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Landscape factors that affect acid-base chemistry of Adirondack Long-Term Monitoring (ALTM) lakes

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Abstract

The Adirondack region has been affected by acid deposition for multiple decades. Atmospheric deposition of sulfur and nitrogen has decreased since the 1970s because of the 1970 and 1990 Clean Air Act Amendments (CAAA) as well as the NO_X Budget Program. Previous studies have related the long-term changes in Adirondack lake water chemistry to decreases in atmospheric deposition and emission controls. However, relatively limited research has been conducted on the spatial patterns and the role of different landscape factors on the recovery of lake water chemistry in the Adirondacks.

The objective of this study was to investigate the relations of volume-weighted concentrations and long-term changes of surface water chemistry of the Adirondack region with landscape characteristics of watersheds to improve the understanding of the factors that drive chemical recovery of surface water from declines in acid deposition. I delineated watersheds of Adirondack Long-Term Monitoring (ALTM) lakes using Geographic Information Systems, and quantified areal fraction of relevant landscape factors within each watershed. Using the GIS and statistical approaches, I compared volume-weighted concentrations and long-term changes of major solutes that affect acid-base chemistry of ALTM lakes (SO_4^{2-}, NO_3^-, Ca^{2+}, Al and DOC) with atmospheric deposition, topography, soil characteristics, surficial processes, wetland and canopy coverage, lake watershed vegetation, and forest disturbance.

I observed that changes in NO_3^- concentrations in precipitation after 2004 had a very similar pattern as SO_4^{2-} at all three National Atmospheric Deposition Program (NADP) sites in the Adirondacks (NY20, NY29, and NY98), and that more than 80 percent of the variation in annual

volume-weighted H^+ concentrations in atmospheric deposition can be explained by the variation in the sum of SO_4^{2-} and NO_3^- concentrations. I also interpolated from 8 NADP sites using the Kriging method to achieve continuous maps of precipitation concentrations of major ions in the Adirondacks, and validated the results against the measurements from an additional NADP site (NY29) at Moss Lake.

Results of this study indicated that spatial variation in volume-weighted lake SO_4^{2-} concentrations and lake SO_4^{2-} decreasing rates were influenced by wet atmospheric deposition of SO_4^{2-} but were also affected a combination of landscape factors including elevation, lake hydraulic residence time, wetland and canopy coverage, and thickness of glacial till deposits. Higher volume weighted concentrations of SO_4^{2-} were found in drainage lakes than seepage lakes and lakes of higher elevation, shorter hydraulic residence time, lesser wetland coverage, and thicker deposits of glacial till. I found a similar relationship between lake SO_4^{2-} and Cl^- which suggests the pattern of higher lake SO_4^{2-} in drainage lakes may be linked to evapotranspiration. Greater wetland coverage within ALTM lake watersheds resulted in more rapid decreases in SO_4^{2-} probably due to the bacterial assimilatory SO_4^{2-} reduction. Watersheds with greater canopy coverage may be linked to interception of greater dry S deposition. More rapid decreases in SO_4^{2-} concentrations were also observed in lakes of higher elevation.

Volume weighted NO_3^- concentrations and NO_3^- decreasing rates in ALTM lakes, in contrast to SO_4^{2-}, showed no relationship with atmospheric deposition. Regression analyses indicated that higher volume weighted NO_3^- concentrations were found in drainage lakes at higher elevation, with steeper land slope, or lower chlorophyll a concentrations. The study also demonstrated that forest disturbance and land slope were the factors most responsible for the spatial variation in rates of NO_3^- decreases. Drainage lake watersheds with shallower land slope or greater area affected by the 1995 and 1950 forest disturbance showed more rapid decreases in NO_3^- concentrations likely due to vegetation uptake of NO_3^- for regrowth following forest disturbance.

The spatial variation in volume weighted Ca^{2+} concentrations and rates of Ca^{2+} decreases in ALTM lakes were attributed to the processes of weathering and leaching from soil exchange complex. I used lake Na^+ and dissolved SiO_2 as indicators of weathering input. Regression analyses demonstrated that ALTM lake watersheds with greater input from weathering and higher concentrations of soil exchangeable Ca^{2+} had higher volume weighted Ca^{2+} concentrations. I also observed more rapid decreases of Ca^{2+} in lake watersheds of more rapid changes in weathering and leaching processes.

Results of this study suggested that spatial variation in volume weighted acid neutralizing capacity (ANC) of ALTM seepage lakes were primarily driven by wet deposition of SO_4^{2-} + NO_3^- and in-lake processes. Volume weighted ANC of ALTM drainage lakes were influenced by atmospheric deposition of SO_4^{2-} + NO_3^-, but were also affected by a combination of landscape factors including wetland coverage, land slope, cation weathering, and cation exchange. No significant relationship was found for ANC increases in ALTM seepage lakes with atmospheric deposition or landscape factors. The regression analysis for ANC increases at ALTM drainage lakes indicated that, in addition to decreases in the sum of SO_4^{2-} and NO_3^- from atmospheric deposition, elevation, wetland coverage, and forest disturbance history play important roles.

Marked decreases in lake concentrations of Al were evident, particularly among thin till drainage lakes. Lakes which are characterized by the highest concentrations of inorganic monomeric Al showed the greatest rates of decrease of inorganic monomeric Al.

Higher volume-weighted DOC was found in lakes with lower concentrations of SO_4^{2-} and NO_3^-, higher O horizon C:N ratio, B horizon base saturation, and greater color. More rapid increases in DOC concentrations were observed in lakes with more rapid decreases in SO_4^{2-} and NO_3^-, more rapid changes in color of lake water, and higher O horizon exchangeable Al and Fe.

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Introduction

Sources of acid rain and ecosystem effects

Acid deposition has been a serious environmental problem since the early 1970s when it was first reported in North America (Likens et al., 1972). Emitted from the burning of fossil fuels by electric utilities and motor vehicles, sulfur dioxide (SO_2) and nitrogen oxides (NO_X) are oxidized in the atmosphere to form acidic compounds. The products, sulfuric acid and nitric acid, are then transported to soil and surface waters through wet and dry deposition and can acidify soil, lakes and streams. In 2011, major sources of SO_2 emissions were fossil fuel combustion at power plants (68 percent), industrial combustion (15 percent), and industrial processes (9 percent) (U.S. EPA, 2013). Major sources of NO_X include transportation (59 percent), fossil fuel combustion (32 percent), and industrial processes (8 percent) (U.S. EPA, 2013). Emissions of SO_2 and NO_X in the United States are highest in the Midwest. Seven states around the Ohio River Valley (Illinois, Indiana, Kentucky, Ohio, Pennsylvania, Tennessee and West Virginia) contributed 35% of the total SO_2 emissions of the nation in 2011, and these states accounted for 19% of national NO_X emissions (U.S. EPA, 2013). High emissions in this region were primarily from electric utilities and from heavy manufacturing. Prevailing winds from west to east caused pollutants emitted in the Midwest to be transported and deposited in eastern North America (Driscoll et al., 2001).

Acid deposition affects sensitive ecosystems by altering soil chemistry, acidifying surface water, stressing forest vegetation and harming aquatic life (Likens et al., 1996). The acid neutralizing capacity (ANC) and pH of surface water decrease following inputs of strong acids. Moreover, in streams and lakes that are hydrologically connected to the watershed, concentrations of Al (especially the toxic inorganic monomeric Al fraction) can increase coincident with decreasing pH and ANC (Driscoll and Newton, 1985). pH, concentrations of Al, and particularly ANC are used as indicators of the acid-base status of waters. Lake water ANC below 0 µeq/L during base flow conditions is considered chronically acidic. Values ranging from 0 to 50 µeq/L are considered sensitive to episodic acidification (Baker et al., 1990). The combination of low pH and high concentration of Al in surface water can decrease the species diversity and abundance of aquatic organisms (Schindler et al., 1985).

Acid deposition also alters soil chemistry by depleting available Ca and other nutrient cations (Likens et al., 1996), facilitating the mobilization of inorganic monomeric Al in soil solutions (Cronan and Schofield, 1990), and increasing the accumulation of sulfur and nitrogen in soil (Driscoll et al., 2001). Over the past forty years, red spruce and sugar maple have declined in the northeastern United States (Siccama et al., 1982; Houston, 1999). The decline of red spruce is attributed to the leaching of Ca from cell membranes in foliage by acid deposition, which renders the trees more susceptible to freezing damage (DeHayes et al., 1999). Effects of red spruce have also been linked with elevated inorganic monomeric Al concentrations in soil solution which hinders water and nutrient uptake (Shortle et al., 1997). Low concentration of soil available Ca and magnesium in naturally base-poor regions that experience depletion of soil available base cations by acidic deposition can also impair health of sugar maple (Horsley et al., 1999; Juice et al., 2006).

Historical atmospheric emission patterns and controls on emissions

Anthropogenic emissions of sulfur and nitrogen are the major sources of acid deposition. Natural phenomena such as volcano emissions and soil and wetland processes contribute acid-producing gases to the atmosphere to a lesser extent (U.S. EPA, 1995). The long-term trends of acid precipitation mirror atmospheric emission trends driven by economic and regulatory controls. The 1970 Amendments to the Clean Air Act (CAAA) established National Ambient Air Quality Standards (NAAQS) which were focused on limiting concentrations of individual air pollutants largely in urban areas. In 1978, the National Atmospheric Deposition Program (NADP) began in the United States and started providing detailed maps of spatial and temporal trends in the chemistry of precipitation. In 1980, the National Acid Precipitation Assessment Program (NAPAP) began as a multi-agency and multi-disciplinary program of policy-focused research. Data from both programs provided important motivation and a scientific foundation of the 1990 Amendments to the Clean Air Act (Driscoll et al., 2010).

Total emissions of sulfur dioxide increased from 9 million tons in 1900 to a peak of 28.8 million tons in 1973, and then declined markedly in the eastern United States after the 1970 Amendments to the Clean Air Act (U.S. EPA, 1995). As a result, concentrations of SO_4^{2-} and H^+ in wet deposition have decreased at most eastern NADP monitoring sites since the late 1970s (U.S. EPA, 2000). After the 1990 CAAA, these trends in emissions and precipitation concentrations of SO_4^{2-} have been more evident. By 2011, the SO_2 emissions for the United States declined to 8.9 million tons. From 1970 to 2011, SO_2 emissions from electric utilities decreased by 69%, largely as a result of the 1970 and 1990 amendments to the Clean Air Act.

In contrast, decreases in NO_X emission and NO_3^- wet deposition were limited in 1990s since no cap on total annual emissions of NO_X was set with the 1990 CAAA. Emissions of NO_X increased from 2.4 million tons in 1900 to 21.8 million tons in 1990 and remained fairly constant until the early 2000s. In 2003, EPA started the NO_X Budget Program (NBP) under the NO_X State Implementation Plan. The NBP was intended to decrease NO_X concentrations during the summer months to control ground-level ozone. Emissions of NO_X and deposition of NO_3^- have decreased since about 2003 in the eastern U.S. in response to this program (Lehmann et al., 2005).

Limited information is available on historical ammonia emissions although ammonium deposition can acidify soil and surface water if it is oxidized to NO_3^- by soil microbes. Agricultural activities are the primary source of US emissions of NH_3 (U.S. EPA, 2000). Deposition of ammonium makes up approximately 30% of the total nitrogen deposition at the eastern U.S. (U.S. EPA, 2012) and has not changed appreciably over the past 30 years. Detailed information on historical emissions of SO_2 and NO_X in the United States are available from U.S. Environmental Protection Agency (2000).

Processes that affect the acid-base status of surface waters

The acid-base status of watersheds and surface waters is regulated by the inputs of acids (e.g., SO_4^{2-}, NO_3^-) and bases (e.g., Ca^{2+}, Mg^{2+}) relative to their outputs. Acid neutralizing capacity (ANC) is a measure of the concentrations of base cations less the concentrations of strong acid anions in solution. Therefore, the addition of strong inorganic acid or bases to surface water affect ANC and significantly influence pH depending on the ANC of the solution.

$$ANC_{calc}=\Sigma C_B-\Sigma C_A=2[Ca]+2[Mg]+[K]+[Na]+[NH_4]-2[SO_4]-[NO_3]-[Cl]-[F]$$

(ANC_{calc} stands for calculated ANC) The base cation inputs are derived primarily from biogeochemical reactions occurring within soil and surficial materials of watershed, such as mineral weathering (slow, potentially infinite), cation exchange (fast, finite), and vegetation processes. For soils in glaciated areas with limited ability to adsorb SO_4^{2-} and with relatively low capacity to store strong acids, large amounts of strong acid anions from atmospheric deposition may be transported through the soil and glacial till into surface water and ground water and contribute to the acidification of a water body. Therefore, the ability of a watershed to neutralize atmospheric acid deposition highly depends on its rate of base supply. At Hubbard Brook, N.H., the rates of base supply are determined by the flow path of water within the watershed (Likens et al., 1998). In northern forest watersheds, the routing of water is a function of thickness of glacial till, hydraulic conductivity, and land slope. However, the dominant flow path is determined by the depth of unconsolidated sediments above the bedrock (Newton et al., 1987). Watersheds with thick deposits of glacial till tend to have large groundwater flow contribution (Peters and Murdoch, 1985). The water from precipitation passes through the soil and stores in ground water before discharging to surface water. By close interaction with the minerals within thick deposits of glacial till in a watershed, these surface waters receive large amount of base cations and have higher ANC.

The input of strong acids are primarily derived from atmospheric deposition of SO_4^{2-} and NO_3^-, decay of organic matter of dead plant and animal material, oxidation of organic sulfur and nitrogen from soil and naturally occurring sulfide minerals (van Breemen et al., 1983). In addition to the neutralization of strong acids by the supply of base cations, ANC may also be increased through SO_4^{2-} and NO_3^- retention within watershed, wetlands and lakes. These basin processes influence strong acid anion concentrations by biological cycling, reduction reactions, and anion adsorption (Munson et al., 1990). NO_3^- concentration can be influenced by biological processes such as vegetation uptake, organic matter decay, nitrification and denitrification (Jenkins et al., 2007). NO_3^- is an important nutrient for terrestrial and aquatic vegetation, therefore the NO_3^- from atmospheric deposition and by nitrification of soil organic nitrogen are largely removed from the waters by watershed processes (Reuss and Johnson, 1986). During the winter, when vegetation uptake is low, NO_3^- formed by mineralization and nitrification accumulates in watersheds. In spring, it can be flushed into surface waters and contribute to the spring acidity (Driscoll et al., 1987).

Plants and microbes can assimilate SO_4^{2-}, producing carbon-bonded and ester-bonded S compounds which make up over 80% of stored sulfur in northeastern forest soils (Likens et al., 2002). In wetland soils, S is often stored in reduced form such as insoluble sulfides or organic S (Jenkins et al., 2007). Mass transfer rates of SO_4^{2-} to lake sediments are relatively slow, and as a result, immobilization of SO_4^{2-} is largely realized in lakes with longer mean residence time (Kelly et al., 1987). SO_4^{2-} reduction in lake sediments is a temperature-dependent and rate-limited reaction which is first order with respect to SO_4^{2-} concentration (Munson and Gherini, 1986). The SO_4^{2-} concentrations in seepage lakes are generally lower than drainage lakes, which is partly due to their differences in residence time (Munson et al., 1990). Adsorption (anion exchange) is an important process by which inorganic S is stored in soil. This removal process is especially important in soils containing high concentration of iron and aluminum oxides (Jenkins et al., 2007). In general, SO_4^{2-} immobilization by soil adsorption is less important in glaciated regions than non-glaciated regions (Rochelle and Church, 1987). In glaciated regions atmospheric S deposition is relatively conservatively transported through watersheds to surface waters (Mitchell et al., 2013).

Weak acids may serve as buffers and help resist changes in pH. Organic acids have strongly acidic and weakly acidic functional groups (Driscoll et al., 1994). Dissociation of strongly acidic functional groups can decrease ANC. Weakly acidic functional groups from organic acids or carbonic acid will dissociate decreasing pH but have no effect on ANC. Nonvolatile acids (primarily organic acids) have the greatest effect on pH in waters with ANC between 0 and 50 μeq/L; volatile acids (mostly carbon dioxide) have the greatest effects on pH in waters with ANC greater than 50 μeq/L. A detailed analysis on the role of weak acid in regulating acid-base chemistry is given by Munson et al., (1990).

Spatial patterns of lake chemistry in the Adirondack region of New York

There are several regions in the eastern U.S. that have been impacted by acidic deposition. These regions are generally forested sites in areas of higher elevation. The Adirondack region of New York receives elevated atmospheric deposition and is among the most sensitive and impacted regions to strong acid inputs. The first survey that demonstrated the spatial pattern in lake chemistry in the Adirondacks was conducted by New York State from 1926 to 1939. In this survey, larger and more productive lakes located at low elevation were sampled. The results suggested that many of these lakes had low ANC, but no lakes showed ANC less than 0 μeq/L (Pfeiffer and Festa, 1980). In 1975, 214 high-elevation lakes (>610m) were surveyed by

Schofield (1976). 55% of these high-elevation lakes had negative ANC. It was concluded that the lake-to-lake differences in ANC were largely due to differences in geological characteristics because much of the variation in ANC was explained by variations in base cation concentration. It was also shown that ANC values are lowest in lakes that are located in basins derived from granitic gneiss and received large amounts of precipitation. These lakes are generally located in high elevation watersheds in the western Adirondacks and are thought to have limited supply of base cations. Lakes with pH>6 were situated near Grenville marble outcrops or within lower elevation surficial deposits and drift, which were considered high in exchangeable bases. Concentrations of SO_4^{2-} were relatively uniform across the region.

In 1984, the U.S. EPA initiated Phase I of the Eastern Lake Survey which was part of the National Surface Water Survey. Lakes sampled in this study have surface area greater than 4 ha. In this study, it was found that lakes with SO_4^{2-} concentrations greater than 150 µeq/L were generally located at northeastern Adirondacks near Lake Champlain or outside Adirondack Park. Lakes with elevated NO_3^- and extractable Al concentrations were generally located in the southwestern area of Adirondack Park where acidic lakes are abundant.

Between 1984 and 1987, Adirondack Lake Survey (ALS) was conducted at 1469 lakes. Lakes with low pH and ANC were found throughout the region, but were concentrated in the western and southwestern Adirondacks. Most of these lakes are small, occurring at high elevation and receive high levels of precipitation. A classification system for the acid-base status of Adirondack Lakes was developed by Baker et al., (1990). This system was based on the characteristics of surficial geology and hydrologic flow paths. Lakes with outlets are referred to as drainage lakes and those without an outlet are seepage lakes. Drainage lakes situated in watersheds with less than 5% watershed area containing deposits of glacial till thicker than 3m are considered thin till lakes; these lakes are typically chronically acidic with ANC less than 0 μeq/L. Medium till lakes contain approximately 5% to 25% watershed area with deposits of glacial till thicker than 3m; these lakes are seasonally or episodically acidic with base flow ANC ranging from 0 to 50 μeq/L. Drainage lakes with watersheds with over 25% thick deposits of glacial till or containing calcite are thick till or calcite impacted lakes; these lakes are relatively insensitive to acidic deposition. The survey also included mounded seepage lakes which receive most of their water directly from precipitation.

Summary of previous studies of lake chemical trends in the Adirondacks

Seventeen Adirondack Long-Term Monitoring Program (ALTM) lakes have been sampled monthly for major solutes to assess seasonal and long-term patterns in the chemistry of lakes since 1982. These lakes were selected from the Regionalization of the Integrated Lake Watershed Acidification study (Driscoll and Dreason, 1993). Driscoll and Dreason (1993) first reported on the long-term trends of lake chemistry in the Adirondacks. In that study, it was found that the long-term trends in acid-base status of ALTM lakes were primarily driven by trends in SO_4^{2-}; Moreover, low ANC during snowmelt coincided with high NO_3^- concentrations. The ALTM program was expanded in 1992 with an additional 35 lakes for a total of 52 sites to provide a better representation of lakes across the region. Updates of the results were made periodically. After 30 years of monitoring, the ALTM program has covered a relatively long period over which the long-term changes in the chemistry of Adirondack lakes can be evaluated. Due to controls on atmospheric emission of SO_2 and NO_X, SO_4^{2-} and NO_3^- concentrations in lake water have decreased in most ALTM lakes, which has resulted in decreases in base cations in these lakes. It was also demonstrated that decreases in strong acid anions has coincided with increases in ANC, resulting in a shift in the speciation from toxic monomeric inorganic Al to less toxic organic monomeric form in many lakes (Driscoll et al., 2003). ANC increases in ALTM lakes were extrapolated and the time frame of chemical recovery of Adirondack Lakes was suggested to be several decades (Driscoll et al., 2003). It was found that lakes in watersheds with thin deposits of glacial till and mounded seepage lakes were generally most responsive to decreases in acid deposition. The number of lakes showing significant declines in NO_3^- has increased as atmospheric deposition of NO_X decreases. Also, DOC concentrations increased in some ALTM lakes coinciding decreases in acid deposition (Driscoll et al., 2007).

Time-series analysis on acidic deposition and subsequent acidification of Adirondack lakes were initiated in the 1970s. Changes in precipitation and lake water chemistry, and fisheries have been monitored across the region since that period (Jenkins et al., 2007). Given the absence of studies prior to 1970 and the poor analytical methods for dilute water, several alternative approaches have been employed to characterize the long-term trends. Two major techniques are the comparison of data from historical lakes surveys with present observations, and the paleoecological analysis from lake sediment records (Charles and Whitehead, 1986).

Asbury et al., (1989) compared the results of 274 Adirondack lakes from the 1929-1924 biological survey with surveys conducted between 1975 and 1985, and found 80% of lakes showed decreases in ANC with a median loss of 50 µeq/L. Kramer et al., (1986) also found a similar mean ANC decline between 0 and 69 µeq/L during the same period. Baker et al. (1990) compared data from 110 high-elevated lakes in the 1975 survey with results from ALSC survey (1984-1987). SO_4^{2-} and base cations concentration declined by 26 µeq/L and 58 µeq/L, respectively, during this short period.

To characterize the acidification history, paleoecological and geochemical data were analyzed in the large-scale study of Paleoecological Investigation of Recent Lake Acidification (PIRLA). The program analyzed lake sediments from 12 Adirondack lakes and other lakes from New England, the northern Great Lakes states and northern Florida (Charles and Whitehead, 1986). A ^{210}Pb dating approach was used to relate changes in sediment assemblages to lake water chemistry. 52 lakes in the Adirondacks were used to calibrate the paleolimnological model. This study found 8 of 12 PRILA lakes showed declines in pH and ANC during the past one hundred years. Similar analysis using diatom reconstruction techniques was made in three Adirondack lakes to describe two-hundred-year history of Woods, Sagamore and Panther Lakes (Davis et al., 1988).

Objectives and hypothesis

The overall objective of this study was to investigate the relations of volume-weighted concentrations and long-term changes of surface water chemistry (SO_4^{2-}, NO_3^-, C_B, ANC, Al, DOC) of the Adirondack region with landscape characteristics of watersheds to improve the understanding of the factors that drive chemical recovery of surface water from declines in acid deposition. My hypotheses for this study are: 1) decreases in strong acid anions (SO_4^{2-}, NO_3^-) in Adirondack lakes are due to decreases in atmospheric deposition but also are affected by variation in elevation, land slope, wetland and canopy coverage, forest disturbance and physical and surficial geological characteristics of lake-watersheds; 2) decreases of base cations are closely regulated by decreases in concentrations of strong acid anions but also are affected by soil and surficial geology of lake-watersheds; 3) changes in ANC are closely related to changes in both strong acid-base systems; and 4) changes in lake DOC are affected by shifts in lake acid-base status driven by decreases in acidic deposition.

Brief description of approach to accomplish objectives

A GIS and statistical approach was used in this study. Watersheds of ALTM lakes were delineated in ArcGIS utilizing the 30-meter Digital Elevation Model (DEM) and the National Hydrography Dataset (NHD) from USGS. Maps of all landscape characteristics were examined within the watersheds to test hypotheses. Long-term trends in lake chemistry from 1992 to 2009 were calculated using Seasonal Kendall Tau (SKT) test. I looked at the relation between mean concentrations and the rate of change of major solutes (i.e., SO_4^{2-}, NO_3^-, C_B) concentrations in each ALTM lake and the landscape characteristics within its watershed. Multiple regression analysis was made to determine the factors that drive spatial patterns in mean volume-weighted solute concentrations and rates of long-term changes. For important data that are not available in the period of this study, estimation and assumptions were made to find best available surrogates.

Methods

Description of the Adirondack region

The Adirondack region (west: -75.326457, east: -73.280739, north: 44.884500, south: 43.041274) is a large (2.4×10^6 ha) predominantly forested mountainous area (Figure 1) characterized by abundant lakes and streams (Driscoll et al., 1991). There are 2796 lakes and ponds larger than 0.2 ha within the Adirondack ecological zone. The total area of these lakes is 101,630 ha. On average, the Adirondack region receives over 1000 mm precipitation annually which varies spatially with its increasing quantity from the northeast to the southwest (Ito et al., 2002). The climate in the Adirondacks is humid continental, with long winter and short cool summers (Trewartha, 1954). The soils are mainly Spodosols. The depth and chemical characteristics of the soils are highly variable spatially in the Adirondacks (Sullivan et al., 2006). The surficial geologic material includes glacial deposits of stratified sand and gravel formed by meltwater streams as the Pleistocene glaciers receded. The receding glaciers also formed basal and ablation till in the Adirondack region (Craft, 1976). The bedrock in the Adirondacks is mostly anorthosite and high grade metamorphic rocks which can be subdivided into granite gneisses, quartz syenite and metasediments (Wiener et al., 1984). The Adirondacks receives elevated inputs of SO_4^{2-}, NO_3^-, NH_4^+ and H^+ from atmospheric deposition. There is a southwest to northeast pattern of decreasing wet deposition that is largely driven by decreases in precipitation (Ito et al., 2002).

Description of the ALTM program and database

The Adirondack Long-Term Monitoring Program (ALTM) was established in 1982 with 17 lakes and was expanded to 52 lakes in 1992 to assess seasonal and long-term patterns in the chemistry of lakes. Four lakes (Barnes Lake, Little Clear Pond, Little Simon Pond and Woods Lake) were previously limed (base addition). A major thrust of this research was the evaluation of factors affecting volume-weighted concentrations and long-term trends in the chemistry in the Adirondacks through analysis of the ALTM lakes.

Samples were collected monthly at the outlet of drainage lakes and at the surface of seepage lakes. They were refrigerated until analysis at the Adirondack Lakes Survey Corporation (ALSC) laboratory. Samples were analyzed for pH, ANC, color, SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Na^+, dissolved Si, dissolved organic carbon (DOC), total organic monomeric Al, total inorganic monomeric Al (calculated), and starting in October 2008 for total phosphorus and chlorophyll a. The analytes examined in this study were analyzed using USEPA standard methods developed and described in previous studies (Morrison et al., 1991; Adirondack Lake Survey Corporation, 2002; Burns et al., 2006).

Soil chemistry data were obtained from a survey that included watersheds of 29 ALTM lakes (Sullivan et al., 2006). Soil samples at O horizon and B horizon were collected within three most predominant land cover types from each watershed. These samples were analyzed for chemical and physical parameters including exchangeable Al, Fe, effective cation exchange capacity, base saturation, total carbon and total nitrogen. Results of chemical analyses from each sample were areally weighted to yield estimates of average conditions for each ALTM watershed.

Intensive hydrology data were available at Arbutus Lake (Mitchell and McHale, 2009). In this study, daily discharges at the outlet were utilized to find the monthly distribution of outflow. Since the month to month variation in precipitation and discharges are approximately uniform across the region (Driscoll et al., 1991), results from Arbutus Lake were applied to all ALTM lakes to calculate volume-weighted concentration of major solutes in lake water. Volume-weighted concentration of chlorophyll a and total phosphorus were calculated for each lake using the 15-month database.

Description of GIS data layers

A GIS approach was used in this study to evaluate how landscape factors drive the spatial patterns of chemical concentrations and long-term trends of Adirondack Lakes. A detailed description of maps used in this analysis is given in Table 1. Digital Elevation Model (DEM) and National Hydrography Dataset (NHD) from USGS played an indispensable role in this study as the basis of watershed delineation and the calculation of land slope. The digital vector of flow network, NHD, contains features such as lakes, ponds, streams, rivers, canals, dams and stream gauges which allow for tracing the upstream and downstream hydrology.

Maps of wetlands coverage were obtained from National Land Cover Database 2001 in which land cover maps are derived from satellite images of Landsat 5 and 7. Maps of land cover were categorized into general land-use classes, for instance, no distinctions were made between herbaceous and woody wetlands or between conifer and hardwoods forests.

A map of tree canopy percentage is included to roughly represent the density of trees. The value of each 30-meter pixel in this map represents the areal percentage of tree coverage as viewed from a satellite perspective. The density of trees is considered proportional to the dry to wet deposition ratio in the Adirondacks because greater leaf area tends to intercept more dry deposition (Chen and Driscoll, 2005).

A map of precipitation quantity from Parameter-elevation Regressions on Independent Slopes Model (PRISM) was used in this study. As the USDA's official climatological dataset, PRISM serves as one of the highest-quality precipitation quantity datasets currently available. Topographic factors are taken into consideration in interpolation. The PRISM covers the entire period of ALTM program (from 1992 to 2009) and provides a relatively fine spatial resolution (approximately 4 km × 4 km) of both monthly and annual maps of precipitation quantity.

Precipitation concentrations of major solutes are available from the NADP/NTN program. Eight NADP sites in New York and Vermont (NY 08, NY 20, NY22, NY52, NY68, NY 98, VT 01 and VT 99) were used to interpolate annual concentration of SO_4^{2-} and NO_3^- in Adirondack region, because all these sites were initiated before the start of ALTM program and are relatively close to Adirondack region (Figure 2). NY29 at Moss Lake started operation in 2003. It covers a short period and cannot be used for interpolation, but served as a validation site to test the results of the interpolation. 72 groups (i.e., monthly data in six year) of interpolated precipitation chemistry at Moss Lake were compared with monthly monitored values at NY29 from 2004 to 2009 to evaluate the best Kriging method of interpolation. Due to the seasonal pattern of precipitation concentrations, different Kriging methods were used for different months. The validation results indicated that ordinary Kriging method with exponential semivariogram model should be used for the interpolation of precipitation concentrations for June, July and August, while Gaussian semivariogram model should be used for the interpolation of precipitation concentrations for December, January, February and March. Spherical semivariogram model should be used for the interpolation of precipitation concentrations for the rest of a year. The precipitation concentrations at each ALTM watersheds interpolated from NADP measurements were used in multiple regression analyses for volume-weighted concentrations and long-term trends of major solutes in lake water.

Forest disturbance history was recorded by Adirondack Park Agency. Vector data for windstorm and fire damages before 1916, in 1950, and in 1995 were compared with trends in lake chemistry. Maps of 1995 blow down were generated from aerial photography captured by DEC Division of Aviation in July and August 1995. Detailed information about degree of damage in 1995 was available, therefore the areal fraction of 1995 storm disturbance within each watershed was weighted by the extent of disturbance. Maps of 1916 and 1950 disturbance were digitized from hardcopy maps. Forest disturbances in all three maps showed the greatest degree of disturbance in the western Adirondacks.

Description of computative methods

Land slopes were calculated for watersheds of all ALTM drainage lakes. Regardless of the shape of the lake or watershed, the assumption of a “circular watershed and lake” was made to estimate the mean slopes of the watersheds. In this assumption, both the lake and its watershed were considered as areas of circles. Assuming the lakes were located at the center of the watersheds, conceptual circular truncated cones were constructed with lake area being the upper base, and watershed area being the lower base. The slopes were calculated using the following equation

$$\alpha=\tan^{-1}\left(\frac{\sqrt{\frac{A}{\pi}}-\sqrt{\frac{a}{\pi}}}{\Delta h}\right)$$

Where α is the mean land slope; a is the area of a lake; A is the area of a watershed; and Δh is the elevation change within a watershed.

To determine the effects of spatial configuration of wetlands to lake water chemistry, 10 evenly distributed buffer areas of each lake were delineated to calculate inverse distance weighted (IDW) wetland coverage. All buffer analyses are further constrained by watershed boundaries. I used the following equation to calculate inverse distance weighted wetland percentage in a watershed (King et al., 2005).

$$\text{IDW \% land cover in watershed} = 100\times\frac{\sum_{i=1}^{C} nx\times Wc}{\sum_{i=1}^{C} nT\times Wc}$$

Where C is the number of distance classes; n_X is the number of cells of the wetlands in distance class I; W_C is the inverse distance weight for distance class I; and n_T is the total number of land-cover cells in distance class I.

Percentage of thick till within the watershed is used as the criteria of classification of lakes in this study. Driscoll et al., (1991) found a relationship between base flow Ca^{2+} concentration and percentage of watershed area covered by thick till and stratified drift.

$$\text{Baseflow } Ca^{2+}=76+3.1(\%\text{ thick till}),\ R^2=0.88$$

Therefore, base flow Ca^{2+} concentration is used as a surrogate of percentage thick till to determine the effect of surficial geology on SO_4^{2-} decreasing rate.

An evapotranspiration rate of 38% proposed for the Adirondacks (Murdoch et al., 1987) was used to estimate the hydraulic residence time (HRT) of ALTM lakes.

$$t=\frac{0.38\cdot P\cdot A}{V}$$

Where t is the hydraulic residence time of a lake; P is the annual precipitation quantity to a lake-watershed; A is the area of a watershed; V is the volume of a lake.

Description of statistical methods

The nonparametric seasonal Kendall Tau (SKT) test was used to detect monotonic trends of lake water chemistry. This test of long-term trend can successfully solve the common complications in time series analysis of water quality data such as non-normal distributions, seasonality, missing values and values below limit of detection (Hirsch and Slack, 1984). Values of same month in different years are calculated for a slope. The median value of these 12 slopes was taken as the long-term slope. In this study, p values less than 0.05 were used as the criteria for significant trends. Multiple regression analysis was made for major solutes in lake waters and land cover and physical lake-watershed characteristics. Sensitivity analysis was also made for each factor in regression equations.

Results

Concentrations and trends in atmospheric deposition of major ions

Long-term changes in the chemistry of precipitation at the two NADP sites in the Adirondacks have been reported for past decades (Driscoll et al., 2003; Driscoll et al., 2007; Waller et al., 2012). Trends in major solutes of precipitation are given from this analysis (Table 2, Figure 3). In July 2003, a new NADP site (NY29) was initiated at Moss Lake. Although the records at the site are relatively short (2003 to 2009) and cannot be used for a long-term analysis, data of NY29 were used to select Kriging methods for concentrations of major ions in precipitation in the Adirondack region. The results of this interpolation were used later in this study for multiple regression analyses for concentrations and changes in major solutes of ALTM lakes.

Annual volume-weighted SO_4^{2-} concentration in precipitation after 2004 showed similar patterns at all three sites. Sites with longer records (i.e., NY20 at Huntington Forest, NY98 at Whiteface Mountain) matched decreases in SO_4^{2-} concentrations in wet deposition through the monitoring period, but particularly after 2004. Volume-weighted concentrations of SO_4^{2-} in 1992 of approximately 30 μeq L^{-1} decreased to approximately 10 μeq L^{-1} in 2010 for both Huntington Forest and Whiteface Mountain.

Wet NO_3^- deposition was found to decrease at all three NADP sites in the Adirondacks after 2004. Changes in NO_3^- concentration in precipitation after 2004 had a very similar pattern as SO_4^{2-} at all three NADP sites in the Adirondacks (NY20, NY29, and NY98). Comparison of the two anions demonstrates that more than 80% of the variation of annual volume-weighted NO_3^- concentration after 2004 can be explained by changes in SO_4^{2-} concentration (Figure 4).

Rapid decreases in H^+ concentration of precipitation were observed at all three NADP monitoring stations. A strong correlation was found between concentrations of H^+ and the sum of SO_4^{2-} and NO_3^- since 2003 (Figure 5). More than 90 percent of the variation in annual volume-weighted H^+ concentration can be explained by the variation in the sum of SO_4^{2-} and NO_3^-.

Relation of sulfate concentrations and trends to landscape pattern

Volume-weighted concentration of lake SO_4^{2-} showed correlations with wet SO_4^{2-} deposition (see Table 3b for the multiple regression analysis) and some landscape characteristics of Adirondack watersheds. The elevation of ALTM lakes ranges from 384m at Grass Pond and Little Clear Pond to 873m at Avalanche Lake. As prevailing winds travel west to east across the Adirondack region, moisture-bearing air is intercepted by the higher elevations of the western Adirondacks and produces a large quantity of precipitation (Driscoll et al., 1991). Volume-weighted concentration of SO_4^{2-} tends to be higher in lakes with higher elevation (R^2=0.09, $p<0.05$). Lakes with shorter hydraulic residence time tend to have higher SO_4^{2-} concentration (Figure 6, R^2=0.55 for all lakes, R^2=0.10 for drainage lakes). The pattern of decreases in lake SO_4^{2-} with increasing hydraulic residence time is strongly influenced by seepage lakes which are characterized by relatively long hydraulic residence times. Inversed distance weighted (IDW) wetland areal fraction showed a negative correlation with volume-weighted concentration of lake SO_4^{2-} (R^2=0.11, $p<0.05$). In this study, base flow Ca^{2+} concentration was calculated as the average of Ca^{2+} concentration from June to September. There is also a strong relationship between volume-weighted concentration of SO_4^{2-} and base flow Ca^{2+} concentration (Figure 7, R^2=0.41). In general, SO_4^{2-} and base flow Ca^{2+} decrease from thick to thin till lakes with marked decreases in SO_4^{2-} relative to base flow Ca^{2+} in seepage lakes. Little Clear Pond with moderate base flow Ca^{2+} concentration but a long residence time over 6 years had a low SO_4^{2-} concentration of 33 μeq L^{-1}. Due to the relatively low and constant concentrations in precipitation and the limited interaction with vegetation, Cl^- is used in this study as an indicator of evapotranspiration. I also observed a relationship between volume-weighted concentrations of SO_4^{2-} and Cl^- in ALTM lakes (Figure 8, R^2=0.44). Multiple regression equations were constructed between the volume-weighted SO_4^{2-} concentration and some factors discussed above (Table 3). In addition to the landscape factors, wet SO_4^{2-} deposition also significantly affected the spatial variation of volume-weighted SO_4^{2-} concentrations. Lake watersheds receiving higher wet deposition of SO_4^{2-} tend to have higher concentration of SO_4^{2-} in lake water. Inclusion of wet SO_4^{2-} deposition to the regression equation increased the R^2 from 0.76 to 0.79. Consistent with results of the single regressions, volume-weighted concentrations of SO_4^{2-} tend to be higher in lakes of higher elevation, shorter hydraulic residence time, lesser wetland coverage, thicker glacial till and greater evapotranspiration (as estimated through the concentration of Cl^-). P values of all factors are less than 0.05, indicating that they all significantly affected the spatial variation of volume-weighted lake SO_4^{2-} concentrations. Sensitivity analysis of the regression model suggests elevation is the most sensitive parameter in the regression equation, as each percent of variation in elevation from the mean value results in the largest variation (0.22 μeq L^{-1}) in volume-weighted SO_4^{2-} concentration.

SO_4^{2-} concentrations in all 48 non-limed ALTM lakes have shown significant ($p<0.05$) decreases during the study period, with a mean rate (±standard deviation) of -2.34±0.70 μeq L^{-1} yr^{-1}. The rate of SO_4^{2-} decreases was more rapid in the thick till class (-2.84±0.75 μeq L^{-1} yr^{-1}) as compared to the medium till (-2.49±0.69 μeq L^{-1} yr^{-1}) thin till (-2.39±0.52 μeq L^{-1} yr^{-1}) and seepage classes (-1.28±0.76 μeq L^{-1} yr^{-1}).

Rates of lake SO_4^{2-} decrease have become more rapid and the standard deviation of SO_4^{2-} declines has become more uniform since 2000 (Table 4). The rates of SO_4^{2-} decline (-0.46 to -4.18 μeq L^{-1} yr^{-1}) show variation across the Adirondacks. A strong correlation was found between the decreasing rate of SO_4^{2-} and the volume-weighted concentration of SO_4^{2-} (Figure 9). For every unit of μeq L^{-1} in SO_4^{2-} concentration, there is a -0.0265 μeq L^{-1} yr^{-1} decrease over time ($R^2=0.61$).

Lake elevation is negatively correlated with the rate of lake SO_4^{2-} decrease (Figure 10, $R^2=0.19$, $p<0.01$). The pattern is evident in lakes of all classes except thick till drainage lakes. The correlation between elevation and decreasing rate of SO_4^{2-} is weak in medium till lakes ($R^2=0.05$) and is stronger in thin till drainage lakes and seepage lakes ($R^2=0.26$). A relationship was evident that the higher the base flow Ca^{2+} concentration the greater the rate of lake SO_4^{2-} decline (Figure 11, $R^2=0.19$, $p<0.01$).

In addition to elevation and surficial geology, changes in wet SO_4^{2-} deposition, canopy percentage and inverse distance weighted wetland areal percentage were found to be negatively correlated with long-term trends in SO_4^{2-} concentration. Lake watersheds with greater canopy coverage and greater inverse distance weighted wetland areal percentage showed more rapid rates of decline in lake SO_4^{2-}. However, these patterns were significant only when incorporated into multiple regression equations with elevation and atmospheric deposition. Unlike volume-weighted concentrations, no relationship was found for rates of SO_4^{2-} decreases with hydraulic residence time or long-term changes in Cl^-.

Soil adsorption of SO_4^{2-} is thought to occur on the surfaces of Al and Fe oxides (Zhang and Sparks, 1990). For the 29 ALTM lakes where soil survey data are available, both exchangeable Al and Fe concentrations in O horizon were negatively correlated with SO_4^{2-} decreasing rate (Figure 12) (R^2=0.13 for Al; R^2=0.12 for Fe). However, this result was not incorporated into the multiple regression equations because no correlation was found for exchangeable Al/Fe with Al/Fe oxides at ALTM watersheds. No relationship was found for SO_4^{2-} decreasing rate with exchangeable Al or Fe in B horizon.

Multiple regression equations were constructed between the SO_4^{2-} decreasing rate and some factors above to describe the response of ALTM lakes to declines in acid deposition (Table 5). Four factors, changes in wet SO_4^{2-} deposition, elevation, wetlands, and canopy coverage, were found to be most strongly correlated with the spatial variation of lake SO_4^{2-} trends. Inclusion of changes in wet SO_4^{2-} deposition to the regression equation increased the R^2 from 0.51 to 0.56. The regression analyses suggest that decreases in lake SO_4^{2-} tend to be more rapid in lake watersheds of more rapid decreases in wet SO_4^{2-} deposition, higher elevation, and greater wetland and canopy coverage. P values of all factors were less than 0.05, indicating that they all significantly affected the spatial variation in rates of SO_4^{2-} decreases. Sensitivity analysis of the regression model suggests elevation is the most sensitive parameter in the regression equation, as each percent of difference in elevation from the mean value results in a difference of 0.021 μeq L^{-1} yr^{-1} in rates of SO_4^{2-} decreases.

Relation of nitrate concentrations and trends to landscape patterns

Unlike volume-weighted SO_4^{2-} concentration, no relationship was evident for volume-weighted NO_3^- concentration with wet NO_3^- deposition. Volume-weighted concentrations of NO_3^- were compared with landscape factors. Volume-weighted concentration of lake NO_3^- appears to increase with lake elevation (Figure 13, R^2=0.39). The pattern of increasing NO_3^- with elevation was strongly influenced by high elevation lakes (Avalanche Lake and Lake Colden) and low elevation lakes (Willis Lake, Grass Pond and Barnes Lake). Volume-weighted concentration of lake NO_3^- also increases with land slope of lake watershed (Figure 14, R^2=0.34). A positive correlation was also found between NO_3^- and dissolved silica concentration (Figure 15, R^2=0.29). Both concentrations of total phosphorus (Figure 16, R^2=0.25) and chlorophyll a (Figure 17, R^2=0.27) showed a strong inverse relationship with lake NO_3^- concentrations. At low concentrations of total phosphorus and chlorophyll a, there are highly variable concentrations of NO_3^-. However, NO_3^- concentration is generally low in lakes with high concentrations of total phosphorus and chlorophyll a. No relationship was found for volume-weighted NO_3^- with wetland or canopy coverage, hydraulic residence time, or land disturbance.

Multiple regression equations were constructed between the volume-weighted concentration of NO_3^- and some of the factors discussed above to describe the response of ALTM lakes (Table 6). Three factors, elevation, land slope, and lake chlorophyll a, were found to be most strongly correlated with the spatial variation of volume-weighted concentration of NO_3^-. The regression analysis suggests that volume-weighted NO_3^- concentration tend to be higher in lake watersheds of high elevation, steeper land slope and lower chlorophyll a. P values of all factors are less than 0.05, indicating that they all significantly affected the spatial variation of volume-weighted lake NO_3^- concentration. Sensitivity analysis of the regression model suggests elevation and land slope being the more sensitive parameters in the regression equation as each percent of variation in elevation and land slope from the mean value result in variation of 0.16 μeq L^{-1} and 0.05 μeq L^{-1} in volume-weighted NO_3^- concentration respectively.

NO_3^- concentrations in 26 of 48 non-limed ALTM lakes have shown significant ($p<0.05$) decreases since 1992 (-0.46±0.27 μeq L^{-1} yr^{-1}). One thick till lake (Owen Pond) showed significant increase in NO_3^- (0.47 μeq L^{-1} yr^{-1}). Six out of twelve medium till lakes showed similar decreases (-0.45±0.15 μeq L^{-1} yr^{-1}) as did nineteen out of twenty-six thin till lakes (-0.46±0.31 μeq L^{-1} yr^{-1}) and a carbonate influenced lake (-0.38 μeq L^{-1} yr^{-1}). No seepage lake had significant decrease in NO_3^- concentration. Unlike SO_4^{2-}, no significant relationship was found for the decreasing rate of NO_3^- with volume-weighted NO_3^- concentration.

Similar to volume-weighted concentration, no relationship was found for decreases in lake NO_3^- with change in wet NO_3^- deposition. Land slope of drainage lake watershed was correlated with NO_3^- decreasing rate for lakes showing significant changes in NO_3^- (Figure 18, $R^2=0.44$). Watersheds with shallower land slope showed more rapid rates of decreases in NO_3^-. The areal fraction of the ALTM watersheds impacted by historical wind blow down (in 1950 and 1995) and land disturbance (before 1916 cutting/fire) were correlated with NO_3^- decreasing rate (Table 7). More rapid decrease in NO_3^- was correlated with greater watershed disturbance in

1995 and 1950, but with lesser watershed disturbance before 1916. P values of the regression equation suggest that land disturbance before 1916 had less impact on long-term decreases in NO_3^- than the more recent wind blow down events in 1950 and 1995. Although land disturbance pattern is significant in the multiple regression model, no significant relation was found for NO_3^- decreasing rate with any individual disturbance event. Inclusion of land slope to the regression equation increased the R^2 from 0.50 to 0.54. Sensitivity analysis indicates that land disturbance in 1995 is the most sensitive parameter in the regression equation, as each percent variation of areal fraction of 1995 disturbance from the mean value results in the largest variation (0.0012 μeq L^{-1} yr^{-1}) in rates of NO_3^- decreases. No significant relationship was found for the rates of NO_3^- decreases with wetland or canopy coverage.

All 48 non-limed ALTM lakes showed significant decreases in SO_4^{2-}+NO_3^- (-2.65±0.87 μeq L^{-1} yr^{-1}). This rate is smaller than values reported for the period from 1992 to 2000 (-3.26 μeq L^{-1} yr^{-1}, Driscoll et al., 2003) but greater than the rate from 1992 to 2004 (-2.50 μeq L^{-1} yr^{-1}, Driscoll et al., 2007). The rate of SO_4^{2-}+NO_3^- decreases was more rapid in the thin till class (-2.82±0.76 μeq L^{-1} yr^{-1}) as compared to the medium till (-2.76±0.82 μeq L^{-1} yr^{-1}) thick till (-2.73±0.47 μeq L^{-1} yr^{-1}) and seepage classes (-1.35±0.77 μeq L^{-1} yr^{-1}).

Relation of calcium concentrations and trends to landscape patterns

Unlike volume-weighted SO_4^{2-} concentration, no relationship was found for volume-weighted Ca^{2+} concentration with wet Ca^{2+} deposition. Volume-weighted concentrations of Ca^{2+} were compared with the sum of lake SO_4^{2-} and NO_3^- concentrations, Na^+, and dissolved SiO_2 concentrations to evaluate the contribution of lake Ca^{2+} from ion exchange and weathering processes. A strong correlation was found between Ca^{2+} concentration and the sum of SO_4^{2-} and NO_3^- (Figure 19, R^2=0.29 for all lakes, R^2=0.19 for drainage lakes). Na^+ (Figure 20, R^2=0.58) and dissolved SiO_2 (Figure 21, R^2=0.45) concentrations were correlated with Ca^{2+} concentration. In general, the highest concentrations of Ca^{2+}, Na^+ and dissolved SiO_2 were found in the thick till lakes with decreasing values in medium till, thin till and seepage lakes. For the 29 ALTM watersheds with soil survey data, a positive correlation was found between soil base saturation in B horizon and lake Ca^{2+} concentration (Figure 22, R^2=0.17).

A multiple regression equation was constructed between the volume-weighted concentration of Ca^{2+} and some of the factors discussed above to describe the response of ALTM lakes (Table 8). Due to the importance of processes in soil on volume-weighted concentration of Ca^{2+}, the only lakes included in this regression equation were the 29 lakes with available soil data from Sullivan et al. (2006). Consistent with results of single regressions, volume-weighted concentrations of Ca^{2+} tend to be higher in lakes of higher concentrations of SO_4^{2-} and NO_3^-, dissolved SiO_2, or higher base saturation in B horizon soil. P values of all factors are less than 0.05, indicating that they all significantly affected the spatial variation of lake Ca^{2+} concentrations. Sensitivity analysis of the regression model suggests that weathering is the most sensitive parameter in the regression equation, as each percent of variation in lake dissolved SiO_2 concentration from the mean value results in the largest variation (0.37 μeq L^{-1}) in volume-weighted Ca^{2+} concentration.

Forty-two of 48 non-limed ALTM lakes showed significant ($p<0.05$) decreases in lake Ca^{2+} (-1.20±0.47 μeq L^{-1} yr^{-1}). Big Hope Pond showed a significant ($p<0.05$) increase in lake Ca^{2+} (0.51

μeq L^{-1} yr^{-1}). Lake Ca^{2+} decreased most rapidly in thick till lakes (-1.94±0.24 μeq L^{-1} yr^{-1}) followed by medium till (-1.40±0.56 μeq L^{-1} yr^{-1}) and thin till lakes (-1.06±0.32 μeq L^{-1} yr^{-1}), which coincides with decreasing rates of SO_4^{2-} + NO_3^- among each surficial geology drainage class. The number of lakes showing significant decreases in Ca^{2+} reported in this study (42 lakes) is much greater than updates in 2000 (29 lakes, Driscoll and Roy, unpublished data) and 2004 (30 lakes, Driscoll and Roy, unpublished data).

A correlation was found between the rate of change in lake Ca^{2+} and its volume-weighted concentration (Figure 23). For every unit of μeq L^{-1} in Ca^{2+} concentration, there is a -0.0069 μeq L^{-1} yr^{-1} decrease over time (R^2=0.23).

Similar to volume weighted concentration, decrease in lake Ca^{2+} showed no correlation with any change in atmospheric Ca^{2+} deposition because most of the changes were not significant. It had been reported that the loss of soil available Ca^{2+} was caused by acidic deposition rather than forest growth (Federer et al., 1989; Likens et al., 1998). Decreasing rates of the sum of SO_4^{2-} and NO_3^- were compared with declines in Ca^{2+} to illustrate the contribution of changes in the displacement of Ca^{2+} from changes in leaching of strong acid anions (Figure 24, R^2=0.17). An equivalent of decrease in strong acid anions leads to a 0.39±0.23 equivalent decrease in Ca^{2+}. These values were smaller for thin till lakes (0.36±0.11 eq eq^{-1}) than in medium till lakes (0.43±0.28 eq eq^{-1}) and thick till lakes (0.73±0.18 eq^{-1}). Each equivalent of decreases in strong acid anion lead to 0.52±0.33 equivalent of decrease in the sum of base cations. These values were again lower in thin till lakes (0.47±0.15 eq eq^{-1}) than in medium till lakes (0.60±0.27 eq eq^{-1}) and thick till lakes (0.89±0.20 eq eq^{-1}).

It is also possible that changes in weathering could contribute to long-term trends in Ca^{2+}. Because of limited interactions with vegetation, silica and sodium have been used as indicators to quantify weathering input (Peters and Driscoll, 1987). Fourteen ALTM lakes showed significant ($p<0.05$) decreases in silica (-0.74 ± 0.38 µmol L^{-1} yr^{-1}) with six lakes showed significant increases (0.69 ± 0.68 µmol L^{-1} yr^{-1}). Only one lake, Big Hope Pond, showed a significant long-term decline in lake sodium (-0.65 µeq L^{-1} yr^{-1}) with six lakes showed significant increases (0.10 ± 0.09 µeq L^{-1} yr^{-1}). Trends in silica and sodium were compared with trends in lake Ca^{2+} to evaluate the contribution of weathering input to Ca^{2+} decreases. Only trends in silica showed a relation with trends in lake Ca^{2+} (Figure 25, $R^2=0.56$). Although many lakes do not show a significant trend, there is a correspondence of changes in lake silica with decreases in lake Ca^{2+} suggesting that declines in acidic deposition may decrease soil weathering rate.

For the 29 ALTM watersheds with soil analysis, twenty-seven showed significant decreases in lake Ca^{2+} concentration. A negative correlation was found between soil base saturation in B horizon and significant decreasing rate of lake Ca^{2+} (Figure 26, $R^2=0.22$). This pattern of changes in lake Ca^{2+} with changes in soil exchangeable base cation status is consistent with the earlier discussion, that the greatest rates of decreases in lake Ca^{2+} are in watersheds that have more base-rich soils.

A multiple regression equation was constructed between the change in lake Ca^{2+} concentration and some of the factors above to describe the response of ALTM lakes (Table 9). Similar to the regression analysis for volume-weighted concentration, due to the importance of processes in soil, the only lakes included in this regression equation were the 29 lakes with available soil data from the Sullivan et al. (2006) survey. Consistent with results of single regressions, more rapid decreases in Ca^{2+} tend to occur in lakes of more rapid decreases in SO_4^{2-}+NO_3^-, dissolved SiO_2, or higher base saturation in B horizon soil. P values of B horizon base saturation is slightly greater than 0.05, indicating that if affected the spatial variation of rate of Ca^{2+} decreases less significantly than other factors. Sensitivity analysis of the regression model suggests change in lake SO_4^{2-}+NO_3^- is the most sensitive parameter in the regression equation, as each percent of variation in rate of SO_4^{2-}+NO_3^- decreases results in the largest variation (0.0085 μeq L^{-1} yr^{-1}) in rate of Ca^{2+} decreases.

Concentrations and trends in lake ANC and pH

Volume-weighted ANC of Adirondack lakes has somewhat increased since 1992 (Figure 27). Multiple regression equations were constructed between mean volume-weighted ANC and factors affecting concentrations of SO_4^{2-}, NO_3^- and Ca^{2+} for seepage lakes and drainage lakes (Table 10). It was shown that, in ALTM seepage lakes, lake watersheds of lower wet deposition of SO_4^{2-}+NO_3^-, longer hydraulic residence time and higher concentration of chlorophyll a showed higher volume-weighted ANC. The influence of hydraulic residence time on volume-weighted ANC was primarily through its influence on SO_4^{2-} in seepage lakes (Figure 6). P values for all three factors are less than 0.05, indicating they all significantly affected volume-weighted ANC of seepage lakes. Based on results of the sensitivity analysis, hydraulic residence time is a more sensitive factor on seepage lake ANC than other factors because each percent variation in hydraulic residence time from the mean value results in a larger variation (0.13 μeq L^{-1}) in volume-weighted ANC of seepage lakes. Spatial variation of volume-weighted ANC in ALTM drainage lakes, on the other hand, was affected by a combination of factors including wet deposition of SO_4^{2-}+NO_3^-, land slope, wetland coverage, weathering input of base cations and soil base saturation. Each of the above factors affected volume-weighted ANC in drainage lakes by altering volume-weighted concentrations of SO_4^{2-}, NO_3^-, or Ca^{2+}. Higher volume-weighted ANC were observed in drainage lake watersheds of lower wet deposition of SO_4^{2-}+NO_3^-, higher wetland coverage, shallower land slope, higher lake SiO_2, and higher base saturation in B horizon soil. P values for B horizon base saturation is slightly greater than 0.05, which indicates that it has less significant impact on the spatial variation in volume-weighted ANC of drainage lakes than other factors. Sensitivity analyses of the regression models suggest lake dissolved SiO_2 is the most sensitive parameter in the regression equation, as each percent of variation in rate of lake dissolved SiO_2 results in the largest variation (0.62 µeq L^{-1}) in volume-weighted ANC. No significant relationship was found for volume-weighted ANC of drainage lakes with hydraulic residence time or chlorophyll a.

Annual updates of long-term trends in lake ANC showed that rates of ANC increases have become more uniform across the ALTM lakes but at a slightly lower rate since 2000 (Figure 28). The analyses indicated that thirty-six of 48 non-limed ALTM lakes showed significant increases ($p<0.05$) in ANC (0.93±0.33 µeq L^{-1} yr^{-1}). One carbonate influenced lake (Windfall Pond), one thick till lake (Owen Pond) and seven medium till lakes showed a mean increasing rate of 1.11 µeq L^{-1} yr^{-1},ranging from 0.71 to 1.53 µeq L^{-1} yr^{-1}. Twenty-three of 26 thin till lakes showed a mean rate of ANC increase of 0.86±0.18 µeq L^{-1} yr^{-1}, while four seepage lakes showed more rapid increase in ANC (1.05±0.50 µeq L^{-1} yr^{-1}). In 2009, 40 lakes had ANC greater than 0 µeq L^{-1}, including 13 with ANC greater than 50 µeq L^{-1}. For each equivalent decrease in strong acid anions, ANC increased 0.55±0.42 equivalent in seepage lakes, 0.28±0.08 eq eq^{-1} in thin till lakes, and 0.31±0.25 eq eq^{-1} in medium till, and 0.14±0.19 in thick till lakes. No significant relationship was found for ANC increases in ALTM seepage lakes with either atmospheric deposition or hydraulic residence time. A multiple regression equation was constructed for the ANC increasing rate in ALTM drainage lakes to describe the response of ALTM lakes to declines in acid deposition (Table 11). Four factors, change in wet SO_4^{2-} + NO_3^- deposition, elevation, wetland area, and a recent forest disturbance event, were found to be correlated with the spatial variation of lake ANC trends (R^2=0.71). Landscape factors included in the regression equation affected spatial variation in changes in ANC by altering changes in either SO_4^{2-} or NO_3^-. Consistent with results for SO_4^{2-} and NO_3^-, lake watersheds of more rapid decreases in wet acidic deposition, higher elevation, greater wetland coverage, or greater watershed disturbance showed more rapid increases in ANC. The p value for change in atmospheric deposition is slightly greater than 0.05, indicating that it affected the spatial variation in changes in ANC less significantly than the landscape factors. Sensitivity analysis indicated elevation is the most sensitive parameter for spatial variation in ANC increases for each percent variation in elevation from the mean value results in 0.0067 μeq L^{-1} yr^{-1} variation in the rate of ANC change. Weathering processes and soil base saturation which played important roles in affecting Ca^{2+} decreases did not show significant influence on changes in ANC.

Thirty lakes showed significant decreases ($p<0.05$) in H^+ concentration (-0.23±0.24 μeq L^{-1} yr^{-1}) while one seepage lake, Sunday Pond, showed significant increase in H^+ concentration (0.26 μeq L^{-1} yr^{-1}). Declines in proton concentration are more rapid in seepage lakes (-0.76±0.07 μeq L^{-1} yr^{-1}) than thin till lakes (-0.21±0.16 μeq L^{-1} yr^{-1}) and medium till, thick till and carbonate influenced lakes (-0.03±0.03 μeq L^{-1} yr^{-1}). On average, lake pH increased by 0.0224 pH unit yr^{-1} with the most rapid increase in seepage lakes (0.0259±0.0231 pH unit yr^{-1}). In 2009, 19 lakes still had mean pH values less than 5.5, including 9 with pH less than 5.

Concentrations and trends in lake monomeric aluminum and dissolved organic carbon (DOC)

Volume-weighted concentrations of inorganic monomeric Al were much higher in thin till class (3.58±2.72 μmol L^{-1}) compared to medium till (1.08±1.06 μmol L^{-1}), thin till (0.34±0.09 μmol L^{-1}) and seepage classes (0.47±0.17 μmol L^{-1}).

Thirty-nine of 48 non-limed ALTM lakes showed significant decreases ($p<0.05$) in concentrations of inorganic monomeric Al (-0.12±0.14 μmol L^{-1} yr^{-1}). These declines were more rapid in thin till lakes (-0.18±0.16 μmol L^{-1} yr^{-1}) than medium till (-0.04±0.04 μmol L^{-1} yr^{-1}), thick till (-0.006±0.002 μmol L^{-1} yr^{-1}) and seepage lakes (-0.02±0.02 μmol L^{-1} yr^{-1}). A strong correlation was found between the volume-weighted concentration of inorganic monomeric Al and its rate of change over time (Figure 29). For every unit of μmol L^{-1} in inorganic monomeric Al concentration, there is a -0.0504 μmol L^{-1} yr^{-1} decrease over time ($R^2=0.83$). The only thick till lake (Owen Pond) and carbonate influenced lake (Windfall Pond) that had significant increases in pH and ANC did not show significant decreases inorganic monomeric Al, while the remainder of thick till and carbonate influenced lakes that had no changes in pH or ANC (Clear Pond, Black Pond Outlet and Middle Pond) all showed significant but small decreases in inorganic monomeric Al. In addition, all five seepage lakes showed moderate decreases in inorganic monomeric Al (-0.02±0.02 μmol L^{-1} yr^{-1}). Only one lake showed significant increase ($p<0.05$) in organic monomeric Al (Carry Pond, 0.04 μmol L^{-1} yr^{-1}) with 8 lakes showing significant decreases (-0.06±0.03 μmol L^{-1} yr^{-1}). No spatial factor was found significantly correlated with volume-weighted concentration or the rate of change in Al.

For the 29 watersheds with intensive soil analysis, volume-weighted concentration of DOC were correlated with C:N molar ratio in O horizon (Figure 30, R^2=0.24). Four lakes (West Pond, Raquette Lake Reservoir, Sagamore Lake, and Willis Lake) with concentration of DOC between 600 μmol L^{-1} and 800 μmol L^{-1} seem the only exceptions to this pattern. Volume-weighted concentration of DOC were also strongly correlated with base saturation in B horizon (Figure 31, R^2=0.45). A multiple regression equation was constructed for the volume-weighted DOC concentrations (Table 12). No significant relationship was found for volume-weighted DOC with atmospheric deposition of SO_4^{2-} and NO_3^-, but a significant relationship was found with the sum of lake SO_4^{2-} and NO_3^-. Higher volume-weighted concentrations of DOC were shown in lakes with lower concentrations of SO_4^{2-} and NO_3^-. A significant relationship was also found for volume-weighted DOC with color of lake water in the multiple regression equation. Although color of lake water is considered a function of DOC concentration, I used color of lake water as an independent variable in this study because it can be used to estimate DOC concentration based on satellite images. P values all factors were less than 0.05, indicating that they all significantly affected the spatial variation of volume-weighted DOC. Sensitivity analysis indicated that O horizon molar C:N ratio is the most sensitive parameter to the spatial variation in volume-weighted DOC concentrations, as each percent variation in C:N ratio from the mean value results in 7.11 μmol L^{-1} variation in volume-weighted DOC concentration.

An increase in DOC is considered an indicator of recovery from acidification (Hedin et al., 1990). Twenty-three out of 48 non-limed ALTM lakes had significant changes ($p<0.05$) in dissolved organic carbon (DOC) with five decreases (-5.63 ± 3.46 µmol L^{-1} yr^{-1}) and eighteen increases (6.39 ± 4.09 µmol L^{-1} yr^{-1}). However, no relationship was found for the rate of change in DOC with its volume-weighted concentration. Trends in DOC were strongly positively correlated with changes in true color of lake water (Figure 32, $R^2=0.51$). Long-term trends in DOC concentration were correlated with exchangeable Al and Fe within O horizon (Figure 33). Soils with larger concentrations of exchangeable Al and Fe in the O horizon tend to have greater increases in DOC concentrations. A multiple regression equation was constructed for the changes in DOC concentration (Table 13). Similar to volume-weighted DOC concentrations, no relationship was found for changes in DOC with changes in atmospheric deposition of SO_4^{2-} and NO_3^-, but a significant relationship was found for changes in DOC and decreases in lake SO_4^{2-} and NO_3^-. More rapid increases in DOC were found in lakes with more rapid decreases in lake SO_4^{2-} and NO_3^-. P values for all factors were less than 0.05, suggesting that they all significantly affected the spatial variation of changes in DOC. Sensitivity analysis suggests that O horizon Al and Fe are the most sensitive parameter, as each percent of variation in O horizon Al and Fe from the mean value results in 0.021 µmol L^{-1} yr^{-1} variation in rate of DOC increases. No significant relationship was found for changes in DOC with soil C:N ratio of O horizon or base saturation of B horizon.

Discussion

Lakes in the Adirondack region have been impacted by acid deposition (Discoll et al., 1991). In recent decades, controls on regional emissions of SO_2 and NO_X have facilitated marked decreases in atmospheric SO_4^{2-} and NO_3^- and H^+ deposition (Figure 3). These decreases have been the most important factors contributing to the chemical recovery of Adirondack lakes. However, there is considerable variability in the response of individual lakes to this decrease in acidic deposition. Thirty-six out of 48 non-limed lakes monitored are showing significant increases in ANC ranging from 0.37 to 2.08 µeq L^{-1} yr^{-1}.

Baker et al. (1990) developed a classification system based on surficial geology to evaluate the sensitivity of lakes to acidic deposition. I have evaluated the effectiveness of that classification system in understanding the recovery of lake-watersheds to decreases in acid deposition. Adirondack lakes were divided into two primary classes: drainage lakes and seepage lakes. Drainage lakes were further subdivided into three additional classes based on the amount of thick till present in the watershed: thin till, medium till and thick till.

Seepage Lakes

The chemical characteristics of seepage lakes and drainage lakes are distinctly different. Moreover they exhibit very different patterns of recovery to decreases in acidic deposition. Seepage lakes that are part of the ALTM program are largely perched or bog seepage lakes (Driscoll et al., 2003). These sites are situated at relatively low elevation (384 to 649 m) and are characterized by relatively small watersheds (i.e., the lake watershed is close to the lake area) and relatively long hydraulic residence time (2.44 to 6.79 yr).

Adirondack seepage lakes show relatively low concentrations of SO_4^{2-} (mean 45 μeq L^{-1}, range 33 to 60 μeq L^{-1}) and their rate of SO_4^{2-} decrease is the lowest of the ALTM lake classes (mean -1.28 μeq L^{-1} yr^{-1}, range -0.46 to -2.53 μeq L^{-1} yr^{-1}). Low SO_4^{2-} concentrations in seepage lakes are likely due to two factors. First, inputs of SO_4^{2-} largely occur due to direct inputs of precipitation to the lake surface and the near-lake region. As a result of the limited watershed canopy cover and low elevation, dry S deposition inputs are likely low compared to largely forest covered drainage lake watersheds. Second, seepage lakes have relatively long hydraulic retention times which facilitate in-lake retention of SO_4^{2-}. Lakes of longer hydraulic residence time exhibit greater removal of SO_4^{2-} by reduction of SO_4^{2-} to S^{2-} in sediments, resulting in organic S compounds and FeS (Cook and Schindler, 1983; Nriagu and Soon, 1985). Long hydraulic residence time may also facilitate algae uptake of SO_4^{2-} (David and Mitchell, 1985).

In addition to low SO_4^{2-}, Adirondack seepage lakes are characterized by very low concentrations of NO_3^-. There is an inverse relation between Adirondack lake NO_3^- and concentrations of total phosphorus and chlorophyll a. Seepage lakes have the lowest NO_3^- of all ALSC classes and relatively high total phosphorus and chlorophyll a. Seepage lakes appear to be productive compared with drainage lakes. This high lake productivity coupled with relatively long hydraulic residence time likely facilitates in-lake retention of NO_3^- (Kelly et al., 1987).

Although seepage lakes have relatively low concentrations of SO_4^{2-} and NO_3^-, they have the lowest ANC. Moreover, although rates of decrease of SO_4^{2-} + NO_3^- are the lowest of the ALSC lake classes, they have the highest rates of ANC increase. These paradoxical characteristics are due to the limited interaction of precipitation with surficial materials and the resulting very low concentrations of Ca^{2+} and other base cations. The fact that concentrations of Na^+ and dissolved Si are also very low in ALTM seepage lakes is strongly indicative of the limited release of solutes from surficial deposits that occurs in seepage lakes. As a result of this limited buffering by watershed processes, decreases in atmospheric deposition of strong acid anions result in a close to stoichiometric increases in ANC (0.55 μeq μeq^{-1}).

Drainage Lakes

The atmospheric deposition affects lake-to-lake variability in acid-base chemistry of drainage lakes through altering both SO_4^{2-} concentrations and their rates of change. The lake-to-lake variability in volume-weighted SO_4^{2-} concentration is primarily driven by the spatial variation in precipitation quantity, while the lake-to-lake variability in SO_4^{2-} decreases is more likely affected by the spatial variation in declines of SO_4^{2-} concentration in precipitation. In addition to atmospheric deposition, the landscape processes driving lake-to-lake variability in the recovery of drainage lakes from acidic deposition also contrast with those driving changes in seepage lakes.

Topographical and physical characteristics: elevation and land slope

Elevation is a key factor that drives the recovery of ALTM lakes from acidic deposition. It affects acid-base chemistry of ALTM drainage lakes primarily through altering their rates of SO_4^{2-} decreases. Concentrations of SO_4^{2-} in drainage lakes are higher than seepage lakes, and their rates of SO_4^{2-} decreases are more rapid (Figure 9). At higher elevation in the western Adirondacks, lake-watersheds receive more precipitation because moisture-bearing air masses are intercepted and resulting in large quantity of precipitation (Driscoll et al., 1991). Therefore, these high-elevation lakes (e.g., Indian Lake, Squaw Lake, Willys Lake) are responsive to decreases in SO_4^{2-} from atmospheric deposition and exhibit relatively rapid increases in lake water ANC. The elevation-dependence of acid-base chemistry in ALTM lakes found in this study connects long-term monitoring data with readily available remote sensing DEM data, which provides an alternative way for roughly evaluating lake water chemistry at remote areas of the Adirondacks in the future. Note I did not observe distinct differences in the rates of lake SO_4^{2-} decrease among drainage lake classes.

Land slope serves as another important factor that affects acid-base chemistry of ALTM drainage lakes. It affects the recovery of ALTM lakes from acidic deposition by altering volume-weighted concentrations of NO_3^- and their rates of change. Watersheds with steeper land slope promote faster drainage particularly after spring melt. In steeper watersheds, water infiltrates rapidly while high concentrations of NO_3^- can be maintained in groundwater. Water with high NO_3^- concentration in watersheds with steeper land slopes infiltrates below the rooting zone and organic-rich upper soil horizons, which keeps NO_3^- from being depleted by vegetation uptake and denitrification (Schafran and Driscoll, 1990). Watersheds with shallower land slopes may promote near-surface flow paths in rooting zone and organic-rich soil horizons, which may facilitate vegetation uptake and denitrification after spring melt. Since land relief can be readily depicted by GIS from DEM data, this finding may help future analysis use remote sensing data to predict where the effects of decreases in atmospheric NO_3^- deposition are most apparent.

Soil chemistry and surficial processes

I observed a linkage between base-flow concentrations of lake Ca^{2+} and lake SO_4^{2-}. Generally, concentrations of SO_4^{2-} are highest and, to a lesser extent, rates of SO_4^{2-} decrease are faster in thick till drainage lakes followed by medium till and thin till lakes. The mechanism driving this pattern is not clear. Mitchell et al. (2013) observed a greater discrepancy in lake-watershed S budgets for ALTM thick and medium till watersheds than thin till watersheds. They speculated that this discrepancy was due to the release of SO_4^{2-} from thicker till deposits that had previously been retained in the watershed during periods of elevated S deposition as a result of decreases in atmospheric S deposition. Alternatively, this pattern could also be due to higher rates of dry deposition or evapotranspiration associated with thicker till watersheds. Note I observed a pattern of increasing concentrations of lake SO_4^{2-} coinciding with increases in Cl^-. Greater rates of evapotranspiration would result in increases in solute concentration and also increase their rate of change.

ALSC drainage lake classes exhibit distinct patterns of Ca^{2+} and base cation supply, with thick till watersheds showing greater base cation supply and decreasing rates in the sum of base cations followed by medium till lakes and thin till lakes. These differences in base cation supply appear to be derived from two processes: weathering and leaching from soil exchange complex associated with changes in concentrations of strong acid anions. Chemical indicators of weathering (i.e., concentrations of Na^+ and dissolved SiO_2) suggest that cation weathering is greatest in thick till lake watersheds followed by medium till and thin till watersheds. I also observed a relationship of increasing concentrations of lake Ca^{2+} with increasing concentrations of strong acid anions from thin till lakes to medium till lakes to thick till lakes, suggesting that the presence of mobile anions (SO_4^{2-}+NO_3^-) facilitates the leaching of Ca^{2+} and the sum of base cations from available surfaces in watershed soils. Limited evidence to support this mechanism is available through soil data (Figure 22) for some of the lake-watersheds. Although there is considerable scatter, generally the percent base saturation and the lake volume-weighted Ca^{2+} concentrations are greater in medium till compared to thin till watersheds (Figure 22), suggesting for a given concentration of strong acid anion, there is greater leaching of Ca^{2+} and sum of base cations in medium till lakes compared to thin till lakes.

These patterns play out in the extent of soil buffering in response to decreases in concentrations of SO_4^{2-}+NO_3^- in drainage lakes. For a unit decrease in SO_4^{2-}+NO_3^-, the rate of decrease in Ca^{2+} and the sum of base cations increased from thin till drainage lakes to medium till drainage lakes to thick till drainage lakes. These changes did translate to expected changes in ANC. Only one thick till lake showed a significant increase in ANC, which is likely due to the near-stoichiometric changes in C_B with changes in SO_4^{2-}+NO_3^- (0.89±0.20 eq eq^{-1}). Unexpectedly, medium till lakes showed somewhat greater increases in ANC per unit decrease in SO_4^{2-}+NO_3^- than thin till lakes. However there is considerable variability in unit rates of ANC increase per unit decrease in SO_4^{2-}+NO_3^- among medium till lakes.

Marked decreases in lake concentrations of Al were evident, particularly among thin till drainage lakes. Lakes which are characterized by the highest concentrations of inorganic monomeric Al show the greatest rates of decrease of inorganic monomeric Al. Lake watersheds with lower C:N ratio in O horizon and base saturation in B horizon may result in more thorough and complete decomposition of soil organic matter and therefore showed lower concentration of DOC in lake water.

Wetland processes

Wetlands affect the acid-base chemistry of ALTM lakes by altering SO_4^{2-} concentrations and their rates of change. There have been some isotopic studies at Plastic Lake and the inlet of Arbutus Lake that suggested the importance of bacterial dissimilatory sulfate reduction in the Adirondack region (Eimers et al., 2004; Mitchell et al., 2006). ALTM drainage lake watersheds with greater wetland coverage adjacent to the lakes exhibit lower concentrations and relatively rapid rates of decreases in SO_4^{2-}. Observed low concentrations and rapid rates of decreases in SO_4^{2-} is likely due to microbial activities under anaerobic conditions by using SO_4^{2-} as electron acceptors to oxidize organic matter.

$$SO_4^{2-}+2H^{+}+2CH_2O\rightarrow 2CO_2+H_2S+2H_2O$$

Microbes sequentially use O_2, NO_3^-, and SO_4^{2-} as electron acceptors under decreasing redox potential. Therefore, both denitrification and bacterial dissimilatory SO_4^{2-} reduction may occur in wetlands. However, no significant relationship was found for NO_3^- concentration with wetland coverage in this study, which is likely due to the relatively large contribution of other landscape factors that affect NO_3^- concentrations and changes such as forest growth, land disturbance and topography.

Spatial arrangement of wetlands plays an important role in modulating their effects on the recovery of ALTM lakes from acidic deposition. I observed relationships of lake SO_4^{2-} with IDW wetland percentage but no relationship with total wetland percentage or wetland percentage within any certain distance, suggesting that patches of wetlands in ALTM watersheds have greater impacts when they occur closer to an ALTM lake.

Forest coverage and disturbance

Canopy coverage affects acid-base chemistry of ALTM lakes by altering dry deposition of S and N into the lake watersheds. I observed a relationship of relatively rapid decreasing rates of SO_4^{2-} with increases in canopy coverage in the ALTM watersheds, suggesting that watersheds of larger density of trees intercept more particulate and gaseous S deposition from entering the surface water (Ollinger et al., 1993; Chen and Driscoll., 2005). This result is consistent with a previous throughfall study in the central Adirondack suggesting that S deposition under coniferous were 2.5 times greater than deciduous forests (Mollitor and Raynal, 1982). No significant relationship was found for NO_3^- with canopy coverage in this study, which is likely due to a combination of the relatively low N deposition compared with S deposition during the growing season and the significant influence of other landscape factors on NO_3^- concentrations and changes such as land slope and vegetation uptake.

Forest disturbance events influence acid-base chemistry of ALTM lakes by affecting their long-term changes in NO_3^-. I observed more rapid decreases in NO_3^- at ALTM lakes with greater portion of watersheds affected by the blow down events in 1995 and 1950, suggesting a higher vegetation uptake of NO_3^- from soil and surface water for forest regrowth following disturbance events in these watersheds. Land disturbance events prior to 1916, however, had a contrasting pattern. Lakes affected by the land disturbance events prior to 1916 showed smaller decreases in lake NO_3^-. The mechanism driving this pattern is not clear but the fire event occurred nearly one century ago and should be interpreted with caution. It may be that watersheds have sufficiently recovered from pre-1916 disturbances and are not influencing rates of NO_3^- decline or ANC increase.

Summary

Results of this study suggest that volume-weighted ANC of ALTM seepage lakes are primarily driven by wet deposition of strong acid anions and in-lake processes which affect bacterial dissimilatory SO_4^{2-} reduction and vegetation NO_3^- uptake. Volume weighted ANC of ALTM drainage lakes are affected by a combination of factors including wet deposition of strong acid anions, inputs of base cations from ground water derived from surficial deposits, wetland coverage, and land slopes of lake-watersheds. ALTM seepage lakes have the most rapid ANC increases but showed no significant relationship with spatial variation in atmospheric deposition or landscape factors. The regression equation for ANC increases at ALTM drainage lakes indicate that, in addition to decreases in strong acids from atmospheric deposition, landscape factors also strongly affect the spatial variation in the recovery of ALTM lakes from acidification, in which elevation, wetland coverage, and forest disturbance history play the most important roles.

Conclusions

- Decreases in atmospheric deposition of NO_3^-, SO_4^{2-} and H^+ were observed in the Adirondack region after 2004 due to the legislation of NO_X Budget Program. More than 80 percent of the variation in annual volume-weighted H^+ concentration in atmospheric deposition after 2004 can be attributed to the variation in the sum of SO_4^{2-} and NO_3^-.
- Higher volume-weighted SO_4^{2-} concentrations were found in ALTM lakes with greater wet atmospheric SO_4^{2-} deposition, higher elevation, shorter hydraulic residence time, lesser wetland coverage, thicker deposits of glacial till, and possibly greater evapotranspiration. More rapid decreases in lake SO_4^{2-} concentrations were observed in ALTM lakes with more rapid decreases in wet atmospheric SO_4^{2-} deposition, higher elevation, and greater wetland and canopy coverage.
- Volume-weighted NO_3^- concentrations and NO_3^- decreasing rates of ALTM lakes were not significantly influenced by atmospheric deposition. Higher volume-weighted NO_3^- concentrations were found in ALTM lake watersheds with higher elevation, steeper land slope, and lower chlorophyll a concentrations; while more rapid decreases in NO_3^- concentrations were observed in lake watersheds with shallower land slope and with greater area affected by forest disturbance.
- Spatial variation in volume-weighted Ca^{2+} concentration and rates of Ca^{2+} decreases of ALTM lakes were attributed to weathering and leaching from the soil exchange complex. Higher volume-weighted Ca^{2+} concentrations were found in lake watersheds with higher concentrations of lake SO_4^{2-} + NO_3^-, dissolved SiO_2, and B horizon base saturation; while

more rapid decreases in Ca^{2+} concentrations were observed in lake watersheds with more rapid decreases in lake SO_4^{2-} + NO_3^-, dissolved SiO_2, and higher B horizon base saturation.

- Spatial variation in volume-weighted ANC of ALTM seepage lakes was primarily driven by precipitation and in-lake processes. Volume-weighted ANC of ALTM drainage lakes, on the other hand, were affected by wet atmospheric deposition of SO_4^{2-} + NO_3^-, and landscape factors including land slope, wetland coverage, weathering, and B horizon soil base saturation.
- The number of ALTM lakes showing significant increases in ANC increased from 21 lakes in 2000 to 36 lakes in 2009. ALTM seepage lakes had more rapid increases in ANC than drainage lakes, but showed no significant relationship with atmospheric deposition or landscape factors. More rapid increases in ANC were found in ALTM drainage lakes with more rapid decreases in wet atmospheric deposition of SO_4^{2-} + NO_3^-, higher elevation, greater wetland coverage, and greater area affected by the 1995 forest disturbance.
- Marked decreases in lake concentrations of Al were evident, particularly among thin till drainage lakes. Lakes which are characterized by the highest concentrations of inorganic monomeric Al showed the greatest rates of decrease of inorganic monomeric Al.
- Higher volume-weighted DOC were found in ALTM lakes with lower concentrations of SO_4^{2-} and NO_3^-, higher O horizon C:N ratio, B horizon base saturation, and greater color. More rapid increases in DOC concentrations were observed in ALTM lakes with more rapid decreases in SO_4^{2-} and NO_3^-, more rapid changes in color of lake water, and higher O horizon exchangeable Al and Fe.

Tables

Table 1. List of maps and data layers used in the analysis.

Name	Source	Website
Adirondack Park Boundary	Adirondack Park Agency	http://www.apa.state.ny.us/gis
Lake Watersheds	Delineated from DEM/NHD using ArcHydro 13	
Wetland Coverage	Multi-Resolution Land Characteristics Consortium	http://www.mrlc.gov
Canopy Coverage	Multi-Resolution Land Characteristics Consortium	http://www.mrlc.gov
Precipitation Concentration	Interpolated from NADP/NTN Sites	
Precipitation Quantity	PRISM Climate Group	http://www.prism.oregonstate.edu
DEM/Elevation	USGS Seamless	http://seamless.usgs.gov
TIN/Slope	Converted from DEM	
NHD/National Hydrography Dataset	USGS	http://nhd.usgs.gov/data.html
Forest Disturbance/1916 Fire	Adirondack Park Agency	http://www.apa.state.ny.us/gis
Forest Disturbance/1950 Blow down	Adirondack Park Agency	http://www.apa.state.ny.us/gis
Forest Disturbance/1995 Blow down	Adirondack Park Agency	http://www.apa.state.ny.us/gis

Table 2. Trends of major solute in precipitation at two NADP sites in the Adirondacks (units are in μeq L^{-1} yr^{-1}, ns indicates no significant trend).

Site	SO_4^{2-}	NO_3^-	C_B	NH_4^+	H^+
Huntington Forest	-0.96	-0.33	ns	ns	-0.74
Whiteface Mountain	-1.03	-0.31	ns	ns	-1.05

Table 3 (a). Regression equation for volume weighted SO_4^{2-} concentration with landscape factors for 48 non-limed ALTM lakes (R^2=0.76).

	Elevation (m)	Hydraulic residence time (yr)	IDW	Base flow Ca^{2+} (μeq/L)	Volume-weighted Cl^- (μeq/L)	Intercept
Coefficients	0.0428	-5.27	-16.2	0.231	0.0751	47.2
P-value	0.0292	6.53E-05	0.032	1.20E-06	0.00389	0.208

Table 3 (b). Regression equation for volume weighted SO_4^{2-} concentration with atmospheric deposition and landscape factors for 48 non-limed ALTM lakes (R^2=0.79).

	Wet SO_4^{2-} deposition (eq/ha)	Elevation (m)	Hydraulic residence time (yr)	IDW	Base flow Ca^{2+} (μeq/L)	Volume-weighted Cl^- (μeq/L)	Intercept
Coefficients	0.0333	0.0393	-5.70	-12.8	0.223	0.00740	37.0
P-value	0.0282	0.0374	1.36E-05	0.022	1.25E-06	0.00478	0.194

Table 4 (a). Significant SO_4^{2-} decreasing rates of non-limed ALTM lakes from 1992.

	2009	2008	2007	2006	2005	2004	2000
Number of significant decreases	48	47	47	47	46	47	37
Mean decreasing rate (μeq L^{-1} yr^{-1})	-2.34	-2.32	-2.35	-2.20	-2.19	-2.16	-2.82
Standard deviation	0.70	0.68	0.72	0.72	0.76	0.81	1.00

Table 4 (b). Mean SO_4^{2-} decreasing rates of all 48 non-limed ALTM lakes from 1992.

	2009	2008	2007	2006	2005	2004	2000
Mean decreasing rate (μeq L^{-1} yr^{-1})	-2.34	-2.27	-2.30	-2.15	-2.10	-2.11	-2.17
Standard deviation	0.70	0.75	0.79	0.78	0.86	0.86	1.48

Table 5 (a). Regression equation for changes in SO_4^{2-} with landscape factors for 48 non-limed ALTM lakes (R^2=0.51).

	Elevation (m)	IDW	Canopy percentage	Intercept
Coefficients	-0.00384	-2.14	-0.0205	1.83
P-value	2.91E-05	0.000205	0.0172	0.0431

Table 5 (b). Regression equation for changes in SO_4^{2-} with atmospheric deposition and landscape factors for 48 non-limed ALTM lakes (R^2=0.56).

	Change in wet SO_4^{2-} deposition (eq/ha-yr)	Elevation (m)	IDW	Canopy percentage	Intercept
Coefficients	0.0577	-0.00386	-2.03	-0.0207	2.38
P-value	0.0459	1.75E-05	0.000299	0.0134	0.0108

Table 6. Regression equation for volume weighted NO_3^- concentration with landscape factors for 48 non-limed ALTM lakes (R^2=0.53).

	Elevation (m)	Land slope	Chlorophyll a (µg/L)	Intercept
Coefficients	0.0302	25.6	-0.221	-5.01
P-value	0.0339	0.00816	0.0481	0.497

Table 7 (a). Regression equation for changes in NO_3^- with forest disturbance history (areal fraction of watershed affected by blow down or fire) for 48 non-limed ALTM lakes (R^2=0.50).

	1995 blow down event	1950 blow down event	1916 forest disturbance	Intercept
Coefficients	-1.39	-0.556	0.348	-0.128
P-value	0.00158	0.000739	0.00171	0.00438

Table 7 (b). Regression equation for changes in NO_3^- with atmospheric deposition, forest disturbance and land slope for 48 non-limed ALTM lakes (R^2=0.54).

	1995 blow down event	1950 blow down event	1916 forest disturbance	Land slope	Intercept
Coefficients	-1.397	-0.575	0.378	0.0135	-0.220
P-value	0.00198	0.000976	0.00558	0.0472	0.319

Table 8. Regression equation for volume weighted Ca^{2+} concentration for 29 non-limed ALTM lakes with available soil data from Sullivan et al. (2006) survey (R^2=0.91).

	Sum of lake SO_4^{2-} and NO_3^- (µeq/L)	Lake dissolved SiO_2 (µmol/L)	B horizon base saturation (%)	Intercept
Coefficients	0.241	0.570	2.29	-1.19
P-value	0.00435	0.000733	0.0251	0.0315

Table 9. Regression equation for changes in lake Ca^{2+} for 29 non-limed ALTM lakes with available soil data from Sullivan et al. (2006) survey (R^2=0.87).

	Change in sum of lake SO_4^{2-} and NO_3^- (µeq/L-yr)	Change in lake dissolved SiO_2 (µmol/L-yr)	B horizon base saturation (%)	Intercept
Coefficients	0.325	1.14	-0.00282	0.156
P-value	1.47E-05	0.0185	0.0884	0.0452

Table 10 (a). Regression equation for volume weighted ANC for 5 non-limed seepage lakes (R^2=0.68).

	Wet deposition of SO_4^{2-} and NO_3^- (eq/ha)	Hydraulic residence time (yr)	Chlorophyll a (µg/L)	Intercept
Coefficients	-0.0204	2.56	0.0156	-0.401
P-value	0.0459	0.0199	0.0487	0.780

Table 10 (b). Regression equation for volume weighted ANC for 28 non-limed drainage ALTM lakes with available soil data from Sullivan et al. (2006) survey (R^2=0.84).

	Wet deposition of SO_4^{2-} and NO_3^- (eq/ha)	IDW	Land slope	Lake dissolved SiO_2 (µeq/L)	B horizon base saturation (%)	Intercept
Coefficients	-0.0544	8.36	-1.44	0.761	1.95	3.04
P-value	0.00595	0.00285	0.00228	8.32E-06	0.0528	0.0245

Table 10 (c). Regression equation for volume weighted ANC for 43 non-limed drainage ALTM lakes (R^2=0.70).

	Wet deposition of SO_4^{2-} and NO_3^- (eq/ha)	IDW	Land slope	Lake dissolved SiO_2 (µeq/L)	Intercept
Coefficients	-0.0926	8.52	-1.93	0.940	5.29
P-value	0.000137	0.0452	0.00377	2.86E-08	0.0480

Table 11. Regression equation for changes in ANC for 43 non-limed drainage ALTM lakes (R^2=0.71).

	Change in wet deposition of SO_4^{2-} and NO_3^- (eq/ha-yr)	Elevation (m)	IDW	1995 blow down event	Intercept
Coefficients	-0.0394	0.00115	0.0598	0.00577	0.000046
P value	0.0790	0.0439	0.0336	9.25E-04	0.00115

Table 12. Regression equation for volume weighted concentration of DOC for 29 non-limed ALTM lakes with available soil data from Sullivan et al. (2006) survey (R^2=0.74).

	Sum of lake SO_4^{2-} and NO_3^- (μeq/L)	O horizon C:N molar ratio	B horizon base saturation (%)	Lake true color (Pt Co)	Intercept
Coefficients	-3.01	22.0	1.35	1.22	108.0
P-value	0.0153	0.00584	0.0487	0.0313	0.254

Table 13. Regression equation for changes in concentration of DOC for 29 non-limed lakes with available soil data from Sullivan et al. (2006) survey (R^2=0.78).

	Change in sum of lake SO_4^{2-} and NO_3^- (μeq/L-yr)	Change in lake true color (Pt Co/yr)	O horizon Al and Fe (meq/100g)	Intercept
Coefficients	-2.48	2.15	0.404	-1.53
P-value	0.0128	2.15E-08	0.000221	0.355

Figures

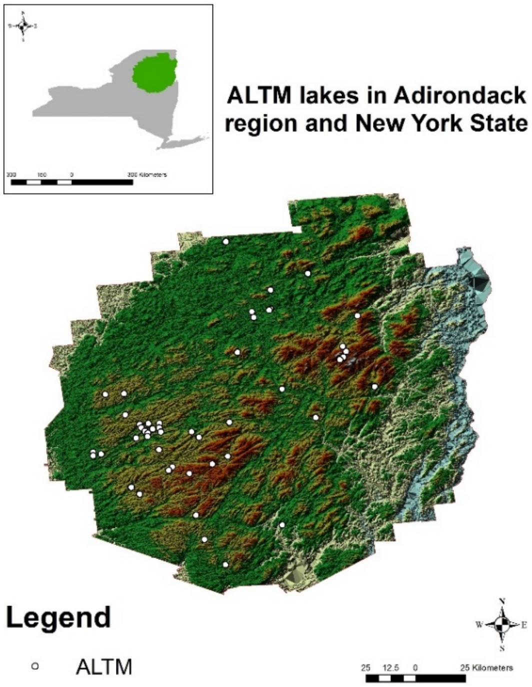

Figure 1. Location of Adirondack Long Term Monitoring lakes in the Adirondack Park of New York State.

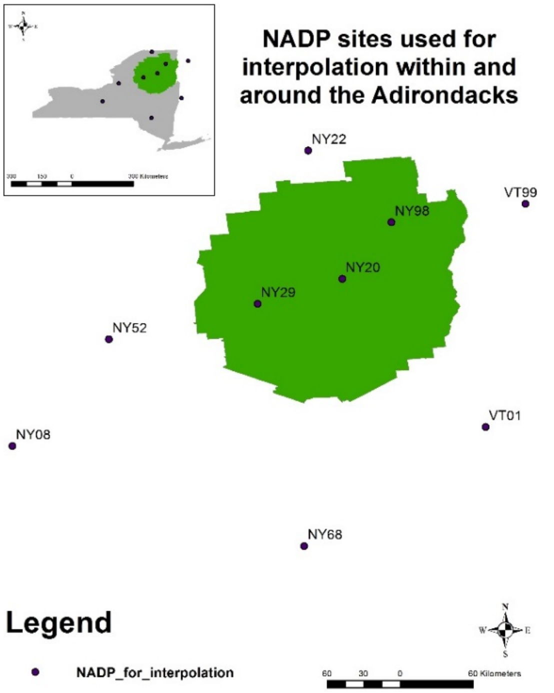

Figure 2. Location of National Atmospheric Deposition Program monitoring sites within and around the Adirondack Park for interpolation of wet deposition.

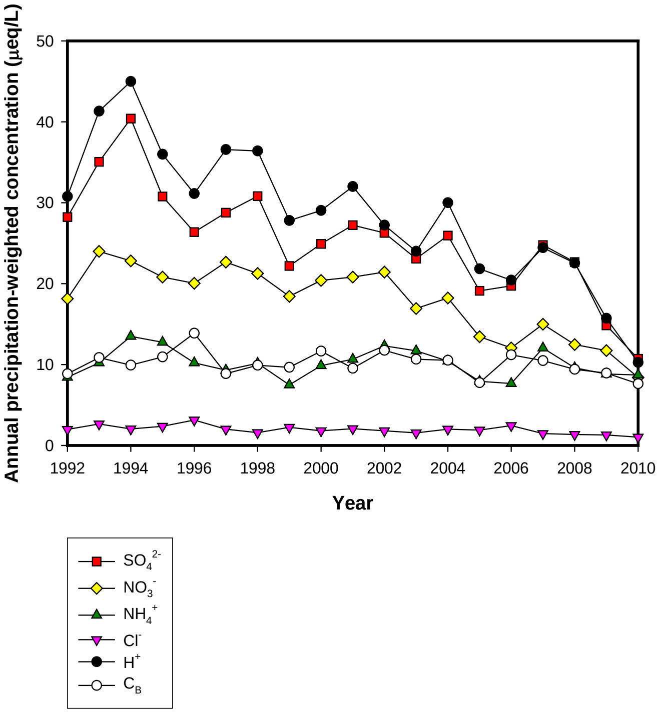

Figure 3 (a). Annual volume-weighted concentrations of major solutes in wet deposition at Huntington Forest from 1992 to 2010.

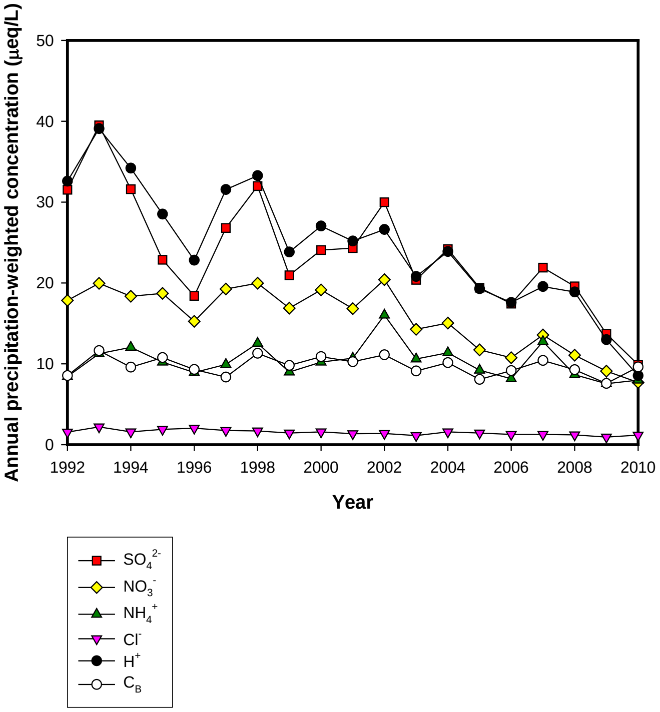

Figure 3 (b). Annual volume-weighted concentrations of major solutes in wet deposition at Whiteface Mountain from 1992 to 2010.

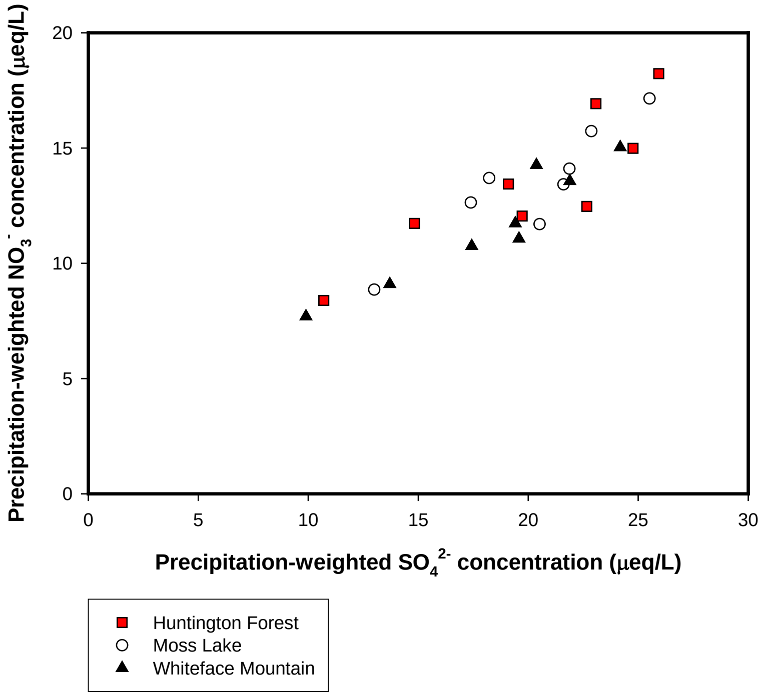

Figure 4. Relation between annual volume-weighted NO_3^- and SO_4^{2-} concentrations in wet deposition at three Adirondack NADP sites from 2003 to 2010 ($R^2=0.82$ $p<0.01$).

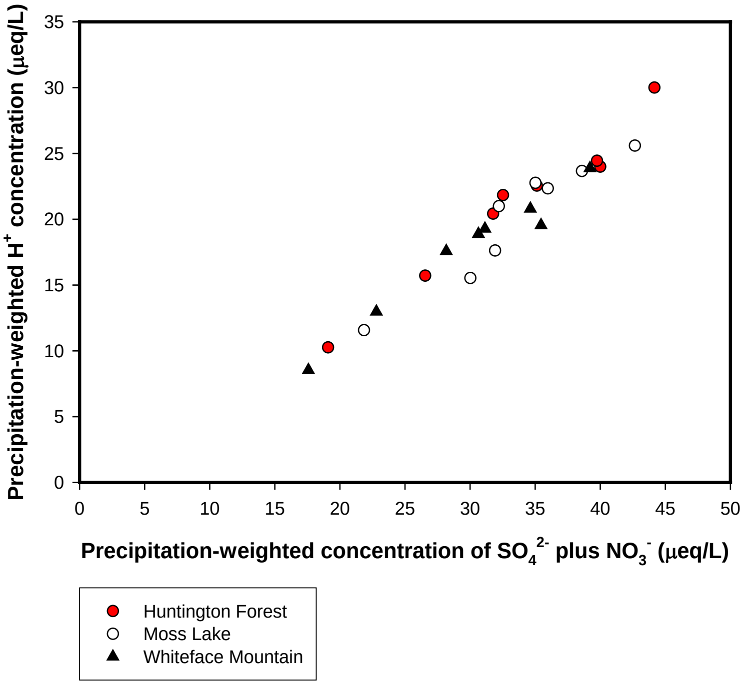

Figure 5. Relation between annual volume-weighted concentrations of proton and the sum of SO_4^{2-} and NO_3^- at three Adirondack NADP sites from 2003 to 2010 ($R^2=0.94$ $p<0.01$).

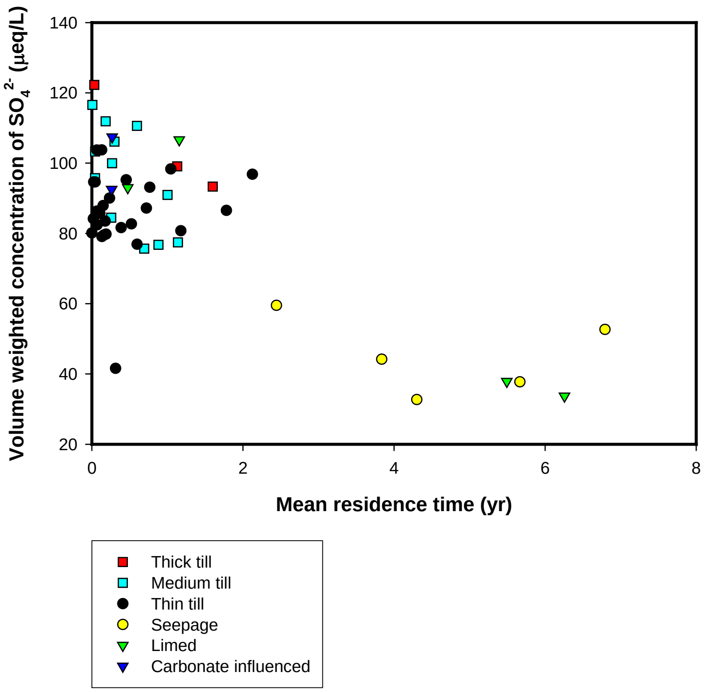

Figure 6. Relation between volume-weighted lake SO_4^{2-} concentration and mean hydraulic residence time (R^2=0.55 p<0.01 for all lakes, R^2=0.10 p<0.05 for drainage lakes).

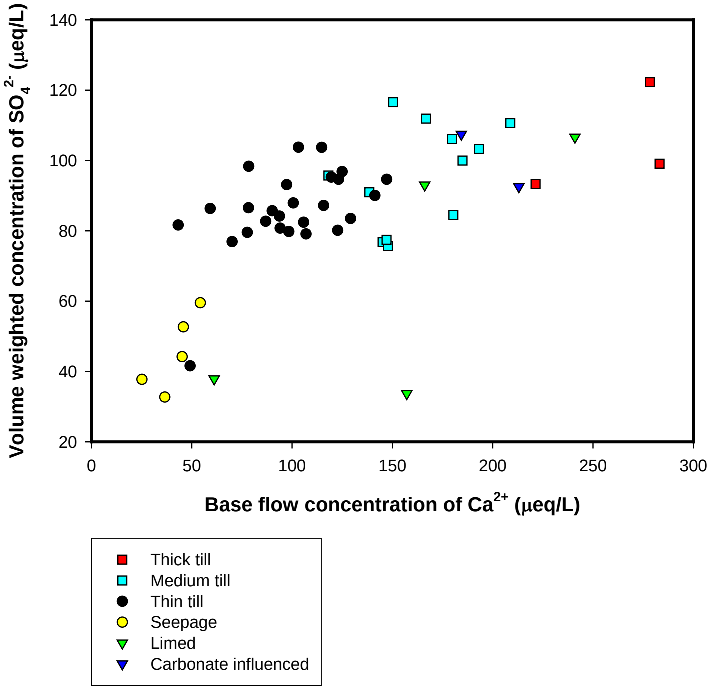

Figure 7. Relation between volume-weighted lake SO_4^{2-} concentration and base flow Ca^{2+} (R^2=0.41 p<0.01).

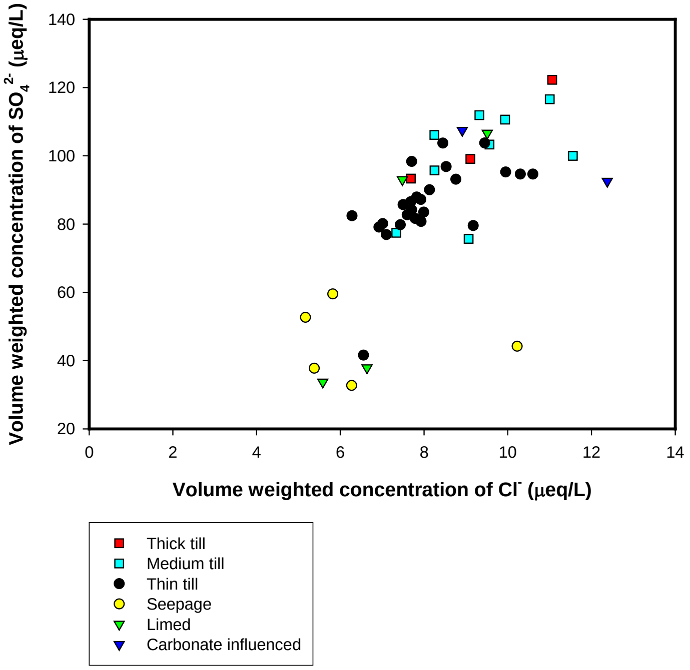

Figure 8. Relation between volume-weighted lake SO_4^{2-} concentration and Cl^- (R^2=0.44 p<0.01)

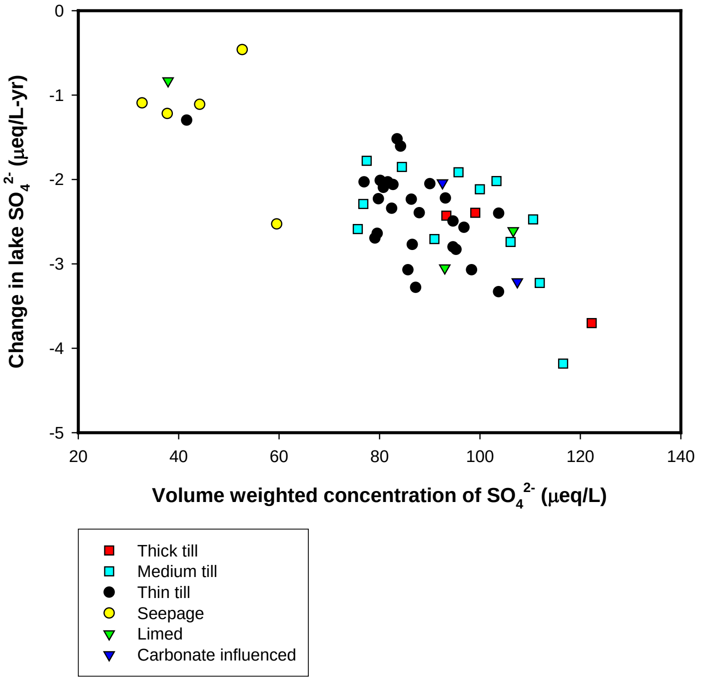

Figure 9. Relation between rate of change in lake SO_4^{2-} concentration and volume-weighted lake SO_4^{2-} concentration (R^2=0.61 p<0.01).

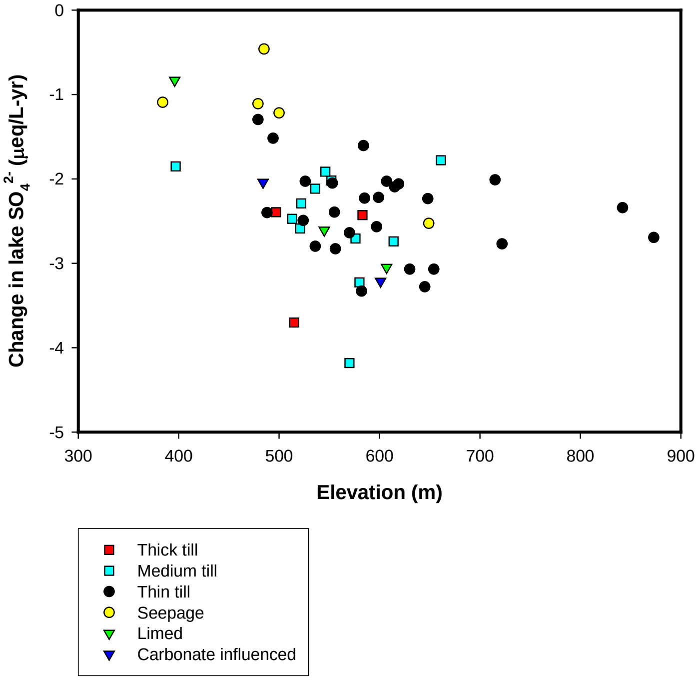

Figure 10. Relation between rate of change in lake SO$_4^{2-}$ concentration and elevation (R^2=0.19 $p<0.01$).

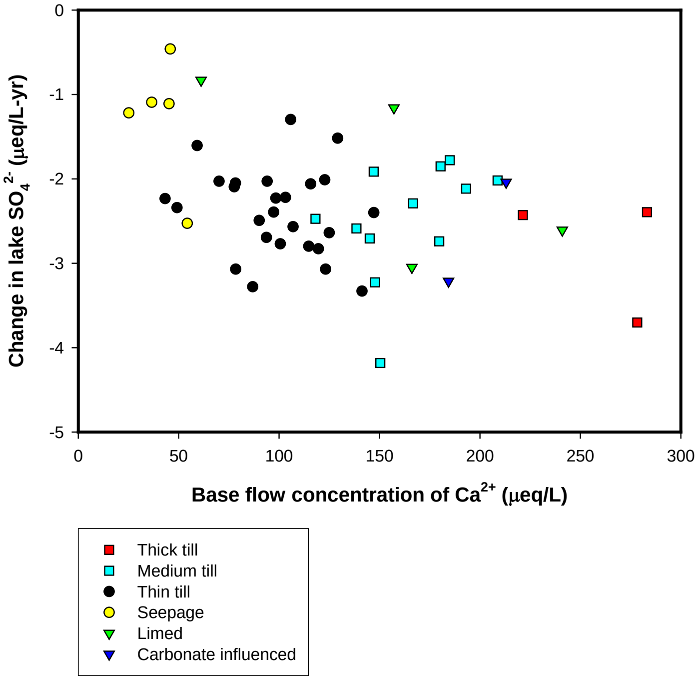

Figure 11. Relation between rate of change in lake SO$_4^{2-}$ concentration and base flow concentration of Ca^{2+} (R^2=0.19 $p<0.01$).

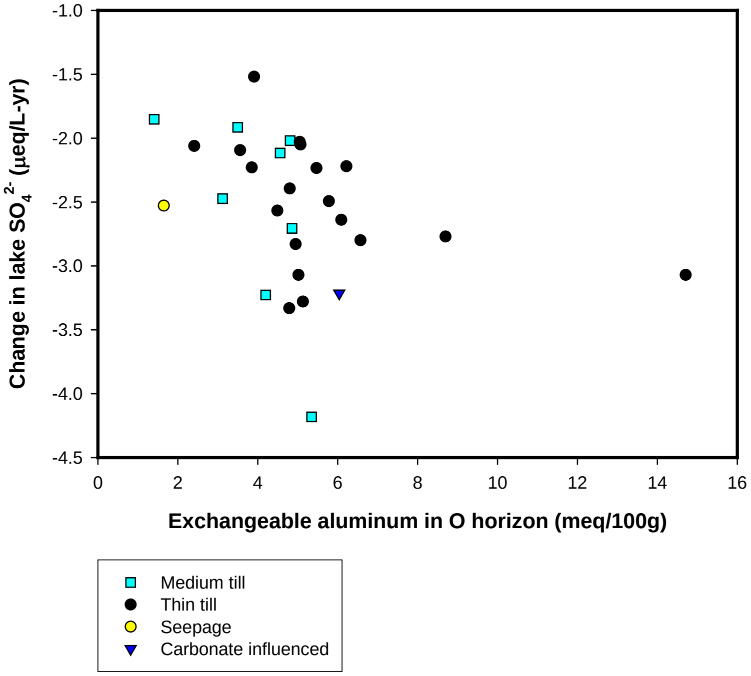

Figure 12 (a). Relation between rate of change in lake SO_4^{2-} concentration and exchangeable Al in the soil O horizon ($R^2=0.13$ $p<0.05$).

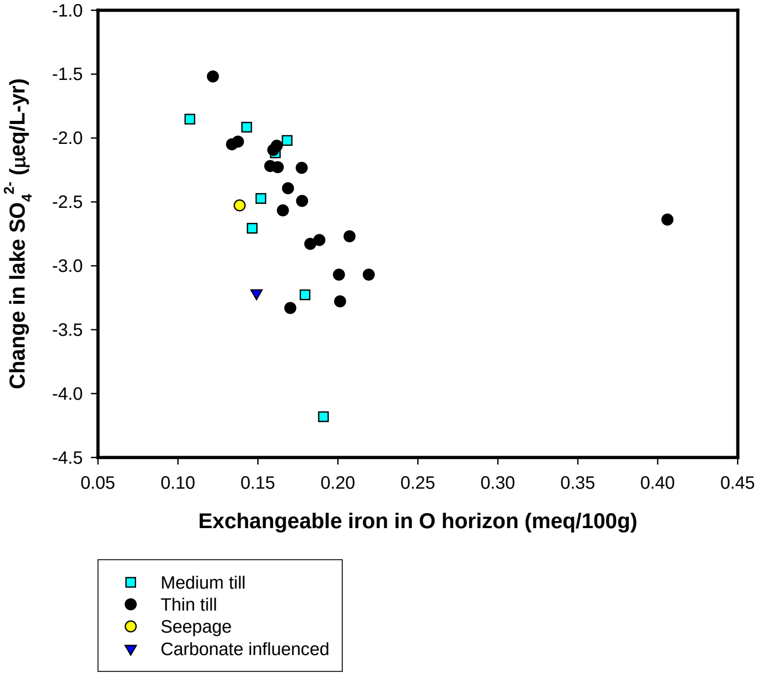

Figure 12 (b). Relation between rate of change in lake SO_4^{2-} concentration and exchangeable Fe in the soil O horizon ($R^2=0.12$ $p<0.05$).

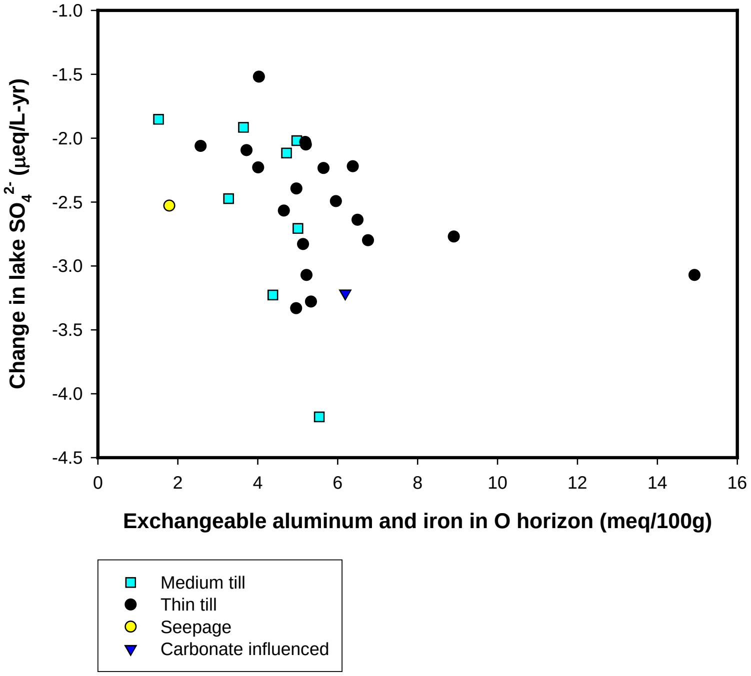

Figure 12 (c). Relation between rate of change in lake SO_4^{2-} concentration and exchangeable iron and Fe in the soil O horizon ($R^2=0.13$ $p<0.05$).

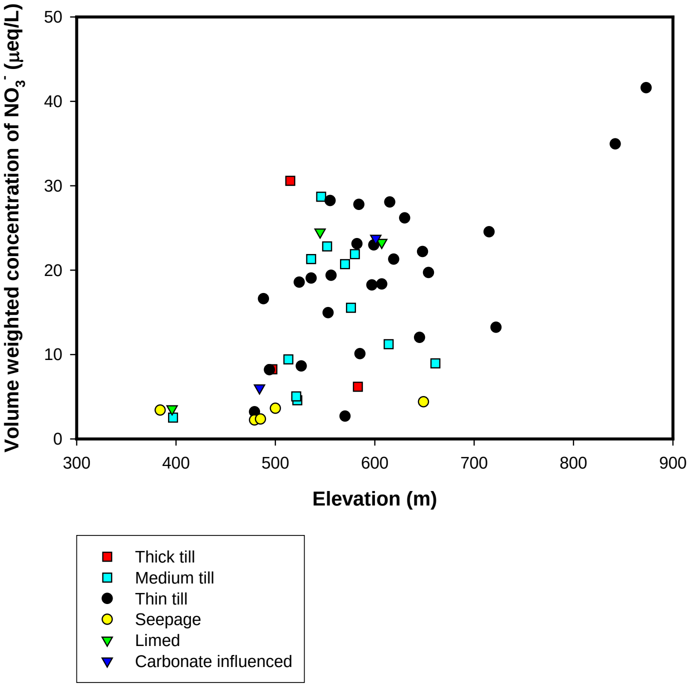

Figure 13. Relation between volume-weighted concentration of lake NO_3^- and elevation ($R^2=0.39$ $p<0.01$).

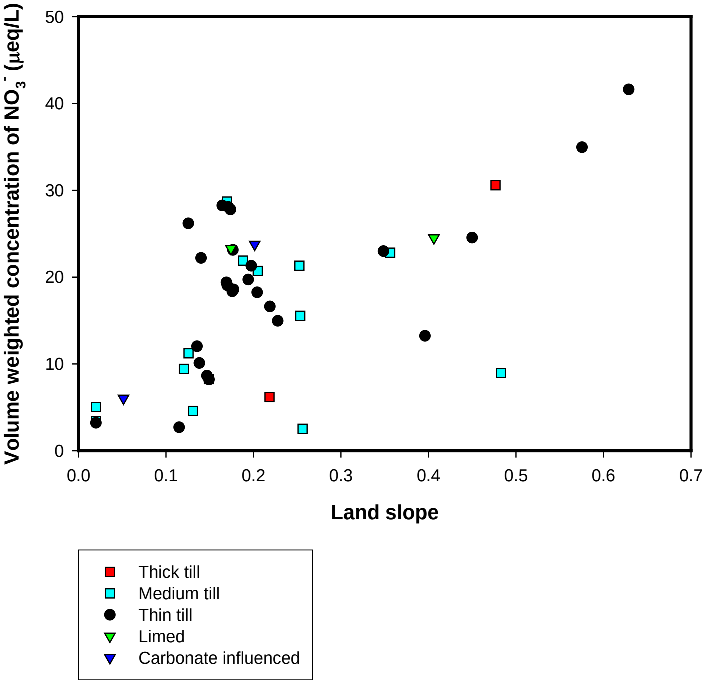

Figure 14. Relation between volume-weighted concentration of lake NO_3^- and land slope (R^2=0.34 $p<0.01$).

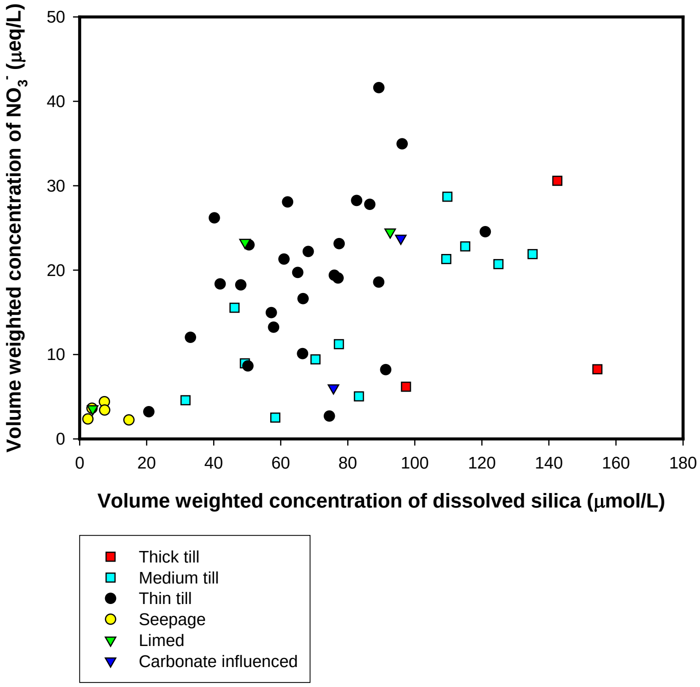

Figure 15. Relation between volume-weighted concentration of lake NO_3^- and dissolved SiO_2 (R^2=0.29 $p<0.01$).

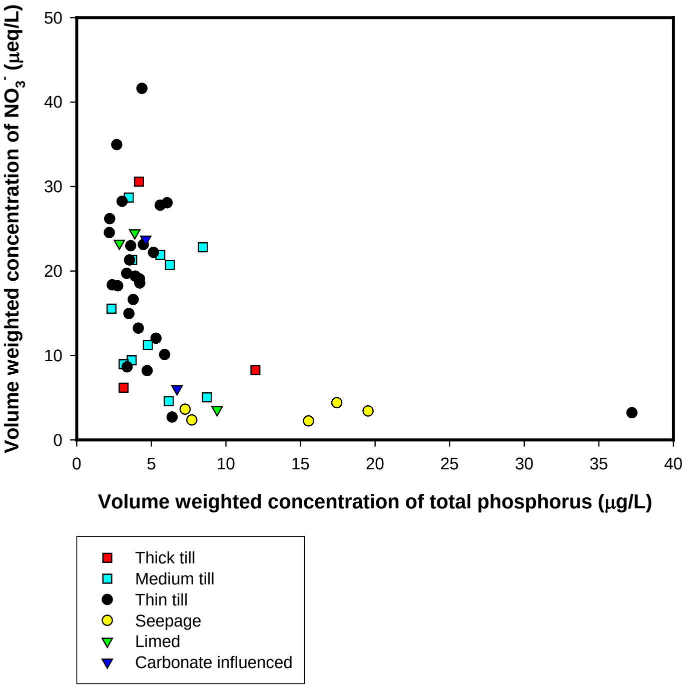

Figure 16. Relation between volume-weighted concentration of lake NO_3^- and total phosphorus ($R^2=0.25$ $p<0.01$).

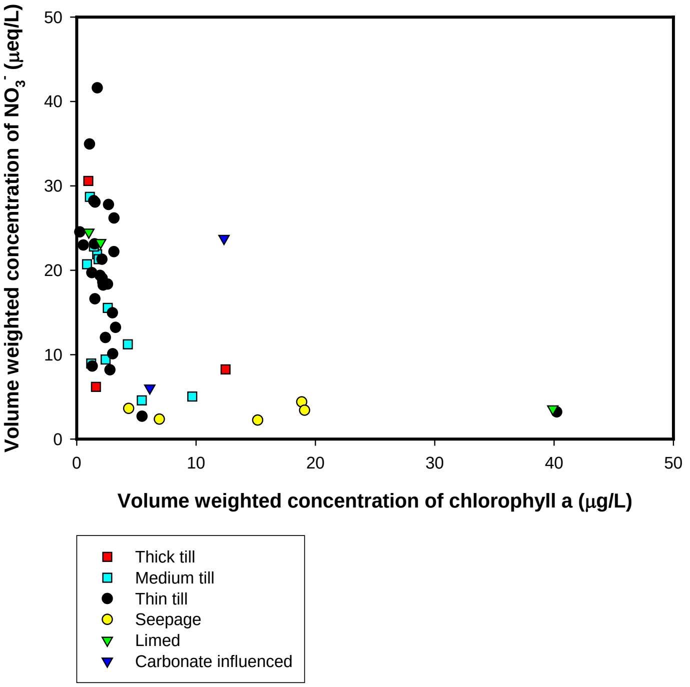

Figure 17. Relation between volume-weighted concentration of lake NO_3^- and chlorophyll a ($R^2=0.27$ $p<0.01$).

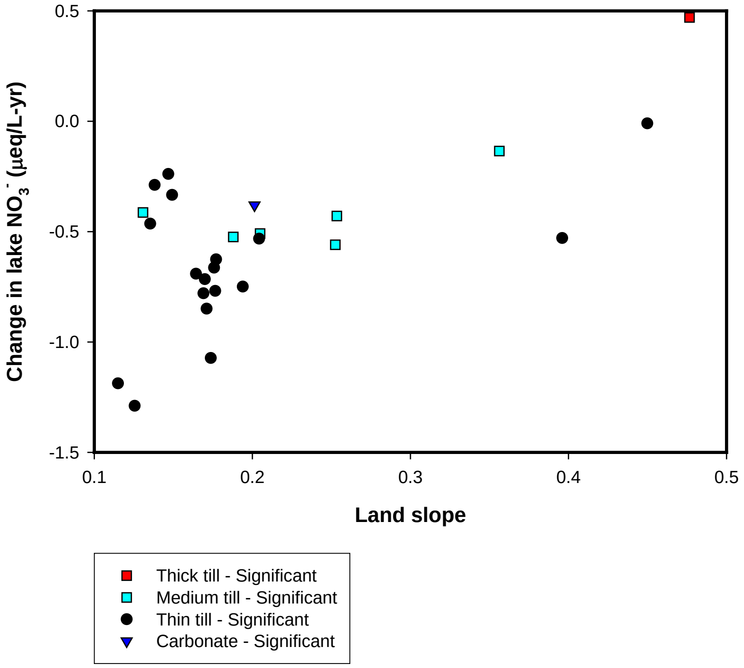

Figure 18. Relation between significant change in lake NO_3^- concentration and land slope (R^2=0.44 p<0.01).

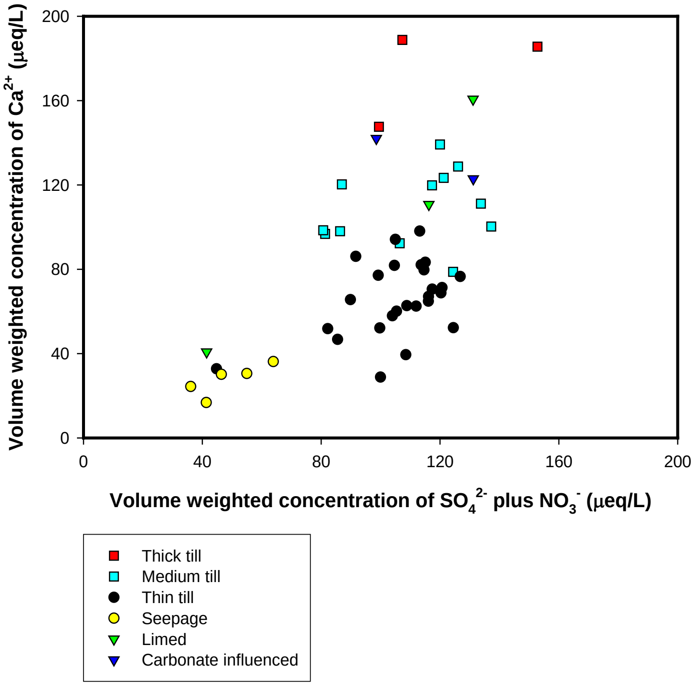

Figure 19. Relation between volume-weighted concentrations of lake Ca^{2+} and the sum of SO_4^{2-} and NO_3^- (R^2=0.29 p<0.01 for all lakes, R^2=0.19 p<0.01 for drainage lakes).

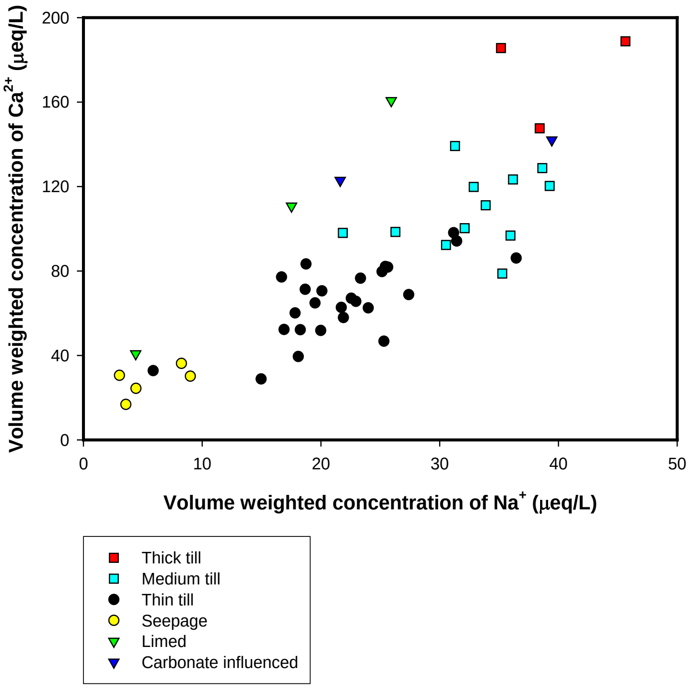

Figure 20. Relation between volume-weighted concentrations of lake Ca^{2+} and Na^{+} (R^2=0.58 $p<0.01$).

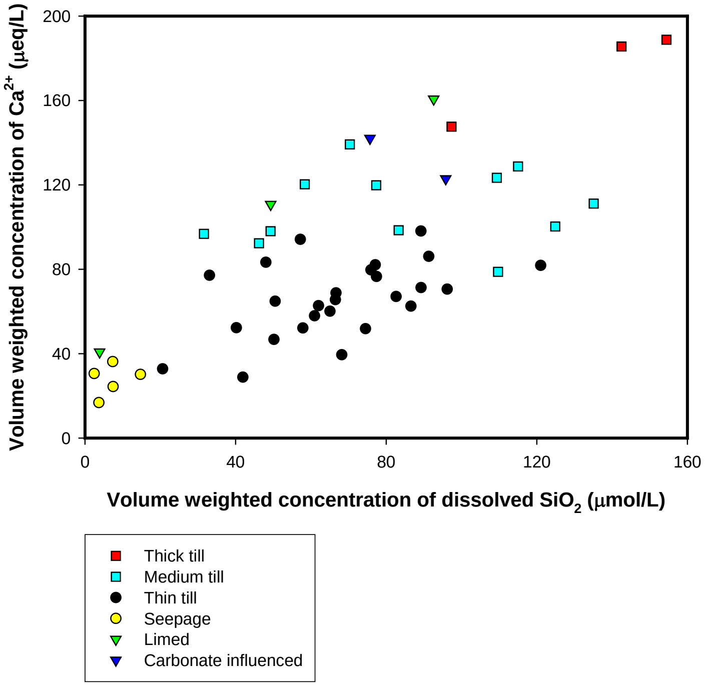

Figure 21. Relation between volume-weighted concentration of lake Ca^{2+} and dissolved SiO_2 (R^2=0.45 $p<0.01$).

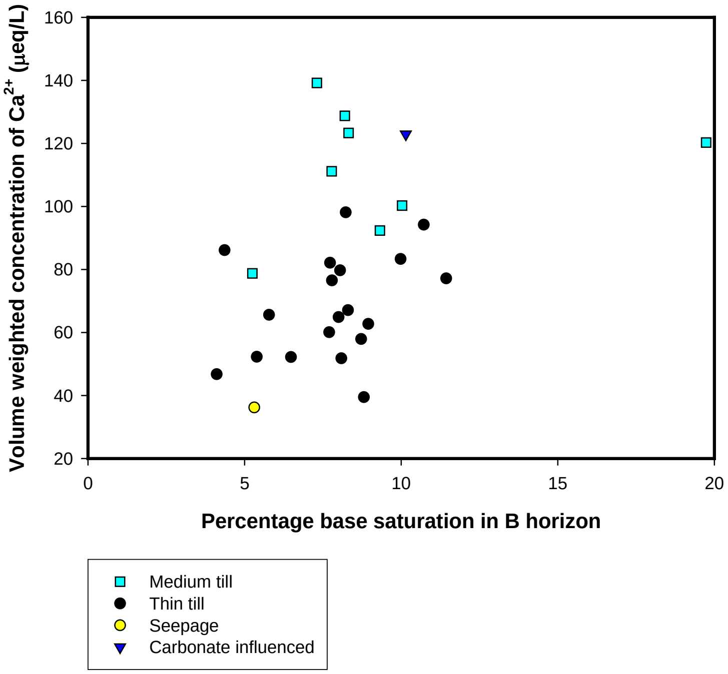

Figure 22. Relation between volume-weighted concentration of lake Ca^{2+} and percentage base saturation in the soil B horizon ($R^2=0.17$ $p<0.05$).

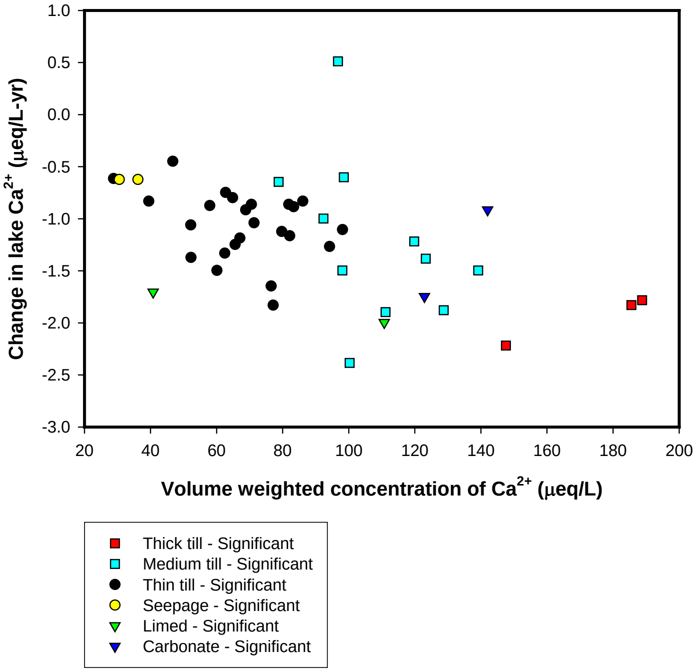

Figure 23. Relation between rate of significant change in lake Ca^{2+} concentration and volume-weighted lake Ca^{2+} concentration ($R^2=0.23$ $p<0.01$).

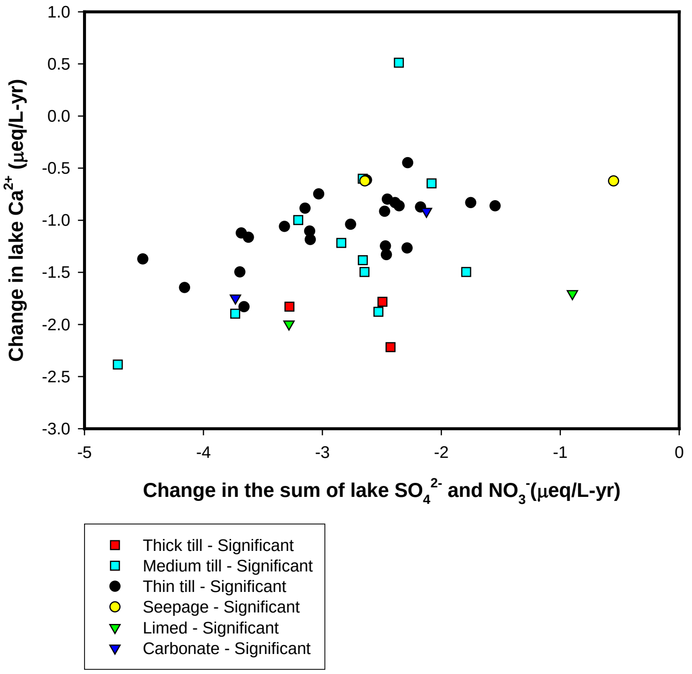

Figure 24. Relation between rates of change in lake Ca^{2+} and the sum of lake SO_4^{2-} and NO_3^- ($R^2=0.17$ $p<0.01$).

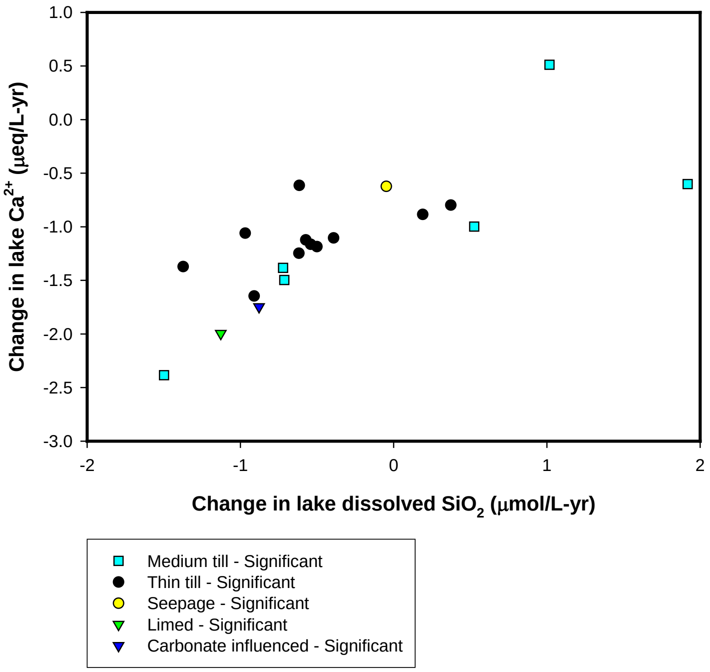

Figure 25. Relation between rates of change in lake Ca^{2+} and dissolved SiO_2 ($R^2=0.56$ $p<0.01$).

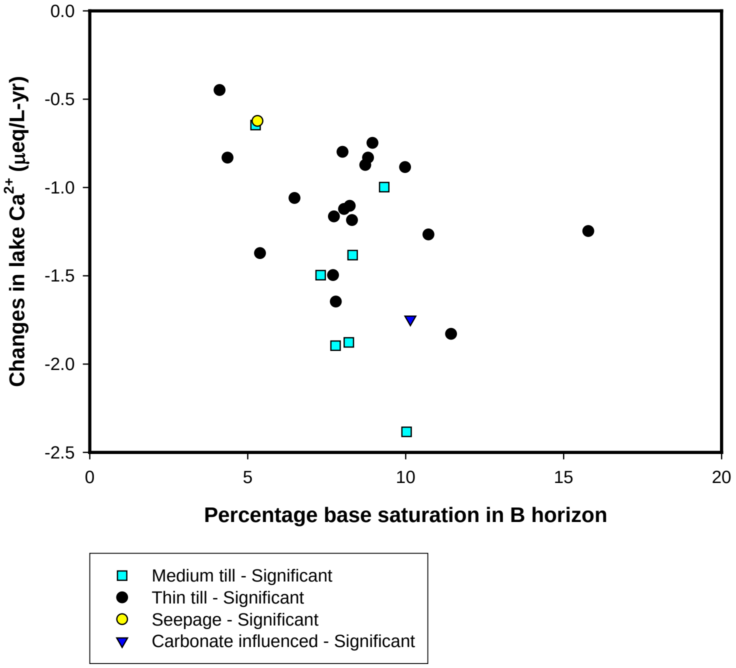

Figure 26. Relation between rates of change in lake Ca^{2+} concentration and percentage base saturation in the soil B horizon (R^2=0.22 p<0.05).

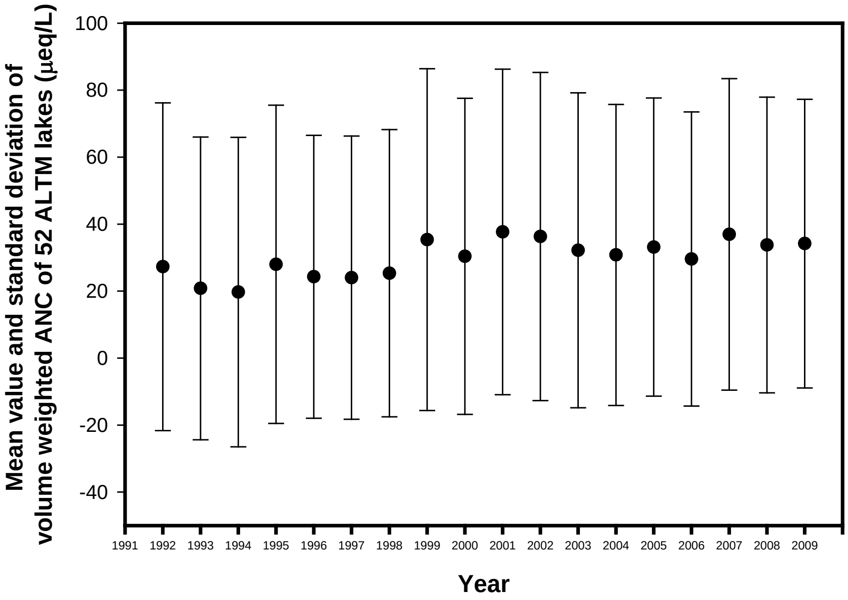

Figure 27. Annual volume-weighted concentrations of ANC starting 1992 (points stand for mean values; vertical bars stand for standard deviations).

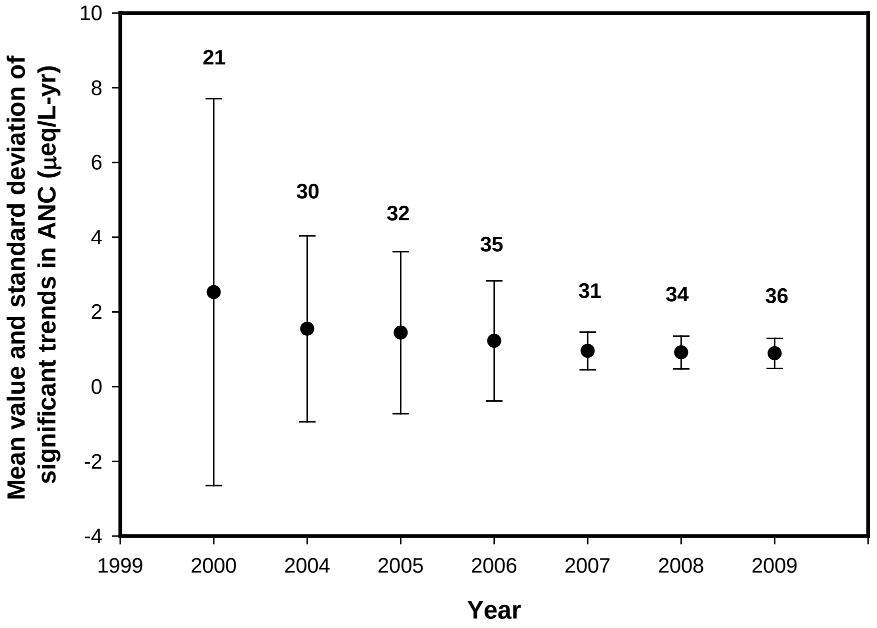

Figure 28. Annual updates of significant long-term trends in ANC starting 1992 (points stand for mean values; vertical bars stand for standard deviations; numbers above vertical bars indicate lakes showing significant trends).

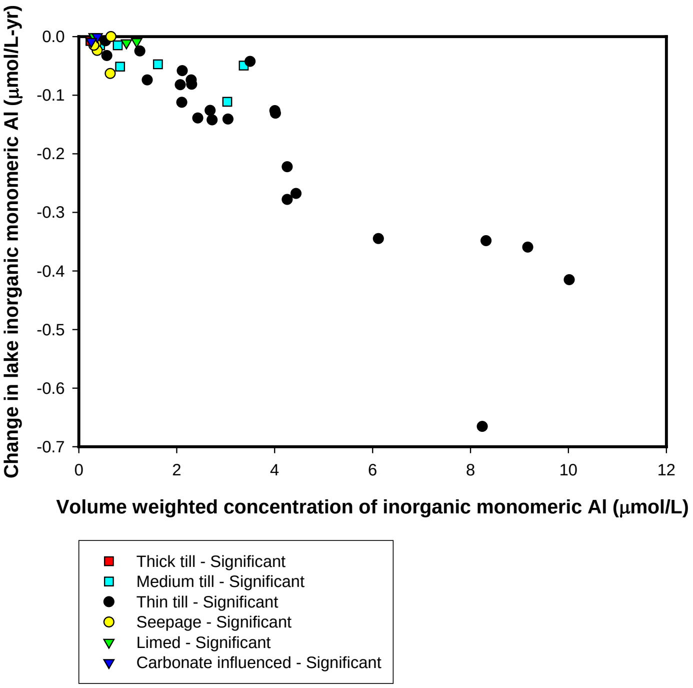

Figure 29. Relation between rate of change in lake inorganic monomeric Al concentration and volume-weighted lake inorganic monomeric Al concentration (R^2=0.83).

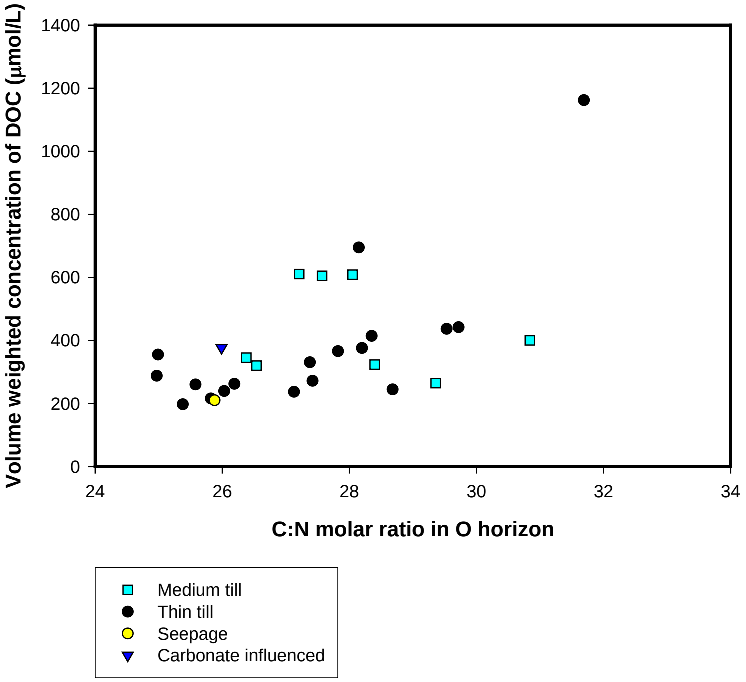

Figure 30. Relation between volume-weighted concentration of lake DOC and C:N ratio in the soil O horizon (R^2=0.24 $p<0.05$).

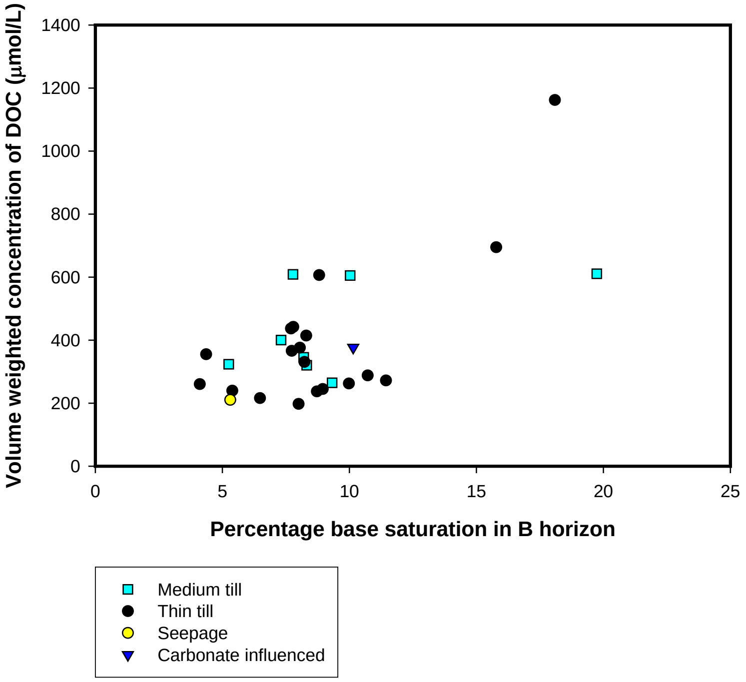

Figure 31. Relation between volume-weighted concentration of lake DOC and percentage base saturation in the soil B horizon (R^2=0.45 $p<0.01$).

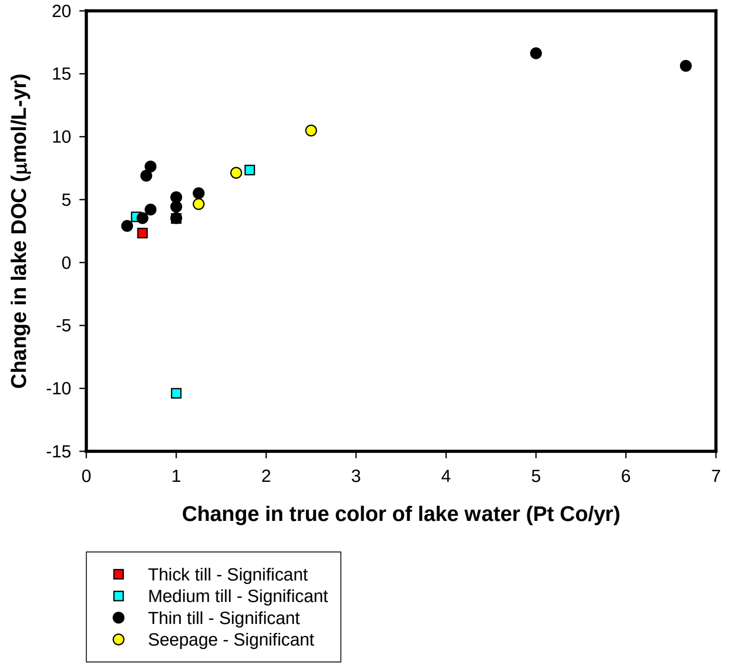

Figure 32. Relation between rates of change in lake DOC concentration and true color of lake water (R^2=0.51 $p<0.01$).

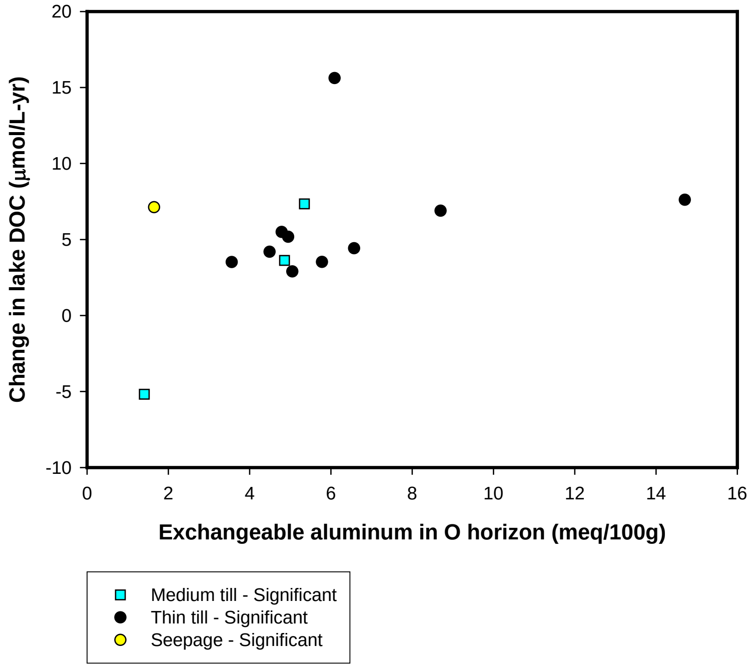

Figure 33 (a). Relation between rate of change in lake DOC concentration and exchangeable Al in the soil O horizon (R^2=0.19 $p<0.05$).

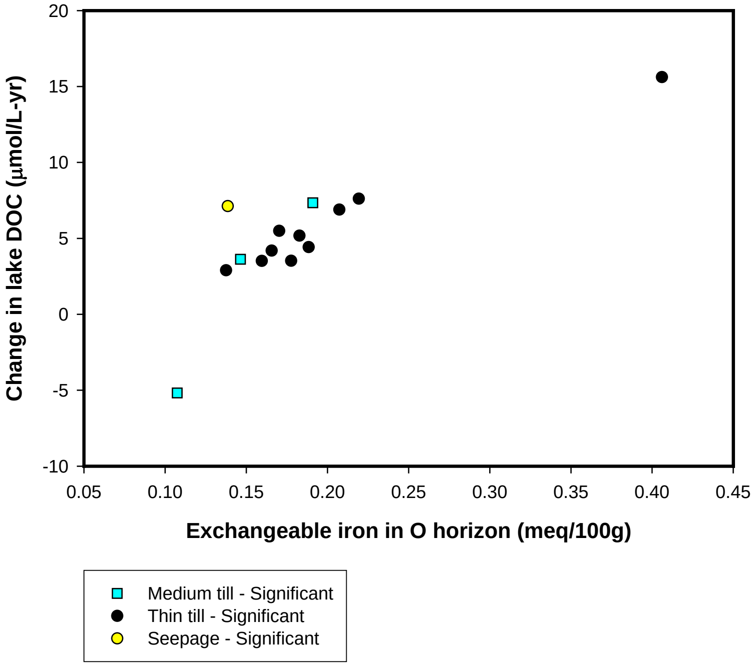

Figure 33 (b). Relation between rate of change in lake DOC concentration and exchangeable Fe in the soil O horizon (R^2=0.66 p<0.01).

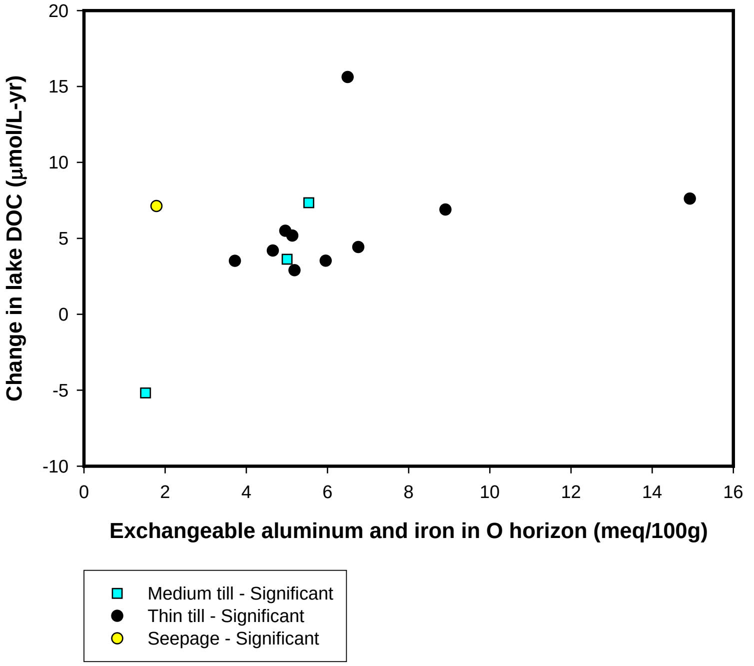

Figure 33 (c). Relation between rate of change in lake DOC concentration and exchangeable Al and Fe in the soil O horizon (R^2=0.21 p<0.05).

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Experience

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Publication

Mitchell, M.J., Driscoll, C.T., McHale, P.J., Roy, K.M., Dong, Z., 2013. Lake/watershed sulfur budgets and their response to decreases in atmospheric sulfur deposition: Watershed and climate controls. Hydrological Processes 27, 710-720.

Conference Presentations

Dong, Z., Driscoll, C.T., Roy, K., 2012. Landscape factors that drive the changes in acid-base chemistry in Adirondack Long-Term Monitoring lakes, Ninth Adirondack Annual Research Forum.

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