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Developing Critical Loads and Dynamic Critical Loads for Acidification for Watersheds in the Adirondack region of New York and Great Smoky Mountain National Park (GRSM)

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Abstract

Critical loads (CLs) and dynamic critical loads (DCLs) are important tools for the management of ecosystems that are impacted by high sulfate, nitrate and ammonium deposition. In this study, a biogeochemical model (PnET-BGC) was applied to 20 watersheds in the Adirondack region and 12 watersheds in Great Smoky Mountain National Park (GRSM) to calculate CLs and DCLs. I evaluated ecosystem changes in response to historical and potential future changes in acidic deposition. I analyzed factors affecting CLs and DCLs for acidification in the acid impacted Constable Pond Watershed in the Adirondack region, specifically evaluating trade-offs of sulfate and nitrate deposition, supply of dissolved organic carbon, land disturbance and lake hydrological residence time. I also calculated CLs and DCLs for 20 watersheds in the Adirondack Region. Based on chemical indicators (acid neutralizing capacity-ANC and soil base saturation) and biological indicators (fish and total zooplankton species richness). I defined two metrics – historical acidification and maximum recovery based on changes in ANC. I explored the factors affecting historical acidification and maximum recovery. I determined the conditions where acidified lakes can recover and the long-term sustained deposition loads that would be required to achieve such recovery and identified the types of watersheds for which recovery is unlikely, regardless of the emission reductions. I also projected the response of aquatic species (fish and total zooplankton species richness) to historical and potential future changes in acidic deposition. Using methods similar to those developed for the Adirondack region, I also applied PnET-BGC to the GRSM region to obtain CLs and DCLs and evaluated how watershed-ecosystems changed in response to historical and future decreases in NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ deposition.
Results from Constable Pond watershed showed that ANC increased more in response to equivalent decreases in SO$_4^{2-}$ deposition than NO$_3^-$ deposition. Moreover, DOC in the surface water, lake hydrological residence time and forest cutting disturbance had substantial effects on historical acidification and the recovery of lake ANC.

Results from lakes of the Adirondack region also showed that future increases in ANC will be accomplished more effectively in response to further decreases in SO$_4^{2-}$ deposition than in NO$_3^-$ deposition. Historical acidification was related to the current deposition of SO$_4^{2-}$+NO$_3^-$, Ca$^{2+}$ weathering rate, and pre-industrial ANC (~1850). Lake recovery was likewise related with the current deposition of SO$_4^{2-}$+NO$_3^-$, Ca$^{2+}$ weathering rate and current ANC. Fish and total zooplankton species richness are projected to increase under decreases in SO$_4^{2-}$ or NO$_3^-$ deposition. However, complete chemical and biological recovery will not be attainable by 2200 even under decreases in atmospheric deposition to pre-industrial conditions.

Results from the GRSM showed that ANC in the future will also increase in response to decreases in acidic deposition. However, ANC increases will be accomplished more effectively with decreases in NO$_3^-$ than in SO$_4^{2-}$ deposition. This difference in response is due to the strong retention of SO$_4^{2-}$ by soil adsorption in this unglaciated landscape, coupled with the limited watershed retention of atmospheric N deposition. Historical acidification and maximum recovery were also related to Ca$^{2+}$ weathering rate and pre-industrial ANC. Some watersheds are projected to achieve target ANC in the future under different DCLs for SO$_4^{2-}$+NO$_3^-$ deposition. Other GRSM watersheds will not be able to achieve target ANC in the future due to sensitive soil conditions and are experiencing watershed N saturation.
Developing Critical Loads and Dynamic Critical Loads for Acidification for Watersheds in the Adirondack region of New York and Great Smoky Mountain National Park (GRSM)

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Chapter 1 Introduction

1.1 Background on acidic deposition

Elevated acidic deposition has adversely affected forest-ecosystems in the eastern U.S. Acidic deposition includes nitrogen (N) oxides (NO\textsubscript{x}), sulfur (S) dioxide (SO\textsubscript{2}), ammonium, and particulate emissions of acidifying and neutralizing compounds. These materials can be emitted from combustion of fossil fuels or agricultural activities (Driscoll et al., 2001). Acidic deposition is a broad term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere containing elevated amounts of acidic and acidifying materials (http://www.epa.gov/acidrain/what/). It was first recognized in North America at the Hubbard Brook Experimental Forest (HBEF) (Likens et al., 1972). Since peak emissions in 1973, SO\textsubscript{2} emissions have significantly decreased in the U.S. as a result of the Clean Air Act and associated rules (Driscoll et al., 2011; Waller et al., 2012). During 2005-2012, total SO\textsubscript{2} emissions from the power sector declined by 68% from 10.2 to 3.3 million tons and total NO\textsubscript{2} declined by 53% from 3.6 to 1.7 million tons based on Acid Rain Program and Clean Air Interstate Rule in U.S (USEPA, 2012). The marked decrease in SO\textsubscript{x} and NO\textsubscript{x} emissions has resulted in decreases in atmospheric sulfate (SO\textsubscript{4}\textsuperscript{2-}) and nitrate (NO\textsubscript{3}⁻) deposition. As a result, some surface waters in acid sensitive regions are recovering from negative impacts of acidic deposition (Warby et al., 2005a; Waller et al., 2012). However, the ecological damage that has been caused by acidic deposition will not likely be reversed over a short period. The rate of recovery of forest ecosystems has been delayed by the retention of S and N and the loss of exchangeable base cations from soil
associated with decades of elevated inputs and leaching of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ (Warby et al., 2009). Acidic deposition remains a major environmental problem despite decreases in emissions as a result of the 1990 Clean Air Act Amendments (Driscoll et al., 2010). Severe effects of acidic deposition have been reported in high-elevation areas of eastern North America, including New England, the Adirondack region of New York, and northern, central and southern Appalachian Mountain regions (Charles, 1991). It is important to evaluate the effectiveness of current emission control programs and provide scientific information for policy makers to determine whether additional decreases of $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ deposition will be needed for the complete recovery in these regions. By complete recovery I am referring to the return of the chemical characteristics to pre-industrial conditions (~1850).

1.2 Critical Loads

There is considerable interest in understanding and quantifying the recovery of ecosystems from impacts of acidic deposition. One approach that has been used widely in Europe and to a lesser extent in North America that has served as an interface between science/engineering understanding and air quality management policy is Critical Loads (CLs).

A Critical load (CL) is a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of ecosystems do not occur according to present knowledge (Sullivan et al., 2008; Nilsson and Grenfelt, 1988; Burns et al., 2008). A related term Dynamic Critical Load (DCL) has been defined as “the level of exposure based on policy, economic, or temporal considerations” (Porter et al., 2005). CLs are thought to depict a steady-state condition, while DCLs represent dynamic conditions and
represent systems that are not at steady-state with respect to acidic deposition, but changing over time. CLs and DCLs are tools and approaches used by scientists and engineers to depict the inputs of air pollutants ecosystems can sustain without damage to its structure or function.

The concept of CLs was introduced through the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutant (LTAP) in Europe, which was established around 1977 in order to monitor and evaluate air pollution. It was developed largely through a common understanding between European scientists and policymakers at two workshops; a Nordic workshop 1986 and a UNECE workshop in Skokloster, Sweden in 1988 (Driscoll et al., 2011). In response to the success of these workshops, CLs became an important element in the revision of the NO₃ Protocol in December 1988.

The U.S. joined LTAP in 1981. During the 1970s, the U.S. focused on the effects of air pollution on human health. Since the 1980s, the U.S. has also addressed the effects of acidic deposition on aquatic and terrestrial species. Programs were established like the National Acid Precipitation and Assessment Program (NAPAP, 1980), National Surface Water Survey (NSWS, 1984), Direct/Delayed Response Project (DDRP, 1988) and Nitrogen Bounding Study (NBS, 1994) to evaluate how acidic deposition affects ecosystems. Based on these studies, a report to Congress in 1995 based on the Acid Deposition Standard Feasibility Study clearly addressed the use of CLs to develop a deposition standard to protect ecosystems and how to obtain CLs in different regions of the U.S. (USEPA, 1995). Since then, the U.S. EPA began to focus more on the application of CLs.

The U.S. EPA recently conducted an integrated review of secondary National Ambient Air Quality Standards for the combined control of two criteria pollutants - oxides of nitrogen.
and oxides of sulfur (USEPA, 2011a). This multi-pollutant effort builds on recent multi-disciplinary research that has developed an integrated understanding of the combined effects of NO$_x$ and SO$_2$ on ecosystems. Critical loads were proposed as the approach for the NO$_x$ and SO$_2$ secondary standard. However, the U.S. EPA Administration decided that scientific understanding of the phenomenon was not adequate enough to implement the standard.

The first methods for deriving CLs were simple and largely based on (semi) empirical data. Following these efforts steady-state models such as the Steady-State Water Chemistry Method have been used in the development of CLs (Kennedy et al., 2001). Recently, with interest in dynamic conditions and the effects of multiple pollutants, dynamic models such as the Model of Acidification and Groundwater in Catchments (MAGIC; Cosby et al., 1985) and Photosynthesis net Evapotranspiration- BioGeoChemical model (PnET-BGC; Wu and Driscoll, 2009) have been used to calculate CLs. Critical loads have been readily adopted as an approach for policy development because they are continually revised and updated with improvements in scientific understanding. They also form an effective bridge allowing for communication and interaction between scientists and policymakers.

1.3 Objectives of the research and research questions

The overarching goal for this dissertation is to assess the response of soils and surface waters to decreases in the acidic deposition by establishing the CLs and DCLs of SO$_4^{2-}$ + NO$_3^-$ deposition for two acid sensitive regions of the U.S: the Adirondack region of New York and Great Smoky Mountain National Park (GRSM) in Tennessee and North Carolina.
The specific objectives for this dissertation are as follows:

1) Compile data, and apply the biogeochemical model PnET-BGC to different watersheds with a range of characteristics in the Adirondacks (based on surficial geology) and GRSM (based on elevation, vegetation, and geology) to evaluate historical conditions and potential future response to a range of atmospheric S and N deposition;

2) Simulate the response of the watersheds to decreases in acidic deposition and assess and compare the CLs/DCLs of S and N for the ecosystems using chemical indicators and biological indicators;

3) Evaluate the factors that affect the CLs/DCLs including watershed physical characteristics, biological processes and the critical chemical indicators; and

4) Compare and contrast the differences in CLs/DCLs between northern (Adirondack) and southern (GRSM) study sites.

Based on the research objectives, I propose the following questions.

1) What are the CLs or DCLs for a chronically acidic lake watershed - Constable Pond Watershed in the Adirondack region, and how do factors such as SO$_4^{2-}$ or NO$_3^{-}$ deposition, land disturbance, hydrological residence time and dissolved organic carbon affect CLs or DCLs?

2) What factors affect historical acidification and recovery for the Adirondack region? How will fish and total zooplankton species richness respond to historical and potential future changes in acidic deposition? What types of watersheds will recover from acidic deposition and what types of watersheds will require more additional remediation efforts beyond controls of acidic deposition?
3) How does PnET-BGC perform in Southeastern sites? Using similar methods, what are the CLs or DCLs for the GRSM and the factors affecting historical acidification and recovery? Are there any differences in the contribution of between S and N deposition to the acidification for these two regions?

1.4 Dissertation Outline

To accomplish these objectives and answer these questions, the model PnET-BGC is used to evaluate the CLs and DCLs of $\text{SO}_4^{2-}$, and $\text{NO}_3^-$ for the watersheds in the Adirondack region and the GRSM. The dissertation is organized into eight chapters. Chapter 1 provides the background on acidic deposition and its effects, and the development of CLs of acidic deposition, and summarizes research objectives and questions; Chapter 2 is a review of relevant literature; in Chapter 3 the methodology for the research is described. Chapters 4-6 provides descriptions of the three main research phases of the dissertation followed by a synthesis (Chapter 7) and conclusions (Chapter 8).

In order to answer the first suite of questions, PnET-BGC was applied to Constable Pond Watershed in the Adirondack region of New York (Chapter 4). Model performance was evaluated by comparing the simulation data with the long-term monitoring data from 1983 to the present (~2008). I reconstructed the meteorological, vegetation, soil and surface water data to run the model. The model was run from the past (1000 A.D.) to the future (2200 A.D.). Forecast scenarios were run for a series on hypothetical deposition conditions, including a range of $\text{SO}_4^{2-}$, $\text{NO}_3^-$ deposition and these combinations. The model was also run under other different
hypothetical scenarios such as intense forest cutting or no land disturbance during the past period; high or low DOC concentrations in the surface water and long or short hydrological residence time (HRT) were applied throughout the simulation period (1000-2200) to improve the understanding that how variation in these factors affect CLs and DCLs for acid impacted Adirondack lake watersheds. I also conducted a sensitivity analysis to evaluate how the model output responded to important model inputs and parameters.

To address the second suite of questions, I used the model to obtain CLs/DCLs of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ deposition for 20 lakes across the Adirondack region (Chapter 5). I compiled data necessary to run the model at study watersheds, including meteorological, vegetation, soil and surface water data. I ran the model initially as a hindcast and simulated historical acidification up to the present period. I then ran the model as a forecast, assuming constant climate and no future land disturbance until steady-state conditions were approximately observed (~2200). I introduced two metrics-historical acidification and potential maximum recovery to quantify the factors that affect the chemical indicator—acid neutralizing capacity (ANC) across the region. I explored factors such as current $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ deposition, $\text{Ca}^{2+}$ weathering rate or historical ANC (1850) that affect historical and potential future ANC across the region. I also evaluated the responses of aquatic biota species richness to historical changes in acidic deposition and the projected changes in deposition in the future.

To address the third suite of questions, I first applied PnET-BGC to 12 stream watersheds in the GRSM and obtained CLs/DCLs for these sites using similar methods as I used for the Adirondack region (Chapter 6). I evaluated the model performances using normal mean error methods (NME) and normal absolute mean error (NAME) methods. I developed the historical,
present and hypothetical future data to run the model over a time series. I ran the model under hypothetical future deposition scenarios, including a range of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ deposition values and their combinations. Based on the model results, I analyzed the factors that affect the historical acidification and potential maximum recovery of GRSM watersheds. I also determined what types of watersheds could not achieve target ANC values for recovery in the GRSM and analyzed the relative importance of SO$_4^{2-}$ or NO$_3^-$ deposition to the acidification and recovery in the stream watersheds.

In Chapter 7, I provided a synthesis of the research conducted in this dissertation. In Chapter 8, I summarized the major findings in this study.
Chapter 2 Literature Review

2.1 Atmospheric Emissions and Deposition

Acidic deposition is largely comprised of sulfuric and nitric acid derived from SO$_2$ and NO$_x$, respectively. These compounds are emitted to the atmosphere primarily by the burning of fossil fuels. Reduced N, largely in the form of ammonia, and largely from agricultural emission sources, also contributes to acidic deposition (Driscoll et al., 2001). Once these compounds enter an ecosystem, they can acidify soil and surface waters, bringing about a series of chemical and ecological changes. The term acidic deposition encompasses all of the forms of these compounds that are transported from the atmosphere to Earth surfaces, including gases, aerosols, particles, rain, snow, clouds, and fog. Acidic deposition occurs as: wet deposition including rain, snow, sleet or hail; as dry deposition involving particles or vapor; or as cloud or fog deposition, which is more common at high elevations and in coastal areas. Wet deposition is fairly well characterized by monitoring at more than 250 National Atmospheric Deposition Programs (NADP) in the U.S (http://nadp.sws.uiuc.edu/). In contrast, dry deposition (gases, aerosols, and particles) is highly dependent on meteorological conditions and vegetation characteristics that affect deposition velocity, which can vary markedly over short distances in complex terrains. Dry deposition varies highly over space and time. Values of dry S deposition range from 10 to 60% of total S inputs at sites in the eastern U.S. (Johnson and Lindberg, 1992). Values of dry N
deposition are also highly variable but average about 50% of total N deposition (Johnson and Lindberg, 1992). Cloud deposition is generally a small contribution to total deposition. However, at high elevations where there is substantial immersion in the cloud layer, cloud deposition can be a substantial component of total atmospheric deposition (Johnson and Lindberg, 1992). Dry deposition is difficult to measure and is estimated based on air concentrations and deposition velocity at over 85 sites through the Clean Air Status and Trends Network (CASTNet; http://www.epa.gov/castnet/index.html). The dry to wet deposition ratios do not change much for each site over several decades based on dry deposition data from CASTNet (http://www.epa.gov/castnet/index.html) and wet deposition data from NADP (http://epa.gov/castnet/javaweb/index.html).

There is considerable variation in atmospheric deposition in the Adirondacks and the Southern Appalachian Mountains. This variation is due to elevation, vegetation, and aspect. For example at Clingmans Dome in the Great Smoky Mountains, total S deposition was estimated to be 36 kg S/ha-yr and total N deposition 27 kg N /ha-yr in the late 1980s – early 1990s (Johnson and Lindberg, 1992; Lindberg and Lovett, 1992; Lovett and Lindberg, 1993). A large fraction of these inputs occurred as dry (25% for S, 50% for N) and cloud (50% for S, 30% for N) deposition. Cloud deposition is thought to be proportional to cloud immersion times (Eagar et al. 1996), so high-elevation forest sites which experience elevated dry and cloud deposition receive particularly high total S and N deposition.

More detailed spatial modeling often reveals complex patterns of atmospheric deposition, particularly in mountainous terrain. Weathers et al., (2006) developed a spatial model of atmospheric N and S deposition for the GRSM. Their maps showed six-fold variations in N and
S deposition across the Park. For total N deposition the area-weighted mean for the year 2000 was 10 kg N/ha-yr, with values ranging from 5 to 31 kg N/ha-yr. For total S deposition the area-weighted mean for 2000 was 14 kg S/ha-yr, with values ranging from 7 to 42 kg S/ha-yr. This spatial variability was largely due to variation in precipitation, elevation and vegetation type, and resulted in “hotspots” or areas of very high inputs of atmospheric deposition across the complex landscape.

In recent years there have been marked decreases in emissions of SO$_2$ and NO$_x$ and acidic deposition. Title IV of the 1990 Amendments of the Clean Air Act (CAAA) established the Acid Rain Program, which implemented major decreases in SO$_2$ emissions from electricity generating units in the U.S. using a market-based cap and trade program for SO$_2$ (USEPA, 2009a). This legislation was followed in 2003 by the Nitrogen Budget Trading Program to control NO$_x$ emissions and ground-level ozone in the eastern U.S., also using a cap and trade approach. Currently the U.S. EPA is implementing the Clean Air Interstate Rule (CAIR).

Waller et al. (2012) showed continuous and significant decreasing trends in wet SO$_4^{2-}$ deposition to Adirondack lake/watersheds. The average annual wet SO$_4^{2-}$ deposition decreased 32.9% over the study period (1991-2007) from 44.5 meq/m$^2$-yr to 29.9 meq/m$^2$-yr, consistent with decreases in SO$_2$ emissions. The average annual wet NO$_3^-$ deposition showed a similar percent decrease to SO$_4^{2-}$ (32.2%). Note, that the rate of decrease in wet NO$_3^-$ deposition was considerably less than that for SO$_4^{2-}$ (-0.69 ± 0.37 meq/m$^2$-yr vs -1.04 ± 0.37 meq/m$^2$-yr). In contrast to SO$_4^{2-}$ the long-term pattern in NO$_3^-$ deposition was characterized by higher year-to-year variability until 2003 when a marked decline in deposition occurred. Again this pattern in wet NO$_3^-$ deposition is consistent with decreases in NO$_x$ emissions that have occurred through
the Nitrogen Budget Program. Similar patterns are evident in the GRSM through NADP data.

2.2 Acidic Deposition Effects

2.2.1 Effects on Soil

Research has shown that acidic deposition has chemically altered soils with consequences for acid-sensitive ecosystems. Soils compromised by acidic deposition lose their ability to neutralize continuing inputs of strong acids, provide poorer growing conditions for plants, and extend the time needed for ecosystems to recover from acidic deposition. Acidic deposition has altered and continues to alter soils in sensitive regions of the eastern U.S. in three important ways: acidic deposition depletes available calcium (Ca\(^{2+}\)), magnesium (Mg\(^{2+}\)) and other nutrient cations from exchangeable sites in soil; it facilitates the mobilization of dissolved inorganic aluminum (Al) into soil-water; and it increases the accumulation of S and N in soil (Driscoll et al., 2001).

Forest soils are heterogeneous, with variations in their physical, chemical and biological characteristics. An important controlling factor of forest ecosystem sensitivity to acidic deposition is elevation. Soils in high-elevation zones are generally shallow, and characterized by high concentrations of soil organic matter and highly acidic conditions (Joslin et al., 1992; Eagar et al., 1996). High-elevation zones are often underlain by unreactive bedrock (e.g., sandstone, granite) which limits the ability of soils to replenish nutrient cations through weathering (Elwood et al., 1991).
Accumulation of sulfur and nitrogen

Acidic deposition results in the accumulation of S and N in forest soils (Driscoll et al., 2001; Likens et al., 2002). In glaciated soils of the Northeast, like the Adirondacks, inputs of \( \text{SO}_4^{2-} \) are not strongly adsorbed to soil or assimilated by vegetation so \( \text{SO}_4^{2-} \) is relatively readily transported to surface waters (Rochelle and Church, 1987). In contrast, old unglaciated soils of the Southeast, like the GRSM, generally strongly retain \( \text{SO}_4^{2-} \) inputs by adsorption associated with the iron and aluminum oxide content (Johnson and Lindberg, 1992). However, the \( \text{SO}_4^{2-} \) adsorption characteristics are not uniform across the Southeastern forest landscape; soil \( \text{SO}_4^{2-} \) adsorption capacity is generally lower at high elevation forests due to shallow soils and high quantities of soil organic matter (Eagar et al., 1996). With decreases in elevation, soil depth increases, soil organic matter content decreases and the iron and aluminum oxide content increases. These characteristics all increase the ability of soil to adsorb \( \text{SO}_4^{2-} \) (Elwood et al., 1991; Eagar et al., 1996). The process of \( \text{SO}_4^{2-} \) adsorption decreases the transport of \( \text{SO}_4^{2-} \) and associated acidity to surface waters.

Soils have a finite capacity to adsorb \( \text{SO}_4^{2-} \). With increases in \( \text{SO}_4^{2-} \) concentration or loading, the ability of soils to retain \( \text{SO}_4^{2-} \) is diminished (or becomes “saturated”) and an increasing fraction of added \( \text{SO}_4^{2-} \) is transported with drainage water (Galloway et al., 1983). Therefore under constant \( \text{SO}_4^{2-} \) loading to forest ecosystems with soils that adsorb \( \text{SO}_4^{2-} \) transport of \( \text{SO}_4^{2-} \) to surface waters will increase with time as soil \( \text{SO}_4^{2-} \) adsorption sites become saturated. Moreover, following decreases in atmospheric S deposition, \( \text{SO}_4^{2-} \) is released from the
soil to drainage waters. This $\text{SO}_4^{2-}$ release is due to desorption of previously adsorbed $\text{SO}_4^{2-}$ or net mineralization of organic S that has accumulated in soil. The recovery of surface waters in response to $\text{SO}_2$ emission controls is therefore likely delayed and will not be complete until the sulfur left by a long legacy of atmospheric deposition is released from the soil.

Similarly, N from atmospheric N has been deposited in some forest soils beyond the amount needed by the forest/vegetation (Stoddard, 1999; Aber et al., 2003). Nitrate is leaching into surface waters in the high-elevation forests of the Adirondacks, and the Central and Southern Appalachians (Nodvin et al., 1995; Aber et al., 2003; Stoddard, 1994). Although forests require N for growth, several studies suggest that some areas of the East receive N inputs through atmospheric deposition above levels forests can use and retain (Stoddard, 1994; Aber et al., 2003; Galloway et al., 2003).

Numerous studies have reported limited retention of atmospheric N deposition and elevated $\text{NO}_3^-$ leaching in the high elevation forests of the Adirondacks and Southern Appalachian regions (Johnson and Lindberg, 1992; Nodvin et al., 1995; Driscoll et al., 2003). This condition appears to be due to elevated N inputs from atmospheric deposition (i.e., particularly high inputs through dry and cloud deposition), low N uptake by vegetation, high concentrations of N in soil, and high rates of N mineralization and nitrification in soil. Forest age appears to be another important factor regulating $\text{NO}_3^-$ leaching, with mature forests requiring less N to sustain new growth than younger forests (Goodale and Aber, 2001). Old-growth red spruce stands in the Southern Appalachians had significantly slower growth rates, and therefore rates of N accumulation, than younger stands (< 120 years old; Smith and Nicholas, 1999).

Loss of calcium, magnesium and other nutrient cations
The cycling of Ca\(^{2+}\) and other nutrient cations (i.e., Mg\(^{2+}\), K\(^{+}\)) in forest ecosystems involves the inputs and losses of these materials. For most forest ecosystems the supply of Ca\(^{2+}\) and other nutrient cations largely occurs by weathering (i.e., the breakdown of rocks and minerals in soil). Calcium and other nutrient cations may also enter forests by atmospheric deposition, although this pathway is generally much smaller than weathering (Johnson and Lindberg, 1992). Atmospheric deposition of Ca\(^{2+}\) and other basic cations have declined in the eastern U.S. over the past decades (Likens et al., 1996). Calcium can be assimilated by vegetation uptake and exported by drainage waters. An important pool of ecosystem Ca\(^{2+}\) and other nutrient cations is the soil available pool, also called the soil cation exchange complex. Plants are generally able to utilize this source of nutrients. Forest ecosystems that are naturally sensitive to acidic deposition are generally characterized by low rates of mineral weathering and generally low quantities of available nutrient cations. Under conditions of elevated inputs of acidic deposition and subsequent transport of SO\(_4^{2-}\) and NO\(_3^-\) in drainage waters, nutrient cations will be displaced from available pools and leached from soil (Reuss and Johnson, 1985). This condition is not problematic for areas with high weathering rates and large pools of available nutrient cations. However, in acid-sensitive areas with shallow soils which contain minerals that are resistant to weathering, the enhanced loss of Ca\(^{2+}\) and other nutrient cations by the accumulation of forest biomass and/or leaching by SO\(_4^{2-}\) and NO\(_3^-\) can deplete soil available pools (Driscoll et al., 2001).

Over the last century, acidic deposition has accelerated the loss of large amounts of available Ca\(^{2+}\) and Mg\(^{2+}\) from soil in acid-sensitive areas in the Eastern U.S. (Likens et al., 1996;
Huntington et al., 2000; Warby et al., 2009). This conclusion is based on data from more than 70 sites using watershed mass balances (Likens et al., 1996), long-term soil measurements (Johnson and Todd, 1990; Knoepp and Swank, 1994) and modeling studies (Gbondo-Tugbawa and Driscoll, 2003). Depletion occurs when nutrient cations are leached from the soil by acidic deposition and/or accumulate in growing trees at a rate faster than these nutrients can be replenished by the slow breakdown of rocks (i.e., weathering) or deposition from the atmosphere. This depletion of nutrient cations fundamentally alters soil processes, compromises the nutrition of some trees, and hinders the capacity for sensitive soils to recover from acidification. Studies suggest that net Ca\textsuperscript{2+} and Mg\textsuperscript{2+} loss from soil is a critical environmental issue for forest ecosystems in the Eastern U.S. (Likens et al., 1996; Driscoll et al., 2001; Huntington et al., 2000).

Mobilization of aluminum

Aluminum is typically released from soil to soil-water, and ultimately to surface waters in forested regions with high acidic deposition, low stores of available Ca\textsuperscript{2+}, and high soil acidity (Cronan and Schofield, 1990; Driscoll and Postek, 1995). One of the most significant ecological effects of acidic deposition is the mobilization of Al from soil and a shift in the form of Al in water from non-toxic organic forms to highly toxic inorganic forms (Driscoll and Postek, 1995). High concentrations of dissolved inorganic Al can inhibit uptake of nutrient cations in plants (Thornton et al., 1994), and be toxic to plants (Cronan and Grigal, 1995), fish, and other organisms (MacAvoy and Bulger, 1995). Concentrations of dissolved inorganic Al in surface waters in acid impacted regions like the Adirondacks and the GRSM are often above levels
considered toxic to some fish (Cook et al., 1994) and greater than concentrations observed in forest watersheds that receive low inputs of acidic deposition (Driscoll et al., 1988).

2.2.2 Effects of Acidic Deposition on Forest Health

Acidic deposition has contributed to the decline of red spruce (*Picea rubens*) and sugar maple (*Acer saccharum*) trees in the eastern U.S (DeHayes et al., 1999; Drohan et al., 1999). Symptoms of tree decline include poor condition of the canopy, reduced growth, and unusually high levels of mortality (DeHayes et al., 1999; Drohan et al., 1999). Declines of red spruce and sugar maple in the eastern U.S. have occurred during the past four decades in the eastern U.S. (Driscoll et al., 2001; Driscoll et al., 2006). Factors associated with declines of both species involve important links to acidic deposition, including leaching and depletion of Ca\(^{2+}\) and mobilization of Al (Driscoll et al., 2001; Fenn et al., 2006).

2.2.3 Effects of Acidic Deposition on the Surface Waters

Acidic deposition degrades surface water quality by lowering pH (i.e., increasing acidity); decreasing acid-neutralizing capacity (ANC); and increasing dissolved inorganic Al concentrations. In particular ANC is widely used as an indicator of the acid-base status of surface waters (Table 1). While emissions of SO\(_2\) have decreased over the past 40 years, concentrations of SO\(_4^{2-}\) in surface waters in acid-impacted regions like the Adirondacks and the Southern Appalachian Mountain regions generally remain high compared to background conditions (e.g., approximately 20 µeq/L; Cosby, 1991; Brakke et al., 1989).
Table 2.1. Categories of ANC and associated biological effects of surface water acidification (after USEPA, 2009).

<table>
<thead>
<tr>
<th>Category of ANC value and associated biological effects</th>
<th>Category of ANC value and associated biological effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chronic &lt; 0 µeq/L</td>
<td>Nearly complete loss of fish populations. Planktonic communities have low diversity, dominated by acidophilic forms. The number of individuals in plankton species present is greatly decreased.</td>
</tr>
<tr>
<td>Severe concern 0-20 µeq/L</td>
<td>Highly sensitive to episodic acidification. During episodes brook trout may experience lethal conditions. Diversity and distribution of zooplankton communities decline sharply.</td>
</tr>
<tr>
<td>Elevated concern 20-50 µeq/L</td>
<td>Fish species richness is greatly diminished (i.e., more than half of the expected species can be missing). On average brook trout experience sub-lethal effects, including decreased health, reproduction capacity and fitness. Diversity and distribution of zooplankton communities decline.</td>
</tr>
<tr>
<td>Moderate concern 50-100 µeq/L</td>
<td>Fish species begin to decline (sensitive species are lost). Possible sub-lethal effects to brook trout. Diversity and distribution of zooplankton begin to decline.</td>
</tr>
<tr>
<td>Low concern &gt; 100 µeq/L</td>
<td>Fish species richness unaffected. Brook trout reproduce where habitat is suitable. Zooplankton communities unaffected.</td>
</tr>
</tbody>
</table>

The Adirondacks is arguably the region in the U.S. most highly impacted by acidic deposition (Driscoll et al., 1991a). The Adirondack Park encompasses 2.4 million ha in northern New York, with about 1 million ha of publicly owned state lands and 1.4 ha of private lands. The region is a complex landscape of forested uplands and wetlands, and includes approximately 2800 lakes (> 0.2 ha). There have been several surveys conducted to quantify the acid-base status of Adirondack lakes. In 1984, the statistically based Eastern Lakes Survey determined that 10% of the Adirondack lakes (> 4 ha) had pH values < 5.0 and 13.9% of the lakes had ANC values < 0.
µeq/L. Note that the geographic boundary of the Eastern Lakes Survey for the Adirondack region was not consistent with the Adirondack Park or the Adirondack Ecological Zone (Driscoll et al., 1991b). In 1984-87 the Adirondack Lakes Survey determined that of 1469 lakes out of a population of 2759 lakes (lake surface area > 0.2 ha), 26% had pH < 5.0, 26% had ANC values < 0 µeq/L and 50% had ANC values < 50 µeq/L (Kretser et al., 1989). Surface waters with ANC less than 0 µeq/L are highly sensitive to acidification (Table 2.1). ANC of 0 µeq/L is a good endpoint for acidification. In the Adirondacks, surface waters with pH<5 generally coincide with ANC<0 µeq/L while in the GRSM, surface waters with pH<6 generally have ANC<0 µeq/L.

Like the Adirondacks, streams of the GRSM have been impacted by acidic deposition. There have been some focused studies on streams in the GRSM. Cook et al. (1994) examined longitudinal and temporal variations in water chemistry of several low-order, high-elevation streams. During base flow, the ANC of the streams studied ranged from –30 to 28 µeq/L and pH values ranged from 4.54 to 6.40. Nitrate and sulfate were the dominant anions in these streams. Cook et al. (1994) also used stable sulfur isotopes to determine that most of the sulfate in stream water was derived from atmospheric deposition.

Streams showed low ANC and pH values, and high Al concentrations at high elevations in the GRSM. Values of ANC and pH increased and Al concentrations decreased with increasing drainage area. Nodvin et al. (1995) studied two streams in the Noland Divide Watershed which is a very sensitive high-elevation watershed in the GRSM. Values of ANC were very low in these streams (-10 to 20 µeq/L), with NO₃⁻ occurring as the dominant anion but also with elevated concentrations of SO₄²⁻. High export of NO₃⁻ and SO₄²⁻ facilitated leaching losses of nutrient cations from these watersheds.
Cai et al., (2010) studied the same two streams in the Noland Divide Watershed. They showed that stream acidification was correlated with inputs of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$; precipitation volume; nitrification rates in the soil A horizon; soil adsorption and desorption of $\text{SO}_4^{2-}$, and export of base cations $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{Na}^+$ from soil. Cai et al., (2010; 2012b) also investigated the $\text{SO}_4^{2-}$ adsorption dynamics of soil samples, finding that soil was actively adsorbing $\text{SO}_4^{2-}$ inputs. Soils from the Noland Divide Watershed are not at their maximum adsorption, which suggests that soil in the watershed will continue to retain $\text{SO}_4^{2-}$, limiting transport to streams.

Atmospheric $\text{SO}_2$ emissions in the eastern U.S. peaked in the early 1970s, and have since been declining in response to emissions controls. Likewise, $\text{NO}_x$ emissions from electric utilities have been declining since 2003. Regional trends in surface water chemistry indicate that recovery of sensitive lakes and streams throughout acid-sensitive areas of the East is slow (Stoddard et al., 1999; Driscoll et al., 2003; Stoddard et al., 2003). Lakes and streams in the Adirondack and Catskill Mountains of New York, northern New England, the Upper Midwest and western Virginia have been intensively monitored since the early 1980s. An analysis shows that these lakes and streams have shown decreases in concentrations of sulfate at all sites except western Virginia (Stoddard et al., 2003). This pattern is consistent with decreases in emissions of $\text{SO}_2$ and atmospheric deposition of $\text{SO}_4^{2-}$. However, these lakes and streams exhibit limited recovery in pH and ANC, and continue to have acidic episodes (Stoddard et al., 1999; Stoddard et al., 2003). In contrast, most streams that have been monitored in the Central and Southern Appalachian Mountain regions have not yet shown signs of regional chemical recovery in response to reductions in S emissions and deposition (Webb, 2004; Stoddard et al. 2003). Indeed, streams have shown continuing increases in $\text{SO}_4^{2-}$ concentrations (Webb. 2004; Elwood et al.,
1991; Robinson et al., 2008). These increases in $\text{SO}_4^{2-}$ have coincided with slight decreases in ANC.

The Adirondack Long Term Monitoring (ALTM) data have shown relatively uniform decreases in $\text{SO}_4^{2-}$ concentrations across virtually all study lakes and decreases in $\text{NO}_3^-$ concentrations in many of the study lakes that are consistent with long-term decreases in atmospheric deposition of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ (Driscoll et al., 2007). These changes have resulted in increases in pH and ANC in many ALTM lakes. Waller et al. (2012) observed that decreases in lake $\text{SO}_4^{2-}$ and to a lesser extent $\text{NO}_3^-$ have generally coincided with increases in ANC, resulting in shifts in lakes among ANC sensitivity classes from the US EPA Temporally Integrated Monitoring of Ecosystems (TIME) program for the Adirondacks. The percentage of acidic Adirondack lakes (ANC <0 μeq/L) decreased from 15.5% (284 lakes) to 8.3% (152 lakes) since the implementation of the Acid Rain Program and the Nitrogen Budget Program from the early 1990s to the late 2000s.

Robinson et al. (2008) investigated the acid-base chemistry of streams at the GRSM over the period 1993 to 2002. They found that long-term temporal patterns in stream chemistry varied by elevation. At lower-elevation, streams showed significant decreasing trends in pH, ANC and $\text{SO}_4^{2-}$. At higher elevation there were no significant trends.

Response of Aquatic Biota to Acidification of Surface Waters by Acidic Deposition

Decreases in pH and elevated concentrations of dissolved inorganic Al have resulted in physiological changes to organisms, direct mortality of sensitive life history stages, and reduced the species diversity and abundance of aquatic life in many streams and lakes in acid-impacted
areas of the East. Fish have received the most attention to date, but entire food webs are often adversely affected (Schindler et al., 1985). Decreases in pH and increases in Al concentrations have diminished the species diversity and abundance of plankton, invertebrates, and fish in acid-impacted surface waters in the East (Baker et al., 1990).

Biological indicators such as fish and total zooplankton reflect the acid-base status of ecosystems through their response to ANC (Table 2.1). Previous studies have demonstrated the effects of acidic deposition and surface water acidification on fish, zooplankton and other biotic communities (Schindler et al. 1985; Bulger et al., 1999; Lovett et al., 2009). Fish and total zooplankton species richness decrease with decreases in ANC on the basis of spatial surveys (Sullivan et al. 2006; Lovett et al. 2009). For example, in the Adirondacks, chronically acidified lakes (ANC<0 µeq/L) are fishless. Fish and total zooplankton species declined greatly for ANC between 0 µeq/L and 50 µeq/L, began to decline for ANC between 50 µeq/L and 100 µeq/L and will not be affected for ANC more than 100 µeq/L. The GRSM National Park Service conducted a survey of the effects of stream water quality on aquatic macroinvertebrates and fish communities with GRSM and a total of 362 streams sites were surveyed between 1990 and 2009 (Cai, M., and Schwartz, 2012). They did not find brook trout (*Salvelinus fontinalis*) in surface waters with ANC<0 µeq/L and adult fish density and biomass were lower where pH <6.0 than where pH>6.0.

2.3 Acidification Models

Several models have been used as research tools to evaluate the effects of acidic deposition on forest watersheds and as management tools to plan and guide air quality
management policy to protect ecosystems from the effects of air pollution, including the determination of CLs. These models range from simple empirical relationships and steady-state models such as the Very Simple Dynamic Model (Posch and Reinds, 2009) and the Simple Mass Balance Model (Kennedy et al., 2001), to more complex and comprehensive dynamic models such as MAGIC (Model Acidification of Groundwater in Catchment; Cosby et al., 1985), and PnET-BGC (Chen and Driscoll, 2005b). Steady state models and dynamic models have their own strengths and weakness. Dynamic model can predict the chemical changes for the ecosystems over time. However, more detailed information is needed for parameterization and application.

2.3.1 Steady state models

The Simple Mass Balance (SMB) model uses an anion/cation balance of the leachate in a typical temperate acid forest soil to describe $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ leaching in terms of acidity, Cl$^-$ and base cation leaching (Kennedy et al., 2001). Soil chemical processes include cation exchange, weathering rate, sulfur oxidization, nitrogen immobilization, nitrogen uptake, and denitrification. The model doesn’t include sulfate adsorption and desorption; sulfur mineralization; or sulfate uptake by vegetation.

The Very Simple Dynamic (VSD) model has a single layer annual time step (Posch and Reinds, 2009). It contains of a set of mass balance equations describing the soil input-output relationships. Soil processes include CO$_2$ equilibrium, mineral weathering, cation exchange and internal production of organic acid. It doesn’t include sulfate adsorption, Al complexation, or
nitrogen mineralization.

2.3.2 Dynamic models

Dynamic models used in Europe and North America for critical loads calculations include MAGIC (Model of Acidification of Groundwater in Catchments) and PnET-BGC model.

MAGIC model is a lumped-parameter model (Cosby et al. 1985) that is used to simulate the watershed response of concentrations of major anions in atmospheric deposition. The biogeochemical reactions in the model include sulfur adsorption based on a Langmuir isotherm, cation weathering and exchange, aluminum dissolution/precipitation/speciation, and inorganic carbon dissolution and speciation.

The PnET-BGC model includes the cycling of all major elements (i.e., C, N, P, S, Ca, Mg, K, Na, Al, Cl, Si). Major biogeochemical reactions are vegetation processes, soil processes and water processes. Vegetation chemical processes include canopy interaction, CO₂ fertilization, litterfall, forest growth, root uptake. Soil processes include sulfur adsorption/desorption, nitrogen mineralization/nitrification, cation exchange, mineral weathering and aluminum dissolution/precipitation/speciation. Water processes include lake element retention (Gbondo-Tugbawa and Driscoll, 2001). The PnET-BGC can depict the N dynamic while MAGIC does not have a carbon cycle algorithm in the model (Wu and Driscoll, 2009).
Chapter 3 Methodology

3.1 PnET-BGC description and application

PnET-BGC is a comprehensive forest-soil-water model that links a C, N and water balance model, PnET-CN (Aber et al., 1997), with a biogeochemical model, BGC (Gbondo-Tugbawa and Driscoll, 2001). Input parameters for the model related to application to a specific site include time series of meteorological data, atmospheric deposition, element weathering, and land-disturbance history. Soil parameters needed for PnET-BGC include soil mass, water holding capacity, cation exchange capacity, cation exchange constants and anion adsorption constants. Vegetation is characterized in PnET-BGC using the major forest cover types represented at a site and incorporating the element stoichiometry associated with various tree cover types. A thorough description of the model including the processes depicted and a detailed sensitivity analysis of the model to inputs and parameter values are provided in Gbondo-Tugbawa et al. (2001), Fakhraei et al. (2014) and Pourmokhtarian et al. (2012). Model outputs include monthly fluxes of water and major elements within and from ecosystem compartments, and volume-weighted concentrations of major solutes in surface water.

PnET-BGC has been widely used in the northeastern U.S. It has been well validated for small watersheds with comprehensive field data for model testing (Gbondo-Tugbawa et al., 2001; Chen and Driscoll, 2004; Pourmokhtarian et al., 2012). Regional
scale applications have also been conducted (Chen and Driscoll, 2004; Chen and Driscoll, 2005a; Zhai et al., 2008). However, my study is the first effort to apply the model to unglaciated watersheds in the southeastern U.S.

3.2 Calculation for CLs and DCLs of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$

Steps that are used to develop CLs and DCLs include (Figure 1): (1) the identification of the ecosystem disturbance of concern from air pollution such as acidification or eutrophication; (2) the determination of biological indicators of air pollution stress- fish or zooplankton that are commonly used for aquatic ecosystems and vegetation species for terrestrial ecosystems; (3) the determination of chemical indicators that can be used to predict biological response to air pollution stress, such as soil base saturation or soil solution Ca/Al for acidification effects on forest vegetation or ANC, or pH for acidification response to aquatic organisms; and (4) finally critical chemical limits are established for chemical indicators. Models (empirical, steady-state or dynamic) are applied to evaluate the level of atmospheric deposition that will result in critical chemical indicators at values below their critical chemical limits and allow for the protection of sensitive biological populations.

The selection of chemical indicators and their limits is an important consideration in determining CLs and DCLs. Different chemical indicators are chosen based on the identification of biological resources (indicators) that should be protected from acidification stress. The U.S. EPA (2009) developed ANC categories of biological
response to acidification stress of surface waters (Table 2.1). Surface waters with ANC below 0 µeq/L often experience chronic acidification with complete loss of fish populations and low diversity of planktonic communities. Surface waters with ANC between 0-20 µeq/L are highly sensitive to episodic acidification. Fishes like brook trout (*Salvelinus fontinalis*) may experience health impacts under these sensitive conditions. Diversity and distribution of zooplankton communities also decline sharply. Surface waters with ANC between 20- 50 µeq/L are moderately sensitive to episodic acidification. Fish species richness is greatly diminished and diversity and distribution of zooplankton communities decline. Surface waters with ANC between 50-100 µeq/L are somewhat sensitive to acidification. Fish species begin to decline (sensitive species are lost) in this ANC range. Diversity and distribution of zooplankton also begin to decline. Surface waters with ANC greater than 100 µeq/L are thought to be insensitive to acidic deposition.

3.3 Model evaluation and sensitivity analysis

I evaluated the agreement between model simulations and observed water data using normalized mean error (NME) and normalized mean absolute error (NMAE) (Janssen and Heuberger 1995). These metrics were obtained as follows:

\[
NME = \frac{\bar{p} - \bar{o}}{\bar{o}}; NMAE = \frac{1}{n} \sum_{i=1}^{n} |p_i - o_i| \]

Equation 1
Where $p_t$ is the predicted value at time t; $o_t$ is the observed value at time t; $\bar{\sigma}$ and $\bar{p}$ are the average observed and predicted values over time t; and n is the number of observations. NME represents the error between a simulation result and an observation. NMAE represents the absolute error between simulation result and observation. Negative values for NME indicate that predicted values are less than observations. Positive values for NME indicate that the predicted values exceed observations.

A sensitivity analysis was conducted to quantify the relative response of model output variables to uncertainty in inputs or parameters of interest. The sensitivity responses can be calculated as follows:

$$S_{Param,x} = \frac{\partial X / X}{\partial Param / Param}$$

Equation 2

where X is the state variable; Param is the model input parameters. The higher the values of $S_{Param,x}$, the more sensitive the system is to the state variables (Gbondo-Tugbawa and Driscoll, 2001).

Sensitivity analyses have been previously conducted for PnET-BGC in the application of the model to watersheds in the Northeast (Aber et al., 1997; Gbondo-Tugbawa et al., 2001; Pourmokhtarian et al., 2012; Fakhraei et al., 2014). These studies show that biological processes depicted in the model are sensitive to meteorological factors such as temperature, precipitation and solar radiation (Pourmokhtarian et al., 2012). Gbondo-Tugbawa et al. (2001) conducted a detailed sensitivity analysis of projections of surface water ANC and soil base saturation to abiotic processes, finding that the model was particularly sensitive to soil partial pressure of carbon dioxide.
(P_{CO2}), cation exchange capacity, soil mass and soil selectivity coefficients for Ca^{2+} and Al^{3+}. I will also conduct a sensitivity analysis of projections of ANC and BS% in Constable Pond to model inputs and parameters including SO_4^{2-} and NO_3^{-} deposition, soil mass, site density, SO_4^{2-} adsorption capacity, CO_2 partial pressure (P_{CO2}), and cation exchange capacity (CEC).
Chapter 4 Factors Influencing Critical Loads and Dynamic Critical Loads for the Acidification of a Lake-Watershed in the Adirondack Region of New York

4.1 Objectives

While many studies have been conducted to quantify DCLs and CLs for ecosystems and regions, few have evaluated the influence of lake-watershed characteristics on these values. The major goal for this phase research was to establish the DCLs and CLs for NO$_3^-$ and SO$_4^{2-}$ deposition, and assess the response of soil and lake water at an acid-impacted lake-watershed in the Adirondack region of New York, U.S., Constable Pond, to various future changes in acidic deposition. I used the dynamic model PnET-BGC to determine CLs and DCLs as well as to probe the role of specific biophysical characteristics in regulating lake-watershed response to changes in atmospheric deposition. The specific objectives were to: 1) determine the DCLs and CLs for NO$_3^-$ and SO$_4^{2-}$ deposition for Constable Pond watershed and evaluate the tradeoffs of controls on these components of acidic deposition to achieve DCL/CLs; and 2) explore the lake-watershed characteristics that affect the calculation of DCL/CLs from the respect of SO$_4^{2-}$ and NO$_3^-$ deposition, specifically the supply of naturally occurring organic acids, historical land disturbance and the hydraulic residence time (HRT) of the lake.
4.2 Methods

4.2.1 Study site

Constable Pond (43°50’N, 74°48’W) is located in the western Adirondacks in the North Branch of the Moose River and experiences among the highest rates of atmospheric deposition in the region (Chen et al., 2004b). Constable Pond is a chronically acidic (ANC<0), thin-till drainage lake, with moderate concentrations of DOC (423 µmol C/L). The watershed area is 945.1 ha and lake elevation is about 584 m. The dominant vegetation type is northern hardwoods, with yellow birch (*Betula alleghaniensis*), red maple (*Acer rubrum*), red spruce (*Picea rubens*), eastern hemlock (*Tsuga Canadensis*); sugar maple (*Acer saccharum*) and American beech (*Fagus grandifolia*; Cronan et al., 1987). The HRT of the lake is 0.06 yr. There is detailed information on the lake and its watershed to facilitate model parameterization and testing (Chen et al. 2004b), including a time-series of water chemistry observations from 1983 to present (~2008).

4.2.2 Deposition Scenarios and Model Application

Sulfur is the major element that contributes to acidic deposition and soil and surface water acidification in the northeastern U.S. (Driscoll et al., 1998). Nitrogen, both oxidized (NO₃⁻) and reduced (NH₄⁺) forms, also contribute to acidic deposition. Ecosystem response to atmospheric N deposition is complex and highly variable over time and space due to multiple transformations that are mediated by plant and microbial
I evaluated different scenarios of future atmospheric NO$_3^-$ NH$_4^+$, SO$_4^{2-}$ deposition and combinations of SO$_4^{2-}$ and NO$_3^-$ and NH$_4^+$ and NO$_3^-$ deposition as model inputs.

Following previous research (Chen et al., 2004b; Zhai et al., 2008), model runs were initiated for Constable Pond watershed in 1000 AD, and run with a monthly time step under the assumption of constant background deposition (10% of current atmospheric deposition (~2008), mean meteorological conditions (average of available meteorological measurements) and no land disturbance until 1850 to achieve steady-state and evaluate “background” (i.e., pre-1850) conditions. Historical changes in atmospheric deposition, meteorology and land disturbance events were initiated after 1850. The model was run from 1850 through 2008 based on a combination of measured values of atmospheric deposition (from 1978 to 2010) extrapolated from detailed observations made at the Huntington Forest (43°58’ N, 74°13’ W) and reconstructions of historical deposition from emission records (1850 to 1978) following the approach described previously for PnET-BGC applications in the Adirondacks (Driscoll et al., 2001; Chen and Driscoll, 2004; Zhai et al., 2008; Fakhraei et al., 2014). Regression analyses were conducted between measured annual volume-weighted concentrations of major solutes in wet deposition at the Huntington Forest (NY20) from the National Atmospheric Deposition Program (NADP; 1978-2010) and emissions from the atmospheric source area for the Adirondacks (Zhai et al., 2008). These regressions were used in conjunction with historical emission estimates (Nizich et al., 1996) to reconstruct wet deposition for the period 1900 to 1978. For the period 1850 to 1900 concentrations of solutes in wet
deposition were assumed to increase linearly from estimated background values. Measured wet deposition (from NY20) was used from 1978 to 2008. The dry to wet deposition ratios for base cations, base anions and other elements for Huntington Forest were derived from Shepard et al. (1989). As there were no consistent trends in dry and wet deposition ratios among Clean Air Status and Trends Network (CASTNET) and nearby NADP sites in the northeastern US (http://epa.gov/castnet/javaweb/index.html), dry to wet deposition ratios for solute inputs were calibrated and held constant during the simulation period based on previous research (Shepard et al., 1989; Chen et al., 2004b) (SO$_4^{2-}$: 0.15; NO$_3^-$: 0.1; Ca$^{2+}$: 0.5; Mg$^{2+}$:0.5).

Historical meteorological data for Constable Pond were extrapolated from detailed time series measurements available from the Huntington Forest for meteorological observations starting from 1955 (air temperature, precipitation, photosynthetically active radiation; http://www.esf.edu/hss/em/huntington/ackerman.html) and from the reconstructions of historical wet deposition using empirical spatial models developed by Ito et al. (2002).

For forecasts, model simulations were continued through the year 2200 considering a range of deposition scenarios of decreasing change from ambient (2008) deposition to “background” deposition (0, 20, 40, 60, 80, 100% reductions) for SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ individually and in combination. Future scenarios included a 12-year linear decrease from current values (2008) to the level of deposition of interest (in 2020) and continued simulation at this deposition level through 2200. This range of values was used to evaluate tradeoffs associated with controls in SO$_2$, NO$_x$ or NH$_3$ emissions to achieve ecosystem recovery from acidic deposition. For future scenarios, meteorological data
conditions were assumed to remain constant as the mean of available measured monthly values.

4.2.3 Land Disturbance and Disturbance Scenarios

The Adirondack region has experienced land cover disturbance and change over the past 200 years (McNeil et al., 2006). Different types of disturbance, such as fire, forest harvest, meteorological events and road construction have occurred, leading to the changes in ecosystem structure and function. Land disturbance events may alter dissolved inorganic nitrogen (DIN) retention and loss, carbon storage and affect the response of watersheds to atmospheric N deposition (Aber et al., 2002).

Unfortunately, historical land disturbance records for specific watersheds in the Adirondacks are limited. McNeil et al., (2006) reconstructed the land disturbance history of the Adirondack region based on the interpretation of historic land disturbance maps assembled by the Adirondack Park Agency. Based on this analysis, it appears that there was a severe clear-cut in Constable Pond watershed around 1900. For the base case hindcast projection, I assumed a cutting occurred in 1900, which impacted 60% of the watershed and involved removal of 80% of the logged tree biomass (Aber and Driscoll, 1997).

To evaluate the role of historical land disturbance in past and potential future changes in surface water ANC, I considered two hypothetical land disturbance scenarios in additional to the base case. The first scenario was a short-rotation intense clear-cut in 1950 and again in 1995, with the cut occurring on 60% of the watershed with removal of
80% of the aboveground biomass (Table 4.1). The base case and the intense cutting scenario are compared with an additional scenario in which simulations were conducted assuming no historical land disturbance occurred.

4.2.4 Supply of Naturally Occurring Organic Acids

Dissolved organic carbon in forest soil and surface waters is mainly derived from humified organic matter formed from plant material (Zsolnay, 1996; Kalbitz et al., 2000). In PnET-BGC, a fraction of soil organic matter is mineralized and converted to dissolved organic carbon that can be mobilized from soil with drainage water. Dissolved organic carbon is depicted as an organic acid analog with the ability to protonate/deprotonate and complex Al (Driscoll et al., 1994; Gbondo-Tugbawa and Driscoll, 2001). For Constable Pond, the mean DOC over the period of record was 423 µmol C/L. To examine the role of supply of DOC in regulating the acid-base status of Adirondack lakes, two scenarios of lake DOC were considered in addition to the base case. The fraction of soil organic matter that is converted to DOC was: 1) increased such that the lake DOC concentration was 905 µmol C/L, indicative of elevated DOC waters; and 2) decreased such that the lake DOC concentration was 125 µmol C/L, indicative of low DOC waters (Driscoll et al. 1994). The elevated and low DOC waters were calculated by decreasing DOC selectivity coefficient to 10% and increasing DOC selectivity coefficient by ten times.

4.2.5 In-lake $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ Retention
The production of ANC can occur by in-lake retention of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$. In PnET-BGC, the removal of $\text{NO}_3^-$ ($R_N$) and $\text{SO}_4^{2-}$ ($R_S$) by in lake-processes is depicted as a mass transfer expression proposed by Kelly et al. (1987):

$$R_S = \frac{S_S}{(\bar{Z}/\tau_w) + S_S}$$  \hspace{1cm} \text{Equation 3}

$$R_N = \frac{S_N}{(\bar{Z}/\tau_w) + S_N}$$  \hspace{1cm} \text{Equation 4}

$\bar{Z}$ is the mean depth of the lake;

$\tau_w$ is the hydrological residence time; and

$S$ is the mass transfer coefficient for $\text{SO}_4^{2-}$ (S) or $\text{NO}_3^-$ (N).

Most lakes in the Adirondack region have short hydrological residence times (HRT <0.1 year) due to relatively large annual precipitation and relatively large watershed areas compared to lake surface areas (Driscoll et al., 1991a). For example, the HRT for Constable Pond is about 0.06 year and the mean depth is 2.11m. As a result, in-lake processes are not an important mechanism of ANC production in Constable Pond compared with watershed processes (e.g. mineral weathering, displacement of exchangeable base cations). However, some lakes in the Adirondacks have longer HRTs and changes in in-lake ANC production may be an important consideration for recovery of Adirondack Lakes from acidic deposition. To evaluate this process, I considered three hypothetical scenarios of HRT for Constable Pond in PnET-BGC simulations: 0.06, 0.6 and 6 years.

4.2.6 Computation Methods
I evaluated the effectiveness of decreases in $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ deposition to obtain a given level of ANC at steady-state (CLs) and under dynamic conditions (DCLs). To visualize the interplay between changes in $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ deposition and resulting lake ANC, I projected lake ANC using PnET-BGC under different loadings of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ individually and in combination for two periods: the mean of 2040-2050 which is the intermediate period prior to the lake-watershed achieving steady-state with respect to the change in deposition and therefore a DCL that may be relevant to a more near-term management perspective; and the mean of 2150-2200 which is a quasi steady-state condition and therefore indicative of the CL. From model output under different loads of $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ deposition for a given time interval (2040-2050 and 2150-2200), I interpolated ANC values to develop ANC isopleths to illustrate the responsiveness of Constable Pond ANC to variations $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ deposition. A similar analysis was done for $\text{NH}_4^+$ and $\text{NO}_3^-$ deposition to evaluate differences in ecosystem response to different loading of N species.

4.3 Results

4.3.1 Time Series of Model Hindcast and Forecast Projections of Lake Chemistry

In general, PnET-BGC reproduced the lake time series for Constable Pond over the period since measurements were initiated in 1983 (Figure 4.2; Table 4.1). Simulations showed a continuous decrease in lake $\text{SO}_4^{2-}$, which is consistent with estimated decreases
in atmospheric S deposition input to the model. The agreement between measured and model simulated SO$_4^{2-}$ was good (NME 0.0048; NMAE 0.073) (Table 4.2). In contrast, PnET-BGC captured the absolute value of lake NO$_3^-$ (NME 0.058; mean measured 28 µmol/L vs modeled 30 µmol/L NO$_3^-$); it failed to depict all of the year-to-year variation in annual NO$_3^-$ concentrations (NMAE 0.44) (Table 4.2). Previous efforts have shown the challenge of simulating forest ecosystem N dynamics and NO$_3^-$ loss due to sensitivity of the N cycle to meteorological variation and uncertainty in historical land disturbance (Chen et al., 2004b; Pourmokhtarian et al., 2012)

PnET-BGC effectively captured the magnitude and trends of lake base cations (Ca$^{2+}$ NME 0.054, NMAE 0.074) (Table 4.2). The model also was able to simulate the magnitude of ANC (NME -0.37), pH (NME 0.0024) and DOC (NME 0.046) (Table 4.2). NME values are probably not a good metric for model agreement with Constable ANC due to values near 0 µeq/L. Nevertheless, the mean observed ANC for Constable Pond over the monitoring period (-6.2 µeq/L) was similar to the measured value (-4.0 µeq/L). The model underpredicted the increase in measured ANC observed in recent years and is not capable of depicting the increase in DOC observed in Constable Pond due to inadequacies in the DOC algorithm in the model or elsewhere in Adirondack waters in response to decreases in acidic deposition (Driscoll et al., 2007). Soil time series data are not available for Constable Pond watershed, but the model simulated the single measurement of soil base saturation (%BS; measured soil %BS 7.8% vs. modeled 6.4%; Table 4.2) and exchangeable cations in 2005 (Sullivan et al., 2007). Accurate hindcasts of pH and ANC with PnET-BGC requires effective simulation of the concentrations and trends in all major solutes as these are used to calculate pH and ANC in the model.
Long-term model hindcasts suggest that in 1850, prior to the advent of acidic deposition, the acid-base status of Constable Pond was considerably different than currently. Projections of pre-industrial (before 1850) $\text{SO}_4^{2-}$ (15 µeq/L) and $\text{NO}_3^-$ (5 µeq/L) are considerably lower and ANC (43 µeq/L), pH (5.9) and soil %BS (22%) are considerably higher than both measured and modeled calculated values for Constable Pond today (Figure 4.2). The trajectory of the model hindcast from 1850 to today shows increases in lake $\text{SO}_4^{2-}$ that closely follow the pattern of reconstruction of the time series of atmospheric $\text{SO}_4^{2-}$ deposition, with a peak around 1975 and marked declines in recent years due to controls on emissions associated with the Clean Air Act. Simulated lake $\text{NO}_3^-$ concentrations are low in the 1800s. There is a peak in lake $\text{NO}_3^-$ in 1900 due to simulation of the cutting event that affects lake water chemistry for a short period (with associated increases in $\text{Ca}^{2+}$ and DOC, decreases in ANC and pH). Following recovery from the clear-cut, lake $\text{NO}_3^-$ increases in the mid 1900s due to maturation of forest in the watershed coupled with increases in atmospheric $\text{NO}_3^-$ and $\text{NH}_4^+$ deposition associated with increases in emissions. Unlike $\text{SO}_4^{2-}$, lake $\text{NO}_3^-$ does not closely follow changes in atmospheric N deposition due to strong vegetation and soil retention and ecosystem N cycling which is altered by year-to-year variation in meteorological conditions.

Concentrations of lake $\text{Ca}^{2+}$, the major base cation, closely match concentrations of strong acid anions ($\text{SO}_4^{2-}+\text{NO}_3^-$) and largely result from displacement from soil cation exchange sites. Note that the mobilization of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ coincides with the loss of cations from the soil exchanger (soil percent base saturation; %BS) and soil acidification during the last century. Coincident with the mobilization of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ are decreases
in ANC from 43 to -4 µeq/L and in pH from 5.9 to 5.0.

4.3.2 ANC and BS% in Response to Future S or N Reduction Scenarios

Calculations using PnET-BGC suggest that decreases in atmospheric SO\(_4^{2-}\) deposition are effective in increasing the ANC and soil BS% of acid impacted lake-watersheds in the Adirondacks, like Constable Pond. Model simulations indicate that following the decrease in atmospheric SO\(_4^{2-}\) deposition in 2020 (Figure 4.1) there is a marked initial decrease in SO\(_4^{2-}\) concentrations until the lake reaches steady-state with respect to the new inputs. In response to these changes, rates of ANC increase rapidly initially, and then diminish over time and approach steady-state around 2150-2200. Under the different scenarios of decreases in atmospheric SO\(_4^{2-}\) deposition of 0%, 20%, 40%, 60%, 80%, and 100% projected ANC are -2.3 µeq/L, 3.2 µeq/L, 8.9 µeq/L, 13.9 µeq/L, 18.8 µeq/L, and 21.9 µeq/L, respectively at quasi steady-state (i.e., 2150-2200) (Figure 4.3). These varying conditions result in rates of lake ANC increase of 0.02 µeq/L/yr, 0.05 µeq/L-yr, 0.08 µeq/L-yr, 0.10 µeq/L-yr, 0.13 µeq/L-yr, and 0.15 µeq/L-yr respectively over the forecast period (2010-2200). I also explored the response of soil %BS to hypothetical future changes in atmospheric deposition. The results of model simulations of %BS illustrate one of the challenges to recovery of forest ecosystems from acidic deposition. From the current modeled soil BS% of 6.4%, projections suggest future BS% ranging from a slight decrease to 6.2% under the 0% decrease scenario to an increase to 15.3% at a 100% decrease in atmospheric SO\(_4^{2-}\) deposition at steady state (2150-2200) (Figure 4.3). Even after complete elimination of anthropogenic SO\(_4^{2-}\) deposition for
nearly 200 years, model simulations suggest that soil BS% will not recover to estimated pre-industrial conditions (~22%).

Decreases in atmospheric N deposition were less effective in recovering ANC than an equivalent SO$_4^{2-}$ deposition. Under scenarios of 0%, 20%, 40%, 60%, 80%, and 100% decreases in atmospheric NO$_3^-$ deposition, steady-state values of ANC are projected to be -2.3 µeq/L, -0.49 µeq/L, 1.6 µeq/L, 3.4 µeq/L, 5.1 µeq/L and 6.7 µeq/L respectively (Figure 4.3). Under the NO$_3^-$ deposition control scenarios, the rate of ANC increase is 0.02 µeq/L/yr, 0.03 µeq/L/yr, 0.04 µeq/L/yr, 0.05 µeq/L/yr, 0.06 µeq/L/yr, and 0.07 µeq/L/yr, respectively over the simulation period. Soil BS% also responded over the simulation period ranging from slight continued soil acidification decreasing soil %BS to 6.2% under a 0% decrease in NO$_3^-$ deposition to an increase to 10% under a scenario of 100% elimination of anthropogenic NO$_3^-$ deposition.

I developed SO$_4^{2-}$-NO$_3^-$ deposition isopleths to examine the relative effectiveness of decreases in atmospheric SO$_4^{2-}$ and NO$_3^-$ deposition in accomplishing increases in the ANC of Constable Pond. I developed two isopleths; one depicting CL conditions for when the lake-watershed is at quasi steady-state with respect to the lower inputs of atmospheric deposition (2150-2200) and one depicting a DCL condition for a near term period that might be more relevant to the time-scale of management decisions (2040-2050) (Figure 4.7). Isopleths are plotted with SO$_4^{2-}$ deposition on the x-axis and NO$_3^-$ deposition on the y-axis with lines of equivalent ANC that are projected for different combinations of atmospheric SO$_4^{2-}$ and NO$_3^-$ deposition for the relevant period of interest. A few observations are evident from these isopleths. There are combinations of SO$_4^{2-}$ and NO$_3^-$ deposition levels at which positive ANC can be achieved for Constable
Pond. However, a unit decrease in atmospheric $\text{SO}_4^{2-}$ deposition is more effective in achieving a unit increase in ANC than a unit decrease in atmospheric $\text{NO}_3^-$ deposition. The slope of ANC for the parallel lines on the $\text{NO}_3^-$-$\text{SO}_4^{2-}$ isopleth at steady-state is about 2 and the slope for the 2040-2050 period is about 4.6 (Figure 4.7), suggesting that decreases in $\text{SO}_4^{2-}$ deposition is about two times and 4.6 times more effective than $\text{NO}_3^-$ deposition at steady-state and 2040-2050, respectively, to achieve the same increases of ANC.

I also examined the degree to which changes in $\text{NH}_4^+$ and $\text{NO}_3^-$ deposition influence lake ANC. In theory, atmospheric deposition of $\text{NH}_4^+$ followed by a given quantity of plant uptake and $\text{NO}_3^-$ leaching should decrease surface water ANC to a greater extent than the equivalent quantity of $\text{NO}_3^-$ (van Breemen et al., 1983) Indeed simulations with PnET-BGC suggest that decreases in atmospheric $\text{NO}_3^-$ deposition (0.049 µeq·L$^{-1}$/eq·ha$^{-1}$) will be slightly more effective in achieving increases in ANC than decreases in $\text{NH}_4^+$ deposition (0.034 µeq·L$^{-1}$/eq·ha$^{-1}$).

4.3.3 Historical Land Disturbance Effects

The model runs were made to evaluate the effects of hypothetical historical land disturbance on future recovery of Constable Pond under the individual decreases in $\text{NO}_3^-$ or $\text{SO}_4^{2-}$ deposition (i.e., 0, 20, 40, 60, 80, 100% decreases). Compared to the base case simulation with a historical clear-cut occurring in 1900, the initial loss of ANC after 1900 under the no-historical land disturbance scenario was delayed slightly. However, through the 20th Century, PnET-BGC simulations suggest limited difference between the base
case and the no-historical land disturbance scenario. The minimum ANC occurred around 2005 at a value of about -10 µeq/L for both scenarios, with a slightly lower BS% under the base-case (5.5%) than the no-historical land disturbance scenario (6.5%) due to the removal of base cations in forest vegetation associated with the historical clear-cut in 1900 (Figure 4.4). Under the potential future decreases in atmospheric NO\textsubscript{3}⁻ or SO\textsubscript{4}\textsuperscript{2⁻} deposition the condition of no historical forest disturbance is projected to recover slightly less ANC than the base case scenario. For example, under the no historical disturbance condition at steady-state (i.e., 2200) if NO\textsubscript{3}⁻ deposition is decreased to pre-industrial values, ANC values are projected to increase to 3.1 µeq/L, slightly lower than the ANC achieved under the base case scenario (5.7 µeq/L) (Figure 4.4). If SO\textsubscript{4}\textsuperscript{2⁻} deposition is decreased to pre-industrial values under the no historical land disturbance scenario, ANC values are projected to increase to 19.8 µeq/L, again lower than the ANC achieved under the base case scenario (29.8 µeq/L) (Figure 4.4).

The contrasting scenario I examined was a more intense forest disturbance scenario, with two clear-cuts occurring in 1950 and again in 1995. Simulations showed pulse decreases in ANC in the years immediately following the cuts associated with short-term elevated leaching losses of NO\textsubscript{3}⁻. These decreases are short-lived, but the long-term effects of repeated cutting disturbance is much more severe acidification resulting in lake ANC of – 14.7 µeq/L in 2005 and a minimum soil BS% of 3.9% (Figure 4.4). Although historical acidification is more severe under this more severe forest disturbance scenario, the extent of ANC recovery following decreases in SO\textsubscript{4}\textsuperscript{2⁻} or NO\textsubscript{3}⁻ deposition is greater than under the less severe historical land disturbance scenarios. Under the severe historical disturbance scenario at steady-state (i.e., 2200) if NO\textsubscript{3}⁻ deposition is decreased
to pre-industrial values, ANC values are projected to increase to 8.8 µeq/L, slightly higher than the ANC achieved under the base case scenario (5.7 µeq/L) (Figure 4.4). If SO$_4^{2-}$ deposition is decreased to pre-industrial values, ANC values are projected to increase to 32 µeq/L, again slightly higher than the ANC achieved under the base case scenario (29.8 µeq/L) (Figure 4.4).

4.3.4 Changes in the Supply of Naturally Occurring Organic Acids

To examine the role of supply of naturally occurring organic acids in changes in historical acidification and recovery under decreases in atmospheric deposition, I altered the extent to which soil organic matter was decomposed to DOC. There are a range of characteristics that affect DOC concentration (e.g., presence of wetlands, temperature, vegetation), but I chose this approach to manipulate concentrations in Constable Pond. In addition to the base-case scenario with a DOC concentration of 423 µmol C/L, simulations were also conducted under higher lake DOC concentration (905 µmol C/L) and lower DOC concentration (125 µmol C/L) (Figure 4.5). These latter two scenarios are considered to be representative of high and low DOC lakes in the Adirondacks. The supply of naturally occurring organic acids will alter lake ANC as well as pH buffering capacity due to occurrence of organic functional groups, particularly strongly acidic functional groups (Driscoll et al., 1994). In comparison with the projected pre-industrial (~1850) ANC of 43 µeq/L in the base-case, under the scenario of elevated supply of naturally occurring organic acids the pre-industrial ANC decreases to 34 µeq/L and under the scenario of limited supply of naturally occurring organic acids (125 µmol C/L) the
pre-industrial ANC increases to 52 μeq/L (Figure 4.5). This difference in ANC (± 9 μeq/L) due to variation in DOC supply to Constable Pond-watershed remains constant through the hindcast and all forecast simulations.

4.3.5 Hydrological Residence Time

Like many Adirondack lakes, Constable Pond has a relatively short HRT (0.06 yr). As a result in-lake processes do not strongly influence the neutralization of acidic deposition and the acid-base status of the lake. However, some Adirondack lakes have greater mean depths and HRTs and therefore in-lake processes can be manifested to a greater extent under these conditions. Lake area and watershed area affect HRTs (Kelly et al., 1987). As indicated earlier, the removal of SO\(_4^{2-}\) and NO\(_3^-\) is determined by HRTs, lake depth and mass transfer coefficients for SO\(_4^{2-}\) and NO\(_3^-\). To evaluate the extent to which in-lake retention of anions could influence historical acidification and the recovery from acidic deposition, I applied two scenarios of hypothetical simulations of longer HRTs (0.6 and 6 yrs) in addition to the base-case. Under the base-case scenario, following the historical clear-cut there was a short-term acidification event. Under conditions of longer HRTs rather than an acidification event after the historical clear-cut, an “alkalization” event is evident (Figure 4.6). Following the simulated historical clear-cut in 1900, there is elevated leaching of NO\(_3^-\) and base cations from the watershed to Constable Pond. Under the scenarios of longer HRTs this NO\(_3^-\) input was retained in the lake while base cations were not strongly retained resulting in marked production of ANC. More diffuse alkalization events are also simulated for the periods 1946-1956 and
1988-1998 due to conditions of elevated NO$_3^-$ leaching associated with variations in meteorological conditions. Finally the simulated minimum lake ANC in 2005 (-7.6 µeq/L under the base case) increases with increases in HRT due to greater retention of SO$_4^{2-}$ and NO$_3^-$ (11.4 µeq/L for 0.6 yr HRT; 20.1 µeq/L for 6 yr HRT).

Projections of future changes in ANC with decreases in atmospheric SO$_4^{2-}$ and NO$_3^-$ deposition show a pattern of recovery that is considerably different under elevated HRT compared to the base case. Increasing HRT greatly increased the ANC value achieved in recovery for a given level of future decreases in atmospheric SO$_4^{2-}$ deposition. In contrast, future decreases in atmospheric NO$_3^-$ deposition have an acidifying effect relative to the base case. This counterintuitive response is due to the relatively higher mass transfer coefficient for in-lake retention of NO$_3^-$. Under higher loading of NO$_3^-$ from the watershed to the lake, there is greater in-lake retention of NO$_3^-$ and therefore, produced ANC. As a result, decreases in atmospheric NO$_3^-$ deposition will result in decreases in NO$_3^-$ leaching from the watershed, less in-lake retention of NO$_3^-$ and lower production of ANC.

4.3.6 Sensitivity analysis for Constable Pond Watershed

I conducted a sensitivity analysis of projections of ANC and %BS to variation in model inputs and parameters, including SO$_4^{2-}$ and NO$_3^-$ deposition, soil mass, site density, SO$_4^{2-}$ adsorption capacity, CO$_2$ partial pressure (P$_{CO2}$), and cation exchange capacity (CEC) (Table 4.3). The range of changes in different inputs and parameters used for this analysis was between ±10% of current values. For example, $S^{(ANC)}$ and $S^{(%BS)}$ for SO$_4^{2-}$
deposition is -2.6 and -1.2, respectively. If \( \text{SO}_4^{2-} \) deposition is increased by 10% of current deposition, ANC will decrease by 26% of the current value while soil base saturation is projected to decrease by 12% of the current value. Model projections of ANC and %BS were found to be sensitive to \( \text{SO}_4^{2-} \) wet deposition, \( \text{NO}_3^- \) wet deposition, \( \text{P}_{\text{CO}_2} \), CEC, and soil mass, which is consistent with the previous studies (Gbondo-Tugbawa and Driscoll, 2001).

The model was found to be most sensitive to \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \) deposition, and soil CEC. \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) are the major strong acid anions in dilute lake water and strongly influence ANC. A unit change in \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) deposition results in changes in the concentrations of these anions in drainage water resulting in a relatively sensitive response in projections of ANC and BS%, compared with other parameters. Model calculations are also sensitive to soil CEC. Variation in CEC affects the pool of exchange sites meaning more or less basic cations are available to be displaced by inputs of acidic deposition. This parameter strongly affects soil %BS and ANC simulations.

The model as applied to Constable Pond is moderately sensitive to soil mass and \( \text{P}_{\text{CO}_2} \). Changes in soil mass affect all soil pools and model processes that are mediated through soil (e.g., mineralization, cation and anion exchange). The model is relatively insensitive to site density, DOC concentration and low \( \text{SO}_4^{2-} \) adsorption capacity. DOC concentration (422 µmol C/L) and soil \( \text{SO}_4^{2-} \) adsorption capacity are relatively low in Constable Pond. Unit variations in these parameters do not substantially affect model projections of ANC or BS%.
4.4 Discussion

4.4.1 Comparisons of Effects of Changes in ${\text{SO}}_4^{2-}$ and ${\text{NO}}_3^-$ Deposition

The model simulations demonstrate that the recovery of lake ANC is accomplished more effectively by equivalent decreases in ${\text{SO}}_4^{2-}$ deposition compared to ${\text{NO}}_3^-$ deposition under all the hypothetical conditions shown for Constable Pond. Inputs of ${\text{SO}}_4^{2-}$ are the main contributor to the acidification of soil and surface waters in the northeastern US (Church et al., 1989). Constable Pond watershed has received greater historical total ${\text{SO}}_4^{2-}$ deposition (dry and wet; currently 311.1 eq/ha-yr) than ${\text{NO}}_3^-$ deposition (dry and wet; 203.7 eq/ha-yr) (Figure 1). Atmospheric deposition of ${\text{SO}}_4^{2-}$ is transported more conservatively through lake-watersheds than ${\text{NO}}_3^-$ and therefore contributes more effectively to the leaching of cations from the ecosystem and the resulting acidification. N saturation is defined as the condition that occurs when the external supply of N to a watershed exceeds the demand for N by plants, microbes and soil within the watershed (Stoddard, 1994; Aber et al., 1989). Studies have shown that watershed ecosystems in the eastern U.S have not generally reached N saturation, and have capacity to retain N inputs (Driscoll et al., 2003). The time for a forest ecosystem to reach N saturation is on the order of multiple decades to centuries (Driscoll et al., 2003). Model calculations show that lake-watershed N retention diminishes over time, although a condition of N saturation is not attained by the end of the simulation period. This long-term increase in ${\text{NO}}_3^-$ leaching as the forest vegetation matures will likely diminish the effects of decreases in atmospheric N deposition.
4.4.2 Land disturbance

Simulation results suggest that land disturbance associated with forest cutting has enhanced historical acidification associated with acidic deposition. Following forest cutting around 1900 in the base case scenario, lake ANC decreased sharply for a few years due to high loss of NO$_3^-$ (Figure 4.2; Figure 4.4; Aber and Driscoll, 1997). The mobilization of Ca$^{2+}$ from soil cation exchange sites to water associated with the leaching of NO$_3^-$ attenuates the pulse decrease in ANC. Forest cutting decreases plant uptake over the short term. As soil N mineralization proceeds in the absence to vegetation uptake the supply of available NH$_4^+$ is nitrified allowing for elevated NO$_3^-$ losses in drainage (Aber and Driscoll, 1997). In addition to these short-term effects, model simulations suggest that forest cutting can enhance the susceptibility of acid-sensitive watersheds to acidification by acidic deposition. The removal of biomass from cutting decreases in the ecosystem pool of nutrient cations and as a result allows for greater soil and water acidification from acidic deposition.

Model simulations also suggest that forest cutting can enhance the extent of ANC recovery over the long-term. Goodale and Aber (2001) evaluated long term effects of logging and fire on northern hardwood forests in the eastern US and found that the old growth sites had higher nitrification rates and higher stream NO$_3^-$ concentrations compared with the historically disturbed sites. High nitrification rate and lower watershed N retention is one possible explanation for the relative lower ANC under the no-historical land disturbance scenario when the model reaches steady state. Another reason could be
due to the second growth or new growth of the forest, which needs more nutrients after
the land disturbance. ANC will increase under historical land disturbance than no
historical land disturbance due to greater retention of N inputs by an aggrading forest.

4.4.3 DOC

Model simulations show that changes in the supply of dissolved organic matter
(DOM) affects the acid-base status of Adirondack waters. In PnET-BGC, the acid-base
character of DOM is modeled as a triprotic analog (Driscoll et al., 1994; Gbondo-
Tugbawa et al., 2001). DOM has strongly acidic functional groups that consume ANC.
Ito et al. (2005) found that concentrations of DOC increase with increasing proportion of
the wetland area in lake-watersheds in the Adirondack region.

Adirondack lakes appear to be experiencing changes in DOM in response to
decreases in acidic deposition. A large fraction of lakes exhibit significant increases in
DOC coincident with decreases in $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ and increases in pH and ANC (Driscoll
et al., 2007). For example, DOC in Constable Pond has increased from 400 µmol C/L
when monitoring was initiated in 1983 to 500 µmol C/L currently. This phenomenon is
consistent with the observations for many monitored surface waters in Europe and North
America (Monteith et al., 2007), including the Adirondacks (Driscoll et al. 2007).

Increases in DOC have important implications for the future structure and
function of aquatic ecosystems. The attenuation of light and the thermal stratification of
Adirondack lakes is strongly regulated by DOM (Effler et al., 1985). Also, DOM is
apparently an important energy source for unproductive Adirondack lakes (Adams et al.,
Scandinavian studies have recently reported increases in fish mercury concentrations coincident with increases in DOC (Akerblom et al., 2012; Hongve et al., 2012). The acidic characteristics of DOM can alter the pH and ANC of Adirondack lakes (Driscoll et al., 1994).

While PnET-BGC can be parameterized to simulate ambient concentrations of DOC and to depict its effects on the acid-base chemistry of surface waters (Gbondo-Tugbawa et al. 2001), it is not able to represent the widespread observation of the compensatory increase in DOM to decreases in acidic deposition as it does not consider changes in DOM partitioning to soil with variations in pH. Given the ongoing decreases in acidic deposition and the need to project accurate targets for ecosystem recovery from acidic deposition, this would seem to be a critical limitation of modeling efforts to project DCLs and CLs.

4.4.4 In-lake processes

In-lake processes are complex biogeochemical phenomena, but generally the net effect is an alkalization process (Schindler et al., 1985; Kilham, 1982). The short-term fluctuation in NO$_3^-$ and ANC around 1900 illustrates some of the intricacies of in-lake process (Figure 4.6). Whether the lake processes generate or consume ANC depends on the supply of major anions and major cations and the specific HRT. The projection of changes in ANC values around 1900 in Constable Pond shifts from negative values under low HRT to positive values at longer HRT due to the preferential retention of SO$_4^{2-}$ and particularly NO$_3^-$ over basic cations that are mobilized following the historical clear-cut
Previous studies have indicated that in-lake $\text{NO}_3^-$ or $\text{SO}_4^{2-}$ removal increases with elevated HRT (Kelly et al., 1987). Based on this theory, a large amount of leaching $\text{NO}_3^-$ or $\text{SO}_4^{2-}$ is removed under the longer HRT scenario than shorter HRT scenario through in-lake processes. Meanwhile, the removal rate of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ is slower than $\text{SO}_4^{2-}$ and $\text{NO}_3^-$. The greater mass transfer coefficient for in-lake $\text{NO}_3^-$ retention than $\text{SO}_4^{2-}$ retention has implications for strategies of achieving lake ANC for recovery. Because many Adirondack lakes are characterized by short HRTs, in-lake processes are not an important consideration in the recovery of these ecosystems. However, in-lake processes can be significant in larger lakes or lakes with smaller watersheds where these processes are manifested. Greater increases in ANC can be achieved in response to decreases in $\text{SO}_4^{2-}$ deposition in lakes with longer HRTs than shorter HRTs due to greater in-lake retention of $\text{SO}_4^{2-}$. In contrast, decreases in $\text{NO}_3^-$ deposition are projected to result in lesser increases in ANC in lakes with longer HRTs due to the relatively efficient in-lake retention of $\text{NO}_3^-$. This differential response of increases in ANC to equivalent decreases in $\text{SO}_4^{2-}$ compared to $\text{NO}_3^-$ deposition are an additional consideration of the greater effectiveness of decreases in $\text{SO}_4^{2-}$ deposition in facilitating recovery of Adirondack lakes (as discussed in section 4.4.1).
Table 4.1. Hypothetical land disturbance scenarios for Constable Pond Watershed.

<table>
<thead>
<tr>
<th>Event</th>
<th>Year</th>
<th>Percent of Land Area Cut</th>
<th>Percent of Biomass Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1900</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>1950</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>

Table 4.2. Simulated and observed mean values for different chemical species in Constable Pond over the monitoring period 1983-2007.

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Ca (ueq/L)</th>
<th>SO₄²⁻ (ueq/L)</th>
<th>NO₃⁻ (ueq/L)</th>
<th>ANC (ueq/L)</th>
<th>pH</th>
<th>DOC (ueq/L)</th>
<th>BS%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation</td>
<td>85.77</td>
<td>120.11</td>
<td>29.85</td>
<td>-3.96</td>
<td>5.02</td>
<td>442.20</td>
<td>6.385</td>
</tr>
<tr>
<td>Observation</td>
<td>81.39</td>
<td>119.54</td>
<td>28.21</td>
<td>-6.24</td>
<td>5.01</td>
<td>422.64</td>
<td>7.790</td>
</tr>
<tr>
<td>NME</td>
<td>0.054</td>
<td>0.0048</td>
<td>0.058</td>
<td>-0.37</td>
<td>0.0024</td>
<td>0.046</td>
<td></td>
</tr>
<tr>
<td>NMAE</td>
<td>0.074</td>
<td>0.073</td>
<td>0.44</td>
<td>-0.95</td>
<td>0.029</td>
<td>0.16</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3. Sensitivity analysis of simulated ANC and BS% for Constable Pond in response to variability in selected parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>S(ANC)</th>
<th>S(BS%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate wet deposition (eq/ha-y)</td>
<td>290.3-365.7</td>
<td>-2.6</td>
<td>-1.2</td>
</tr>
<tr>
<td>Nitrate wet deposition (eq/ha-y)</td>
<td>172.5-233.5</td>
<td>-0.64</td>
<td>-0.4</td>
</tr>
<tr>
<td>Soil mass (kg/m²)</td>
<td>465.7-630.1</td>
<td>-0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>SO₄²⁻ adsorption capacity (mmol/g)</td>
<td>3.6-36</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>CEC (kmol/ha)</td>
<td>139-181</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Site density (mol/mol c)</td>
<td>0.015-0.030</td>
<td>0.02</td>
<td>0.1</td>
</tr>
<tr>
<td>pCO₂</td>
<td>1.5-2.5</td>
<td>0.27</td>
<td>-0.77</td>
</tr>
</tbody>
</table>

Note: $S^{(ANC)}$ and $S^{(BS%)}$ are sensitivity of ANC and base saturation for each parameter or input. CEC is the cation exchange capacity. Soil Mass, soil mass per unit area; Site DOC, moles of organic anion sites per moles of organic carbon; pCO₂, partial pressure of CO₂ in the soil.
Figure 4.1. Hindcast and forecast deposition scenarios for SO$_4^{2-}$ (a) and NO$_3^-$ (b) at Constable Pond.
Figure 4.2. Long-term model simulations concentrations of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$, ANC, pH, and DOC in lakewater and BS% in soil at Constable Pond from 1800 to 2200.
Figure 4.3. Long term simulations of $\text{NO}_3^-$, $\text{SO}_4^{2-}$, ANC and soil BS% in response to past and different future scenarios of $\text{NO}_3^-$, $\text{SO}_4^{2-}$ deposition at Constable Pond.
Figure 4.4. Simulations of ANC for Constable Pond from 1800 to 2200 under three hypothetical land disturbance scenarios (1900 land disturbance; no forest harvesting; 1950 and 1995 land disturbance) in response to past and hypothetical future decreases in NO$_3^-$ (a) and SO$_4^{2-}$ (b).
Figure 4.5. Simulations of ANC at Constable Pond over 1800 to 2200 under scenarios of high, ambient, and low DOC concentration (i.e., 1000 µmol C/L, 450 µmol C/L, 100 µmol C/L) in response to past and hypothetical future decreases in NO$_3^-$ (a) and SO$_4^{2-}$ (b).
Figure 4.6. Simulations of ANC for Constable Pond over 1800 to 2200 under scenarios of three different hydrological residence times (6 year, 0.6 year and 0.06 year) in response to past and hypothetical decreases in \( \text{NO}_3^- \) (a) and \( \text{SO}_4^{2-} \) (b) deposition.
Figure 4.7. Isopleths of ANC for 2150 to 2200 (a) and for 2040 to 2050 (b) at Constable Pond showing the combinations of total $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ deposition that result in projected values of ANC.
Chapter 5 Responses of 20 lake-watersheds in the Adirondack region of New York to historical and potential future acidic deposition

5.1 Objectives

While insight was gained in the analysis for Constable Pond, it is essential to quantify how diverse lake-watersheds of the Adirondacks respond to changes in acidic deposition. I used the dynamic model PnET-BGC to quantify historical acidification and project the future response of 20 lake-watersheds in the Adirondacks due to changes in SO$_4^{2-}$+NO$_3^-$ deposition. Moreover, I determined the CLs and DCLs of NO$_3^-$ and SO$_4^{2-}$ deposition needed to achieve target ANC values for Adirondack lakes; and evaluated the application of biological indicators (Fish and total zooplankton species richness) as a proxy to assess historical effects of acidic deposition and response to hypothetical future recovery.

5.2 Methods

5.2.1 Site description

I selected 20 lake watersheds from the Adirondack region of New York for analysis based on chemical and physical characteristics (Table 5.1). These sites were chosen as a subset of lakes from Adirondacks Long Term Monitoring Program (ALTM) (Driscoll et al. 2007). The 20 sites represented chronically acidic (ANC < 0 μeq/L; n= 5), episodically
acidic (0 < ANC < 50 µeq/L; n= 11) and relative acid-insensitive lakes (ANC > 50 µeq/L; n= 4) based on presumed lake sensitivity to acidification (Driscoll et al., 2001; USEPA 2009). The 20 sites were also characteristic of a range of acid sensitivity based on lake-watershed classification derived from surficial geology - 11 drainage lakes are situated in thin glacial till, seven medium till drainage lakes, one thick till drainage lake, and one seepage lake (Driscoll et al. 2003). Normally the thin till and seepage lakes are low ANC lakes (Tale 5.1). The study sites encompass a range of watershed areas (1.5-186.9 ha), and elevation (421-743 m) to depict characteristics of lake-watersheds in the Adirondack region.

Lake water chemistry data are available through the Adirondack Long Term Monitoring Program (ALTM) (http://www.adirondacklakessurvey.org/). The ALTM provides monthly concentration data of major solutes (e.g., SO$_4^{2-}$, NO$_3^-$, Ca$^{2+}$, Mg$^{2+}$, ANC, pH). The program was initiated in 1983 with 17 lakes and expanded with the addition of 35 additional lakes in 1992. Two of the 20 sites selected for modeling (Arbutus Lake and Constable Pond) are from the original suite of lakes. Soil chemistry data are available for these sites from a detailed survey of Adirondack watersheds (Sullivan et al., 2006a). I integrated the soil data for the 20 sites and prepared all required data for inputs, parameters and model testing.

5.2.2 Model Data Development

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

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

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

PnET-BGC estimates dry deposition of chemical constituents based on the use of dry to wet deposition ratios. Dry to wet deposition ratios for base cations, NH$_4^+$ and Cl$^-$ were estimated from throughfall studies at the Huntington Forest (Shepard et al., 1989). Since a consistent temporal trend was not observed in dry to wet S and N deposition ratios among
CASTNET and nearby NADP sites in the northeastern US (http://epa.gov/castnet/javaweb/index.html), a constant dry to wet deposition ratio over time was assumed. Spatial patterns in dry to wet deposition for the $\text{SO}_4^{2-}$ and $\text{NO}_3^{-}$ were calculated based on spatial models developed by Ollinger et al. (1993) and then modified by Chen and Driscoll (2004) to incorporate effects of forest composition (Cronan, 1985).

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

Land disturbance history was developed for each watershed from historical records of disturbance including fire and logging prior to 1916, blow down events in 1950 and 1995 and an extensive ice storm in 1998 (McNeil et al., 2006). These data were obtained through Adirondack Park Agency geographical information system (GIS) data layers, ALSC website (http://www.adirondacklakessurvey.org/) and a written history by McMartin (1994).

5.2.3 Projected future deposition scenarios for Adirondack lake-watersheds

I applied a series of scenarios to evaluate the response of Adirondack lake watersheds to hypothetical future decreases in acidic deposition. Using an acid-sensitive lake watershed, Jockeybush Lake, as an example (lake ANC=2.7 µeq/L), I illustrate the hindcast and suite of forecast projections of atmospheric $\text{SO}_4^{2-}+\text{NO}_3^{-}$ deposition, similar to the approach applied to
all sites studied (Figure 5.1(a)). The hindcast time series of \( \text{SO}_4^{2-} + \text{NO}_3^- \) deposition was developed using the approach described above (section 5.2.2; Figure 5.1(a)). The mean of \( \text{SO}_4^{2-} + \text{NO}_3^- \) deposition for 2004-2008 was used as an estimate of current deposition. From current deposition, I projected a suite of hypothetical future deposition scenarios that included a 12-year linear decrease from current deposition in 2008 to the level of deposition of interest in 2020 and that continued at this deposition until 2200. These deposition scenarios (0, 20, 40, 60, 80, 100% reductions) reflect 20% increments of the difference between ambient deposition of \( \text{SO}_4^{2-} + \text{NO}_3^- \) (~2008) and historical deposition (1850).

5.2.4 Estimates of CLs and DCLs of \( \text{SO}_4^{2-} + \text{NO}_3^- \) for Adirondack lake-watersheds

I chose the critical chemical criteria for ANC of 0, 20 and 50 \( \mu \text{eq}/\text{L} \) as targets for DCLs and CLs. These values have been used in previous calculation of CLs (USEPA 2009). Surface waters with ANC less than 0, between 0 to 20 \( \mu \text{eq}/\text{L} \), and between 20 to 50 \( \mu \text{eq}/\text{L} \) experience chronic, episodic and relative insensitive to acidification (Table 2.1). The loss of biological species also shows different patterns to the acidification in these ranges of ANC values (Table 2.1). So ANC of 0, 20 and 50 \( \mu \text{eq}/\text{L} \) are good critical chemical criteria for the acidification. Initially the model was run for all scenarios of \( \text{SO}_4^{2-} + \text{NO}_3^- \) deposition for every study site. Simulations show that lake ANC increases as future \( \text{SO}_4^{2-} + \text{NO}_3^- \) deposition is decreased. Then, based on the six model projections for individual sites, lake ANC values were interpolated for a given year to determine the load of \( \text{SO}_4^{2-} + \text{NO}_3^- \) necessary to achieve a target ANC of interest (i.e., 0, 20, 50 \( \mu \text{eq}/\text{L} \)). Note that in some cases model calculations suggest that, even under pre-industrial deposition values, the target ANC could not be
achieved. Some of these sites are naturally acidic; some of these sites are acidified by the acidic deposition. Using these interpolated data for the 20 sites for a given year, linear regression analysis was conducted to establish relationships between current lake ANC and the deposition of $\text{SO}_4^{2-}+\text{NO}_3^-$ to achieve a target ANC.

5.2.5 Multiple stepwise regression analysis

I define historical acidification (HA) as the change in simulated ANC from the pre-industrial value of 1850 to the lowest ANC value that occurred over the recent period (1990-2008). These values are illustrated in Figure 5.1(b) for hindcast and future projections of Jockeybush Lake. I used linear and multiple regression analysis to explore the relationships for historical acidification with site specific factors including current $\text{SO}_4^{2-}+\text{NO}_3^-$ deposition, $\text{Ca}^{2+}$ weathering rate, historical ANC (1850), elevation, watershed area, and DOC. The regression analysis was performed in statistical analysis software (SAS. 9.0) using F-test with a significant level of $p<0.01$.

5.2.6 Fish species and total zooplankton species richness

Projections of the chemical indicator ANC were used to evaluate the application of biological indicators (fish species and total zooplankton species richness) and estimated the response of fish and total zooplankton species richness to changes in past and future acidic deposition. Empirical relationships between fish and zooplankton species richness and lake ANC have been developed from spatial surveys (Sullivan et al., 2006). A logistic relationship
between fish species richness and ANC was developed based on the Adirondack Lakes Survey or water chemistry and fish conducted in the 1980s (Equation 5; Baker et al. 1990; Lovett et al. 2009). A relationship between total zooplankton species richness and ANC was also developed based on datasets from three surveys: U.S. EPA’s Eastern Lakes Survey in 1986; EMAP during the period of 1991-1994; EPA Science to Achieve Results (STAR) during the period of 1999-2001 (Equation 6) (Sullivan et al., 2006). These empirical relationships together with simulated ANC values, were used to depict the temporal responses of fish and zooplankton species richness to changes in atmospheric \( \text{SO}_4^{2-} + \text{NO}_3^- \) deposition in the study lakes.

\[
\text{Fish Species Richness} = 0.18 + \left[ \frac{5.7}{1 + \left( \frac{\text{ANC}}{28} \right)^{1.63}} \right] (r^2 = 0.9) \quad \text{Equation 5;}
\]

\[
\text{Zooplankton Species Richness} = 15.65 + 0.089\text{ANC} (r^2 = 0.46) \quad \text{Equation 6;}
\]

5.3 Results

5.3.1 Model performance

Generally PnET-BGC was able to effectively simulate Adirondack lake chemistry data. The mean of simulated \( \text{SO}_4^{2-}, \text{NO}_3^- \), divalent base cations (\( \text{Ca}^{2+} + \text{Mg}^{2+} \)), and ANC matched well with the mean of observed values for the 20 lakes for the period 1992 to 2008 (Figure 5.2). The mean simulated \( \text{SO}_4^{2-} \) (94.0 ± 14.0 µeq/L) is similar to the mean observed \( \text{SO}_4^{2-} \) (95.7 ± 14.1µeq/L; mean NME: -0.02) for the 20 sites. Simulated \( \text{NO}_3^- \) is slightly
overpredicted compared with observed NO$_3^-$\textsuperscript{-}. The discrepancy between measured (14.6 ± 7.9 meq/L) and model simulated NO$_3^-$ (23.2 ± 8.7 meq/L; mean NME: 0.36) is greater than other solutes due to the challenges in simulation of lake-watershed N dynamics (Pourmokhtarian et al. 2012). In particular, projections of NO$_3^-$ are sensitive to meteorological conditions and historical land disturbance. Uncertainty in these inputs for individual sites likely contributes to errors in simulations of lake NO$_3^-$\textsuperscript{-}. The mean simulated divalent base cations (112.4 ± 57.2 µeq/L) for the 20 lakes matched well with the mean observed value (110.0 ± 40.7 µeq/L; mean NME: 0.03). Mean simulated ANC (19.5 ± 28.4 µeq/L) also agreed well with the mean observed value (21.9 ± 31.5 µeq/L; mean NME: -0.15). The mean simulated base saturation (11.3% ± 9.3%) was somewhat overestimated compared with observed value (7.9% ± 3.3%; mean NME: 0.03).

5.3.2 Long-term simulations of lake response to historical and potential future changes in acidic deposition.

Simulations of historical and hypothetical future deposition scenarios were made for the 20 Adirondack lake watersheds. Jockeybush Lake is used as an example showing the time-series of lake ANC responses following the deposition scenarios from 1850 to 2200 (Figure 5.1). Before 1850, the ANC of Jockeybush was estimated to be around 60 µeq/L. After about 1900, the ANC was simulated to decrease markedly with increases in atmospheric SO$_4^{2-} \text{+NO}_3^-$ deposition until 2008. Historical acidification for Jockeybush Lake is 61.2 µeq/L. After 2008, the suite of hypothetical scenarios of decreases in acidic deposition were invoked, ranging from 0 to 100%. Simulations for the high-reduction scenarios
exhibited relatively rapid patterns of ANC increase shortly after the decrease in deposition was realized (2020), with the rate of ANC increase decreasing over time. The simulations reached steady-state with respect to the new lower deposition approximately by 2200. Under the scenario of a 100% decrease in $\text{SO}_4^{2-}+\text{NO}_3^-$ deposition, the maximum ANC of 41.5 $\mu$eq/L was attained, a value considerably lower than the estimate of pre-industrial ANC. This apparent hysteresis in the lake-watershed response to increases then decreases in $\text{SO}_4^{2-}+\text{NO}_3^-$ deposition is attributed to the loss of exchangeable Ca$^{2+}$ and Mg$^{2+}$ from soil during the historical period of elevated deposition. Under the lower reduction scenarios (0, 20% decreases) following a period (several decades) of increases in ANC, a long-term decline in ANC was simulated due to the maturation of forest stands and simulated long-term declines in lake-watershed retention of atmospheric N inputs.

I also evaluated the acid-base status of the 20 lake-watersheds under pre-industrial conditions. Simulations of mean lake concentrations prior to 1850 were $14.8 \pm 5.3 \mu$eq/L for $\text{SO}_4^{2-}$ and $3.8 \pm 1.2 \mu$eq/L for $\text{NO}_3^-$ (Figure 5.3). These values are considerably less than current concentrations and illustrate the effect of atmospheric deposition on lake chemistry. Model hindcasts of the pre-industrial conditions suggested that none of the 20 study lakes were chronically acidic (ANC < 0 $\mu$eq/L). The mean pre-industrial ANC of the study sites was $77.0 \pm 45.1 \mu$eq/L (Figure 5.3). All the lake-watersheds simulated decreases in ANC from pre-industrial to the current conditions, indicative of the acidification associated with historical increases in acidic deposition. The mean of simulated ANC in 2200 increased from $27.8 \pm 42.6 \mu$eq/L under 0% reduction scenario to $71.9 \pm 43.4 \mu$eq/L under 100% reduction scenario. Soil base saturation exhibited a temporal pattern that is similar to that of lake ANC. The mean simulated base saturation under preindustrial conditions was $23\% \pm 11.1\%$. 

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compared to the current simulated values of 11.3% ± 9.3% (Figure 5.3). The mean of the simulated base saturation for the 0% reduction scenario and for the 100% reduction scenario in 2200 were 9.5% ± 6.7% and 18.7% ± 10.0%, respectively.

5.3.3 Historical acidification

There is considerable variation among sites in the calculated values of historical acidification, ranging from 26.0 µeq/L to 100.4 µeq/L. I observed higher values of simulated historical acidification for lake-watersheds with higher ambient SO$_4^{2-}$+NO$_3^-$ deposition (2008; $r^2=0.30$), Ca$^{2+}$ weathering rate ($r^2=0.42$), and pre-industrial ANC (1850) ($r^2=0.44$) (Figure 5.4). Ca$^{2+}$ weathering rate can compensate for inputs of such as SO$_4^{2-}$ or NO$_3^-$ and mitigate acidification. Sites with higher pre-industrial ANC (1850) have relatively higher acid buffering capacity and can more effectively neutralize acidic deposition than sites with inherently lower ANC. However, The apparently counterintuitive response of historical acidification with Ca$^{2+}$ weathering rate and pre-industrial ANC is likely due to the effects of changes in the mobilization of Al$^{3+}$. Aluminum is an important pH buffer. I found relationships between increases in surface water Al$^{3+}$ between the current period and pre-industrial conditions (i.e., historical Al$^{3+}$ mobilization) and Ca$^{2+}$ weathering rates (\[
\Delta \text{Al}^{3+} (\mu \text{eq} / \text{L}) = -0.62[\text{Ca}^{2+ \text{ weathering rates}}] (\text{meq} / \text{m}^2 \cdot \text{yr}) + 45.50; r^2 = 0.18,\]
and pre-industrial ANC
\[
(\Delta \text{Al}^{3+} (\mu \text{eq} / \text{L}) = -0.31[\text{preindustrial ANC}] (\text{meq} / \text{m}^2 \cdot \text{yr}) + 39.91; r^2 = 0.18).\]
So enhanced mobilization of Al$^{3+}$ from soil to surface waters is an important mechanism neutralizing acidic deposition in the most acid-sensitive watersheds.
I also conducted stepwise regression for historical acidification showing that current
\( \text{SO}_4^{2-} + \text{NO}_3^- \) deposition (meq/m\(^2\)-yr) (p<0.01) and pre-industrial ANC (\( \mu\text{eq/L} \)) (p<0.01) are significantly related to historical acidification and recovery. Note that each of the two factors entered the model with \( p<0.05 \). Multiple regression did not show a significant contribution of Ca weathering rate due to the correlation between Ca weathering rate and pre-industrial ANC (Pearson Correlation Coefficient=0.87; \( p<0.01 \)).

\[
\text{Historical Acidification} = -13.76 + 0.60[\text{total}(S + N)\text{deposition}] (\text{meq/m}^2 - \text{yr}) + 0.23[\text{pre-\text{anthropogenic ANC}}] (\mu\text{eq/L}) (r^2 = 0.66)
\]

5.3.4 DCLs and CLs of SO\(_4^{2-}\) and NO\(_3^-\) deposition

I calculated the load of \( \text{SO}_4^{2-} + \text{NO}_3^- \) needed to achieve target ANC values of 0, 20 and 50 \( \mu\text{eq/L} \) for two years: 2040, representing a DCL and 2200, representing the CL. I observed that in general the \( \text{SO}_4^{2-} + \text{NO}_3^- \) deposition needed in a given year to achieve a given target ANC (0, 20, 50 \( \mu\text{eq/L} \)) increased with ambient lake ANC (Figure 5.5). Sites with low current lake ANC require lower \( \text{SO}_4^{2-} + \text{NO}_3^- \) deposition to achieve the target ANC values by a future date. I am particularly interested in lakes with current ANC less than target ANC values, and do not consider the DCL/CL for the sites where current ANC is greater than target ANC values. The DCLs of \( \text{SO}_4^{2-} + \text{NO}_3^- \) deposition for 2040 ranged from 0-42 meq/m\(^2\)-yr to achieve ANC of 0 \( \mu\text{eq/L} \) for five sites with current ANC<0 \( \mu\text{eq/L} \). Two lakes are projected to achieve ANC > 0 \( \mu\text{eq/L} \) and three lakes will not reach the target. The DCLs of \( \text{SO}_4^{2-} + \text{NO}_3^- \) deposition ranged from 0-51 meq/m\(^2\)-yr to achieve ANC of 20 \( \mu\text{eq/L} \) for 11 sites with current ANC < 20 \( \mu\text{eq/L} \). Two lakes are projected to achieve ANC > 20 \( \mu\text{eq/L} \) and
nine lakes will not reach the target. Finally, the DCLs of SO$_4^{2-} +$ NO$_3^-$ deposition ranged from 0-35 meq/m$^2$-yr to achieve ANC of 50 μeq/L for 16 sites with current ANC < 50 μeq/L. Two lakes are projected to achieve ANC > 50 μeq/L and 14 lakes will not reach the target by 2040. The CLs of SO$_4^{2-} +$ NO$_3^-$ deposition ranged from 41-62 meq/m$^2$-yr for the five sites with current ANC < 0 μeq/L to achieve ANC of 0 μeq/L (all these lakes will achieve ANC > 0 μeq/L); 0-83 meq/m$^2$-yr for the 11 sites with current ANC < 20 μeq/L to achieve ANC of 20 μeq/L (ten lakes will achieve ANC > 20 μeq/L), and 0-93 meq/m$^2$-yr for the 16 sites with current ANC < 50 μeq/L to achieve ANC of 50 μeq/L (ten lakes will achieve the target ANC > 50 μeq/L) by 2200. Based on the results of model simulations, most of the sites are able to achieve target ANCs (0, 20, or 50 μeq/L) within the CL of SO$_4^{2-} +$ NO$_3^-$ deposition ranges (figure 5.5). These relations suggest that the higher the target ANC the lower the DCL or CL that will be needed to achieve this target. Note, simulations indicate that some sites will not be able to reach target ANCs of 20 μeq/L or 50 μeq/L, even if atmospheric deposition decreased to preindustrial conditions; these sites have DCL or CL values of 0 meq/m$^2$-yr.

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

I explored the potential responses of aquatic biota species richness to historical and projected future changes in deposition. Species richness is a measure of the diversity of species for a community. Information is not available on the populations. Based on the empirical logistic relationship (Equation 5), estimated fish species richness in the 20 lakes under pre-industrial conditions ranged from 2.1 to 5.6 (ANC: 18 μeq/L to 163 μeq/L) (Figure 5.6a). This range compares with ambient fish species richness from zero to 5.3 (ANC: -25
µeq/L to 103 µeq/L; Figure 5.6a). Based on simulated ANC in 1850, fish might have been present in all study lakes. From 1850 to the present, (the shift from blue line (preindustrial conditions) to the red line (current conditions)) simulations suggest that lakes lost fish species coincident with increases in acidic deposition (25% of study lakes are projected to be fishless under current conditions). The average fish species richness decreased from 4.5 in 1850 to 2.2 under ambient conditions (Figure 5.6a). Comparison among the future projections showed that lakes could gain fish species under an aggressive future emissions reduction scenarios of 100% decrease, with a mean species richness of 4.3 by 2200, similar to pre-industrial conditions. In contrast, the scenario of no future change in acidic deposition from 2008 values suggests that there would be no apparent change in fish species richness from ambient conditions.

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

5.4 Discussion

5.4.1 DCLs and CLs of SO$_4^{2-}$+NO$_3^-$ deposition loading for the Adirondacks
DCLs and CLs of SO$_4^{2-}$ + NO$_3^-$ deposition were variable for Adirondack lake-watersheds to achieve a given target ANC value. My analysis suggests that for chronically acidic lake-watersheds (ANC < 0 µeq/L; Table 1) it will be difficult to achieve a positive target ANC (e.g., 20, 50 µeq/L). Many of these sites have low estimated pre-industrial ANC values. For example the mean estimated pre-industrial ANC of the thin-till drainage lakes and the seepage lake simulated is 55.4 µeq/L.

Sullivan et al. (2012) calculated DCLs of SO$_4^{2-}$ deposition using the Model of Acidification of Groundwater in Catchments (MAGIC) for two future dates (2050 and 2100) and three target ANC values (0, 20 and 50 µeq/L). It was estimated that only about 30% of 600 Adirondack lakes with SO$_4^{2-}$ deposition < 50 meq/m$^2$-yr would achieve an ANC of 50 µeq/L by 2100. My study is not exactly comparable because I examined decreases in the combination of SO$_4^{2-}$+NO$_3^-$ deposition. Because NO$_3^-$ is also an important atmospheric pollutant, I calculated CLs for both SO$_4^{2-}$ and NO$_3^-$. The CLs of SO$_4^{2-}$+NO$_3^-$ to achieve an ANC of 50 µeq/L by 2200 ranged from 8.4 to 339.0 meq/m$^2$-yr. Similar to the pattern observed by Sullivan et al (2012), several of our sites (n=5) could not achieve an ANC of 50 µeq/L under any deposition scenario.

Sullivan et al. (2012) found that DCLs of SO$_4^{2-}$+NO$_3^-$ deposition were variable for lake watersheds for achieving the same target ANC value and also variable for the same site for achieving different target ANC values by 2100. It is likely that the highly acid sensitive sites (ANC < 0 µeq/L) will have difficulty achieving target ANC values (20, 50 µeq/L) by 2100. These highly acid-sensitive sites often are situated at relatively higher elevation compared with less sensitive sites. High elevation sites receive greater amounts of SO$_4^{2-}$+ NO$_3^-$ than other lower elevation sites (Weathers et al., 2006). Greater decreases in SO$_4^{2-}$+
NO$_3^-$ deposition would be needed to achieve higher target ANC values (20, 50 µeq/L) over the same period (2008-2100) for the specific site.

5.4.2 Factors that affect historical acidification and recovery

There are some factors that affect historical acidification. Additional inputs of SO$_4^{2-}$ +NO$_3^-$ deposition will accelerate acidification to the ecosystems (Figure 5.4a). This is because acidic deposition increases the leaching loss of exchangeable base cations, resulting in decreases in ANC. Sites with higher weathering rate and pre-industrial ANC appear to exhibit greater loss of ANC from historical inputs of acidic deposition than the sites with relatively lower weathering rate and pre-industrial ANC. The mobilization of Al$^{3+}$ from soil is an important mechanism to neutralize elevated acidic deposition in acid sensitive watersheds (Driscoll and Postek, 1995). Unfortunately the acid-base chemistry of this process is not adequately depicted in ANC measurements (Sullivan et al., 1989). Moreover, Al$^{3+}$ is highly toxic to aquatic biota (Driscoll et al. 2001).

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

The magnitude of decreases in \(\text{SO}_4^{2-}+\text{NO}_3^-\) deposition and the time scale of response are important considerations in ecosystem recovery. Under scenarios of limited or no future decrease in acidic deposition, lake-watershed recovery is projected to be short lived. Model simulations suggested that under continued elevated atmospheric N deposition (without forest disturbance), forest watersheds will progress toward a condition of N saturation, exhibit increasing leaching losses of \(\text{NO}_3^-\), and resume acidification. In contrast, under scenarios of more aggressive decreases in acidic deposition, lake recovery will continue over the long-term (Figure 5.1b). In addition to the effects of decreases in \(\text{SO}_4^{2-}\) deposition, decreases in \(\text{NO}_3^-\) deposition were simulated to delay the progression toward a condition of N saturation. Much of the benefits to ecosystems associated with implementing emission controls to decrease acidic deposition will be realized within a few decades, although simulated recovery does proceed slowly for more than a century. This time-dependent response illustrates the advantages in the application of dynamic models for determining DCLs and CLs.
5.4.3 Application of biological indicators of acidification stress

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

DCL and CL calculations are generally made using chemical indicators of acidification stress. However, there are compelling reasons to use biological relationships in CL calculations. I illustrate the potential application of biological indicators of acidification stress in the calculation of CLs through the use of empirical relations of species richness obtained from spatial lake surveys. While these relationships relate the extent of acidification and recovery to easily understandable measures, there are a number of limitations in this approach. First, the empirical relationships were obtained from a spatial survey with measured ANC. It is not clear if this spatial relationship can be applied to quantify temporal
changes. Second, there are many physiochemical and biological factors that influence lake ANC, acidic deposition being only one. Biotic species richness is likely controlled by several lake-watershed characteristics (e.g. lake size, watershed characteristics). Last, the empirical spatial relationships do not consider lags in biological recovery that might occur. Organisms are not responding to ANC, but rather some combination of factors that are linked to ANC (e.g., pH, Al). There may be additional stressors other than acidification that contribute to the losses of the biotic species such as shifts in stocking policy, or habitat alteration (Driscoll et al., 1991b). The specific mechanisms by which fish and total zooplankton communities respond to decreases in acidic deposition have not yet been defined. More work is needed on the development and application of relationships between aquatic biota responses and recovery from acidification stress.
Table 5.1. Characteristics of 20 simulation sites in the Adirondack region.

<table>
<thead>
<tr>
<th>LAKE</th>
<th>LATITUDE</th>
<th>LONGITUDE</th>
<th>ELEVATION (M)</th>
<th>LAKE AREA (HA)</th>
<th>MEAN ANC (µEQL)</th>
<th>ALSC LAKE CLASS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arbutus Lake</td>
<td>43.9877</td>
<td>74.2416</td>
<td>538</td>
<td>47.93</td>
<td>68.3</td>
<td>Medium till</td>
</tr>
<tr>
<td>Brook Trout Lake</td>
<td>43.5999</td>
<td>74.6624</td>
<td>725</td>
<td>28.70</td>
<td>2.5</td>
<td>Thin till</td>
</tr>
<tr>
<td>Bubb Lake</td>
<td>43.7708</td>
<td>74.8542</td>
<td>596</td>
<td>18</td>
<td>46.5</td>
<td>Thin till</td>
</tr>
<tr>
<td>Carry Pond</td>
<td>43.6816</td>
<td>74.4891</td>
<td>651</td>
<td>2.80</td>
<td>-5.9</td>
<td>Seepage</td>
</tr>
<tr>
<td>Clear Pond</td>
<td>44.4869</td>
<td>74.1603</td>
<td>520</td>
<td>40.01</td>
<td>102.6</td>
<td>Thick till</td>
</tr>
<tr>
<td>Constable Pond</td>
<td>43.8332</td>
<td>74.7958</td>
<td>693</td>
<td>21.30</td>
<td>-6.2</td>
<td>Thin till</td>
</tr>
<tr>
<td>Grass Pond</td>
<td>43.6903</td>
<td>75.0650</td>
<td>548</td>
<td>5.30</td>
<td>27.2</td>
<td>Medium till</td>
</tr>
<tr>
<td>Indian Lake</td>
<td>43.6163</td>
<td>74.7533</td>
<td>719</td>
<td>34.83</td>
<td>-4.4</td>
<td>Thin till</td>
</tr>
<tr>
<td>Jockeybush Lake</td>
<td>43.3022</td>
<td>74.5858</td>
<td>610</td>
<td>17.30</td>
<td>2.7</td>
<td>Thin till</td>
</tr>
<tr>
<td>Limekiln Lake</td>
<td>43.7133</td>
<td>74.8130</td>
<td>629</td>
<td>186.90</td>
<td>26.4</td>
<td>Medium till</td>
</tr>
<tr>
<td>Middle Branch Lake</td>
<td>43.6978</td>
<td>75.1022</td>
<td>517</td>
<td>17</td>
<td>52.9</td>
<td>Thin till</td>
</tr>
<tr>
<td>Middle Settlement Lake</td>
<td>43.6839</td>
<td>75.1000</td>
<td>547</td>
<td>15.80</td>
<td>9.6</td>
<td>Thin till</td>
</tr>
<tr>
<td>North Lake</td>
<td>43.5381</td>
<td>74.9269</td>
<td>674</td>
<td>178.01</td>
<td>3.2</td>
<td>Thin till</td>
</tr>
<tr>
<td>Queer Lake</td>
<td>43.8136</td>
<td>74.8069</td>
<td>610</td>
<td>54.50</td>
<td>11.4</td>
<td>Thin till</td>
</tr>
<tr>
<td>Raquette Lake</td>
<td>43.7950</td>
<td>74.6514</td>
<td>595</td>
<td>1.50</td>
<td>30.9</td>
<td>Medium till</td>
</tr>
<tr>
<td>Squash Pond</td>
<td>43.8263</td>
<td>74.8897</td>
<td>680</td>
<td>1.70</td>
<td>-25.0</td>
<td>Thin till</td>
</tr>
<tr>
<td>Sagamore Lake</td>
<td>43.7658</td>
<td>74.6286</td>
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<td>Medium till</td>
</tr>
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<td>43.8111</td>
<td>74.8792</td>
<td>592</td>
<td>8.90</td>
<td>8.0</td>
<td>Thin till</td>
</tr>
<tr>
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<td>43.3714</td>
<td>74.2463</td>
<td>421</td>
<td>14.60</td>
<td>65.6</td>
<td>Medium till</td>
</tr>
<tr>
<td>Willys Lake</td>
<td>43.9693</td>
<td>74.9547</td>
<td>640</td>
<td>22.93</td>
<td>-10.0</td>
<td>Thin till</td>
</tr>
</tbody>
</table>

Note: ALSC is the abbreviation for Adirondack Long Term Survey Corporation.
Figure 5.1. Time series of historical and hypothetical future deposition scenarios of $\text{SO}_4^{2-} + \text{NO}_3^-$ for Jockeybush Lake (a) and simulated ANC of Jockeybush Lake in response to changes in $\text{SO}_4^{2-} + \text{NO}_3^-$ deposition (b). For future projections, linear decreases are assumed between 2008 and 2020 from the present deposition to the deposition of interest (0, 20, 40, 60, 80, 100% decrease of current value). These future deposition scenarios range from the present deposition to historical deposition at 20% intervals. Deposition before 1850 or after 2020 is held constant for the model runs. The terms historical acidification (61 $\mu$eq/L) and maximum (49 $\mu$eq/L) recovery are illustrated based on ANC response.
Figure 5.2. Comparison of observed and simulated average of $\text{SO}_4^{2-}$ (a), $\text{NO}_3^-$ (b), ANC (c) and sum base cations (SBC) (Ca$^{2+}$+Mg$^{2+}$) (d) for 20 study lakes. The observed values are average of the measured annual data from ALTM from 1993 to the present. The simulated values are average of the annual simulation data. A 1:1 line is shown.
Figure 5.3. Comparison of distribution of simulated ANC (a) and percentage of base saturation (b) classes in 1850 and 2008; comparison of simulated ANC and base saturation for the 0% reduction scenario (c) and the 100% reduction scenario (d) in 2200 for the 20 sits in the Adirondacks. X-axis is ANC classes and the percent of soil base saturation classes at 5% intervals. Y-axis is the number of lakes within ANC and BS% classes.
Figure 5.4. Relationships between historical acidification and (a) current total deposition of \( \text{SO}_4^{2-} + \text{NO}_3^- \), (b) Ca weathering rate, and (c) historical ANC (1850) for simulated sites; and relationships between \( \text{Al}^{3+} \). Note that historical acidification is lake ANC loss between ANC in 1850 and the lowest ANC that occurred over the recent period (1990-2008).
Figure 5.5. Relationships between current lake ANC and total deposition of $\text{SO}_4^{2-} + \text{NO}_3^{-}$ necessary to achieve target ANC of 0, 20 and 50 $\mu$eq/L in 2040 and 2200. Shaded areas represented current total deposition of $\text{SO}_4^{2-} + \text{NO}_3^{-}$ for the Adirondacks from 80 meq/m$^2$-yr to 120 meq/m$^2$-yr.
Figure 5.6. Projections of cumulative distribution functions of species richness of aquatic biota for the 20 lakes in the Adirondack region, including (a) fish species richness and (b) total zooplankton species richness developed from model estimated ANC and empirical relationships between aquatic biota species richness and lake water ANC. Results for four conditions are shown: pre-industrial (1850; blue), current (2008; red) and a range of future conditions in 2200. Shaded areas represent the range of species richness that could occur under two projected deposition scenarios: 0% reduction and 100% reduction of $\text{SO}_4^{2-}+\text{NO}_3^-$. 
Chapter 6 Developing Critical Loads of Nitrate and Sulfate Deposition to Watersheds of the Great Smoky Mountains National Park, United States

6.1 Introduction and Objectives

The Great Smoky Mountains National Park (GRSM) is a 1,999 km$^2$ Class I Airshed in the Southern Appalachian Mountains of Tennessee and North Carolina, USA. The GRSM receives high atmospheric sulfur (S) and nitrogen (N) deposition (Johnson and Lindberg, 1992). In 2000, total S deposition ranged from 7 to 42 kg S/ha-yr and total N deposition ranged from 5 to 31 kg N/ha-yr (Weathers et al., 2006). Air quality management, through the Clean Air Act and the U.S. Environmental Protection Agency NO$_x$ Budget Trading Program and the Clean Air Interstate Rule (CAIR) has resulted in decreases in atmospheric sulfate (SO$_4^{2-}$) and nitrate (NO$_3^-$) deposition in the eastern U.S. (Lehmann et al., 2005). Currently (2004-2008) atmospheric S and N deposition across the GRSM range from 6.8 to 27.8 kg S/ha-yr and 6.1 to 16.6 kg N/ha-yr, respectively.

Watersheds of the GRSM are sensitive to acidic deposition due to high elevation topographic features coupled with highly weathered, unglaciated, base-poor soils, shallow hydrologic flow paths and mature forests (Johnson and Lindberg, 1992; Cai et al., 2012a; Neff et al., 2013). Atmospheric S and N deposition have resulted in acidification of the soil and the stream water in the GRSM (Nodvin et al., 1995; Robinson et al., 2008) and throughout the other portions of the Appalachian Mountains (Kahl et al., 2004). Section 303(d) of the Clean Water Act requires states to list waters for which technology-based
effluent limitations are not adequate to meet water quality standards. In 2008, Tennessee listed 12 impaired streams in the GRSM due to acidity, two of which are included in this research, as not supporting designated use classification (i.e., impaired), associated with pH values below 6.0 (Goshen Prong and Cannon Creek; TDEC 2010; Neff et al., 2009). A total maximum daily load (TMDL) analysis for acid-impaired watersheds was conducted by the Tennessee Department of Environment and Conservation, determining that the source of acidity was largely from regional atmospheric sources of acidic deposition (TDEC 2010). A TMDL pertains to loading of acidic deposition from the perspective of the Clean Water Act. CLs examine inputs from an air quality management perspective. They are both used for calculating the maximum load deposition for the acid-impaired watersheds.

The overall objective of this chapter was to apply and test the biogeochemical model PnET-BGC to 12 watersheds characteristic of GRSM, including two 303(d) listed streams, to ultimately establish CLs/DCLs for GRSM and evaluate stream water chemistry in response to decreases in acidic deposition. The specific objectives were to: 1) compile data and apply the dynamic biogeochemical model (PnET-BGC) to test model simulations of hydrochemistry of watersheds in the GRSM; 2) simulate the response of different watersheds to historical increases in acidic deposition and project their responses to hypothetical decreases in atmospheric SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ deposition; 3) evaluate the physical and biogeochemical factors that affect the response of GRSM watersheds to changes in atmospheric SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ deposition; and 4) determine the CLs/DCLs of atmospheric SO$_4^{2-}$ and NO$_3^-$ deposition and time required to reach target ANCs (if possible) for various time periods.
6.2 Methods

6.2.1 Sites

I selected 12 watersheds for model application, ten of which represented a large proportion of the variability within GRSM based on stream water acid neutralizing capacity (ANC), elevation, watershed area, historical land disturbance, NO$_3^-$ leaching, and the presence/absence of Anakeesta in the watershed (Neff et al., 2013; Table 6.1). Anakeesta is a sulfur bearing rock which can release SO$_4^{2-}$ to drainage waters if the watershed is disturbed by a rock slide or road cut (Elwood et al., 1991). Goshen Prong and Cannon Creek were selected because they contained streams on the Tennessee 303(d) list, indicating they do not meet water quality pH standards for intended use (i.e., mean stream pH<6.0) (TDEC, 2010). Noland Divide Watershed was selected because atmospheric deposition and stream chemistry have been monitored since 1991 by the University of Tennessee - Knoxville (UTK). The extensive data record from the Integrated Forest Study and UTK was used for the validation of the model and assessment.

6.2.2 Data sets

6.2.2.1 Model input data

Meteorological data used to help drive model simulations include monthly minimum and maximum air temperatures, precipitation and solar radiation. Several meteorological datasets were used. For Noland Divide Watershed (35° 34' N, 83° 28' W; elev: 1798m),
meteorological data between 1993 and 2007 were obtained from Clingman’s Dome (35° 32' 59"N, 83° 30' 0"W; elev: 2003m), which is the highest peak in GRSM and a monitoring site for the National Park Service. Meteorological data for the period 1931 to 1993 were extrapolated using Waterville 2 coop station (35° 46' N, 83° 5' 59"W; EL: 439m) as a reference site. Meteorological data for Waterville 2 are available from 1931 to present (http://www.ncdc.noaa.gov). For hindcast simulations prior to 1931, monthly meteorological data were assumed to be constant at the mean of monthly values from 1931 to 1941. For forecast projections, temperatures and precipitation data are assumed to be constant as of the mean of monthly values from 1993 to 2007. Available solar radiation data (1993-2007) are from National Park Service Air Resources Division (http://ard-request.air-resource)

Clingmans Dome air quality monitoring station. The mean values of solar radiation from 1993-2007 were used for hindcast and forecast simulations.

Atmospheric deposition (1981– present) was reconstructed for the 12 watersheds in the GRSM. The wet deposition data for major ions (Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, NO$_3^-$, SO$_4^{2-}$, Cl$^-$, NH$_4^+$) at Noland Divide were available through the University of Tennessee-Knoxville (UTK). I developed spatial relationships of precipitation quantity (Table 6.2) and precipitation chemistry (e.g., Table 6.3) for the GRSM using monthly data at five nearby monitoring sites (NC25, NC45, TN00, TN04, TN11) from the National Atmospheric Deposition Program (NADP). Empirical relationships for precipitation quantity and solute concentrations were developed using geographic position (latitude, longitude) and elevation (Table 6.2 and Table 6.3). As the product of precipitation quantity and solute concentrations, monthly wet deposition values were estimated for each of the study watersheds based on values that were scaled to wet deposition at Noland Divide. This is similar to the approach
used by Ollinger et al. (1993) and Ito et al. (2002) for the Northeast.

The historical wet deposition data from 1900 to 1980 for use in hindcast simulations were estimated from the Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model (Shannon, 1981). The ASTRAP model was applied as part of the Southern Appalachian Mountain Initiative (SAMI) (Shannon, J.D. unpublished) to estimate historical deposition at five-year intervals, with results that are representative of a moving average centered about a particular year. For the pre-industrial period (prior to 1850), I assumed that the deposition was 10% of current deposition (Gbondo-Tugbawa et al., 2001). I also assumed that there was a linear increase for the wet deposition from 1850 to 1900. The relative temporal pattern of historical deposition was assumed to be the same for each of the watersheds, with values scaled to deposition at Noland Divide.

To estimate dry deposition, I used dry to wet deposition ratios for major cations and anions. For Noland Divide Watershed, I assumed that dry deposition of SO$_4^{2-}$ and Cl$^-$ can be calculated as the difference between throughfall and wet deposition (i.e., net throughfall). Dry and cloud deposition represented approximately 75% for total SO$_4^{2-}$ deposition and about 80% total NO$_3^-$ deposition at the high elevation Noland Divided Watershed during 1986-1989 (Johnson and Lindberg, 1992). For other watersheds, dry to wet deposition ratios were prorated from the distribution of hardwood and conifer forest cover in the watershed. Dry to wet deposition ratios were assumed to be constant for the simulation period.

Land disturbance included logging, agriculture and settlement, fire, BWA (Balsam Woolly Adelgid) damage (Smith and Nicholas, 2000), windstorms (White and Cogbill, 1992) and ice storms (Nicholas and Zedaker, 1989; Moore et al., 2008). Historical land disturbance was estimated by digitizing the land disturbance records of the National Park Service for the
study watersheds. Hurricanes, logging, farming and fire have affected and changed landscape patterns (Pyle, 1985). More recently, the infestation of exotic pests and air pollution have impacted the forests. The BWA has caused heavy mortality of *Abies balsamea*, killing virtually every individual fir tree less than 10 cm diameter at breast height (Moore et al., 2008). There were also three hurricanes in 1989, 1995 and 2004 that caused extensive forest damage (Moore et al., 2008). Estimates of the fraction of the watershed impacted by disturbance and fraction of biomass removal were estimated based on archive records for GRSM.

Weathering rates for the GRSM watershed were estimated through model calibration. There are no weathering rate data for the GRSM. The range of weathering rate observed was similar to that estimated for the Adirondack region (see chapter 5). Weathering rate estimates were obtained by matching rates to observations of stream watershed output of base cations.

6.2.2.2 Stream data

Stream monitoring data for strong acid anions (NO$_3^-$, SO$_4^{2-}$, Cl$^-$), NH$_4^+$, ANC and pH at Noland Divide are available from 1991 to 2008. Base cation data (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$) are available from 1993 to 2008. All of the data are biweekly based on the long-term monitoring program conducted by the University of Tennessee-Knoxville (UTK) and the National Park Service (Robinson et al., 2008). Biweekly data of chemical species were converted to monthly volume-weighted concentrations and then converted into annual volume-weighted concentrations for comparison with simulated annual data. For the other eleven sites, stream water samples were collected on a monthly basis by GRSM staff from 1994-1996, quarterly
1997-2003, and bi-monthly from 2004-2008 (Schwartz et al., 2012). Monthly, quarterly and bi-monthly data from these sites were converted into annual volume-weighted concentrations. Stream discharge data are available for Noland Divide Watershed. GRSM stream water quality data and Noland Divide chemistry and discharge data are accessible via the EPA STORET data warehouse (http://www.epa.gov/storet/dw_home.html) using the “11NPSWRD” Organization ID.

6.2.2.3 Model application

Following previous research (Zhai et al., 2008), model runs were started for individual GRSM watersheds in 1000 AD, and run under constant background deposition and no land disturbance until 1850 to achieve steady-state and evaluate “background” (i.e., pre-1850) conditions. Changes in atmospheric deposition and land disturbance events were initiated after 1850. The model was run from 1850 through 2010 based on measured values of atmospheric deposition and reconstructions of historical deposition from emission records. Model simulations continued through the year 2100 with a series of forecasts, which included a range of deposition scenarios from current to “background” deposition at 20% intervals (0%, 20%, 40%, 60%, 80% and 100% reductions) for SO$_4^{2-}$, and NO$_3^-$ individually and in combination. Future scenarios involved a 12-year linear decrease from 2008 values to the level of deposition of interest in 2020 and continued simulation at this deposition level until 2200. This range of deposition values was used to evaluate tradeoffs associated with reductions in SO$_2$ or NO$_x$ emissions to achieve ecosystem recovery from acidic deposition.
I also evaluated the degree to which decreases in NH$_4^+$ deposition influenced the rate of watershed recovery from atmospheric deposition. As described above, I examined a range of future scenarios in which NH$_4^+$ deposition was incrementally decreased which were compared to the simulated response to incremental decreases in atmospheric NO$_3^-$ deposition. These comparisons were conducted for four watersheds: Lost Bottom Creek, which exhibits limited NO$_3^-$ loss in stream water and three sites which are characterized by elevated concentrations of NO$_3^-$ in stream water, Noland Divide, Walker Camp Prong and Indian Camp Creek.

6.3 Results

6.3.1 Model performance

Generally PnET-BGC effectively simulated the hydrology and chemistry of stream waters at the GRSM (Figure 6.1; Table A2). Measured annual discharge (1422 ± 335mm) was similar to simulated values (1330 ± 429mm; NME -0.064, NMAE 0.11). For most stream solutes, model values were in agreement with simulated concentrations, with little difference or bias for individual sites (simulated NME Mg$^{2+}$ -0.13 to 0.17; Ca$^{2+}$ -0.24 to 0.19; SO$_4^{2-}$ -0.07 to 0.39; ANC -0.46 to 0.32; pH -0.04 to 0.07). While generally the agreement for Ca$^{2+}$ was good, Indian Camp Creek (NME -0.24) and Cosby Creek (NME -0.24), the sites with the highest Ca$^{2+}$ concentrations were underpredicted. Model simulations did exhibit some bias for NO$_3^-$ (NME -0.63 to 0.05). Stream NO$_3^-$ is underpredicted compared to
measured values, particularly for Pretty Hollow (NME = -0.63), Sugar Fork (NME = -0.53), Cannon Creek (NME = -0.45) and Thunderhead (NME = -0.43). Watersheds where NO$_3^-$ is overpredicted are generally at lower elevation and exhibit relatively low NO$_3^-$ leaching (annual volume-weighted NO$_3^-$ < 20 µeq/L). PnET-BGC simulated ANC (NME: -0.46 to 0.32) reasonably well, although simulations that underpredicted NO$_3^-$ tended to overpredict ANC.

6.3.2 Hindcasts (1850-2010) for stream chemistry at the GRSM

The hindcast simulations showed a time series of annual volume weighted concentrations of SO$_4^{2-}$, NO$_3^-$, and ANC from 1850 to 2010 for each of the stream study sites (Figure 6.2). Pre-industrial stream SO$_4^{2-}$ has a mean of 9.5 ± 7.1 µeq/L. Three of the study watersheds have some Anakeesta in the bedrock, and those streams have higher pre-industrial SO$_4^{2-}$ than the non-Anakeesta streams (mean SO$_4^{2-}$ for Anakeesta watersheds 13.3 ± 8.9 µeq/L vs. 8.2 ± 6.2 µeq/L for non-Anakeesta watersheds). Generally, stream SO$_4^{2-}$ increased over the past 150 years with peak values occurring in the 1970s to 1980s coinciding with maximum values in SO$_2$ emissions and SO$_4^{2-}$ deposition in the eastern U.S., decreasing to current values (Figure 6.2). The mean simulated value for current (1999-2009) SO$_4^{2-}$ is 38.0 ± 13.5 µeq/L, and this agrees well with the mean measured current value (35.5 ± 16.1 µeq/L). On average, model simulations suggest that stream SO$_4^{2-}$ in GRSM increased on average 26 ± 12.5 µeq/L from pre-industrial values (~1850) to present. Although the long-term temporal pattern of increases in stream SO$_4^{2-}$ in response to increases in atmospheric SO$_4^{2-}$ deposition was comparable across the study watersheds, the magnitude of
increase in stream $SO_4^{2-}$ was highly variable (Figure 6.2). The variability in stream $SO_4^{2-}$ response can partially be explained by variability in atmospheric $SO_4^{2-}$ deposition superimposed on variation in elevation

$$(\text{stream } SO_4^{2-} \text{ concentration (\mu eq/L)} = 0.019[\text{elevation (m)}] + 17.2; r^2 = 0.15)$$

and variation in soil $SO_4^{2-}$ adsorption capacity

$$(\text{[stream } SO_4^{2-} \text{ concentration (\mu eq/L)}] = -0.25 \times [SO_4^{2-} \text{ adsorption capacity (meq/kg)}] + 46.8; r^2 = 0.23).$$

Simulations of pre-industrial stream $NO_3^-$ concentrations are low for the study watersheds (1.2 ± 0.7 μeq/L; Figure 6.2). Model hindcasts showed low stream $NO_3^-$ until the 1950s and 1960s when some study watersheds started to show increasing leaching losses that have continued to the present. Average current simulated annual volume-weighted stream $NO_3^-$ (17.6 ± 12.4 μeq/L) compares well with current measured values (23.2 ± 13.3 μeq/L). The mean increase in stream $NO_3^-$ from pre-industrial values to present is 22 ± 12.2 μeq/L, with a large range from 39.5 ± 4.5 μeq/L at Indian Camp Creek Watershed to 3.2 ± 3.7 μeq/L at Sugar Fork. This variation in simulated stream $NO_3^-$ in part coincides with variation in watershed elevation

$$(\text{[NO}_3^- \text{ concentration (\mu eq/L)]} = 0.028 \times [\text{elevation (m)}] - 3.59; r^2 = 0.40).$$

There is considerable variability in watershed sensitivity to acidic deposition among the study sites. Projections of pre-industrial ANC (ANC projected for 1850) at these sites ranged from 28 μeq/L at Noland Divide to 107 μeq/L at Sugar Fork, with a mean of 70.8 ± 10.5 μeq/L. Variations in preindustrial stream ANC at the GRSM were somewhat related to watershed elevation ([ANC (μeq/L]) = -0.029[elevation (m)] + 61.9; $r^2=0.15$). Hindcasts of stream ANC from 1850 to present coincide with increases in acidic deposition and leaching
of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$. Simulated current mean annual volume-weighted ANC is $32.8 \pm 21.5 \mu$eq/L, a volume that is consistent with the current measured mean ANC ($33.1 \pm 25.9 \mu$eq/L). Hindcasts suggest that on average across the 12 GRSM modeled streams, acidic deposition resulted in a decrease in ANC of $37.6 \mu$eq/L from pre-industrial values to present. Model simulations indicate that current values of stream ANC are correlated with estimates of pre-industrial ANC values ($r^2 = 0.38$; Figure 6.4).

6.3.3 Future projections

For each of the study watersheds, I made future projections of hypothetical decreases in $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ deposition individually and together since 2008. To illustrate this response, I show detailed hindcasts and the suite of forecast projections for one of the GRSM watersheds, Goshen Prong, indicating the response to projected decreases in $\text{NO}_3^-$ deposition with: (a) $\text{SO}_4^{2-}$ deposition remaining at current values; (b) decreases in $\text{SO}_4^{2-}$ deposition with $\text{NO}_3^-$ deposition remaining at current elevated values; and (c) decreases in both $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ deposition (Figure 6.3). Simulations of hindcast and future forecast projections for all 12 study watersheds are given in the Appendix.

Goshen Prong (~1046m) exhibits relatively high $\text{NO}_3^-$ leaching (~21 $\mu$eq/L), is sensitive to acidic deposition (ANC=21 $\mu$eq/L) and is a 303(d) listed stream. Current model simulations of stream chemistry at Goshen Prong generally agreed with measured values (i.e., $\text{SO}_4^{2-}$ NME = 0.20; $\text{NO}_3^-$ NME = -0.07; $\text{Ca}^{2+}$ NME = 0.12; ANC NME = 0.11; pH NME = -0.04). Simulations of a range of future conditions of $\text{NO}_3^-$ deposition suggest that the watershed would be responsive to changes in $\text{NO}_3^-$ loading (Figure 6.3a). In the absence of
controls on NO$_3^-$ deposition, the watershed is projected to exhibit increases in leaching losses of NO$_3^-$ to high concentrations (~100 µeq/L) through about 2200, resulting in marked decreases in ANC and pH. Incremental future controls on NO$_3^-$ deposition lessen the extent and rate of increases in NO$_3^-$ leaching and mitigate decreases in pH and ANC. However, model projections suggest that acidification will progress even under 100% decrease in deposition.

The suite of SO$_4^{2-}$ deposition control scenarios (with no controls on NO$_3^-$ deposition) show that decreases in SO$_4^{2-}$ in Goshen Prong and other watersheds in GRSM will effectively decrease SO$_4^{2-}$ concentrations in stream water (Figure 6.3b). However, as NO$_3^-$ deposition is unchanged, ongoing elevated NO$_3^-$ drives the watershed toward a condition of N saturation and increasing concentrations of NO$_3^-$ in stream water. As a mobile anion, NO$_3^-$ strongly contributes to the continued acidification of Goshen Prong, resulting in continuing decreases in ANC and pH. Simultaneous control of NO$_3^-$ and SO$_4^{2-}$ is the most effective approach to decrease concentrations of total strong acid anion concentrations in stream water of GRSM watersheds arresting acidification and allowing for limited recovery. Note that even under marked decreases in NO$_3^-$ loading as the forest biomass matures, NO$_3^-$ leaching losses are expected to increase over time, because the GRSM is an unmanaged forest.

6.3.4 Factors affecting the historical acidification and recovery of watersheds at the GRSM

As before, I define historical acidification (HA) as the change in simulated ANC from the pre-industrial value of 1850 to the current value (2010). I evaluated characteristics of the 12 GRSM study watersheds to assess factors that control HA. Modeled HA for the GRSM
watersheds increased with decreasing pre-industrial estimates of ANC ranging from 54.2 µeq/L to 19.6 µeq/L (Figure 6.4a). The lower the pre-industrial estimated ANC, the greater the modeled change (HA) in comparison to current ANC values. HA was positively related to current SO$_4^{2-}$ + NO$_3^-$ deposition ($r^2 = 0.66$; Figure 6.4b), indicating the greater the input of acidic deposition the greater the historical acidification. The extent of HA also decreases with increases in estimated soil SO$_4^{2-}$ adsorption capacity ($r^2 = 0.19$; Figure 6.4c). I conducted multiple regression analysis of HA with total current SO$_4^{2-}$ + NO$_3^-$ deposition, historical ANC and soil SO$_4^{2-}$ adsorption capacity which explained most of the watershed variation in the extent of HA.

$$HA(\mu eq / L) = 35.9 + 7.4 \times [current \ SO_4^{2-} + NO_3^- \ deposition(keq / ha - yr)] + 0.002 \times [preindustrial \ ANC(\mu eq / L)] - 0.06 \times [SO_4^{2-} \ adsorption \ capacity(\text{meq} / \text{kg})](r^2 = 0.73)$$

I define maximum recovery (MR) as the difference between stream ANC projected for 2200 under the scenario which atmospheric NO$_3^-$ + SO$_4^{2-}$ deposition are lowered to pre-industrial values and the scenario which atmospheric NO$_3^-$ + SO$_4^{2-}$ deposition remains at current deposition. As observed for HA, MR decreases with increasing current (2010) ANC ($r^2 = 0.65$; Figure 6.4d; 21.8 µq/L to 121.0 µeq/L). I found a similar relationship between MR and pre-industrial (historical) ANC ($r^2 = 0.62$; Figure 6.4e). In contrast, MR was positively related to current NO$_3^-$ + SO$_4^{2-}$ deposition ($r^2 = 0.37$; Figure 6.4f).

6.3.5 Projections of DCLs

I am ultimately interested in developing CLs and DCLs for all streams in the entire GRSM. To illustrate how this extrapolation might be accomplished using simulations from
the 12 study watersheds, I interpolated the results of stream ANC projections for the
hypothetical years (2050, 2100, and 2200) from future decreases in NO$_3^-$ + SO$_4^{2-}$ deposition
to a series of target ANC values: 0, 20 and 50 µeq/L (Table 6.4). These target ANC values
were selected because they are values that have been selected as potential target ANC in the
U.S. CL assessment (USEPA, 2009a). Based on the six model projections (0, 20, 40, 60, 80,
100% decreases) for individual sites, stream ANC values were interpolated in 2050 to
determine the load of SO$_4^{2-}$+NO$_3^-$ necessary to achieve target ANC (i.e., 0, 20, 50 µeq/L). I
found that the DCL in 2050 necessary to achieve a given ANC target for GRSM sites was
approximately a linear function of current stream ANC (Figure 6.5). DCLs of NO$_3^-$ + SO$_4^{2-}$
deposition for the 12 study stream ranged from 0.27-3.37 keq/ha-yr to reach an ANC of 0
µeq/L by 2050; 0-2.34 keq/ha-yr to reach ANC of 20 µeq/L by 2050; and 0-1.40 keq/ha-yr to
reach an ANC of 50 µeq/L by 2050 (Table 6.4). For example, the DCLs for Goshen Prong is
0.32 keq/ha-yr to reach an ANC of 20 µeq/L, but cannot achieve the target ANC of 50 µeq/L
even if deposition is decreased to pre-industrial conditions by 2050. Note that for some study
streams, ANC targets cannot be met under the deposition reductions and time periods used
for this study (Table 6.5). From PnET-BGC projections I developed three empirical
relationships of NO$_3^-$ + SO$_4^{2-}$ deposition necessary to achieve a target DCL (Figure 6.5).
These projections suggest that the higher the target ANC the lower the DCL necessary to
achieve this value of ANC. Moreover, the lower the current stream ANC the lower the DCL
necessary to achieve a target ANC value by 2050. As most stream sites modeled have ANC
values <50 µeq/L, the modeled relationships suggest that this target ANC will not be
achievable at many low ANC sites.
6.4 Discussion

6.4.1 Comparison of controls on $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{NH}_4^+$ deposition

I evaluated watershed responses to relative controls on $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ deposition under future projections of hypothetical decreases individually, and in combination. ANC projections for Goshen Prong increased from -73 $\mu$eq/L to -36 $\mu$eq/L by 2200 under no additional controls of $\text{SO}_4^{2-}$ (or $\text{NO}_3^-$) deposition scenario (0% reduction, constant deposition) and the aggressive $\text{SO}_4^{2-}$ deposition scenario (100% reduction to preindustrial conditions) with no change in atmospheric $\text{NO}_3^-$ deposition, respectively. Sulfate adsorption plays an important role in regulating the acid-base status of streamwater, particularly in the decades immediately following decreases in atmospheric $\text{SO}_4^{2-}$ deposition. Soil $\text{SO}_4^{2-}$ adsorption is depicted in PnET-BGC to be a pH-dependent process in which an adsorbed OH$^-$ ligand is replaced by $\text{SO}_4^{2-}$ to decrease the solution $\text{SO}_4^{2-}$ concentration and consequently increase ANC. The relationship between HA (historical acidification) and $\text{SO}_4^{2-}$ adsorption capacity among the different watershed sites showed that HA was limited by soil $\text{SO}_4^{2-}$ adsorption capacity. In PnET-BGC soil $\text{SO}_4^{2-}$ adsorption is assumed to be a reversible chemical equilibrium process. As a result, the legacy $\text{SO}_4^{2-}$ that has accumulated in soil under historical elevated acidic deposition can completely desorb under decreases in atmospheric $\text{SO}_4^{2-}$ deposition, and serve to delay stream recovery.

When atmospheric deposition of $\text{NO}_3^-$ was decreased by 100% to pre-industrial conditions, the projected ANC responses in Goshen Prong Watershed were similar to $\text{SO}_4^{2-}$ responses (Figure 6.3a). Decreases in $\text{NO}_3^-$ deposition will be important in decreasing stream
acidity and improving habitat for the aquatic community. When atmospheric NO$_3^-$ deposition is decreased to the same level as historical deposition (100% decrease scenarios) with no change in atmospheric SO$_4^{2-}$ deposition, ANC increased 73 µeq/L while stream NO$_3^-$ decreased 90 µeq/L by 2200. In the GRSM, ANC = 0 is a lethal threshold for brook trout (Salvelinus fontinalis) and rainbow trout (Oncorhynchus mykiss; Cai and Schwartz, 2012). With less leaching losses of NO$_3^-$ from soil, H$^+$ leaching will decrease, corresponding with increases in pH and ANC. The pH-dependent algorithm for SO$_4^{2-}$ adsorption suggests that initially under decreases in atmospheric NO$_3^-$ deposition, increases in soil pH will drive desorption of SO$_4^{2-}$ from soil, offsetting the recovery associated with decrease in NO$_3^-$.

In contrast, the simulations in which atmospheric NO$_3^-$ deposition is projected to remain constant, increases in NO$_3^-$ leaching associated with decreases in N retention by the watershed acidify soil and enhance SO$_4^{2-}$ adsorption. Over the course of the simulation, stream SO$_4^{2-}$ concentrations increase as the soil comes to steady-state with respect to atmospheric SO$_4^{2-}$ deposition. Field studies show that the pH-dependence of SO$_4^{2-}$ adsorption/desorption is an important process controlling the recovery of GRSM watersheds (Cai et al., 2012b).

For simulations of decreases in a combination of SO$_4^{2-}$ and NO$_3^-$ deposition to pre-industrial conditions, maximum recovery under the combinations of decreases in SO$_4^{2-}$ and NO$_3^-$ is much greater than under the scenarios of decreases in SO$_4^{2-}$ or NO$_3^-$ individually. ANC increased 99.2 µeq/L when the model reached steady state around 2200. This relatively large increase in ANC is due to the effects of decreases in NO$_3^-$, which delays the progression of the watersheds toward a condition of N saturation, coupled with decreases in
SO$_4^{2-}$, which facilitates the desorption of SO$_4^{2-}$ that has been accumulated in soil under decades on elevated atmospheric SO$_4^{2-}$ deposition.

Note that simulations suggest that the ANC of Goshen Prong does not recover to the estimated preindustrial value (ANC ~ 59 µeq/L) by 2200. The loss of ANC is largely due to soil acidification associated with the depletion of base cations from soil exchange sites. While my analysis suggests that controls on atmospheric NO$_3^-$ deposition are more effective in facilitating increases in ANC than decreases in SO$_4^{2-}$ deposition, to maximize the recovery of GRSM watersheds it will be necessary to decrease concentrations of total strong acid anion concentrations in stream water by decreasing both NO$_3^-$ and SO$_4^{2-}$ in combination.

I also evaluated the relative effectiveness of controls on NH$_4^+$ deposition as compared to controls on NO$_3^-$ deposition, both of which increase the ANC of streams. PnET-BGC is structured to address differences in ecosystem response to changes in NH$_4^+$ compared with NO$_3^-$ deposition, because it simulates the acid-base chemistry associated with watershed involving different N species transformations. I conducted simulations to address variations in NH$_4^+$ deposition for four sites; one that exhibits limited NO$_3^-$ leaching (Lost Bottom Creek) and three that experience higher NO$_3^-$ leaching (Noland Divide, Walker Camp Prong, Indian Camp Creek) (Table 6.5). One might expect that controls on NH$_4^+$ deposition would be more effective at increasing ANC, because NH$_4^+$ is an acidifying compound when it is assimilated or nitrified by vegetation of microbes. In contrast retention of NO$_3^-$ is on ANC generating process (van Breemen et al., 1983). In Lost Bottom Creek I found little difference between controls of NH$_4^+$ and NO$_3^-$ deposition because both N compounds are relatively strongly assimilated within the watershed over a simulation period until 2050. In contrast, the other watersheds that exhibit elevated NO$_3^-$ leaching show that controls on NH$_4^+$ deposition
are more effective in increasing stream ANC than equivalent controls on NO$_3^-$ deposition, similar to a pattern expected from ion chemistry theory. The extent of increases in ANC per equivalent decrease in NH$_4^+$ or NO$_3^-$ deposition decreased over the simulation period because the watershed initially responded rapidly to controls on N deposition and the response diminished over time.

6.4.2 Developing CLs/DCLs for GRSM

As mentioned earlier, some watersheds can achieve target ANC (0, 20, 50 µeq/L) by 2050 under DCLs of SO$_4^{2-}$+NO$_3^-$ and projections suggest that some watersheds will not achieve target ANC (0, 20, 50 µeq/L) by 2050 even under the condition that atmospheric SO$_4^{2-}$+NO$_3^-$ were decreased to pre-industrial conditions. For example, Noland Divide (current ANC = 4.2 µeq/L), Walker Camp Prong (ANC = -13.3 µeq/L), Goshen Prong (ANC = 19.3 µeq/L) and Indian Camp Creek (ANC = 16.9 µeq/L) would not achieve ANC of 20 µeq/L by 2050. These sites have received elevated acidic deposition and are highly sensitive to acidic deposition (e.g., Noland Divide Watershed) or are affected by natural soil properties (i.e., Anakeesta in Walker Camp Prong; Cai et al., 2012b; Grell, 2010). These sites appear to have inherently low ANC (Table 6.1). The soils in these watersheds are naturally low in exchangeable base cations. Moreover, simulations suggest that acid-sensitive soils of the GRSM have exchangeable cation pools that have been depleted by historical acidic deposition, have accumulated SO$_4^{2-}$ through adsorption, and exhibit high nitrification rates. The recovery of these sensitive and acidified watersheds will not only depend on the control of atmospheric deposition, but on inherent soil properties. Due to the inherent soil properties
such as low weathering rate, low percent base saturation and high $\text{SO}_4^{2-}$ adsorption capacity, the recovery process of soils will be delayed in these watersheds, and possibly take decades or even centuries for total recovery.

The empirical relationships for HA with total acidic deposition, and preindustrial ANC (1850) are similar to the empirical relationships for maximum recovery with total acidic deposition, and preindustrial ANC (1850). There is inherent variability in watershed ANC due to elevation, soil characteristics and land disturbance history that influences the sensitivity to acidic deposition and the response to decreased deposition. In addition, the watersheds clearly show the variation in the historical acidification and recovery that are driven by the magnitude of acidic deposition and subsequent decreases in deposition. In GRSM, deposition of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ varies by elevation and total $\text{SO}_4^{2-}$ deposition closely corresponds with total $\text{NO}_3^-$ deposition.

Historical acidification (HA) was related with $\text{SO}_4^{2-}$ adsorption capacity. The soil adsorption and the varying ability of soil $\text{SO}_4^{2-}$ surfaces to bind is an important process. Process studies and watershed mass balance have demonstrated that a large fraction of $\text{SO}_4^{2-}$ entering the watershed from atmospheric deposition, historically and currently, is retained by soil $\text{SO}_4^{2-}$ adsorption (Johnson and Lindberg, 1992; Cai et al., 2012b). Field studies show that $\text{SO}_4^{2-}$ adsorption/desorption has the potential capability to control the recovery of GRSM watersheds (Cai et al., 2012b). Sulfate adsorption/desorption from soil is related to soil solution pH. The release of previously bound $\text{SO}_4^{2-}$ will delay the ecosystem recovery from acidification (Driscoll et al., 2001). For the application of PnET-BGC to the GRSM, estimates of soil $\text{SO}_4^{2-}$ adsorption are obtained through the development of parameters from laboratory soil adsorption isotherms and model calibration. The $\text{SO}_4^{2-}$ adsorption capacity is
held constant during the simulation period. In reality, the soil SO₄²⁻ adsorption capacity and adsorption parameters may change over time. This SO₄²⁻ adsorption algorithm has been well-tested in glaciated landscapes (Gbondo-Tugbawa and Driscoll, 2002), but not for unglaciated soils such as GRSM. Additional experimentation and improved parameterization should be conducted to improve characterization of SO₄²⁻ adsorption and its pH-dependence in GRSM soils.
Table 6.1. Characteristics of watersheds from GRSM that are used to test and apply PnET-BGC. These values represent average between 1995-2006 except Noland Divide Watershed between 1994-2008.

<table>
<thead>
<tr>
<th>Site</th>
<th>Elevation (m)</th>
<th>Area (km²)</th>
<th>%Anakeesta</th>
<th>NO₃⁻ (µeq/L)</th>
<th>SO₄²⁻ (µeq/L)</th>
<th>ANC (µeq/L)</th>
<th>Impaired</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noland Divide</td>
<td>1798</td>
<td>0.174</td>
<td>No</td>
<td>44.3</td>
<td>40.9</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Indian Camp Creek</td>
<td>1205</td>
<td>2.17</td>
<td>No</td>
<td>42.1</td>
<td>57.0</td>
<td>17.8</td>
<td></td>
</tr>
<tr>
<td>Walker Camp</td>
<td>1168</td>
<td>10.73</td>
<td>81.89%</td>
<td>38.0</td>
<td>71.2</td>
<td>-13.8</td>
<td></td>
</tr>
<tr>
<td>Goshen Prong</td>
<td>1046</td>
<td>7.29</td>
<td>26.83%</td>
<td>21.2</td>
<td>30.3</td>
<td>20.8</td>
<td>303d</td>
</tr>
<tr>
<td>Lost Bottom</td>
<td>1000</td>
<td>5.15</td>
<td>No</td>
<td>7.7</td>
<td>16.5</td>
<td>50.3</td>
<td></td>
</tr>
<tr>
<td>Left Prong Anthony</td>
<td>909</td>
<td>1.61</td>
<td>No</td>
<td>23.4</td>
<td>26.1</td>
<td>34.8</td>
<td></td>
</tr>
<tr>
<td>Pretty Hollow</td>
<td>903</td>
<td>11.18</td>
<td>No</td>
<td>16.6</td>
<td>20.6</td>
<td>47.0</td>
<td></td>
</tr>
<tr>
<td>Cosby Creek</td>
<td>783</td>
<td>5.78</td>
<td>No</td>
<td>38.2</td>
<td>46.1</td>
<td>37.3</td>
<td></td>
</tr>
<tr>
<td>Sugar Fork</td>
<td>780</td>
<td>2.14</td>
<td>No</td>
<td>3.7</td>
<td>22.5</td>
<td>90.3</td>
<td></td>
</tr>
<tr>
<td>Cannon Creek</td>
<td>751</td>
<td>4.19</td>
<td>0.64%</td>
<td>20.6</td>
<td>39.7</td>
<td>16.2</td>
<td>303d</td>
</tr>
<tr>
<td>Thunderhead</td>
<td>664</td>
<td>11.26</td>
<td>34.73%</td>
<td>14.4</td>
<td>31.2</td>
<td>33.2</td>
<td></td>
</tr>
<tr>
<td>Mill Creek</td>
<td>545</td>
<td>10.92</td>
<td>No</td>
<td>12.1</td>
<td>24.8</td>
<td>46.2</td>
<td></td>
</tr>
</tbody>
</table>

Data are from Great Smoky Mountains National Park, National Park Service, and adapted from Neff et al., (2013).
Table 6.2. Regression equations for mean monthly precipitation quantity based on longitude, latitude, and elevation in GRSM.

<table>
<thead>
<tr>
<th>Quarter</th>
<th>Constant</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Elevation</th>
<th>Adj. $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(µeq/L)</td>
<td>(µeq/L deg)</td>
<td>(µeq/L deg)</td>
<td>(m)</td>
<td></td>
</tr>
<tr>
<td>January</td>
<td>-198.232</td>
<td>-2.93</td>
<td>-1.02</td>
<td>0.00427</td>
<td>0.985</td>
</tr>
<tr>
<td>February</td>
<td>-304.497</td>
<td>-5.193</td>
<td>-3.331</td>
<td>0.004</td>
<td>0.987</td>
</tr>
<tr>
<td>March</td>
<td>-206.915</td>
<td>-4.482</td>
<td>-4.454</td>
<td>0.00676</td>
<td>0.978</td>
</tr>
<tr>
<td>April</td>
<td>-198.232</td>
<td>-2.93</td>
<td>-1.02</td>
<td>0.00427</td>
<td>0.938</td>
</tr>
<tr>
<td>May</td>
<td>-69.424</td>
<td>-2.178</td>
<td>-2.827</td>
<td>0.00378</td>
<td>0.541</td>
</tr>
<tr>
<td>June</td>
<td>355.77</td>
<td>2.311</td>
<td>-4.172</td>
<td>0.00151</td>
<td>0.935</td>
</tr>
<tr>
<td>July</td>
<td>287.745</td>
<td>3.431</td>
<td>0.377</td>
<td>-0.00091</td>
<td>0.275</td>
</tr>
<tr>
<td>August</td>
<td>508.106</td>
<td>5.403</td>
<td>-1.336</td>
<td>0.00148</td>
<td>0.997</td>
</tr>
<tr>
<td>September</td>
<td>-36.912</td>
<td>-2.851</td>
<td>-5.373</td>
<td>0.0041</td>
<td>0.99</td>
</tr>
<tr>
<td>October</td>
<td>62.165</td>
<td>-0.612</td>
<td>-3.016</td>
<td>0.00397</td>
<td>0.998</td>
</tr>
<tr>
<td>November</td>
<td>78.386</td>
<td>-0.973</td>
<td>-4.14</td>
<td>0.00292</td>
<td>0.995</td>
</tr>
<tr>
<td>December</td>
<td>72.583</td>
<td>-0.736</td>
<td>-3.438</td>
<td>0.000736</td>
<td>0.987</td>
</tr>
</tbody>
</table>

Table 6.3. Regression equations for mean quarterly $SO_4^{2-}$ and $NO_3^-$ concentrations in wet deposition dependent on longitude, latitude and elevation at GRSM.

<table>
<thead>
<tr>
<th>Quarter</th>
<th>Constant</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Elevation</th>
<th>Adj. $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(µeq/L)</td>
<td>(µeq/L deg)</td>
<td>(µeq/L deg)</td>
<td>(m)</td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_3$(µeq/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>-1.48×10$^3$</td>
<td>-1.68×10</td>
<td>2.45</td>
<td>1.03×10$^{-2}$</td>
<td>0.828</td>
</tr>
<tr>
<td>Spring</td>
<td>-1.82×10$^3$</td>
<td>-2.11×10</td>
<td>1.58</td>
<td>1.64×10$^{-2}$</td>
<td>0.974</td>
</tr>
<tr>
<td>Summer</td>
<td>-2.69×10$^3$</td>
<td>-3.19×10</td>
<td>0.80</td>
<td>2.79×10$^{-2}$</td>
<td>0.987</td>
</tr>
<tr>
<td>Autumn</td>
<td>-2.04×10$^3$</td>
<td>-2.39×10</td>
<td>1.38</td>
<td>2.04×10$^{-2}$</td>
<td>0.962</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_4$(µeq/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>-1.78×10$^3$</td>
<td>-1.83×10</td>
<td>7.44</td>
<td>1.06×10$^{-2}$</td>
<td>0.452</td>
</tr>
<tr>
<td>Spring</td>
<td>-1.46×10$^3$</td>
<td>-1.52×10</td>
<td>5.70</td>
<td>1.48×10$^{-2}$</td>
<td>0.875</td>
</tr>
<tr>
<td>Summer</td>
<td>-1.55×10$^3$</td>
<td>-1.57×10</td>
<td>7.56</td>
<td>1.41×10$^{-2}$</td>
<td>0.987</td>
</tr>
<tr>
<td>Autumn</td>
<td>-2.77×10$^3$</td>
<td>-3.10×10</td>
<td>5.07</td>
<td>2.64×10$^{-2}$</td>
<td>0.954</td>
</tr>
<tr>
<td>Stream</td>
<td>ANC</td>
<td>SO$_4^-$</td>
<td>NO$_3^-$</td>
<td>Deposition</td>
<td>2010</td>
</tr>
<tr>
<td>-------------------------</td>
<td>-----</td>
<td>----------</td>
<td>----------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>Mill Creek</td>
<td>2.03</td>
<td>30.7</td>
<td>14.4</td>
<td>0.48</td>
<td>0.30</td>
</tr>
<tr>
<td>Thunderhead</td>
<td>6.05</td>
<td>1.34</td>
<td>1.71</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>Cannon Creek</td>
<td>2.77</td>
<td>7.33</td>
<td>2.14</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>Sugar Fork</td>
<td>4.93</td>
<td>0.34</td>
<td>1.13</td>
<td>0.56</td>
<td>0.56</td>
</tr>
<tr>
<td>Coosy Creek</td>
<td>1.14</td>
<td>0.94</td>
<td>0.30</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>Pretty Hollow</td>
<td>2.24</td>
<td>0.84</td>
<td>0.36</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>Little Ford安东尼</td>
<td>1.71</td>
<td>0.51</td>
<td>0.22</td>
<td>1.34</td>
<td>1.34</td>
</tr>
<tr>
<td>Lost Bottom Creek</td>
<td>87.5</td>
<td>4.31</td>
<td>1.33</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Goosebom Point</td>
<td>0.28</td>
<td>0.41</td>
<td>0.41</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>Water Camp Fire</td>
<td>0.70</td>
<td>1.49</td>
<td>1.49</td>
<td>1.49</td>
<td>1.49</td>
</tr>
<tr>
<td>Indian Camp Creek</td>
<td>0.36</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Table 6. Dynamic critical loads (DCL) of NO$_3^-$, NO$_2^-$ deposition necessary to reach ANC targets (0.30 to 0.50) and SO$_4^-$ deposition necessary to reach ANC targets (0.50 to 0.70) based upon the BEST model forecasts for 12 study streams within Great Smoky Mountains National Park. Simulated pre-industrial ANC, current 2010 and DCL are key values for ANC are recalculation.
Table 6.5. Changes in stream acid neutralizing capacity per unit equivalent decrease in ammonium and nitrate deposition for watersheds of the Great Smoky Mountain National Park over the period to 2050. Note that the sites studied exhibit a different response depending on the extent of nitrate leaching.

<table>
<thead>
<tr>
<th>Site</th>
<th>Volume-weighted NO$_3^-$ (µmol/L)</th>
<th>$\Delta$ANC/ $\Delta$NH$_4^+$ (µeq/L)/( keq/ha-yr))</th>
<th>$\Delta$ANC/ $\Delta$NO$_3^-$ (µeq/L)/( keq/ha-yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lost Bottom Creek</td>
<td>7.7</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>Walker Camp Prong</td>
<td>38</td>
<td>0.31</td>
<td>0.46</td>
</tr>
<tr>
<td>Indian Camp Creek</td>
<td>42.1</td>
<td>0.46</td>
<td>1.02</td>
</tr>
<tr>
<td>Noland Divide</td>
<td>44.3</td>
<td>0.31</td>
<td>0.36</td>
</tr>
</tbody>
</table>
Figure 6.1. Model comparisons between measured and model-predicted mean annual volume-weighted concentrations of selected stream solutes for 12 sites in GRSM. The line is 1:1 line. Observations values are means values for 1994 to 2008 for each site.
Figure 6.2. Simulations of hindcasts of $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and acid neutralizing capacity (ANC) for stream chemistry sites in GRSM.
Figure 6.3. Time series of stream $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$, ANC and pH for Goshen Prong watershed (y-axis) that include hindcasts and future projections to atmospheric deposition decreases in: (a) $\text{NO}_3^-$ only, (b) $\text{SO}_4^{2-}$ only, and (c) both $\text{NO}_3^-$ and $\text{SO}_4^{2-}$. Also shown are measured values.
Figure 6.4. Relationships between (a) pre-industrial ANC (1850); (b) current total deposition of SO$_4^{2-}$ + NO$_3^-$; and (c) estimated soil sulfate adsorption capacity with historical acidification HA; ANC in 1850- ANC in 2010. Relationships between (d) current ANC (2010); (e) pre-industrial ANC(1850); and (f) current total deposition of SO$_4^{2-}$ + NO$_3^-$ with maximum recovery (MR) ANC under decreases in total deposition of SO$_4^{2-}$ + NO$_3^-$ to pre-industrial values in 2200. Results of linear regression analysis are shown.
Figure 6.5. Empirical relationships between current ANC of GRSM streams and the deposition of \( \text{NO}_3^- + \text{SO}_4^{2-} \) necessary to achieve target ANC values of 0, 20 and 50 \( \mu \text{eq/L} \) in 2050. These values were developed from simulations from 12 study sites with PnET-BGC. Regression lines were also developed individually between different CLs and current stream ANC. They are 

\[
y = 0.028x + 1.00 \quad (r^2 = 0.64) \text{ for ANC 0 \( \mu \text{eq/L} \);} \quad y = 0.019x + 0.61 \quad (r^2 = 0.69) \text{ for ANC 20 \( \mu \text{eq/L} \);} \quad \text{and} \quad y = 0.013x + 0.38 \quad (r^2 = 0.61) \text{ for ANC 50 \( \mu \text{eq/L} \)}. \]

Also shown as cross hatching the range of \( \text{NO}_3^- + \text{SO}_4^{2-} \) deposition currently observed in GRSM.
Chapter 7 Synthesis

While there are many differences between the Adirondacks and the GRSM in terms of climate, soils, hydrology, surface water features (i.e., lakes vs. streams) and vegetation, it is useful to compare the similarities and differences on their response to changes in acidic deposition to summarize the CLs study for these two regions and to provide scientific support for the policy makers on strategies for controlling acidic deposition in these two regions, I investigated 20 sites in the Adirondacks and 12 sites in the GRSM to historical and potential future changes in acidic deposition specially site characteristics, response to changes in SO\(_4^{2-}\) vs NO\(_3^-\) deposition, DCLs and CLs, and policy implications.

7.1 Comparisons between the Adirondacks and the GRSM

The Adirondacks and GRSM have common characteristics such as that they are forest dominated, are at high elevations and receive elevated atmospheric deposition. They also exhibit a range of site characteristics.

The selection criteria for the study sites used to conduct simulations in these two regions differ by the various regional geophysical and ecological characteristics. I had two main approaches for the two regions. First, I aimed to select sites with diverse characteristics from the thousands of lake-ecosystems in the Adirondacks and many stream ecosystems in the GRSM. The second criteria of even greater importance was to select sites that are more acidified (low ANC or low pH) because they are of particular concern for the ecosystem restoration. The
Adirondacks contains diverse lake ecosystems, including drainage lakes (thin till, medium and thick till), and seepage lakes. The ANC values of the 20 simulation sites range from -10 µeq/L to 70 µeq/L, with most of lakes exhibiting low ANC. For the GRSM sites, the specific selection criteria was primarily based on a block design that was developed by the National Park Service. The 12 simulation sites were selected based on elevation, ANC, pH, NO₃⁻ and presence/absence of Anakeesta. Similarly, I focused more on sites with pH<6 and low ANC values, with a range of NO₃⁻ leaching. An important difference in the selection criterion between these two regions is that I included presence/absence of Anakeesta for the GRSM. Anakeesta is a potential source of SO₄²⁻ through the oxidation of pyrite. Winger et al. (1987) collected different stream samples from the Southern Blue Ridge and found that the concentrations of sulfate were 8 to 9 times higher in streams with Anakeesta than without Anakeesta, and similarly NO₃⁻ were 2 to 3 times higher in streams with Anakeesta than without Anakeesta. This indicates that ANC might have some relationship with the SO₄²⁻ and NO₃⁻; however, my model simulation results do not show any evidence for the watersheds containing higher percentage of Anakeesta exhibits greater acidification than watersheds containing lower percentage of Anakeesta. The reason may be due to the limited understanding of the Anakeesta effects on the ecosystem and how hydrologic flowpaths affect the supply of SO₄²⁻ derived from Anakeesta.

The Adirondacks is a glaciated area. The processes of the glaciation determined that the soils were generally young, thin and acidic. Based on the data from the Adirondack Park Agency, 49% of the soils in the Adirondacks are acidic glacial till soils and 24% are shallow to bedrock soils (Driscoll et al., 1991a). GRSM is an unglaciated area. Based on the Integrated Forest Study (Johnson and Lindberg, 1992), soil types for the study sites in the GRSM were generally classified as Umbric Dystrochrepts derived from the Ankaesta formation and that are
characterized by a high $\text{SO}_4^{2-}$ adsorption capacity. Considering the contribution to stream acidification, these soil types are classified as no risk, low risk, moderate, and high risk to stream acidification (Winger et al., 1987). Most of the sites have a low or moderate risk for stream acidification.

7.2 Trade off of watershed response to decreases in $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ deposition

The Adirondacks and GRSM showed different patterns in their response of ANC to the changes in $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ deposition. The relative importance of decreases in $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ in accomplishing increases in surface water ANC differed in the two regions.

Surface water ANC for sites in both regions have decreased since the onset of acidic deposition in 1850 and continuously decreased until the present under current deposition regimes. However, after the present time, a time series of future projections under different scenarios exhibits an increasing pattern of ANC in the Adirondacks, while ANC continues to decrease in the GRSM. There are two possible reasons for this phenomenon. One is that much of the $\text{SO}_4^{2-}$ deposition to GRSM is retained in the soil. Studies have shown that soil $\text{SO}_4^{2-}$ adsorption capacity in the GRSM is relatively high compared to the Adirondacks (Rochelle and Church, 1987; Johnson and Lindberg; 1992; Cai et al., 2012b). As the accumulated $\text{SO}_4^{2-}$ in the GRSM soil is slowly released to water over several years or decades, ecosystem recovery will be delayed. Another important reason is $\text{NO}_3^-$ leaching from the soil. The mean of measured stream $\text{NO}_3^-$ for the 12 sites (23.5 $\mu$eq/L) in the GRSM is considerably higher than the mean of measured lake $\text{NO}_3^-$ for the 20 sites (14.6 $\mu$eq/L) in the Adirondacks. The watersheds in the GRSM are not able to assimilate atmospheric N deposition as effectively as the Adirondacks.
Moreover, in-lake retention of NO$_3^-$ in the Adirondacks likely also contributes to this difference between the regions. Differences in stand age, land disturbance history, or landscapes with wetlands and lakes, or deposition patterns could also contribute to the differences between the regions. Thus, more NO$_3^-$ could be leached from the ecosystem, and acidification in GRSM may potentially occur for decades even maybe centuries.

My research has demonstrated that ANC increased more effectively under equivalent SO$_4^{2-}$ decreases than equivalent NO$_3^-$ decreases in the Adirondacks, while ANC increased more effectively under equivalent NO$_3^-$ decreases than SO$_4^{2-}$ decreases in GRSM. In order to quantify and compare the response of ANC to SO$_4^{2-}$, NO$_3^-$, and SO$_4^{2-}$ and NO$_3^-$ deposition, reductions were expressed on an equivalence basis under two deposition scenarios (0% reduction scenario and 100% reduction scenario) in relative change to deposition load for SO$_4^{2-}$ or NO$_3^-$ under 0% reduction scenario and 100% reduction scenario over two time periods (i.e., 2007-2050 or 2007-2200). These ratios represented the extent of increases in ANC with an equivalent decrease of SO$_4^{2-}$ or NO$_3^-$ per year for a target time (2050 or 2200). In 2050 or 2200, ratios for lake SO$_4^{2-}$ in the Adirondacks were higher than for GRSM and ratios for NO$_3^-$ in the Adirondacks are lower than for GRSM due to inherent soil properties (Table 7.1), such as base cation weathering rate, depth, cation exchange capacity and SO$_4^{2-}$ at adsorption capacity. Note that Adirondack watersheds are projected to show a decrease in ANC with decreases in NO$_3^-$ deposition for 2050. This pattern is due to associated decreases in in-lake ANC generation as discussed in Chapter 4.
Table 7.1. Differences in simulated increases in ANC per equivalent change in atmospheric \( \text{SO}_4^{2-} \) or \( \text{NO}_3^- \) deposition for the GRSM and the Adirondacks for two simulation periods 2050 and 2200.

<table>
<thead>
<tr>
<th></th>
<th>DCLs (2050)</th>
<th>CLs (2200)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta \text{ANC} (\mu \text{eq.L}^{-1}) / \Delta \text{SO}_4^{2-} (\text{eq.ha}^{-1}) )</td>
<td>( \Delta \text{ANC} (\mu \text{eq.L}^{-1}) / \Delta \text{NO}_3^- (\text{eq.ha}^{-1}) )</td>
</tr>
<tr>
<td>Adirondacks</td>
<td>0.6(±0.2)</td>
<td>-0.2(±0.1)</td>
</tr>
<tr>
<td>GRSM</td>
<td>0.3(±0.1)</td>
<td>0.7(±0.3)</td>
</tr>
</tbody>
</table>

7.3 Comparisons for CLs and DCLs of \( \text{SO}_4^{2-} + \text{NO}_3^- \) between the Adirondacks and the GRSM

CLs or DCLs of \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) deposition vary for the two regions due to different site characteristics. The DCLs of \( \text{NO}_3^- + \text{SO}_4^{2-} \) deposition by 2050 for the 12 study streams in the GRSM is generally higher than the DCLs of \( \text{NO}_3^- + \text{SO}_4^{2-} \) deposition for the 20 lakes in the Adirondacks by 2040 to achieve the same target ANCs (i.e., 0, 20, 50 \( \mu \text{eq.L} \)). The loading of wet deposition in the GRSM is higher than in the Adirondacks. Dry and cloud deposition can contribute greater inputs than wet deposition at the GRSM. Dry and cloud deposition is approximately three times more than wet deposition for \( \text{SO}_4^{2-} \) and four times more than wet deposition for \( \text{NO}_3^- \) at the high elevation Noland Divide Watershed during 1986-1989 (Johnson and Lindberg, 1992). In comparison in the Adirondacks, the dry deposition only accounts for about 20%-30% of wet deposition for both \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \).

Elevated \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) deposition may play an important role as \( \text{SO}_4^{2-} \) in the acidification in certain regions such as GRSM. It is well known that the atmospheric pollutants
such as SO$_2$ and NO$_x$ can cause acidification to soil, water, and vegetation through biogeochemical processes. In the 1970s, elevated S deposition was recognized as a significant contributor to acidification. In the 1990s, N was also recognized as a significant pollutant in acidification. Air quality management has focused on controls of SO$_2$ and NO$_x$ emissions and ignored reduced nitrogen (NH$_4$$^+$). Recently, NH$_4$$^+$ has attracted increasing interest because it is also an acidifying compound, which can be nitrified and enhance basic cations leaching through cation exchange processes in the soil water and contribute to the acidification of soil and water. The relative importance of NH$_4$$^+$ and NO$_3^-$ and interaction between these two chemical species is still not well known. I found small differences in the ANC responses to controls on NO$_3^-$ and NH$_4$$^+$ deposition among the sites in the Adirondacks and sites in the GRSM that exhibit low NO$_3^-$ leaching, like Lost Bottom Creek. However, the high NO$_3^-$ leaching sites in the GRSM exhibit greater ANC increases resulting from decreases in NH$_4$$^+$ deposition than controls of NO$_3^-$ deposition by 2200.

7.4 Policy implications

My research has improved the understanding of the relative contribution of SO$_4^{2-}$, NO$_3^-$ and NH$_4$$^+$ to the acidification of ecosystems and provides important information for ecosystem management.

CLs are an appropriate approach for justifying emission abatement strategies to guide policies designed to protect ecosystems from the adverse effects of acidic inputs. Dynamic models such as PnET-BGC can help in assessing the implications of various air quality
management policies. CLs of SO$_4^{2-}$ and NO$_3^-$ were calculated on a site-by-site basis in the Adirondacks and the GRSM to demonstrate what might be done to prevent future impacts from SO$_4^{2-}$ and NO$_3^-$ deposition. My analysis and detailed field studies show that the current emission control programs are not adequate to prevent acidification and additional reduction of SO$_4^{2-}$ + NO$_3^-$ is needed. Implementing CLs or DCLs of SO$_4^{2-}$ + NO$_3^-$ deposition in the Adirondacks and GRSM can provide reliable information for policy makers to determine the degree of emission controls needed to recover ecosystems from the effects of acidic deposition.

My research shows that N is more important than S in the acidification of soil and surface water in the GRSM while the opposite pattern is evident for the Adirondacks. The relative importance of sulfur or nitrogen in acidification largely depends on the watershed characteristics such as glaciated or unglaciated areas. For example, in regions where N plays an important role in acidification, controls on N emission will be more effective in mitigating effects of acidification than decreases in SO$_2$ emissions. In regions where S is relatively more important than nitrogen, controls on S emission will be more effective in facilitating recovery.

Given the relative importance of N and S in acidification across diverse regions, a policy targeting air pollutants would seem to be sound strategy. Establishing CLs of SO$_4^{2-}$ + NO$_3^-$ to achieve target ANC will depend on different regional characteristics (e.g. SO$_4^{2-}$ adsorption capacity, watershed N retention), future dates, and different target ANCs. Some sites will require much greater decreases in atmospheric deposition than others to achieve recovery. However, note that complete chemical recovery will not likely be achieved everywhere even with under a scenario that SO$_4^{2-}$ + NO$_3^-$ deposition is decreased to pre-industrial value.
7.5 Future work

Future work could be done to improve the representation of soil processes in PnET-BGC. In this study, a single soil layer version of PnET-BGC was used. An algorithm of multiple soil layers may better depict the biogeochemical and geophysical processes of cations and anions by considering the whole soil profile, which would potentially improve the model performance by better simulating the dynamics of soil processes.

Future work could focus on a pH dependent soil DOC adsorption algorithm. DOC shows an increasing trend at Constable Pond and other waters of the Adirondacks based on the long-term monitoring data (Driscoll et al., 2007). One possible reason for this pattern is due to recent increases on pH associated with decreases in acidic deposition. With increasing pH, the partitioning of DOC with soil would decrease. However PnET-BGC does not have pH-dependent algorithm for DOC adsorption.

Future work could be done to improve the estimation of cloud and dry deposition at the GRSM. As mentioned earlier, cloud and dry deposition could contribute a large fraction of total deposition of S and N in mountainous areas. However cloud and dry deposition can not be as easily measured as wet deposition.

Future work could be done on developing an algorithm to simulate the release of $\text{SO}_4^{2-}$ from Anakeesta. Anakeesta can supply the sulfate through oxidation of pyrite. Currently, there is no algorithm for pyritic phyllite oxidation.

Future work could also be done to explore how climate change and changes in forest assimilation of $\text{CO}_2$ will affect the CLs or DCLs of S or N deposition. I have already evaluated how land disturbance, DOC or hydrological residence time affects the CLs or DCLs of N or S
deposition. The effects of climate change and CO₂ were not considered here, but should be considered for future work.

Chapter 8 Conclusions

The PnET-BGC model was applied to 20 sites in the Adirondacks and 12 sites in the GRSM and performed well in these two regions. I calculated CLs/DCLs for SO₄²⁻ and NO₃⁻ deposition using the model and also examined ecosystem changes in response to historical and hypothetical future decreases in atmospheric deposition. The specific conclusions for the three phases of this dissertation are as follows.

In Phase 1 of the study (Chapter 4), I determined the CLs and DCLs of SO₄²⁻ and NO₃⁻ for Constable Pond. I also assessed the factors that affect historical acidification and maximum recovery of the lake. I found that factors such as loadings of SO₄²⁻ or NO₃⁻ deposition, forest cutting disturbance, supply of naturally occurring organic acids, and in-lake processes have potential influences on lake-watershed response to historical acidic deposition as well as future response to decreases in atmospheric deposition. Firstly, lake ANC will increase in response to decreases in SO₄²⁻ or NO₃⁻ deposition. Greater increases in ANC will occur in response to a decrease in SO₄²⁻ deposition than an equivalent decrease in NO₃⁻ deposition. Secondly, model simulations showed that forest cutting likely enhanced historical acidification due to the removal of nutrient cations associated with the removal of forest biomass over the short-term. However, over the long-term forest cutting can also enhance recovery from acidic deposition due to the greater retention of atmospheric N deposition in an aggrading forest ecosystem. Thirdly, DOM supply affects the acid-base status of surface water. The greater recovery of ANC can be
achieved in lakes with lower DOC concentrations than higher DOC concentrations due to strongly acidic functional groups associated with DOM. The inability of PnET-BGC and other acidification models to depict the compensatory response of watershed DOM to decreases in acidic deposition may limit the ability to establish accurate targets for acidification and recovery.

Lastly, in-lake processes also affect ANC and the extent of recovery of Adirondack lakes. For lakes with longer HRTs, decreases in SO$_4^{2-}$ deposition will result in greater ANC values than lakes with shorter HRT lakes. In contrast, in longer HRT lakes, decreases in NO$_3^-$ deposition will offset the extent of ANC recovery due to more efficient in-lake retention of NO$_3^-$.

In Phase 2 of the study (Chapter 5) I expanded the application of PnET-BGC to 19 additional lake-watersheds in the Adirondacks. Model performance for these sites were also good. I calculated CLs/DCLs for SO$_4^{2-}$ and NO$_3^-$ for the 20 sites and evaluated factors that affected historical acidification and maximum recovery across the region. I also evaluated the changes of biological indicators, fish and zooplankton species richness, in response to historical and future decreases in SO$_4^{2-}$ and NO$_3^-$ deposition using empirical relationships between lake ANC and species richness. For the acidification of the lake-watersheds, the modeled estimates of pre-industrial ANC showed that the magnitude of historical acidification varied from site to site. I found that historical acidification of the lake-watersheds was related with the total current deposition of SO$_4^{2-}$+NO$_3^-$, Ca weathering rate, and pre-industrial ANC (~1850). For the maximum recovery of Adirondack lake ecosystems, the magnitude of the recovery varied across sites based on the magnitude of decreases in SO$_4^{2-}$+NO$_3^-$ deposition and the value of the target ANC. Some lakes can reach targetANCs of 0, 20 or 50 µeq/L over the short-term (2050) with or without additional emission controls. However, some lakes are projected not to be able to reach the target ANC over the long term (2200) even under a scenario of complete reduction of
anthropogenic acidic deposition. Complete recovery from acidification is not possible for all lake ecosystems largely due to the depletion of exchangeable basic cations from watershed soils. Extrapolation of empirical spatial relationships for biological indicators with projections of ANC suggests that Adirondack lake ecosystems have lost fish and total zooplankton species richness starting with the onset of the acidic deposition that has continued until the present time. However recovery of these species could occur under future decreases in deposition.

In Phase 3 of the dissertation (Chapter 6) a similar approach that was used for the Adirondacks was applied to stream-watersheds in the GRSM. This study was the first application of PnET-BGC to watersheds in the southeastern U.S. The model was successfully calibrated in 12 sites. As for the Adirondacks, I evaluated the changes in GRSM ecosystems to historical and future decreases in atmospheric deposition. Hindcast simulations suggest that historical atmospheric deposition resulted in marked increases in stream SO$_4^{2-}$ and NO$_3^-$, resulting in decreases in the pH and ANC. The extent of changes in stream chemistry in response to changes in atmospheric deposition is largely driven by watershed variability across the GRSM, associated with variations in acidic deposition, historical land disturbance and soil characteristics. I observed a relationship between historical acidification and potential watershed recovery with changes in NO$_3^- + $SO$_4^{2-}$ deposition and historical ANC (1850). Stream ANC in GRSM watersheds increases to a greater extent in response to decreases in atmospheric NO$_3^-$ deposition than to an equivalent decrease in SO$_4^{2-}$ deposition due to the SO$_4^{2-}$ adsorption capacity of soils in the region. I also developed a relationship between current ANC and the level of deposition needed to achieve a target ANC. This relationship could be utilized with stream survey data for the GRSM to develop a park-wide TMDL or CL/DCL.
Appendix

Table A1 Summary of dry to wet deposition ratios for SO$_4^{2-}$ and NO$_3^-$ for the 12 sites in GRSM.

<table>
<thead>
<tr>
<th>Dry to wet ratios</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noland Divide</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Indian Camp Creek</td>
<td>0.5</td>
<td>7</td>
</tr>
<tr>
<td>Walker Camp Prong</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>Goshen Prong</td>
<td>0.2</td>
<td>4</td>
</tr>
<tr>
<td>Lost Bottom Creek</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Left Prong Anthony</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>Pretty Hollow</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>Cosby Creek</td>
<td>1</td>
<td>4.5</td>
</tr>
<tr>
<td>Sugar Fork</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Cannon Creek</td>
<td>0.2</td>
<td>4.5</td>
</tr>
<tr>
<td>Thunderhead</td>
<td>0.2</td>
<td>3</td>
</tr>
<tr>
<td>Mill Creek</td>
<td>0.1</td>
<td>3</td>
</tr>
</tbody>
</table>
Table A2. Summary of the results of model simulations of mean annual volume-weighted concentrations for selected stream solutes for 12 sites in GRSM. Shown are simulated (S) and observed (O) concentrations and metrics of agreement between measured and model simulated values (NME, NMAE).

<table>
<thead>
<tr>
<th></th>
<th>Mg(S)</th>
<th>Mg(O)</th>
<th>NME</th>
<th>NMAE</th>
<th>Ca(S)</th>
<th>Ca(O)</th>
<th>NME</th>
<th>NMAE</th>
<th>NO₃(S)</th>
<th>NO₃(O)</th>
<th>NME</th>
<th>NMAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noland Divide</td>
<td>24.22</td>
<td>20.67</td>
<td>0.17</td>
<td>0.17</td>
<td>60.11</td>
<td>51.68</td>
<td>0.16</td>
<td>0.17</td>
<td>35.47</td>
<td>44.31</td>
<td>-0.20</td>
<td>0.29</td>
</tr>
<tr>
<td>Indian Camp Creek</td>
<td>23.90</td>
<td>21.77</td>
<td>0.10</td>
<td>0.13</td>
<td>64.80</td>
<td>85.76</td>
<td>-0.24</td>
<td>0.23</td>
<td>36.80</td>
<td>42.08</td>
<td>-0.13</td>
<td>0.25</td>
</tr>
<tr>
<td>Walker Camp Prong</td>
<td>31.23</td>
<td>34.04</td>
<td>-0.08</td>
<td>0.15</td>
<td>62.72</td>
<td>52.49</td>
<td>0.19</td>
<td>0.22</td>
<td>31.91</td>
<td>38.04</td>
<td>-0.16</td>
<td>0.21</td>
</tr>
<tr>
<td>Goshen Prong</td>
<td>18.33</td>
<td>20.49</td>
<td>-0.11</td>
<td>0.26</td>
<td>44.91</td>
<td>40.11</td>
<td>0.12</td>
<td>0.36</td>
<td>19.70</td>
<td>21.17</td>
<td>-0.07</td>
<td>0.29</td>
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<tr>
<td>Lost Bottom Creek</td>
<td>21.13</td>
<td>18.08</td>
<td>0.17</td>
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<tr>
<td>Left Prong Anthony</td>
<td>22.61</td>
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<td>51.68</td>
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<td>0.31</td>
</tr>
<tr>
<td>Pretty Hollow</td>
<td>19.93</td>
<td>18.86</td>
<td>0.06</td>
<td>0.18</td>
<td>37.09</td>
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<td>48.34</td>
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<td>12.61</td>
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<table>
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<tr>
<th>SO₄(S)</th>
<th>SO₄(O)</th>
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<th>NMAE</th>
<th>ANC(S)</th>
<th>ANC(O)</th>
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<td>0.08</td>
<td>0.15</td>
<td>19.02</td>
<td>16.59</td>
<td>0.15</td>
<td>0.53</td>
<td>5.87</td>
<td>5.94</td>
<td>-0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>34.39</td>
<td>31.16</td>
<td>0.10</td>
<td>0.12</td>
<td>34.23</td>
<td>32.55</td>
<td>0.05</td>
<td>0.28</td>
<td>6.13</td>
<td>6.25</td>
<td>-0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>29.21</td>
<td>24.78</td>
<td>0.18</td>
<td>0.26</td>
<td>47.92</td>
<td>46.18</td>
<td>0.04</td>
<td>0.10</td>
<td>6.29</td>
<td>6.40</td>
<td>-0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Note: S - model simulation values; O - observed values (most of sites between 1995-2006; Noland Divide Watershed between 1994-2008); Values represent annual volume weighted concentrations; Units for Mg²⁺, Ca²⁺, NO₃⁻, SO₄²⁻, ANC are μeq/L. NME is normalized mean error; NMAE is normalized mean absolute error.
Table A3. Available measurements and model simulations of element fluxes for Noland Divide Watershed. UTK measured values are mean annual values for 1994-2008. IFS measurements were made during 1986-1989.

<table>
<thead>
<tr>
<th></th>
<th>( \text{NH}_4^+ ) (keq/ha-yr)</th>
<th>( \text{NO}_3^- ) (keq/ha-yr)</th>
<th>( \text{SO}_4^{2-} ) (keq/ha-yr)</th>
<th>( \text{Ca}^{2+} ) (keq/ha-yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IFS</td>
<td>UTK</td>
<td>Model</td>
<td>IFS</td>
</tr>
<tr>
<td>Throughfall</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deposition</td>
<td>0.02</td>
<td>0.3</td>
<td>0.29</td>
<td>1.40</td>
</tr>
<tr>
<td>Weathering Rate</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mineralization</td>
<td>1.0</td>
<td>2.38</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nitrification</td>
<td>-1.69</td>
<td>1.69</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Plant uptake</td>
<td>-0.91</td>
<td>-1.89</td>
<td>-2.27</td>
<td>-0.22</td>
</tr>
<tr>
<td>Sorption</td>
<td>0</td>
<td></td>
<td>-1.24</td>
<td>0</td>
</tr>
<tr>
<td>Drainage losses</td>
<td>-0.02</td>
<td>0</td>
<td>-0.71</td>
<td>-0.54</td>
</tr>
<tr>
<td>Total input</td>
<td>2.67</td>
<td></td>
<td>2.71</td>
<td>2.71</td>
</tr>
<tr>
<td>Total output</td>
<td>2.60</td>
<td></td>
<td>2.81</td>
<td>2.73</td>
</tr>
</tbody>
</table>

Note: Measured data for throughfall, weathering rate, mineralization, nitrification, plant uptake, sorption, drainage losses are from University of Tennessee (UTK) and the Integrated Forest Study (IFS). Simulation values are average from 1994 to 2008. Positive values indicate ecosystem inputs. Negative values indicate ecosystem losses.
Table A4 Element and ANC budgets for Goshen Prong Watershed for preindustrial (1850-1860) and current (1999-2009) periods. Preindustrial data (1850-1860) are from Shannon’s ASTRAP model. Current period (1999-2009) is from model parameterization or simulation.

<table>
<thead>
<tr>
<th>Flux</th>
<th>$C_2$ (keq/ha-yr)</th>
<th>$NO_3^-$ (keq/ha-yr)</th>
<th>$SO_4^{2-}$ (keq/ha-yr)</th>
<th>$NH_4^+$ (keq/ha-yr)</th>
<th>ANC (keq/ha-yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition</td>
<td>0.0</td>
<td>0.1</td>
<td>0.2</td>
<td>1.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Weathering rate</td>
<td>0.7</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Canopy exchange</td>
<td>0.0</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Uptake</td>
<td>-2.8</td>
<td>-4.2</td>
<td>-0.1</td>
<td>-4.2</td>
<td>-0.5</td>
</tr>
<tr>
<td>soil sorption</td>
<td>0.0</td>
<td>0.8</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Mineralization</td>
<td>2.7</td>
<td>3.6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Nitrification</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Drainage losses</td>
<td>-0.6</td>
<td>-1.3</td>
<td>0.0</td>
<td>-0.4</td>
<td>-0.1</td>
</tr>
<tr>
<td>Sources</td>
<td>3.4</td>
<td>5.5</td>
<td>0.2</td>
<td>4.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Sinks</td>
<td>-3.4</td>
<td>-5.5</td>
<td>-0.1</td>
<td>-4.6</td>
<td>-0.6</td>
</tr>
</tbody>
</table>
Table A.5

| Element and ANC budgets for hypothetical recovery of Goshen Prong Watershed. Element fluxes values are shown for 2200 comparing values under scenarios of current deposition (without reduction) with 100% decrease in anthropogenic deposition to preindustrial values. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flux | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction | Without 100% Reduction |
| NO$_3$- (keq/ha-yr) | 0.1 | 0.1 | 1.7 | 0.2 | 0.5 | 0.1 | 0.3 | 0.3 | 1.9 | 0.2 | 0.7 | | |
| SO$_4$-2 (keq/ha-yr) | | | | | | | | | | | | | | |
| NH$_4$+ (keq/ha-yr) | | | | | | | | | | | | | | |
| ANC (keq/ha-yr) | | | | | | | | | | | | | | |
| Sources | | | | | | | | | | | | | | |
| Deposition | | | | | | | | | | | | | | |
| Weathering | | | | | | | | | | | | | | |
| Uptake | | | | | | | | | | | | | | |
| Soil sorption | | | | | | | | | | | | | | |
| Mineralization | | | | | | | | | | | | | | |
| Nitrification | | | | | | | | | | | | | | |
| Nitrogen fixation | | | | | | | | | | | | | | |
| Drainage losses | | | | | | | | | | | | | | |
| Precipitation | | | | | | | | | | | | | | |
| Canopy exchange | | | | | | | | | | | | | | |
| Lef | | | | | | | | | | | | | | |
| Miscellaneous | | | | | | | | | | | | | | |
| Period | 1/01 | 3/03 | 1/07 | 6/01 | 6/04 | 1/07 | 6/07 | 6/04 | 1/07 | 6/01 | 1/04 | 1/07 | 1/04 | 1/07 |
| Flux | | | | | | | | | | | | | | |
| NH$_4$+ (keq/ha-yr) | 0.7 | 0.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 | 0.7 |
| SO$_4$-2 (keq/ha-yr) | | | | | | | | | | | | | | |
| NO$_3$- (keq/ha-yr) | | | | | | | | | | | | | | |
| ANC (keq/ha-yr) | | | | | | | | | | | | | | |
| Sources | | | | | | | | | | | | | | |
| Deposition | | | | | | | | | | | | | | |
| Weathering | | | | | | | | | | | | | | |
| Uptake | | | | | | | | | | | | | | |
| Soil sorption | | | | | | | | | | | | | | |
| Mineralization | | | | | | | | | | | | | | |
| Nitrification | | | | | | | | | | | | | | |
| Nitrogen fixation | | | | | | | | | | | | | | |
| Drainage losses | | | | | | | | | | | | | | |
| Precipitation | | | | | | | | | | | | | | |
| Canopy exchange | | | | | | | | | | | | | | |
| Lef | | | | | | | | | | | | | | |
| Miscellaneous | | | | | | | | | | | | | | |
| Period | 1/01 | 3/03 | 1/07 | 6/01 | 6/04 | 1/07 | 6/07 | 6/04 | 1/07 | 6/01 | 1/04 | 1/07 | 1/04 | 1/07 |
| Flux | | | | | | | | | | | | | | |
| NH$_4$+ (keq/ha-yr) | 0.7 | 0.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 | 0.7 |
| SO$_4$-2 (keq/ha-yr) | | | | | | | | | | | | | | |
| NO$_3$- (keq/ha-yr) | | | | | | | | | | | | | | |
| ANC (keq/ha-yr) | | | | | | | | | | | | | | |
| Sources | | | | | | | | | | | | | | |
| Deposition | | | | | | | | | | | | | | |
| Weathering | | | | | | | | | | | | | | |
| Uptake | | | | | | | | | | | | | | |
| Soil sorption | | | | | | | | | | | | | | |
| Mineralization | | | | | | | | | | | | | | |
| Nitrification | | | | | | | | | | | | | | |
| Nitrogen fixation | | | | | | | | | | | | | | |
| Drainage losses | | | | | | | | | | | | | | |
| Precipitation | | | | | | | | | | | | | | |
| Canopy exchange | | | | | | | | | | | | | | |
| Lef | | | | | | | | | | | | | | |
| Miscellaneous | | | | | | | | | | | | | | |
| Period | 1/01 | 3/03 | 1/07 | 6/01 | 6/04 | 1/07 | 6/07 | 6/04 | 1/07 | 6/01 | 1/04 | 1/07 | 1/04 | 1/07 |
| Flux | | | | | | | | | | | | | | |
| NH$_4$+ (keq/ha-yr) | 0.7 | 0.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 | 0.7 |
Time series of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$ and ANC for Cosby Creek that include hindcast and future projections to atmospheric deposition decreases in a) $\text{NO}_3^-$ only; b) $\text{SO}_4^{2-}$ only; c) combination of ($\text{NO}_3^- + \text{SO}_4^{2-}$). Also shown are measured values.
Time series of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$ and ANC for Indian Camp Creek that include hindcast and future projections to atmospheric deposition decreases in a) $\text{NO}_3^-$ only; b) $\text{SO}_4^{2-}$ only; c) Combination of ($\text{NO}_3^- + \text{SO}_4^{2-}$). Also shown are measured values.
Time series of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$ and ANC for Left Prong Anthony that include hindcast and future projections to atmospheric deposition decreases in a) $\text{NO}_3^-$ only; b) $\text{SO}_4^{2-}$ only; c) Combination of ($\text{NO}_3^- + \text{SO}_4^{2-}$). Also shown are measured values.
Time series of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$ and ANC for Mill Creek that include hindcast and future projections to atmospheric deposition decreases in a) $\text{NO}_3^-$ only; b) $\text{SO}_4^{2-}$ only; c) combination of ($\text{NO}_3^- + \text{SO}_4^{2-}$). Also shown are measured values.
Time series of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$ and ANC for Pretty Hollow that include hindcast and future projections to atmospheric deposition decreases in a) $\text{NO}_3^-$ only; b) $\text{SO}_4^{2-}$ only; c) combination of ($\text{NO}_3^- + \text{SO}_4^{2-}$). Also shown are measured values.
Time series of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$ and ANC for Sugar Fork that include hindcast and future projections to atmospheric deposition decreases in a) $\text{NO}_3^-$ only; b) $\text{SO}_4^{2-}$ only; c) Combination of ($\text{NO}_3^- + \text{SO}_4^{2-}$). Also shown are measured values.
Time series of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$ and ANC for Thunderhead that include hindcast and future projections to atmospheric deposition decreases in a) NO$_3^-$ only; b) SO$_4^{2-}$ only; c) combination of (NO$_3^-$ + SO$_4^{2-}$). Also shown are measured values.
Time series of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$ and ANC for Goshen Prong that include hindcast and future projections to atmospheric deposition decreases in a) $\text{NO}_3^-$ only; b) $\text{SO}_4^{2-}$ only; c) Combination of ($\text{NO}_3^- + \text{SO}_4^{2-}$). Also shown are measured values.
Time series of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$ and ANC for Walker Camp Prong that include hindcast and future projections to atmospheric deposition decreases in a) $\text{NO}_3^-$ only; b) $\text{SO}_4^{2-}$ only; c) combination of ($\text{NO}_3^- + \text{SO}_4^{2-}$). Also shown are measured values.
Time series of $SO_4^{2-}$, $NO_3^-$, $Ca^{2+}$ and ANC for Lost Bottom Creek that include hindcast and future projections to atmospheric deposition decreases in a) $NO_3^-$ only; b) $SO_4^{2-}$ only; c) combination of ($NO_3^- + SO_4^{2-}$). Also shown are measured values.
Time series of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Ca}^{2+}$ and ANC for Noland Divide that include hindcast and future projections to atmospheric deposition decreases in a) $\text{NO}_3^-$ only; b) $\text{SO}_4^{2-}$ only; c) combination of ($\text{NO}_3^- + \text{SO}_4^{2-}$). Also shown are measured values.
Time series of $SO_4^{2-}$, $NO_3^-$, $Ca^{2+}$ and ANC for Cannon Creek that include hindcast and future projections to atmospheric deposition decreases in a) $NO_3^-$ only; b) $SO_4^{2-}$ only; c) Combination of ($NO_3^- + SO_4^{2-}$). Also shown are measured values.
References


USEPA (2012). SO\textsubscript{2} and NO\textsubscript{x} Emissions, Compliance, and Market Analyses. (Clean Air Interstate Rule, Acid Rain Program, and Former NO\textsubscript{x} Budget Trading Program.).


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