	13.78	17.73	-22.85	NS[b]	NS	11.49	-50.0
SO_2	9.86	5.43	15.29	-7.78	NS	NS	4.97	-70.0
NH_3	0.002	5.000	5.002	+2.46	NS	NS	5.115	+4.77

[a] Includes on-road, non-road, and area sources

[b] NS - not specified - emissions reductions for the aggressive scenario will require some reductions in NO_x and SO_2 from the non-EGU sectors

NO_x and SO_2 emissions from electric generating units (EGU) under the Base Case will be capped at about 4.01 and 9.22 million tons, respectively, by the year 2015 (U.S. EPA 2004). Overall, by 2015 the Base Case scenario represented a 30.6% reduction in NO_x emissions compared with 2001 emissions, and a 10.9% reduction in SO_2 emissions. NH_3 emissions were assumed to increase by 4.8%. Emissions were held constant at 2015 levels for the remainder of the scenario (to 2050). This is a conservative assumption and may result in an underestimate of actual NO_x emissions reductions that will occur between 2015 and 2050. This is because the recent mobile source rules that are incorporated into the Base Case scenario are expected to result in gradual, long-term NO_x emissions reductions as new clean-burning vehicles are incorporated into the automotive fleet throughout the U.S. We do not have data at this time with which to quantify such further NO_x emissions reductions after 2015, and therefore such further emissions reductions beyond 2015 were not included in the modeling.

The Moderate Additional Controls scenario assumed Base Case scenario emissions levels from 2001 to 2010, followed by more marked reductions in emissions from 2010 to 2015, and constant emissions thereafter. For this scenario, it was assumed that, by 2015, EGU emissions of

NO_x will be capped at 1.7 million tons and that EGU emissions of SO_2 will be capped at 2.25 million tons (Table 2-4), in general agreement with several policy recommendations currently under consideration. Assuming non-EGU emissions follow those specified in the Base Case scenario with no further reductions, the total reductions for all sectors from 2001 values under the Moderate Additional Controls scenario are equal to 40.69% for NO_x and 52.96% for SO_2 (Table 2-4).

For the Aggressive Additional Emissions Control scenario, we assumed Base Case scenario emissions for the period 2001 to 2010. Additional reductions in emissions were imposed in a linear fashion during the period 2010 to 2015. By 2015, the assumed total reductions from 2001 emissions levels would be equal to 50% for NO_x and 70% for SO_2. As shown in Table 2-4, such large emissions reductions could not be achieved by only further controlling the EGU sector. Additional reductions in non-EGU NO_x and SO_2 emissions would also be required to achieve the total emissions levels specified for this scenario.

A breakdown of assumed future scenarios scenario according to emissions sector (EGU versus non-EGU) is provided in Table 2-4. However, it is the estimates of total emissions and deposition that ultimately drive the model estimates of effects. In other words, the total emissions reduction specified in Table 2-4 might be achieved through various combinations of reductions from the different emissions sectors. For example, under the Moderate Additional Emissions Control scenario, total SO_2 emissions were reduced by about 53% by the year 2015. Such a reduction could be achieved by enacting smaller EGU emissions reductions and larger non-EGU emissions reductions than those shown in the table, or vice versa. Regardless, the scenario provides an estimate of the expected response to an overall 53% reduction in SO_2 emissions.

On March 10, 2005, EPA issued the Clean Air Interstate Rule (CAIR), which will further reduce power plant emissions of SO_2 and NO_x beyond those represented in our Base Case scenario. CAIR will cap SO_2 and NO_x emissions in the eastern United States. Full implementation will not occur for more than two decades. EPA estimated that, under CAIR emissions reductions, SO_2 emissions from power plants throughout the United States will be about 5 million tons in 2015; NO_x emissions at that time are projected to be 2.2 million tons (http://www.epa.gov/cair/). When combined with non-EGU emissions, those represent levels of total SO_2 and NO_x emissions in 2005 that are roughly midway between our Base Case and Moderate Additional Emissions Control scenarios. With full implementation of CAIR, the SO_2

emisisons will be further reduced beyond 2015 levels, but will still be higher than is represented by the Moderate Additional Controls scenario.

2.6.2.3 Deposition

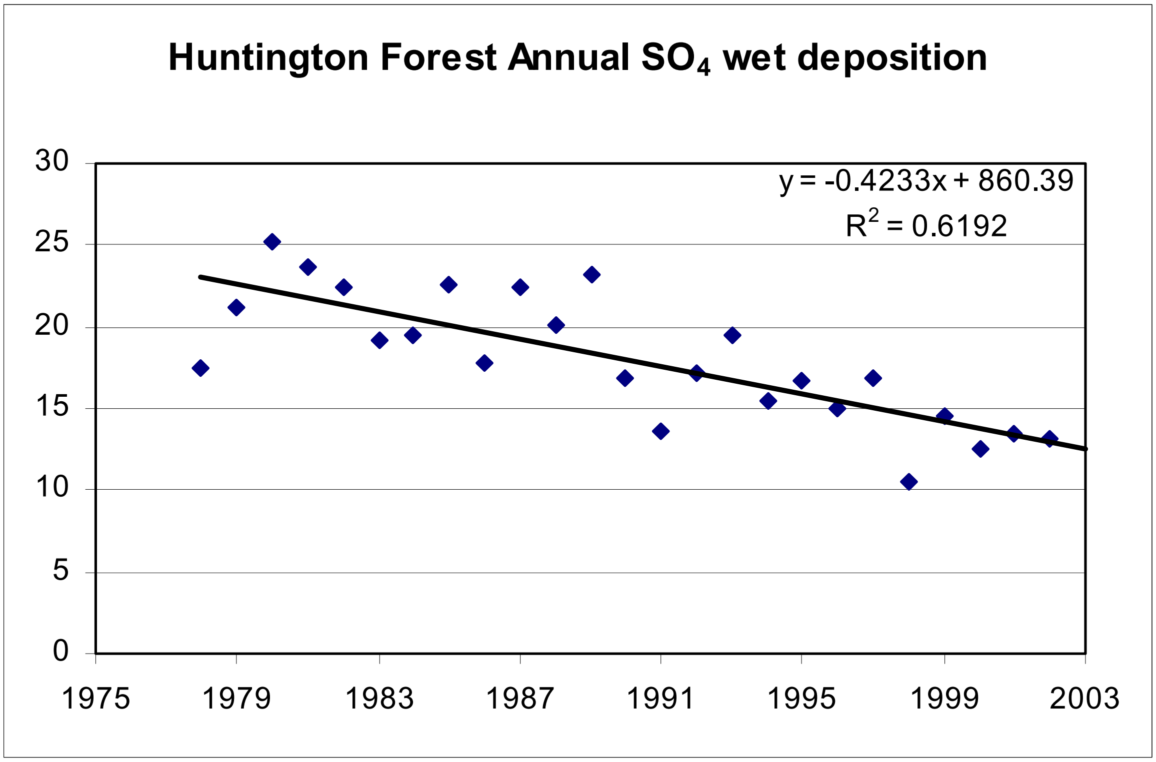
Wet deposition in the Adirondacks has been monitored by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) since 1978 at two sites: Huntington Forest and Whiteface Mountain. Measured values of recent and current wet deposition were derived from NADP/NTN through the year 2002. Base Year wet deposition of S, NO_x-N, and NH_4-N were estimated as three-year averages of annual wet deposition for the period 2000 through 2002. Over the past 20 years, wet S deposition at the two NADP/NTN sites in the Adirondacks has declined by about 40% to 50% (Figure 2-2).

Empirical relationships between regional emissions and ionic concentrations in precipitation (Figure 2-3), coupled with historical regional emissions inventories, were used to estimate the time series of historical wet S deposition to the midpoint of each study watershed (c.f., Driscoll et al. 2001). Similarly, these empirical relationships were used to estimate future wet S deposition from estimated emissions for the period 2003 to 2015 under each of the three emissions control scenarios. These future estimates assumed continued long-term average precipitation amounts. For estimating future NO_x deposition, it was assumed that NO_x deposition would change in proportion to regional NO_x emissions.

It was assumed that NH_4^+ deposition in the past, prior to the availability of monitoring data, varied with NO_3^- deposition. The spatial coverage of Ollinger et al. (1993) was used to interpolate NADP/NTN wet deposition data to the midpoint of each study watershed. Dry deposition was estimated as a percentage of wet deposition. Enhancement factors were used to depict the higher dry deposition that occurs in coniferous and mixed forest stands, as compared with hardwood stands. Based on the forest composition in each watershed, the dry-to-wet S deposition ratio for the entire watershed (DRW_n) was calculated as:

$$DRW_n = DRW_d * (P_d + EF_c * P_c + EF_m * P_m) \qquad (2\text{-}1)$$

where DRW_d is the dry-to-wet S deposition ratio for deciduous forest; P_d, P_c, and P_m are the percentages of deciduous, coniferous, and mixed forest coverages within the watershed; and EF_c



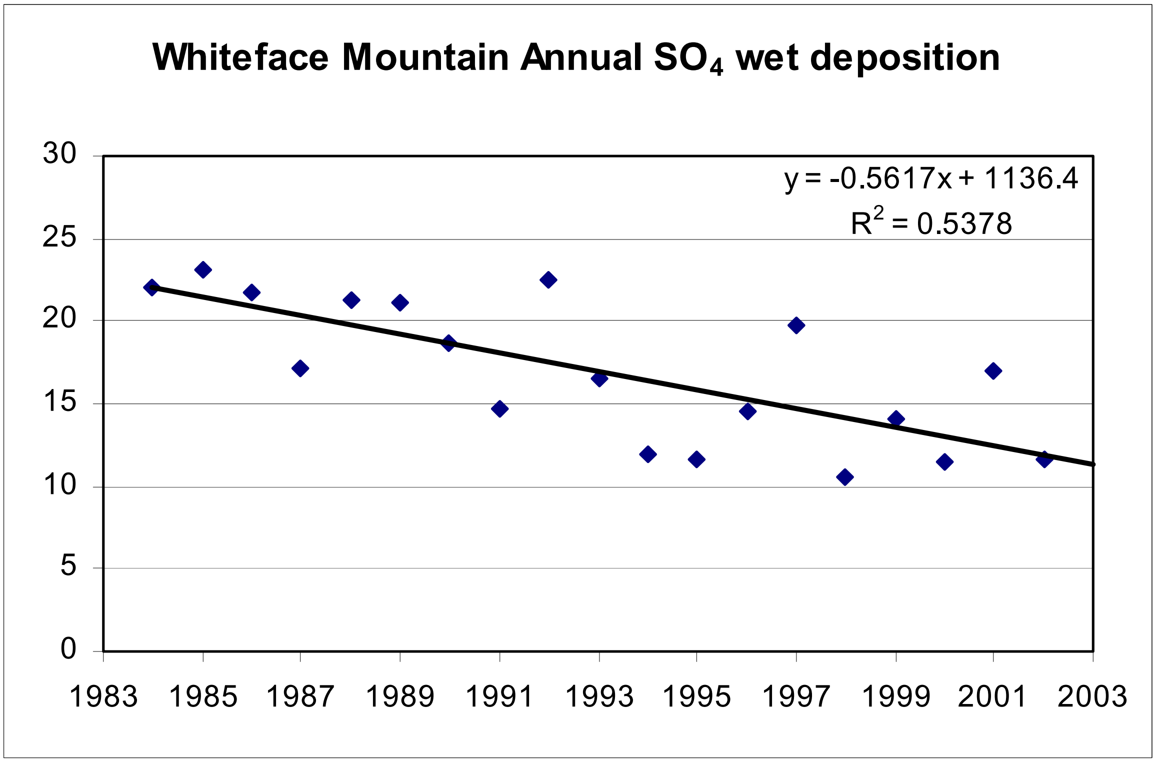


Figure 2-2. Annual SO_4^{2-} wet deposition (kg SO_4^{2-}/ha/yr) measured by NADP/NTN at a) Huntington Forest and b) Whiteface Mountain over the period of record.

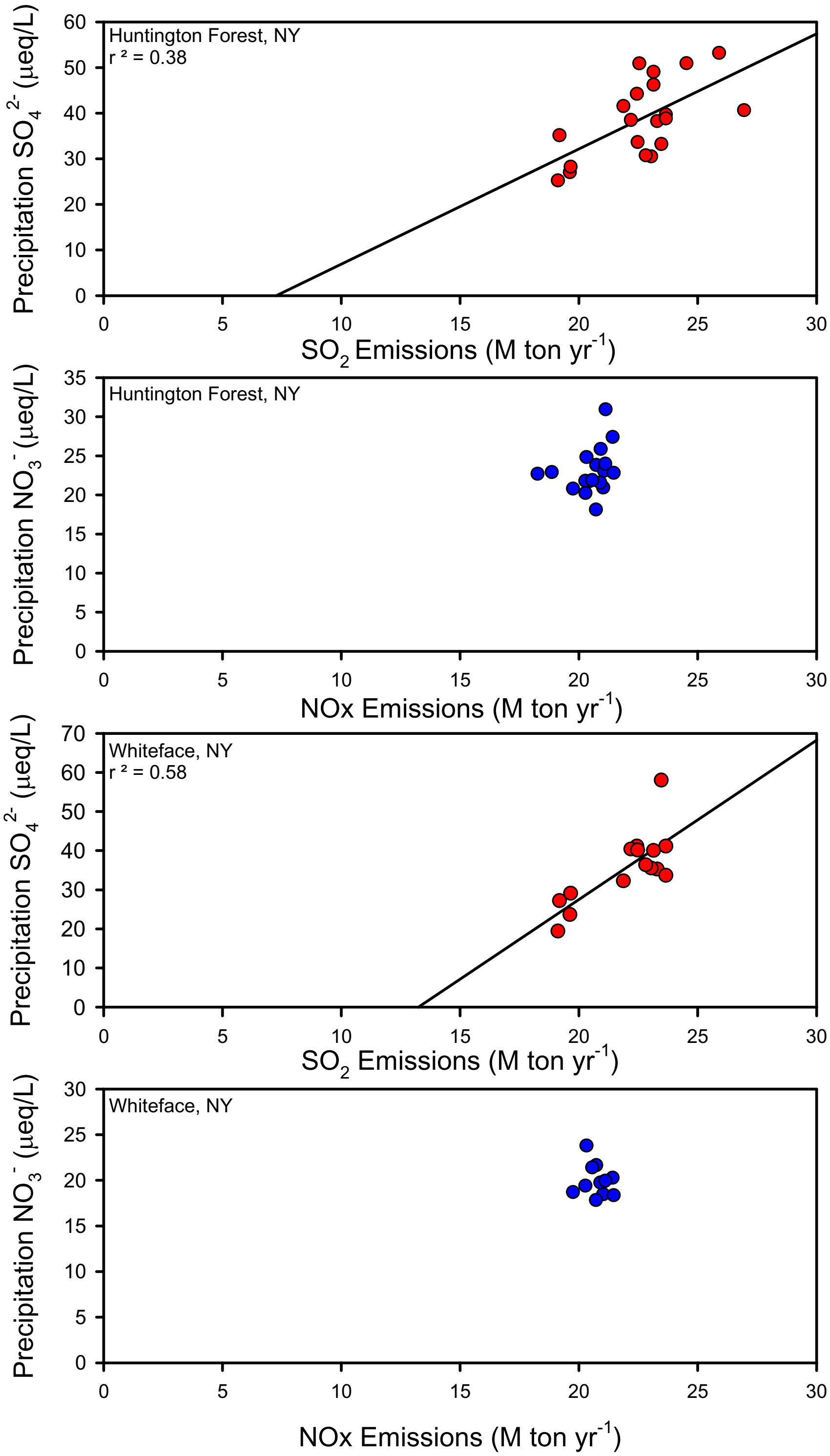


Figure 2-3. Observed relationships between regional emissions of SO_4^{2-} and NO_x and the concentrations of SO_4^{2-} and NO_3^- in precipitation at Huntington Forest and Whiteface Mountain in the Adirondacks.

and EF_m are the enhancement factors for coniferous and mixed forests, respectively. These enhancement factors were assumed to be 2.5 for coniferous and 1.75 for mixed forests (Mollitor and Raynal 1982, Chen and Driscoll 2004).

Recent data suggest that the ratio of dry-to-wet S deposition has changed over time. For example, dry S deposition decreased much faster than wet S deposition in response to recent decreases in SO_2 emissions in the U.K. (Downing et al. 1995). Similar results have been found for some sites in the northeastern United States (Palmer et al. 2004). We therefore employed time-varying dry-to-wet S deposition ratios for this study, based on current spatial distributions of dry-to-wet ratios from the Clean Air Status and Trends Network (CASTNet) and NADP/NTN. Chen and Driscoll (2004) demonstrated a positive relationship between the dry-to-wet S deposition ratio and ambient SO_2 concentrations in air samples of seven CASTNet and Atmospheric Integrated Research Monitoring Network (AIRMon) monitoring sites across the northeastern United States (Figure 2-4). Extending the empirical relationship over the past century, Chen and Driscoll (2004) inferred that the dry-to-wet S deposition ratio has changed over time at Huntington Forest in the Adirondacks (Figure 2-5). This relationship was applied in this project to historical emissions inventory data in order to estimate historical patterns in the dry-to-wet S deposition ratio in the Adirondacks.

Cloud deposition was not considered, because the study watersheds are almost completely lacking in land above 1,000 m elevation. Only three study lakes (Carry Falls Reservoir, Blue Mountain Lake, Sagamore Lake) included any land in its watershed that was higher than 1,000 m. The Sagamore Lake watershed included the highest percentage of such high-elevation land, but it only accounted for 2.4% of the watershed.

Current wet deposition of base cations and Cl^- was available from the NADP/NTN monitoring station at Huntington Forest. For each of these ions, background pre-industrial deposition was assumed to be 10% of current deposition. Deposition inputs after 1850 were assumed to increase linearly to estimated values obtained for 1950. 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 wet to dry deposition ratio. This value was assumed to be 0.3 for each of the base cations and 0.24 for Cl^-.

Past, current, and future total deposition amounts of major ions were interpolated to the midpoint of each study, as described above. Although the absolute values of total deposition

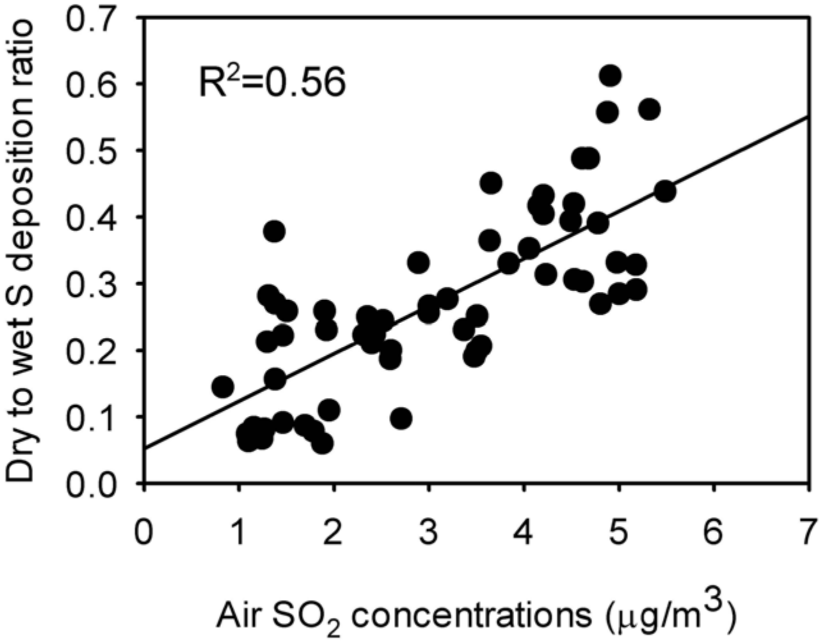


Figure 2-4. Relationship between air SO_2 concentrations and the measured dry-to-wet S deposition ratio across seven CASTNet and AIRMon monitoring sites in the northeastern United States. (Source: Chen and Driscoll 2004)

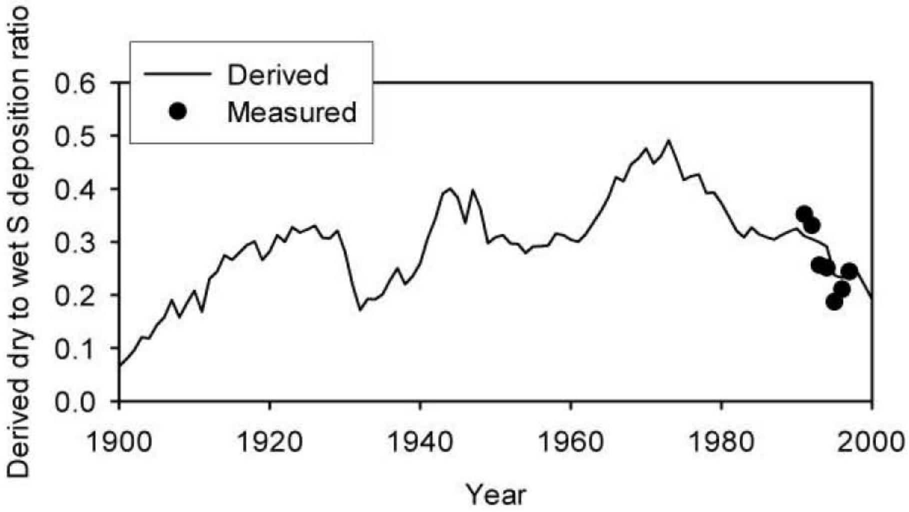


Figure 2-5. Historical dry-to-wet S deposition ratio reconstructed by Chen and Driscoll (2004) at Huntington Forest, based on the empirical relationship between air SO_2 concentrations and dry-to-wet S deposition ratio shown in Figure 2-4.

were variable from watershed to watershed, the patterns of change over time were the same. Figure 2-6 shows the estimated pattern of change in deposition over time at one illustrative watershed.

2.7 Watershed Disturbance

The extent of past disturbance was estimated for each watershed on the basis of existing records of logging activities, fire, and blow-down. Land disturbance prior to 1916 was assessed using the 1916 fire map (Roy et al. 1997) to identify areas that had previously been logged or burned. More recent disturbances were identified from the data compilation of McMartin (1994), anecdotal information in Barbara McMartin's files, perusal of historical records, and interviews with land-owners and woodland managers. The extent of blow-down during the large windstorms of 1950 and 1995 was estimated from New York State Department of Environmental Conservation (NYSDEC) blow-down maps (NYSDEC 1950, Roy et al. 1997). The spatial extent of all identified past land disturbances were clipped to study watershed boundaries using an ArcInfo GIS. The percent of each study watershed impacted by each known past land disturbance, and the estimated severity of impact, were calculated. These disturbance estimates were provided as inputs for PnET-BGC model simulations.

Data from the 1916 land cover map indicated that many of the EMAP study watersheds had been logged prior to 1916, whereas others were largely forested at that time (Figure 2-7). Most (78%) of the ALTM/AEAP study watersheds were more than 75% forested in 1916, compared with only 41% of the EMAP study watersheds.

There were two large blowdown events in the Adirondacks in the 20th century, in 1950 and 1995. Salvage logging occurred in many of the affected areas, especially following the 1950 storm. Estimates of blowdown severity for the study watersheds are given in Figure 2-8. Blowdown severity was generally similar between the two groups of study watersheds.

Data regarding more recent disturbances (post-1916) have also been compiled, including type and approximate date of disturbance, percent of watershed impacted, and a severity rating (0-5). Most of these disturbances involved selective logging of part or all of the subject watersheds.

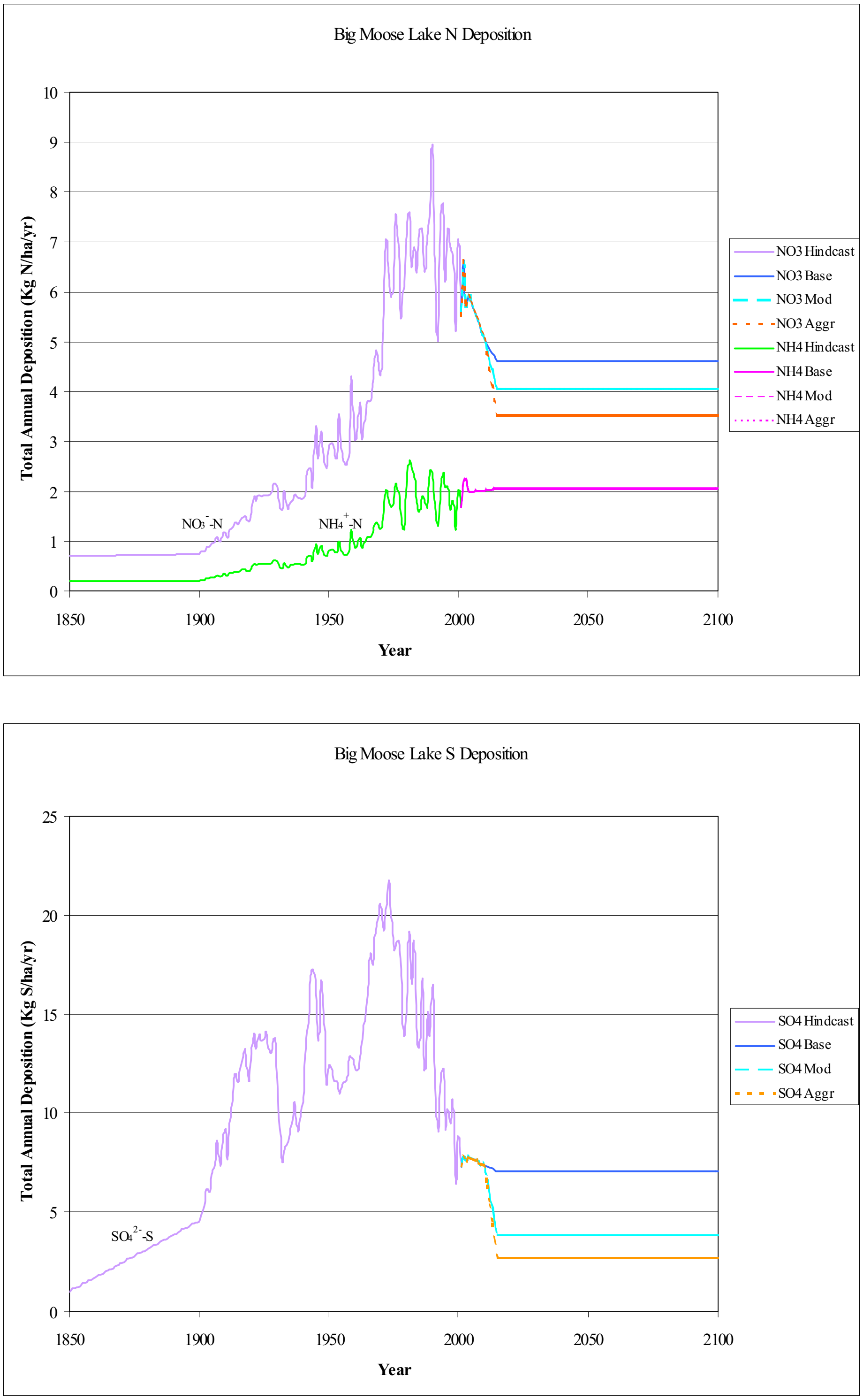
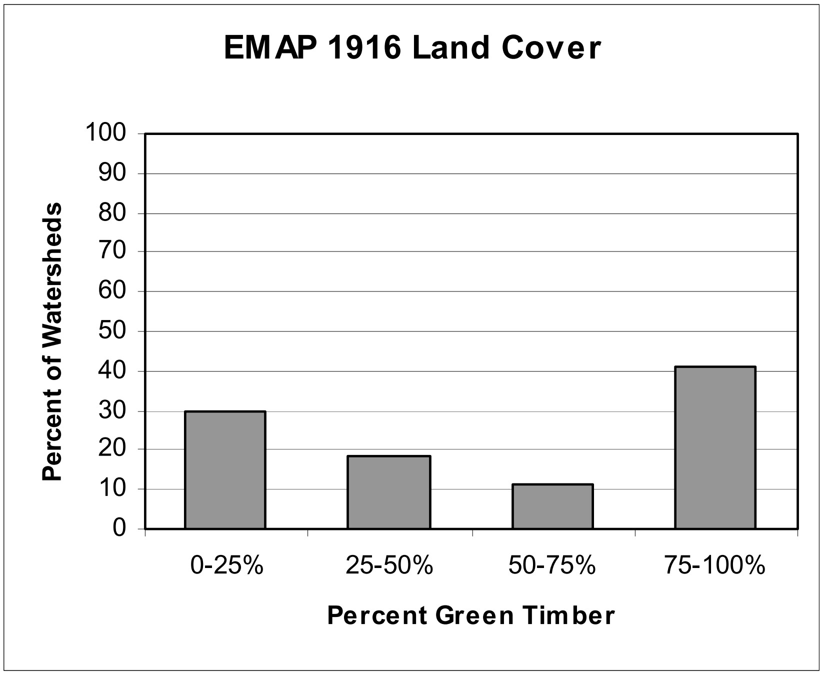


Figure 2-6. Estimated total deposition of N and S at one representative watershed (Big Moose Lake) in the southwestern Adirondack Mountains.



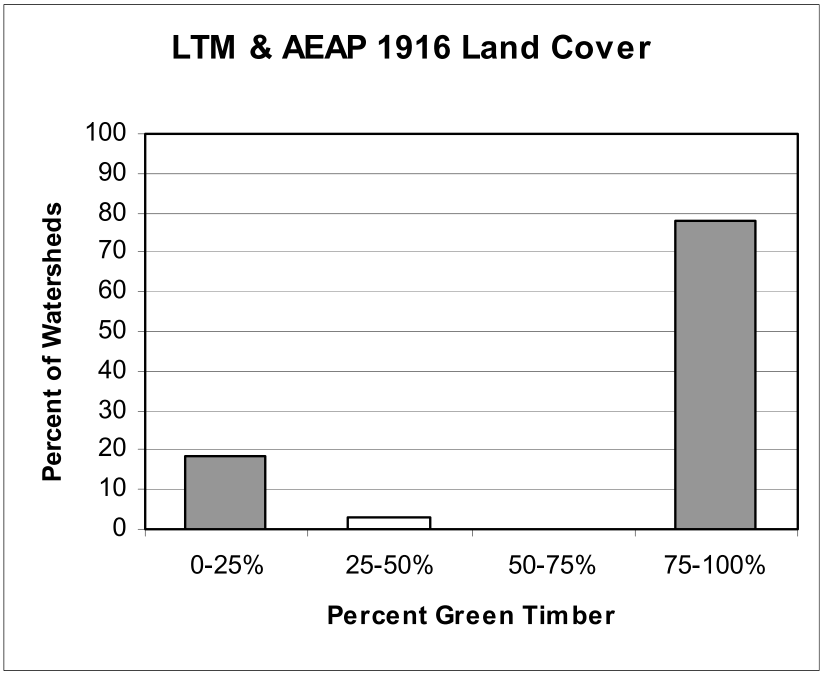


Figure 2-7. Estimated percent of terrestrial watershed (excluding the lakes) covered by green timber in 1916. Results are reported for A) EMAP study watersheds, and B) ALTM/AEAP study watersheds.

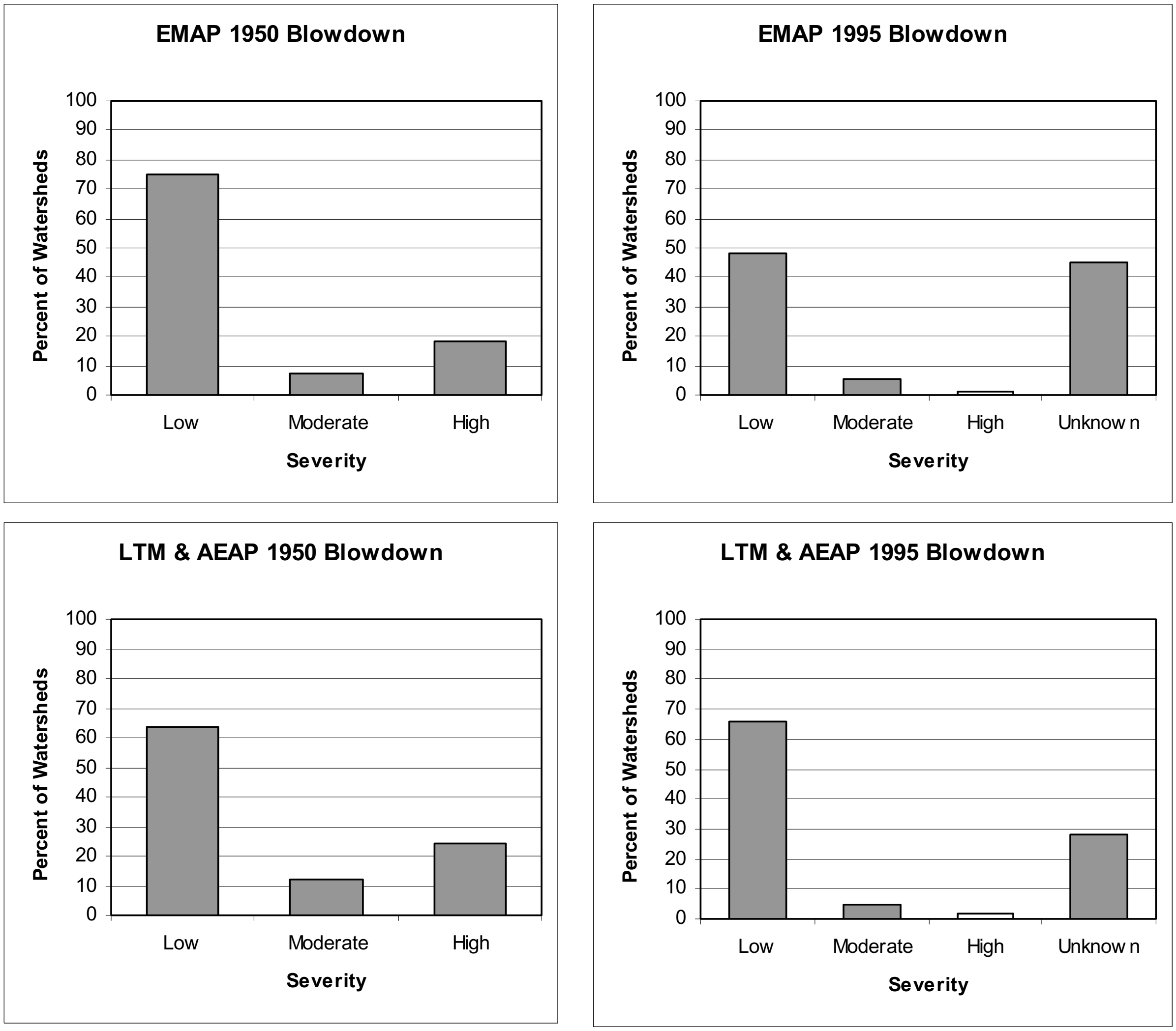


Figure 2-8.. Estimates of blowdown severity in the study watersheds during the 1950 and 1995 wind storms.

2.8 Regional Extrapolation of Model Output

Regional extrapolation of model results focused on numbers and percentages of lakes that the models predict might respond in a certain way to various future emissions control scenarios. The only statistically rigorous spatial frame available for quantitative extrapolation that covered the geographical extent of the Adirondack Mountain region and included lakes as small as 1 ha was that of EMAP. By applying modeling results from the 44 statistically-selected modeled watersheds to the EMAP statistical frame, we were able to estimate future changes in lake water acid-base chemistry for all of the watersheds in the region that were represented by the statistical design.

We used the EMAP Adirondack data as the basis for developing different approaches to extrapolating spatially limited data: hydrogeologic lake classes, model-based extrapolations, and clustering. Any model or lake classification scheme developed or applied using data from well-studied Adirondack sites can be extrapolated to the region using the 115 EMAP lake data, or a statistically-selected subset of those lakes, and their sample weights. The only condition is that predictor variables in the model must have been measured or can be estimated at the EMAP lakes used to represent the population frame.

Both the probability-based EMAP sites and the judgment-based long-term monitoring sites were assigned to hydrogeologic lake classes, based on the expectation that the likelihood of recovery of a given lake in response to decreasing acidic deposition would be determined on the basis of its hydrogeochemical characteristics (Young and Stoddard 1996). Because response functions tend to vary from lake to lake within a region, classification of lakes in both the probability and judgment samples into response classes maximizes the capability of assessing regional recovery trends (Stoddard et al. 1996).

This classification provides a foundation for integrating the data collected by the EMAP and ALTM/AEAP approaches. If the lakes within a given subpopulation are shown to respond similarly to changes in acidic deposition, relationships observed for the intensively-monitored lakes can be extrapolated to the results of the probability sampling, thereby yielding information that could not be gained through one project alone (Stoddard et al. 1998). As long as the critical sub-populations are adequately defined and the intensively-monitored lakes are representative of those critical sub-populations, then it is possible to make inferences about regional recovery based solely on ALTM and/or AEAP lakes (Stoddard et al. 1998).

Newton and Driscoll (1990) developed a hydrogeochemical lake classification system for Adirondack lakes. Classes were identified largely on the basis of hydrologic lake type (drainage or seepage), concentration of dissolved organic carbon (high or low), and inferred depth of glacial till (thin, intermediate, or thick) based on measured lakewater Ca^{2+} concentration. Stoddard et al. (1998) used this system, with some modification, as a basis for extrapolating site-specific trends in lakewater chemistry throughout the northeastern United States. The system was found to isolate much of the inter-annual variability of the overall lake population in the least sensitive sub-populations. This is important because variability greatly obfuscates regional trends analysis (Urquart et al. 1998, Stoddard et al. 1998).

Young and Stoddard (1996) developed a modification of the Adirondack hydrogeochemical lake classification model of Newton and Driscoll (1990) for the larger, more heterogeneous northeastern U.S. region. They then compared this classification model to a geographical model, a multivariate statistical model, and an integrated model that combined elements of the other approaches. Because of its simplicity and success in designating homogeneous lake classes, the hydrogeochemical classification model was recommended as the preferred method for sample stratification in the U.S. EPA's TIME monitoring project (Young and Stoddard 1996).

The results of this classification effort were placed into the context of the Adirondack region using the statistical frame of lakes developed by EMAP. Model projections and biogeochemical assessment of the regional population of lakes were compared with similar data for the intensively-studied sites. A series of statistical weighting factors and watershed classification systems were developed. These factors and relationships provide the basis for regional assessments based solely on the documented, monitored, or modeled responses of intensively-studied watersheds.

Model-based extrapolations: Data from intensively studied sites were used to develop models of conditions that could not be developed from survey data, and the overall probability design was used to make regional estimates of condition. Eshleman (1988) used this approach to estimate the extent of episodic lake acidification in the Adirondacks by developing a model of episodic acidification from long-term monitoring data based on fall index ANC and applying that model to all lakes in the probability-based Eastern Lake Survey to estimate the extent of episodic lake acidification region-wide.

Clustering: Clustering of regional survey data provides a useful way to place spatially-limited data or data from well-studied sites into a regional context. Multivariate cluster analysis of the regional EMAP data was used to identify significant regional groupings of sites. The spatial extent of each of these clusters (e.g., number of lakes in region) was also calculated using the EMAP site weights. Discriminant function analysis was used to identify the environmental data that best predicted cluster membership. The discriminant function was then applied to the well-studied sites to calculate their probability of being in each of the different regional clusters. This approach helped to identify the "representativeness" of each of the well-studied sites in the context of important regional clusters or types of lakes. There are many potential types of clustering schemes that could be developed for lakes in the Adirondacks, some based on biology (e.g., fish, zooplankton), others based on water chemistry, and still others based on physical attributes (e.g, size, elevation). We conducted a cluster analysis of zooplankton assemblage data to identify biological clusters of lakes. Other clusters were constructed using water chemistry and environmental data to devise classification schemes for responsiveness of watersheds to changes in acidic deposition reflected in lakewater and soils chemistry and lakewater biology. The significance of the principal variables and species that determined each cluster were evaluated.

Based on identified clusters, we tested how each cluster might respond to N and S deposition using model projections from PnET-BGC and MAGIC. We predicted cluster membership based on water chemistry and watershed characteristics and then performed regional extrapolations to estimate the number of watersheds within the region represented by each cluster. This provided a mechanism for placing well-studied sites into classification schemes to predict future responses to acidic deposition.

2.9 Quality Assurance/Quality Control (QA/QC)

2.9.1 Soils

Quality assurance soil samples included field replicates, sample replicates, blanks, repeated analyses of an in-house standard that was a field composite sample, certified reference materials for instrumental precision, and spiked recovery as appropriate. During the first several days of sampling, composite soil samples were prepared for both O and mineral B horizons. These composites consisted of air-dried, homogenized, and sieved subsamples from eight soil pedons excavated in four different watersheds. After air-drying and thoroughly homogenizing each of the two composites, each was partitioned into multiple sealed plastic bags and kept refrigerated until shipped to the analytical laboratory. Each week during the sampling period, a shipment of soil samples was packaged in coolers and one of each of the composite samples (O and B horizon) was added to the shipment. Results of repeated analyses of each of these composite soil samples (Table 2-5) provide important information regarding analytical reproducibility throughout the study. The percent coefficient of variation for most analytes was less than about 10%. Exceptions to this pattern included mainly analytes having very low concentration (e.g., exchangeable K and Na).

Duplicate soil pedons were excavated and sampled at 14 sites, providing the ability to compare paired measurements for each of the soil variables of interest. These paired samples

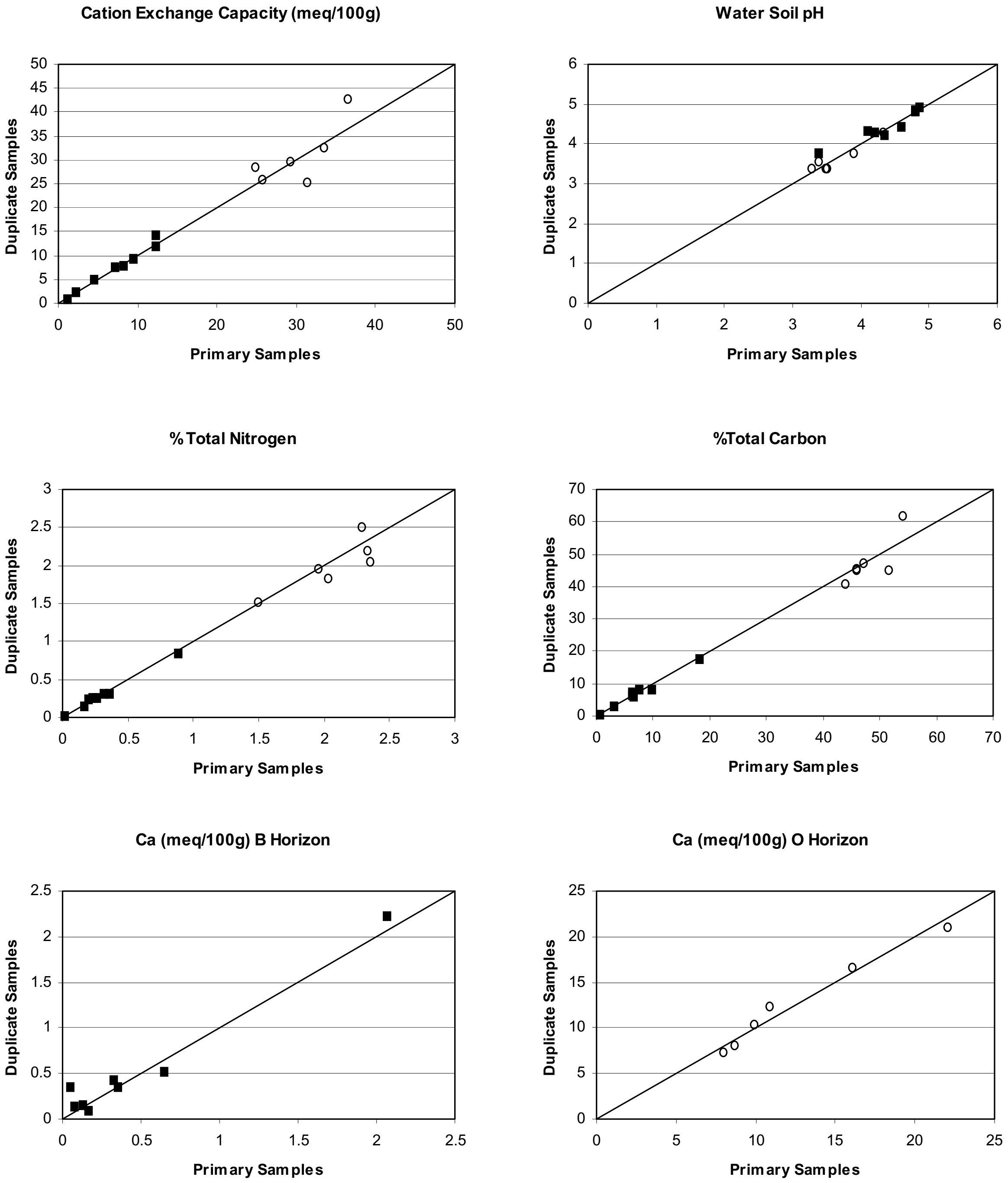
Table 2-5. Results of repeated (n=6) analyses throughout the duration of the field study of aliquots from composite samples of organic and mineral soils representative of the study area.

	Mean	Standard Deviation	Percent CV	Mean	Standard Deviation	Percent CV
	O Horizon Composite			B Horizon Composite		
pH_H_2O	3.81	0.02	0.65	4.21	0.17	4.08
% TN	1.81	0.02	1.31	0.31	0.02	6.35
% TC	40.57	1.26	3.11	7.17	0.47	6.49
Acidity ($cmol_c$/kg)	15.08	1.27	8.46	6.19	0.34	5.50
ECEC ($cmol_c$/kg)	29.56	1.40	4.75	6.91	0.34	4.94
Ca ($cmol_c$/kg)	11.51	0.40	3.48	0.51	0.05	10.42
K ($cmol_c$/kg)	0.90	0.14	15.41	0.07	0.03	41.98
Mg ($cmol_c$/kg)	1.88	0.06	3.37	0.12	0.02	13.50
Na ($cmol_c$/kg)	0.13	0.03	26.11	0.02	0.01	53.21
Al ($cmol_c$/kg)	5.88	0.21	3.53	4.06	0.47	11.60
BS (%)	48.90	2.33	4.77	10.48	0.90	8.54

provided information with which to evaluate the combined uncertainties and/or errors associated with fine-scale spatial variability in soil conditions, soil collection procedures, and laboratory analytical methods. The identities of the replicated soil pedons were not revealed to the analytical laboratory in advance of testing. There was good agreement between analytical results for the duplicate pairs (original soil pit and the nearby duplicate soil pit) for each of the principal soils chemistry variables (Figure 2-9). For soil samples exhibiting low BS (< 10%), the root mean squared error (RMSE) of the BS measured in the duplicate soil pits was 4.2%.

2.9.2 Lakewater

The water chemistry of the 13 new lakewater samples, measured at Syracuse University, exhibited good internal consistency, with calculated and titrated ANC values in reasonable agreement and the expected relationship between pH and ANC (Figure 2-10). The overall database also exhibited internal consistency (Figure 2-11), suggesting that the water chemistry data are of high quality.



Cation Exchange Capacity (meq/100g)

Water Soil pH

% Total Nitrogen

%Total Carbon

Ca (meq/100g) B Horizon

Ca (meq/100g) O Horizon

Figure 2-9. Comparison of results of chemical measurements for selected variables from samples collected of the mineral soil (B horizon, filled squares) and organic soil (O horizon, open circles) at sites at which duplicate soil pits were excavated. For the plots showing results for Ca and Mg, results were split into two panels (O and B horizon data) for display purposes because of the large differences in results for the O and B horizons.

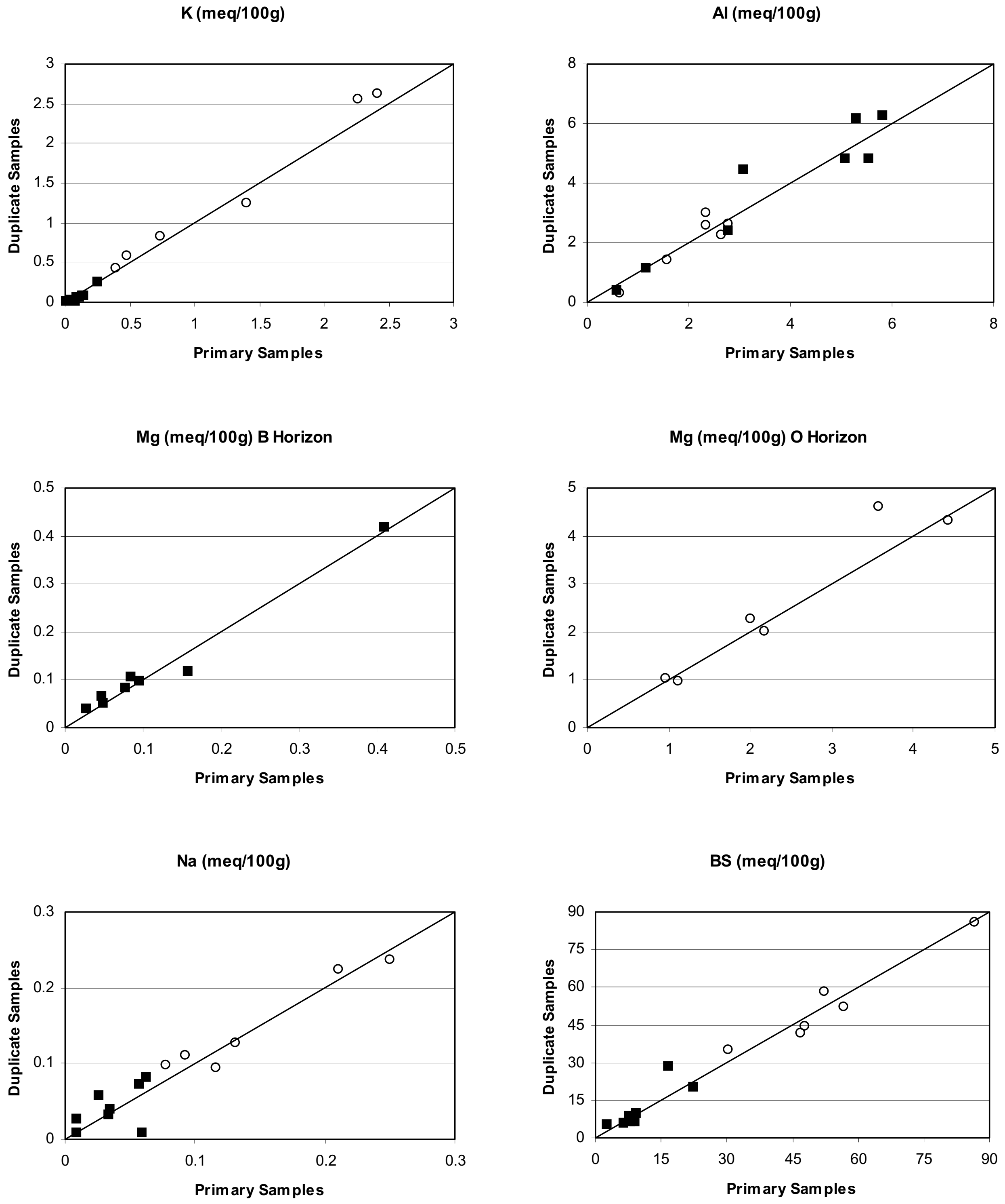


Figure 2-9. Continued.

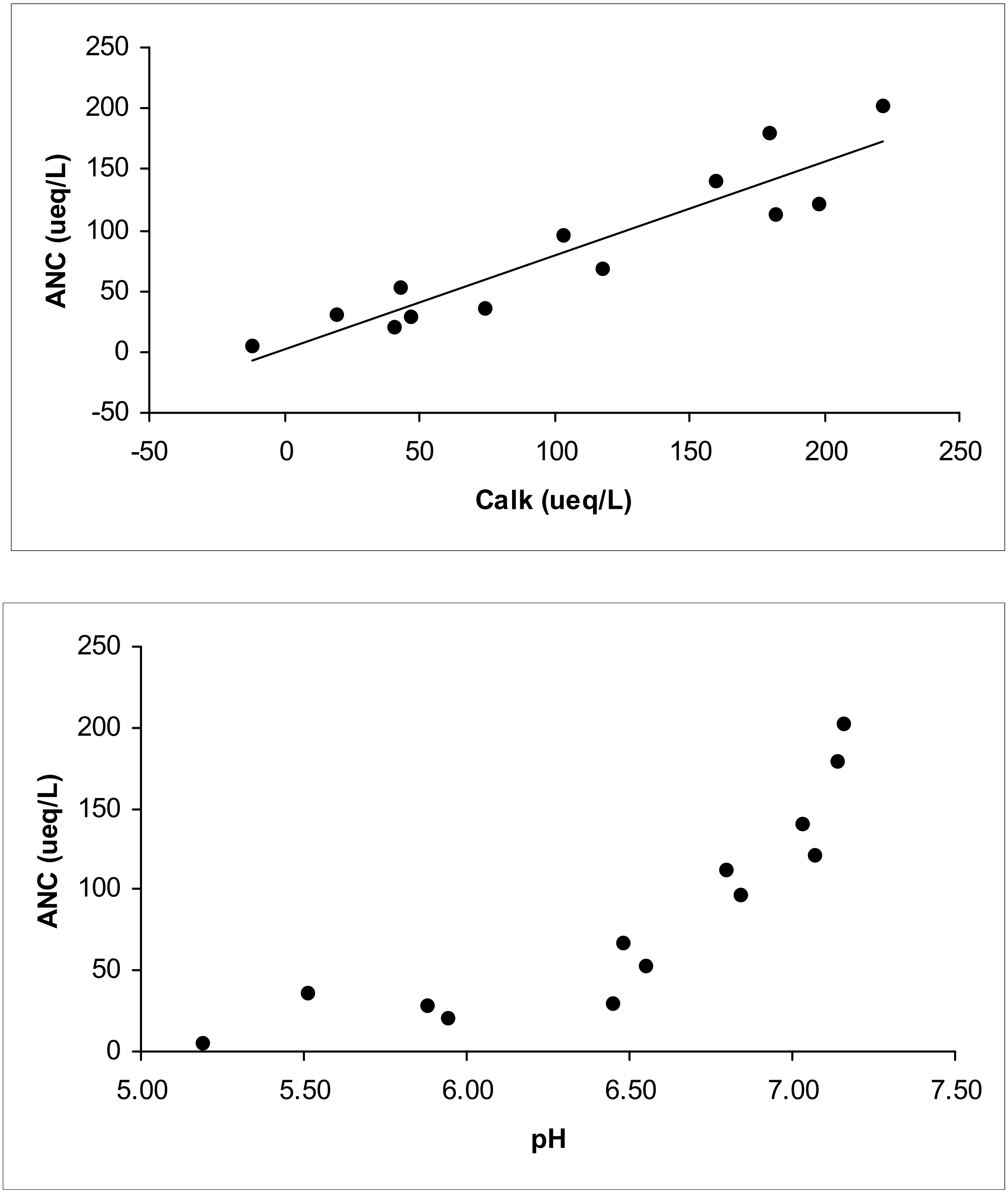


Figure 2-10. Relationships between a) titrated and calculated ANC and b) titrated ANC and pH for 13 lakewater samples collected in 2003.

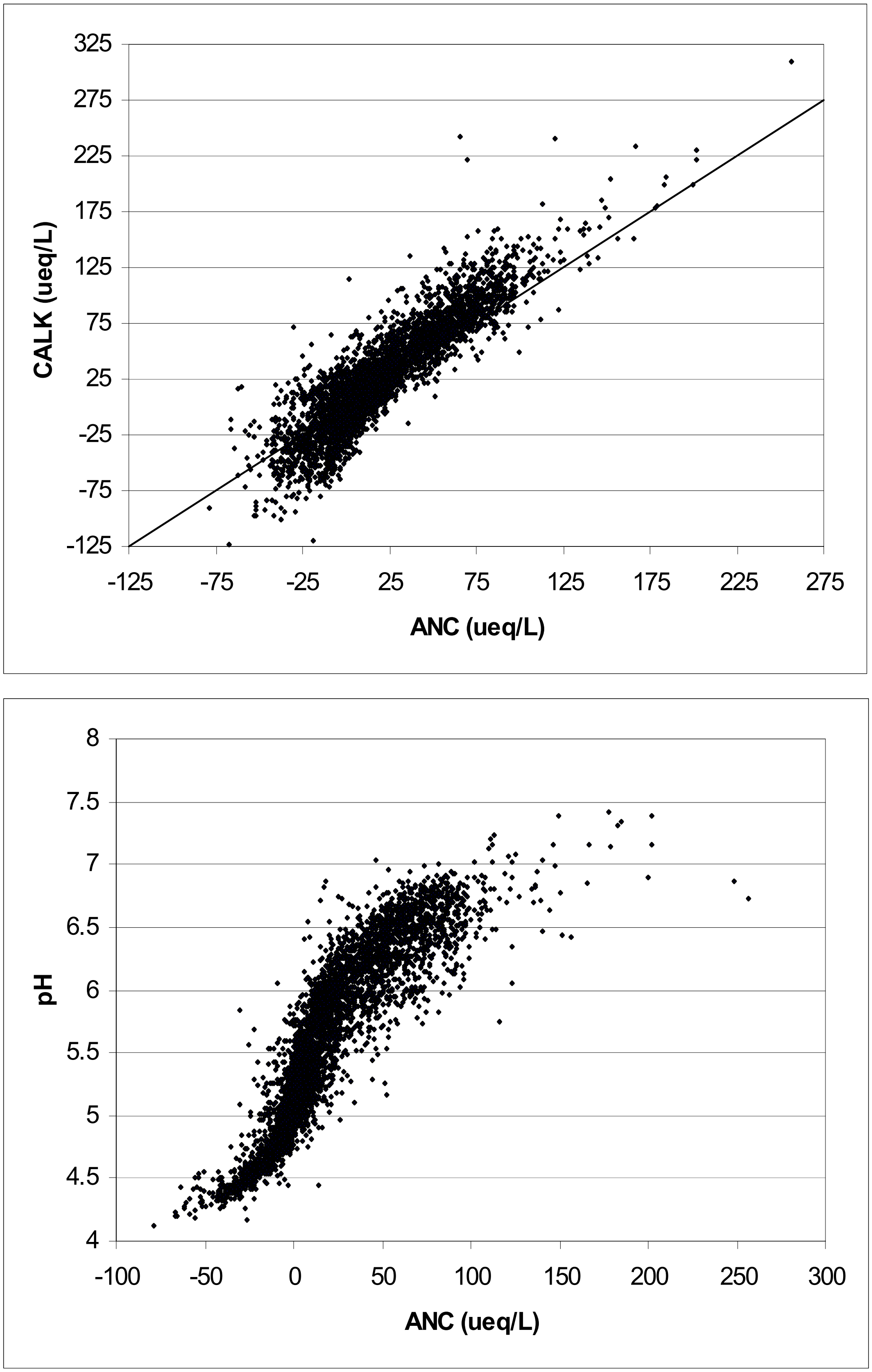


Figure 2-11. Internal consistency of lakewater chemistry data collected and compiled for the modeling effort. A) relationship between titrated and calculated ANC, and B) relationship between pH and ANC.

2.10 Biological Monitoring

2.10.1 Fish

There are 30 AEAP long-term biological monitoring lakes, which are approximately equally divided between those having pH 4 to 5, 5 to 6, and > 6. Biological sampling began in 1994. Fisheries information is available for the majority of the lakes (0 to 16 fish species per lake). Eight of the 30 Program waters are fishless and seven waters are either too large or inaccessible for fisheries surveys. The AEAP includes all ALTM lakes in the southwest quadrant of the Adirondack Park, excluding treated lakes (e.g., lime, rotenone) and lakes less than 3m deep.

Potential future recovery of fish communities was assessed using two matrices: fish species richness and the presence of brook trout. Empirical relationships were developed with which to project future increases in species richness and the probability of brook trout presence in individual lakes as a consequence of improved chemical conditions.

To evaluate fish response to changes in acidic deposition, fish response algorithms were developed and applied to PnET-BGC simulations of past, current, and future lakewater chemistry. To evaluate change in fish species richness, we utilized data from the ALSC survey database. Species richness was calculated for lakes within ANC classes. The ANC classes were established for each 10 μeq/L value.

We also applied a relationship for the probability of the presence of brook trout ($P_{\text{Brook Trout}}$), based on lakewater pH, that was previously developed by Baker and Christensen (1991) for the ALSC lake survey database.

$$P_{Brook\ Trout} \left(\frac{1}{1+e^{8.62-1.76*pH}} \right) \tag{2-2}$$

2.10.2 Zooplankton

In this study we incorporated three zooplankton datasets collected for northeastern U.S. lakes:

1) In the summer of 1986, 145 low base cation lakes were sampled as part of U.S. EPA's Eastern Lakes Survey (ELS-II). Zooplankton were collected with a 30 cm diameter, 80 μm mesh Wisconsin style plankton net. These data were downloaded from the EPA website (http://www.epa.gov/emap/html/dataI/surfwatr/data/napap/els.html). Individual chemistry, morphometry, and zooplankton data files were merged by lake. Zooplankton species data were combined into functional or

taxonomic richness categories in accordance with methods outlined by Stemberger et al (2001).

2) From 1991-1994, EMAP sampled 385 lakes using a stratified random selection design. This sample population was intended to represent the population of lakes in the northeastern United States.

3) During 1999-2001 an EPA Science to Achieve Results (STAR) grant, awarded to Dartmouth College, sampled 60 headwater lakes in the Adirondacks, Vermont, and New Hampshire. The lakes were selected to represent a wide range in total-N and total-P concentrations (Stemberger and Miller 2003). Thirty of these lakes had previously been sampled in the EMAP survey.

The latter two surveys used a bongo style net having a 30 cm, 200 μm mesh Wisconsin net for macrozooplankton and a 30 cm, 54 μm mesh net with a 15 cm reducing collar for microzooplankton (small crustaceans and rotifers). These nets are more efficient for collecting both large and small zooplankton species than the single 30 cm, 80 μm mesh net (Stemberger and Lazorchak 1994) employed in ELS-II. Therefore, some bias in the species lists exists between the ELS-II zooplankton data and the other two surveys, especially for microzooplankton richness. Also, differences in taxonomic skills of the technicians in the ELS-II survey vs. the EMAP and STAR surveys is a potential source of variation that has not been evaluated. However, even if the ELS-II rotifer richness data are omitted from the analysis there is no improvement in the explained relationship between ANC and rotifer richness. Hence, we included the ELS-II rotifer data in the analyses.

A primary goal of the zooplankton analysis was to establish a robust relationship between ANC and metrics of zooplankton richness among the three datasets. We calculated a defined ANC so that the independent variable in the models would be consistent for all datasets and also consistent with model projections for MAGIC and PnET-BGC. We also aggregated zooplankton species data for each survey into taxonomic groups as defined in Stemberger et al. (2001) so all metrics were consistent across datasets. After first inspecting the frequency distributions of key variables, a simple regression analysis was performed on each dataset based on the entire regional sample and then separately for lakes in geographic subregions (e.g., Adirondack Mountains, Coastal Plain, and New England Uplands).

Two consistent patterns emerged from this evaluation. First, the variation in the relationship between variables like ANC or pH and taxonomic richness was so great for lakes across the entire NE region as to be essentially unusable. This lack of relationship likely occurs because the extensive spatial coverage for the entire region reflects a variety of environmental factors in addition to acidity that can also affect species richness (e.g., land use, fish population structure, DOC and ultraviolet radiation (UV-B) tolerance, lake area and depth, temporal variation, etc.) and that exhibit varying impact across the region. We first eliminated lakes at the extremes of their ANC concentration distributions. This improved the relationships of interest but variation still remained too high to be useful for predictive purposes. Second, we tried regression analysis by geographic subregion. This significantly improved the explained variance, probably because the smaller subregional spatial scale better reflects the dominant environmental gradients that affect species richness. Overall, the three survey subsets for the Adirondack region gave the most consistent relationships between ANC and metrics of zooplankton richness. Hence, we combined the three survey subsets for the Adirondack Mountains into a single file. Further inspection of the combined Adirondack dataset suggested that relationships between ANC and richness was linear between -50 and 250 μeq/L. Hence, we selected lakes in this range for our analysis.

Further analysis of the combined Adirondack lake dataset by year also showed that there was high variability between ANC and taxonomic richness in the 1992 EMAP survey but not in the other years. Richness in that year has been shown to be higher than in other years because of cooler and wetter climatic conditions due to global cooling by SO_4 aerosols after the 1991 Mt. Pinatubo volcanic eruption (Stemberger et. al. 1996). Therefore, we omitted EMAP data for 1992 for further analysis. This significantly improved the explained variance in the regression models for the combined dataset.

The combined Adirondack dataset (which excludes the 1992 EMAP data) contained zooplankton data for 123 lakes. Of these, 37 lakes had been sampled at least twice, either as a repeat visit in the same or in different years (EMAP and STAR), or were resampled in different surveys (EMAP vs. STAR). None of the ELS-II lakes matched those sampled in the EMAP or STAR surveys. In total this file contained 160 lake visits. If a lake was sampled two or more times we included only a single visit in the analysis unless the time between revisits was 6 or more years. These revisits were treated in regression analysis as distinctive lake samples. Several lake samples were omitted from the analysis because they were collected from shallow (<1m depth) lakes and/ or the zooplankton population count data indicated that the sample was too sparse to get a reliable estimate of taxonomic richness (e.g., Antediluvian Pond). Taking all the data restrictions into consideration (ANC range, 1992 EMAP survey, and reliability of taxonomic richness estimates based on lake depth and sample count) the final Adirondack dataset includes 111 lake visits representing 97 lakes.

2.11. Lake Classification

In order to provide a basis for lake classification, we used a multiple regression approach to identify the lake chemical, watershed soil B horizon, and environmental variables most strongly related to future ANC change as predicted by both the MAGIC and PnET-BGC models. The future change in ANC between 2100 (aggressive scenario) and 1990 was used as the dependent variable in the regression model in order to reflect maximal chemical recovery for the study lakes. We used an all-subsets multiple regression approach for model selection. Using SAS PROC REG, all possible model subsets from one variable to n variable models were constructed and Aikake's Information Criteria (AIC) values for each model were calculated. AIC was used as a way of identifying the model with the best fit without overfitting the model (too many variables; Burnham and Anderson 1998). Given the low sample size relative to the number of variables, AIC was corrected (AIC_c) by

$$AIC_c = AIC + 2K(K+1) / (n-K-1) \qquad (2\text{-}3)$$

where n is the number of sample sites and K is the number of variables plus 2 (for intercept and variance estimate terms). The model with the lowest AIC_c may be considered the best model but models with very similar AIC_c exhibit similar goodness. We chose to consider for further analysis any model with AIC_c within 4 of the minimum model AIC_c. For each of these models, we calculated a deviation from the minimum AIC_c as:

$$\Delta i = AIC_{c,i} - \text{Minimum}(AIC_c) \qquad (2\text{-}4)$$

As described in Burnham and Anderson (1998), each model was assigned a weight (Wi) as:

$$Wi = \exp(-0.5 * \Delta i) / \Sigma (\exp(-0.5 * \Delta i)) \qquad (2\text{-}5)$$

Wi can be considered to be the probability that model i is the best model given all the models considered. We then looked at which independent variables occurred in all these top models and calculated the importance of each variable one at a time by summing the Wi of all models in which that variable occurred. If a variable occurred in every one of the models, it would have an AIC weighted variable importance of 1. If it occurred in none of the models it would have a value of zero. All variables that had an AIC weighted importance greater than 0.5 were considered significant and used in the final regression model relating predicted future ANC change to observed current conditions. Regressions were run separately for MAGIC and PnET-BGC future ANC projections.

To derive candidate lake clusters or types of lakes that would be expected to respond similarly with respect to future ANC change, a principal components analysis (PCA) was performed on all the variables that were significant in either the MAGIC or PnET-BGC regression model. This reduced the dimensionality to 3 significant axes. The axis or factor scores were then clustered via cluster analysis to look for groups of generally similar lakes. The PCA was done using SAS PROC FACTOR, method=PRINCOMP. Cluster analyses were done using PC-ORD using the Flexible Beta method (beta=-0.25) and Euclidean distance.

3.0 RESULTS

3.1 Site Selection and Characterization

Soil sampling sites were selected within the predominant landscape types in each study watershed. A total of 70 watersheds was sampled for soil chemistry and modeled with the MAGIC and PnET-BGC models. Of those 70 watersheds, 44 were statistically selected to be representative of the wider regional lake population (N = 1,320). Landscape type was determined across each study watershed by overlaying general soil type (Figure 3-1) and general forest cover type (Figure 3-2). The number of soil pits excavated within each of the landscape types and median associated chemical values are given in Table 3-1. Soils were sampled and analyzed at 199 sites within the 70 study watersheds. Soil pit locations throughout the region are shown in Figure 3-3. One illustrative watershed (Rock Pond watershed) is highlighted in Figures 3-1 through 3-3. Soil pits excavated in the Rock Pond watershed and the landscape characterization from which soil pits were selected are shown in Figure 3-4.

3.2 Soil Acid Base Chemistry

3.2.1 Exchange Phase Composition

Acid-base chemistry was determined for the O and B horizons of each soil pit location. O horizon soils typically exhibited substantially lower pH and higher concentrations of exchangeable cations, C and N than did B horizon samples. Variability of median chemical values among landscape types was high, and there were no obvious differences in the range of the data among soil classes (Table 3-1).

The overall mean soil exchange phase composition from this sample population of O and B horizons for all watersheds sampled is shown in Figure 3-5. These data provide a general representation of the contrasts between the O horizons and underlying mineral B horizons that are characteristic of cool, temperate climate forest soils. The O horizons were highly acidic, being dominated by weak organic acidity despite the relatively high base saturation (BS; 45.2%). All of the O horizon exchangeable base cation concentrations were higher than mineral soil values. Exchangeable Ca dominated in these O horizons and the mean exchangeable Ca:Al ratio for these data in the O horizon was 2.3 to 1. Exchangeable acidity in the O horizon, operationally defined by the methods employed, was dominated by exchangeable H^+, reflecting the importance of organic functional groups in these highly organic soil materials. Mean B horizon CEC_e was 8.3 $cmol_c/kg$ with a % BS of 10.0%, compared to 29.6 $cmol_c/kg$ in the O horizon, with a % BS of

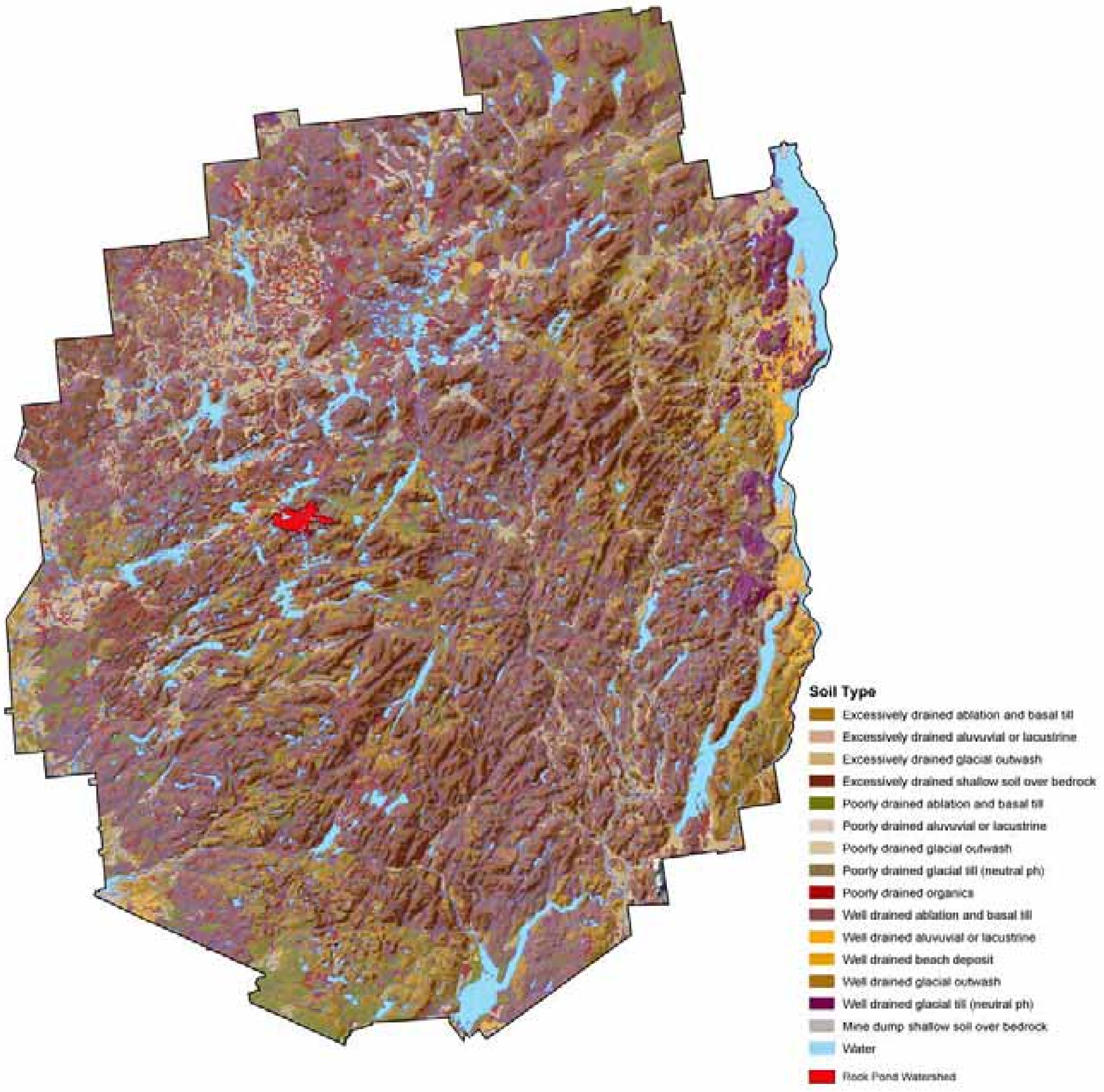


Figure 3-1. Regional soils types of the Adirondacks.

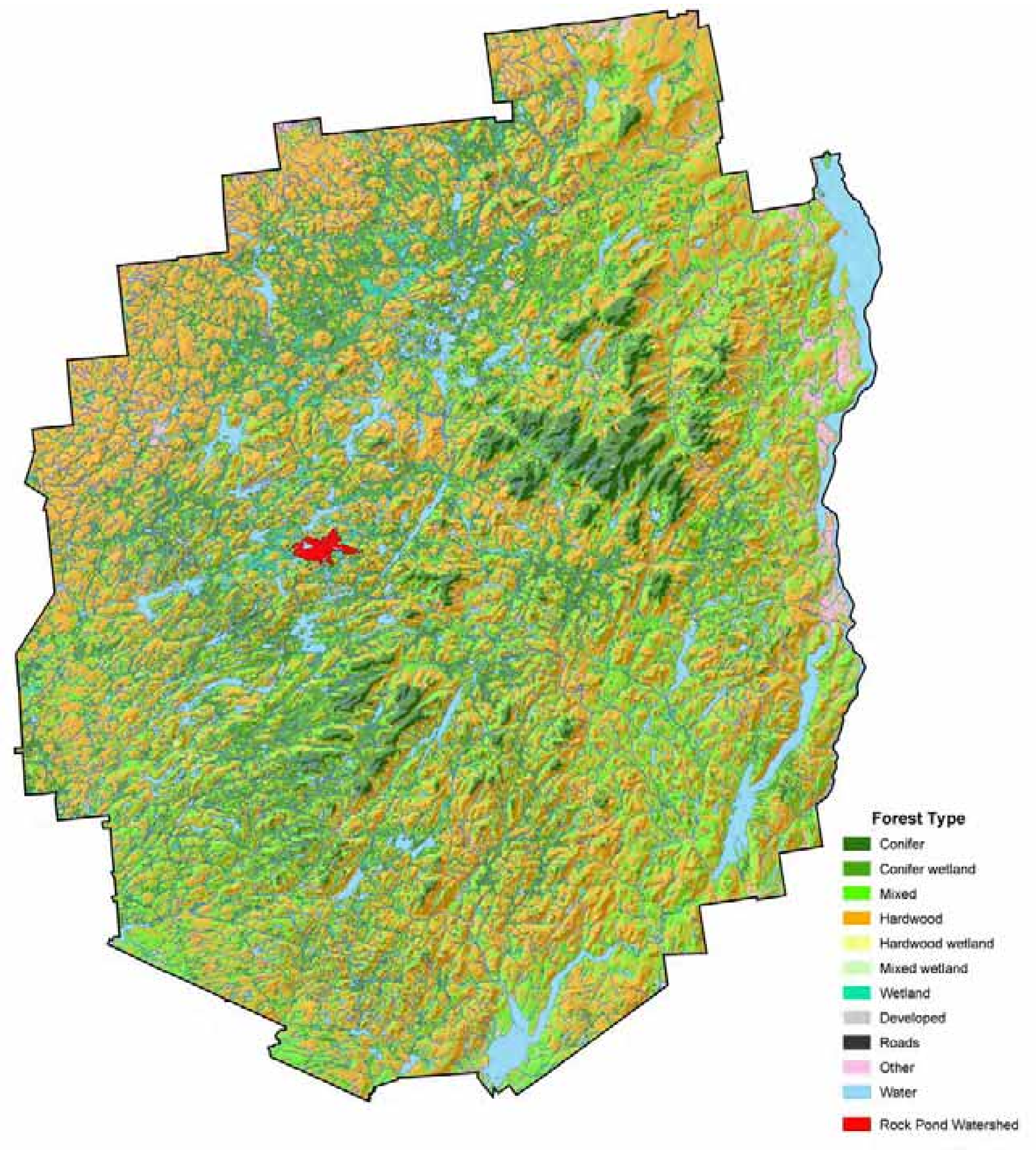


Figure 3-2. Regional forest types of the Adirondacks.

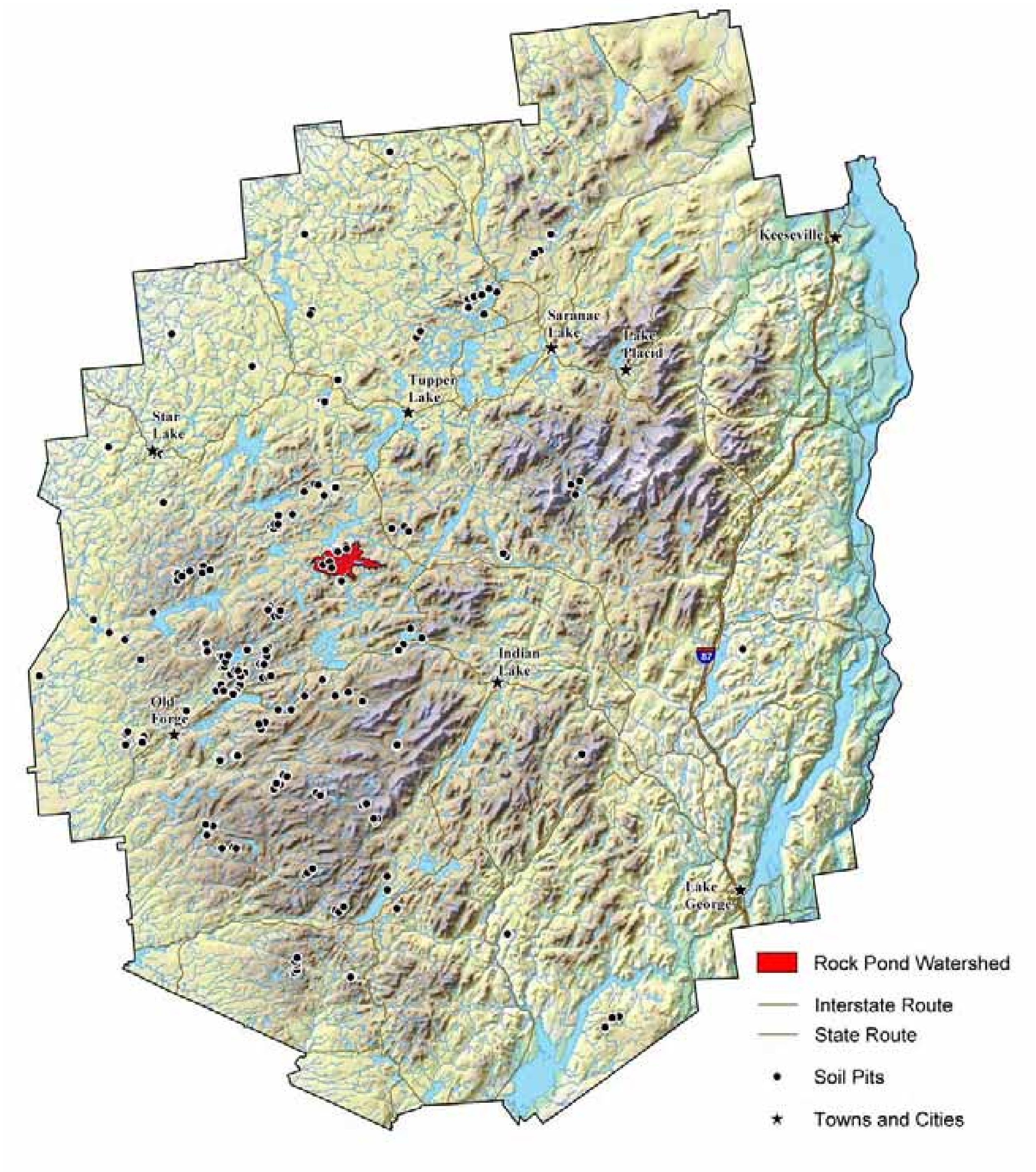


Figure 3-3. Locations of soil pits sampled for this study in the Adirondacks. The boundary of one representative watershed (Rock Pond) is provided.

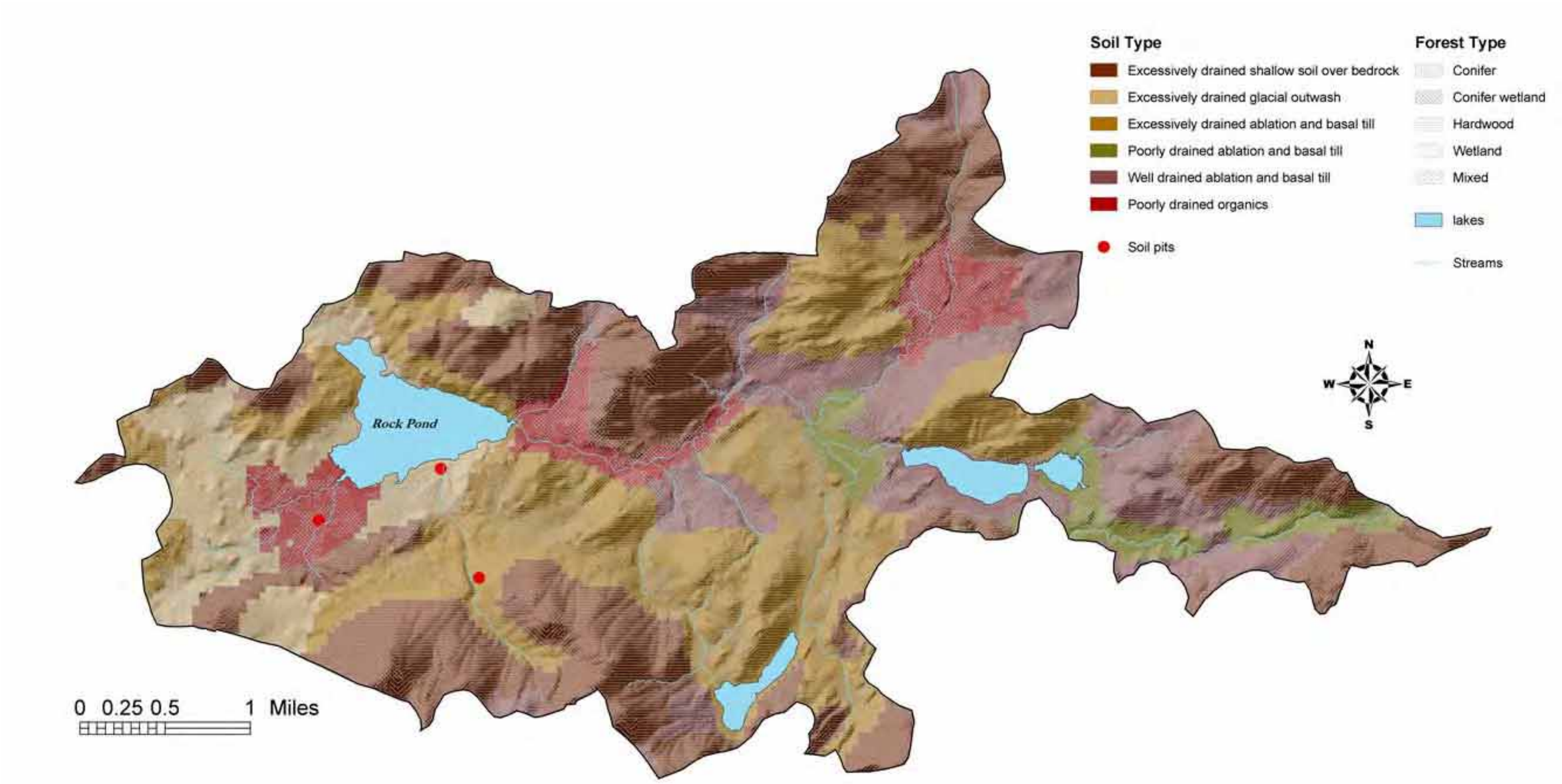


Figure 3-4. Mapped landscape units and soil pit locations for one illustrative study watershed (Rock Pond watershed). Its location is shown in Figure 3-3.

Table 3-1. Number of sampled sites and median measured values of selected soil acid-base chemistry values for landscape types defined according to general forest type and general soil type.

Soil and Forest Type[a]	Number of Sampled Pedons	pH (H_2O)	LOI[b] (%)	Exch. Ca ($cmol_c$/kg)	Effective CEC[v] ($cmol_c$/kg)	Base Saturation (%)	Total C (%)	Total N (%)
O Horizon								
Conifer								
Excessively drained ablation and basal till	10	3.49	81.2	12.33	32.5	45.84	50.88	1.86
Excessively drained glacial outwash	15	3.48	73.1	11.8	32.68	51.43	47.29	1.81
Excessively drained shallow soil over bedrock	11	3.69	73.4	9.2	25.45	43.41	47.16	2.19
Well drained ablation and basal till	20	3.42	77.8	9.77	30.37	42.01	50.56	2.07
Well drained glacial outwash	6	3.84	58.5	11.49	22.35	58.37	34.87	1.68
Poorly drained ablation and basal till	8	3.54	77.7	12.61	36.75	40.93	51	1.96
Poorly drained glacial outwash	4	3.22	83	11.4	32.16	48.27	53.21	1.71
Poorly drained organics	7	3.47	75	6.42	28.92	29.1	47.98	2.15
Wetland; well drained ablation and basal till	3	3.71	81.9	12	34.57	38.24	52.42	2.09
Wetland; poorly drained organics	4	3.26	77.4	10.12	35.24	31.73	49.66	1.81
Hardwood								
Excessively drained ablation and basal till	5	3.6	55.5	8.58	22.22	49.5	43.05	1.57
Excessively drained glacial outwash	3	3.66	62.1	13.27	25.85	53.31	37.11	1.55
Excessively drained shallow soil over bedrock	18	3.71	67.5	9.99	26.02	48.67	41.16	1.92
Well drained ablation and basal till	13	3.78	72.1	8.73	27.99	40.18	44.98	2.1
Well drained glacial outwash	4	3.55	61.9	10.28	27.67	49.65	40.6	2.02
Mixed								
Excessively drained ablation and basal till	7	6.63	72.2	14.83	26.19	60.88	47.27	1.81
Excessively drained glacial outwash	5	3.8	71.2	14.75	31.06	78.61	45.61	2.01
Excessively drained shallow soil over bedrock	16	3.43	77.8	10.98	29.88	46.92	49.02	1.99
Well drained ablation and basal till	13	3.45	70.88	11	30.33	42.61	46.32	1.69
Poorly drained glacial outwash	3	3.37	79.96	9.41	28.94	48.96	50.38	2.09

Table 3-1. Continued.

Soil and Forest Type[a]	Number of Sampled Pedons	pH (H_2O)	LOI[b] (%)	Exch. Ca ($cmol_c$/kg)	Effective CEC[b] ($cmol_c$/kg)	Base Saturation (%)	Total C (%)	Total N (%)
B Horizon								
Conifer								
Excessively drained ablation and basal till	9	4.39	12.4	0.34	8.21	6.41	5.76	0.25
Excessively drained glacial outwash	14	4.62	9.4	0.2	5.77	7.05	4.69	0.17
Excessively drained shallow soil over bedrock	10	4.29	9.3	0.37	7.49	6.65	4.89	0.22
Well drained ablation and basal till	20	4.22	10.4	0.32	8.39	6.64	5.35	0.2
Well drained glacial outwash	6	4.55	11.3	0.19	6.78	6.5	5.38	0.21
Poorly drained ablation and basal till	8	4.08	10.4	0.41	9.16	7.23	5.77	0.22
Poorly drained glacial outwash	3	4.58	12.3	0.28	9.18	4.57	5.83	0.19
Poorly drained organics	7	4.39	8.8	0.19	5.16	5.36	4.54	0.15
Wetland; Poorly drained organics	4	4.21	8.1	0.17	6.85	5.07	4.41	0.19
Hardwood								
Excessively drained ablation and basal till	5	4.42	11.8	0.36	8.15	6.57	6.38	0.25
Excessively drained glacial outwash	4	4.77	9	0.24	4.56	12.39	4.74	0.21
Excessively drained shallow soil over bedrock	17	4.37	12.1	0.4	8.85	6.17	6.62	0.27
Well drained ablation and basal till	13	4.3	19.4	0.53	9.2	8.95	10.7	0.43
Well drained glacial outwash	4	4.29	8.1	0.19	6.91	4.05	4.59	0.16
Mixed								
Excessively drained ablation and basal till	7	4.61	12.4	0.65	9	19.77	7.08	0.26
Excessively drained glacial outwash	4	4.68	11.9	0.3	5.46	7.32	6.32	0.27
Excessively drained shallow soil over bedrock	13	4.43	11.3	0.36	7.37	7.73	5.99	0.22
Well drained ablation and basal till	14	4.59	13.6	0.35	7.58	7.32	7.68	0.26
Poorly drained glacial outwash	3	4.32	10.3	0.2	6.15	5.02	4.98	0.18

[a] Only landscape types represented by 3 or more sampled pedons are included here.
[b] LOI - Loss on ignition; CEC - Cation exchange capacity

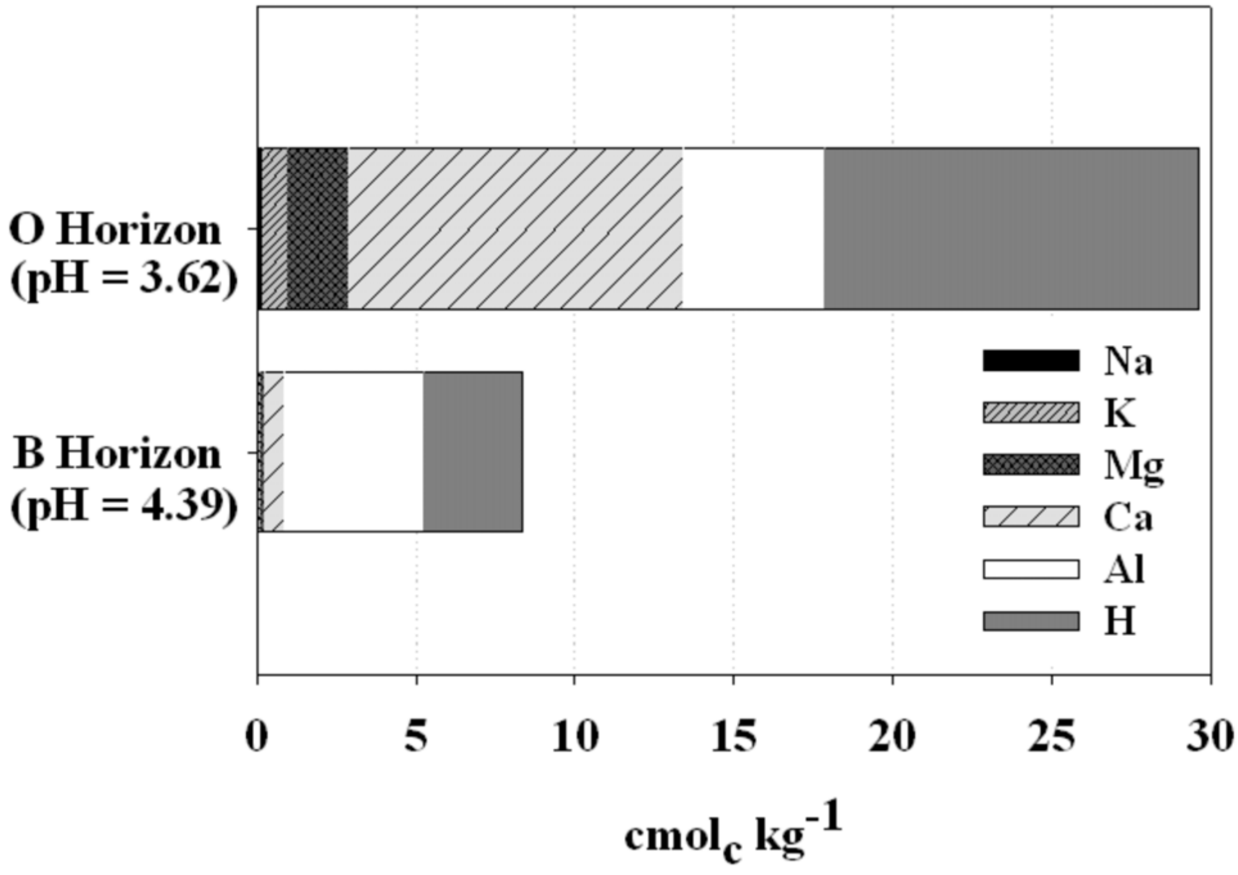


Figure 3.5. Mean composition of the CEC $_e$ and pH$_s$ from all watershed samples analyzed in the Adirondack watershed sampling conducted in 2003.

45.2%. While there was a strong contribution of organic acidity in the B horizon, as evidenced by the considerable amount of exchangeable H$^+$, exchangeable Al clearly dominated the cation exchange complex in the mineral soil and the mean B horizon exchangeable Ca:Al ratio was only 0.13.

3.2.2 Distribution of Soil Characteristics Across Target Watersheds

B horizon soil samples collected from 113 pits within the statistically-representative EMAP watersheds indicated a high degree of acid-sensitivity. Acid-sensitive soils were found to be widely distributed throughout the western Adirondacks. The results of % BS estimates for B horizon samples collected in the EMAP study watersheds are shown in Figure 3-6. Sites having B horizon % BS less than 10% were found throughout the western region of the Adirondack Park. The common occurrence of pedons having low B horizon % BS (Figure 3-6) is important,

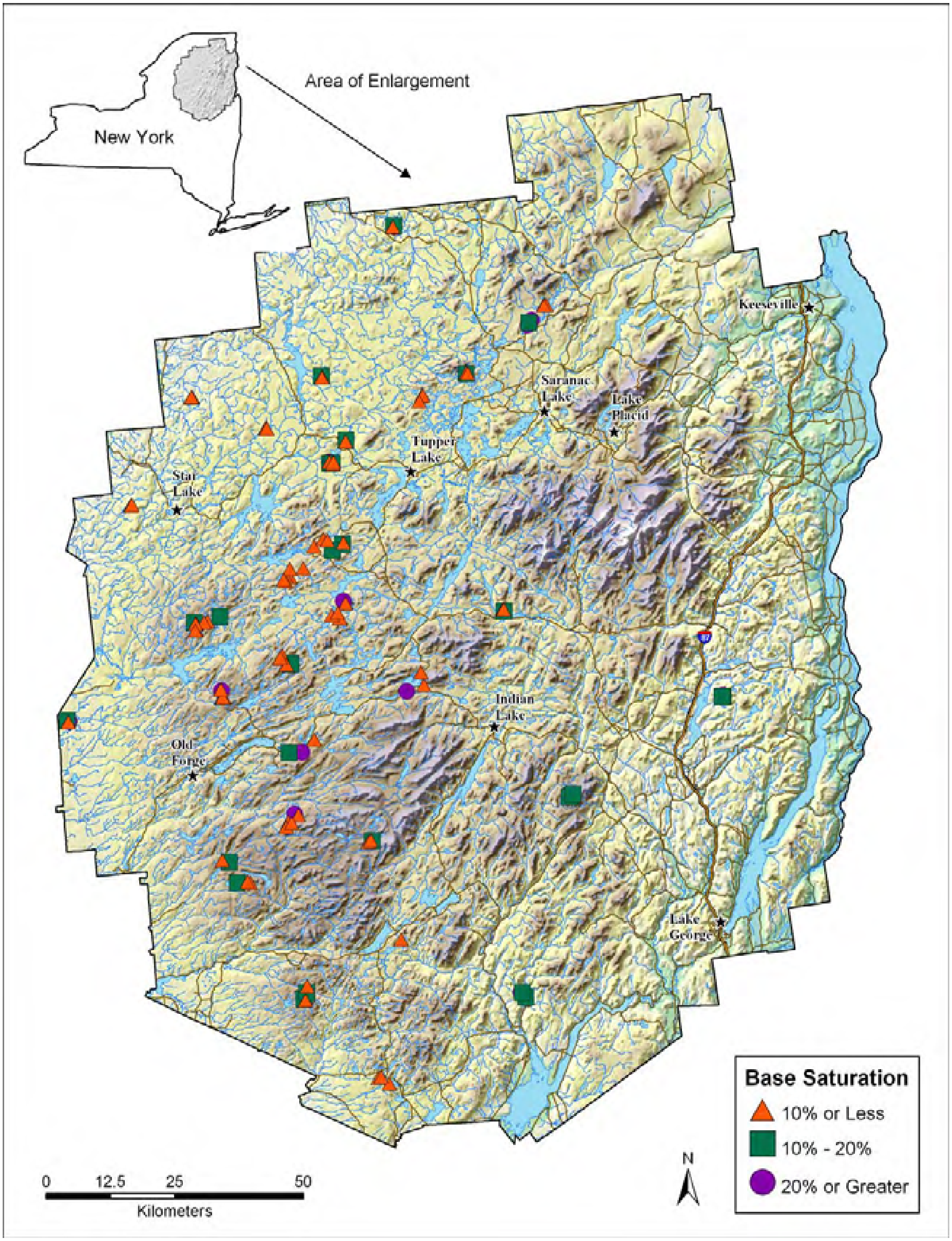


Figure 3-6. Soil base saturation for soil samples collected within the statistically-selected EMAP study watersheds in the Adirondacks.

in part, because concentrations of inorganic Al in soil solution increase as % BS decreases, with the increase in dissolved Al being pronounced when the % BS decreases below ~15% in the presence of strong acid anions (Reuss, 1983; Cronan and Schofield 1990).

Soil data for each watershed were aggregated to yield areally-weighted average values for each parameter in a given watershed. These average values were based on soil pits sampled within the watershed plus nearest-neighbor soil pit data for landscape units not sampled within that watershed. Thus, the soil aggregation procedure provided a mechanism for spatially averaging data from individual soil pedons excavated within each study watershed. This approach also provided the basis for including averaged regional data for landscape units that were not sampled for soil within a particular watershed.

The distributions of soil acid-base chemical characteristics within Adirondack lake watersheds containing potentially acid-sensitive lakes are given in Table 3-2. These distributions were developed from the aggregated data for each of the statistically-selected study watersheds.

The watersheds draining into an estimated three-fourths (N = 990) of Adirondack lakes having ANC $\leq$ 200 μeq/L contained average % BS less than about 10% in the B horizon, with 5% having % BS less than ~5% (Table 3-2). Soil pH values were also very low. Median watershed-average soil pH (H_2O) was 4.3 in the B horizon and 3.5 in the O horizon.

There were not large differences observed among soil classes in parameters that reflect soil acid-base status (Table 3-1). This was probably, in part, because soil classes were designated based on information regarding drainage and geologic parent material. In a glaciated region such as the Adirondack Mountains, we would not necessarily expect soil acid-base chemistry to be clearly associated with such soil classes. Somewhat greater variability was noted in the distribution of values for such variables as CEC, acidity, BS, and exchangeable Ca^{2+} (Table 3-2). Nevertheless, the distribution of values for these parameters across the target population was relatively narrow for the middle 50% of lake watersheds. For example, the 25th and 75th percentile values for % BS in the B-horizon were 6.5 and 10.3% (a relative difference of only 58%). It is important to note, however, that the population frame for this distribution includes only watersheds that drain into lakes having ANC less than 200 μeq/L. Thus, all are relatively low in buffer capacity.

Although variability within a given forest type was high, the Ca and (Ca + Mg) saturation values and the % BS tended to be lowest in soils under coniferous forest and highest in soils under hardwood forest, with intermediate values for soils under mixed forest cover. This pattern

Table 3-2. Population statistics for Adirondack soils based on a statistically-selected group of 44 potentially acid-sensitive Adirondack lake watersheds, representative of 1,320 lake watersheds with lakes larger than 1 ha that have acid neutralizing capacity less than 200 µeq/L.

Variable	Unit	Min	Percentile					
			10	25	50	75	90	Max
O horizon								
Air-dried moisture content	%	6.14	8.03	8.91	10.4	11.1	11.89	13.52
pH ($CaCl_2$)	pH	2.67	2.71	2.76	2.82	2.93	3.1	3.53
pH (H_2O)	pH	3.26	3.29	3.38	3.49	3.6	3.74	4.08
Loss on ignition	%	52.8	62.9	66	69.4	72.8	76.6	81.4
Total N	%	1.29	1.46	1.72	1.84	1.92	2	2.24
Total C	%	31.5	39.2	40.4	45.2	47.2	49.41	51.53
Extractable P	mg/kg	26.5	43.5	52.2	61.1	71.1	86.86	107
Extractable SO_4-S	mg/kg	20.4	21.5	27	29.4	34.2	35.9	47.06
Acidity	cmol$_c$/kg	5.52	11	12.7	16.5	17.8	18.91	24.93
Effective cation exchange capacity	cmol$_c$/kg	21.1	25.6	26.5	29.6	32.5	33.34	37.72
Extractable H (acidity-Al)	cmol$_c$/kg	4.82	8.25	10.2	11.9	13.7	14.64	15.82
Exchangeable Ca	cmol$_c$/kg	2.93	8.29	9.4	11.1	12.3	16.44	22.12
Exchangeable K	cmol$_c$/kg	0.46	0.5	0.66	0.78	0.96	1.1	1.44
Exchangeable Mg	cmol$_c$/kg	0.69	1.42	1.64	1.99	2.36	2.74	3.42
Exchangeable Na	cmol$_c$/kg	0.07	0.12	0.13	0.15	0.16	0.17	0.26
Exchangeable Al	cmol$_c$/kg	0.7	1.92	2.46	2.98	4.68	5.68	14.71
Exchangeable Fe	cmol$_c$/kg	0.06	0.13	0.15	0.17	0.2	0.23	0.26
Exchangeable Mn	cmol$_c$/kg	0.09	0.14	0.22	0.31	0.49	0.796	1.318
Base saturation	%	15.4	37.8	41.8	49	53.9	58.55	82.86
C:N	mol	23.4	24.9	27.1	28.7	30.8	31.97	32.92
B horizon								
Air-dried moisture content	%	2.59	3.39	3.72	4.22	4.84	5.5	6.39
pH ($CaCl_2$)	pH	2.84	3.45	3.53	3.71	3.94	3.99	4.06
pH (H_2O)	pH	3.86	4.09	4.21	4.33	4.51	4.68	4.73
Loss on ignition	%	7	7.8	9	10.3	11.9	13.9	16.5
Total N	%	0.12	0.17	0.18	0.21	0.25	0.31	0.39
Total C	%	3.67	4.15	4.61	5.28	6.6	7.45	9.14
Extractable P	mg/kg	1.33	2.61	3.1	3.39	4.18	4.49	5.51
Extractable SO_4-S	mg/kg	7.63	12	17.2	21.1	48.2	110.3	150.9
Acidity	cmol$_c$/kg	3.42	4.29	5.89	6.97	8.13	9.41	12.62
Effective cation exchange capacity	cmol$_c$/kg	3.81	4.91	6.43	7.84	9	10.01	13.69
Extractable H (acidity-Al)	cmol$_c$/kg	0.86	1.7	2.28	2.93	3.68	4.17	5.01
Exchangeable Ca	cmol$_c$/kg	0.12	0.24	0.27	0.38	0.52	0.7	1.39
Exchangeable K	cmol$_c$/kg	0.03	0.04	0.05	0.06	0.07	0.1	0.14
Exchangeable Mg	cmol$_c$/kg	0.04	0.06	0.07	0.09	0.1	0.13	0.23
Exchangeable Na	cmol$_c$/kg	0.01	0.02	0.03	0.04	0.05	0.07	0.11
Exchangeable Al	cmol$_c$/kg	2.01	2.18	3.42	4.05	4.61	5.19	7.61
Exchangeable Fe	cmol$_c$/kg	0.07	0.09	0.12	0.17	0.23	0.25	0.33
Exchangeable Mn	cmol$_c$/kg	0	0	0	0	0.01	0.021	0.056
Base saturation	%	2.96	5.07	6.47	7.94	10.3	12.8	29.6
C:N	mol	19	24	27.9	29.6	31	33	44.81

held for both O horizon and B horizon soil samples (Table 3-3). In contrast, H saturation was highest for O horizon soils under coniferous forest and Al saturation was highest for B horizon soils under coniferous forest.

3.3 Lakewater Acid Base Chemistry

Results of water chemistry analyses performed for this project are provided in Table 3-4. The 13 lakes listed in the table were sampled during 2003 because of the lack of recent chemical data. These new data were combined with existing data from EMAP, ALSC, ELS, and ALTM in developing the water chemistry database.

Average values for the calibration period of selected water chemistry variables are given in Table 3-5 for each of the study watersheds. The ALTM lakes are primarily low-ANC dilute lakes. The EMAP probability lakes span a wider spectrum of acid-base chemistry conditions, from highly acidic lakes to those having ANC near 200 μeq/L.

3.4 Simulated Versus Observed Chemistry

Results of predicted versus observed average lakewater chemistry during the calibration/evaluation period are given in Figure 3-7 for the MAGIC and PnET-BGC models. Both models showed close agreement with measured values at most sites. For the ANC simulations, the root mean squared error (RMSE) for predicted versus observed values, based on

Table 3-3. Mean and standard deviation of percent cation saturation values in O and B horizon soils, by vegetation type.

	Mean (Standard Deviation)		
Parameter	Conifer	Mixed	Hardwood
O horizon			
Ca Saturation	30.9 (13.4)	35.7 (16.9)	38.7 (15.2)
Ca+Mg Saturation	37.2 (14.9)	42.1 (18.9)	44.9 (17.3)
H^+ Saturation	44.2 (12.8)	35.3 (11.7)	37.7 (12.1)
Al Saturation	15.2 (12.2)	19.1 (21.1)	13.6 (15.9)
Base Saturation	40.5 (15.5)	45.5 (19.2)	48.5 (17.9)
B horizon			
Ca Saturation	4.4 (3.5)	6.1 (6.0)	7.9 (9.5)
Ca+Mg Saturation	5.7 (4.2)	7.7 (7.1)	9.4 (10.6)
H^+ Saturation	35.3 (10.9)	34.9 (9.7)	37.4 (10.8)
Al Saturation	57.3 (10.7)	55.8 (8.8)	51.5 (10.7)
Base Saturation	7.4 (5.2)	9.3 (7.5)	11.0 (11.1)

Table 3-4. Measured water chemistry data for 13 lakes sampled during summer 2003 in this project.

Lake Name	ALSC[a] Pond #	ANC (μeq/L)	Calc ANC (μeq/L)	pH	pH-air	Ca (μeq/L)	Mg (μeq/L)	Na (μeq/L)	K (μeq/L)	NH4 (μeq/L)	SO4 (μeq/L)	NO3 (μeq/L)
Antediluvian Pond	060126	5.18	-12.19	5.19	5.07	77.23	17.32	14.12	2.728	4.74	103.15	14.90
Bennett Lake	050182	30.10	19.45	6.45	6.37	65.97	17.34	24.46	2.353	3.61	79.99	0.83
Blue Mountain Lake	060304	120.86	198.22	7.07	7.31	194.61	49.78	394.87	17.637	0.88	92.35	6.22
Bog Pond	060175	67.45	118.10	6.48	6.76	137.03	42.13	27.88	3.709	7.22	87.23	0.71
Canada Lake	070717	53.11	43.36	6.55	6.93	107.04	41.64	200.39	5.970	2.55	90.50	7.82
Clear Pond	020070	202.28	221.86	7.16	7.49	165.42	86.16	44.45	12.763	7.53	76.61	0.88
Gull Pond	050418	140.34	159.55	7.03	7.37	188.17	45.92	29.62	5.525	1.96	76.53	0.80
Hitchins Pond	060144	112.66	181.97	6.80	7.10	104.99	54.06	38.97	6.829	1.80	20.18	0.73
Long Pond	030170	20.70	40.61	5.94	5.82	43.40	15.88	10.25	11.934	9.19	38.56	0.77
McCuen Pond	060039	35.59	74.52	5.51	6.50	50.09	20.42	17.67	10.095	12.64	28.30	0.89
Piseco Lake	050234	96.44	103.21	6.84	6.94	130.14	63.03	134.54	7.315	2.24	77.98	6.69
Rocky Lake	040137	28.60	47.30	5.88	6.26	62.67	27.24	31.45	5.929	6.09	76.26	1.02
Seventh Lake	040787A	179.16	179.89	7.14	7.52	212.43	70.11	227.01	15.960	1.69	103.60	16.14

Lake Name	ALSC Pond #	Cl (μeq/L)	Al (m)[a] (μmol/L)	Al (o)[a] (μmol/L)	Al (i)[a] (μmol/L)	F (μmol/L)	Total P (ug/L)	DOC[a] (μmol/L)	DIC[a] (μmol/L)			
Antediluvian Pond	060126	10.28	1.098	1.883	2.749	90.28	896.05	0.73	100			
Bennett Lake	050182	13.46	0.935	0.112	1.319	37.33	141.86	80.72	100			
Blue Mountain Lake	060304	361.00	0.888	0.037	3.502	39.10	141.03	191.99	12			
Bog Pond	060175	11.93	1.053	0.105	2.981	48.47	486.34	141.78	50			
Canada Lake	070717	215.91	0.951	0.107	1.689	57.54	183.47	102.78	25			
Clear Pond	020070	16.96	0.878	0.079	2.340	28.35	300.32	266.74	33			
Gull Pond	050418	34.31	0.857	0.253	2.204	5.30	298.80	193.11	50			
Hitchins Pond	060144	3.78	1.075	0.119	1.714	74.42	498.02	156.38	50			
Long Pond	030170	10.70	1.457	0.165	0.926	2.70	569.66	109.32	50			
McCuen Pond	060039	7.21	2.461	0.405	3.952	17.40	121.26	147.50	100			
Piseco Lake	050234	149.39	0.961	0.097	1.894	50.62	231.59	147.30	33			
Rocky Lake	040137	8.79	1.840	0.604	7.217	18.99	422.28	164.22	100			
Seventh Lake	040787A	227.57	0.959	0.148	2.819	71.38	272.14	253.58	20			

[a] ALSC - Adirondack Lakes Survey Corporation; Al(m) - monomeric aluminum; Al(o) - organic monomeric aluminum; Al(i) - inorganic monomeric aluminum; DOC - dissolved organic carbon; DIC - dissolved inorganic carbon

Table 3-5. Average observed lakewater chemistry during the calibration period for each study lake.

			Average Summer and Fall Value*			
Lake Name	ID	ANC**	pH	SO4	NO3	Sum of Base Cations
Long-Term Monitoring Lakes* **						
Arbutus Pond***	50684	84.41	6.95	110.42	2.16	204.93
Big Moose Lake	40752	14.56	5.71	93.88	11.91	127.78
Brook Trout Lake	40874	4.35	5.81	87.64	2.41	100.71
Bubb Lake	40748	71.51	6.86	88.82	5.04	171.74
Carry Pond	50669	-9.52	5.06	69.01	0.77	63.78
Cascade Lake	40747	59.98	6.85	105.52	11.09	184.35
Constable Pond	40777	21.52	5.66	99.38	5.84	134.12
Dart Lake	40750	19.97	5.89	94.61	11.84	134.32
G Lake	70859	19.88	6.23	83.79	2.04	111.75
Grass Pond	40706	47.43	6.55	96.75	3.96	154.95
Hell Diver	40877	53.52	5.25	88.81	0.63	151.7
Indian Lake***	40852	4.4	5.24	81.49	1.78	93.88
Jockeybush Lake	50259	-0.94	5.67	94.82	8.05	107.63
Lake Rondaxe	40739	63.09	6.74	93.86	8.24	173.67
Limekiln Lake	40826	36.6	6.57	92.15	8.79	158.14
Long Pond (12)	50649	17.89	4.66	74.48	0.83	100.56
Middle Branch Lake	40707	78.86	6.87	86.48	1.22	173.63
Middle Settlement Lake	40704	14.53	6.07	80.89	1.62	96.98
Moss Lake	40746	98.95	7.08	102.35	8.47	220.31
North Lake***	41007	19.32	5.76	87.79	8.85	122.18
Queer Lake	60329	12.63	5.84	99.93	13.76	133.13
Raquette Lake Reservoir	060315A	93.26	6.55	113.48	3.61	222.17
Round	040731A	0.58	5.14	58.95	1	64.76
Sagamore Lake	60313	74.74	6.41	108.02	6.96	198.1
South Lake***	41004	5.26	5.75	83.57	16.02	111.77
Squash Pond	40754	-24.82	4.54	77.23	5.96	64.68
Squaw Lake***	40850	27.02	6.33	89.94	2.67	126.74
West Pond	40753	30.01	5.02	69.39	3.16	108.52
Wheeler	40731	95	6.57	76.16	2.32	178.1
Willis Lake	50215	114.34	6.67	75.36	0.65	208.65
Willys Lake***	40210	-32.61	4.92	101.92	16.2	91.48
Windfall Pond	040750A	90.02	6.8	99.38	7.35	206.71
Probability Lakes						
Antediluvian Pond	60126	71.5	6.28	55	0.75	133.85
Arbutus Pond ***	50684	84.41	6.95	110.42	2.16	204.93
Bennett Lake	50182	30.98	6.55	85.61	0.51	126.2
Bickford Pond	30273	21.88	5.93	81.65	0.34	108.63
Big Alderbed	70790	67.5	6.43	77.5	3.6	158.65
Blue Mountain Lake	60307	115.12	7.31	105.12	1.94	570.23

Table 3-5. Continued.

			Average Summer and Fall Value*			
Lake Name	ID	ANC**	pH	SO4	NO3	Sum of Base Cations
Bog Pond	60175	118.1	6.76	87.23	0.71	210.75
Boottree Pond	30374	58.97	6.77	33.67	0.1	97.73
Canada Lake	70717	55.09	6.8	94.83	7.27	318.41
Carry Falls Reservoir	060035C	121.2	7	94	11.6	271.1
Clear Pond (61)	20070	218.1	7.51	86	0	315.1
Clear Pond (82)	60176	85.9	7.02	73	0	165.9
Dismal Pond	40515	-20.97	4.62	81	1.97	63.33
Dry Channel Pond	30128	23.83	5.82	89	0	116.17
Effley Falls Pond	40426	53.87	6.52	85.67	13.03	160.87
Gull Pond	50418	157.78	7.3	76.33	0	242.62
Hitchins Pond	60144	150.2	7.24	71	0.17	227.45
Hope Pond	20059	62.6	6.39	80	0	172.6
Horseshoe Pond	30373	51.17	6.54	66.67	0.17	124
Indian Lake***	40852	4.4	5.24	81.49	1.78	93.88
Little Lilly Pond	40566	46.67	5.59	60.13	0.42	112.6
Long Lake	70823	-32.07	4.91	98.67	14.2	86.23
Long Pond (65)	30170	66.07	6.56	51.5	0	123.78
Lower Beech Ridge Pond	40203	-18.7	4.87	78.67	4.63	68.6
Mccuen Pond	60039	56.84	5.4	57.9	0.52	115.33
North Lake***	41007	19.32	5.76	87.79	8.85	122.18
Parmeter Pond	30331	67.53	5.96	60	1.8	136.87
Payne Lake	40620	53.93	6.47	26	0.93	88
Piseco Lake	50234	103.21	6.94	77.98	6.69	335.02
Razorback Pond	40573	34.7	6.49	89.33	11.8	142.53
Rock Pond	60129	88.55	6.36	77	0.55	172.7
Rocky Lake	40137	56.5	6.37	69.16	0.72	131.54
Second Pond	50298	73.05	6.72	82.75	0.7	163.77
Seven Sisters Pond	60074	-14.1	4.42	51.45	0.38	45.15
Seventh Lake	050631A	179.89	7.52	103.6	16.14	525.51
Snake Pond	40579	13.71	5.54	88.67	4.02	112.87
South Lake***	41004	5.26	5.75	83.57	16.02	111.77
Squaw Lake***	40850	27.02	6.33	89.94	2.67	126.74
Trout Pond	60146	39.24	6.54	93.2	3.56	142.04
Upper Sister Lake	40769	30.96	5.54	81.5	0	125.26
Whitney Lake	70936	26.75	6.24	83.5	0.35	115.55
Willys Lake***	40210	-32.61	4.92	101.92	16.2	91.48
Witchhopple Lake	40528	28.77	6.03	84.67	2.33	122.9
Wolf Pond	30360	-10.79	4.91	70.54	0.37	64.21

* all values expressed in μeq/L except pH

** ANC is reported as the calculated ANC (CALK = SBC-SAA)

*** asterisk indicates lakes that occurred within both the probability and long-term monitoring categories

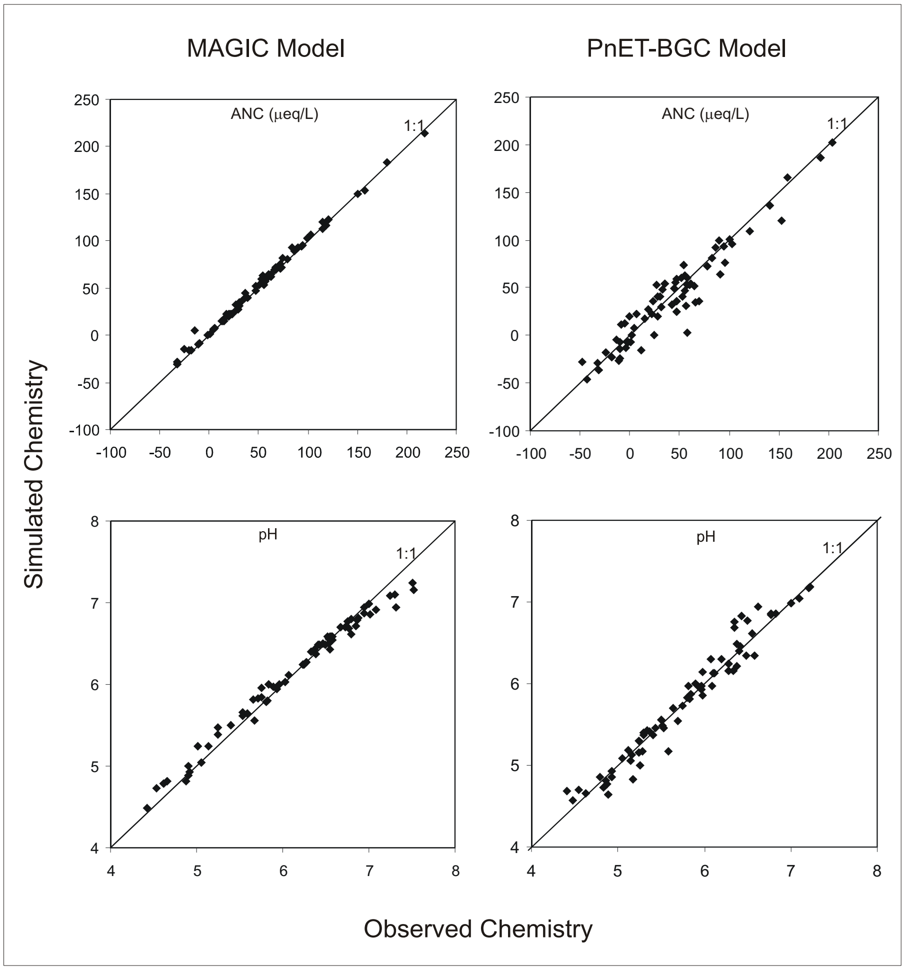


Figure 3-7. Simulated versus observed average lakewater ANC (calculated from the charge balance) and pH during the model calibration/evaluation period for each of the 70 study lakes.

average ANC over a five-year period, was 4.3 μeq/L for MAGIC and 15 μeq/L for PnET-BGC. Plots of simulated and observed calculated ANC for individual lakes are provided in Appendix A, for those lakes that had two decades of monitoring data.

3.5 Model Projections of Regional Acidification and Recovery

Regional extrapolation of model output focused on estimating numbers and percentages of Adirondack lakes that the models predict might respond in certain ways to past and future emissions of S and N. Results of model projections were extrapolated to the entire population of Adirondack lakes having ANC less than 200 μeq/L using the original EMAP sample weights adjusted for our random subsampling procedure. For this analysis, ANC is defined by the charge balance as the difference between the sum of the concentration of the base cations and the strong acid anions:

$$\text{ANC} = (\text{Ca}^{2+} + \text{Mg}^{2} + \text{Na}^{+} + \text{K}^{+} + \text{NH}_4^{+}) - (\text{SO}_4^{2-} + \text{NO}_3^{-} + \text{Cl}^{-}) \qquad (3\text{-}1)$$

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

3.5.1 MAGIC Projections

Based on MAGIC model outputs extrapolated to the regional lake population, annual volume-weighted lakewater chemistry population statistics were generated for various years from 1850 to 2100. Results suggested that the median lake, from among the 1,320 Adirondack lakes larger than 1 ha that have ANC < 200 μeq/L, had pre-industrial (1850) ANC near 100 μeq/L. An estimated 10% of those lakes had pre-industrial ANC < 26 μeq/L, and one-fourth had ANC < 68 μeq/L (Table 3-6). Maximum past acidification occurred by about 1980 or 1990, with median ANC of about 61 μeq/L (reduced from a median of 92 μeq/L estimated for the pre-industrial period). By 1990, 10% of the EMAP target lakes had decreased in ANC to below -16 μeq/L and 25% had ANC < 28 μeq/L. Percentile values in 2000 illustrate limited chemical recovery (3 to 5 μeq/L) compared with simulated values in 1980 and 1990.

Future projections with the MAGIC model under the Base Case Emissions Control scenario suggest that chemical recovery will continue in the future, but only for the lakes having higher ANC. The 10th, 25th, and 50th percentile ANC values suggested a partial future reversal of the ANC recovery that occurred between about 1980 and 2000 (Table 3-6). However, simulations under the more restrictive emissions control scenarios suggest continued ANC recovery into the future across the range of lakes from 10th to 90th percentile ANC levels. Greatest chemical recovery was projected to occur under the Aggressive Additional Emissions Control scenario. Ninety percent of the target lakes were projected to increase in ANC to above 8 μeq/L under that scenario. Such an increase in ANC would only represent partial recovery of simulated pre-industrial ANC levels, but nevertheless would suggest the potential for long-term biological recovery of the more acidic lakes.

The MAGIC model simulations suggest that none of the target lakes were chronically acidic (had ANC < 0 μeq/L) under pre-industrial conditions, but that by 1980 there were about

Table 3-6. Simulated water chemistry percentile values for the population of potentially acid-sensitive Adirondack lakes, based on the MAGIC model, for the period from 1850 to 2100, assuming three scenarios of S and N emissions control. (Units: μeq/L except pH)

Variable	Year	Emissions Control Scenario	Percentile				
			10	25	50	75	90
ANC	1850		26	68	92	178	257
	1900		26	68	96	183	259
	1980		-15	24	61	134	186
	1990		-16	28	62	120	177
	2000		-13	32	67	119	180
	2050	Base	-16	34	64	131	197
	2050	Moderate	-1	44	76	146	214
	2050	Aggressive	4	48	80	151	220
	2100	Base	-19	29	58	134	197
	2100	Moderate	2	42	71	154	219
	2100	Aggressive	8	47	76	161	228
pH	1850		5.6	6.3	6.7	7.4	7.7
	1900		5.6	6.3	6.7	7.4	7.7
	1980		4.8	5.4	6.5	7.0	7.6
	1990		4.8	5.5	6.5	7.0	7.5
	2000		5.0	5.7	6.6	7.1	7.5
	2050	Base	5.0	5.6	6.5	7.0	7.5
	2050	Moderate	5.4	5.9	6.6	7.2	7.6
	2050	Aggressive	5.5	6.0	6.7	7.3	7.6
	2100	Base	4.9	5.5	6.5	7.0	7.5
	2100	Moderate	5.4	6.0	6.6	7.2	7.6
	2100	Aggressive	5.5	6.0	6.6	7.3	7.6
SO_4^{2-}	1850		5	7	9	15	23
	1900		17	20	23	32	38
	1980		86	95	107	123	138
	1990		71	81	93	108	129
	2000		49	55	71	81	94
	2050	Base	36	40	50	57	62
	2050	Moderate	21	24	32	41	43
	2050	Aggressive	15	18	25	34	38
	2100	Base	36	40	49	57	59
	2100	Moderate	20	22	29	34	43
	2100	Aggressive	14	16	22	27	36

Table 3-6. Continued.

Variable	Year	Emissions Control Scenario	Percentile				
			10	25	50	75	90
NO_3^-	1850		0	0	0	0	1
	1900		0	0	0	0	1
	1980		0	0	1	3	15
	1990		0	0	1	2	13
	2000		0	0	1	2	11
	2050	Base	0	0	0	2	10
	2050	Moderate	0	0	0	2	9
	2050	Aggressive	0	0	0	1	8
	2100	Base	0	0	0	2	10
	2100	Moderate	0	0	0	2	9
	2100	Aggressive	0	0	0	1	8
Sum of Base Cations	1850		45	88	111	199	293
	1900		65	109	134	232	320
	1980		101	145	172	260	342
	1990		85	131	151	239	320
	2000		68	114	133	215	295
	2050	Base	46	95	117	195	286
	2050	Moderate	45	87	110	191	285
	2050	Aggressive	44	85	106	190	285
	2100	Base	41	89	115	191	286
	2100	Moderate	40	83	109	190	285
	2100	Aggressive	40	82	106	189	285

204 acidic Adirondack lakes. That number decreased by an estimated 14% between 1980 and 2000. Similarly, the MAGIC model simulations suggest that there were no Adirondack lakes having ANC < 20 μeq/L in 1850, but by 1990 there were 263 such lakes. Many lakes ($\hat{N}$ = 191) were estimated to have had pre-industrial ANC below 50 μeq/L, and this estimate increased three-fold by 1990, followed by a decrease to 399 lakes in 2000. Future projections suggest that the number of acidic lakes will remain stable, at 2000 levels, into the future under the Base Case scenario. Under the two more restrictive emissions control scenarios, the number of acidic lakes was projected to continue to decline in the future. For example, under the Aggressive Additional Emissions Control scenario, the model projected that all except 93 target lakes would recover to ANC > 0 μeq/L (Table 3-7).

Table 3-7. Estimated number of Adirondack lakes below ANC criteria values for the population of 1,320 Adirondack lakes larger than 1 ha that have ANC less than 200 µeq/L based on MAGIC model simulations for 44 statistically-selected lakes.

	ANC (µeq/L)								
Year	**≤0**			**≤20**			**≤50**		
Past									
1850	0			93			191		
1900	93			109			216		
1980	204			279			519		
1990	204			263			581		
2000	175			217			399		
Future	**Base**	**Mod.**	**Ag.**	**Base**	**Mod.**	**Ag.**	**Base**	**Mod.**	**Ag.**
2020*	175	159	159	229	191	191	437	407	398
2050*	175	142	93	229	191	175	437	381	365
2100*	175	125	93	243	191	175	437	381	336

* Simulations for future years (2020, 2050, and 2100) are based on three scenarios of emissions controls: the Base Case which included controls that have been or are expected to be enacted under existing regulations and scenarios of Moderate (Mod.) and Aggressive (Ag.) Additional Emissions Controls.

Simulation results for lakewater pH were similar to ANC results. The number of lakes having pH ≤ 5.0 was estimated to be 93 lakes in 1850, increasing to 175 lakes by 1990. The simulated number of lakes having pH ≤ 5.5 tripled between 1900 and 1990. Again, partial chemical recovery was simulated between 1980 and 2000, but under the Base Case Scenario a reversal of this short-term pH recovery was suggested in the near future. Under the Moderate and Aggressive Additional Emissions Control scenarios, the numbers of lakes having pH below 5, 5.5, and 6 were projected to continue to decline in the future. In particular, the estimated number of lakes having pH < 5 was projected to return to pre-industrial conditions (Table 3-8).

The temporal development of chemical acidification and recovery responses, as represented by MAGIC simulations, is shown in Figure 3-8 for all modeled lakes that had ANC below 20 µeq/L in 2000. These are the lakes that are most sensitive to biological impacts. Each would be expected to acidify seasonally to ANC < 0 during spring snowmelt (Stoddard et al. 2003). All of the modeled low-ANC lakes showed substantial simulated historical acidification, with historical ANC minima occurring near 1980 or 1990. Recent ANC recovery is evident during the 1990s and is projected to continue to about 2020. Thereafter, reacidification is

Table 3-8. Estimated number of Adirondack lakes below pH criteria values for the population of 1,320 Adirondack lakes larger than 1 ha that have ANC less than 200 μeq/L based on MAGIC model simulations for 44 statistically-selected lakes.

Year	pH ≤5.0			pH ≤5.5			pH ≤6.0		
Past									
1850	93			110			251		
1900	93			110			281		
1980	175			342			443		
1990	175			342			426		
2000	175			284			406		
Future	**Base**	**Mod.**	**Ag.**	**Base**	**Mod.**	**Ag.**	**Base**	**Mod.**	**Ag.**
2050*	143	110	93	284	158	142	406	355	339
2100*	159	110	93	314	158	142	422	339	322

* Simulations for future years (2050 and 2100) are based on three scenarios of emissions controls: the Base Case which included controls that have been or are expected to be enacted under existing regulations and scenarios of Moderate (Mod.) and Aggressive (Ag.) Additional Emissions Controls.

projected for all of these lakes under the Base Case scenario. For most of these lakes, continued chemical recovery is projected under the Moderate and Aggressive Additional Emissions Control scenarios.

3.5.2 PnET-BGC Projections

PnET-BGC model simulations generated output generally similar to results that were based on MAGIC model simulations (presented in the previous section). PnET-BGC simulations suggested that lakewater SO_4^{2-}, NO_3^-, and base cation concentrations under pre-industrial conditions were much lower than current values (Figure 3-9). In 1850, simulated SO_4^{2-} concentrations in all study lakes were less than 25 μeq/L, and the median value was about 15 μeq/L. By 1980, the median simulated SO_4^{2-} concentration had increased more than six-fold to about 100 μeq/L. Simulated lake NO_3^- concentrations also increased markedly during that time, with the median value increasing from about 4 μeq/L in 1850 to 12 μeq/L in 1980. Simulated increases in the sum of divalent base cation concentrations were less than for SO_4^{2-} concentrations, with the median value increasing from 93 μeq/L in 1850 to 140 μeq/L in 1980. This large change in SO_4^{2-} + NO_3^- relative to the change in the sum of base cation concentrations

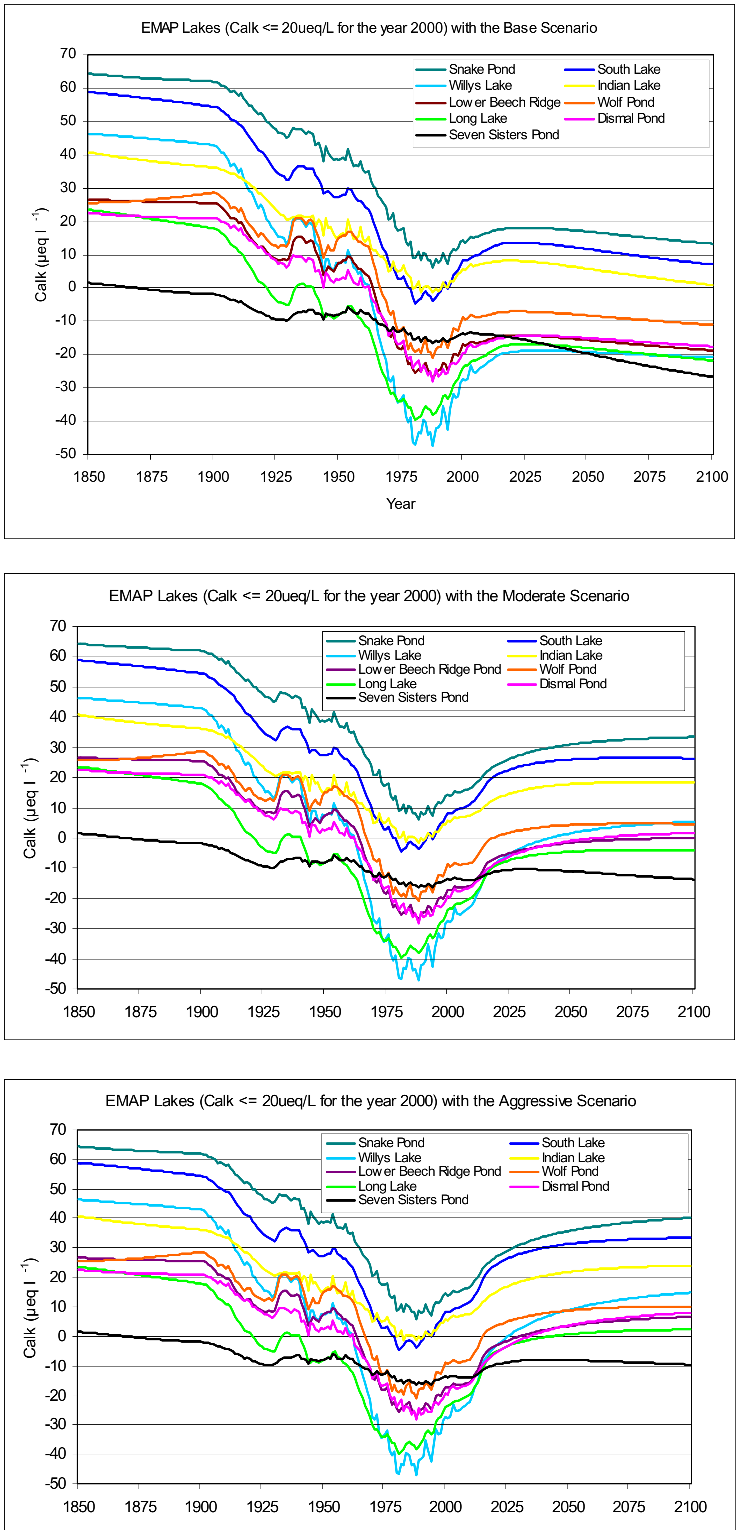


Figure 3-8. MAGIC simulations for the probability lakes that had ANC ≤ 20 μeq/L in 2000 under three scenarios of emissions controls. These are the lakes expected to have the greatest biological impacts from acidification and chemical recovery.

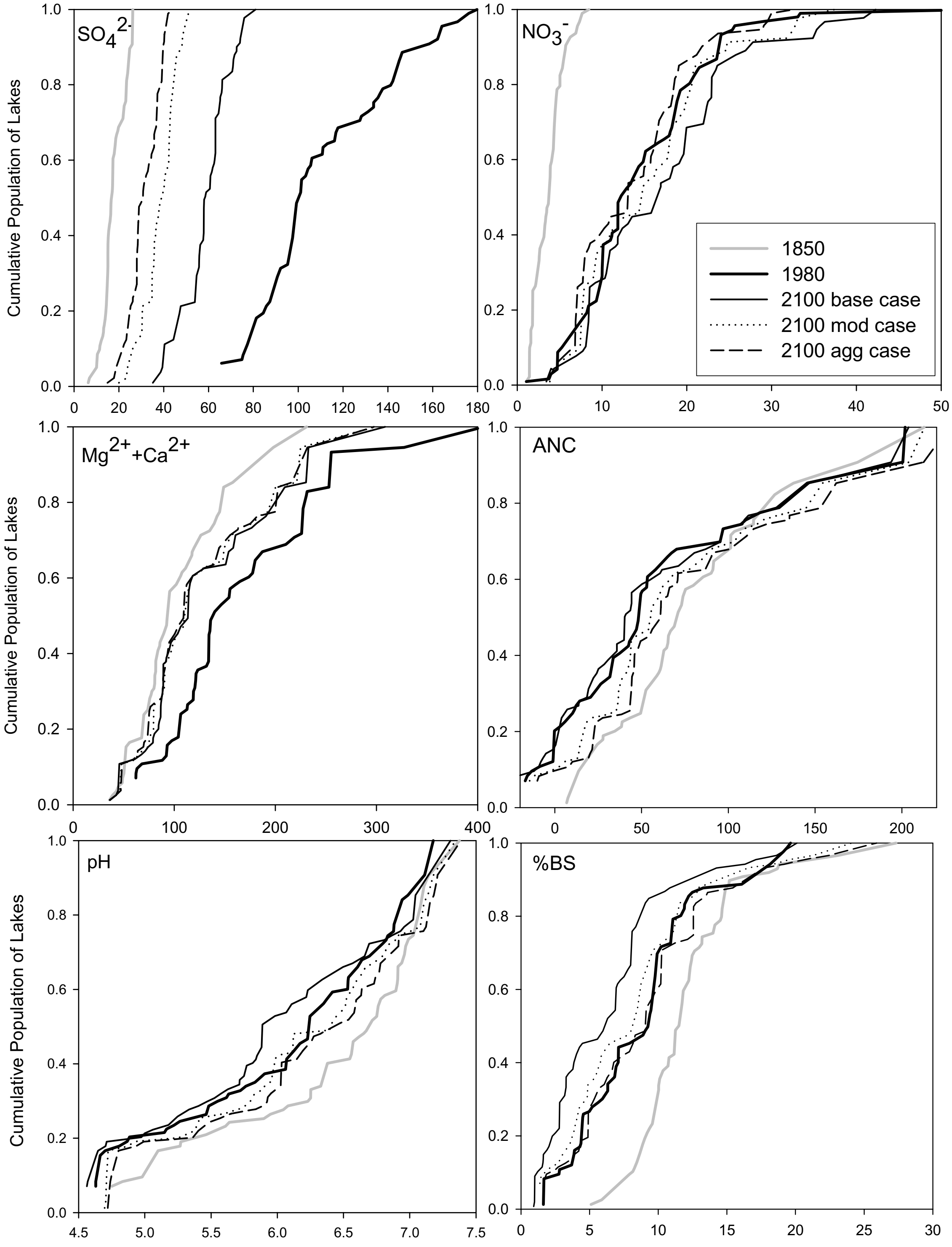


Figure 3-9. Cumulative distributions of PnET-BGC simulated water chemistry and soil base saturation for the population of Adirondack lakes (1320 lakes) in pre-industrial time (1850), 1980, and 2100 under three future emissions scenarios. Values are expressed as μeq/L, except pH and soil % BS.

was the major mechanism driving the decreases in ANC and pH associated with historical increases in acidic deposition.

Simulated lakewater ANC and pH and soil base saturation decreased from pre-industrial conditions to recent times. Results from PnET-BGC suggested that the median Adirondack lake, from among the estimated 1,320 lakes in the population larger than 1 ha that had measured recent ANC < 200 μeq/L, had pre-industrial ANC near 80 μeq/L; an estimated 10% of the lake population had pre-industrial ANC < 41 μeq/L; and one-fourth had pre-industrial ANC < 64 μeq/L (Table 3-9). Percentiles for the year 2000 suggest decreases in SO_4^{2-}, NO_3^-, and sum of base cations, and small increases in ANC since 1990 for lower-ANC lakes.

The median simulated pH decreased from 6.7 in 1850 to 6.2 in 1985. About 27% of the population of lakes had pH less than 6.0 in 1850, and 38% had pH less than 6.0 in 1980. The median value for soil % BS decreased over this same period from 11.5% to 9.2%. About 25% of the population of lake-watersheds had soil % BS less than 10% in 1850, and 70% had soil % BS less than 10% in 1980. These model results suggest long-term acidification of both soil and surface waters in the Adirondack region.

Simulated lake SO_4^{2-} concentrations showed large decreases under all three future scenarios (Figure 3-9). The median lakewater SO_4^{2-} concentrations in 2100 for the Base Case, Moderate, and Aggressive Additional Controls scenarios were 59, 39, and 30 μeq/L, respectively, compared to the median value in 1980 of 100 μeq/L. Despite these large decreases, projected SO_4^{2-} concentrations for 2100 were still considerably higher than the estimated pre-industrial values (median 16 μeq/L).

The projected NO_3^- concentrations under the three future scenarios were similar, with median values of 17, 14, and 13 μeq/L, respectively, in 2100. The median simulated value in 1980 was 12 μeq/L. Although it is anticipated that there will be decreases in future emissions of NO_x, the projected concentrations of NO_3^- in lake water remained high.

The projected concentrations of divalent base cations (Ca + Mg) were similar under the three future emissions control scenarios (median 114, 111, and 100 μeq/L, respectively), and suggest modest decreases compared with 1980 values (median 138 μeq/L).

For ANC and pH, there is little evidence to suggest future chemical recovery for most lakes under the Base Case scenario (Table 3-9). A major reason for this pattern of response was the simulated decline in soil base saturation under this scenario. These results suggest that

Table 3-9. Simulated water chemistry percentile values of annual concentrations for the population of potentially acid-sensitive Adirondack lakes, based on the PnET-BGC model, for the period from 1850 to 2100, assuming three scenarios of S and N emissions control. (Units: µeq/L, except pH).

Variable	Year	Emissions Control Scenario	Percentile				
			10	25	50	75	90
ANC	1850		41	64	81	125	182
	1900		36	62	81	132	187
	1980		-17	27	48	114	150
	1990		-26	23	55	113	198
	2000		-21	25	54	107	181
	2050	Base	-12	21	50	109	184
	2050	Moderate	7	36	57	116	194
	2050	Aggressive	12	39	63	123	200
	2100	Base	-11	20	50	113	202
	2100	Moderate	13	43	66	126	212
	2100	Aggressive	22	49	71	131	221
pH	1850		5.0	5.9	6.7	7.0	7.1
	1900		4.9	5.9	6.7	7.0	7.1
	1980		4.6	5.3	6.2	6.9	7.1
	1990		4.7	5.4	6.1	6.9	7.2
	2000		4.7	5.3	6.0	6.9	7.1
	2050	Base	4.6	5.3	6.0	6.9	7.1
	2050	Moderate	4.7	5.4	6.3	6.9	7.1
	2050	Aggressive	4.7	5.4	6.4	7.0	7.2
	2100	Base	4.6	5.2	5.9	6.9	7.1
	2100	Moderate	4.7	5.4	6.4	7.0	7.2
	2100	Aggressive	4.7	5.6	6.4	7.0	7.2
SO_4^{2-}	1850		11	15	15	23	25
	1900		19	23	27	33	41
	1980		77	87	100	134	158
	1990		61	71	76	96	107
	2000		45	61	67	80	87
	2050	Base	43	57	62	67	77
	2050	Moderate	32	42	46	51	56
	2050	Aggressive	29	34	38	47	50
	2100	Base	40	54	59	65	73
	2100	Moderate	27	35	39	43	48
	2100	Aggressive	22	27	30	37	40

Table 3-9. Continued.							
Variable	Year	Emissions Control Scenario	Percentile				
			10	25	50	75	90
NO_3^-	1850		1.5	1.8	3.7	4.5	5.7
	1900		1.5	2.7	4.1	5.4	8.7
	1980		5.3	9.5	12.3	18.9	23.6
	1990		8.6	14.2	22.1	29.9	33.4
	2000		9.5	11.2	16.1	24.8	27.3
	2050	Base	4.7	6.5	10.5	16.4	22.3
	2050	Moderate	4.2	5.8	9.2	14.9	20.7
	2050	Aggressive	4.5	5.4	8.2	13.7	15.9
	2100	Base	8.1	8.6	16.9	22.4	26.9
	2100	Moderate	6.9	7.9	14.5	19.7	24.6
	2100	Aggressive	6.1	7.1	13.0	18.2	21.8
Sum of Base Cations	1850		61	81	108	162	251
	1900		76	103	120	187	281
	1980		103	149	188	271	329
	1990		84	142	159	263	316
	2000		70	118	136	215	284
	2050	Base	62	101	127	208	270
	2050	Moderate	61	93	120	198	266
	2050	Aggressive	59	90	116	199	274
	2100	Base	56	103	131	222	290
	2100	Moderate	58	95	128	214	281
	2100	Aggressive	59	94	120	212	289

emission controls represented by the Base Case scenario would not be sufficient to achieve chemical recovery of lakes from acidic deposition over the long term. In contrast, some recovery of lake ANC and pH is evident under the Moderate and Aggressive Additional Controls scenarios. The median simulated ANC in 2100 increased to 55 and 61 μeq/L, respectively, for these two scenarios, compared with 48 μeq/L in 1980.

Greatest chemical recovery was projected under the Aggressive Additional Emissions Control scenario. Ninety percent of the target lakes were projected to increase in ANC to above 22 μeq/L by 2100 under the Aggressive scenario. This represents recovery of a substantial component of the ANC loss that was simulated to have occurred between 1850 and 1990 (Table 3-9).

Results from PnET-BGC suggest that none of the lakes in the Adirondack population had pre-industrial ANC below 20 μeq/L. By 1990, there were 289 lakes having ANC ≤ 20 μeq/L and 217 acidic (ANC ≤ 0 μeq/L) lakes according to PnET-BGC simulations (Table 3-10). There were 202 lakes in the population simulated to have had pre-industrial ANC below 50 μeq/L, and this number increased 2.8 times by 1980 under the PnET-BGC simulations. Future projections suggest that the numbers of acidic and very low-ANC (≤ 20 μeq/L) lakes would stabilize into the future near year-2000 levels under the Base Case scenario. Under the more restrictive emissions control scenarios, the numbers of acidic and low-ANC (≤ 20 μeq/L, ≤ 50 μeq/L) lakes were projected to continue to decline into the future (Table 3-10). Under either the Moderate or Aggressive Additional Emissions Control scenarios, the number of acidic Adirondack lakes was projected to decrease to 17 by the year 2050.

PnET-BGC simulation results for pH were generally similar to the pattern of response for ANC. The model estimated that there were many (estimate of N = 110) lakes with pH < 5.0 under pre-industrial conditions, but this estimate increased to 284 lakes by the year 2000 (Table 3-11). The estimated numbers of lakes having pH ≤ 5.5 or ≤ 6.0 also increased markedly between 1850 and 2000. Estimates for the numbers of lakes having pH below 5.5 or 6.0

Table 3-10. Estimated number of Adirondack lakes below ANC criteria values for the population of 1,320 Adirondack lakes larger than 1 ha that have ANC less than 200 μeq/L based on PnET-BGC model simulations for 44 statistically-selected lakes.

Year	**ANC (μeq/L)**								
	≤0			**≤20**			**≤50**		
Past									
1850	0			0			202		
1900	0			17			218		
1980	201			289			563		
1990	217			289			533		
2000	200			289			517		
Future	**Base**	**Mod.**	**Ag.**	**Base**	**Mod.**	**Ag.**	**Base**	**Mod.**	**Ag.**
2020*	188	159	126	289	260	260	644	563	563
2050*	188	17	17	289	201	188	639	551	471
2100*	200	17	17	305	188	110	639	390	344

* Simulations for future years (2020, 2050, and 2100) are based on three scenarios of emissions controls: the Base Case which included controls that have been or are expected to be enacted under existing regulations and scenarios of Moderate (Mod.) and Aggressive (Ag.) Additional Emissions Controls.

Table 3-11. Estimated number of Adirondack lakes below pH criteria values for the population of 1,320 Adirondack lakes larger than 1 ha that have ANC less than 200 μeq/L based on PnET-BGC model simulations for 44 statistically-selected lakes.

Year	pH								
	≤5.0			≤5.5			≤6.0		
Past									
1850	110			252			240		
1900	126			252			240		
1980	268			378			492		
1990	268			353			524		
2000	284			378			577		
Future	**Base**	**Mod.**	**Ag.**	**Base**	**Mod.**	**Ag.**	**Base**	**Mod.**	**Ag.**
2050*	268	268	268	378	336	336	658	477	477
2100*	284	268	252	394	336	320	658	465	423

* Simulations for future years (2050 and 2100) are based on three scenarios of emissions controls: the Base Case which included controls that have been or are expected to be enacted under existing regulations and scenarios of Moderate (Mod.) and Aggressive (Ag.) Additional Emissions Controls.

decreased into the future between 2000 and 2050 under the Moderate and Aggressive Additional Controls scenarios, but not under the Base Case scenario. Similarly, the number of lakes estimated to have pH < 5.0 in 2100 did not decrease under the Base Case scenario, but did decrease under the more restrictive emissions control scenarios.

The temporal development of the acidification response for lakewater ANC is shown in Figure 3-10, as represented by PnET-BGC simulations, for all modeled lakes that had ANC below 20 μeq/L in 2000. All of these modeled low-ANC lakes showed substantial historical acidification. Recent recovery of lakewater ANC was projected for the latter part of the 20th century. Reacidification was projected for most of these lakes under the Base Case scenario, beginning after sometime between 2010 and 2050.

3.6 Comparisons Between Intensively-Studied Watersheds and the Regional Population

3.6.1 Soil Comparison

Soils having low % BS in the B horizon were found to be widely distributed throughout the western portion of the Adirondack Park. In particular, soils collected within watersheds included in the ALTM and AEAP monitoring programs frequently exhibited low % BS (Figure 3-11). Of 84 soil pits (excluding duplicates, which were averaged) collected within ALTM/AEAP watersheds, 24 had % BS less than 5% and 47 had % BS between 5 and 10%. Only six of the

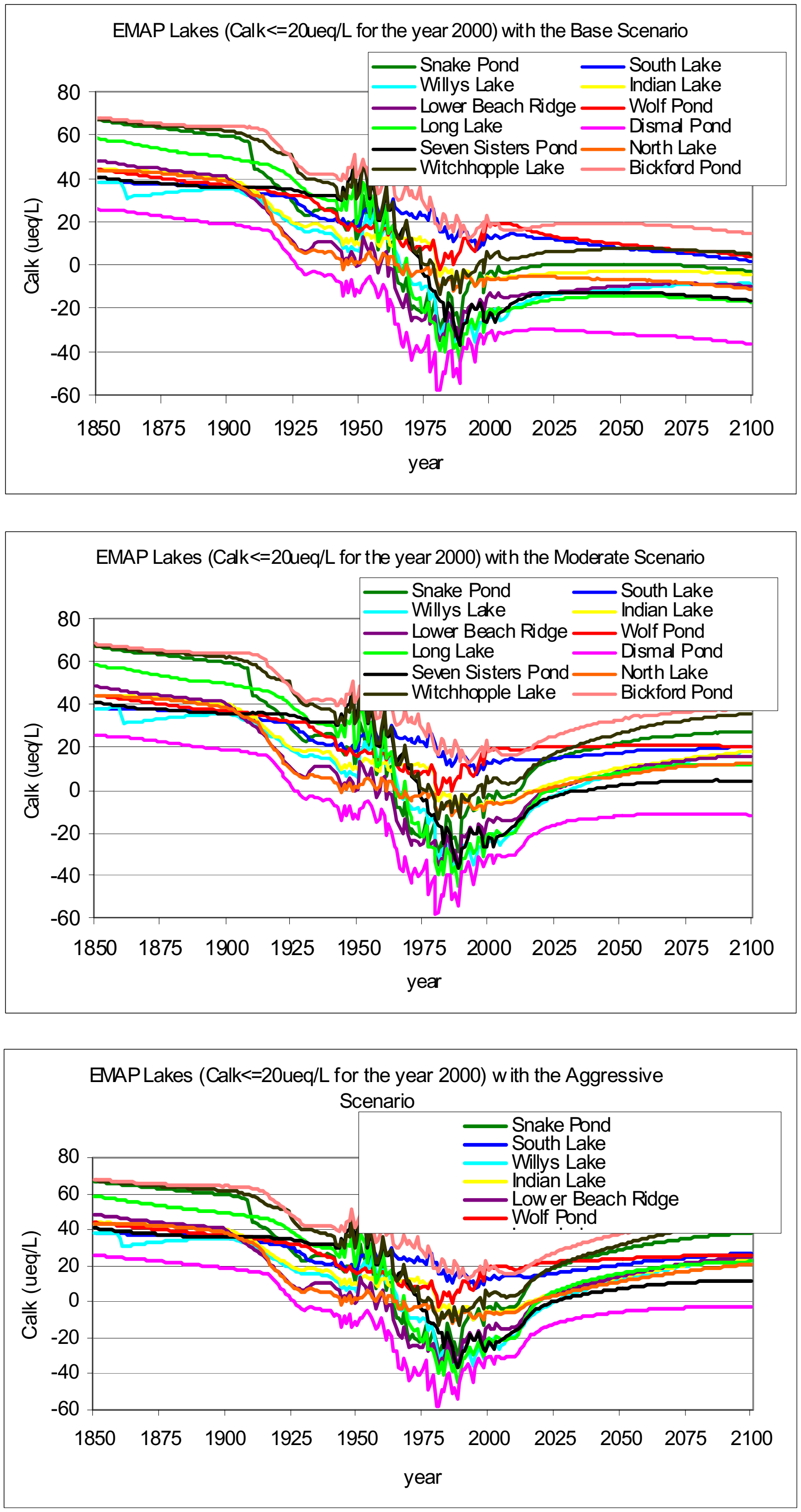


Figure 3-10. PnET-BGC simulation results for the probability lakes that had ANC ≤ 20 µeq/L in 2000 under three scenarios of emissions controls. These are the lakes expected to have the greatest biological impacts from acidification and chemical recovery.

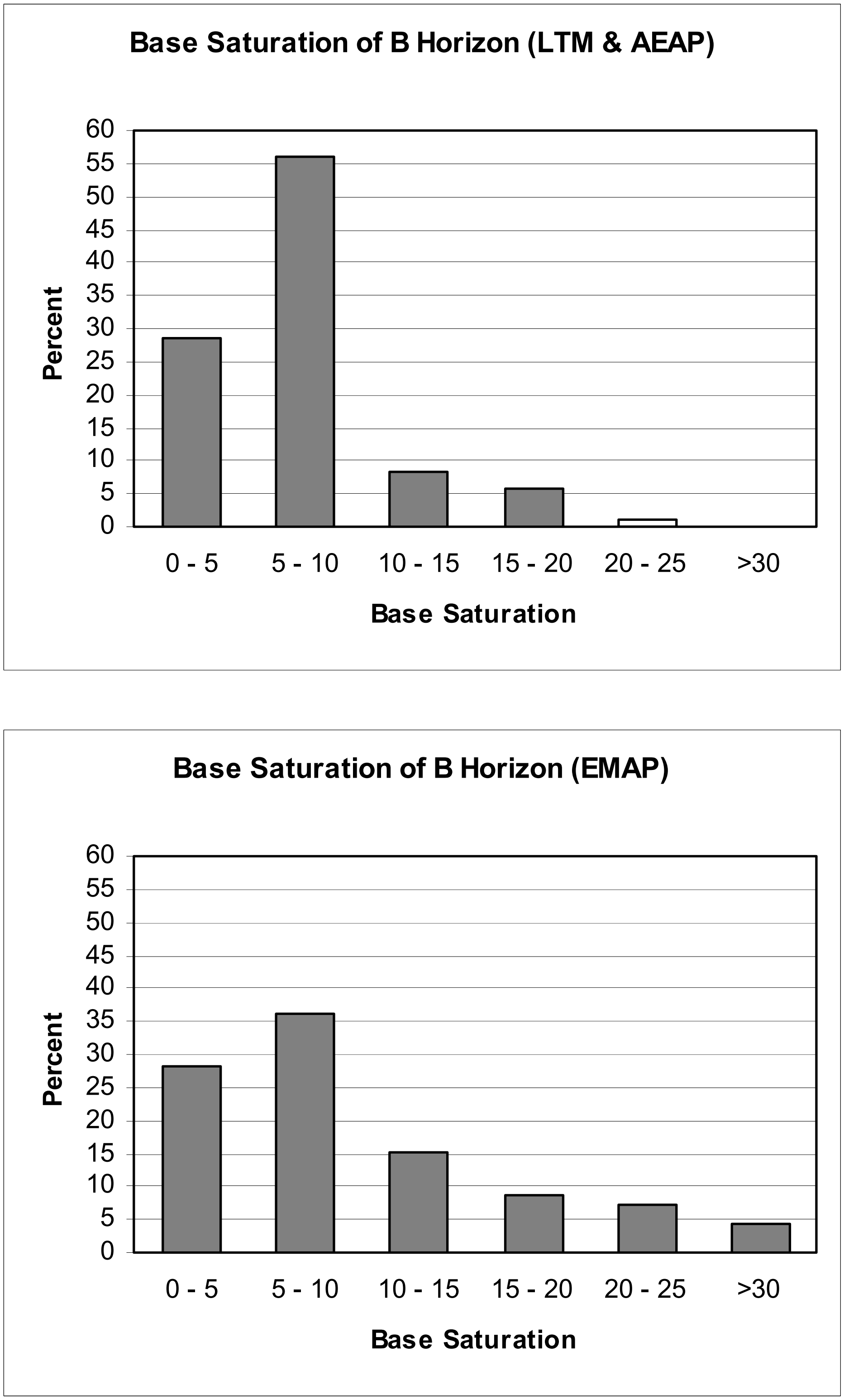
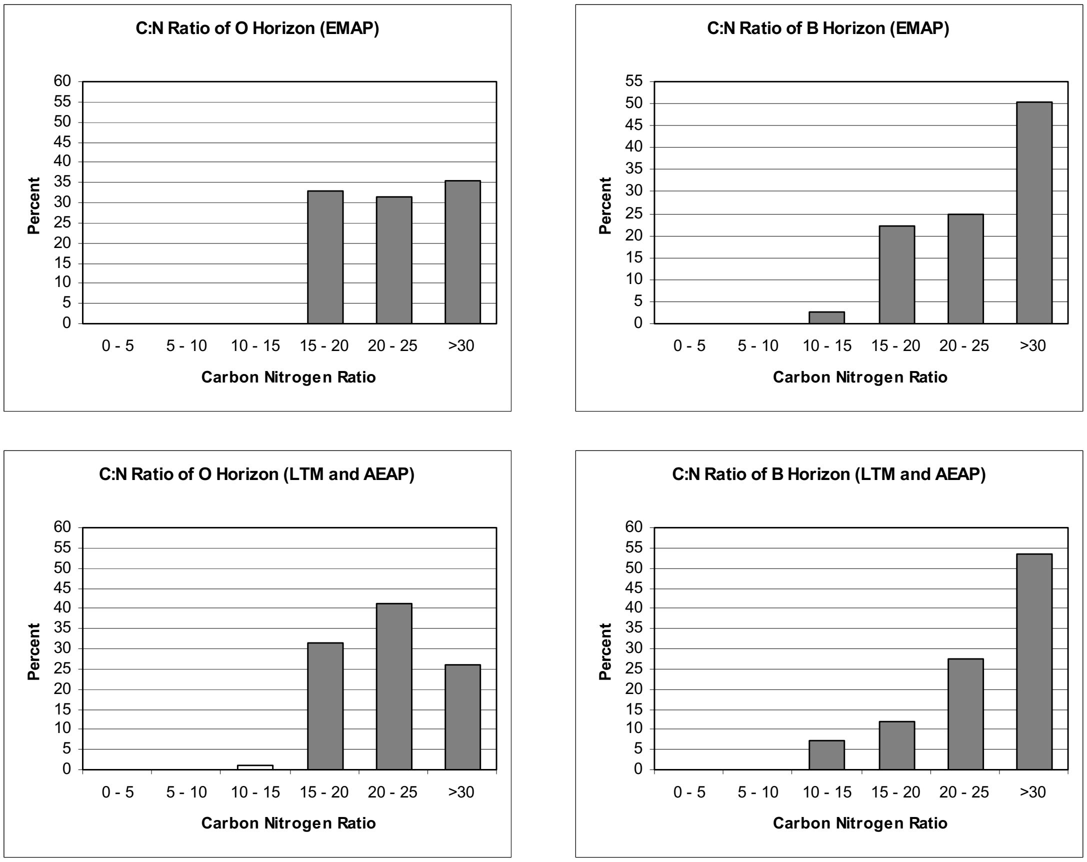


Figure 3-11. Percent base saturation of soils sampled from the B horizon of A) ALTM and AEAP watersheds and B) EMAP watersheds. Base saturation is reported as percent frequency of occurrence within value ranges.

ALTM/AEAP soil pit sites had % BS higher than 15%, a commonly-used threshold value to suggest soil acid-sensitivity. Thirty-two soil pits excavated within EMAP watersheds had B horizon % BS less than 5% and an additional 41 soil pits had % BS between 5 and 10% (Figure 3-11). The major difference in % BS estimates for the EMAP sites, as compared with the ALTM/AEAP soil pit sites, was the somewhat increased frequency of EMAP sites having % BS higher than 10% (35% versus 15%, Figure 3-11). Thus, soils conditions in the EMAP watersheds, while including a large number of highly acid-sensitive sites, also included appreciable numbers of sites that could be considered moderately sensitive or perhaps insensitive to acidification.

There were no major differences observed in soil nitrogen status in the EMAP, as opposed to the ALTM/AEAP, watersheds (Figure 3-12). Few sites exhibited C:N below 15 in either of the horizons analyzed but values between 15 and 20 were common (> 12% of samples) in both horizons and in both data sets.



C:N Ratio of O Horizon (EMAP)

C:N Ratio of B Horizon (EMAP)

C:N Ratio of O Horizon (LTM and AEAP)

C:N Ratio of B Horizon (LTM and AEAP)

Figure 3-12. C:N molar ratio of O horizon and B horizon soil samples collected within the EMAP and ALTM/AEAP study watersheds.

MAGIC model simulated soil B horizon % BS generally increased between pre-industrial time (~ 1850) and 1980 for both the population of Adirondack lake watersheds and for the ALTM/AEAP lake watersheds (Figure 3-13). This simulated increase in mineral soil % BS can be attributed to increased atmospheric deposition of base cations in association with industrialization. It was less pronounced for the long-term monitoring lake watersheds than for the overall EMAP population of lake watersheds. The model suggested a rapid decline in % BS between 1980 and 2000, with continued decline (albeit at a lower rate of change) into the future under the Base Case Emissions Control scenario. The projected change is similar for the two groups of lake watersheds through 2000, but a somewhat more rapid decline in % BS is projected into the future for the ALTM/AEAP lake watersheds as compared with the overall EMAP watershed population.

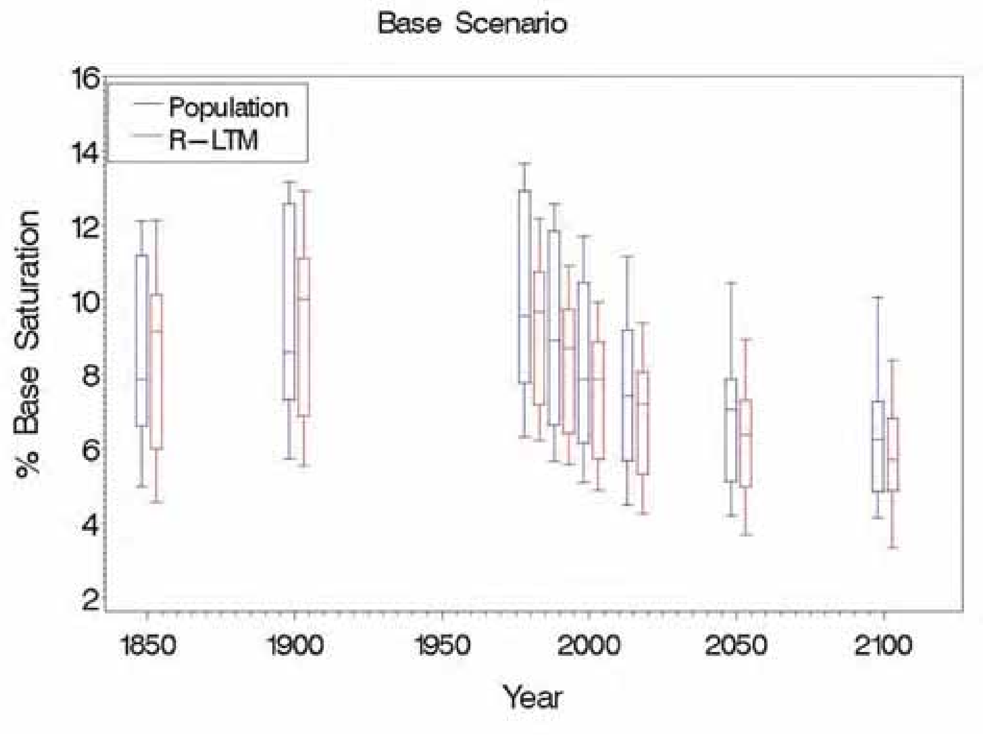


Figure 3-13. MAGIC model simulated watershed B horizon soil percent base saturation from pre-industrial times to the year 2100 for two sets of study lakes: the population represented by the EMAP lakes and the ALTM/AEAP long-term monitoring lakes. Future conditions were modeled under the Base Case emissions control scenario. Median and quartile values are indicated by a box; 10th and 90th percentiles are indicated by vertical bars.

PnET-BGC also simulated a small increase in B horizon soil % BS between 1850 and 1900. This simulated initial increase in % BS was followed by projected decreases in % BS between 1900 and the current time, and continuing through the next century under the Base Case Emissions Control scenario (Figure 3-14). In general, simulated B horizon % BS was higher in the long-term monitoring watersheds than in the population as a whole during pre-industrial times. This pattern was reversed for simulations of future conditions. Under the Aggressive Additional Emissions Control scenario, PnET-BGC simulated a future increase in B horizon % BS for both the long-term monitoring watersheds and the population of Adirondack lake watersheds (Figure 3-14).

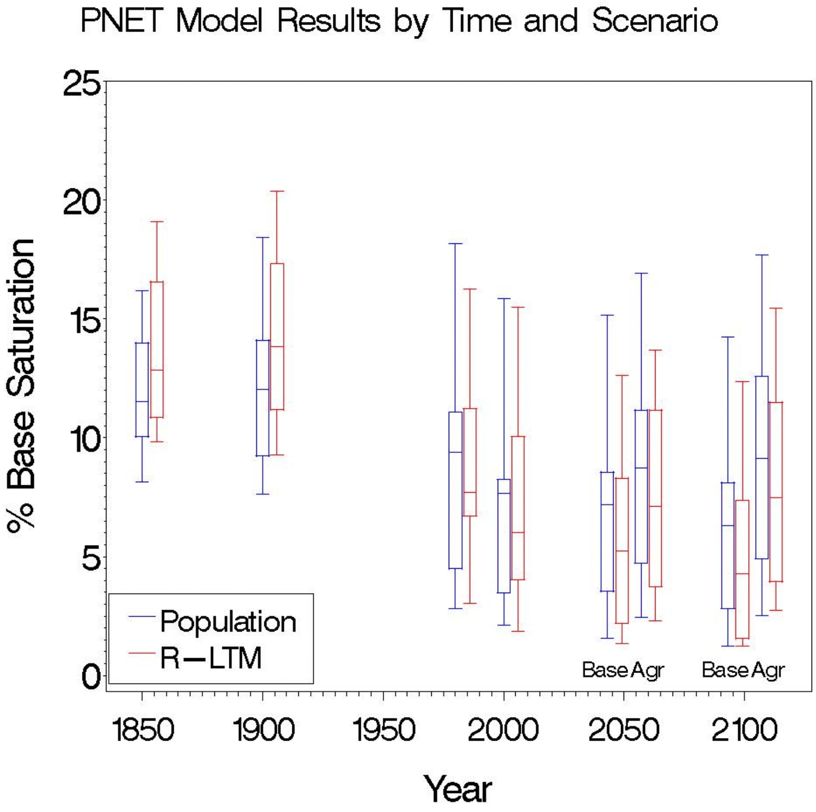


Figure 3-14. PnET-BGC model simulated values of watershed B horizon soil percent base saturation from pre-industrial times (~1850) to the year 2100 for two sets of study lakes: the population represented by the EMAP lakes and the ALTM/AEAP long-term monitoring lakes. Future conditions were modeled under the Base Case (Base) and Aggressive Additional (Agr) Emissions Control scenarios. Median and quartile values are indicated by a box; 10th and 90th percentiles are indicated by vertical bars.

To examine the extent to which each of the ALTM/AEAP lake watersheds was representative of the overall watershed population, we compared MAGIC soil chemistry modeling results for each with extrapolated results for the population. These comparison results are summarized for soil acid-base chemistry in Table 3-12. Using B horizon % BS as the principal indicator of soil acid base chemistry, Middle Settlement Lake, Middle Branch Lake, Carry Pond, and Round Pond watersheds exhibited soil conditions that were most acidic. Less than 10% of the lake watersheds in the population have lower B horizon % BS than these watersheds (Table 3-12).

3.6.2. Lakewater Comparison

Lakewater SO_4^{2-} concentration was projected by the MAGIC model to increase from pre-industrial levels (that were generally near 10 μeq/L) to peak values around 1980 that were over 100 μeq/L in most lakes. Simulated lakewater SO_4^{2-} concentrations decreased markedly after 1980 in response to decreased atmospheric S deposition, and were projected to continue to decline in the future in response to existing and expected emissions controls under the Base Case Emissions Control scenario. In general, simulated lakewater SO_4^{2-} concentrations were lower and less variable among the ALTM/AEAP lakes as compared with the regional population during pre-industrial conditions. In contrast, under the more heavily impacted conditions of recent and future time periods, simulated lakewater SO_4^{2-} concentrations were generally higher in the ALTM/AEAP lakes (Figure 3-15).

Simulated patterns of response were similar for PnET-BGC , although the model estimates of SO_4^{2-} concentration were generally higher than were simulated by the MAGIC model (Figure 3-16). Under the Aggressive Additional Emissions Control scenario, PnET-BGC simulated lakewater SO_4^{2-} concentrations continued to decrease into the future, with the greatest magnitude of decrease found for the long-term monitoring lakes.

PnET-BGC simulations for ALTM/AEAP lakes had lower ANC values, on average, as compared with the Adirondack lake population (Figure 3-17). This differential was generally consistent across time from 1850 to future conditions simulated under the Base Case Emissions Control scenario. This result was also shown for the MAGIC model. The patterns in the simulated future increase in ANC were similar for the two groups of lakes: long-term monitoring and Adirondack lake population (Figure 3-18).

Table 3-12. Relationship between each of the long-term monitoring study watersheds and the EMAP population of Adirondack lake watersheds[1] with respect to modeled soil base status, based on the MAGIC model.

Study Watershed		Estimated Percentage of Lake Watersheds in the Population Having:					
		Lower B horizon Base Saturation		Lower B horizon Exchangeable Ca^{2+}		Lower B horizon Exchangeable Ca^{2+} + Mg^{2+}	
Name	ID	2000	2050[2]	2000	2050[2]	2000	2050[2]
Middle Settlement Lake	40704	2.8	5.3	0	2.2	0.9	2.2
Middle Branch Lake	40707	4.1	6.3	28.8	26.7	24	30.1
Round Pond	040731A	8.7	5.3	10.4	11.6	22.7	18.7
Grass Pond	40706	11.6	10.9	56.5	41.6	56.5	41.6
Carry Pond	50669	11.6	6.3	7.2	7.2	7.2	6
Willys Lake	40210	14.7	10.9	7.2	8.5	7.2	8.5
West Pond	40753	16.7	14.7	30.1	32.3	33.9	30.1
Helldiver Pond	40877	16.7	23.1	30.1	32.3	24	30.1
Wheeler	40731	26	30.1	36.2	41.6	36.7	40.7
Brook Trout Lake	40874	26	29.1	36.2	35.9	46.7	40.7
Arbutus Pond	50684	33.1	32	79.2	80.3	75.8	77
Dart Lake	40750	46.6	33.1	61.8	61.8	60.8	59.6
Constable Pond	40777	46.6	37.5	73.6	71.3	72.4	68.9
Sagamore Lake	60313	46.6	39.7	80.4	84.8	80.4	83.6
Indian Lake	40852	46.6	37.5	60.8	53.2	60.8	52
Jockeybush Lake	50259	47.9	38.7	56.5	41.6	58.4	52
Big Moose Lake	40752	50.2	38.7	75.8	75.8	72.4	72.4
Long Pond	50649	50.2	38.7	30.1	24.8	30.1	30.1
Lake Rondaxe	40739	51.2	40.7	75.8	75.8	72.4	72.4
Cascade Lake	40747	51.2	50	75.8	75.8	72.4	73.6
Moss Lake	40746	52.2	65.4	79.2	82.5	75.8	80.1
North Lake	41007	52.2	39.7	61.8	61.8	71.1	61.8
G Lake	70859	61.5	50	73.6	71.3	75.8	72.4
Squash Pond	40754	62.6	39.7	82.7	80.3	81.6	73.6
South Lake	41004	62.6	60.3	82.7	76.9	82.7	79.2
Limekiln Lake	40826	63.8	65.4	79.2	75.8	75.8	73.6
Windfall Pond	040750A	70.2	79.7	73.6	76.9	75.8	82.4
Raquette Lake Reservoir	060315A	70.2	78.5	86	86	83.9	86
Queer Lake	60329	70.2	73.7	92.5	86	91.5	86
Bubb Lake	40748	78.5	79.7	86	86	92.5	87
Squaw Lake	40850	80.7	79.7	73.6	63	78.1	73.6
Willis Lake	50215	98.1	98.1	95.9	95.9	95.9	95.9

[1] Based on the EMAP population of 1,320 acid sensitive Adirondack lake watersheds containing lakes larger than 1 ha.

[2] Estimates for 2050 are based on the Aggressive Additional S and N Controls Scenario

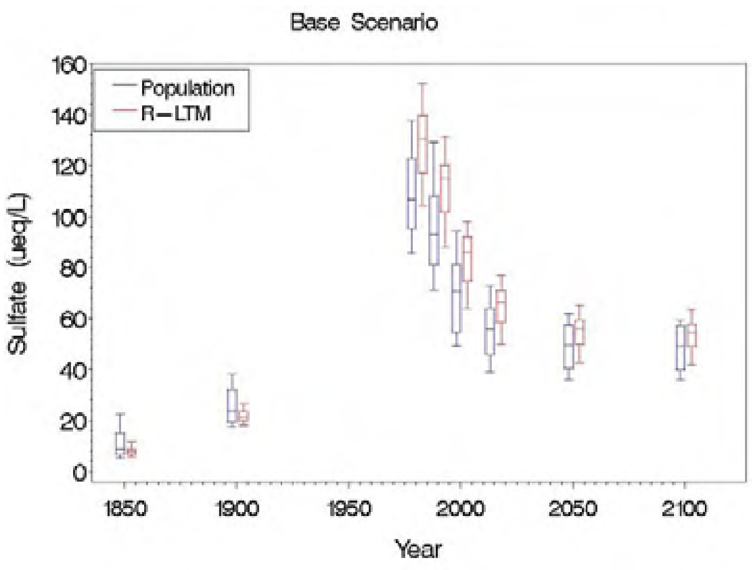


Figure 3-15. MAGIC model simulated lakewater sulfate concentration from pre-industrial times (~1850) to the year 2100 for two sets of study lakes: the population represented by the EMAP lakes and the ALTM/AEAP long-term monitoring lakes. Future conditions were modeled under the Base Case Emissions Control scenario. Median and quartile values are indicated by a box; 10th and 90th percentiles are indicated by vertical bars.

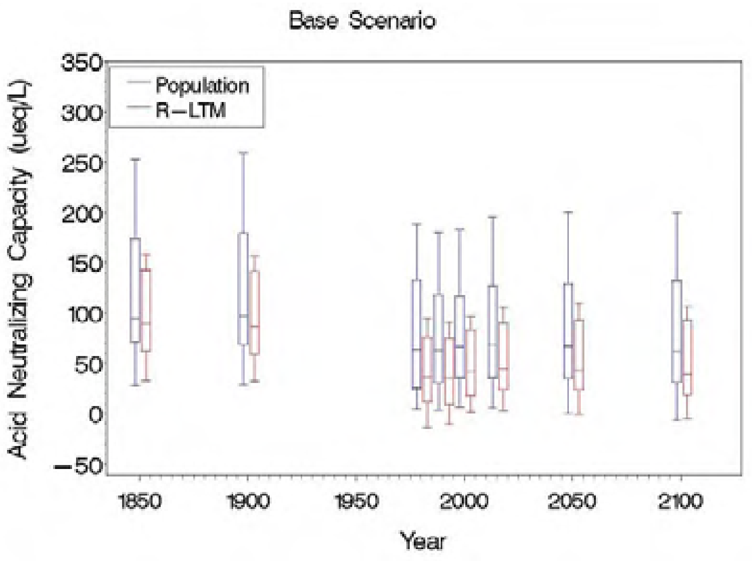


Figure 3-16. PnET-BGC model simulated lakewater sulfate concentration from pre-industrial times (~1850) to the year 2100 for two sets of study lakes: the population represented by the EMAP lakes and the ALTM/AEAP long-term monitoring lakes. Future conditions were modeled under the Base Case (Base) and Aggressive Additional (Agr) Emissions Control scenarios. Median and quartile values are indicated by a box; 10th and 90th percentiles are indicated by vertical bars.

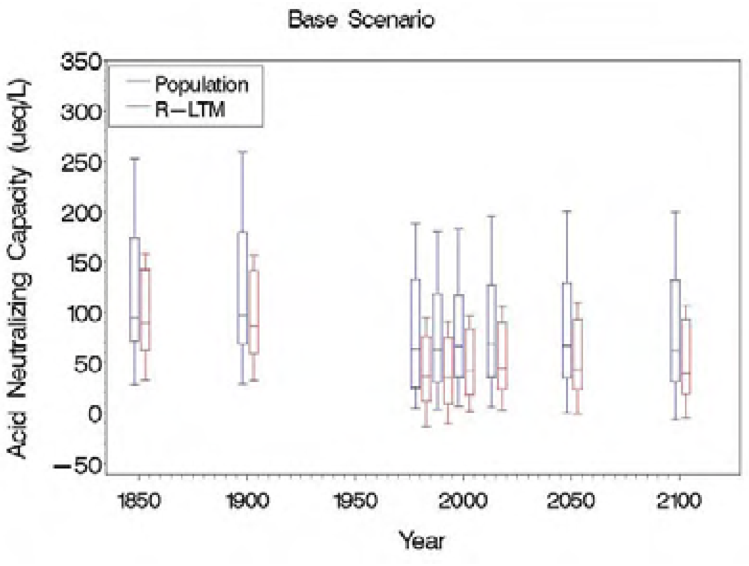


Figure 3-17. MAGIC model simulated lakewater acid neutralizing capacity from pre-industrial times to the year 2100 for two sets of study lakes: the population represented by the EMAP lakes and the ALTM/AEAP long-term monitoring lakes. Future conditions were modeled under the Base Case emissions control scenario. Median and quartile values are indicated by a box; 10th and 90th percentiles are indicated by vertical bars.

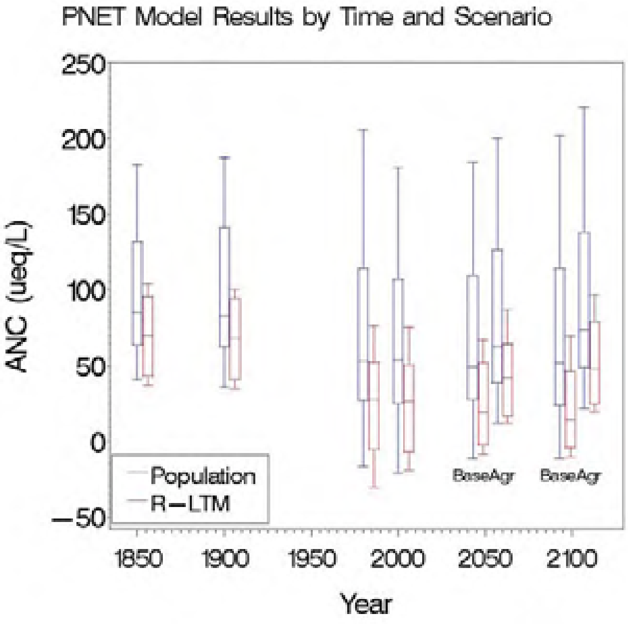


Figure 3-18. PnET-BGC model simulated lakewater acid neutralizing capacity from pre-industrial times (~1850) to the year 2100 for two sets of study lakes: the population represented by the EMAP lakes and the ALTM/AEAP long-term monitoring lakes. Future conditions were modeled under the Base Case (Base) and Aggressive Additional (Agr) Emissions Control scenarios. Median and quartile values are indicated by a box; 10th and 90th percentiles are indicated by vertical bars.

3.7 Uncertainty Analysis

3.7.1 Uncertainty in MAGIC

There are numerous uncertainties associated with conducting an assessment of this type, some of which are quantifiable, some not. The major sources of uncertainty in the assessment based on MAGIC model simulations are several: input data quality; temporal variability (especially seasonal and episodic) 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 discussion, we focus on the elements of uncertainty arising from the MAGIC model simulations.

The aggregated nature of the MAGIC model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration of MAGIC for each watershed is accomplished by specifying the model inputs (forcing functions), setting the values of those parameters for which measurements were available (fixed parameters), and then determining the values of the remaining parameters for which data were not available (adjustable parameters). The latter step is accomplished through an optimization procedure that selects values of the adjustable parameters such that the squared errors between the simulated and observed values of important state variables in the model for which observed data are available (target variables) are minimized. Formal procedures for estimation of optimal values of the adjustable parameters (and their error variances) customarily ignore several sources of uncertainty in this calibration procedure, 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.

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. 2002, 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. Those studies led to the development of a multiple (also called “fuzzy”) optimization procedure for MAGIC that can be used for both regional and site specific applications (see Cosby et al. 1990, Wright et al. 1994). 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.

3.7.2 Sensitivity Analysis of PnET-BGC

It is useful to quantify the sensitivity of parameters in the PnET-BGC model to the state variables of greatest interest. Aber et al. (1997) previously conducted sensitivity analysis of the vegetation parameters on productivity for PnET, and Schecher and Driscoll (1995) conducted uncertainty analysis on the chemical equilibrium constants for Al speciation in solution. As a follow-up to this earlier work, the sensitivity analysis conducted here for PnET-BGC focused on the canopy interaction parameters, the equilibrium constants for cation exchange and adsorption reactions, the exchange and adsorption capacity of the soil, the soil mass, and P_{CO_2} (Gbondo-Tugbawa et al. 2001). The state variables selected to assess the sensitivity of these parameters were the B horizon soil base saturation and the ANC of the adjoining surface water because of their importance as indicators of the acid-base status of soil and water, respectively. The analysis was conducted by examining the relative change in each state variable (X values) divided by the relative change in the value of the parameter (Param) tested. Thus the sensitivity of a parameter, $S_{\text{Param,X}}$ is defined as follows:

$$S_{\text{Param, X}} \quad \frac{\partial \text{X} / \text{X}}{\partial \text{Param} / \text{Param}} \tag{3-2}$$

The higher the value of S_{Param}, the more sensitive the model is to the parameter of interest (Jorgensen, 1988). Estimated or observed ranges for model parameters were obtained, and the maximum and minimum possible values for each parameter were used in this analysis. The range of values for canopy interaction parameters was selected utilizing available data for northern forest ecosystems. For soil parameters, the ranges of values were estimated from the observed data. The average of the absolute $S_{\text{Param,X}}$ values was calculated for each state variable (in Table 3-13). Positive and negative values (in parentheses) indicate whether a relationship between the change in parameter value and the change in model output is positive or negative.

Sensitivity analysis on abiotic parameters showed that model predictions of ANC and B horizon soil % BS are most responsive to changes in the partial pressure of CO_2 in the soil, soil CEC, soil mass, and the selectivity coefficients of Ca^{2+} and Al^{3+}. Model predictions of the % BS of the soil were more sensitive to changes in these parameters than were predictions of surface water ANC.

Since Ca^{2+} and Al^{3+} are major constituents of the soil exchange pool in acid-sensitive soils, the use of incorrect selectivity coefficients for these species can cause instability in the simulation of soil solution and soil chemistry. Running the model for long periods indicated that the selectivity coefficients may vary with soil solution pH. This condition can affect the results of long-term simulations if significant changes in the pH occur. Changes in the CEC and soil mass affect the pool of total exchange sites and anion adsorption sites available in the soil chemical reactions. Variations in these pools can also affect model simulations. Changes in P_{CO2} will affect the % BS through changes in pH in the soil (Reuss and Johnson, 1986). As the soil water emerges as runoff, CO_2 is released from the water to the atmosphere. Although the ANC remains unchanged, increases in surface water pH affect the speciation of monomeric Al, an important model output used to assess the biological effects of acidification. Some biogeochemical models do not include H^+ in exchange reactions (e.g. MAGIC, Cosby et al., 1985), because of the difficulty in separating H^+ exchange and Al hydrolysis reactions. The concentration of H^+ in solution is determined in PnET-BGC by charge balance, in contrast to total concentrations in the system as is done for other ions. Several studies have shown the importance of including H^+ in exchange reactions for the accurate prediction of soil pH (Ross et al., 1996; Tipping et al., 1995; Tipping and Hurley, 1988, 1992).

The foliar uptake of H^+, SO_4^{2-} adsorption capacity, DOC and SO_4^{2-} adsorption coefficients, and the Na^+, Mg^{2+} and K^+ selectivity coefficients were found to be moderately sensitive parameters. The sensitivity of these model parameters ranged from 0.1 to 0.4 (Table 3-13). The fraction of Na^+ associated with the soil exchange complex was low but the concentration of Na^+ in solution compared to other ions enabled variations in its selectivity coefficient to affect calculations of the soil % BS. The soil adsorption coefficient of DOC affects ANC because of the triprotic organic acid analog used in the simulation of solution acid-base chemistry.

Table 3-13. Summary of the sensitivity of PnET-BGC model output of lakewater acid neutralizing capacity (S_{ANC}) and B horizon soil % base saturation ($S_{\% BS}$) to selected model parameters[a].

Parameter	Range	S_{ANC}	$S_{\% BS}$
fH_{FUP}	0.65 - 0.79	0.09 (-)	0.19 (-)
SiteDen (DOC)	0.014 - 0.028	0.06 (-)	0.03 (-)
CEC		0.35 (-)	0.94 (+)
$k_{min,DOC}$	0.05 – 0.34	0.02 (-/+)	0.02 (-)
$fNH_{4,FUP}$	0.20-0.30	0.06 (-/+)	0.11 (-/+)
SoilMass	300-350	0.23 (-/+)	0.60 (-/+)
SAdCap		0.06 (-)	0.14 (+)
K^{add}_{PO4}		<0.01 (-)	<0.01 (+)
K^{add}_{Cl}		0.02 (+)	0.02 (-)
K^{add}_{DOC}		0.26 (-)	<0.01 (-)
K^{add}_{F}		0.02 (+)	0.05 (-)
K^{add}_{1}		0.05 (-)	0.09 (-)
K^{add}_{2}		0.05 (-)	0.09 (-)
K^{add}_{SO4}		0.19 (-)	0.43 (+)
K^{ex}_{H-Al}		0.19 (+)	1.81 (-)
K^{ex}_{H-Ca}		0.19 (-)	2.33 (+)
K^{ex}_{H-Na}		0.02 (-)	0.43 (+)
K^{ex}_{H-Mg}		0.06 (-)	0.66 (+)
K^{ex}_{H-K}		0.04 (-)	0.32 (+)
$K^{ex}_{H-NH_4}$		0.03 (-)	0.06 (+)
P_{CO2}	1.6 – 2.9	0.21 (+)	3.20 (-)

[a] (+) indicates a positive relation between the change in parameter and change in state variable and (-) indicates a negative relation.

The model was relatively insensitive to changes in the other abiotic parameters considered, such as the DOC site density, sorption coefficients for anions other than SO_4^{2-}, and the selectivity coefficient of NH_4^+. The concentrations of anions like PO_4^{3-} and F^- in solution are relatively low and therefore transformations involving these solutes do not strongly influence the acid-base status of soil or water. Although the sensitivity analysis conducted here showed that the model is relatively insensitive to changes in the site density of the organic acid analog, note that this result is dependent on the total DOC concentration in surface water. Model calculations of ANC would increase in sensitivity to the value of DOC site density in lakes having higher DOC concentrations.

3.8. Linkages Between Water Chemistry and Aquatic Biota

3.8.1 Fish

The relationship between fish species richness and ANC class, developed using ALSC data, is shown in Figure 3-19. These observations were fit to a logistic relationship by a non-linear regression analysis. The relationship for species richness as a function of ANC is:

$$\textit{Fish Species Richness} \;=\; 0.18 \;+\; \left[\frac{5.7}{1+\left(\dfrac{ANC}{28}\right)^{-1.63}} \right] \; (r^2 \quad 0.9) \qquad (3\text{-}3)$$

where ANC is in μeq/L.

The relationship shows that under chronically acidic conditions (summer index or annual average ANC< 0 μeq/L), Adirondack lakes are generally fishless. There is a marked increase in mean species richness with increases in ANC up to near values of 100 μeq/L. The asymptote for the fish species equation is 5.7.

The observed marked increase in fish species richness with increases in ANC may have important management implications. Many assessments of effects of acidic deposition on surface waters place an upper sensitivity limit at ANC values of 50 μeq/L (Driscoll et al. 2001) and even

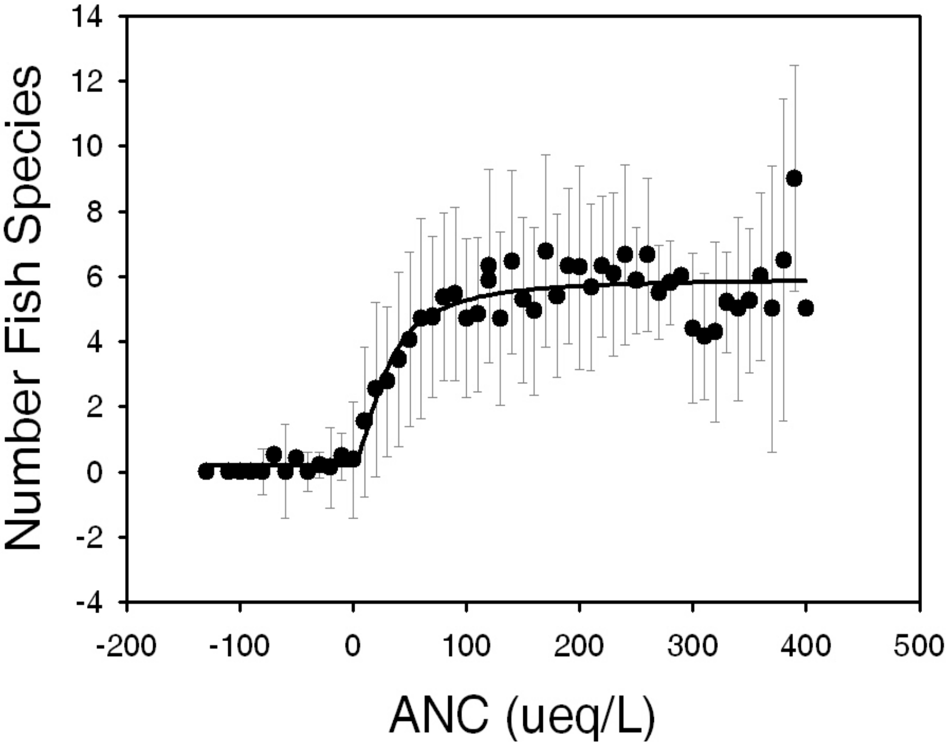


Figure 3-19. Fish species richness of Adirondack lakes as a function of ANC. The values shown represent the mean (filled circles) and standard deviation (bars) of 10 μeq/L ANC classes. Also shown as a solid line is the application of the logistic model.

as low as 30 μeq/L. This analysis suggests that there could be loss of fish species with decreases in ANC starting at values around 100 μeq/L. It does not account, however, for the possibility that lakes having higher ANC often tend to be larger, and therefore support more fish species due to increased habitat diversity and complexity. In addition, mean fish species richness for ANC classes between 50 and 100 μeq/L were similar to mean values for many of the higher ANC classes, and there is substantial variation in fish species richness for all ANC classes.

We examined the source of the variation for lakes with ANC values above 100 μeq/L (to eliminate the effects of surface water acidification). For these lakes, no strong relationships were evident for fish species richness and other lake attributes that might be expected to influence fish habitat such as lake size, lake volume and dissolved silica concentrations (a measure of groundwater inputs). Nevertheless, we would expect that some of the variability in fish species richness for a given ANC class would be due to variations in these physical factors.

3.8.2 Zooplankton

Results of zooplankton taxonomic richness analyses are presented in Figure 3-20 and Table 3-14. Taxonomic richness expressed as number of species of crustaceans, rotifers, large cladocerans, and total zooplankton, increased with increasing ANC. In general, lakewater ANC explained nearly half of the variation in total zooplankton and crustacean taxonomic richness, but less for large cladoceran and rotifer richness. These results (Table 3-14) provide the basis for estimating changes in zooplankton richness in response to past or future changes in lakewater ANC.

Table 3-14. Observed relationships between zooplankton species richness (R) and lakewater ANC.

Taxonomic Group	Equation	r^2	p
Total Zooplankton	R=15.65 + 0.089ANC	0.46	0.001
Crustaceans	R=6.35 + 0.028ANC	0.47	0.001
Rotifers	R=9.04 + 0.053ANC	0.30	0.001
Large Cladocerans	R=1.95 + 0.017ANC	0.41	0.001

3.9 Lake Classification

A regression analysis was conducted in an attempt to classify modeled lakes with respect to their sensitivity to change in ANC in response to change in acidic deposition. All variables considered in the regression analysis are listed in Table 3-15. The regression on MAGIC projections of future ANC change (1990 to 2100) identified 10 variables that were significant predictors of ANC change, based on Aikake's Information Criteria (AIC; Burnham and Anderson 1998) weighted importance > 0.5 (Table 3-15). Year 2000 lakewater SO_4^{2-}, Ca^{2+}, Mg^{2+}, Si, and % mixed forest in the watershed were included in all models with an AIC within 4 units of the best model. The final regression model using the 10 significant variables had r^2=0.83 and RMSE of 6.3 ueq/L.

The similar regression for PnET-BGC future ANC change also identified 10 significant variables. The final PnET-BGC regression had fewer lakewater chemistry variables than the MAGIC regression model and also included three soil chemistry variables (Table 3-15). The final PnET-BGC model was somewhat weaker than the MAGIC results with an r^2=0.52 and

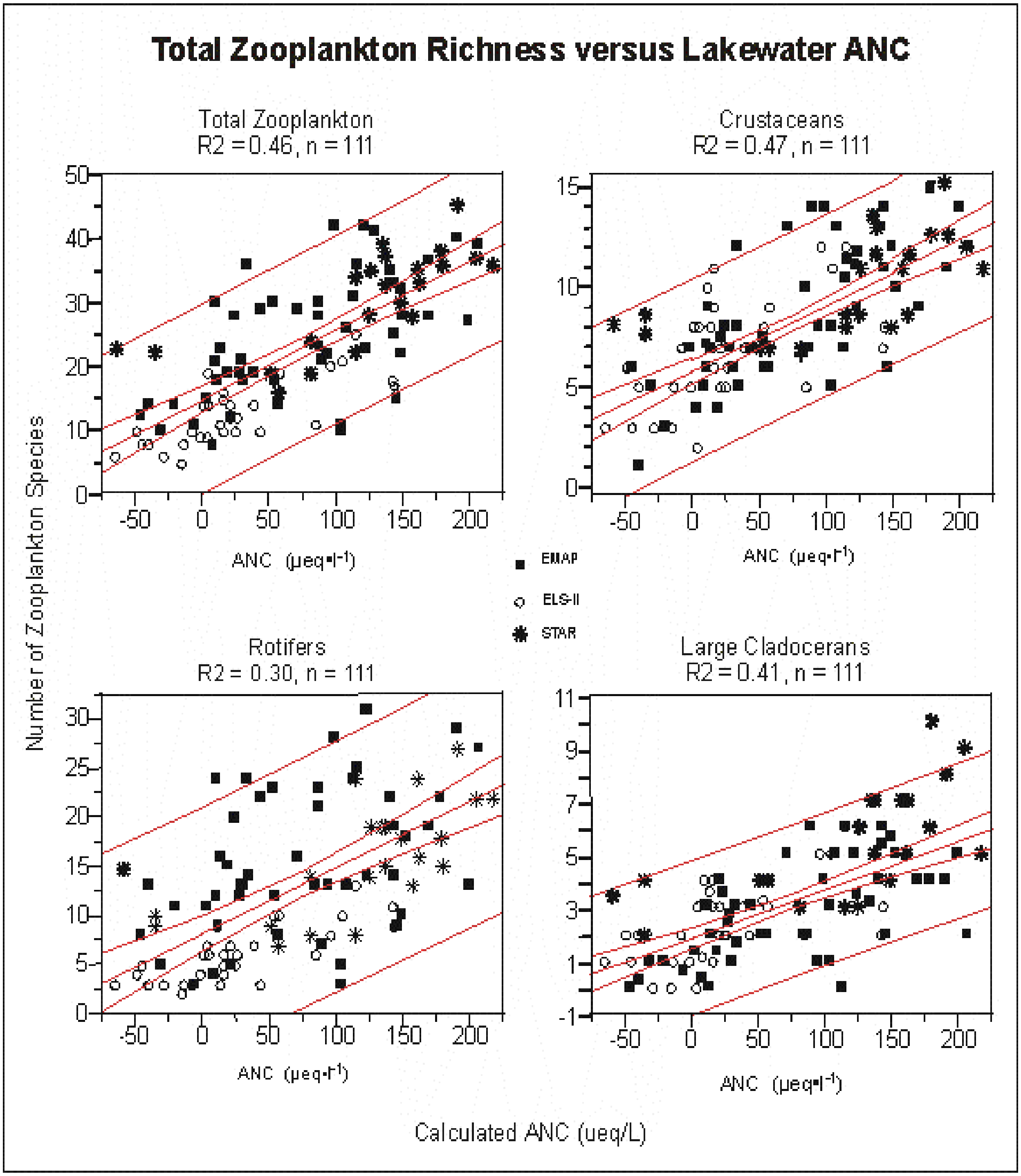


Figure 3-20. Zooplankton taxonomic richness versus ANC for the combined Adirondack dataset, based on 111 lake visits to 97 lakes in the EMAP, ELS, and STAR zooplankton surveys.

Table 3-15. Best all-subsets regression model relating simulated future ANC change (2100-1990, aggressive scenario) for MAGIC and PnET-BGC to current conditions.

MAGIC (r^2=0.83, RMSE=6.27)			PnET-BGC (r^2=0.52, RMSE=13.3)		
Variable[a]	Coefficient	AIC Imp.[b]	Variable[a]	Coefficient	AIC Imp.[b]
2000 Lake SO4	0.241	1.00	% Wetland	-0.602	1.00
2000 Lake Mg	-0.414	1.00	% Mixed Forest	-0.416	1.00
2000 Lake Ca	0.209	1.00	Watershed Area	0.0133	0.915
2000 Lake Si	0.162	1.00	Max Lake Depth	-0.851	0.857
% Mixed Forest	-0.262	1.00	Soil % Base Sat.	-1.47	0.785
Lake Volume	2.31×10^{-7}	0.994	2000 Cb Deposition	8.17	0.742
Soil % Base Saturation	-1.46	0.984	Soil Acidity	-6.51	0.603
% Wetland	-0.180	0.912	Soil CEC	3.91	0.582
Lake Area	-0.0296	0.909	2000 Lake NO3	0.544	0.556
1990 S Deposition	0.215	0.776	2000 Lake Si	-0.102	0.554

[a] Variables considered that were not significant include lakewater Na, K, Cl, DOC, conductivity, elevation, mean lake depth, shoreline length, watershed area:lake area ratio, residence time, runoff, soil pH, total C, total N, C:N, extractable SO_4^{2-}, percent air-dried moisture content, % conifers, and % hardwoods.

[b] AIC Imp. is the Aikake's Information Criteria weighted importance value (Burnham and Anderson 1998)

RMSE=13.3. Of interest was that the MAGIC regression included current lakewater SO_4^{2-} concentration as a significant variable whereas the PnET-BGC regression included lakewater NO_3^- concentration.

The principal components analysis (PCA) analysis identified three axes that together explained 58% of the variance in the 16 variables that were significant in either the MAGIC and/or the PnET-BGC regression analysis (Table 3-16). The first axis was most strongly related to lakewater ionic strength and lake size variables; higher axis scores were found in lakes with higher lakewater concentrations of base cations and anions and in larger, deeper lakes. The second axis was most strongly related to deposition (sulfur and base cations), whereas the third axis was related to soil chemistry variables (Table 3-16).

From the cluster analysis of the three axis scores, seven lake clusters were identified based on major breakpoints in the resulting dendrogram (Figure 3-21). Based on the dendrogram, there were three major divisions (labeled A, B, C). Group A had two divisions (A1, A2) and group B had three divisions (B1, B2, B3). Group C initially had two divisions and had the most distinct separation from the other lakes. It only contained five lakes in both divisions so it was combined into one group C cluster. Specific lakes, their cluster assignments, and environmental data are given in Table 3-17. Based on these results and the cluster locations on factor 1 vs. 2 and factor 2 vs. 3 plots (Figure 3-22), the clusters were described as:

Table 3-16. Principal components analysis pattern showing correlations of variables with top three factor components. Correlations greater than 0.6 are shown in bold. Only variables that were significant in the multiple regression model predicting future ANC change were used in this analysis.

Variable Correlations	Factor 1	Factor 2	Factor 3
2000 Lake SO_4^{2-}	**0.64**	0.39	---
2000 Lake Mg	0.52	-0.51	---
2000 Lake Si	**0.61**	0.33	---
2000 Lake Ca	**0.61**	-0.50	---
2000 Lake NO_3^-	0.57	---	0.25
Lake Volume	**0.69**	-0.45	---
Lake Area	**0.73**	-0.51	---
Watershed Area	0.39	-0.41	---
Maximum Lake Depth	**0.67**	-0.25	**---**
% Mixed Forest	0.34	0.33	0.43
% Wetland	---	---	-0.41
1990 S Deposition	0.36	**0.78**	0.20
2000 SBC Deposition	0.41	**0.65**	0.29
Soil % Base Saturation	---	---	**0.64**
Soil Acidity	0.43	0.40	**-0.77**
Soil CEC	0.47	0.40	**-0.68**
% Variance Explained	26.3%	18.7%	12.8%

[a] --- = $-0.2 < r < 0.2$

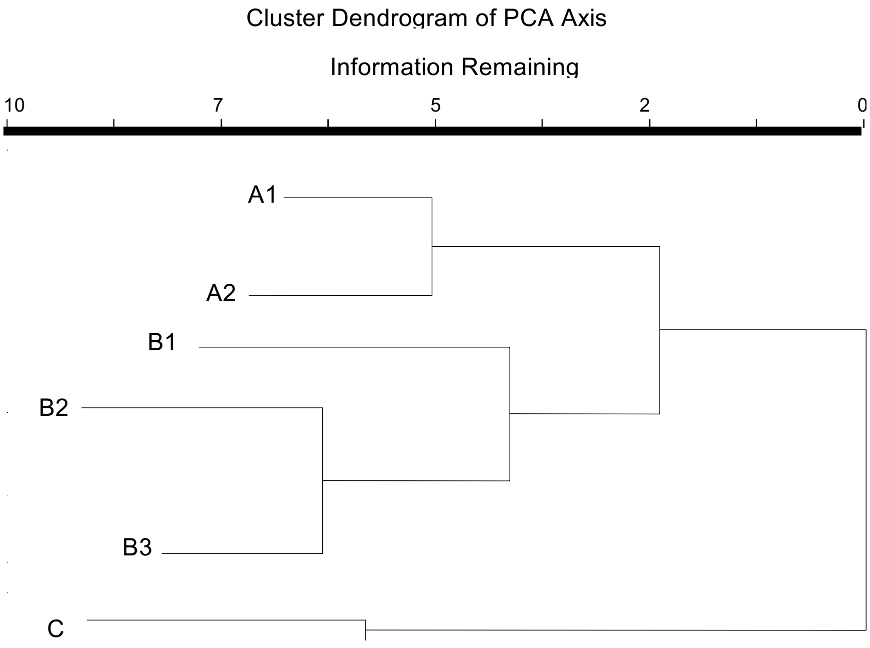


Figure 3-21. Cluster dendrogram of the three PCA axis scores.

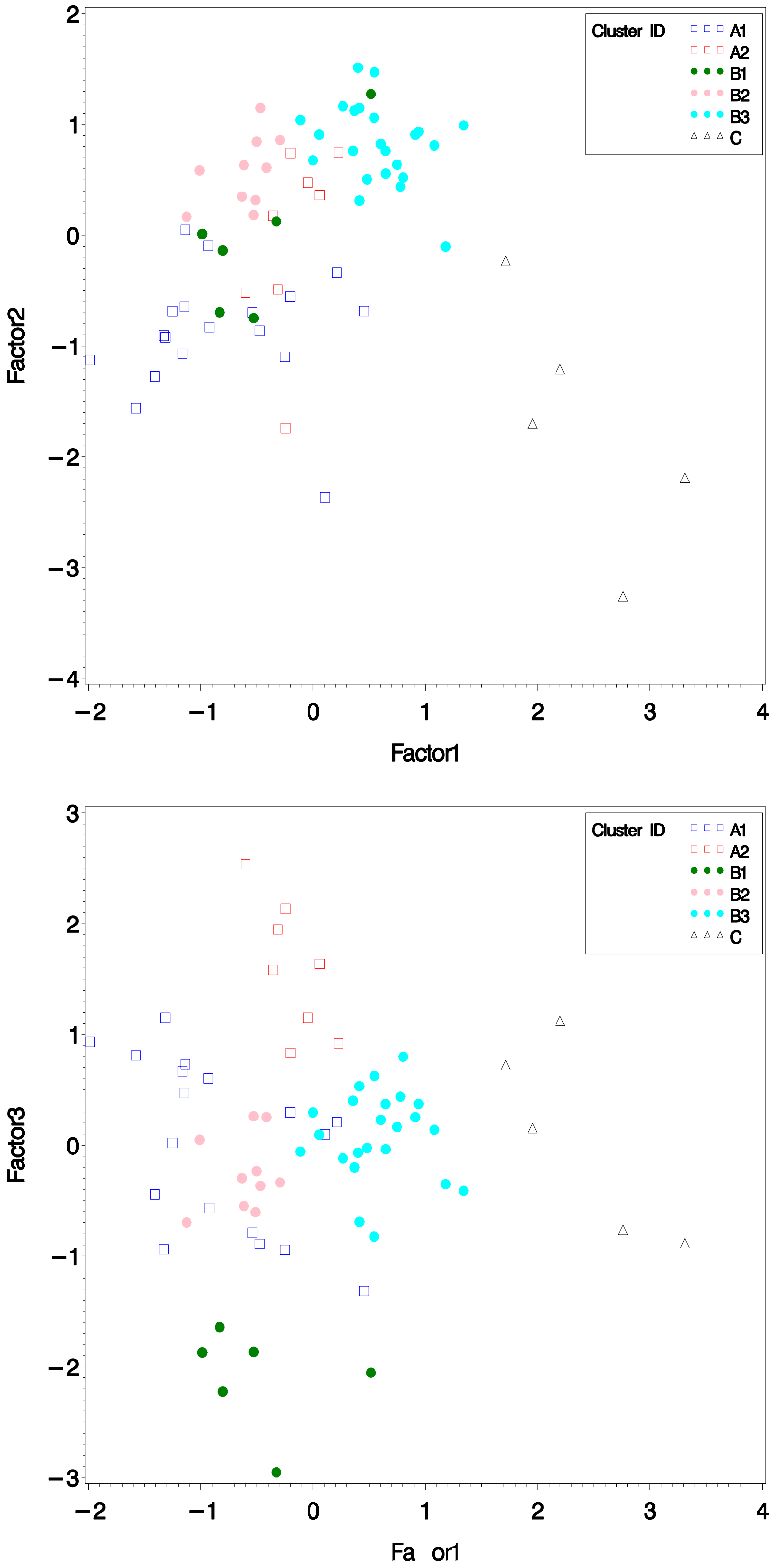


Figure 3-22. Factor axis plots showing separation of clusters.

Table 3-17. List of lakes and their characteristics by cluster ID.

Lake Name	ID	Source	Lake Ca (μeq/L)	Lake SO4 (μeq/L)	Watershed Area (km^2)	Watershed % Wetland	Soil CEC (meq/100g)	1990 Sulfate Deposition (meq/m^2/yr)
Cluster A1 Antediluvian Pond	060126	EMAP	74	56	1.53	13.5	7.59	79.1
Bickford Pond	030273	EMAP	59.9	71.9	0.68	0	6.21	62.4
Bog Pond	060175	EMAP	137	87.2	27.33	25.2	9.48	78.9
Boottree Pond	030374	EMAP	46	30	0.12	0	4.13	71.3
Clear Pond	020070	EMAP	165.4	76.6	1.57	3.8	6.82	51.4
Effley Falls Pond	040426	EMAP	90	81	640.78	11.4	7.27	94.2
Hitchins Pond	060144	EMAP	105	20.2	133.28	13	8.73	74.5
Hope Pond	020059	EMAP	83.3	84	0.53	0	9.07	56.5
Horseshoe Pond	030373	EMAP	65	65	0.92	0	5.09	71.8
Long Pond	030170	EMAP	43.4	38.6	0.6	0	7.18	46.8
Lower Beech Ridge	040203	EMAP	32	74	0.33	11.4	5.43	100.2
Mccuen Pond	060039	EMAP	74.9	45	0.59	10.9	8.11	64.4
Parmeter Pond	030331	EMAP	88	45	0.51	0	8.01	61.8
Payne Lake	040620	EMAP	61	30	1.68	8.4	4.91	86
Rock Pond	060129	EMAP	96	67	35.86	31.9	8.5	72.5
Seven Sisters Pond	060074	EMAP	25	51.9	0.69	6.1	3.81	63.7
Trout Pond	060146	EMAP	81	89	2.5	1.8	6.97	83.4
Long Pond	050649	ALTM	43.4	81	0.26	0	5.77	110.8
Cluster A2 Squaw Lake	040850	BOTH	73.4	88.9	1.25	15.7	6.91	108.7
Willys Lake	040210	BOTH	48.9	101.2	1.28	0	6.2	114.8
Bennett Lake	050182	EMAP	75.8	87.1	2.67	0	6.08	68.9
Gull Pond	050418	EMAP	188.2	76.5	0.15	0	4.92	44.8
Razorback Pond	040573	EMAP	65	84	0.23	0	6.43	107.5
Second Pond	050298	EMAP	96	79	4.42	0	7.26	104.3
Willis Lake	050215	ALTM	125.2	64.6	1.39	0	6.8	77
Windfall Pond	040750A	ALTM	94.8	87.1	0.44	0	7.83	116.4
Cluster B1 Clear Pond	060176	EMAP	98.3	73	0.91	46.1	9.05	66.3
Dry Channel Pond	030128	EMAP	81.3	93	1.77	2.6	13.69	58.8
Rocky Lake	040137	EMAP	68.4	48.5	1.06	0	10.82	69.9
Wolf Pond	030360	EMAP	31.9	71.2	0.2	23.7	9.84	67
Grass Pond	040706	ALTM	70.4	99.2	2.37	4.7	12.35	95.3
Helldiver Pond	040877	ALTM	105.1	84	0.85	86.7	7.48	69.4
Cluster B2 Indian Lake	040852	BOTH	44.4	82.9	10.85	22.3	8.82	120.3
Dismal Pond	040515	EMAP	31	71	2.14	9.5	6.8	113.5
Little Lilly Pond	040566	EMAP	60.9	58.7	2.22	8.1	8.11	98.6
Upper Sister Lake	040769	EMAP	63.4	84	13.92	12.8	9.15	98.5
Witchhopple Lake	040528	EMAP	62	80	19.68	1.8	7.43	96.3
Carry Pond	050669	ALTM	31.9	69.6	0.2	31.8	7.17	100.5
Middle Settlement	040704	ALTM	47.4	86.7	0.98	0	7.2	104.3
Round Pond	040731A	ALTM	40.8	67.4	0.12	21.4	8.43	87.7
Squash Pond	040754	ALTM	27.9	68.5	0.41	0	9.58	120.9
West Pond	040753	ALTM	50.4	63.3	1.08	11.2	8.89	109.1

Table 3-17. Continued.

Lake Name	ID	Source	Lake Ca (µeq/L)	Lake SO4 (µeq/L)	Watershed Area (km^2)	Watershed % Wetland	Soil CEC (meq/100g)	1990 Sulfate Deposition (meq/m^2/yr)
Cluster B3								
Arbutus Pond	050684	BOTH	118.8	108.1	3.23	0	10.25	97.5
North Lake	041007	BOTH	60.9	90.4	75.37	16	8.43	123.5
South Lake	041004	BOTH	60.9	82.9	14.45	6.3	9.33	114.5
Big Alderbed	070790	EMAP	67	68	15.88	0.2	10.63	129.9
Long Lake	070823	EMAP	49.9	97	0.72	0	9.56	123.1
Snake Pond	040579	EMAP	65.9	83.5	0.46	0	8.06	103.6
Whitney Lake	070936	EMAP	70	81	2.25	18.2	9	123.2
Big Moose Lake	040752	ALTM	76.8	94.8	95.85	8.9	9.13	102.7
Brook Trout Lake	040874	ALTM	50.4	83.9	1.77	7.5	9.23	127
Bubb Lake	040748	ALTM	99.3	85	1.86	0	9.38	102.2
Cascade Lake	040747	ALTM	100.3	105.6	4.75	1.7	9.26	103.4
Constable Pond	040777	ALTM	59.4	98.9	9.45	1.4	8.73	122.8
Dart Lake	040750	ALTM	76.8	95.8	107.57	7.9	8.64	102.1
G Lake	070859	ALTM	57.9	85.4	4.13	3.3	9.52	115.4
Jockeybush Lake	050259	ALTM	58.4	95.6	1.49	0	8.42	112.6
Lake Rondaxe	040739	ALTM	95.3	93.7	142.83	6.8	9	109.1
Limekiln Lake	040826	ALTM	84.3	93.1	13.93	2	8.09	105.5
Middle Branch	040707	ALTM	85.8	88.9	3.63	0	10.5	101.8
Moss Lake	040746	ALTM	117.8	102.7	13.15	2.4	9.53	104.8
Queer Lake	060329	ALTM	78.3	99.4	1.55	0	9.51	103.4
Raquette Lake Res.	060315A	ALTM	93.8	106.9	1.86	6.1	8.49	100.7
Sagamore Lake	060313	ALTM	97.8	111.6	49.46	5.5	10.49	126.3
Wheeler	040731	ALTM	111.3	101.2	0.41	7.9	8.12	98.2
Cluster C								
Blue Mountain Lake	060307	EMAP	192.6	99.4	51.67	5.4	9.43	85.2
Canada Lake	070717	EMAP	117	92	101.46	2.4	7.86	110.1
Carry Falls Reservoir	060035C	EMAP	145.2	94	2265.06	11.7	8.42	72.5
Piseco Lake	050234	EMAP	130.1	78	143.73	14.9	10.01	92.5
Seventh Lake	050631A	EMAP	212.4	103.6	43.1	7.5	7.84	92.4

Group A – Lower ionic strength, small lakes; cluster A1 lakes had lower ionic strength and were smaller than A2 lakes, whereas A2 lakes had higher watershed soil % BS, and lower soil CEC and soil acidity than A1 lakes.

Group B – Separated from groups A and C by higher sulfur and base cation deposition; cluster B1 had the lowest factor 3 scores of any cluster (high soil CEC and acidity, low % BS). Cluster B3 had higher ionic strength and larger lake sizes than cluster B2.

Group C – Larger lakes with high ionic strength, and lower sulfur and base cation deposition.

Based on extrapolation of cluster IDs to the EMAP lakes, an estimated 49% of the low ANC lake population in the Adirondacks is in cluster A1 (Table 3-18). The high ionic strength, large lakes represented by cluster C account for 10% of the lake population. ALTM lakes are concentrated in clusters B2 and B3 (Figure 3-23) with 25 of the 32 ALTM lakes occurring in those clusters (Table 3-18). No ALTM lakes were found in cluster C.

Table 3-18. Number of lakes in PCA clusters.

Cluster	Number of Lakes in Population*	Percent of Population	Number of ALTM Lakes
A1	647	49.0%	1
A2	186	14.1%	4
B1	115	8.7%	2
B2	94	7.1%	6
B3	147	11.1%	19
C	132	10.0%	0
Total	1,320		32

* Estimated number of lakes in target population

There was a gradient in ANC related to PCA axis 1-2. Lower ANC was found in lakes with higher factor 2 and lower factor 1 scores. Higher ANC lakes were located in the opposite quadrant with lower factor 2 scores and higher factor 1 scores (Figure 3-23).

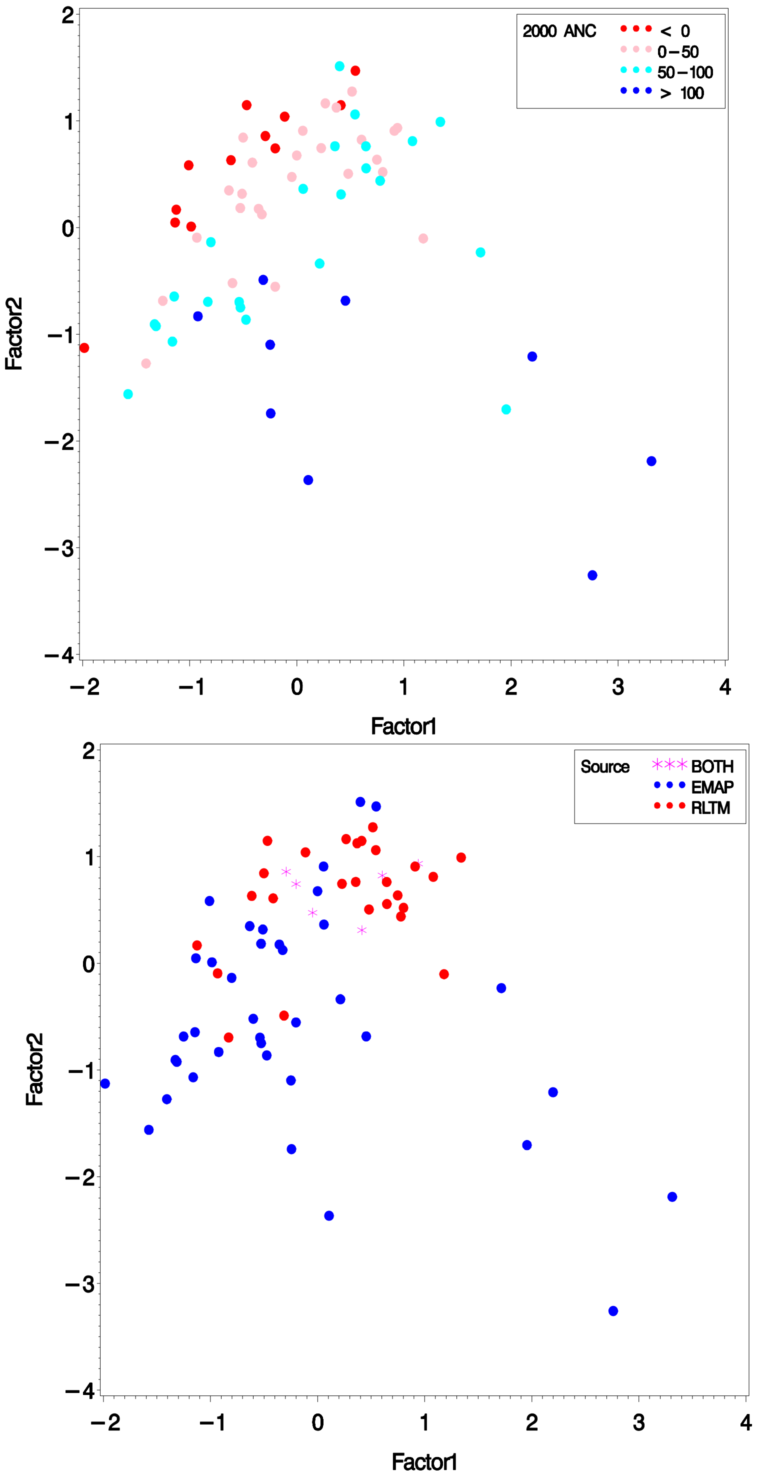


Figure 3-23. *Top panel*: 2000 lakewater ANC and site source distribution across PCA axis 1-2 scores. *Bottom panel*: distribution of data points across datasets.

4.0 ANALYSIS OF MODEL PROJECTIONS AND DISCUSSION

4.1 Projections of Acidification and Recovery

4.1.1 Lakewater Chemistry

To date, the strongest empirical evidence for regional surface water response to decreasing acidic deposition has been surface water SO_4^{2-} concentration trends (Stoddard et al. 1999, Driscoll et al. 2003). Sulphate has declined in most monitored lakes and streams in Europe and North America, including the Adirondack Mountains, with the most rapid declines during the 1990s. Within-region similarities in magnitude of SO_4^{2-} trends suggest that this pattern is driven by declines in S deposition (Stoddard et al. 1999). However, aquatic biota respond to changes in acidity status rather than to changes in SO_4^{2-} concentration (Baker et al. 1990, Stoddard et al. 2003, Kahl et al. 2004). Surface water ANC is the main target indicator of chemical recovery from acidification (Kahl et al. 2004).

The expectation that ANC would respond to observed large decreases in SO_4^{2-} concentrations has partially been realized. Both measurements (Driscoll et al. 2003) and model output produced in this study suggested that by 2000 there were fewer acidic and low-ANC lakes in the Adirondack Mountains than there were in 1990. Kahl et al. (2004) reported a median ANC increase near 1 μeq/L/yr for Adirondack lakes during the 1990s, and this was characterized as important progress toward recovery from acidification.

On the basis of seasonal variability in lakewater chemistry and paleolimnological reconstructions, Kahl et al. (2004) concluded that chronic ANC above about 30 μeq/L would prevent short-term acidification to ANC ≤ 0 during snowmelt and would approximate full chemical recovery for most currently-acidic Adirondack lakes. Trends analysis suggested that the median acidic lake in the Adirondacks would meet the chemical recovery target of 30 μeq/L within two decades if ANC recovery continued at the rates documented during the 1990s (Kahl et al. 2004). The authors cautioned, however, that it was not known whether this rate of recovery would continue without further reductions in acidic deposition. We note that a chemical recovery target of ANC = 30 μeq/L is modest. Data from ALTM lakes show that acid episodes during snowmelt occur with baseflow ANC values above about 50 μeq/L. Results of modeling reported here suggest that the ongoing chemical recovery will not only fail to continue, but that low-ANC lakes might actually reacidify, even under the small further decreases in acidic deposition that were expected under emissions controls regulations in place in January, 2004, at the time of development of this modeling effort. However, our model analysis further suggests that Adirondack lakes could, in fact, continue to recover if moderate additional controls on emissions and acidic deposition were implemented, beyond those represented in our Base Case emissions scenario.

Both the MAGIC and PnET-BGC models simulated past acidification of Adirondack lakes throughout much of the 20th century, ANC recovery since about 1990, and associated recent reduction in the simulated number of Adirondack lakes having ANC less than biologically-relevant threshold values of 0, 20, and 50 μeq/L (Tables 4-1 and 4-2). However, under future emissions and deposition expected to occur in response to Base Case regulations, we projected future decreases in the ANC of most acidic and low-ANC Adirondack lakes. The 25th percentile of ANC recovery by 2050, as projected by the MAGIC model under the Base Case scenario, was only 0.4 μeq/L. Many lakes were projected to re-acidify rather than recover chemically. The median projected recovery by 2050 was only 5.9 μeq/L, compared with a median historical acidification of 38 μeq/L (Table 4-1). Simulations that assumed further emissions reductions beyond the Base Case did not result in reacidification, but rather resulted in a continued chemical recovery as represented by simulated decreases in the numbers of acidic and low-ANC lakes in the future. Median MAGIC model projected increases in ANC by 2050 under the Moderate and Additional Emissions Control scenarios were 18.6 and 22.6 μeq/L, respectively (Table 4-1).

Cumulative distribution functions of modeled lakewater ANC for the population of lakes illustrate chemical acidification and recovery responses from 1850 to 2100 (Figure 4-1 and 4-2). The ANC distribution for 1990 indicates a marked shift to lower values as compared with simulations for 1850. These model decreases in ANC accompanied increases in median SO_4^{2-} + NO_3^- concentrations from about 9 (MAGIC) to 19 (PnET-BGC) μeq/L/yr in 1850 to levels of 88 (PnET-BGC) to 94 (MAGIC) μeq/L/yr in 1990. The Base Case scenario shows little or no future improvement over 1990 conditions. The more restrictive emissions controls scenarios suggest greater future improvement, but do not approach the simulated pre-industrial ANC distribution.

The pattern of reacidification under the Base Case scenario is illustrated in Figure 4-3, using MAGIC model output for all modeled EMAP lakes that had ANC $\leq$ 20 μeq/L in the year 2000. These are representative of the lakes in the population that would be expected to be most biologically-responsive to changes in acidic deposition. Each would be expected to acidify

Table 4-1. MAGIC model projections of acidification and recovery (change in lakewater acid-base chemistry) for the population of potentially acid-sensitive Adirondack lakes, based on estimates of historical emissions and three scenarios of future emissions controls.

Variable	Historical Change from 1850 to 1990 (μeq/L) Percentile			Future Recovery from 1990 to 2050 (μeq/L)								
				Base Case Percentile			Moderate Controls Percentile			Aggressive Controls Percentile		
	25th	50th	75th	25th	50th	75th	25th	50th	75th	25th	50th	75th
ANC	-55.5	-38.3	-22.4	0.42	5.89	11.1	12	18.6	25.5	16.2	22.6	31.3
H	0.02	0.18	2.32	-0.43	-0.02	0	-1.84	-0.1	-0.01	-2.07	-0.12	-0.01
SO_4^{2-}	64.2	77.8	99.6	-53.2	-42.4	-35.2	-70	-58.9	-49.9	-75.6	-64.6	-55.3
NO_3	0	0.49	2.13	-0.63	-0.16	0	-0.81	-0.21	0	-0.98	-0.26	0
SBC	27.3	39.8	48.5	-44.5	-36.9	-33.5	-47.8	-41.4	-34.8	-49.8	-43.1	-35.2

Table 4-2. PnET-BGC model projections of acidification and recovery (change in lakewater acid-base chemistry) for the population of potentially acid-sensitive Adirondack lakes, based on estimates of historical emissions and three scenarios of future emissions controls.

Variable	Historical Change from 1850 to 1990 (μeq/L) Percentile			Future Recovery from 1990 to 2050 (μeq/L)								
				Base Case Percentile			Moderate Controls Percentile			Aggressive Controls Percentile		
	25th	50th	75th	25th	50th	75th	25th	50th	75th	25th	50th	75th
ANC	-47.1	-29.5	0.4	-13.9	-3.7	4.0	-11.8	1.8	8.4	-6.4	9.3	23.2
H	0.01	0.29	0.97	0.01	0.06	1.33	-0.04	0.01	0.41	-0.31	-0.01	0.07
SO_4^{2-}	48.4	57.3	78.0	-24.9	-18.0	-12.1	-44.1	-32.2	-25.5	-52.2	-38.3	-30.4
NO_3	12.3	18.2	27.3	-16.0	-11.0	-7.7	-17.7	-12.8	-8.2	-18.9	-12.8	-8.7
SBC	45.8	65.7	77.8	-47.6	-32.0	-22.5	-57.3	-41.6	-32.0	-61.1	-43.5	-34.0

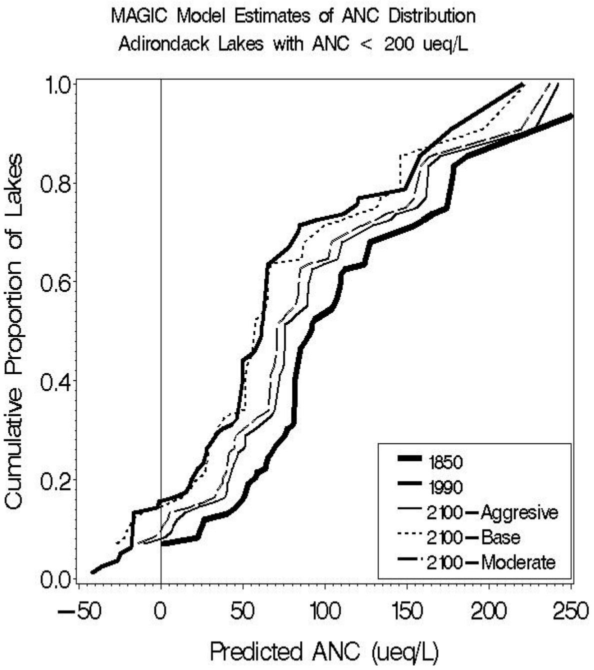


Figure 4-1. Cumulative distribution functions of lakewater ANC at three periods for the population of Adirondack lakes, based on MAGIC model simulations. Distributions for 2100 are based on three alternative scenarios of emissions control. Distribution shifts to the left indicate acidification; shifts to the right indicate chemical recovery.

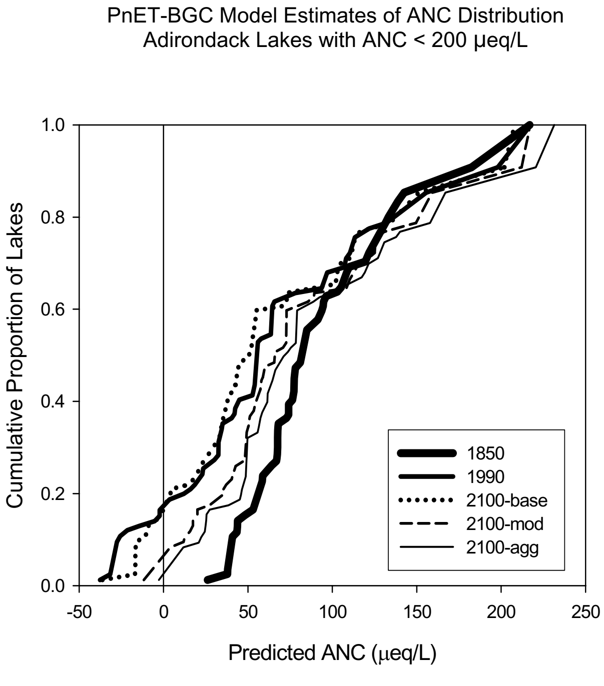


Figure 4-2. Cumulative distribution functions of lakewater ANC at three periods for the population of Adirondack lakes, based on PnET-BGC model simulations. Distributions for 2100 are based on three alternative scenarios of emissions control. Distribution shifts to the left indicate acidification; shifts to the right indicate chemical recovery.

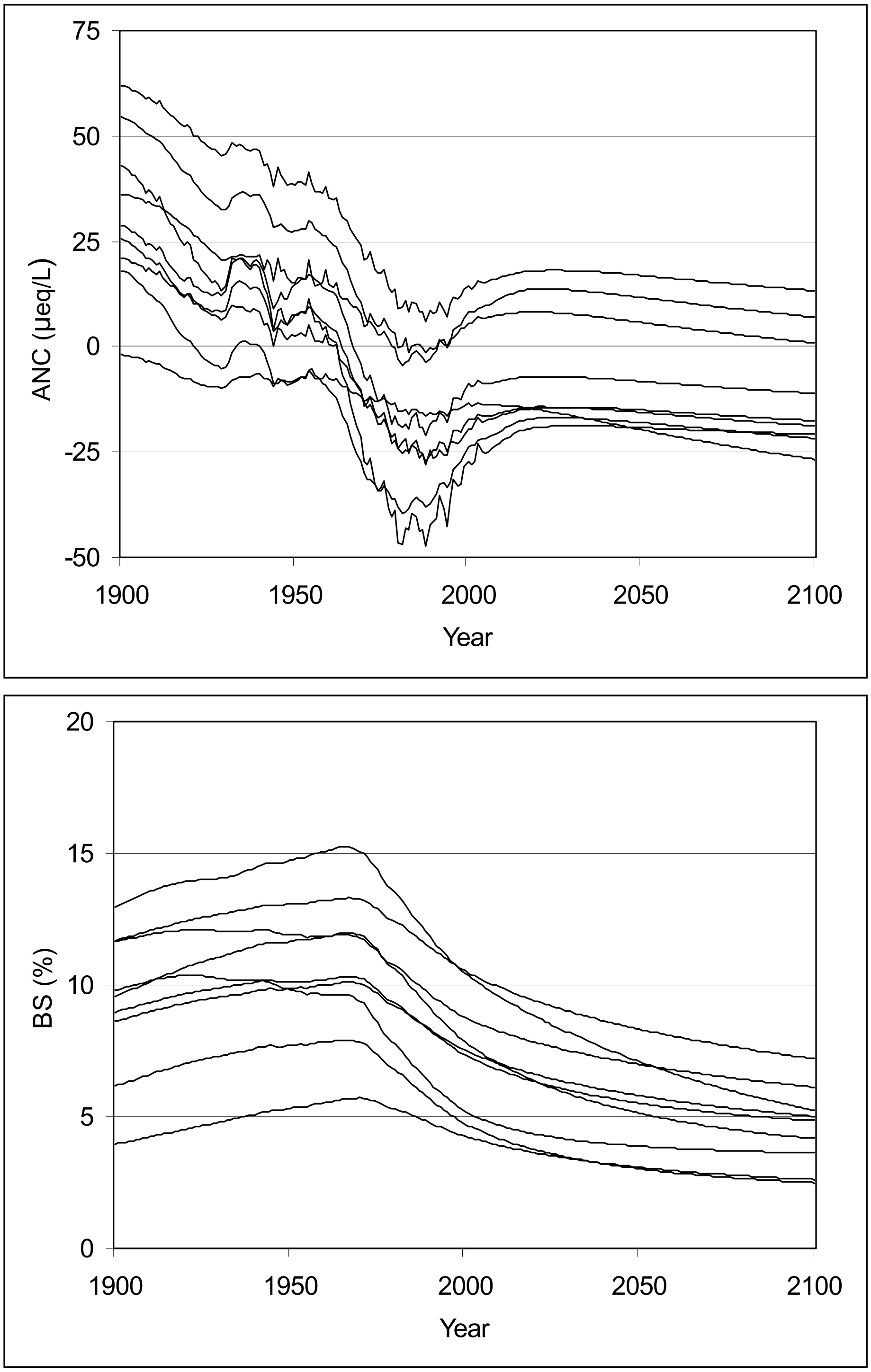


Figure 4-3. MAGIC model projections of lakewater ANC (top panel) and watershed soil % base saturation (bottom panel) for the period 1900 to 2100 for all modeled lakes that had ANC in the year 2000 less than or equal to 20 µeq/L. Future conditions were simulated under the Base Case emissions control scenario.

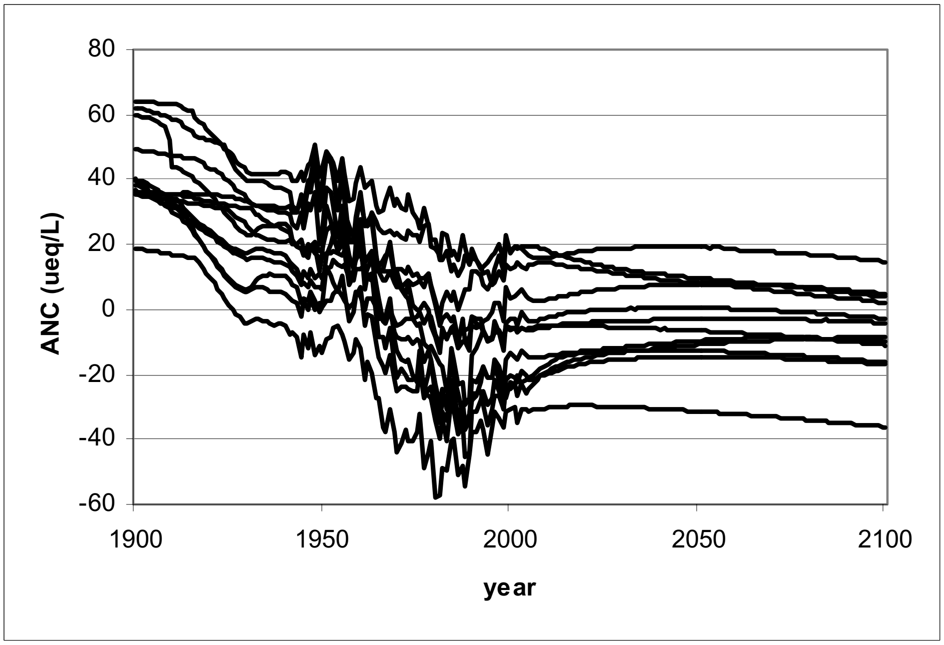
seasonally to ANC < 0 during spring snowmelt (Stoddard et al. 2003). All of the modeled low-ANC lakes showed substantial simulated historical acidification, with ANC minima near 1980 or 1990. Recent ANC recovery is evident during the 1990s and is projected to continue to about 2020. Thereafter, reacidification is projected for all of these lakes under the Base Case scenario. Simulation results for these low-ANC lakes, using the PnET-BGC model, showed similar ANC patterns (Figure 4-4). However, the time at which reacidification began was more variable than for MAGIC simulations (Figure 4-3).

4.1.2 Soil Chemistry

Our survey of Adirondack soil chemistry was undertaken to provide the basis for regional soil characterization, assessment of soil/surface water linkages, and to support the watershed modeling reported here. This survey not only provided information regarding regional soil conditions for low-ANC (< 200 μeq/L) Adirondack lake-watersheds (including those potentially susceptible to adverse impacts from acidic deposition; Sullivan et al. 2006), but it also provided the necessary soil data with which to calibrate and implement the S and N effects models. The soil survey provided a regionally-representative soil database for the Adirondacks that will serve as a benchmark against which future soil conditions can be compared. The establishment of a high quality and documented watershed soil database for this vulnerable and highly valued region is also critical to provide meaningful assessments of terrestrial ecosystem recovery, or lack thereof, in the future.

In general, recent lakewater ANC and the extent to which lakes have acidified during the past century show strong spatial patterns in the Adirondack region. The most acid-sensitive and most acidified lakes are found in the southwestern portion of the Adirondack Park (Driscoll et al. 1991, Sullivan et al. 1997). Nevertheless, the distribution of soils having low % BS does not show such strong spatial patterns (Figure 3-6). Soils having % BS < 10% are widely distributed throughout the western Adirondack region.

All MAGIC simulations showed an increase in soil % BS during the first half of the 20th century in response to increased atmospheric deposition of base cations, followed by a marked decrease in % BS after 1970 and continuing throughout the next century. Mean % BS for soils in these lake catchments decreased from 10.5% in 1950 to 7.4% in 2000, and was projected to decrease steadily to 4.6% by 2100 (Figure 4-3). The steadily decreasing levels of acidic deposition through 2015 (Figure 2-6) were sufficient to result in improved water quality.



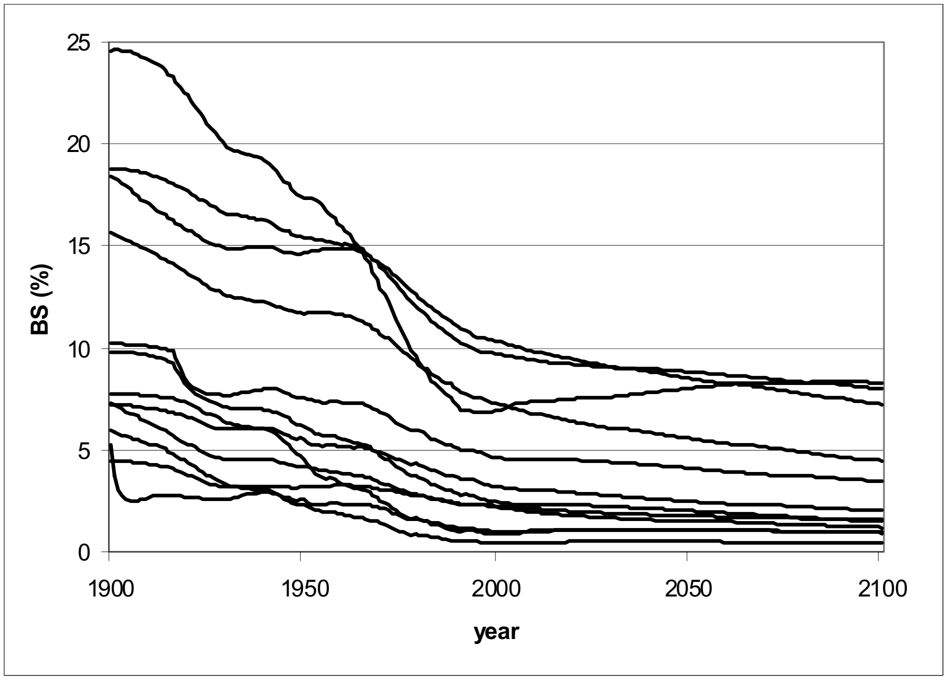


Figure 4-4. PnET-BGC model projections of lakewater ANC (top panel) and watershed soil % base saturation (bottom panel) for the period 1900 to 2100 for all modeled lakes that had ANC in the year 2000 less than or equal to 20 μeq/L. Future conditions were simulated under the Base Case emissions control scenario.

However, emissions and deposition were held constant beyond 2015 in the Base Case simulations. Under these conditions, the continuing decline in simulated soil % BS caused the reacidification response among the lakes that were lowest in ANC. PnET-BGC also projected substantial declines in B horizon soil % BS since pre-industrial time in the watersheds of lakes having very low ANC (Figure 4-4), but did not show a pattern of increasing % BS during the first half of the 20th century. Both models showed a leveling off of future % BS declines at % BS values below about 4%.

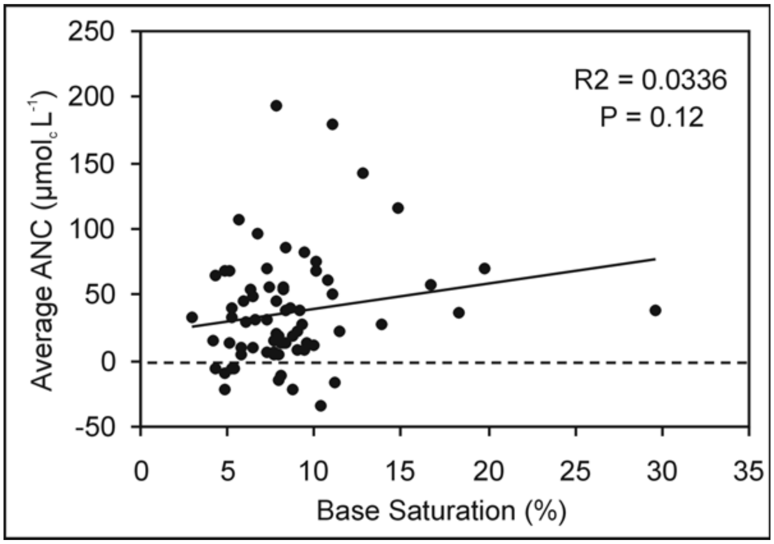


Figure 4-5. Relationship between watershed-aggregated B horizon soil percent base saturation and lakewater ANC for the 70 study lake watersheds.

A comparison of watershed-aggregated soil % BS with available data on average summer and fall lakewater ANC for all 70-study lake-watersheds is shown in Figure 4-5. For this analysis, lakewater ANC data were compiled for each lake over the most data-rich five-year period of record within the recent past. Soil BS and lakewater ANC constitute the master acid-base chemical variables for soils and drainage water, respectively. In general, it is expected that watersheds containing soils having low % BS would be most likely to be those that contain lakes having low ANC. The converse would also be expected to be true.

There was not a significant ($p > 0.1$) overall relationship between watershed soil % BS and lakewater ANC for Adirondack watersheds (Figure 4-5). Although such a correlation might logically be expected, the scale of this study did not accommodate smaller-scale differences in hydrologic flowpaths or regolith distribution such that clear soil/lakewater linkages could be defined. This result was likely due, in part, to the influence of past glaciation on the distribution of till in these watersheds and the importance of hydrologic flowpaths in determining acid neutralization (Driscoll et al., 1991). In other words, soil chemistry is only one among many important factors that influence lakewater chemistry. Nevertheless, lakes having lowest ANC generally had low watershed soil % BS in the B horizon. As was found by Sullivan et al. (2003)

for streamwater in Shenandoah National Park in Virginia, all of our Adirondack study lakes that had ANC below 20 µeq/L also had B horizon watershed soil % BS less than 12%; most were less than 10% (Figure 4-5). There were also many watersheds that had low B horizon base saturation (< 10%), but still had lakewater ANC well above 20 µeq/L (Figure 4-5). Thus, low % BS in watershed B horizon soils appears to be a necessary, but not sufficient, condition for having Adirondack lakewater ANC below 20 µeq/L, a level at which adverse impacts to fisheries become more likely. Low B horizon % BS may be insufficient as a cause of low lakewater ANC if, for example, drainage water flowpaths, in-lake water residence time, or pockets of rock material having high base cation supply result in proportionately greater acid neutralization within a given watershed. The relationship between depth of till and watershed acid-base status has been well established for Adirondack watersheds (Newton and Driscoll 1990).

In a study of episodic stream acidification processes in eight small watersheds (11 to 967 ha) throughout the northeastern United States, Lawrence (2002) found that exchangeable Ca concentrations in the O_a horizon were strongly correlated with high-flow stream ANC ($r^2 = 0.84$). In contrast, we found no significant relationship between average lakewater ANC and exchangeable Ca in the O horizon ($p = 0.25$) of soils collected in this study. Thus, although watershed soil base cation supply is clearly important to surface water acid-base chemistry, the linkages are apparently not simple or straight-forward.

Soil base cation depletion can occur if the leaching of base cations from the soil by acidic deposition occurs faster than the combined replenishment by rock weathering and base cation deposition from the atmosphere. Long-term depletion of soil base cations, reflected in the low soil % BS values, represents a natural pattern of soil formation in humid environments. Modern atmospheric chemical inputs of S and N appear to have accelerated the rate of cation leaching, and therefore base cation loss, in watersheds where base cation acid neutralization mechanisms have not been depleted. After exposure to long-term elevated deposition of atmospheric pollutants, soil base cation acid neutralization mechanisms become less effective as % BS declines and acid neutralization through Al mobilization becomes increasingly important, as does exchangeable Al on the CEC_e (Norton et al., 2004; Fernandez et al., 2003). Soils in the population studied here from the Adirondack region appear to typify these characteristics, with low pH and % BS, and relatively high exchangeable Al. This presumed accelerated soil acidification, which is supported by the modeling conducted within this study, may have resulted in a fundamental alteration of soil processes, potentially impacting the nutritional status of vegetation and the extent to which soils and drainage waters can recover from acidification. Indirect chemical effects of soil base cation depletion include the acidification of soil solution and increased mobilization of potentially-toxic inorganic monomeric Al from soil to solution (Cronan and Grigal, 1995). Such effects have been linked with the observed decline of red spruce (*Picea rubens*) at high elevations throughout the northeastern United States (DeHayes et al., 1999) and of sugar maple (*Acer saccharum*) in Pennsylvania (Horseley et al., 2000).

One focus of this study has been on the implications of % BS and the composition of the CEC_e in O and B horizons of Adirondack forested watersheds for soil and surface water acid-base status. Two parameters in this data set provide information on the amount of organic matter in these soils. Soil total C is primarily found in organic matter. Also, LOI (determined as the percent loss of mass of a soil sample when combusted at 450^o C) is considered an estimate of soil organic matter, although it is taken to be less accurate than direct C measurements. In these soils, LOI proves to be a good estimator of total soil C and, by inference, organic matter content (LOI = 1.5 x TC + 2.44; $r^2 = 0.99$; where both LOI and total C are given in percent).

The relationship between total C and CEC_e in both O and B horizons is shown in Figure 4-6. Given that the Adirondack region is dominated by coarse textured parent materials of glacial origin, it is evident that variations in soil CEC_e have less to do with clay content than with soil organic matter content in these soil materials. Similar results were found in the Catskill Mountains of New York by Johnson et al. (2000). The correlations found here are relatively strong considering that these data represent total soil C, with some minor contribution of carbonate minerals, and without any consideration of differences in the extent of organic matter humification that could govern the degree of surface reactivity, and thus influence CEC_e. Organic matter derived CEC_e in these soils takes on additional importance when we consider that essentially all of the CEC_e on soil organic materials is pH-dependent. We can expect that there will be, and perhaps have been, significant changes in CEC_e to the extent that soils have been influenced by acidic deposition (c.f., Lapenis et al. 2004). In addition, the quality of organic matter and the degree of humification are governed by plant community composition, productivity, and rate of microbial processing in soil. All of these factors are expected to be influenced by a changing physical climate.

Since total C in these soils plays such a critical role in determining the reactive CEC_e, it is reasonable to question the role of total C in determining soil pH. The correlation between total

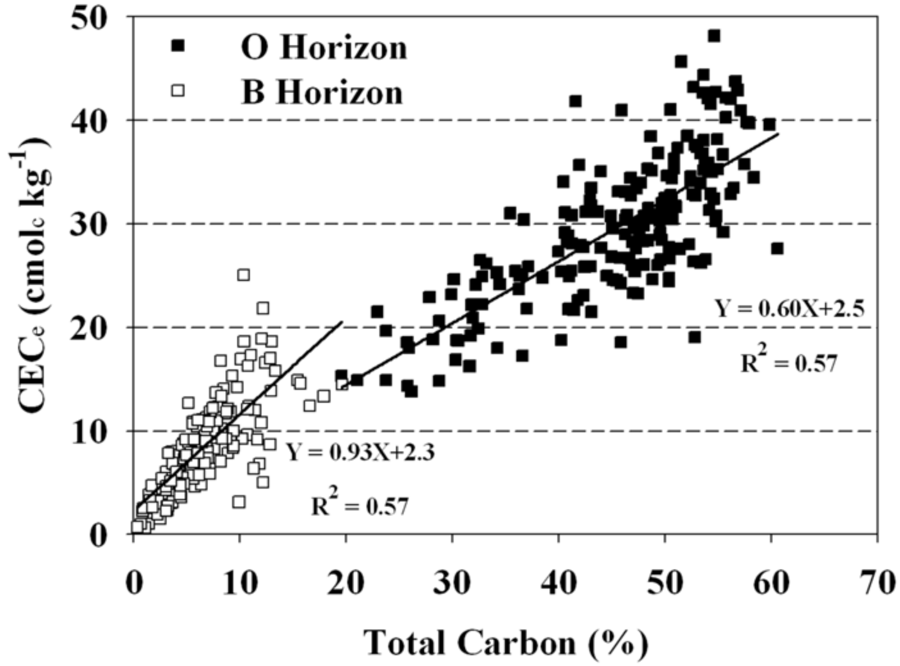


Figure 4-6. Correlations between total C and CEC_e from all soil samples analyzed in the Adirondack watershed sampling conducted in 2003.

C in the O and B horizons with a measure of acidity expressed as H^+ activity in the equilibrium soil water pH solutions (pH_w) is shown in Figure 4-7. These data suggest that variation in soil C, primarily reflecting soil organic matter differences, influences pH in both the O- and B horizons. However, the slope and r^2 for this relationship in the O horizon suggests a major control on soil pH attributable to percent organic matter whereas the influence of organic matter in the B horizon is much weaker.

The stronger positive correlation in the O horizon reflects the importance of organic functional groups in contributing to reactive H^+ in these soils. Higher concentrations of organic matter contribute to higher H^+ activity and lower pH. The O horizons were also much more acidic than B horizons. The pH_w values ranged from 2.66 to 4.87 for the O horizons, and 3.54 to 5.66 for the B horizons sampled in this study. Organic matter in the B horizon would be expected to be relatively humified and absolute differences in the amount of organic matter appear to have little influence on soil pH but do influence the exchangeable cation composition of organic matter reactive surfaces.

Although this research was intended to conduct and support ecosystem modeling and extrapolation, the soil data developed and samples archived within the project constitute valuable assets in ecological and environmental research for evaluation of changing conditions over time.

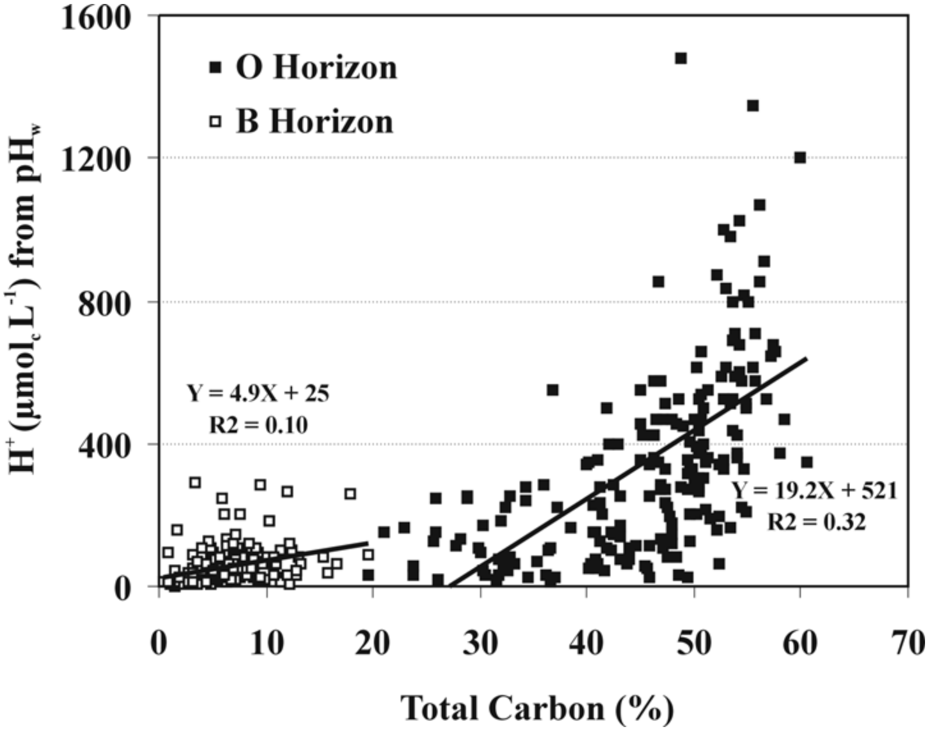


Figure 4-7. Correlations between total C in the soil and H^+ in equilibrium soil solutions from the soil pH in water measurements.

Soils sampled within this project from Adirondack watersheds selected to be representative of the region and geo-referenced with a global positioning system (GPS) will serve as baseline data for future comparisons, while simultaneously supporting the immediate objectives of this project. Long-term concerns for carbon sequestration, base cation depletion, metal accumulation and forest productivity are classic issues that rely on informed data regarding changes in ecosystem condition over time. This database will be available for use in future research and environmental policy development on issues both known and not yet identified.

4.1.3 Comparison with DDRP Data from the 1980s

In order to compare distributions of watershed soil chemistry between our study and those of the 1980s DDRP project, we constructed subsets of both datasets so they defined a common population of lakes and associated watersheds. The original DDRP population had been constrained by excluding lakes with area < 4 ha, maximum depth < 1.5 m, watershed area > 30 km^2, and ANC > 400 µeq/L (Church et al., 1989). Because our soil survey of EMAP lake watersheds only included lakes with ANC ≤ 200 µeq/L, for this comparison we excluded DDRP lakes with ANC > 200 µeq/L and excluded lakes from our EMAP sample that exceeded DDRP lake area, depth, and watershed area limits. Using these data subsets (n=32 for EMAP, n=36 for DDRP) and the sample weights from each survey, cumulative distribution functions were constructed so that we could compare the EMAP and DDRP population distributions of lake watersheds for lakewater ANC, and B horizon soil % BS and exchangeable Ca (Figure 4-8). Differences between the two surveys in terms of population estimates (% of lake watersheds) for specific criteria values were evaluated for significance using a z-test (z=difference between estimates/pooled standard error). The pooled standard error was calculated as the square root of the sum of the squared standard error of the estimate for each survey.

Distributions of lakewater ANC were very similar between the two surveys at values above 50 μeq/L and 56% of the lake watersheds in each population had ANC $\leq$ 50 μeq/L (Figure 4-8A). In the lower half of the ANC distribution, there were more acidic lakes in the DDRP (20.0%) than EMAP (10.2%; z=1.32, p=0.074). In terms of B horizon soil chemistry, there were small proportions of high % BS (>15%) and high exchangeable Ca (>0.6 $\text{cmol}_c\ \text{kg}^{-1}$) lake watersheds in EMAP that were not present in DDRP (Figures 4-8B, 4-8C). In the lower 60% of the population distributions, however, EMAP lake watersheds had both lower % BS and exchangeable Ca than did DDRP watersheds. An estimated 79.9% (SE=9.52) of the EMAP lake watersheds had % BS < 10% versus 61.9% (SE=9.11) of the DDRP lake watersheds. The difference between these two estimates is significant at a p-value of 0.1, but not 0.05, with a z-score of 1.37 (p=0.085). Similarly, 58.5% of the EMAP lake watersheds had exchangeable Ca < 0.4 $\text{cmol}_c\ \text{L}^{-1}$ compared to 46.2% of the DDRP lake watersheds (z=0.85, p=0.20).

These populations of Adirondack lake watersheds defined by the DDRP study in the mid 1980s and our analyses of EMAP lake watersheds in the 1990s (water chemistry) and 2003 (soil chemistry) are not totally comparable. For example, our soil analyses were standardized to the top 10 cm of B horizon soil whereas DDRP upper mineral soil samples exhibited varying depths (Church et al., 1989). Nevertheless, the data shown in Figure 4-8 suggest that while lakewater chemistry was improving subsequent to large decreases in acidic deposition (Figure 4-8A, a result also shown in other studies, c.f., Driscoll et al., 2003), Adirondack soil acid-base chemical conditions may have been continuing to deteriorate in most of the acid-sensitive watersheds (Figure 4-8 B,C). This result was also consistent with our model projections of % BS (Figure 4-3, 4-4). Such an effect would be expected to restrict the extent to which surface water chemistry will be able to recover from acidification in the future and may contribute to future adverse effects on forest soils and vegetation.

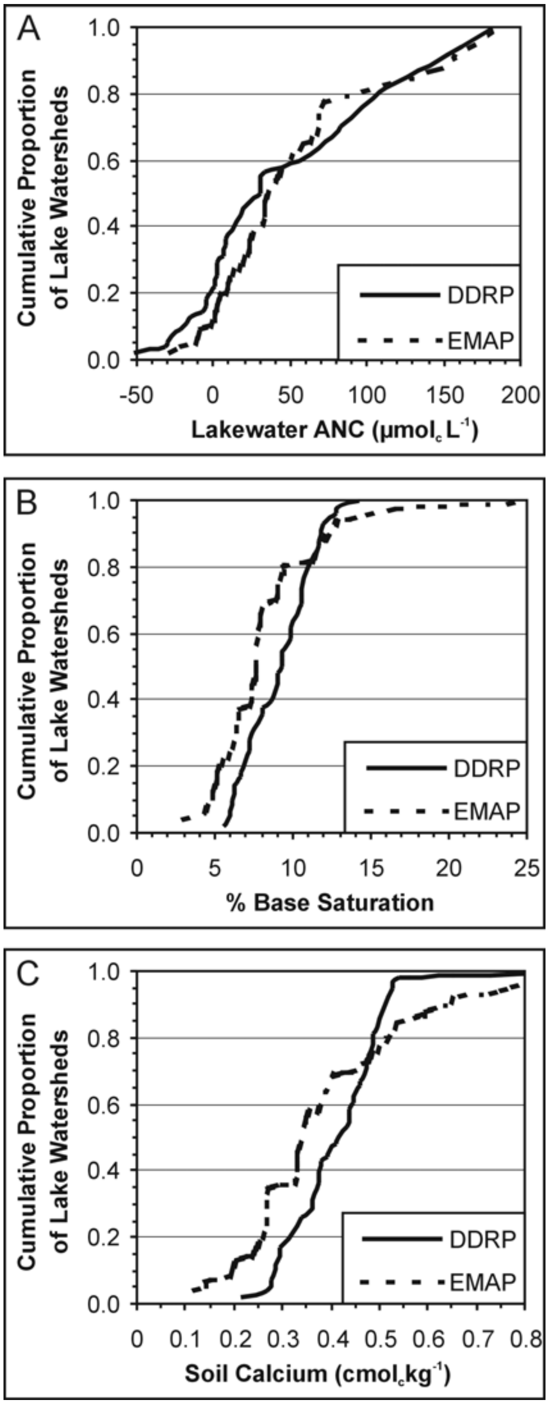


Figure 4-8. Cumulative distribution functions for a common population of Adirondack lake watersheds constructed for DDRP data collected in the mid 1980s and data compiled or collected in this study for EMAP lake watersheds in the early 1990s (lake chemistry) and in 2003 (soil chemistry). Comparisons are shown for A) lakewater ANC, B) B horizon soil base saturation, and C) B horizon soil exchangeable Ca^{2+}.

4.1.4 Biota

4.1.4.1 Zooplankton Response to Changes in Acidic Deposition

Using the empirical relationships developed between species richness of zooplankton and lakewater ANC (Table 3-14) for lakes in the Adirondacks, we evaluated the potential level of response of total zooplankton to historical and potential future changes in acidic deposition in the EMAP lakes. PnET-BGC model output of hindcasts and future scenario projections of lakewater ANC were used together with the relationship between total zooplankton species richness and ANC (Table 3-14) to make lake population estimates of changes in zooplankton diversity that would be consistent with model estimates of changes in lakewater chemistry in the Adirondacks over the time period of this study (i.e., 1850-2100). The empirical relationship developed between zooplankton species richness and ANC was based on spatial survey data. In this analysis we assume that these spatial relationships can be used to extrapolate temporal change driven by changes in acidic deposition. This space-for-time substitution relationship is an important assumption. Note that many factors in addition to acid-base chemistry may affect zooplankton abundance, including climate, land disturbance, changes in nutrient inputs, and introductions and changes in fish species. Such factors might alter this relationship. In addition, we make no attempt to account for possible zooplankton dispersal limitations that could affect the ability of zooplankton to recolonize a lake in the process of chemical recovery from previous acidification. Thus, these estimates should be interpreted as indicating the level of change in zooplankton taxonomic richness that, on average, would be consistent with the model projections of change in lakewater chemistry.

Over the range of ANC values observed in EMAP lakes, the zooplankton species richness ranged from 15 in highly acidic lakes to 35 at the highest values of ANC observed. For 1850, the median number of zooplankton species in the target lake population was estimated to be 21.9 (Figure 4-9A). From 1850 to 1990, increases in acidic deposition contributed to median decreases in zooplankton species richness to 20.0. The change in number of zooplankton species for a given lake between 1850 and 1990 ranged from 6 species lost to 4.9 species gained, with a median value of 1.9 species lost (Figure 4-10).

The model projections also suggested changes in zooplankton species richness under the future scenarios. Future decreases in acidic deposition generally resulted in further changes in estimated zooplankton species richness, with median values from 20.0 in 1990 to 19 in 2100 for the Base Case, to 20.6 in 2100 for the Moderate Additional Controls scenario and to 21.0 in 2100

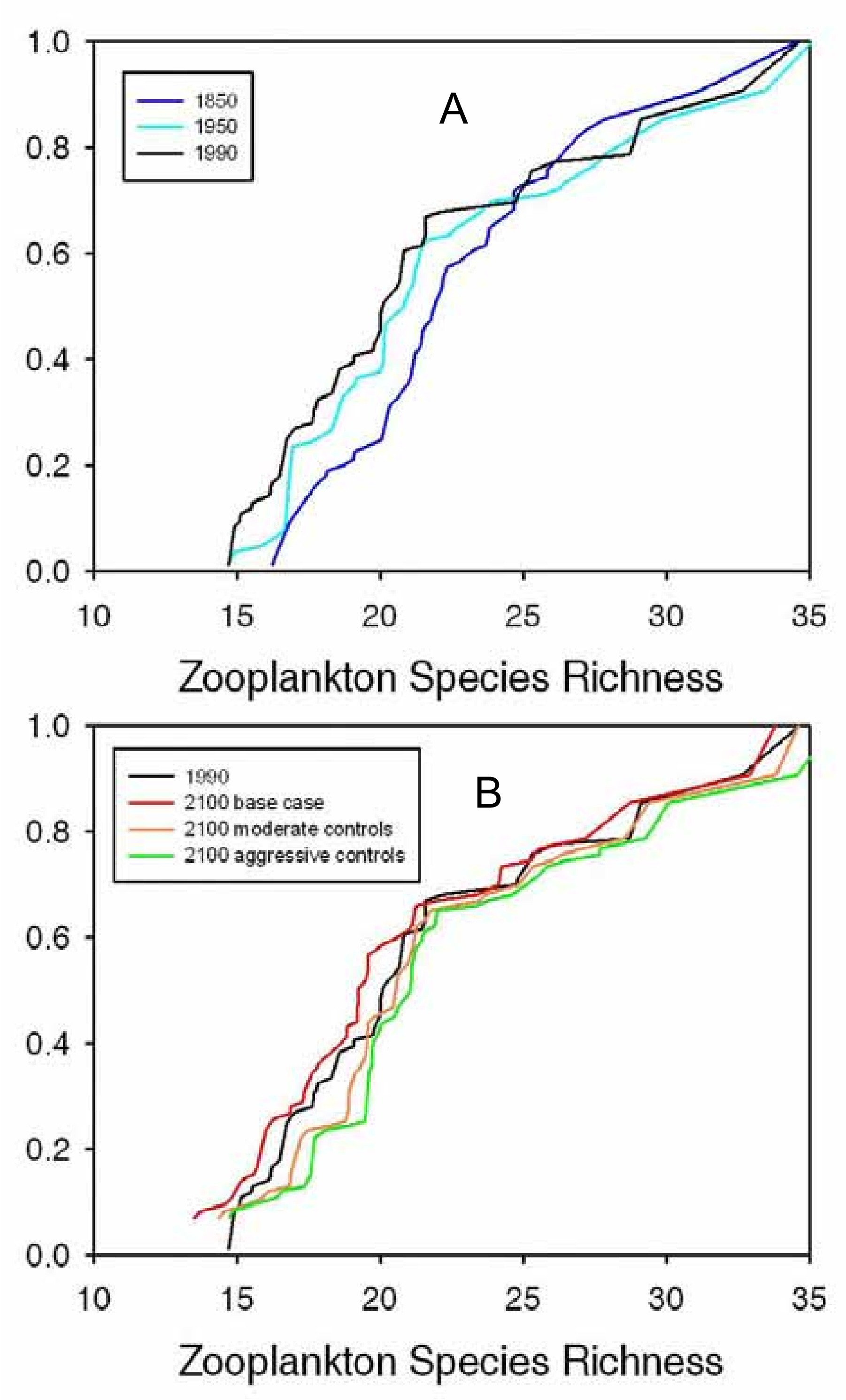


Figure 4.9. Cumulative distribution functions of estimated total zooplankton species richness for the population of Adirondack lakes, based on PnET-BGC model estimates of lakewater ANC and the empirical relationship between total zooplankton species richness and lakewater ANC in Adirondack lakes (Figure 3-20). In the upper panel, distributions are compared for three points in time: 1850, 1950, and 1990. In the lower panel, the three scenarios of future emissions control for the year 2100 are compared with results for 1990.

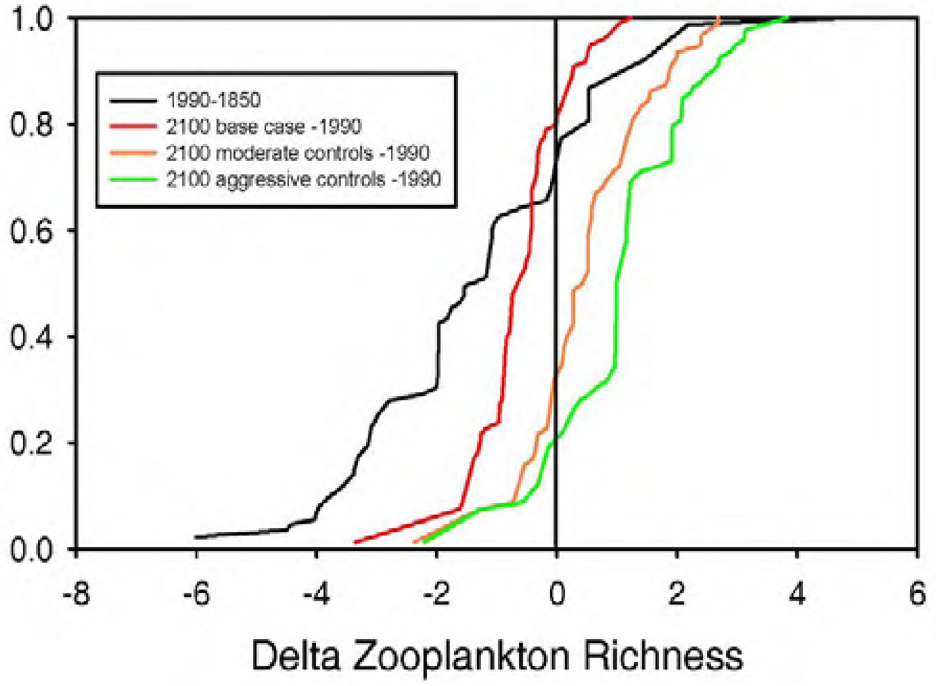


Figure 4.10. Cumulative distribution functions of changes in estimated total zooplankton species richness for the population of Adirondack lakes, based on PnET-BGC model estimates of lakewater ANC and the empirical relationship between total zooplankton species richness and ANC in Adirondack lakes (Figure 3-20). Changes are depicted over the historical period (1850 to 1990) and into the future (1990 to 2100) under each of the emissions control scenarios. Positive values indicate increase in species richness; negative values indicate decrease.

for the Aggressive Additional Controls scenario (Figure 4-9B). The estimated change in number of zooplankton species from 1990 to 2100 ranged from –3.4 to 1.2, with a median loss of 1.0 species for the Base Case, from –2.4 to 2.7, with a median gain of 0.6 species for the Moderate scenario and –2.2 to 3.8, with a median gain of 1.0 species for the Aggressive scenario (Figure 4-10). Note that the estimated general loss of zooplankton species richness through 2100 for the Base Case is consistent with the future model projections of decrease in ANC (re-acidification) in many lakes under this scenario.

These calculations may be viewed as an extension of the model representation of effects of acidic deposition beyond simulations of chemical change because ecological and management concerns are largely focused on biological resources associated with lake ecosystems. However these estimates are highly uncertain because there is considerable variability in the empirical relationships (see Figure 3-20) and because it is unclear whether it is appropriate to use the space-for-time substitution assumption. Nevertheless, these calculations suggest that the potential exists for some change in zooplankton species richness given the levels of change simulated in lake water chemistry in response to future decreases in acidic deposition and subsequent chemical recovery of lakewater. However, the estimated changes in zooplankton species richness in response to simulated changes in lake chemistry are small on an absolute basis and also in comparison with the observed variability in the empirical relationship between zooplankton species richness and ANC. Based on simulations of future change in zooplankton richness (Figure 4.10), the maximum increase in total zooplankton species from 1990 to 2100 in any Adirondack lake would only be an increase of four species. In order to achieve such an increase, aggressive emissions controls would be required. The PnET-BGC model hindcast simulations suggested that the largest historic decrease in zooplankton species richness (1850 to 1990) was only slightly larger (six species). It will be useful to develop zooplankton time-series data for ALTM lakes, as is presently being done in the AEAP project, to validate the relationships and calculations developed here.

4.1.4.2 Fish Response to Changes in Acidic Deposition

Using the empirical relationship developed between fish species richness and ANC (Figure 3-19), we evaluated the response of fish species richness to historical and potential future changes in acidic deposition in the EMAP lakes. Model output of hindcasts and scenario predictions of lake ANC from PnET-BGC were used together with the relationship between total fish richness and ANC (Equation 3-3) to make lake population estimates of changes in fish species richness in the Adirondacks over the time period of this study (i.e., 1850-2100). The empirical relationship developed between fish species richness and ANC was based on the spatial patterns observed in the ALSC survey data. In this analysis and the subsequent analysis for brook trout presence (see below), we assume that these spatial relationships can be used to extrapolate temporal change driven by changes in acidic deposition. This space-for-time relationship is an important assumption for fish, as it was for zooplankton (discussed in the previous section). Many factors in addition to acid-base chemistry may affect fish abundance, including climate, land disturbance, changes in nutrient inputs, and fish species introductions. Such factors might alter this relationship with ANC. Therefore, the estimates presented here can be interpreted as representing the possible effects of changes in acid-base chemistry on fish species richness in the absence of any other factors that also might influence fish occurrence. The actual loss or gain of fish species in the past or future might be different.

Over the range of ANC values simulated in EMAP lakes, the fish species richness ranged from zero in highly acidic lakes to 5.7 at the highest values of ANC observed. For 1850, the median number of fish species in EMAP lakes was estimated to be 5.0, with a 20th percentile value of 4.1 (Figure 4-11A). From 1850 to 1990, increases in acidic deposition generally resulted in median decreases in fish species richness to 4.6 and a 20th percentile value of 2.0. The number of fish species lost from 1850 to 1990 ranged from 4.4 to – 0.3 (i.e., 0.3 species gained), with a median value of 0.4 lost (Figure 4-12). The model projections also suggest changes in fish species richness under the future scenarios. Future decreases in acidic deposition generally resulted in changes in fish species richness, with median values from 4.6 in 1990 to 4.3 in 2100 for the Base Case, to 4.8 in 2100 for the Moderate scenario and to 4.9 in 2100 for the Aggressive scenario (Figure 4-11B). The estimates of change for the 20th percentile values of fish species richness were larger. Fish species richness for the 20th percentile changed from 1.9 in 1990 to 0.6 in 2100 for the Base Case, to 2.8 in 2100 for the Moderate scenario and to 3.4 in 2100 for the Aggressive scenario (Figure 4-11B). The number of fish species gained from 1990 to 2100 ranged from –2.4 to 0.5, with a median of 0 for the Base Case, from –1.2 to 3.2, with a median of +0.3 for the Moderate scenario, and –1.2 to 3.7, with a median increase of 0.4 for the Aggressive scenario (Figure 4-12). As expected, the estimated general loss of fish species richness in 2100 for the Base Case is consistent with the simulated future decrease in ANC under this scenario.

Using the empirical relationship between the probability of brook trout presence ($P_{\text{brook trout}}$) and lakewater pH, we evaluated the response of brook trout in the EMAP lakes to historical and potential future changes in acidic deposition. Model output of hindcasts and scenario predictions of lake pH from PnET-BGC were used together with the relationship between the probability of brook trout presence and pH (Equation 3-4) to make lake population estimates of changes in the probability of brook trout presence in the Adirondacks over the time period of this study (i.e., 1850-2100). This relationship was developed for lakes in the Adirondacks with confirmed presence of brook trout in the past and no obvious confounding factors. In applying this relationship to the EMAP lakes, it is assumed that these lakes have suitable habitat and conditions for brook trout survival (other than impact from acidic deposition). Such an assumption would not necessarily be expected to hold. Thus, this analysis reflects the

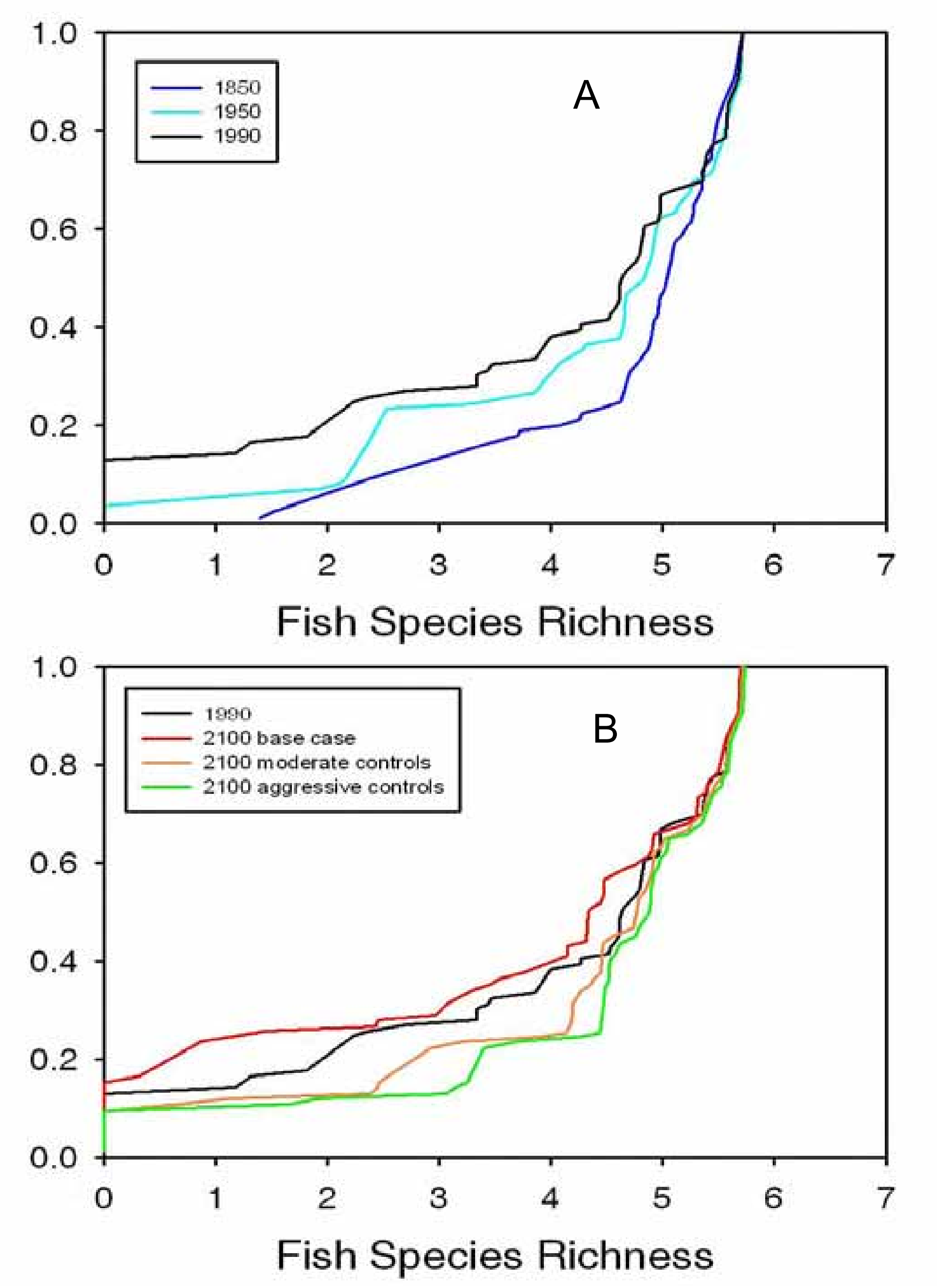


Figure 4-11. Cumulative distribution functions of the probability of fish species richness for hindcasts (A) and forecasts (B) for the EMAP population of Adirondack lakes using PnET-BGC. For hindcasts, the probability of a value of fish species richness is shown for 1850 (assumed background conditions) and for 1950 and 1990. For forecasts, the probability of fish species richness values are shown for three future scenarios in 2100: a Base Case, a Moderate Scenario and an Aggressive Scenario. The simulated values for 1990 are shown for comparison. Larger differences across years and across emissions control scenarios were found for lakes having low fish species richness. Smaller differences were found for lakes having high fish species richness.

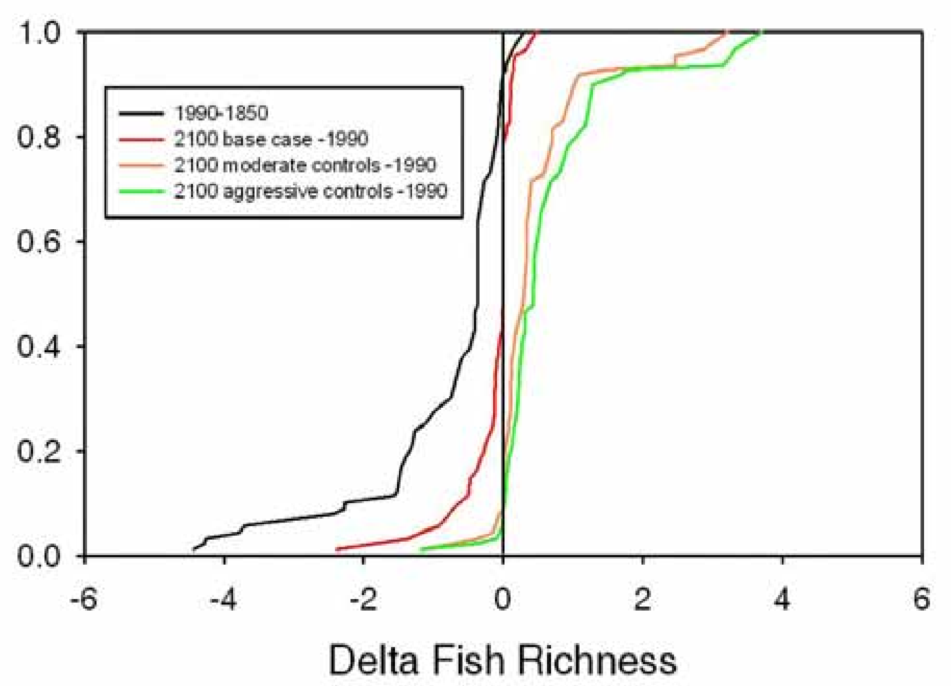


Figure 4-12. Cumulative distribution functions of the difference in probability of fish species richness between 1850 and 1990; between 1990 and 2100 for the Base Case scenario; between 1990 and 2100 for the Moderate scenario; and between 1990 and 2100 for the Aggressive scenario for the EMAP population of Adirondack lakes using PnET-BGC.

probability of brook trout presence if other habitat characteristics, other than acid-base chemistry, are suitable.

Over the range of pH values simulated in the EMAP lakes, the probability of brook trout presence ranged from 0.4 in the lakes having lowest pH to 0.99 at the highest values of pH observed. For 1850, the median probability of brook trout presence in EMAP lakes was estimated to be 0.96, with a 20th percentile of 0.7 (Figure 4-13A). From 1850 to 1990, increases in acidic deposition resulted in a median decrease in the probability of brook trout presence to 0.90, with the 20th percentile decreasing to 0.52. The change in probability of brook trout presence from 1850 to 1990 ranged from a loss of 0.44 to a gain of 0.03 with a median value of 0.02 lost (Figure 4-14).

The model projections also suggested changes in probability of brook trout presence under the future scenarios. Future decreases in acidic deposition generally resulted in changes in probability of brook trout presence, with median values from 0.9 in 1990, to 0.85 in 2100 for the

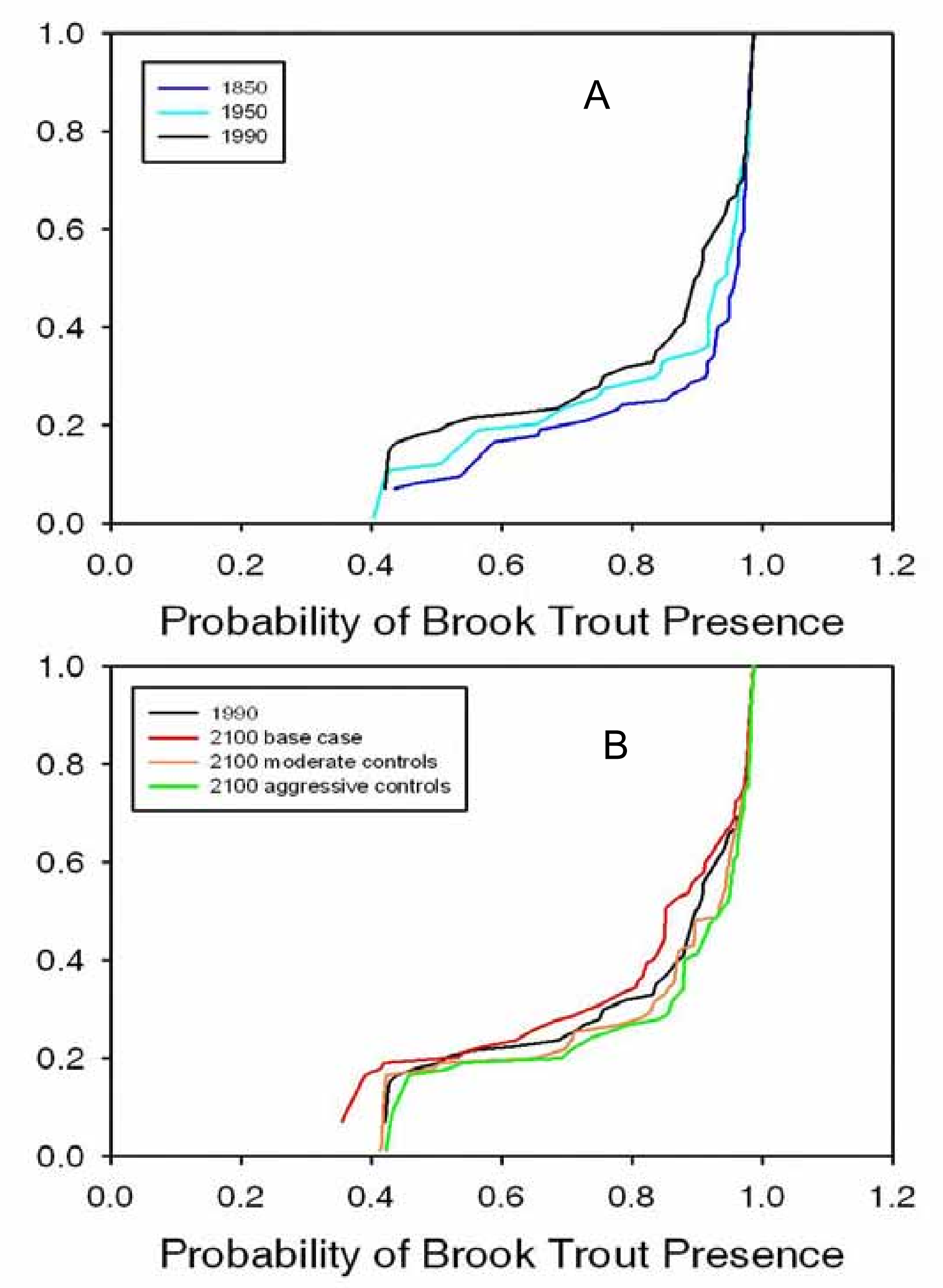


Figure 4-13. Cumulative distribution functions of the probability of brook trout presence for hindcasts (A) and forecasts (B) for the EMAP population of Adirondack lakes using PnET-BGC. For hindcasts, the probability of brook trout presence is shown for 1850 (assumed background conditions), 1950, and 1990. For forecasts, the probability of brook trout presence is shown for three future scenarios in 2100: Base Case, Moderate Scenario and Aggressive Scenario. The simulated values for 1990 are shown for comparison.

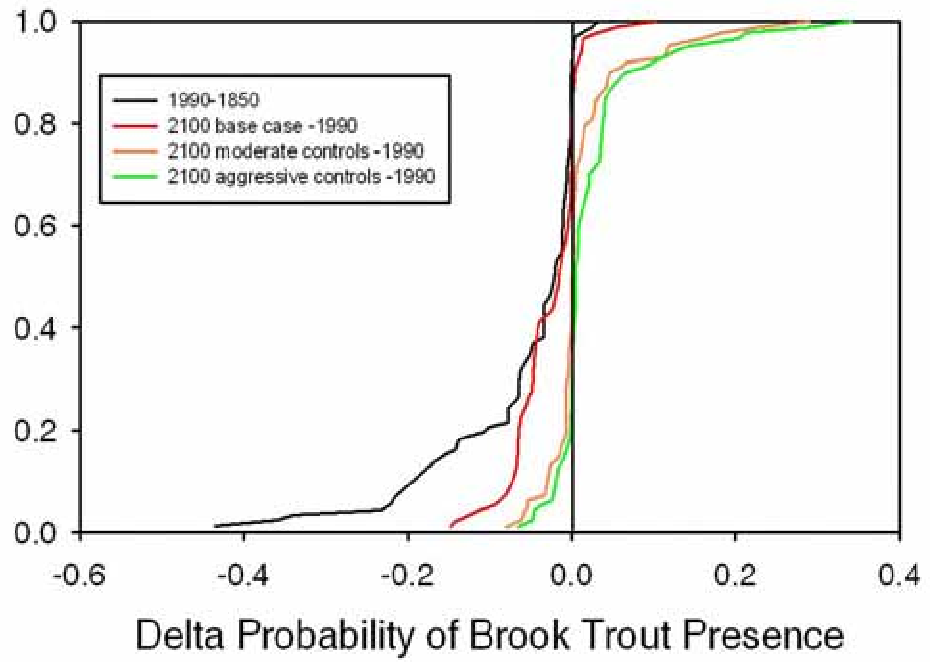


Figure 4-14. Cumulative distribution functions of the difference in the probability of brook trout presence between 1850 and 1990; between 1990 and 2100 for the Base Case scenario; between 1990 and 2100 for the Moderate scenario; and between 1990 and 2100 for the Aggressive scenario for the EMAP population of Adirondack lakes using PnET-BGC.

Base Case, to 0.93 in 2100 for the Moderate scenario and to 0.94 in 2100 for the Aggressive scenario (Figure 4-13B). As was observed for fish species richness, the 20th percentile values revealed more pronounced changes. The 20th percentile values for the probability of brook trout presence changed from 0.52 in 1990, to 0.53 in 2100 for the Base Case, to 0.65 in 2100 for the Moderate scenario and to 0.69 in 2100 for the Aggressive scenario (Figure 4-13B). The change in probability of brook trout presence from 1990 to 2100 ranged from –0.15 to 0.10, with a median of –0.02 for the Base Case, from –0.08 to 0.29, with a median of 0.0 for the Moderate scenario, and –0.07 to 0.34, with a median increase of 0.01 for the Aggressive scenario (Figure 4-14). Note that the general decrease in probability of brook trout presence in 2100 for the Base Case is consistent with the modeled future decrease in pH of many lakes under this scenario.

4.2 Similarities and Differences Between Models

The discussion of model comparisons between PnET-BGC and MAGIC is divided into the following sections:

1. **Site-by-site comparisons of simulation outputs from the two models using x-y scatterplots.**. The site-by-site comparisons are arranged in two sub-groups. For each subgroup, the comparisons are provided for the following output (unless specified otherwise): SO_4^{2-}, NO_3^-, Ca^{2+} + Mg^{2+}, SBC, pH and CALK concentrations in the lakes, and the B horizon % BS of the soil. The years for which comparisons are made differ for each sub-group, as follows:
    a) Comparisons of the outputs from each model with observed data. These comparisons are provided for the years 1990 and 2000.
    b) Comparisons of the outputs of the models with each other. These comparisons are provided for 1990 and 2000 (to supplement the comparisons above), for 1850 (an estimate of pre-industrial conditions), and for the year 2100 for each of the future deposition scenarios – Base, Moderate, and Aggressive.
2. **Regional comparisons of simulation outputs from the two models using cumulative distribution functions (CDFs) describing the weighted regional population estimates**. These comparisons are provided for selected output variables in selected years. The variables selected for comparison are: SO_4^{2-}, NO_3^-, SBC and CALK concentrations in the lakes and the B horizon % BS of the soil. The years selected for comparison are 1850 (an estimate of pre-industrial conditions), 1990 (an estimate of the approximate period of lowest CALK in the lakes), and 2100, with the CDFs compared in 2100 for each of the future deposition scenarios – Base, Moderate, and Aggressive.
3. **Comparisons of patterns of historical and future changes in simulated CALK produced by the two models**. In these comparisons, the changes from 1850 to 1990 (estimates of historical acidification) and the changes from 1990 to 2100 for the Aggressive scenario (estimates of maximum chemical recovery) are examined. The simulated historical and future changes in CALK are evaluated in comparison with three site-specific characteristics: the 1990 S deposition used in the simulations; the 1990 simulated lake CALK; and the 1990 simulated mineral soil % BS.

4.2.1 Site-by-Site Comparisons of Simulation Outputs from the Two Models

4.2.1.1 Comparisons of the Outputs from Each Model with Observed Data.

Comparisons of model outputs with observed data are *not* the same as comparisons of the model outputs to observed data used for calibration. The two models used different procedures and different periods of time for calibration. Because of these differences there is no common set of data to which the model calibrations can be compared, and thus no way to directly compare calibration goodness-of-fit for the two models. In this section, we provide a comparison of simulated and observed variable values that attempts to "normalize" for the differences in calibration procedures and differences in calibration data used for each model. Comparisons are provided for the following variables (unless specified otherwise) SO_4^{2-}, NO_3^-, $Ca^{2+} + Mg^{2+}$, SBC, pH, and CALK concentrations in the lakes, and the B horizon % BS of the soil.

The observed data available for model calibration and comparison cover the period from 1983 through 2003. However, the sampling frequency of these data differs among the 70 sites that were modeled. Some sites have monthly data extending over decades (some of the ALTM sites) while others may have only a few samples for the whole period of interest. In order to provide a common set of observed data to compare with model simulations, the following procedure was adopted. First, all available data at each site were averaged on a calendar year basis, using a straight arithmetical average (no discharge weighting was used). Then, all yearly values were averaged for the period 1985-1994 and the period 1995-2003. This resulted in two sets of data that could be compared to model outputs for the year 1990 (compared to the 85-94 averages) and model outputs for the year 2000 (compared to the 95-03 averages). While these comparisons are not strictly comparisons of simulated and observed calibration data for either model, they do provide a means of assessing the calibration success of both models using a common data set that is broadly representative of the data to which the models *were* calibrated. Note that, due to the averaging procedure and the designation of the two time periods, the number of sites that can be compared to model output is not 70 for either time period (i.e., not all sites had observed data in *both* time periods).

The PnET-BGC simulated values of CALK agreed well with the observed average values for both comparison periods, 1990 (Figure 4-15) and 2000 (Figure 4-16), over all sites modeled. MAGIC simulations of CALK were also in good agreement with observed data for the two time periods, 1990 (Figure 4-17) and 2000 (Figure 4-18), for all sites. For both models, the data cluster around the 1:1 line, indicating that both models simulated sites with high and low CALK

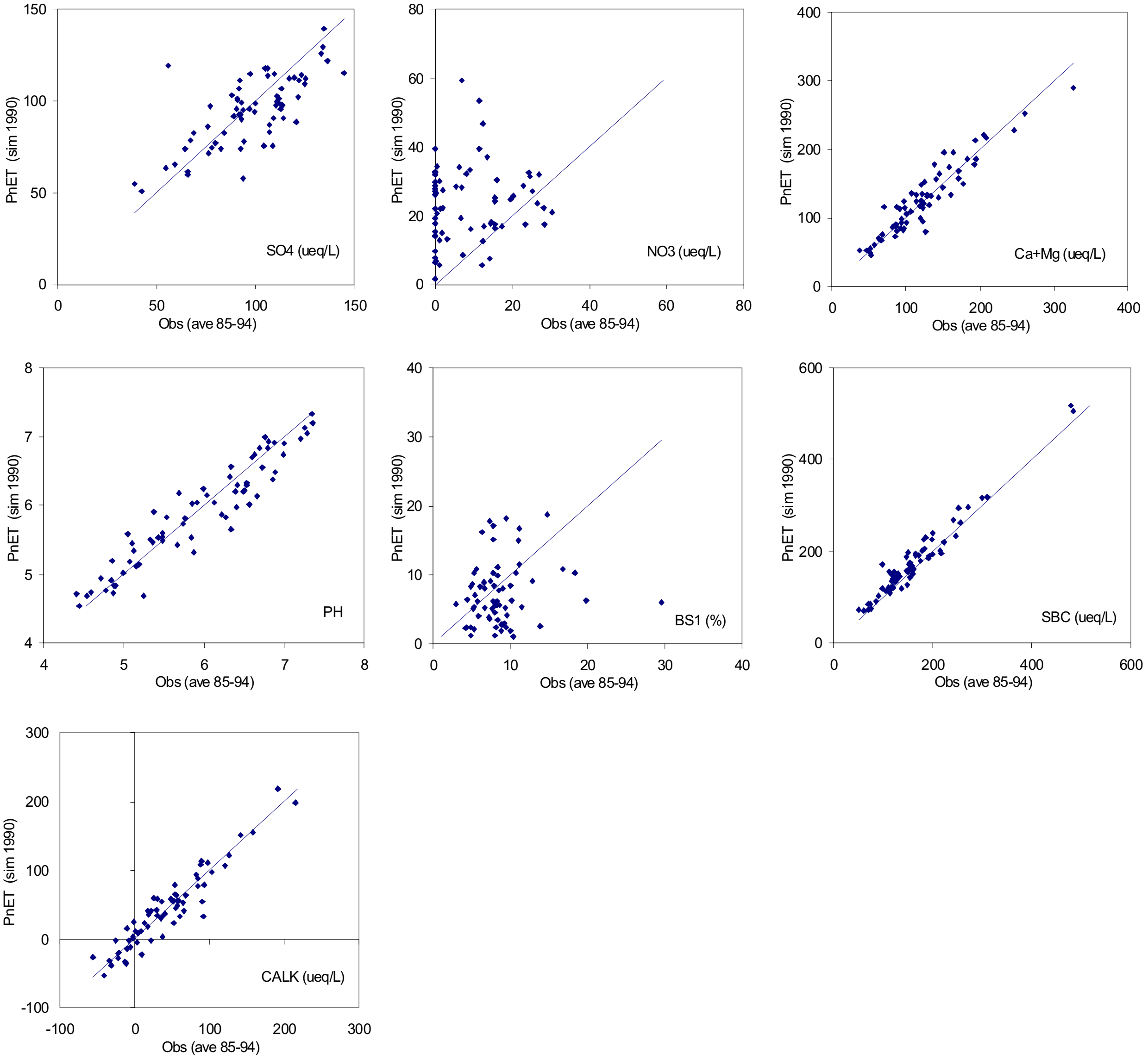


Figure 4-15. Comparison of 1990 values simulated by PnET-BGC with averages of observed values for the period 1985-1994 for several variables. The comparisons are presented for 69 sites. Simulated values from PnET-BGC are plotted on the Y-axes and average observed values are plotted on the X-axes of each panel. The upper three panels compare (from left to right) SO_4^{2-} concentrations, NO_3^- concentrations, and the sum of Ca^{2+} + Mg^{2+} concentrations (all in ueq/L). The middle three panels compare (from left to right) pH, soil B horizon % base saturation, and the sum of all base cations (SBC=Ca+Mg+Na+K; ueq/L). The lower panel compares CALK (ueq/L). The straight line in each panel is the 1:1 line.

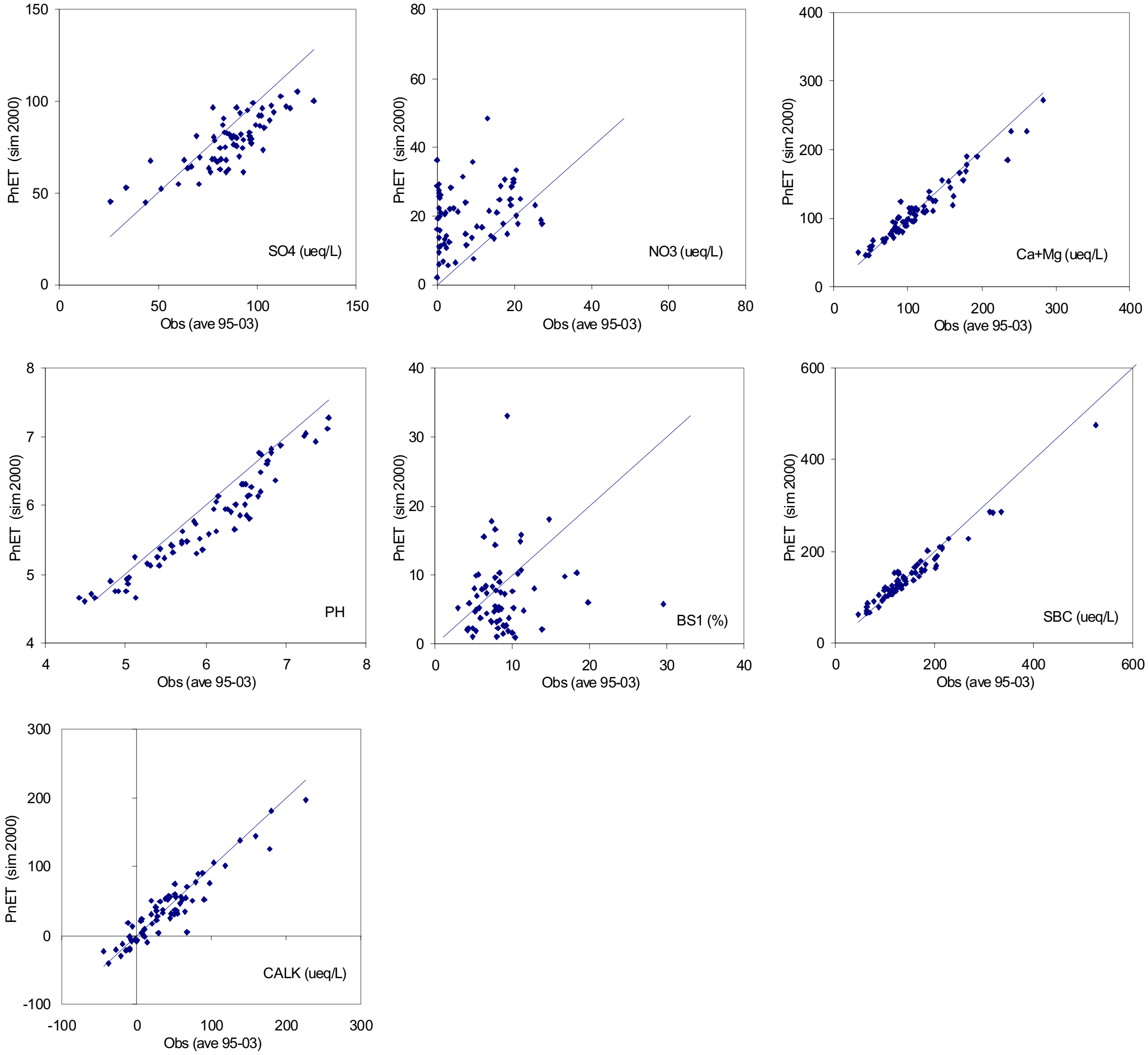


Figure 4-16. Comparison of 2000 values simulated by PnET-BGC with averages of observed values for the period 1995-2003 for several variables. The comparisons are presented for 67 sites. Simulated values from PnET-BGC are plotted on the Y-axes and average observed values are plotted on the X-axes of each panel. The upper three panels compare (from left to right) SO_4^{2-} concentrations, NO_3^- concentrations, and the sum of Ca^{2+} + Mg^{2+} concentrations (all in ueq/L). The middle three panels compare (from left to right) pH, soil B horizon % base saturation, and the sum of all base cations (SBC=Ca+Mg+Na+K; ueq/L). The lower panel compares CALK (ueq/L). The straight line in each panel is the 1:1 line.

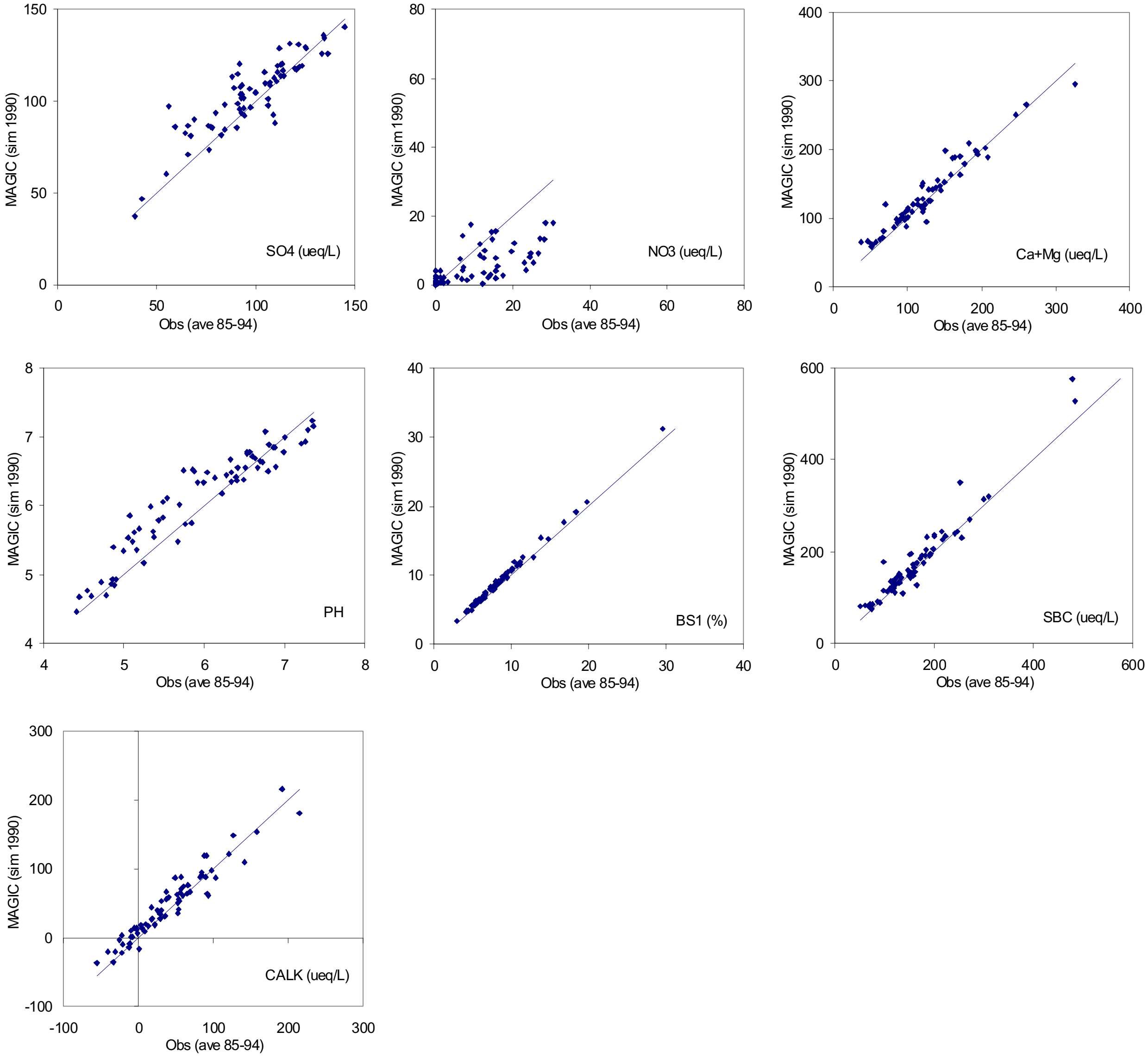


Figure 4-17. Comparison of 1990 values simulated by MAGIC with averages of observed values for the period 1985-1994 for several variables. The comparisons are presented for 69 sites. Simulated values from MAGIC are plotted on the Y-axes and average observed values are plotted on the X-axes of each panel. The upper three panels compare (from left to right) SO_4^{2-} concentrations, NO_3^- concentrations, and the sum of Ca^{2+} + Mg^{2+} concentrations (all in ueq/L). The middle three panels compare (from left to right) pH, soil B horizon % base saturation, and the sum of all base cations (SBC=Ca+Mg+Na+K; ueq/L). The lower panel compares CALK (ueq/L). The straight line in each panel is the 1:1 line.

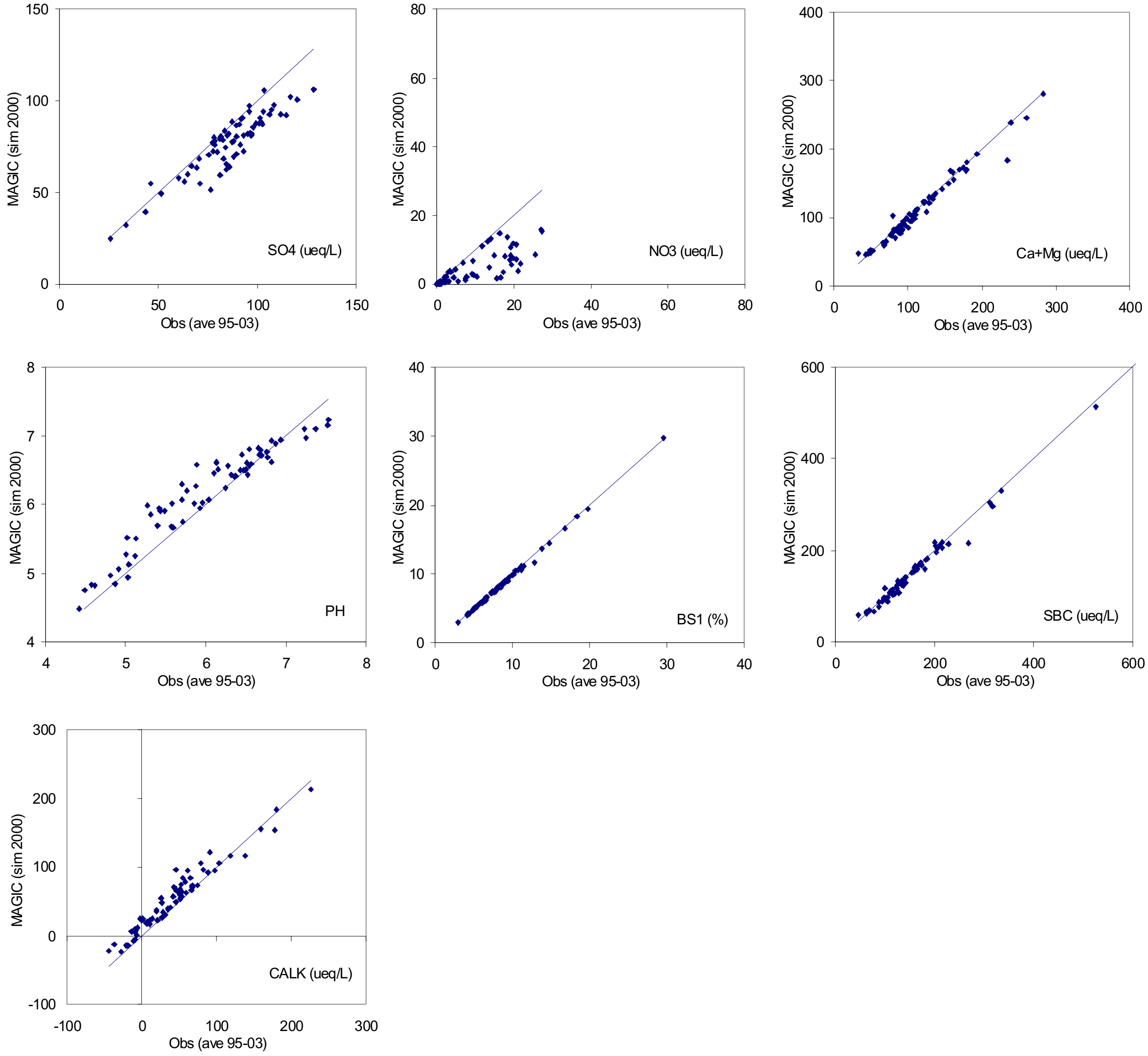


Figure 4-18. Comparison of 2000 values simulated by MAGIC with averages of observed values for the period 1995-2003 for several variables. The comparisons are presented for 67 sites. Simulated values from MAGIC are plotted on the Y-axes and average observed values are plotted on the X-axes of each panel. The upper three panels compare (from left to right) SO_4^{2-} concentrations, NO_3^- concentrations, and the sum of Ca^{2+} + Mg^{2+} concentrations (all in ueq/L). The middle three panels compare (from left to right) pH, soil B horizon % base saturation, and the sum of all base cations (SBC=Ca+Mg+Na+K; ueq/L). The lower panel compares CALK (ueq/L). The straight line in each panel is the 1:1 line.

values equally well, and that any biases in simulated CALK were negligible for both models. The comparisons for SO_4^{2-} and NO_3^- illustrate some basic differences in simulations between the two models. These differences in simulation response reflect the underlying differences in the model structures with respect to biological and geochemical processes that affect SO_4^{2-} and NO_3^- and model calibration, as discussed above. The MAGIC model tends to under-simulate NO_3^- in both 1990 and 2000 (Figures 4-17 and 4-18), while PnET-BGC tends to over-simulate NO_3^- in both years (Figures 4-15 and 4-16). Note, however, that the absolute magnitudes of these biases in the models are not very large (as compared to the range of CALK being simulated). With respect to SO_4^{2-}, the MAGIC model tends to over-simulate in 1990 and under-simulate in 2000 (Figures 4-17 and 4-18). PnET-BGC slightly under-simulates SO_4^{2-} for both periods (Figures 4-15 and 4-16) but the bias is negligible compared to the range of CALK across all sites being modeled. Note that there is considerable temporal variability in surface water NO_3^-. The EMAP data, which were generally sampled during the low flow summer period, do a poor job of representing annual volume-weighted concentrations which are simulated by the model. The slight biases detectable in both models in the two years may be due to the fact that year-to-year variability in deposition inputs are driving the model outputs away from the 10 year averages used for the observed data.

Comparisons of the SBC and the sum of Ca^{2+} + Mg^{2+} concentrations agreed well with observed data for both models for both periods of comparison (Figures 4-15 through 4-18). There are no indications of bias in either model with respect to these variables. This reflects the similarity of the processes affecting base cations in both model structures. The differences in B horizon soil base saturation comparisons to observed data (PnET-BGC Figures 4-15 and 4-16; MAGIC Figures 4-17 and 4-18) probably reflect differences in calibration procedures used in the two models.

4.2.1.2 Comparisons of the Outputs of the Models with Each Other

Direct MAGIC to PnET-BGC comparisons were made for 1850 (Figure 4-19; an estimate of pre-industrial conditions), for 1990 (Figure 4-20: the period of lowest CALK in the lakes), for 2000 (Figure 4-21; to supplement the comparisons in part 2a above), and for the year 2100 for each of the future deposition scenarios – Base (Figure 4-22), Moderate (Figure 4-23), and Aggressive (Figure 4-24). Comparisons are provided for the following variables (unless

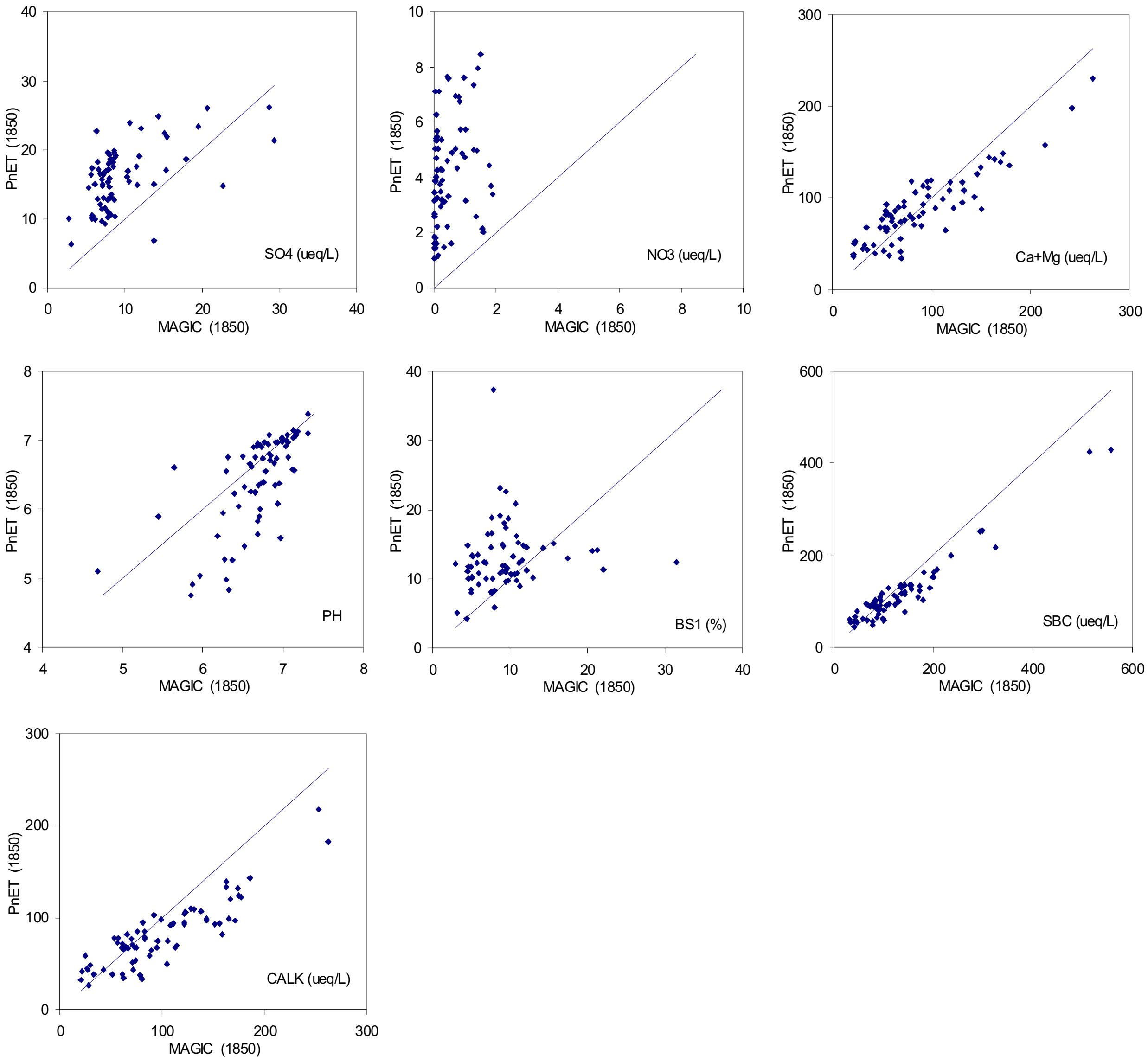


Figure 4-19. Comparison of 1850 simulated values for several variables for the two models. Simulated values from PnET-BGC are plotted on the Y-axes and simulated values from MAGIC are plotted on the X-axes of each panel. The upper three panels compare (from left to right) SO_4^{2-} concentrations, NO_3^- concentrations, and the sum of Ca^{2+} + Mg^{2+} concentrations (all in ueq/L). The middle three panels compare (from left to right) pH, soil B horizon % base saturation, and the sum of all base cations (SBC=Ca+Mg+Na+K; ueq/L). The lower panel compares CALK (ueq/L). The straight line in each panel is the 1:1 line.

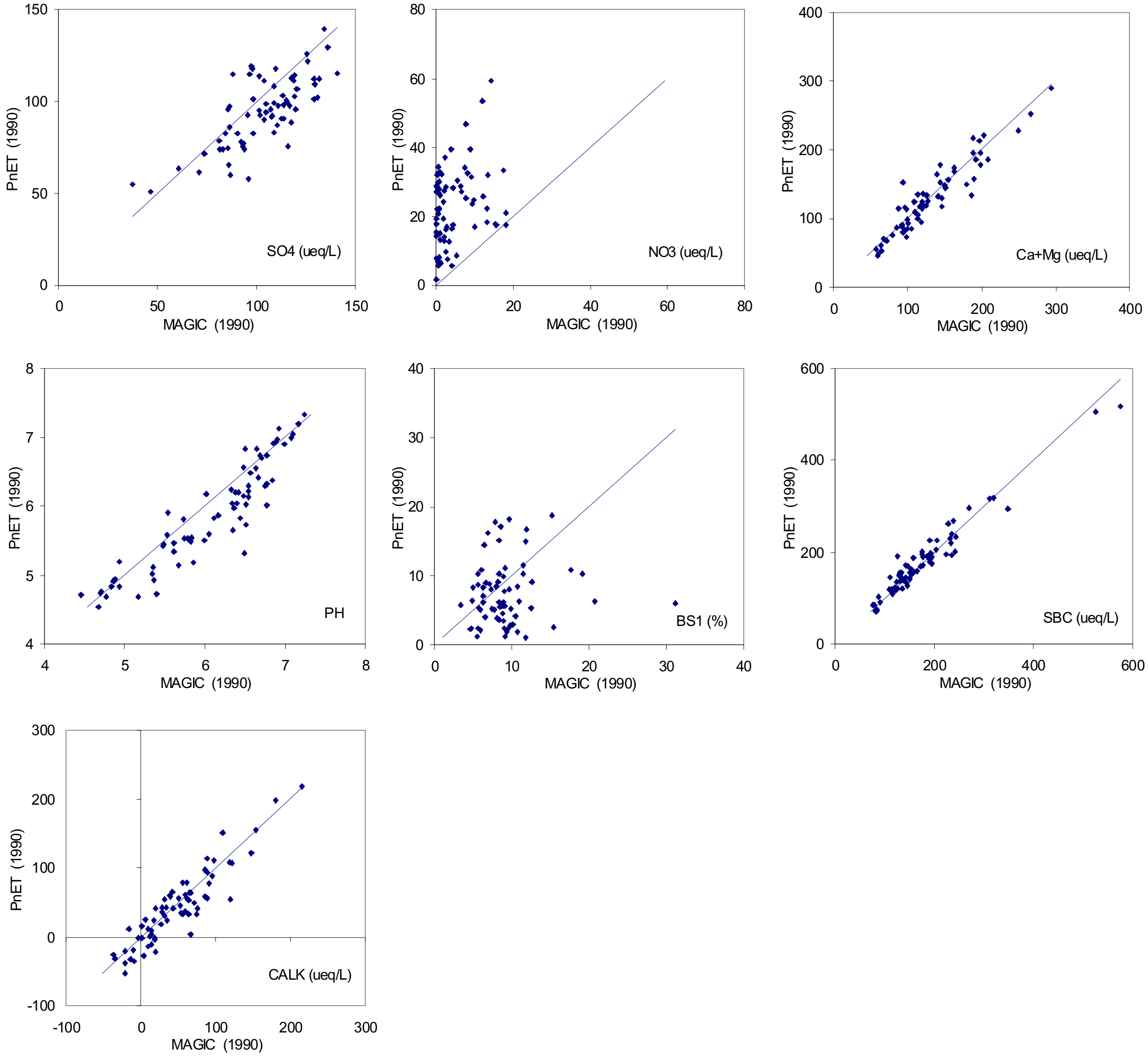


Figure 4-20. Comparison of 1990 simulated values for several variables for the two models. Simulated values from PnET-BGC are plotted on the Y-axes and simulated values from MAGIC are plotted on the X-axes of each panel. The upper three panels compare (from left to right) SO_4^{2-} concentrations, NO_3^- concentrations, and the sum of Ca^{2+} + Mg^{2+} concentrations (all in ueq/L). The middle three panels compare (from left to right) pH, soil B horizon % base saturation, and the sum of all base cations (SBC=Ca+Mg+Na+K; ueq/L). The lower panel compares CALK (ueq/L). The straight line in each panel is the 1:1 line.

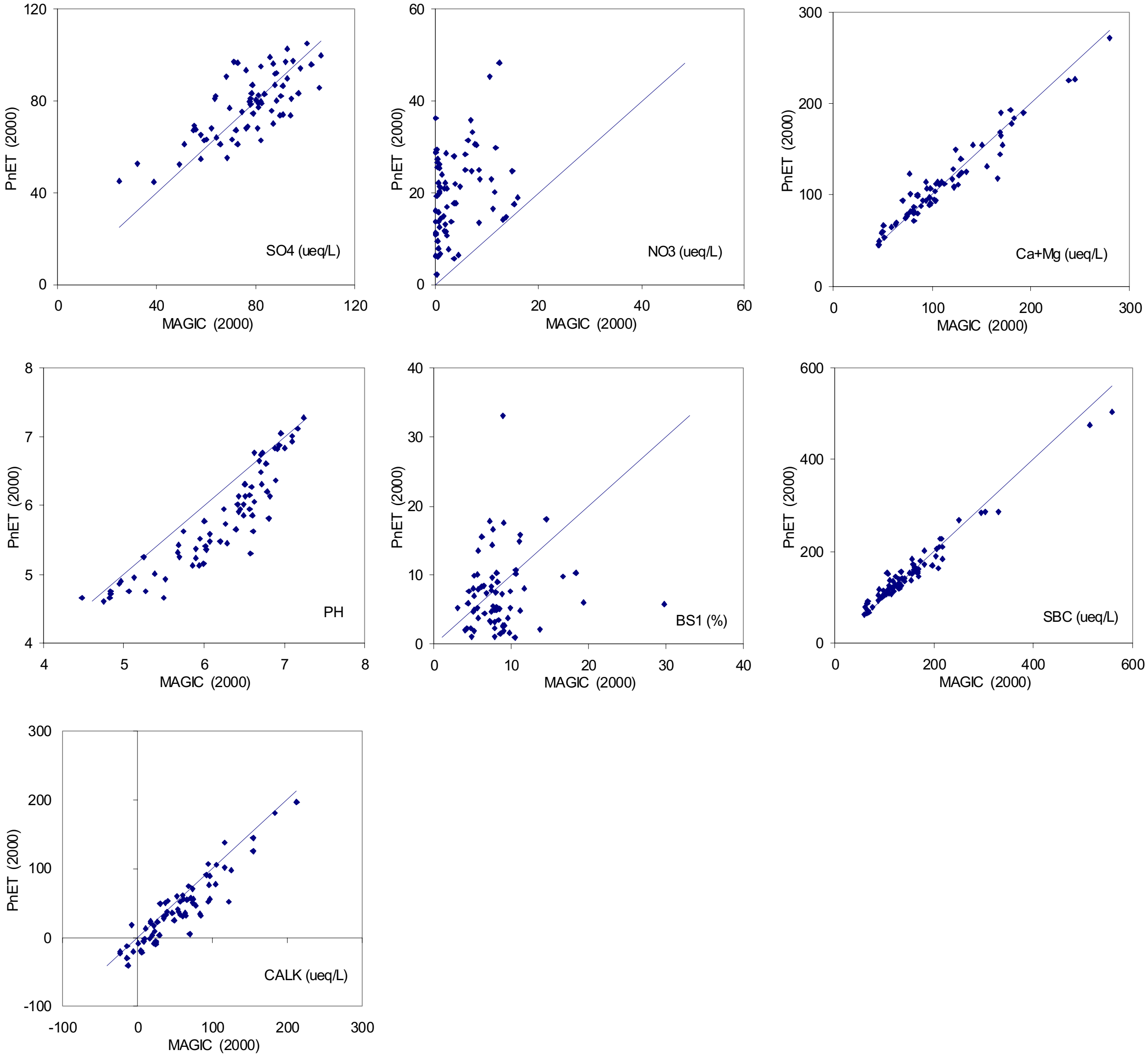


Figure 4-21. Comparison of 2000 simulated values for several variables for the two models. Simulated values from PnET-BGC are plotted on the Y-axes and simulated values from MAGIC are plotted on the X-axes of each panel. The upper three panels compare (from left to right) SO_4^{2-} concentrations, NO_3^- concentrations, and the sum of Ca^{2+} + Mg^{2+} concentrations (all in ueq/L). The middle three panels compare (from left to right) pH, soil B horizon % base saturation, and the sum of all base cations (SBC=Ca+Mg+Na+K; ueq/L). The lower panel compares CALK (ueq/L). The straight line in each panel is the 1:1 line.

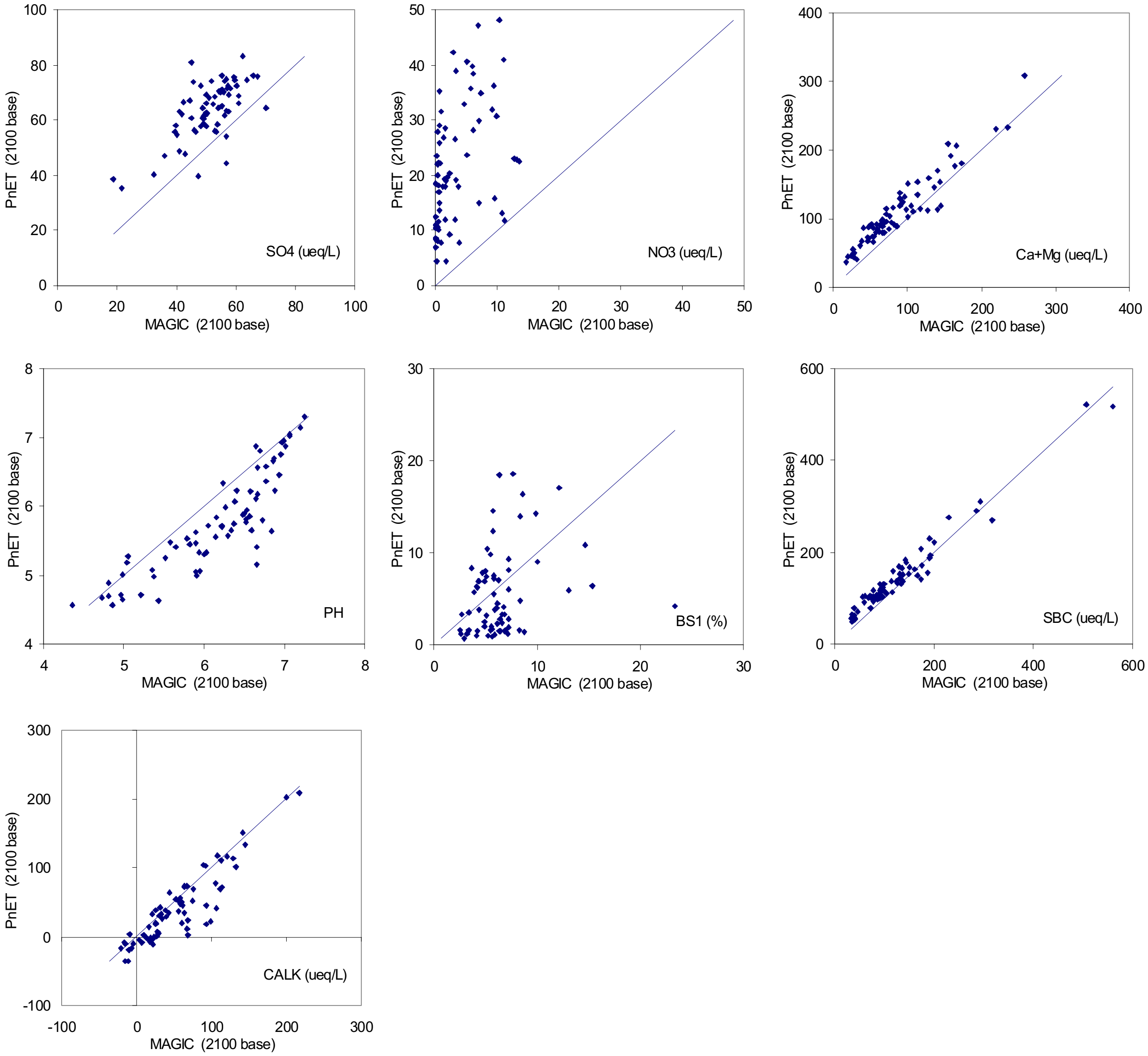


Figure 4-22. Comparison of 2100 simulated values for several variables for the two models for the Base Case future deposition scenario. Simulated values from PnET-BGC are plotted on the Y-axes and simulated values from MAGIC are plotted on the X-axes of each panel. The upper three panels compare (from left to right) SO_4^{2-} concentrations, NO_3^- concentrations, and the sum of Ca^{2+} + Mg^{2+} concentrations (all in ueq/L). The middle three panels compare (from left to right) pH, soil B horizon % base saturation, and the sum of all base cations (SBC=Ca+Mg+Na+K; ueq/L). The lower panel compares CALK (ueq/L). The straight line in each panel is the 1:1 line.

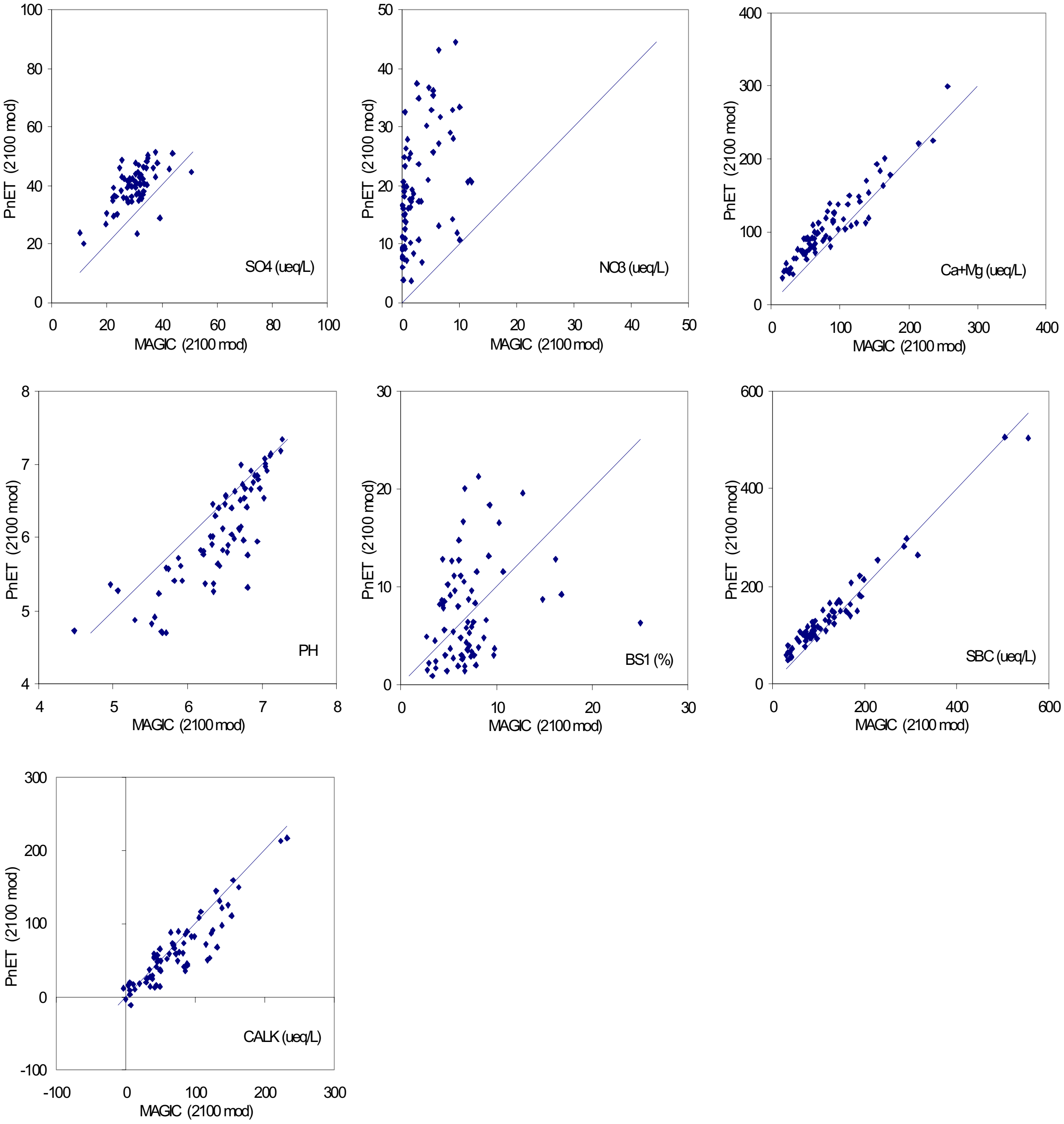


Figure 4-23. Comparison of 2100 simulated values for several variables for the two models for the moderate future deposition scenario. Simulated values from PnET-BGC are plotted on the Y-axes and simulated values from MAGIC are plotted on the X-axes of each panel. The upper three panels compare (from left to right) SO_4^{2-} concentrations, NO_3^- concentrations, and the sum of Ca^{2+} + Mg^{2+} concentrations (all in ueq/L). The middle three panels compare (from left to right) pH, soil B horizon % base saturation, and the sum of all base cations (SBC=Ca+Mg+Na+K; ueq/L). The lower panel compares CALK (ueq/L). The straight line in each panel is the 1:1 line.

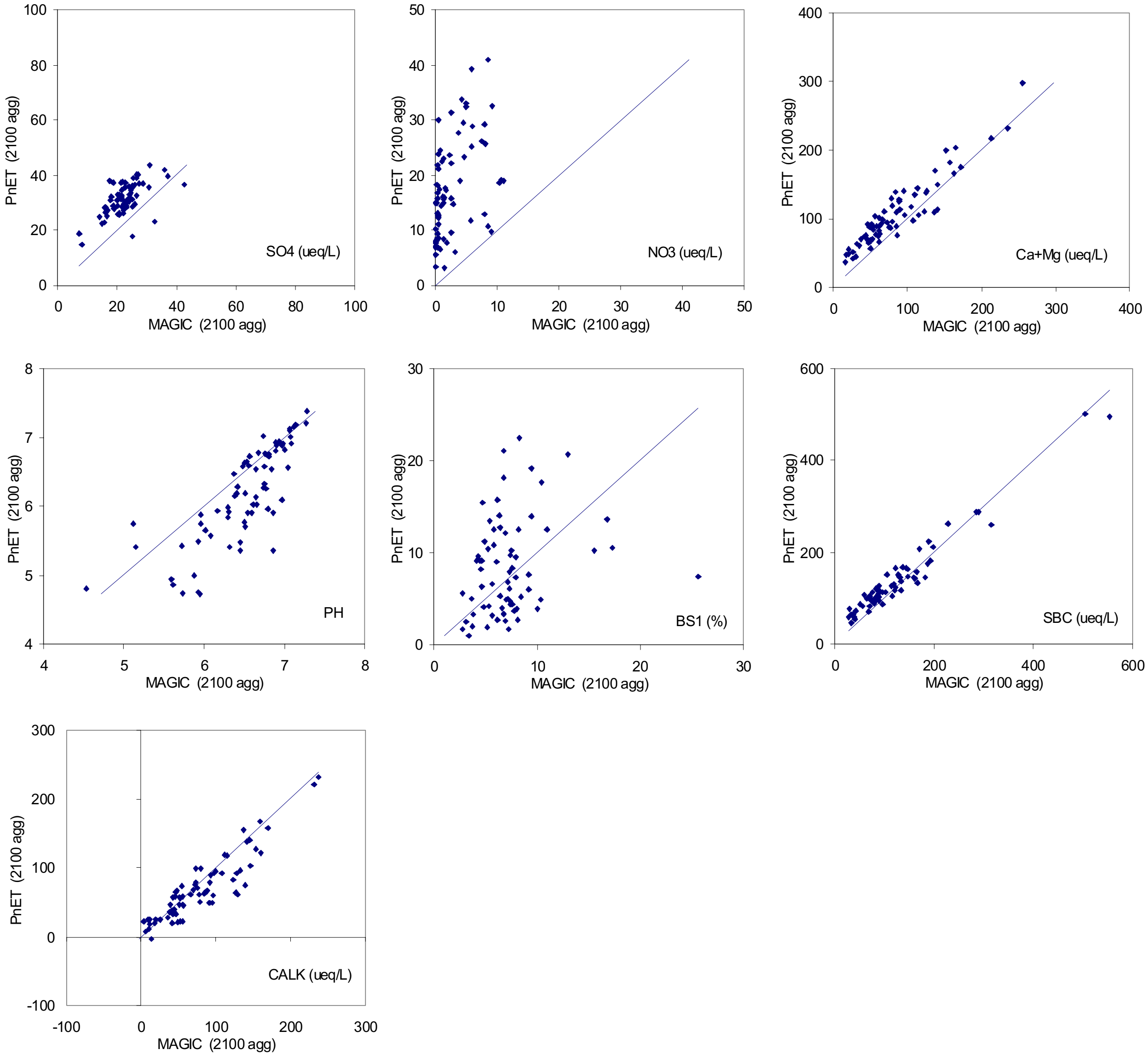


Figure 4-24. Comparison of 2100 simulated values for several variables for the two models for the aggressive future deposition scenario. Simulated values from PnET-BGC are plotted on the Y-axes and simulated values from MAGIC are plotted on the X-axes of each panel. The upper three panels compare (from left to right) SO_4^{2-} concentrations, NO_3^- concentrations, and the sum of $Ca^{2+} + Mg^{2+}$ concentrations (all in ueq/L). The middle three panels compare (from left to right) pH, soil B horizon % base saturation, and the sum of all base cations (SBC=Ca+Mg+Na+K; ueq/L). The lower panel compares CALK (ueq/L). The straight line in each panel is the 1:1 line.

specified otherwise): SO_4^{2-}, NO_3^-, Ca^{2+} + Mg^{2+}, SBC, pH and CALK concentrations in the lakes, and % BS of the soil B horizon.

The PnET-BGC and MAGIC simulations of CALK were generally unbiased (relative to each other) for the 1990 (Figure 4-20) and 2000 (Figure 4-21) comparisons. There was some indication that MAGIC-simulated CALK was slightly lower than PnET-BGC-simulated CALK for these years, but only for a few of the sites modeled. Greater differences in simulated CALK between the two models were apparent in the comparison of the 1850 values (Figure 4-19) which probably reflects differences in the calibration procedures for the two models. In general, PnET-BGC estimates of historical CALK were lower at all sites than MAGIC estimates of historical CALK. These differences in simulated CALK between the two models were also apparent in the simulations for the year 2100 provided for all three future scenarios (Figures 4-22 through 4-24). As the simulations reflect chemical recovery from acidification, the PnET-BGC estimates of future CALK are generally lower at all sites than the MAGIC estimates. Given the initial differences in the model estimates of CALK in 1850, this bias in 2100 is to be expected. The models are both simulating a return to a CALK level that approaches a partial recovery of historical conditions as deposition declines.

Differences in simulations of SO_4^{2-} and NO_3^- are apparent for all years compared (Figures 4-19 through 4-24). The general pattern is one of higher simulated NO_3^- by PnET-BGC (relative to MAGIC) and higher simulated SO_4^{2-} by MAGIC (relative to PnET-BGC). These differences arise from underlying differences in the model structures with regard to processes affecting SO_4^{2-} and NO_3^-, as discussed above. Note, however, that these biases are not large compared to the range of CALK values across all sites, and, in addition, the directions of the biases tend to cancel each other with respect to CALK. Base cation concentrations (both SBC and Ca^{2+} +Mg^{2+}) are similar between the models for all years. The differences in B horizon soil % BS are due to differences in calibration procedures and persist in all years compared.

4.2.2 Comparison of CDFs for Results from the Two Models

In addition to the previous analyses to compare results from MAGIC and PnET-BGC on a lake by lake basis, we also determined simulated cumulative distribution functions (CDFs) for the population of Adirondack lakes for different years of the simulations (Figure 4-25). The model projections for lake and soil chemistry for the EMAP population of lakes were generally in good agreement for 1990, due to the fact that this is near the period when data were available for model

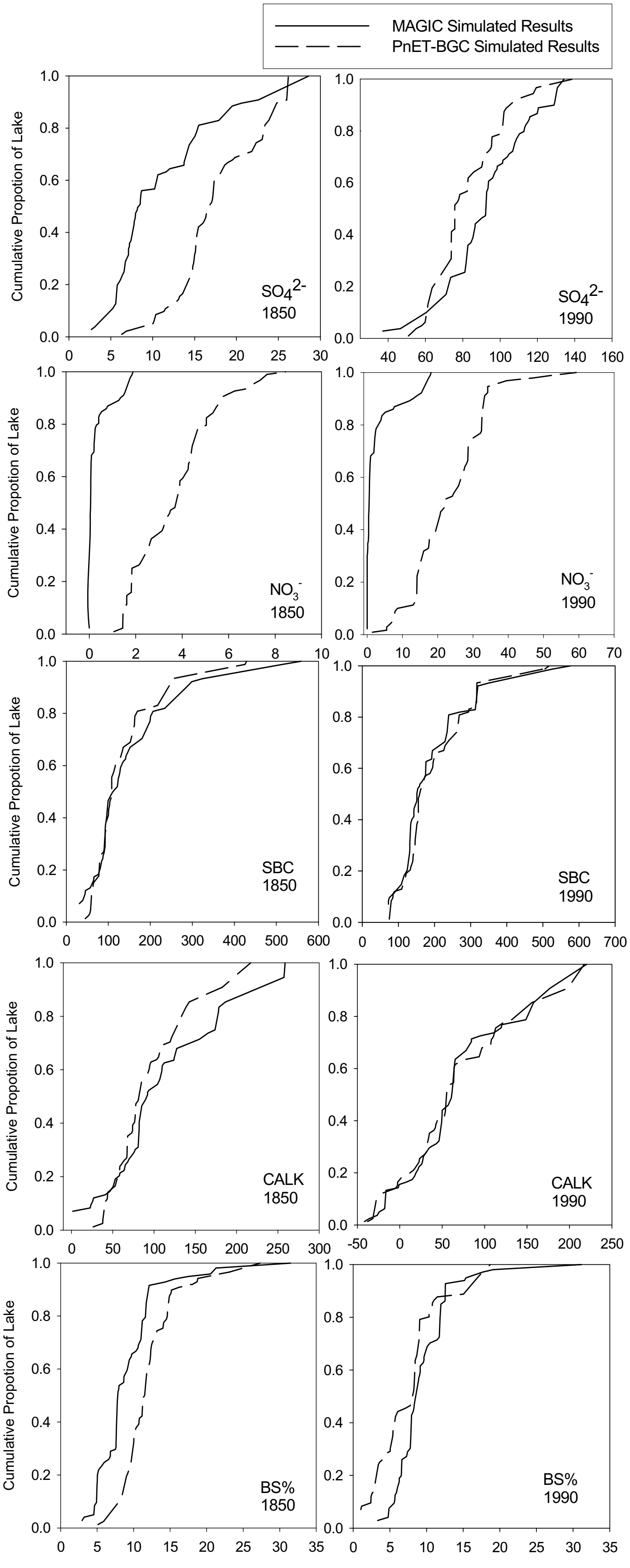


Figure 4-25. Cumulative distribution functions of selected major ions (μeq/L), calculated ANC of lakewater (μeq/L), and B horizon soil % base saturation for the MAGIC and PnET-BGC models. Results are shown for 1850 (left side) and for 1990 (right side).

calibration. There were some differences in model population-level predictions of SO_4^{2-} and large differences in NO_3^- for 1990, but these differences were largely due to structural differences in the two models and in the manner in which the models were calibrated for these elements (see discussion above). The models show very good agreement for population-level projections for the sum of base cations (SBC) and CALK. For the model hindcasts (e.g., 1850), model discrepancies for SO_4^{2-} and NO_3^- persist. Despite these differences, the model hindcasts of population-level projections of CALK and SBC showed good agreement. While there were differences for some variables (i.e., MAGIC showed greater soil acidification) and clear lake-to-lake differences, this analysis suggests that the population-level projections with both models represent robust indicators of the extent and magnitude of changes in lake chemistry associated with historical inputs of acidic deposition. The differences observed in the nature of acidification between the two models may again be linked to model structural differences. In MAGIC, soil water is assumed to be in equilibrium with an aluminum trihydroxide mineral at all times (Cosby et al. 1985a,b,c). Inputs of strong acids, therefore, drive the mobilization of Al. This Al strongly displaces exchangeable base cations from the soil exchange complex. In PnET-BGC, the soil-phase is in equilibrium only when solutions are oversaturated with the aluminum trihydroxide solid phase. As a result, there is less Al available in PnET-BGC to displace exchangeable soil base cations and greater acidification of the solution is realized.

These patterns of population-level estimates of lake water and soil chemistry were also evident in the future projections (Figure 4-26). There were some differences in model forecasts of SO_4^{2-} and NO_3^- concentrations, but population-level model projections of SBC, CALK and B horizon soil % BS were similar. This analysis suggests that although there are some differences in model structure and calibration approach, a model of moderate complexity (i.e., MAGIC) and a model of somewhat greater complexity (i.e., PnET-BGC) show similar population-level projections of changes in soil and lake chemistry in response to changes in acidic deposition. This result is encouraging, especially if model projections are to be used as a basis for formulating public policy.

4.2.3 Comparisons of the Historical and Future Changes in Simulated CALK

We also compared and evaluated the response of the models to factors that drive historical and future change in CALK. We begin this section by presenting summary plots (Figure 4-27) showing comparisons of simulated CALK from PnET-BGC and MAGIC for 1850 (an estimate of

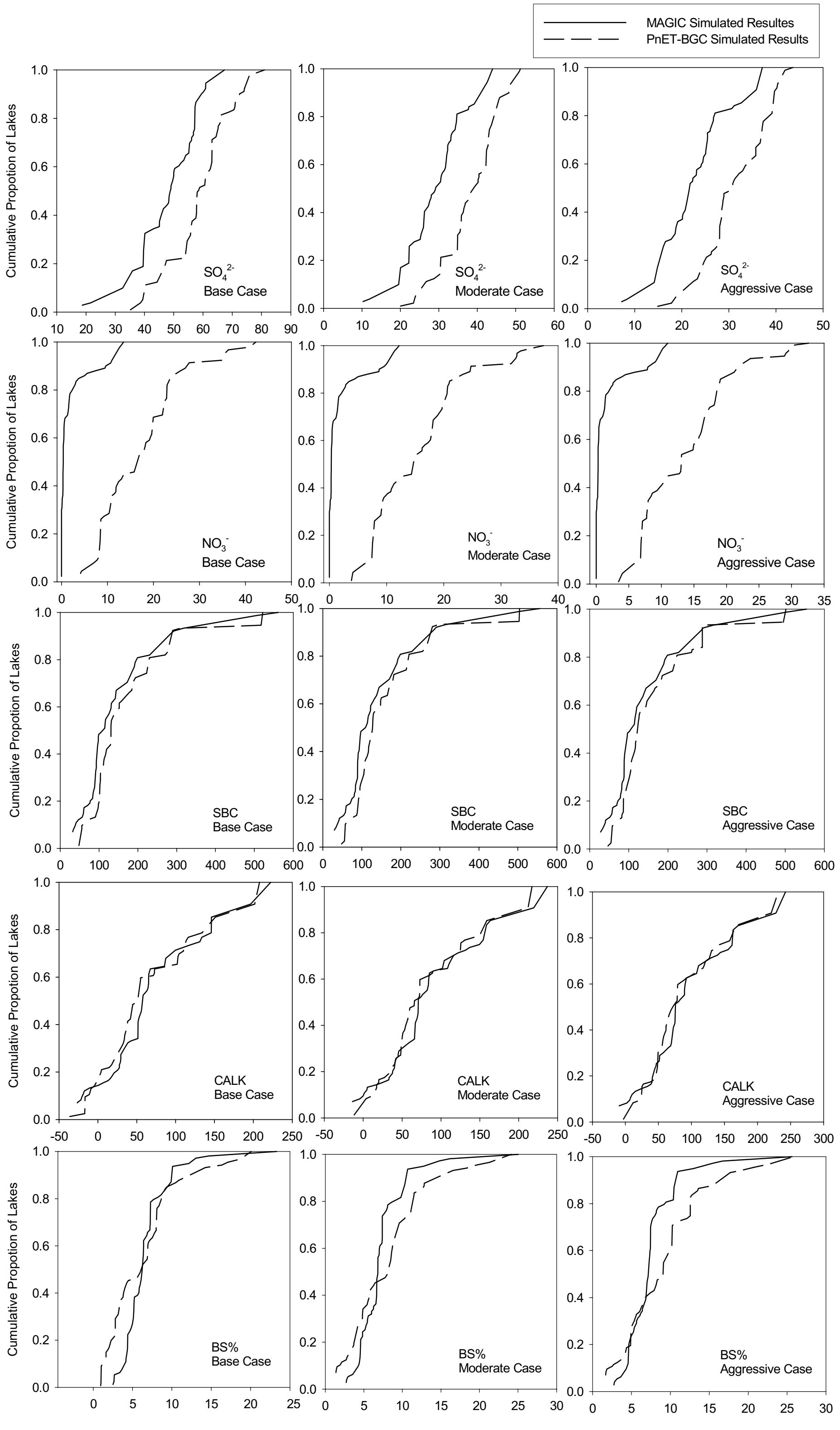


Figure 4-26. Cumulative distribution functions of selected major ions and calculated ANC of lakewater (μeq/L) and of soil B horizon % base saturation for the MAGIC and PnET-BGC models. Results are shown for 2100 under the three scenarios of emissions control.

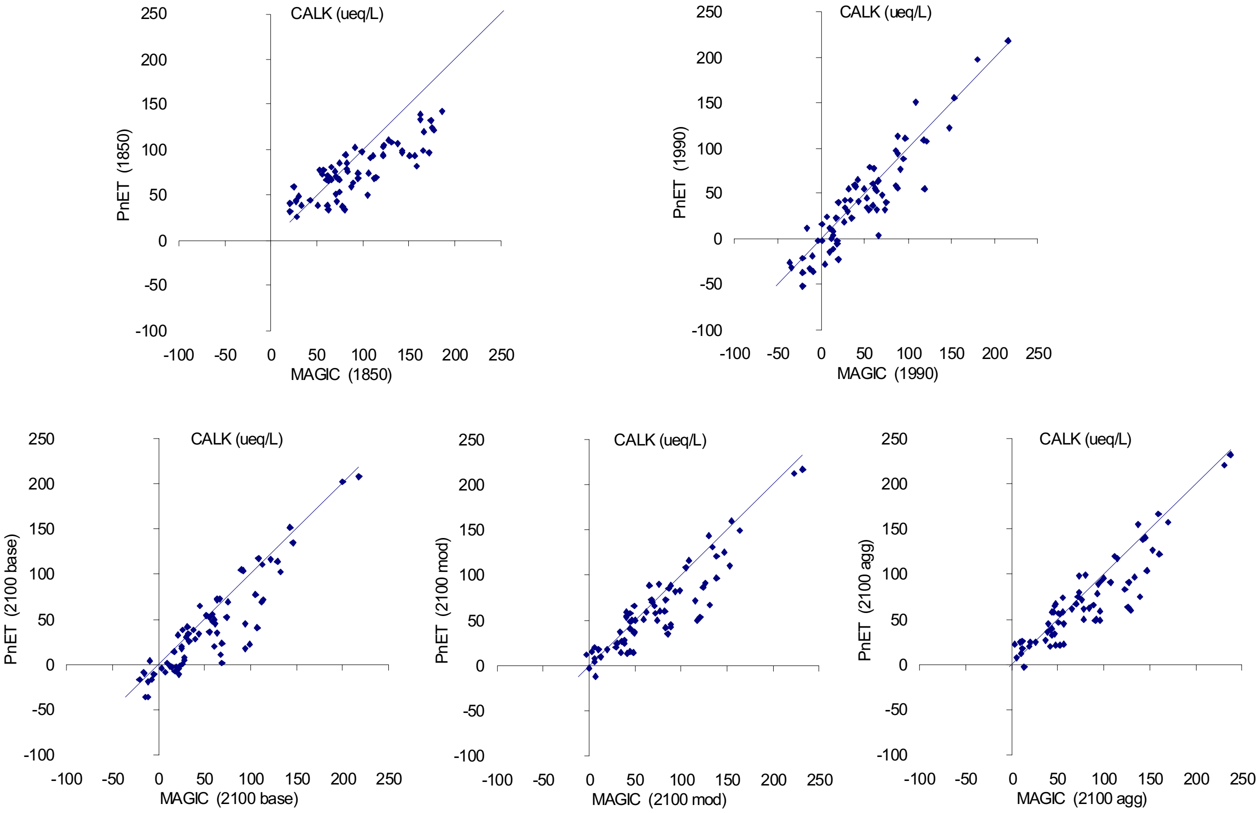


Figure 4-27. Comparison of simulated values of CALK (ueq/L) for the two models. Simulated values from PnET-BGC are plotted on the Y-axes and simulated values from MAGIC are plotted on the X-axes of each panel. The upper left panel compares simulated pre-industrial CALK. The upper right panel compares simulated CALK for 1990 (these are the data used to calibrate the models). The lower three panels compare simulated CALK in the year 2100 for the three different future deposition scenarios (lower left = "Base"; lower center = "Moderate"; lower right = "Aggressive").

pre-industrial conditions), for 1990 (the period of approximate lowest CALK in the lakes), and for 2100 for each of the future deposition scenarios – Base, Moderate, and Aggressive. With these comparisons of simulated CALK between the two models in mind, we turn to an analysis of the factors that apparently affect simulated changes in CALK for each model.

Not surprisingly, the models showed a strong response of changes in CALK to long-term changes in atmospheric S deposition, as reflected by S deposition in 1990 (Figure 4-28). While both models showed a qualitatively similar response, the correlations between simulated CALK change (decrease in hindcast and increase in forecast simulations) and changing atmospheric S deposition was somewhat greater for MAGIC than PnET-BGC.

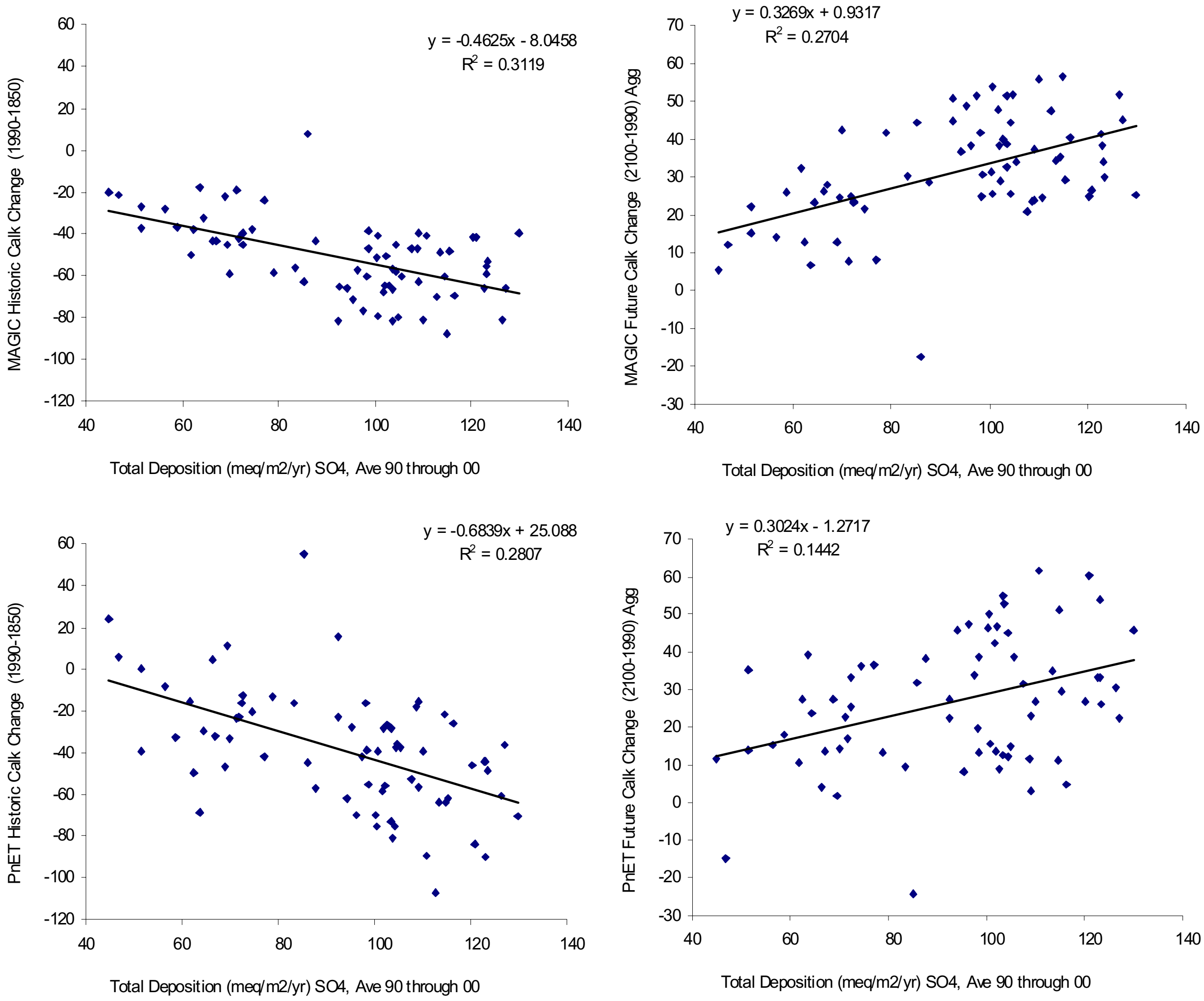


Figure 4-28. *Left:* Model estimates of historical change in CALK from 1850 to 1990 (negative changes imply acidification since pre-industrial times) versus average estimated S deposition for 1990-2000 to the midpoint of each study watershed (MAGIC projections are given in upper left panel and PnET-BGC projections are given in lower left). *Right:* Simulated changes in lakewater CALK from 1990 to 2100 under the Aggressive Additional Emissions Controls scenario versus average estimated S deposition for 1990-2000 to the midpoint of each study watershed (MAGIC projections are given in upper right panel and PnET-BGC projections in lower right).

Note that three of the modeled EMAP lakes exhibited historical increases in CALK and future decreases in CALK in simulations with PnET-BGC. These responses are consistent with the alkalization hypothesis advanced by Kilham (1982). All three lakes are characterized by relatively long hydraulic residence times and relatively high CALK values. Following increases in atmospheric S and NO_3^- deposition, a nearly stoichiometric release of base cations was simulated in the upland watersheds of these lakes in response to increases in drainage water concentrations of SO_4^{2-} and NO_3^-. Subsequently, retention of some of these strong acid anions in wetlands and the lakes resulted in simulated net production of CALK. This process would be expected to reverse under future decreases in atmospheric deposition.

We also examined the model calculated change in CALK as a function of the average simulated CALK in 1990 and 2000 (Figure 4-29). PnET-BGC showed a strong dependence of change in CALK on the CALK simulated in 1990, while MAGIC did not. For PnET-BGC, this pattern is consistent with the idea that the largest extent of historical acidification and subsequent recovery occurs in lakes with the lowest CALK. This pattern is similar to the results of paleoecological studies of historical acidification (Sullivan et al. 1990) and synoptic resurveys of lake chemistry to assess recovery (Warby et al. 2005) in the Adirondacks. These differences in response between the two models are likely due to differences in the way they are calibrated, as the models have similar structure regarding cation exchange and weathering.

Whereas the simulated changes in historical and future CALK differ between the models, the simulated changes in CALK for the period when both models were being constrained by observed data (1990-2000) were similar (Figure 4-30). This result and the comparisons discussed in the paragraph above are consistent with the expectation that the model outputs should be similar (despite structural differences between the models) during the period to which the models are calibrated, and that the effects of structural differences between the models should become more pronounced as the simulations move away from the calibration periods.

Finally, both models showed similar changes in historical and future CALK as a function of simulated soil B horizon % base saturation (Figure 4-31). Both models suggest that historical acidification has been greater (and future recovery will be greater) for sites with lower current B horizon soil % base saturation. This pattern was weak for both models, but slightly more pronounced for PnET-BGC than for MAGIC.

Overall, the two models produced very different results on a lake-by-lake basis. They also differed substantially in their representation of N dynamics. Nevertheless, population level projections of historical acidification and future changes in ANC in response to various levels of emissions control were generally in good agreement.

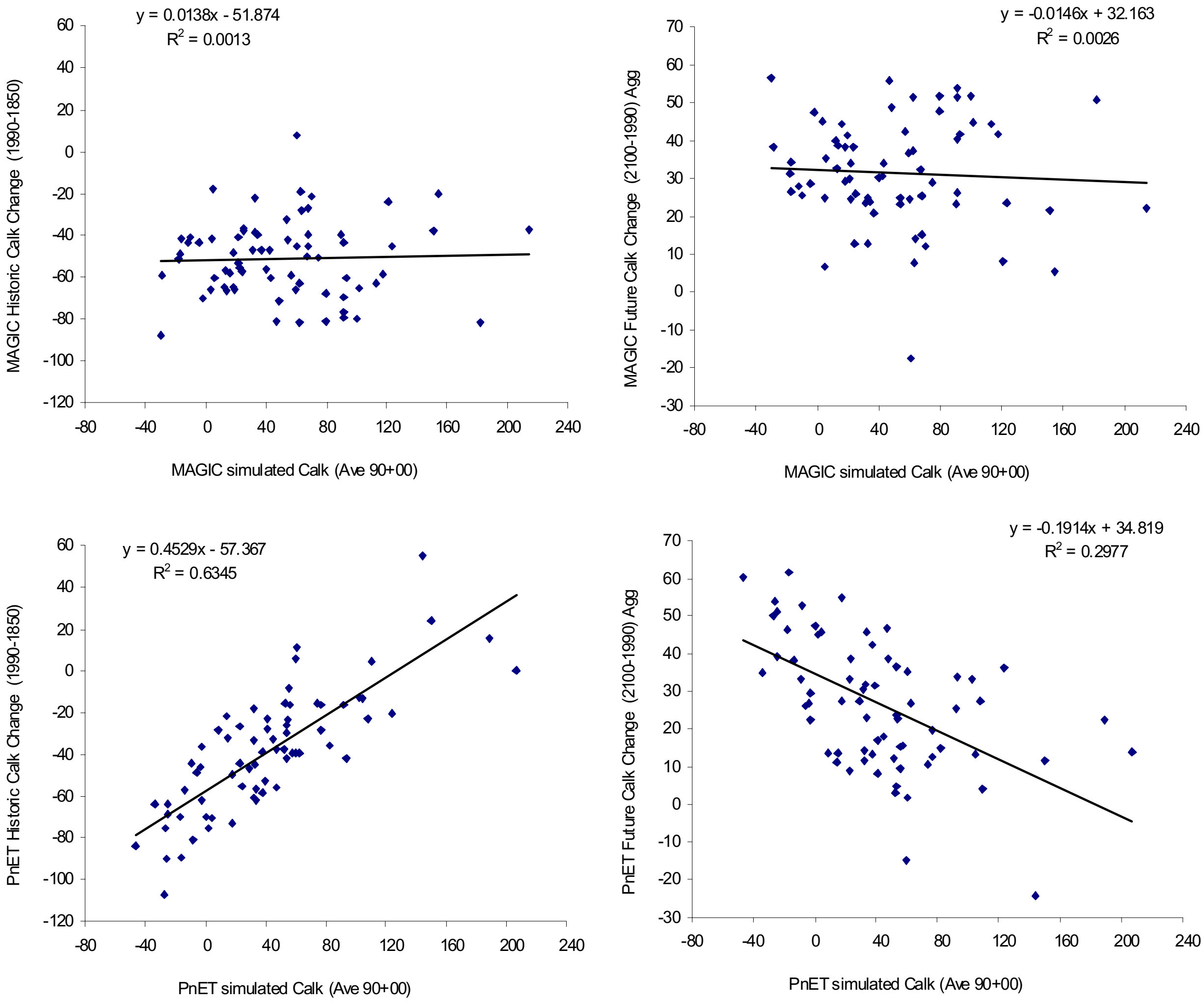


Figure 4-29. *Left:* Model estimates of historical change in CALK from 1850 to 1990 (negative changes imply acidification) versus simulated CALK (average of 1990 and 2000 values). MAGIC projections are given in upper left panel and PnET-BGC projections are given in lower left. *Right:* Simulated changes in lakewater CALK from 1990 (approximate period of lowest CALK) to 2100 under the Aggressive Additional Emissions Controls scenario versus simulated CALK (average of 1990 and 2000 values). MAGIC projections are given in upper right panel and PnET-BGC projections in lower right.

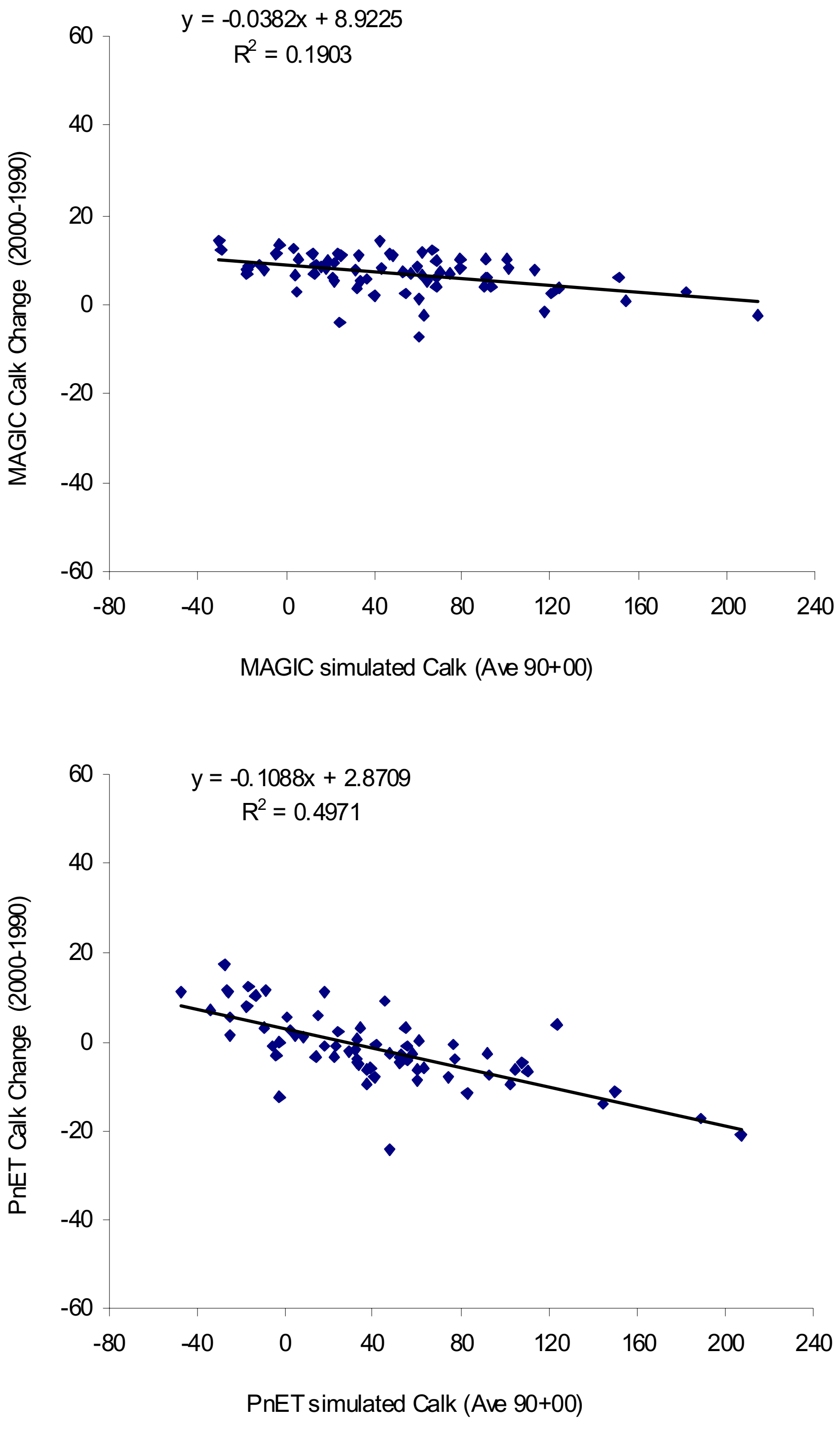


Figure 4-30. Model estimates of change in CALK from 1990 to 2000 (negative changes imply continuing acidification) versus simulated CALK (average of 1990 and 2000). MAGIC projections are given in the upper panel and PnET-BGC projections are given in the lower panel.

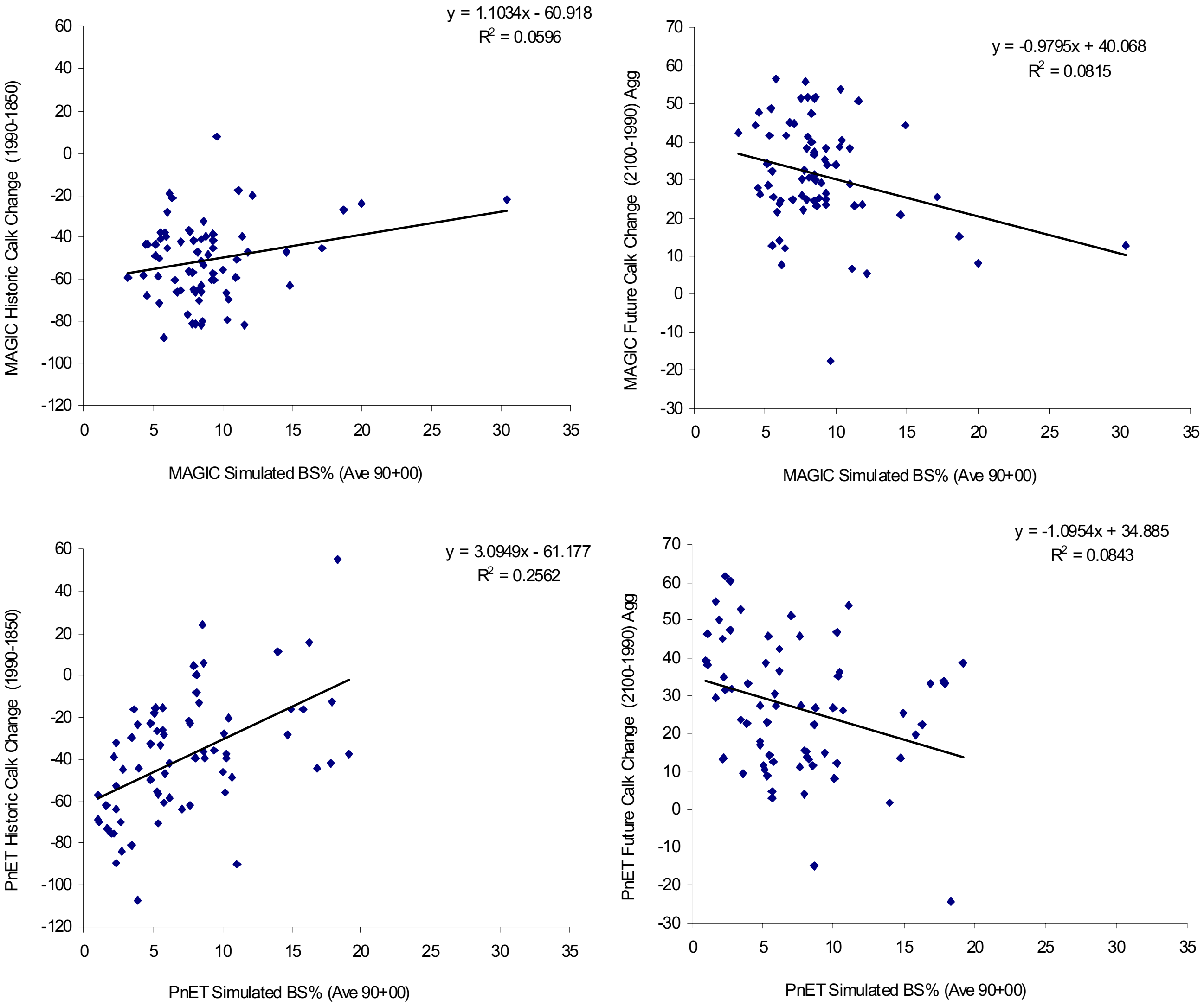


Figure 4-31. *Left*: Model estimates of historical change in CALK from 1850 to 1990 (negative changes imply acidification) versus simulated B horizon soil % BS (average of 1990 and 2000 values). MAGIC projections are given in upper left panel and PnET-BGC projections are given in lower left. *Right*: Simulated changes in lakewater CALK from 1990 (approximate period of lowest CALK) to 2100 under the Aggressive Additional Emissions Controls scenario versus simulated B horizon soil % BS (average of 1990 and 2000 values). MAGIC projections are given in upper right panel and PnET-BGC projections in lower right.

4.3 Representativeness of Long-Term Monitoring Lakes

In the sentinel-site approach to monitoring environmental systems, as has been adopted by ALTM and AEAP, a relatively small number of sites is subjected to intensive study. Intensive monitoring can result in development of an understanding of the nature of variability at the monitored sites and the cause-effect relationships that operate over the time scale of monitoring. Nevertheless, the efficacy of the location as a sentinel site rests on our ability to generalize to the broader class of systems (Jassby 1998).

Chemical monitoring data collected within the long term monitoring ALTM and AEAP programs provide important information regarding the aquatic resources that have been most impacted by acidic deposition, and the spatial and temporal patterns of recovery as atmospheric sulfur deposition continues to decline (Driscoll et al. 2003). However, there was previously not a mechanism available with which to extrapolate results of ALTM studies to the regional population of Adirondack lakes, and this limited the ultimate utility of these important data. Resource managers and policymakers need to know the extent to which current and projected future emissions reductions are leading, and will continue to lead, to ecosystem recovery for the population of Adirondack lakes, not just those that are the focus of intensive study. Such recovery is being quantified at these monitoring site locations, but could not previously be directly linked to the regional situation. Regional knowledge will provide a stronger basis for setting emissions reduction goals, evaluating incremental improvements, and conducting cost/benefit analyses.

The relationship between each of the modeled ALTM/AEAP lakes and the overall lake population was determined with respect to current chemistry, past acidification, and future chemical recovery, based on both the MAGIC and PnET-BGC model simulations. Results of this analysis are summarized in Tables 4-3 and 4-4 for each lake. These model estimates allow evaluation of each ALTM/AEAP monitoring lake to determine the number and percentage of lakes in the population that are more or less acid-sensitive than each individual intensively-studied lake. This will allow researchers to place lake-specific monitoring and research results into the context of the overall population. For example, we can address such questions as: How many Adirondack lakes will improve their acid-base chemistry more than Lake X in response to future emissions controls?

Table 4-3. Modeled relationship between each of the studied ALTM/AEAP lakes and the population of Adirondack lakes with respect to acid-base chemistry status, acidification, and recovery responses, based on MAGIC model simulations.

ALTM Lake		Estimated Percentage of Lakes in the Population Having:			
Name	ID	Lower 2000 ANC	Greater Historical Acidification (1850 to 1990)	Greater ANC Recovery Under Base Case Scenario (1990 to 2050)	Lower 2050 ANC Under Base Case Scenario
Willys Lake	40210	1.2	1.3	1	8.3
Squash Pond	40754	2.4	46.6	25.4	0
Carry Pond	50669	13.3	46.6	49	12
Round Pond	040731A	13.3	40.1	26.4	13.3
Jockeybush Lake	50259	13.3	11.1	12.3	14.5
Indian Lake	40852	14.5	46.6	45.5	14.5
Brook Trout Lake	40874	14.5	12.1	12.3	15.5
South Lake	41004	15.5	15.5	18.8	15.5
Big Moose Lake	40752	16.4	13.3	14.7	17.4
Queer Lake	60329	16.4	11.1	18.8	17.4
Middle Settlement Lake	40704	16.4	21.5	14.7	18.4
Long Pond	50649	16.4	46.6	45.5	17.4
North Lake	41007	17.4	26.7	34	18.4
G Lake	70859	17.4	31	28.6	18.4
Dart Lake	40750	17.4	13.3	18.8	19.6
Constable Pond	40777	18.4	12.1	15.9	20.8
Squaw Lake	40850	22.1	34.5	60	19.6
West Pond	40753	24	49.9	50	20.8
Limekiln Lake	40826	27.3	15.5	26.4	30.1
Grass Pond	40706	30.2	11.1	12.3	44
Helldiver Pond	40877	35	38.8	79.7	33.1
Lake Rondaxe	40739	47.8	13.3	19.8	59
Cascade Lake	40747	47.8	6.7	6.9	63.5
Bubb Lake	40748	61.2	27.9	34	63.5
Middle Branch Lake	40707	63.5	11.1	13.5	67.9
Sagamore Lake	60313	63.5	6.7	6.9	63.5
Arbutus Pond	50684	66.9	11.1	3.5	71.3
Windfall Pond	040750A	71.3	11.1	22.2	67.9
Wheeler	40731	71.3	15.5	19.8	71.3
Raquette Lake Reservoir	060315A	71.3	7.7	1	71.3
Moss Lake	40746	71.3	7.7	6.9	71.3
Willis Lake	50215	72.5	74.6	81.7	71.3

Table 4-4. Modeled relationship between each of the studied ALTM/AEAP lakes and the population of Adirondack lakes with respect to acid-base chemistry status, acidification, and recovery responses, based on PnET-BGC model simulations.

ALTM Lake		Estimated Percentage of Lakes in the Population Having:			
Name	ID	Lower 2000 ANC	Greater Historical Acidification (1850 to 1990)	Greater ANC Recovery Under Base Case Scenario (1990 to 2050)	Lower 2050 ANC Under Base Case Scenario
Willys Lake	40210	2.5	15.2	10.5	10.8
Squash Pond	40754	0	1.2	2.2	0
Carry Pond	50669	10.8	2.1	9.3	2.4
Round Pond	040731A	12	17.5	14.0	12.0
Jockeybush Lake	50259	10.8	0	0	13.0
Indian Lake	40852	14.2	24.5	38.1	14.2
Brook Trout Lake	40874	15.2	38.5	36.9	14.2
South Lake	41004	19.7	54.8	58.8	19.7
Big Moose Lake	40752	21.9	50.9	76.8	19.7
Queer Lake	60329	23.2	2.1	0	28.4
Middle Settlement Lake	40704	16.4	2.1	19.6	21.0
Long Pond	50649	13.1	1.2	0	14.2
North Lake	41007	13.1	21.6	39.1	13.0
G Lake	70859	12.0	16.4	50.8	15.2
Dart Lake	40750	18.7	50.9	50.8	15.2
Constable Pond	40777	12.0	28.5	20.6	13.0
Squaw Lake	40850	28.5	57.8	70.7	24.3
West Pond	40753	42.6	60.7	76.8	41.7
Limekiln Lake	40826	36.3	36.3	39.1	59.7
Grass Pond	40706	39.2	50.9	58.8	30.6
Helldiver Pond	40877	61.6	8.7	50.8	58.8
Lake Rondaxe	40739	31.3	17.5	76.8	21.0
Cascade Lake	40747	63.5	50.9	61.9	61.6
Bubb Lake	40748	39.2	17.5	12.7	59.7
Middle Branch Lake	40707	35.3	17.5	36.9	45.5
Sagamore Lake	60313	31.3	17.5	55.9	24.3
Arbutus Pond	50684	66.9	29.8	19.6	69.9
Windfall Pond	040750A	49.7	50.9	76.8	39.8
Wheeler	40731	63.5	60.7	33.7	63.5
Raquette Lake Reservoir	060315A	59.7	33.2	60.0	48.4
Moss Lake	40746	63.5	38.5	70.6	63.5
Willis Lake	50215	49.7	29.8	19.6	59.7

Four CDFs of lakewater ANC are provided in Figure 4-32 for MAGIC model simulations of the population of Adirondack lakes represented by the EMAP statistical frame. Super-imposed on each CDF is the position of each ALTM/AEAP study lake as compared with the overall population. Lakes having lowest current ANC are Willys Lake (-37 μeq/L), Squash Pond (-21 μeq/L), Carry Pond (-14 μeq/L), Round Pond (-10 μeq/L), and Jockeybush Lake (-9 μeq/L; Figure 4-32a). These same lakes are projected to have the lowest ANC in 2050 in response to the Base Case emissions control scenario (Figure 4-32b). Lakes that acidified the most in the past in response to acidic deposition also included the highly-acidic Willys Lake (Figure 4-32c). However, other lakes simulated to have acidified by a large margin since 1850 were not currently low in ANC. They included, in addition to Willys Lake, Cascade Lake, Sagamore Lake, Raquette Lake Reservoir, Moss Lake, and Arbutus Pond (Figure 4-32d); all had 1990 ANC between 50 and 100 μeq/L. Similarly, the lakes projected to recover the most by 2050 in response to emissions reductions under the Base Case emissions control scenario (Willys Lake, Raquette Lake Reservoir, Arbutus Pond, Cascade Lake, Sagamore Lake, and Moss Lake) primarily (all except Willys Lake) had 1990 ANC between 50 and 100 μeq/L. Thus, based on MAGIC simulation results, the lakes that are most chemically responsive to both increases and decreases in acidic deposition are not those lowest in ANC. Rather, the most responsive lakes appear to be those having intermediate ANC.

PnET-BGC simulations of historical acidification also suggested that ALTM/AEAP lakes were skewed toward the portion of the population distribution that was most acid-sensitive. All modeled ALTM/AEAP lakes fall within about the 60th percentile of past acidification, based on PnET BGC (Table 4-4). In contrast, the modeled ALTM/AEAP lakes were more evenly distributed across the population distribution of projected ANC recovery between 1990 and 2050 under the Base Case scenario (Table 4-4).

Smol et al. (1998) integrated many paleolimnological studies in the Adirondack Mountains and the Sudbury, Ontario region of Canada to provide evidence as to why some lakes were inferred to recover from decreased acid loading faster than other lakes. Using cluster analysis, they identified four categories of lake responsiveness to acidic deposition, based on diatom and chrysophyte inferred pre-industrial chemistry and the timing of inferred acidification. Background acidity was the most important factor in discriminating among paleolimnological inferences of acidification response. In general, lakes that were naturally low in ANC in pre-industrial times were the first to acidify based on paleolimnological reconstructions, but showed

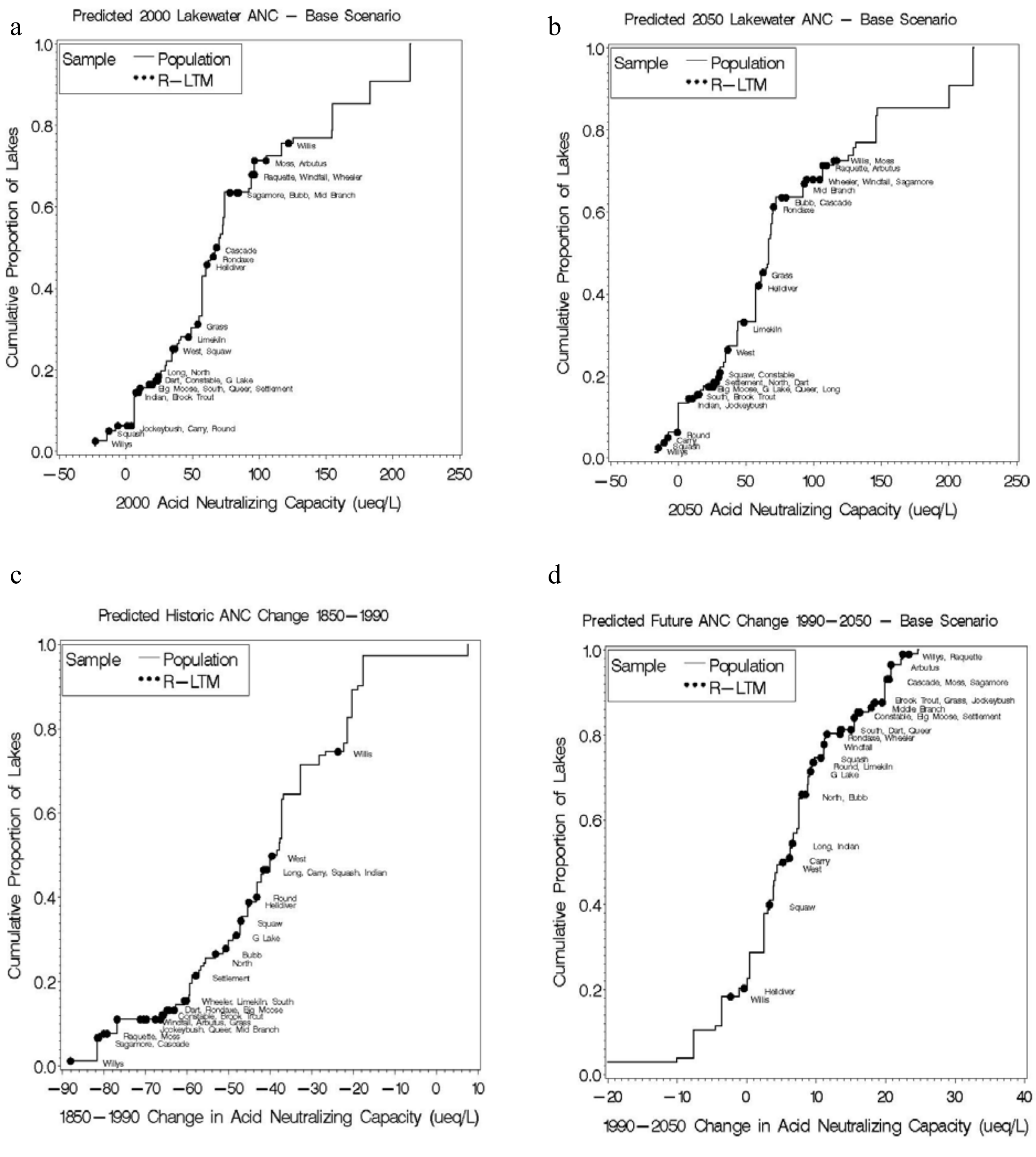


Figure 4-32. Cumulative distribution functions (CDF) of lakewater acid base chemistry and acidification/recovery responses simulated with the MAGIC model for the population of Adirondack lakes having ANC ≤ 200 μeq/L. Superimposed on each CDF is the location of each ALTM/AEAP study lake within the population distribution. The distributions represent a) lakewater ANC in 2000, b) lakewater ANC in 2050 in response to the Base Case emissions control scenario, c) historical acidification between 1850 and 1990, and d) future recovery in ANC from 1990 to 2050 in response to the Base Case emissions control scenario.

little evidence of recovery in response to decreases in acidic deposition in the 1970s and 1980s. Our MAGIC modeling results suggested that these lowest-ANC lakes are generally not among those expected to show the most recovery in the future in response to reduced levels of acidic deposition. In contrast, PnET-BGC projections suggested that the lakes having lowest current ANC are generally those that will show the greatest chemical recovery in the future (Table 4-4).

Jassby (1998) and Stoddard et al. (1998) cautioned against using judgment samples (those not statistically selected) to represent regional estimates of change in lakewater acid-base status. A major concern expressed by Stoddard et al. (1998) was that measured trends within subpopulations were not observed to be homogeneous. Stoddard et al. (1998) analyzed ALTM data through 1994, and found no consistent pattern of recovery in the Adirondacks. Each lake watershed system is different. Important inherent sources of variation include geology, distribution and amount of glacial till, soils, drainage water flow paths, vegetation, climate, and disturbance history (Charles 1991). In addition, the histories of acidic deposition have varied from watershed to watershed with such factors as location, elevation, topography, and forest cover type. Thus, it is expected that watersheds would exhibit variable acidification and recovery responses.

The future projected distribution of ANC values for the modeled long-term monitoring lakes was consistently lower than the population distribution, regardless of evaluation year and regardless of the extent of emissions reduction (Figure 4-33). This pattern was due, in part, to the generally higher concentrations of SO_4^{2-} in the long-term monitoring lakes (Figure 4-34). MAGIC model estimates suggested, however, that SO_4^{2-} concentration was not always higher in the ALTM/AEAP lakes. Rather, simulated pre-industrial SO_4^{2-} concentrations were uniformly low in ALTM/AEAP lakes, and more variable across the population of lakes (Figure 4-35). The Aggressive Additional Emissions Control scenario resulted in projections of higher lakewater ANC than the Base Case scenario, and these differences became more pronounced in 2050 as compared with 2020. However, median and quartile ANC values were always lower for the long-term monitoring lakes than they were for the population (Figure 4-33).

There are 1,829 lakes in the EMAP statistical frame for the Adirondacks. For this project, modeling was conducted for a subsample of the 1,320 of those that had measured ANC $\leq$ 200 μeq/L. Assuming that the balance of 509 lakes having ANC > 200 μeq/L are less acid-sensitive that those that provided the basis for selecting candidate modeling lakes, we can calculate statistics for the entire population of 1,829 lakes based on the results of the modeling

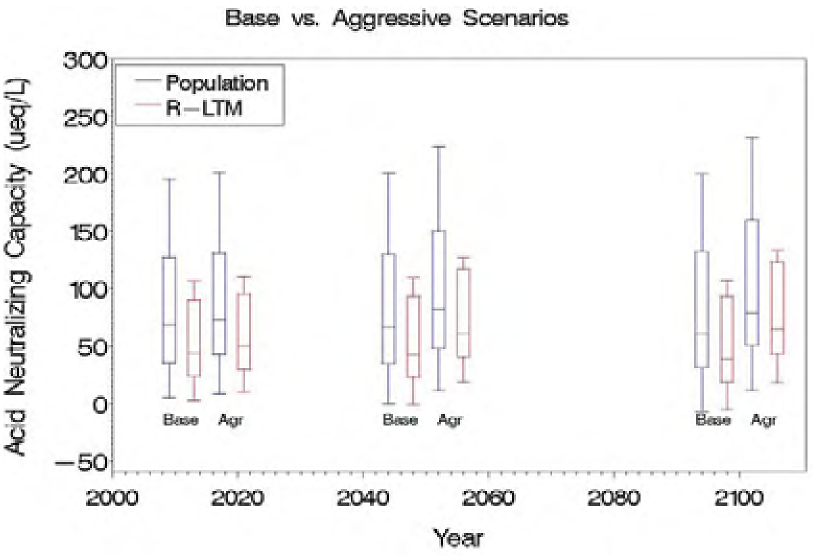


Figure 4-33. Box and whisker plots of lakewater ANC at three future points in time: 2020, 2050, and 2100. Results are presented for MAGIC model simulations under the Base Case and Aggressive Additional Emissions Control scenarios for two groups of lakes: the modeled ALTM/AEAP long-term monitoring lakes and the population of Adirondack lakes having ANC ≤ 200 μeq/L.

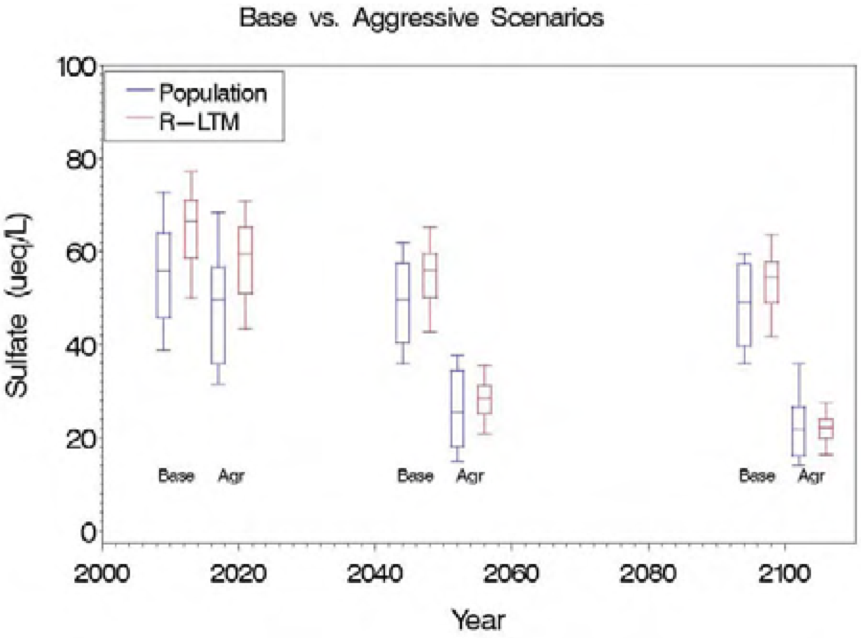


Figure 4-34. Box and whisker plots of lakewater SO_4^{2-} concentration at three future points in time: 2020, 2050, and 2100. Results are presented for MAGIC model simulations under the Base Case and Aggressive Additional Emissions Control scenarios for two groups of lakes: the modeled ALTM/AEAP long-term monitoring lakes and the population of Adirondack lakes having ANC ≤ 200 μeq/L.

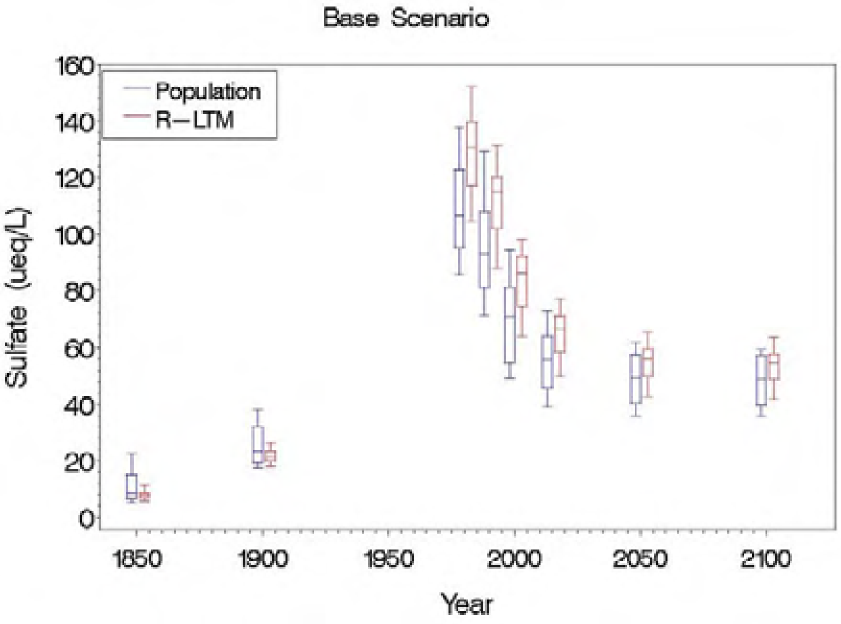


Figure 4-35. Box and whisker plots of lakewater SO_4^{2-} concentrations in pre-industrial and more recent times, based on MAGIC model simulations under the Base Case emissions controls scenario. Results are presented separately for ALTM/AEAP lakes and for the population of Adirondack lakes having ANC ≤ 200 µeq/L.

conducted for this project. Such calculations indicate that nearly all of the ALTM lakes modeled for this project were among the 50% of the overall population that was modeled to be most acid-sensitive. This finding holds for measures of acid-sensitivity based on both simulated historical acidification and simulated future chemical recovery.

Based on MAGIC simulations, 985 lakes (74.6% of 1,320) showed greater historical acidification than the least acid-sensitive lake as represented by past change (Willis Lake, Table 4-3). Only 659 lakes (36% of population) showed greater historical acidification than the next least acid-sensitive modeled ALTM lake (West Pond). Two modeled ALTM lakes (Willis Lake and Helldiver Pond) showed relatively small amounts of future chemical recovery. For all other modeled ALTM lakes, fewer than 792 lakes in the population (43%) showed greater future recovery (Table 4-3).

Results for PnET-BGC hindcast, and to a lesser extent forecast, simulations were generally similar. All modeled ALTM lakes were within the top 60.7% (N = 801) of the ANC ≤ 200 µeq/L lake population with respect to the simulated amount of past acidification and within the top 76.8% (N = 1,014) of the ANC ≤ 200 µeq/L lake population with respect to the simulated amount of future chemical recovery (Table 4-4). Thus, in comparison with the overall Adirondack lake population, across the full spectrum of ANC (N = 1,829), PnET-BGC simulations also suggested that the modeled ALTM lakes are approximately within the upper 50% of the population distribution of lake sensitivity to changes in acid-base chemistry in response to changing levels of acidic deposition.

Using MAGIC model output as an example, the modeled ALTM lakes were well distributed across the lower 75% of the ANC distribution for the years 2000 and 2050 (Base Case scenario, Figure 4-32 a,b). The 75th percentile of the low-ANC ($\leq$ 200 μeq/L) lake population of 1,320 lakes represents the lower 54% of the entire population of 1,829 lakes. Similarly, most, but not all, ALTM lakes were well distributed across the upper 50% of the low-ANC lake distribution with respect to amount of simulated past acidification and amount of simulated future chemical recovery (Figure 4-32 c,d). The upper 50% of the low-ANC ($\leq$ 200 μeq/L) lake distribution of 1,320 lakes corresponds to the upper 36% of the overall lake distribution of 1,829 lakes. Therefore, the modeled ALTM lakes are not representative of the overall populations of Adirondack lakes with respect to current chemistry, past amount of acidification, or future chemical recovery from acidification. Rather, the modeled ALTM lakes are broadly representative of the most acid-sensitive subset of the overall lake population.

4.4 Implications

This research provided a linkage between lakewater acidification and chemical recovery potential for two groups of Adirondack lakes: those included in intensive long-term monitoring programs and the overall population of Adirondack lakes that have ANC less than 200 μeq/L. Model outputs using two commonly-applied watershed models, MAGIC and PnET-BGC, were used to place the intensively-studied lakes into the regional context. This will increase the utility of the long-term monitoring data.

The modeling results reported here raise the possibility that Adirondack lakes that are currently recovering from past acidification might reacidify in the near future under emissions controls enacted prior to January, 2004. The models simulated near-term reacidification of the lowest-ANC lakes because of continued depletion of soil B horizon percent base saturation. Newly-enacted emissions controls, under the CAIR, may affect the probability of future reacidification.

This research project also constructed a statistically-based database for Adirondack soil acid-base chemistry, which will be useful as a benchmark for evaluation of future change in soil conditions. In addition, a rigorous intermodel comparison was conducted to compare and contrast model projections derived from the MAGIC and PnET-BGC models. Finally, this research provided empirical relationships with which to evaluate the level of changes in biological communities (fish and zooplankton) that would be consistent with modeled values of lake chemistry in the past and in the future under alternative scenarios of emissions controls.

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Appendix A

Plots of MAGIC and PnET-BGC model prejections and measurements of calculated ANC for the lakes having two decades of monitoring data

Modeled projections and observed values for the data-rich lakes are provided in Figures A-1 and A-2 for the MAGIC and PnET-BGC models, respectively. These include lakes from the original group of ALTM lakes. Each has two decades of monitoring data. These figures illustrate the extent to which each of the models captures the changes in lakewater ANC that have occurred over the monitoring period.

MAGIC

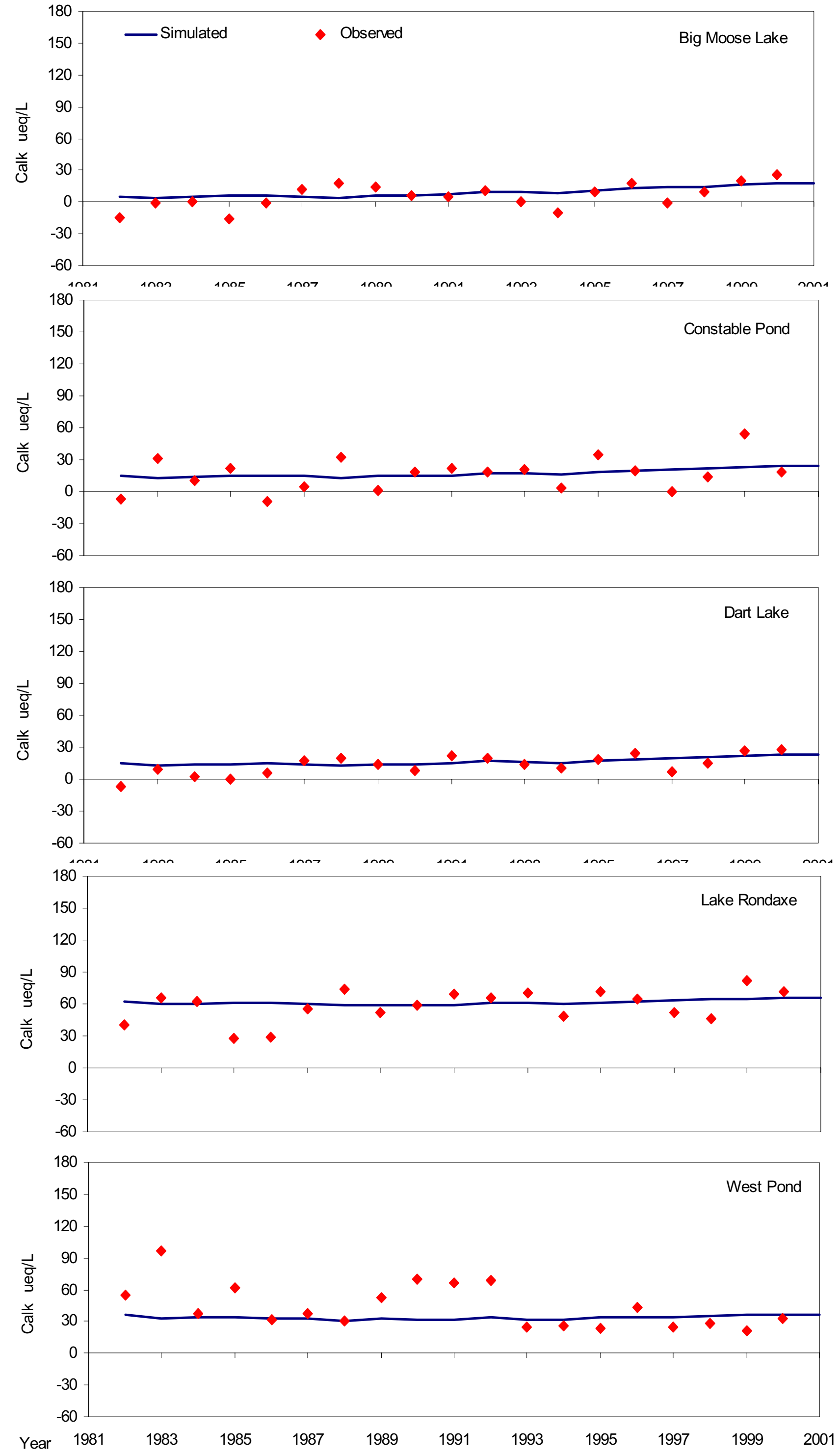

Figure A-1. MAGIC projected and observed values of calculated ANC for the data-rich modeled lakes.

MAGIC

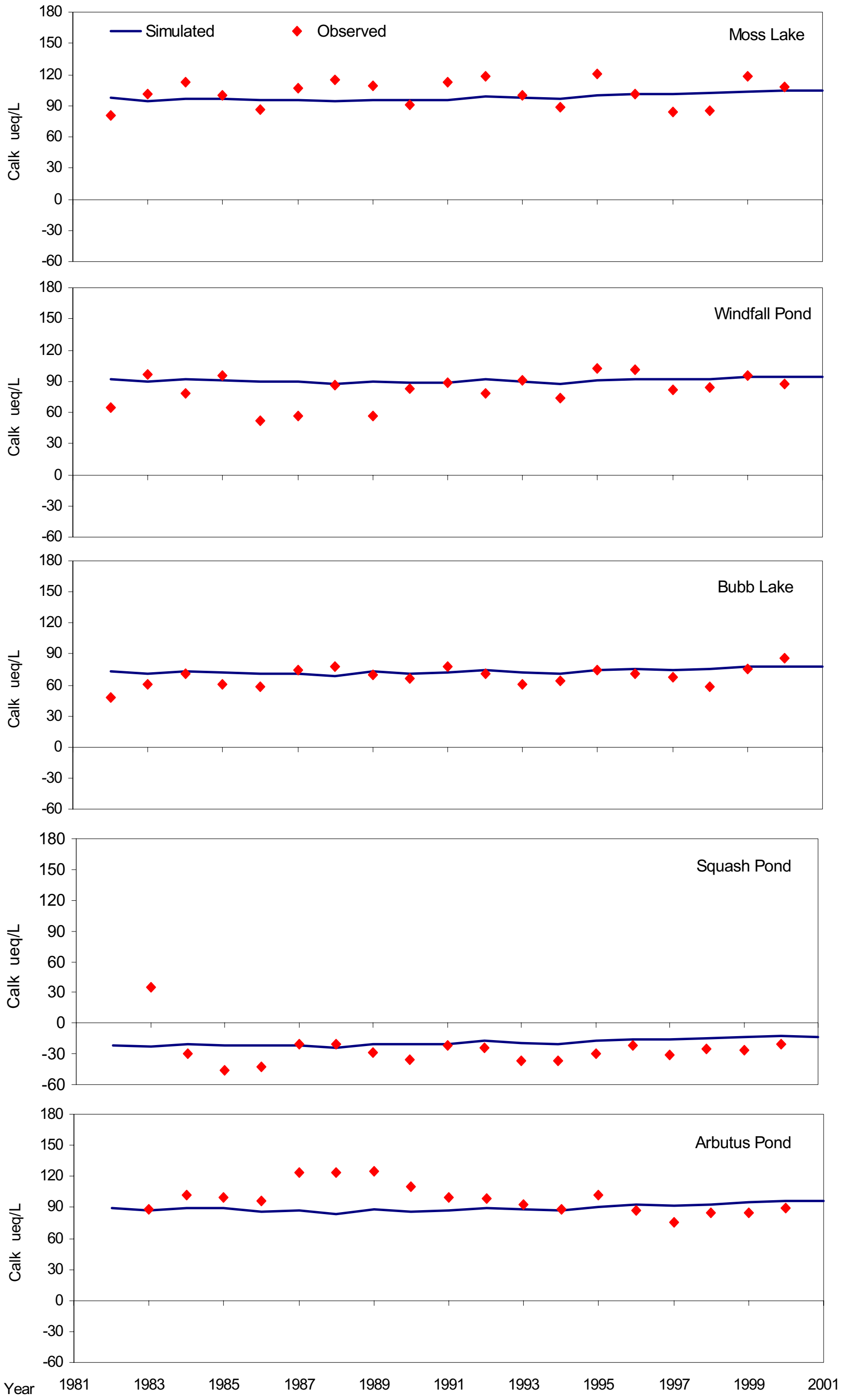

Figure A-1. Continued.

PnET-BGC

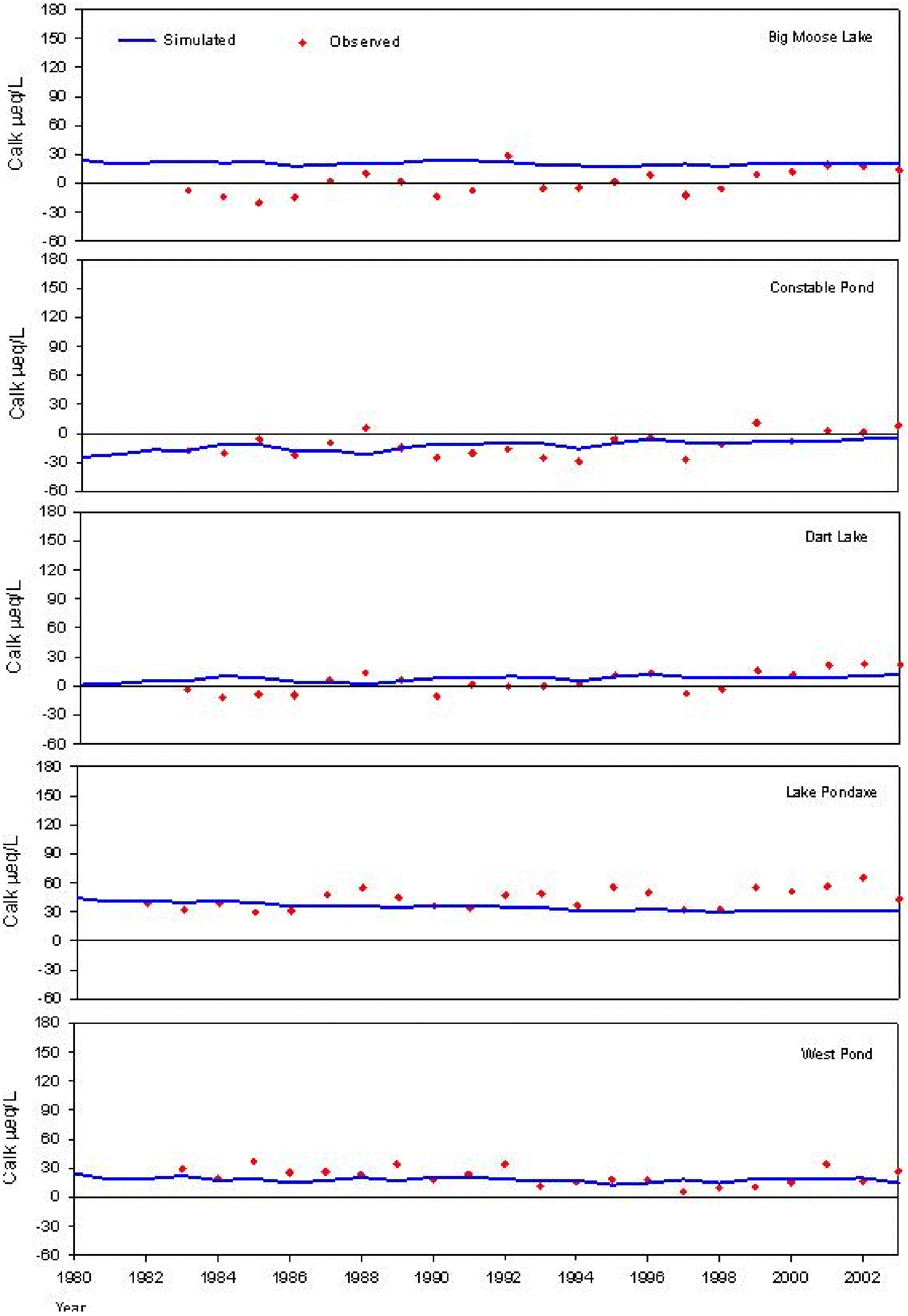

Figure A-2. PnET-BGC projected and observed values of calculated ANC for the data-rich modeled lakes.

PnET-BGC

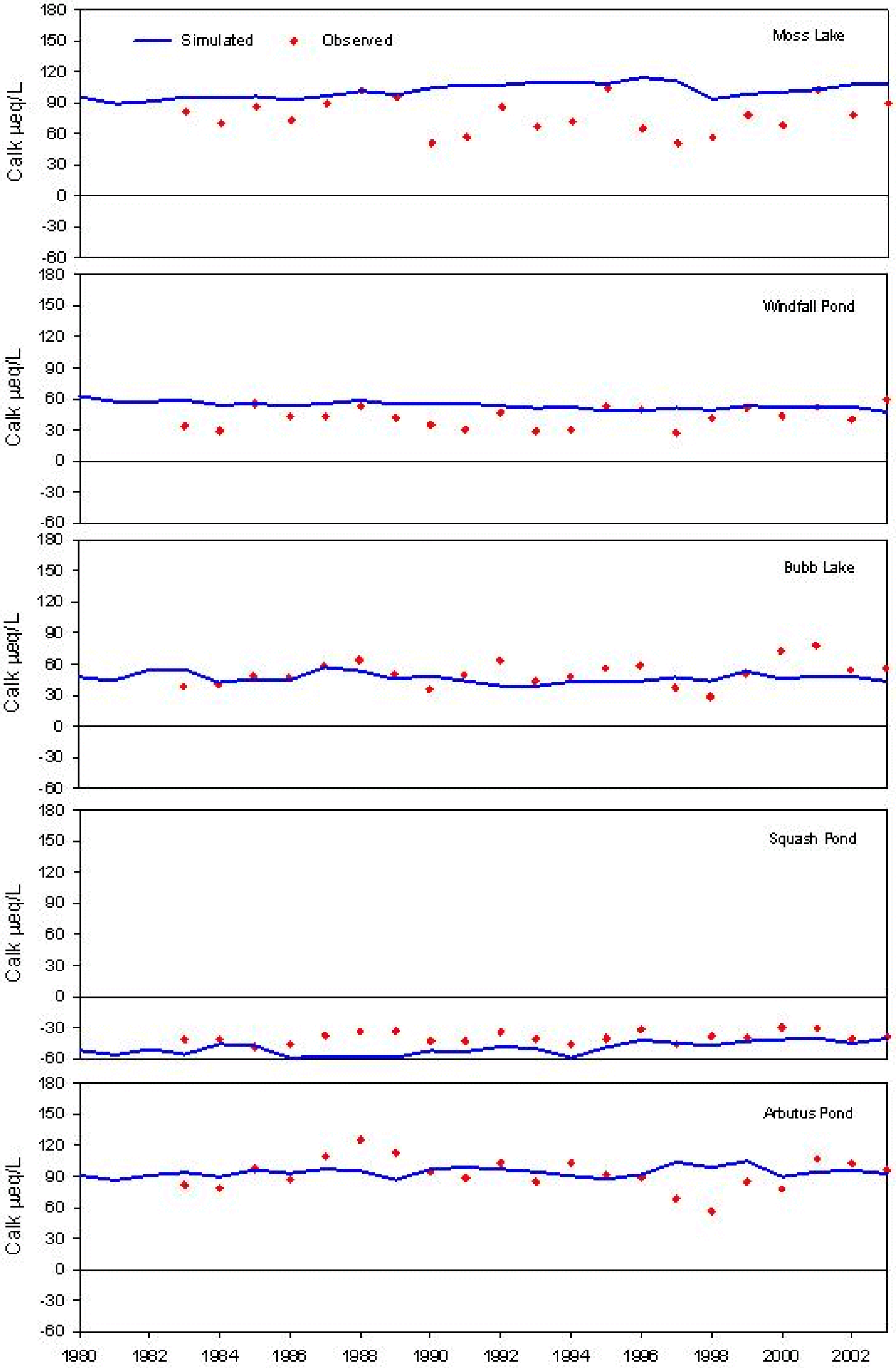

Figure A-2. Continued.

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ASSESSMENT OF THE EXTENT TO WHICH INTENSIVELY STUDIED LAKES ARE REPRESENTATIVE OF THE ADIRONDACK MOUNTAIN REGION

FINAL REPORT 06-17

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