Post-Clean Air Act pH, Alkalinity, and Ecosystem Recovery of 26 Bodies of Water in the Hudson Highlands

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ABSTRACT

In 1985, 25 of 43 bodies of water surveyed in Black Rock Forest and the surrounding New York Hudson Highlands were measured as having low to nonexistent alkalinity, in addition to endangered or critical pH values. This poor regional water quality was ascribed to acid precipitation resulting from anthropogenic emissions of sulfate (SO_4^{2-}) and nitrogen oxides (NO_χ). Since 1985, however, the 1990 Clean Air Act amendment led to a significant decrease in acidic sulfate and nitrate emissions in the northeastern United States. While the local average annual precipitation pH has increased from 4.2 in 1985 to 5.1 in 2017, still not much is known about the area's potential corresponding recovery in lake chemistry and aquatic life. Six ponds in Black Rock Forest and 20 ponds in the surrounding Hudson Highlands were revisited, for a total of 26 water bodies sampled. Water samples were collected at the surface and bottom of each water body, and pH, temperature, conductivity, alkalinity, anion and cation concentrations, and pH variation with depth were measured and analyzed. Historical water chemistry and biological data on fish populations were also compiled. On the basis of pH, a greater proportion of water bodies were classified as satisfactory in 2018 than in 1985, a smaller proportion were classified as endangered, and none were classified as critical. Additionally, 13 ponds had statistically significantly higher pH in 2018 than in 1985. On the basis of alkalinity, a smaller proportion of the water bodies were classified as vulnerable to acid deposition in 2018 than in 1985, and 16 ponds had statistically significantly higher alkalinity in 2018 than in 1985. Furthermore, 15 lakes had statistically significantly lower sulfate concentrations in 2018 than in 1985, but comparisons for other anions and cations were limited due to a lack of historical data. Comparing the chemistry of six Black Rock Forest ponds to precipitation revealed that all the ponds had higher pHs and ion concentrations than precipitation, and that pH increased as pond elevation decreased. Finally, most of the ponds in BRF, except for Arthur's Pond, have gained more acid-sensitive species since 1987, with 2018 fish species abundance in both BRF and Harriman State Park appearing to positively correlate with pH. These findings suggest that most of the lakes have experienced increases in pH and alkalinity since 1985, but also that the rate and extent of chemical and biological recovery depend on other variables such as the underlying geology and surrounding environment. The results of this study serve as a baseline for future studies by providing insight on the rate and extent of chemical and biological recovery of these waters, some of which have seldom been studied since 1985. The success and importance of the Clean Air Act amendments and similar emissions controls will be quantified, and recommendations for future research and management strategies can be made for not only the U.S., but also for other anthropogenically acidified areas like Europe and eastern Asia.

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1. INTRODUCTION

The recovery of 26 lakes in the New York Hudson Highlands from the severe acidification documented in the 1980s has been evaluated in this study. First, acid deposition is defined and its deleterious effects on lake chemistry and ecology are illustrated. pH, alkalinity, and acid neutralizing capacity are then presented as three chemical measurements that are critical for quantifying and understanding how acidification harms lake ecosystems. The ways in which the Clean Air Act has mitigated these parameters are then reviewed. Finally, the experimental site of the Hudson Highlands, including Black Rock Forest, is described, as is the historic acidification of the region and the general characteristics of the sampled lakes.

1.1. History of Acid Deposition

First identified by R.A. Smith in 19th century England, acid deposition refers to the addition of strong acids from the atmosphere to the Earth's surface (Driscoll et al., 2001). Acid deposition can include rain, snow, vapors, particles, or fog. Based on data collections beginning in the early 1960s, Gene E. Likens first reported acid precipitation in North America at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire (Driscoll et al., 2001). Defined as having a pH less than 5.6, acid precipitation is caused by both natural and anthropogenic emissions of sulfur dioxide (SO_2), sulfate (SO_4^{2-}), and nitrogen oxides (NO_χ) (Hasan, 1999). Natural sources of these emissions include volcanoes, sea spray, and decomposition of vegetation, while anthropogenic sources include fossil fuel burning, smelters, vehicles, and agricultural activity (Hasan, 1999; Richardson et al., 2018).

As acid deposition reaches the surface of the Earth, its acidic components chemically react with both terrestrial and aquatic ecosystems. Surface waters are frequently subjected to acid

deposition, especially acid rain and snow, particularly at high elevations where acid precipitation has yet to be neutralized by soils during runoff. As a result of increasing anthropogenic emissions and peak acid rain formation in the 1980s, ponds and lakes in the northeastern United States have undergone significant acidification, often marked by pH values less than 5.0 and reduced alkalinity levels (McKinsey, 1997). Consequently, these regional waters have also experienced chronic and episodic toxicity that has negatively affected aquatic life (Baldigo et al., 2016). Acid precipitation represents one of the major ways through which anthropogenic pollution influences the natural environment and can be felt all over the world (Likens, 2013).

1.2. Alkalinity, Acid Neutralization Capacity, and Ion Concentrations

In addition to increases in surface water acidity, changes in a lake's alkalinity, acid neutralization capacity (ANC), and ion concentrations can further increase its susceptibility to acidification. Both alkalinity and ANC generally refer to the capacity of water to neutralize an acid, but are calculated slightly differently. While alkalinity is the difference between the total unprotonated bases of the weak acids and the protonated strong acids in the solution, ANC equals the sum of all the basic species below a specified pH threshold (Anderson, 2018). The levels of both ANC and alkalinity are largely dependent on processes such as mineral weathering and cation exchange (Driscoll et al., 2001). Specifically, the presence of hydroxides, bicarbonates, and carbonates largely determines the levels of alkalinity in natural waters, expressed as milligrams per liter (mg/L) of calcium carbonate ($CaCO_3$) or microequivalents per liter (μEq/L), where 1 mg/L of $CaCO_3$ equals 20 μEq/L. As a result, lakes with underlying geology that is rich in sedimentary carbonate rocks are high in dissolved carbonates and therefore often have high alkalinity and ANC, whereas lakes with underlying granite or

metamorphic rocks are low in dissolved carbonates and thus are also low in alkalinity and ANC. An important reference pH level for both ANC and alkalinity is pH 4.5 - the pH at which the concentration of bicarbonate ions (HCO_3^-) is 1% of the carbonic acid concentration (H_2CO_3). At this reference level, alkalinity and ANC are not only roughly equal to each other, but are also nearly zero (Anderson, 2018).

In the soils and surface waters of the northeastern United States, such as the New York Hudson Highlands region on which this study focuses, acidic deposition has increased the concentrations of protons and strong acid anions like sulfate (SO_4^{2-}) and nitrate (NO_3^-), which are thought to have leached base cations from ecosystems as they are exchanged for protons (Driscoll et al., 2001). Data from the Hubbard Brook Experimental Forest (HBEF) in New Hampshire have shown a strong correlation between high streamwater sulfate, which is itself positively correlated to SO_2 emissions, and low base cation concentrations. This correlation led to the discovery that as much as one-half of the amount of exchangeable calcium and other base cations have been depleted by decades of acid deposition (Figure 1; Likens et al., 1996, 1998). These discoveries suggest that if SO_2 and NO_χ emissions decrease, then ANC and alkalinity will subsequently increase because the amount of base cations will remain sufficient to neutralize the acidity of the soil and surface water (Likens, 2013). However, if base cations are continually exchanged and leached as a result of prominent acid precipitation, then alkalinity and ANC are reduced, and proton neutralization will not be as effective. As shown at HBEF, the declining concentrations of base cations like calcium and magnesium cause aquatic ecosystems to become increasingly sensitive to the addition of acidic substances into the atmosphere (Likens, 2013).

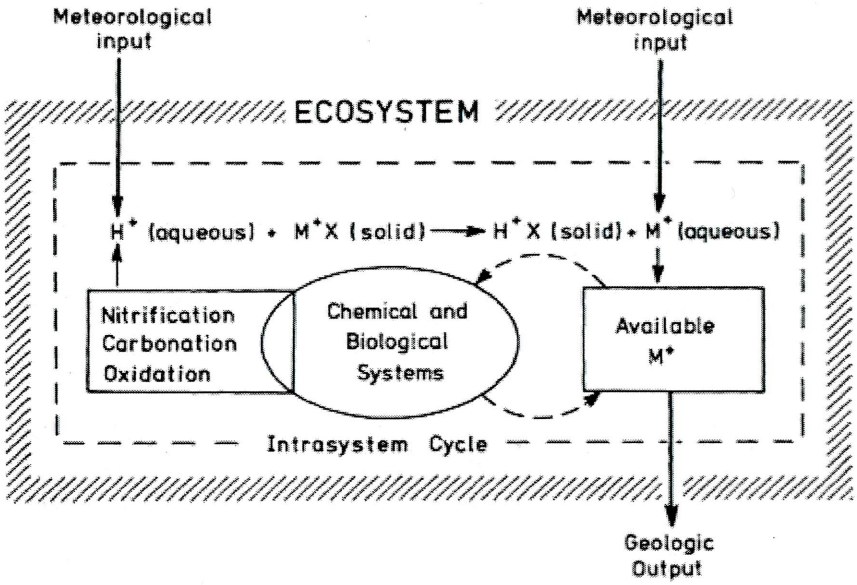

Figure 1: Diagram of theoretical leaching of base cations as a result of added H^+. M^+ represents a base cation while X is some ionic exchange substrate. When protons are added to the system, base cations are leached from the system (Likens, 2013).

The vulnerability of water bodies can be defined by their alkalinity or ANC values. According to Andrew Becker and Robert H. Boyle, waters with total alkalinity of 25 mg/L, or 500 μEq/L, are not considered vulnerable to acid deposition, while waters with total alkalinity less than or equal to 6 mg/L, or 120 μEq/L, are deemed vulnerable because their neutralizing ability can be exhausted over time with recurring acid rain (Becker & Boyle, 1986). As of 2016, the Massachusetts Acid Rain Monitoring Project ranked freshwater according to alkalinity as follows: 0 mg/L (0 μEq/L) with a pH below 5.0 = Acidified, 0-2 mg/L (0-40 μEq/L) = Critical, 2-5 mg/L (40-100 μEq/L) = Endangered, 5-10 mg/L (100-200 μEq/L) = Highly Sensitive, 10-20 mg/L (200-400 μEq/L) = Sensitive, and 20+ mg/L (400+ μEq/L) = Not Sensitive (Massachusetts Water Watch Partnership, 2016). Both alkalinity and ANC are therefore closely linked to the level of acidification of surface waters and the effects of long-term acid deposition.

Commonly used as indicators of water quality, the concentrations of the major anions and cations in bodies of water are also important for evaluating a lake's recovery from acidification. As previously mentioned, measuring the concentrations of the major base cations such as Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+} over time can determine if the alkalinity and ANC of a body of water have been depleted, and therefore if the body of water is particularly vulnerable to acidification. Measuring the base cation concentrations over time can also reveal weathering patterns and potentially the type of underlying bedrock of the surrounding watershed (Berner & Berner, 2012). Similarly, because major anions like SO_4^{2-} and NO_3^{-} are often correlated with SO_2 and NO_χ emissions, measuring the concentrations can reveal how acid deposition affects bodies of water. This directly facilitates the evaluation of lake recovery from acidification over time. Adding in measurements of other anions like chloride (Cl^{-}) can allow further conclusions to be drawn about other types of anthropogenic impacts such as road salt pollution, and can also lead to the classification of different water types based on their water chemistry (Richardson et al., 2018). Calculating the charge balance between the cations and anions can also indicate to what extent the ecosystem obeys electroneutrality, as well as reflect the sampling precision and accuracy (Anderson, 2018).

1.3. Impact on Aquatic Ecosystems

Through its relation to air pollution and complex effects on the chemical composition of surface waters, acid deposition contributes greatly to biological and ecosystem stress. In 1985, the New York State Department of Environmental Conservation classified bodies of water with a pH of 6.0 or greater as "satisfactory," meaning that fish populations were generally present. Meanwhile, waters with a pH of 5.0-6.0 were classified as "endangered," meaning fish

populations were present but at reduced levels. Furthermore, bodies of water with a pH of less than 5.0 were deemed "critical," in which fish populations were low to non-existent (Becker & Boyle, 1986). The negative effect of low pH on fish populations was demonstrated by the Adirondack Lakes Survey Corporation, which monitored 1469 lakes between 1984 and 1987 in the New York Adirondack region. This survey found that over three-fourths of the lakes in which fish were not captured had pHs below 5.0, in addition to zero or negative acid neutralizing capacities and low calcium concentrations (Adirondack Lakes Survey Corporation, 2019).

This correlation between low pH and fishless lakes occurs because low pH alters the salt balance in the body tissue and blood plasma of freshwater fish, causing physical deformities, behavioral modifications, and death (Becker & Boyle, 1986; Charifson et al., 2015). At a pH between 5.0 and 6.0, fish such as the fathead minnow (*Pimephales promelas*) can survive but show abnormal behavior, modified swimming patterns, hunchbacks, and smaller-than-average heads (Charifson et al., 2015). For many species of fish and other acid-sensitive organisms like reptiles, lake acidification inhibits reproduction by reducing egg production and viability (Charifson et al., 2015). These deleterious effects are largely due to the mobilization of aluminum (Al) and similar metals at low pHs. Because the solubility of aluminum increases with decreasing pH, acidic deposition on soil and in water increases aluminum mobilization and produces toxic inorganic forms (Driscoll et al., 2001). For example, aluminum can bind to phosphorus and inhibit phosphorus uptake by organisms - the injurious effects of which are amplified through bioaccumulation at higher levels of the food chain (Sparling, 1990).

Numerous studies have successfully shown the correlation between decreasing pH values - accompanied by increasing aluminum concentrations and therefore water toxicity - and

decreasing species richness by the elimination of acid-sensitive species. In the Adirondack and Hudson Highland regions, some of the first species to be negatively affected by pH values less than 6.0 are Atlantic salmon (*Salmo salar*), redbreast sunfish (*Lepomis auritus*), and minnows (*Phoxinus phoxinus*). In contrast, the fish species most commonly caught in the same environments were yellow perch (*Perca flavescens*), chain pickerel (*Esox niger*), brown bullhead (*Ameiurus nebulosus*), golden shiner (*Notemigonus crysoleucas*), and brook trout (*Salvelinus fontinalis*), thus showing greater tolerance of acidic conditions (Driscoll et al., 2001). In addition to the effects on fish, the impact of acid rain on turtles, specifically the painted turtle (*Chrysemys picta picta*) has also been investigated. Studies throughout the 1990s on the painted turtle population at Black Rock Forest, for example, have indicated positive correlations between pH and pond health with turtle abundance and growth rate, as well as relationships with sex, age, and size distribution (McKinsey, 1997).

The first phase of ecosystem recovery from acidification is the chemical recovery of the water, including increases in pH, ANC, and alkalinity, as well as corresponding decreases in toxic metals like aluminum (Baldigo et al., 2016). Studies suggest that the time scale of water chemistry recovery varies widely and greatly depends on factors such as the magnitude of acid deposition decrease, the balance between depletion and input of exchangeable base cations in soils, and the extent and rate at which sulfate and nitrate are released into drainage waters. The second phase of ecosystem recovery is biological recovery, which can occur only if the water chemistry recovers enough to promote survival and reproduction. While the time scale on chemical recovery for a specific body of water may be predicted using experimental models, the time required for biological recovery is still uncertain (Driscoll et al., 2001).

1.4. The Clean Air Act

Following the recognition of acid deposition as a severe environmental threat that affects chemical and aquatic ecosystem health, the United States federal government enacted policy changes to specifically target acid precipitation. The 1970 Clean Air Act Amendment (CAAA) saw the beginning of sulfur dioxide (SO_2) emissions controls in the United States, while more rigorous regulations decades later further required significant decreases in both sulfur dioxide and nitrogen oxides (NO_χ). In 1990, Congress passed Title IV of the CAAA's Acid Deposition Control Program to further reduce SO_2 and to start controlling NO_χ emissions from electric utilities. One of the program's goals as part of the 1990 CAAA was, by the year 2000, to reduce SO_2 emissions by 9.1 million metric tons/year and NO_χ emissions by 1.1 million metric tons/year (Likens, 2013). As a result of these policies, national SO_2 emissions decreased by as much as 38% by the early 2000s, but NO_χ emissions remained relatively constant, indicating that additional reductions in NO_χ emissions were required after 2000 (Driscoll et al., 2003).

To address this need, the Acid Deposition Control Program redefined new goals for 2010, now aiming to reduce the original 1980 SO_2 emissions by 50% and to decrease NO_χ emissions by 1.8 million metric tons per year (Driscoll et al., 2001). Though the legislation failed to establish this specific cap on NO_χ emissions, it did successfully provide caps on total utility and non-utility emissions of SO_2 on the order of millions of metric tons per year (Driscoll et al., 2001). As a result, there were still significant additional declines in the national U.S. emissions for both SO_2 and NO_χ between 2000 and 2010 (Figure 2; Likens, 2013).

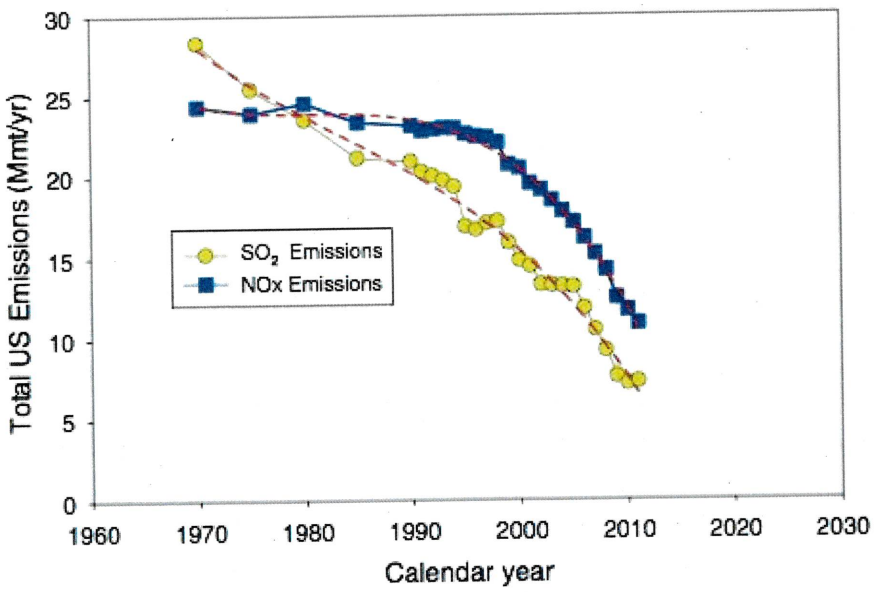

Figure 2: Total US SO_2 and NO_x emissions from 1970 to 2010. Total emissions are in million metric tons per year (Mmt/yr), which is equal to 1,000,000 metric tons per year. The third-order polynomial regressions have an R^2 values of 0.99. Data from U.S. Environmental Protection Agency (Likens, 2013).

More recently, there have been even further decreases in SO_2 and NO_X emissions that are thought to be an indirect benefit of the reduction in CO_2 emissions by the 2015 Clean Power Plan (Baldigo et al., 2016). In correlation with these decreases in anthropogenic sulfur and nitrogen emissions, there was an observed increase in precipitation pH in the northeastern United States from 4.2 in 1985 to 5.1 in 2017 (National Atmospheric Deposition Program, 2019).

1.5. Site Description: Hudson Highlands and Black Rock Forest

Studying historically acidified areas such as the Hudson Highlands can quantify the effects of the Clean Air Act and similar emissions controls. Located about 50 miles north of New York City on both sides of the Hudson River, the Hudson Highlands are part of the Reading Prong, which spans nearly 200 miles northeast from Reading, Pennsylvania to western Connecticut (Becker & Boyle, 1986). The Highlands are also south of the more substantial mountain ranges of the Catskills and Adirondacks. The climate in the Hudson Highlands is

temperate, meaning it has warm summers and cold winters, with a mean maximum July temperature of 30 ◦C (86 ◦F) and a mean minimum January temperature of −7 ◦C (19.4 ◦F). Mean monthly precipitation is nearly uniformly distributed over the year, and varies between 88 mm and 100 mm (Warrach et al., 2006).

At the intersection of the Hudson Highlands and the Hudson River Basin is Black Rock Forest (BRF), a 3,870-acre private, non-profit forest in Cornwall, NY that conducts and fosters research, education, and conservation programs (Figure 3; Black Rock Forest, n.d.). The preserve is home to oak-dominated, secondary growth forests that developed after the Pleistocene glaciers retreated nearly 14,000 years ago (Black Rock Forest, n.d.; Warrach et al., 2006). The forest features seven ponds/reservoirs and spans elevations from 110 meters to roughly 400 meters above sea level (Hasan, 1999).

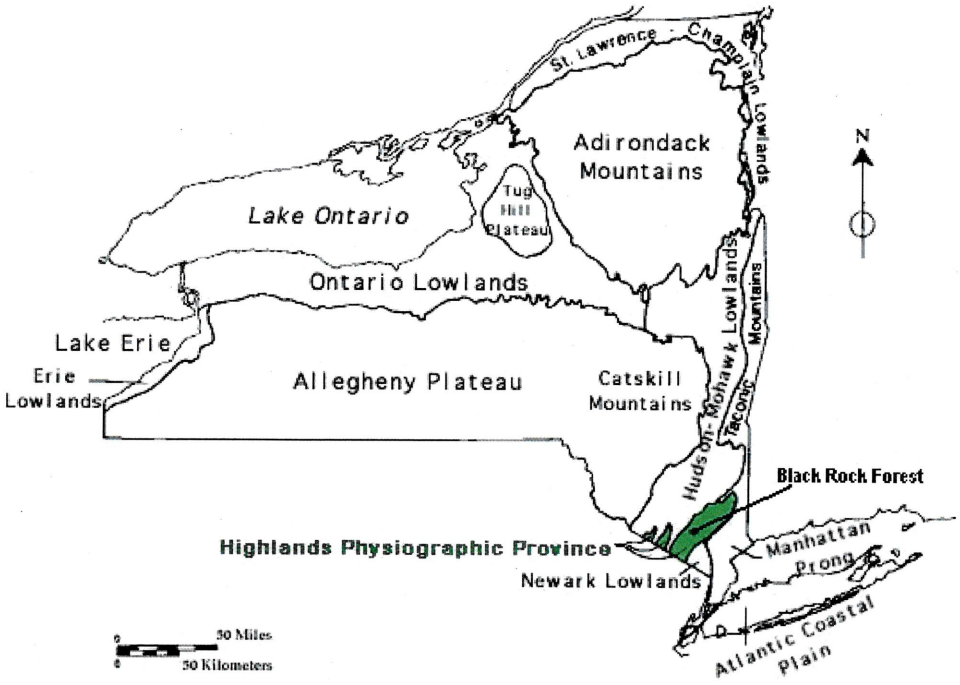

Figure 3: Location of the Hudson Highlands region and Black Rock Forest relative to the other regions of New York state. The area highlighted in green represents the Hudson Highlands, labeled as Highlands Physiographic Province in the map, while the black dot within the highlighted area locates Black Rock Forest (Black Rock Forest, n.d.).

While six ponds were studied in Black Rock Forest, the remaining 20 bodies of water were located in Harriman State Park, Sterling Forest State Park, Clarence Fahnestock State Park, or on private property adjacent to these nature preserves. Located in Rockland and Orange counties just south of Black Rock Forest, Harriman State Park features 31 lakes and reservoirs, making it the second largest park in the system (New York State Parks, Recreation and Historic Preservation, 2019b). Just west of Harriman and southwest of BRF is Sterling Forest State Park in Tuxedo, NY. The park comprises 21,935 acres of deep-forest habitat that is critical for the survival of many resident and migratory species (New York State Parks, Recreation and Historic Preservation, 2019c). Clarence Fahnestock State Park is located directly east across the Hudson River from BRF in Putnam and Dutchess counties. It covers 14,086 acres with two lakes and four ponds thought to contain bass, pickerel, perch, and brook trout (New York State Parks, Recreation and Historic Preservation, 2019a).

The geologic characteristics of the entire Hudson Highlands - including Black Rock Forest and Harriman, Sterling Forest, and Clarence Fahnestock state parks - make the region especially susceptible to the effects of acid rain. Underlying the Highlands and the entire Reading Prong Province are one billion-year old Precambrian meta-granites, amphibolite gneisses, and marble that metamorphosed from volcanic rocks, sandstones, and glacially-deposited limestone till (Léger et al., 1996). Additionally, Black Rock Forest is known to contain magnetite (Fe_3O_4) and chloride-rich biotite ($K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$) (Léger et al., 1996). Consisting of large, bare expanses of this bedrock, the hills and mountains of the region reach a maximum elevation of 400 meters and therefore receive direct inputs of acid precipitation. Aside from the marble, much of the underlying metamorphic and igneous bedrock

is low in calcium carbonate, resulting in poor buffering ability and therefore naturally low alkalinity values (Hasan, 1999). These geologic features characterize the region as having soils with limited available exchangeable cations, thus increasing the proportion of bodies of water that are acidic and acid-sensitive (Driscoll et al., 2003).

1.6. Acidification of the Hudson Highlands Water Bodies

Though acid deposition threatens ecosystems all over the United States and the world, the New York Hudson Highlands region in the northeastern United States is a particularly vulnerable region. As a result of the prevailing westerly winds, pollutants emitted in the midwestern United States are often deposited in the northeastern United States (Richardson et al., 2018). During this transport, some of the emitted SO_2 and NO_χ are converted to sulfuric and nitric acid, thus forming acid precipitation that enters the surface waters of the northeastern United States. Black Rock Forest and the surrounding Hudson Highlands have historically experienced acidification of the soil and surface water, with the lowest precipitation pH of 4.2 occurring in 1985, as measured by the precipitation collection station located at BRF (Figure 4). The precipitation pH measured at Black Rock Forest has since increased to 5.1 in 2017, which is a ten-fold decrease in the hydrogen ion concentration. Despite observing this statistically significant increase in pH ($p < 0.001$), still not much is known about the area's potential corresponding recovery in lake chemistry and aquatic life (Figure 4; National Atmospheric Deposition Program, 2019).

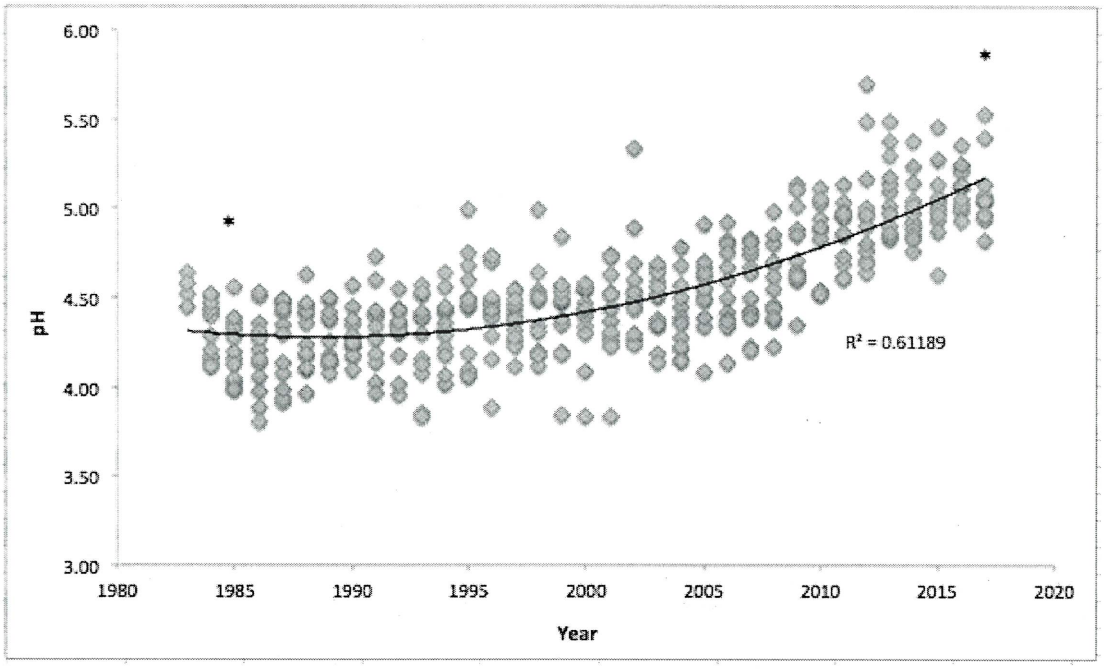

Figure 4: pH of precipitation collected at site NY99 from 1983 to 2017. The gray diamonds represent monthly pH values for each year, and the solid black line shows a 2nd order polynomial trendline with an R^2 value of 0.61189. The asterisks above the years 1985 and 2018 indicate statistically significant differences ($p < 0.05$). Data was retrieved from the National Atmospheric Deposition Program National Trends Network (NTN) Site NY99 operated by Black Rock Forest Consortium in Cornwall, NY (National Atmospheric Deposition Program, 2019).

Corresponding to the significant increase in pH, BRF's collection station has also monitored a statistically significant decrease in sulfate ($p < 0.001$; Figure 5a) and nitrate ($p < 0.001$) concentrations from 1985 to 2017. The precipitation was also found to slightly decrease in chloride ($p = 0.047$, Figure 5b) and magnesium ($p = 0.0499$, Figure 5d), while potassium, sodium, calcium (Figure 5c), and ammonium were not significantly different in 2018 than in 1985.

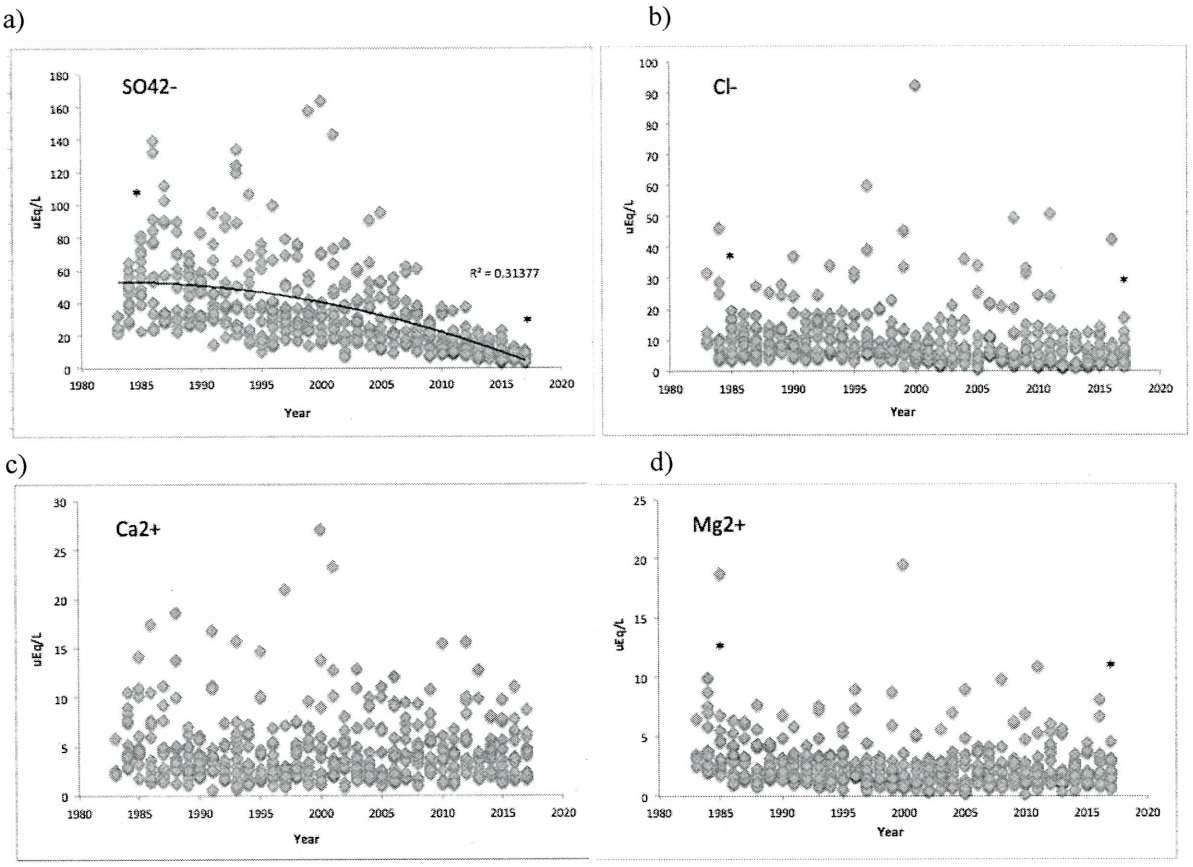

Figure 5: Concentrations of sulfate, chloride, calcium, and magnesium in precipitation collected at site NY99 from 1983 to 2017. Panel a (top left) shows monthly sulfate (SO_4^{2-}) concentrations for each year with a 2nd order polynomial trendline ($R^2 = 0.31377$), while panel b (top right) represents monthly chloride (Cl^-) concentrations for each year. Panel c (bottom left) shows monthly calcium (Ca^{2+}) concentrations for each year, and panel d (bottom right) represents monthly magnesium (Mg^{2+}) concentrations for each year. The asterisks above the years 1985 and 2018 indicate statistically significant differences ($p < 0.05$). Data was retrieved from the National Atmospheric Deposition Program National Trends Network (NTN) Site NY99 operated by Black Rock Forest Consortium in Cornwall, NY (National Atmospheric Deposition Program, 2019).

Following the recognition of acid rain as a major concern for aquatic ecosystem viability in this area, Andrew Becker and Robert H. Boyle conducted a chemical survey in 1985 of 43 bodies of water in Black Rock Forest and the surrounding Hudson Highlands. These water bodies were first classified as "vulnerable to acid deposition" if they had alkalinity of 120 μeq/L or less. On the basis of pH, they were then categorized as satisfactory, endangered, or critical according to the New York State Department of Environmental Conservation's pH ranges,

described in section 1.3 (Becker & Boyle, 1986). Of the 43 water bodies sampled, 25 of them were found to be significantly acidified or threatened, with low to non-existent alkalinity (Figure 6). These 25 lakes were considered the most vulnerable in 1985, and therefore make up 25 of the 26 bodies of water re-visited in 2018.

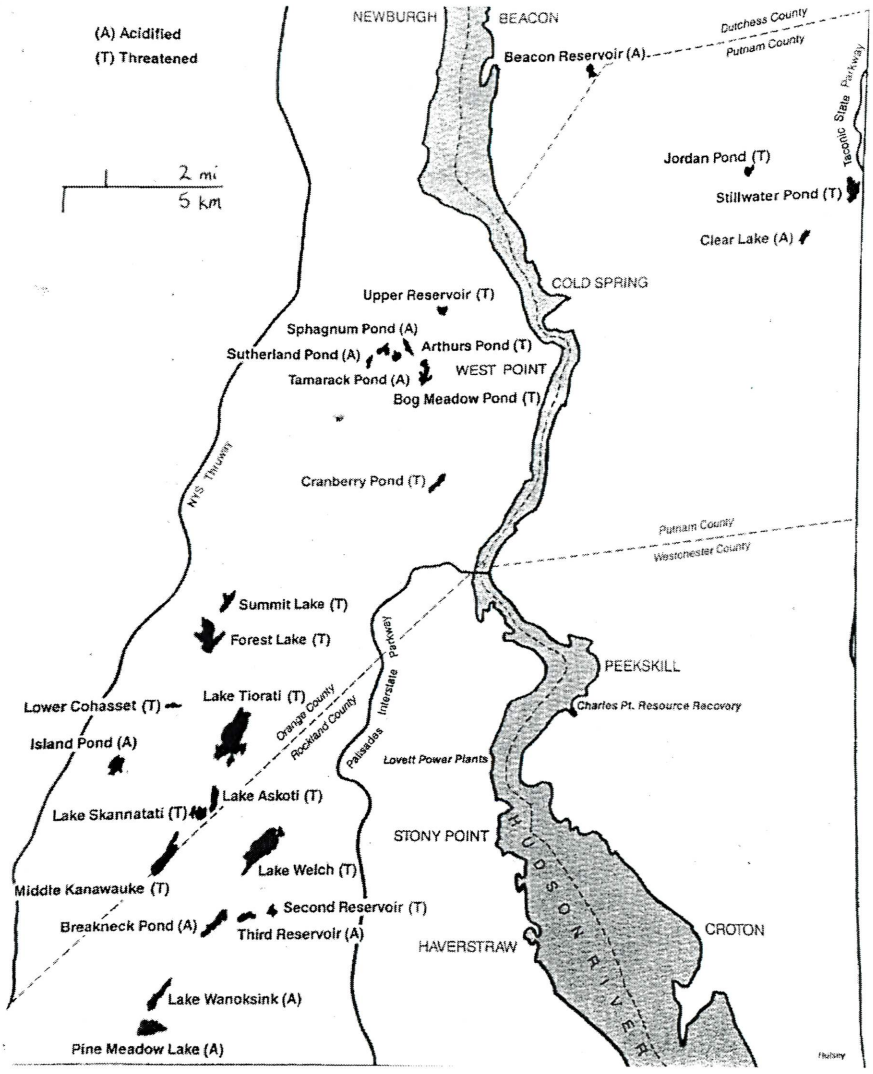

Figure 6: Map of 25 lakes sampled in 1985 with low to non-existent alkalinity. Lakes are marked acidified (A) or threatened (T) based on pH and alkalinity levels. The 10 lakes labeled "A" have low to non-existent alkalinity and pH 4.8-5.5. The 15 lakes labeled "T" have slightly higher alkalinity, and pH 6.0 or greater (Becker & Boyle, 1986).

Additionally, in 1987, the Adirondack Lakes Survey Corporation conducted a survey of the fish species that were present in Black Rock Forest. The fish species associated with the Black Rock Forest reservoirs in 1987 were 133 brown bullheads, 12 chain pickerels, 18 pumpkinseed (*Lepomis gibbosus*), 75 yellow perches, 30 golden shiners, and 9 banded sunfish (*Enneacanthus obesus*) (Table 1; Adirondack Lakes Survey Corporation, 1987). Through this survey, it was discovered that the most acid-tolerant species like brown bullhead, chain pickerel, and pumpkinseed were found in all of the reservoirs, including the most acidic ponds that were deemed critical by Becker & Boyle two years earlier, such as Tamarack Pond (Schuster, personal communication). In contrast, the relatively more sensitive species like golden shiner and banded sunfish were only found in the reservoirs with the highest pHs that were classified as satisfactory for aquatic life by Becker & Boyle two years earlier, such as the Upper Reservoir (Schuster, personal communication).

Table 1: Major ponds in Black Rock Forest and associated fish species in 1987. The "X" indicates the presence of the fish species in that reservoir in 1987 (Adirondack Lakes Survey Corporation, 1987).

Pond name	Elevation (m)	Mean pH	Brown Bullhead	Chain Pickerel	Pumpkin-seed	Yellow Perch	Golden Shiner	Banded Sunfish
Tamarack Pond	390	5.59	X	X	X			
Sphagnum Pond	381	5.64	X	X		X		
Sutherland Pond	380	5.88	X	X	X	X		
Arthur's Pond	375	6.27	X				X	X
Aleck Meadow Res.	314	6.43	X	X	X		X	X
Upper Reservoir	298	6.77	X				X	

Years later in 1992, Black Rock Forest data still showed substantial acidification of ponds, streams, and soils, remaining as an unfavorable environment for many different types of

aquatic life, especially the acid-sensitive species (Schuster, personal communication). Though surface pH values for the water bodies in Black Rock Forest and the surrounding Hudson Highlands have been sporadically measured since the 1990s, a comprehensive chemical and biological analysis of ecosystem recovery since 1985 has yet to be performed.

1.7. Basic Descriptions and Hydrology of 26 Water Bodies

As previously stated, six of the ponds sampled are located in Black Rock Forest, and the remaining 20 were located throughout Harriman State Park, Sterling Forest State Park, and Clarence Fahnestock State Park, as well as private property surrounding these preserves. A table of the 26 bodies of water, their name abbreviations, and their basic features can be found in Appendix A (Table A1).

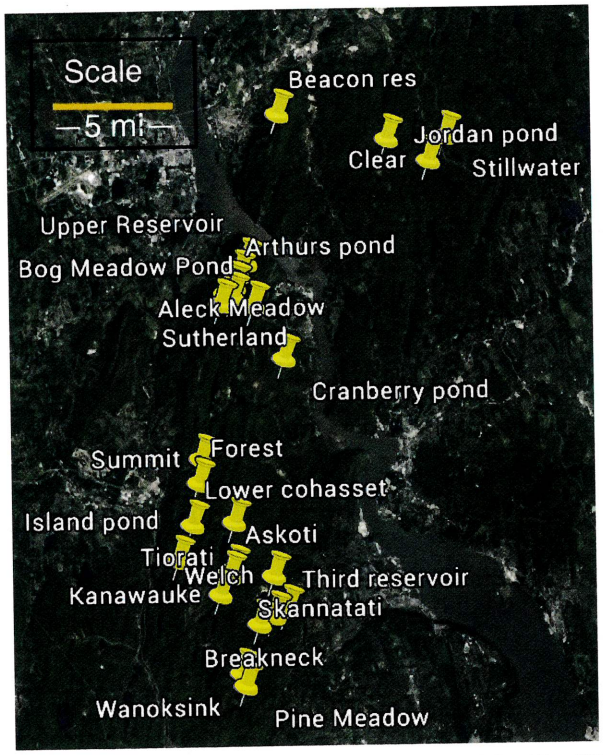

Figure 7: GPS locations of 26 bodies of water in the Hudson Highlands. GPS coordinates were measured during sampling using KoboCollect software for Android. Image from Google Earth.

All of the 26 bodies of water are man-made and dammed, except for Sutherland Pond, Breakneck Pond, and Island Pond. Additionally, the reservoirs at Black Rock Forest - and many of the ponds in the other sites - have a specific hydrological order that influences their water chemistry. For example, Tamarack Pond (TP) - with the highest elevation in BRF of 390 meters - is predominantly ombrotrophic (rain-fed) and flows roughly 0.3 km into Sphagnum Pond (SPP), which is at a lower elevation of 381 meters. Meanwhile, Sutherland Pond (SUP) - slightly lower at 380 meters above sea level - does not have any input streams and flows through a wetland in the opposite direction of Tamarack and Sphagnum. In contrast, water from Sphagnum flows roughly 2.1 km through a wetland to a man-made bifurcation, with one part flowing into Aleck Meadow Reservoir (AMR) at 314 meters elevation. Arthur's Pond (AP), located at 375 meters above sea level, joins the stream connecting SPP and AMR and travels a total of ~1 km into AMR. Like Sutherland Pond, Upper Reservoir (UR) - with an elevation of 298 meters - remains separate from this main hydrological pathway and is thought to receive a greater input of groundwater in addition to direct rainfall and runoff (Brady, personal communication). Similar to the ponds at BRF, several lakes in Harriman are connected by streams, such as Lake Skannatati and Lake Kanawauke; Lake Welch and Breakneck Pond; 3rd Reservoir and 2nd Reservoir; and Lake Wanoksink and Pine Meadow Lake.

It is important to understand these hydrologic pathways and approximate stream lengths because they, along with the availability of neutralizing base cations in the soil, dictate the full effect of the strong acid anions on a water body (Likens, 2013). It is known that as water moves through a hydrologic pathway downstream, the strong acid anions become increasingly neutralized as a result of cation-exchange and weathering reactions (Likens, 2013). For example,

higher elevation ponds and streams like Tamarack Pond have relatively low pHs, precluding the presence of significant quantities of bicarbonate. As the water continues down longer flow paths, as in Tamarack to Sphagnum to Aleck Meadow, it increasingly interacts with base cations, such as those from the glacially-deposited limestone till. Subsequently, the pH increases and carbonic acid can dissociate, promoting further carbonation weathering reactions. Thus, bicarbonate alkalinity is also expected to increase downstream. This concept is important for setting and maintaining downstream water quality standards (Likens, 2013).

1.8. Terminology

When discussing the 26 bodies of water studied, it is important to consider the difference between a lake and a pond. While some of the water bodies are called lakes, such as Lake Tiorati in Harriman State Park, others are called ponds, such as Island Pond, also in Harriman State Park. Others still are called reservoirs, such as Upper Reservoir in Black Rock Forest or Beacon Reservoir in the City of Beacon, which are used as town water supplies. Though both lakes and ponds are inland surface waters, there are limnological and ecological differences between the two. In general, lakes are considered to be deeper than ponds, but because historical naming conventions have been somewhat arbitrary, some bodies of water called "ponds" are actually deeper than some called "lakes" (New Hampshire Department of Environmental Services, 2003). Limnologists have attempted to differentiate lakes and ponds based on area and depth, in which lakes are specified as being deep enough to exhibit thermal stratification in temperate summers. They have also tried to distinguish lakes and ponds according to plant growth, in which a pond is shallow enough for total sunlight penetration and rooted plant growth. With that said, consistent and precise differentiation between lakes and ponds has yet to be universally established (New

Hampshire Department of Environmental Services, 2003). As a result, this study going forward will use the terms "lake," "pond," "water bodies," and "bodies of water" interchangeably.

2. THESIS STATEMENT

The replication and extension of Becker and Boyle's study to gauge the extent of lake recovery from acidification in the Hudson Highlands since 1985 is the goal of this thesis. The 26 most vulnerable waterbodies in the Hudson Highlands according to Becker and Boyle were revisited in order to measure the current pH, alkalinity, and conductivity levels, perform a full anion and cation analysis, and investigate the potential recovery of aquatic life. As a result of the post-Clean Air Act increase in precipitation pH, 26 lakes in Black Rock Forest and the surrounding Hudson Highlands are hypothesized to exhibit increased pH and alkalinity to healthy levels, as well as more viable aquatic ecosystem populations since 1985, though the extent of such recovery is expected to depend on each lake's underlying geology and surrounding environment.

3. METHODS

3.1. Water Collection

The following methods were adapted from two different lake water sampling procedure manuals, the Standard Operating Procedures from the Minnesota Pollution Control Agency (Egge et al., 2018) and the Inland Lakes Sampling Procedure Manual (Ohio Environmental Protection Agency, 2010). Becker and Boyle's 1986 sampling and testing procedures were not directly followed, as they had collected samples solely from the surface at the lakes' outlets, or from a dam or rock outcropping (Becker & Boyle, 1986). These samples were also collected in early August, once stratification had already set in. In an effort to expand and improve on these

past studies, water samples were collected using a deep water sampler from a rowboat at both the surface and the bottom of each water body at its greatest depth. Stratification of the bodies of water was also monitored, and most remained well-mixed during the sampling period. However, the last six ponds that were sampled in July began to stratify, which means that the two samples that were taken at different depths more closely represent the epilimnion and hypolimnion, rather than top and bottom samples from a well-mixed lake. Although these methodological differences were purposefully performed to obtain a more accurate and holistic depiction of the lakes' chemistry that could be used as a baseline for future studies, the sampling methods still allow data to be compared between 2018 and 1985.

For each water body sampled, two 2-L Nalgene Lab Quality HDPE bottles were labeled with researcher name, lake/pond name, date collected, and the depth from which the sample was taken. An Accumet portable pH/mV meter and an Oakton handheld ECtestr 11 conductivity meter were calibrated the morning of sampling, and a cooler for storage was filled with ice packs. A rowboat and a deep water sampler were used to find the deepest part of each lake (Figure 8). The date, time, lake name, GPS coordinates, weather conditions, color of the water, site depth, surface pH, surface water temperature, surface conductivity, and other notes were recorded using the KoboCollect software for Android. The deep water sampler and collection bottles and caps were rinsed three times with lake water. Using the deep water sampler, two liters of water were collected from 0.5 meters from the bottom and 0.5 meters from the surface, and the bottles were stored in the cooler (Figure 8). Bottles were filled completely to eliminate headspace and prevent chemical reactions during storage. Samples were immediately stored in the refrigerator at or below 4 degrees C. Additional pH measurements of each sample were taken

in the lab before and during alkalinity titrations. The average pH and standard deviation of each sample were later calculated.

a) b) c)



Figure 8: Beacon Reservoir sampling on July 5, 2018. Panel a (left) depicts the measurement of the surface pH, panel b (center) shows the pre-collection rinsing of the deep water sampler, and panel c (right) depicts the collection of a 2-L sample from 8.25 meters deep. Photos by Dr. William Schuster.

3.2. Alkalinity Titrations

Alkalinity titrations were conducted using a Hach Alkalinity Test Kit. In a 250 mL Erlenmeyer flask with a magnetic stirrer, 100 mL of each sample were mixed with one Phenolphthalein indicator powder pillow to determine the Phenolphthalein (P) alkalinity. All samples were colorless with phenolphthalein and required no initial titration. One Bromcresol green-methyl red indicator powder pillow was added before the digital pipette was used to titrate a sample with 0.1600 N Sulfuric Acid to a pH of 4.5, as measured by the Accumet pH/mV meter. The amount of acid added to a sample was represented by the number of drops displayed on the screen of the digital pipette. This number was then multiplied by the given calibration constant (0.01) to yield the alkalinity value in units of mg/L as $CaCO_3$. These experimentally determined alkalinity values in mg/L were later converted to μEq/L. Three to four trials were conducted for each sample, $[H^+]$ vs. alkalinity was graphed, and a linear regression was performed to find the

alkalinity value precisely at pH 4.5. Historical water chemistry data were compiled for all 26 lakes sampled, and year vs. alkalinity and year vs. pH were graphed.

3.3. pH with Depth

The pH, temperature, and conductivity levels with increasing depth of the six Black Rock Forest reservoirs were measured in August to analyze possible variation from the first set of measurements, as well as to monitor the stratification process and to clarify the vertical structure of the ponds. As in the water collection procedure, an Accumet portable pH/mV meter and an Oakton handheld ECtestr 11 conductivity meter were calibrated the morning of sampling. The previously-recorded GPS coordinates were followed in order to sample from roughly the same location with the rowboat and deep water sampler in each pond. The date, time, lake name, GPS coordinates, weather conditions, color of the water, site depth, surface pH, surface water temperature, surface conductivity, and other notes were recorded using the KoboCollect software for Android. The deep water sampler was rinsed three times with lake water. Unlike in the water collection procedure, the deep water sampler was used to collect water from every 0.5 meters, which was then measured for pH, temperature, and conductivity. All measurements were made on site and no samples were saved.

3.4. Anion and Cation Analysis

In order to comprehensively measure water quality and recovery from acidification, the major anions and cations in the waters of each lake at both surface and depth were measured. Two trays (52 vials) of 20 mL glass scintillation vials were labeled with researcher name, lake/pond name, date, and depth. For each 2-L sample, a sterile 50 cc syringe and sterile Thermo Fisher Scientific 45 μm syringe filters were used to filter the water into three vials additionally

labelled "anions," and three vials marked "cations." Vials were filled two-thirds full and frozen for storage. For anion analysis, 3 mL of each thawed sample were pipetted into 5-mL labeled ion chromatography vials topped with a septa and cap. For cation analysis, 5 mL of each thawed sample were pipetted into 10-mL test tubes and diluted with 200 µL of 8 Molar nitric acid.

Anion analysis was conducted on the Ion Chromatograph (IC) at Barnard College, following the established procedure. Concentrations in parts per million (ppm) of chloride (Cl^-), nitrite (NO_2^-), bromide (Br^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), and phosphate (PO_4^{3-}) were generated. Cation analysis was initially performed on the Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at Lamont-Doherty Earth Observatory, but after instrument failure, subsequent cation analysis was instead performed on the Inductively Coupled Plasma Optical Emissions Spectrometer (ICP-OES) at Lamont-Doherty Earth Observatory. Concentrations in ppm of calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}), and sodium (Na^+) were calculated. Because only the ICP-OES generated results for the cation analysis, no comparison of results between the OES and MS could be made.

Following the measurement of anion and cation concentrations, the charge balances for all 26 lakes were calculated by converting the concentrations in ppm, which is equal to mg/L, to microequivalents per liter (µEq/L), and then subtracting the sum of the anions from the sum of the cations: $CB = \Sigma cation\ equivalents - \Sigma anion\ equivalents$. Additionally, the charge balance can be expressed as the percent difference between positive charges and negative charges relative to positive charges, per the equation: $\%\ difference = (\frac{\Sigma cations - \Sigma anions}{\Sigma cations}) * 100$ (Anderson, 2018). The concentration of bicarbonate (HCO_3^-) was calculated from the alkalinity values and added to the total anion concentrations used to calculate electroneutrality. The charge balance

error (CBE) was also calculated by the following equation: $CBE = (\frac{\Sigma cations - \Sigma anions}{\Sigma cations + anions}) * 100$. The maximum CBE value accepted is +/-10% (Andersen, 2015).

3.5. Comparison with Precipitation

Precipitation data was obtained from the National Atmospheric Deposition Program for station NY99 operated by Black Rock Forest. Data for precipitation pH and ion concentrations in mg/L were available monthly from 1983 to 2017. Using the known ratios by weight of ion to Na^+ for seawater (Table 2), the amount of sea salt contribution to the precipitation was calculated as a percentage for sulfate, chloride, calcium, and magnesium (Appendix B, Table B1). Using this precipitation data, the amount of total precipitation contribution and overall sea salt contribution to the six BRF ponds were also calculated as a percentage for the same four ions.

Table 2: Ratios of ion to Na^+ for seawater and marine island rain in terms of weight. Only the ratios for seawater and sulfate, chloride, calcium, and magnesium were used (Berner & Berner, 2012).

	Seawater	South Atlantic Rain	Pacific Rain	Bermuda Rain	Hawaii Rain	Amsterdam Is. Rain
Ion						
Na^+	1	1	1	1	1	1
Cl^-	1.797	1.92	1.79	1.83	1.76	1.83
SO_4^{2-}	0.252	0.266	0.333	0.515	0.352	0.29
Mg^{2+}	0.12	0.137	----	----	0.168	0.117
Ca^{2+}	0.038	0.032	0.179	0.056	0.086	0.039
K^+	0.037	0.034	0.042	0.05	0.068	0.023

3.6. Black Rock Forest Fish Populations

Historical data on the fish populations at Black Rock Forest from the 1987 Adirondack Lakes Survey were compiled with the help of Dr. William Schuster, the Executive Director of Black Rock Forest. The Adirondack Lakes Survey used four different methods to catch fish in

the BRF ponds: a 150-foot gill net, a 30-foot minnow net, a minnow trap, and a beach seine (Adirondack Lakes Survey Corporation, 1987). The beach seine was only used in Sutherland Pond and Upper Reservoir, but the other three methods were used in all of the ponds. The type of fish captured, the number of each species caught, and the minimum and maximum fish length in inches were then measured (Adirondack Lakes Survey Corporation, 1987). The total number of fish captured in the six BRF ponds was 277. The historical data was then compared to current anecdotal data on the forest's fish populations, provided by the forest manager at Black Rock Forest, Matthew Brady. Fish population data was also available on the New York State Department of Environmental Conservation website for seven bodies of water in Harriman State Park. The effect of pH on fish population presence and diversity in the Hudson Highlands was qualitatively examined.

3.7. Statistical Analysis

The primary method of statistical analysis used in this study was a one-way paired t-test, performed in Microsoft Excel. This statistical test was chosen based on its use in similar studies (Richardson et al., 2018). The paired 2-sample t-test was used to assess whether each of the 26 lakes had pH and alkalinity values that were significantly higher in 2018 than in 1985. The same statistical method was also used to test for significant differences in anion and cation concentrations when enough historical data was available. The critical p value was set as 0.05. Box and whisker plots were also constructed to visualize differences in pH and ion concentrations between different water samples.

4. RESULTS

4.1. Surface Water pH

Assessing pH over time for bodies of water is a simple and direct way of evaluating the possible recovery from acidification. The results of this study generally show increases in pH for the 26 bodies of water between 1985 and 2018. Four more lakes have pHs of 6.0 or greater and are classified as satisfactory for aquatic life in 2018 than in 1985 (to 95% confidence; Figure 9). Additionally, all three ponds that had pHs below 5.0 and were classified as critical in 1985 now have pHs above 5.0 and are classified as either endangered or satisfactory (to 95% confidence; Figure 9). However, nine ponds have pHs between 5.0 and 6.0 and are classified as endangered in 2018, which is the same number as in 1985 (to 95% confidence; Figure 9).

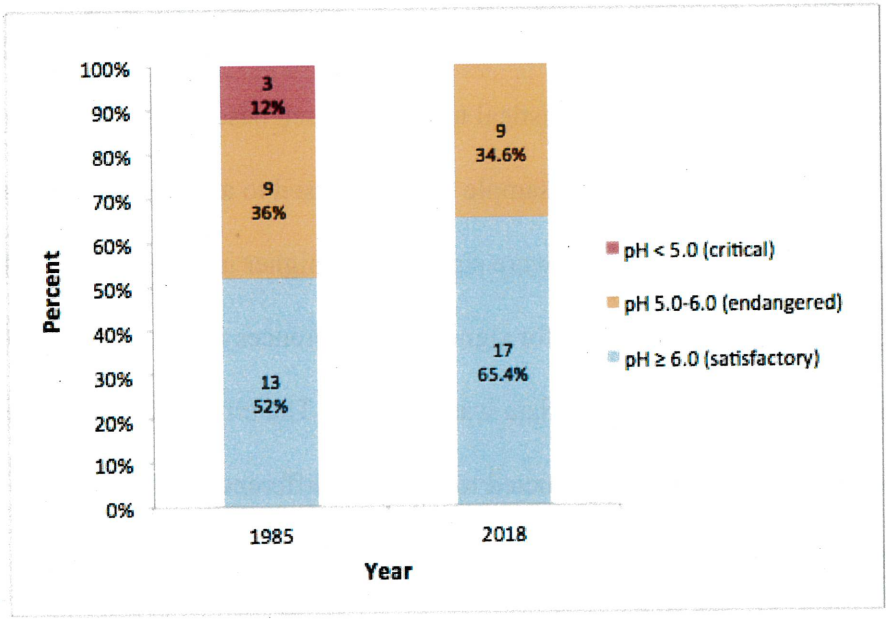

Figure 9: Number and percent of lakes sampled in 1985 vs. 2018 classified as satisfactory, endangered, or critical based on pH. The blue bars represent pH of 6.0 or greater (satisfactory), the orange bars show pH of 5.0-6.0 (endangered), and the red bar indicates a pH less than 5.0 (critical). Note that 25 lakes were sampled in 1985, while 26 lakes were sampled in 2018.

Within the category of satisfactory pH, the 13 lakes in 1985 varied from 6.37 at Lake Skannatati to 7.35 at the Upper Reservoir, while the 17 lakes in 2018 vary from 6.16 at Beacon Reservoir to 7.29 at Lake Welch (Figure 10). Within the category of endangered pH, the nine lakes in 1985 varied from 5.00 at Beacon Reservoir to 5.97 at Summit Lake, while the nine lakes in 2018 vary from 5.59 at Tamarack Pond to 5.99 at Breakneck Pond (Figure 10). Within the category of critical pH, the three lakes in 1985 ranged from 4.73 at Tamarack Pond to 4.90 at Island Pond, and, as previously stated, no lakes in 2018 fall in the critical category (Figure 10).

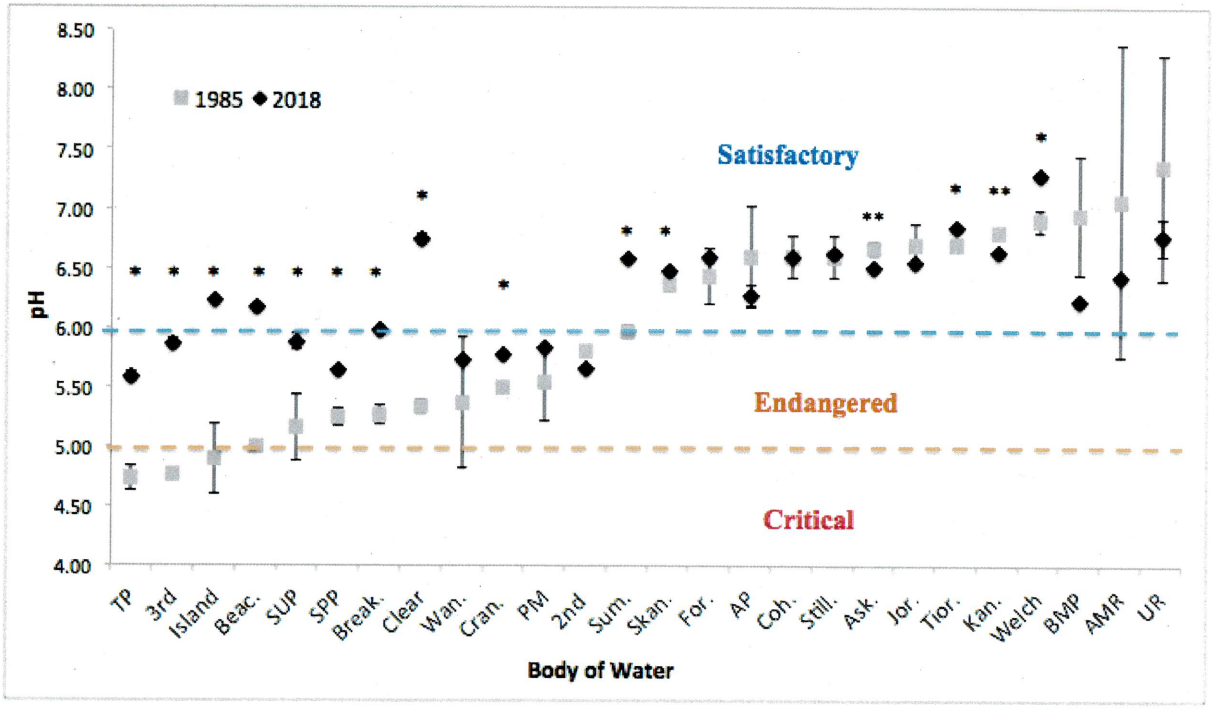

Figure 10: Distribution of surface pH values for 26 bodies of water in 1985 and 2018. The gray squares represent the average surface pH values for 26 lakes sampled in 1985, ordered from lowest pH (Tamarack Pond [TP]) to highest pH (Upper Reservoir [UR]). The black diamonds show the average surface pH values for the same 26 lakes sampled in 2018. The dotted orange line marks the boundary between "critical" and "endangered" at pH 5 while the dotted blue line marks the boundary between "endangered" and "satisfactory" at pH 6. The single asterisks indicate the lakes with statistically significantly higher pH values in 2018 ($p<0.05$), while the double asterisks mark lakes with significantly lower pHs in 2018. Error bars show +/-1 standard deviation from the mean.

After categorizing the bodies of water sampled in 1985 and 2018 based on Becker and Boyle's classifications, 2-sample t-tests were performed for all 26 bodies of water comparing the mean pH values in 1985 and 2018. Of the 26 bodies of water, 13 lakes have pH values in 2018 that are statistically significantly higher than the pH values in 1985 ($p < 0.05$; Appendix C, Table C1). These lakes include Tamarack Pond ($p = 0.03$), Sutherland Pond ($p = 0.01$), Sphagnum Pond ($p = 0.03$), Lake Tiorati ($p = 0.003$), Lake Skannatati ($p = 0.047$), Breakneck Pond ($p < 0.001$), Lake Welch ($p = 0.01$), Third Reservoir ($p < 0.001$), Island Pond ($p = 0.001$), Summit Lake ($p = 0.001$), Cranberry Pond ($p = 0.008$), Beacon Reservoir ($p < 0.001$), and Clear Lake ($p < 0.001$). Of these ponds, three had been critical and seven had been endangered in 1985, but are now either endangered or satisfactory (Figure 10). Two of the 26 lakes have pHs that are statistically significantly lower in 2018 than in 1985: Lake Askoti ($p < 0.01$) and Lake Kanawauke ($p < 0.001$), both of which were satisfactory in 1985 and remain satisfactory in 2018 (Figure 10). The remaining 11 lakes do not have statistically significantly different surface pHs in 2018 than in 1985, eight of which had already been satisfactory in 1985 (Figure 10).

An example of a statistically significant, but non-linear increase in pH over time is Breakneck Pond, which is a natural pond in Harriman State Park. In 1981 and 1982, Breakneck had critical pH values of 4.60 and 4.95 respectively, before increasing to endangered in 1983 with a pH of 5.33 (Figure 11). Breakneck Pond remained endangered in 1984, 1985, and 1994, before increasing to satisfactory in 2005 and 2008 with values of 6.10 and 6.12 respectively (Figure 11). The pH drops a bit below satisfactory in 2018 to 5.99, but this is still the third highest pH since 1985 (Figure 11). However, this rate of increase in pH is not constant/linear.

Rather, the trend fits a second-order polynomial trendline with a 91% correlation from 1981 to 2018 (Figure 11), suggesting that multiple variables influence pH recovery.

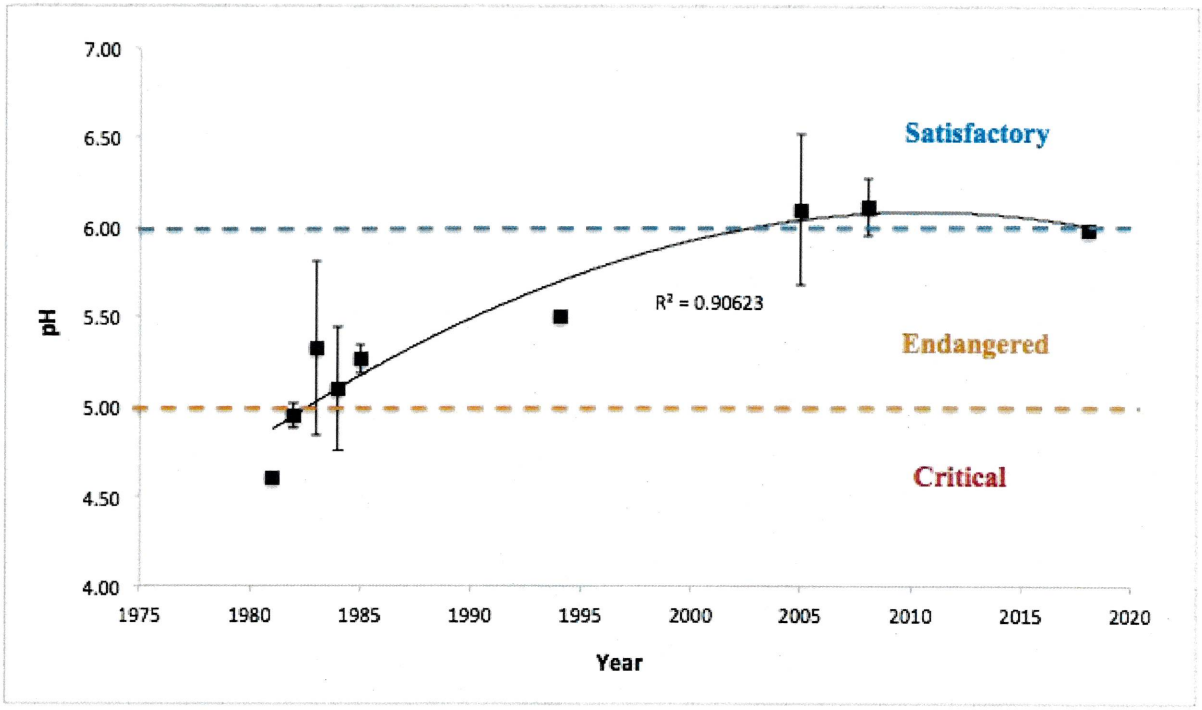

Figure 11: Increase in pH for Breakneck Pond from 1981 to 2018. The black line represents a 2nd order polynomial trendline with an R^2 of 0.90623. The dotted blue line marks the separation between endangered and satisfactory at pH 6, while the dotted orange line marks the boundary between endangered and critical at pH 5. The error bars are +/- the standard deviation for each point.

4.2. Surface Water Alkalinity

Though more complex than pH, alkalinity is a useful parameter for assessing the vulnerability of the bodies of water to acid deposition. The results indicate overall increases in alkalinity for most of the bodies of water from 1985 to 2018. For example, 10 fewer lakes in 2018 compared to 1985 are classified as vulnerable to acid deposition by having alkalinity values less than or equal to 120 μEq/L (to 95% confidence; Figure 12). As previously mentioned, there were no lakes in 1985 that fell into the "less vulnerable" to acid deposition category, but the 10 lakes in 2018 that do fall into this category have alkalinities ranging from 132.3 μEq/L at Lake

Tiorati to 200.0 µEq/L at Lake Welch (Figure 13). Within the category of "more vulnerable" to acid deposition, the lakes in 1985 ranged from 0.0 µEq/L at 10 different lakes to 114.4 µEq/L at Lake Kanawauke (Figure 13), while the lakes in 2018 vary from 40.6 µEq/L at Sphagnum Pond to 89.2 µEq/L at Cranberry Pond (Figure 13).

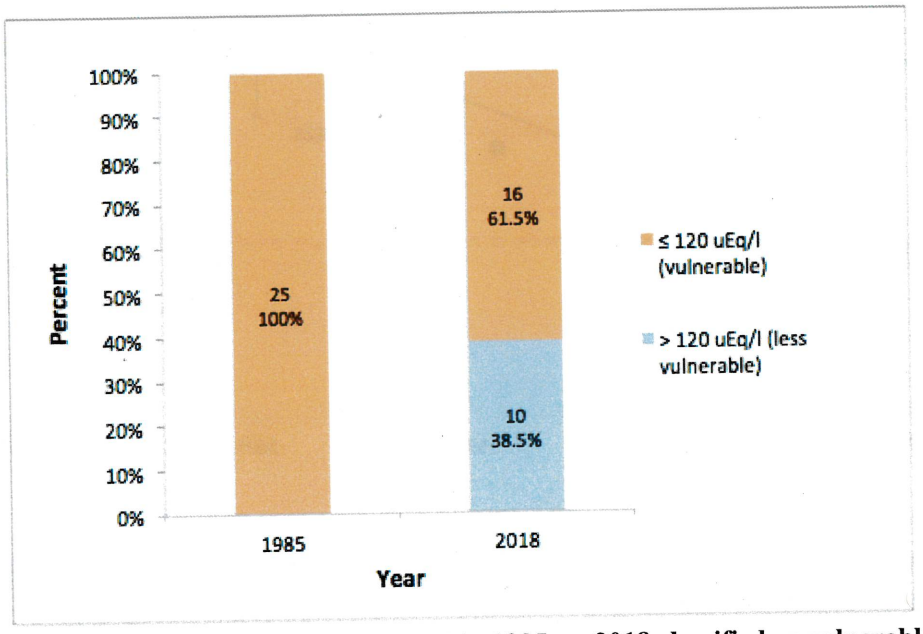

Figure 12: Number and percent of lakes sampled in 1985 vs. 2018 classified as vulnerable or less vulnerable based on alkalinity. The blue bar represents alkalinity greater than 120 µEq/L (less vulnerable), while the orange bars represent alkalinity of 120 µEq/L or less (vulnerable to acid rain). Note that 25 lakes were sampled in 1985, while 26 lakes were sampled in 2018.

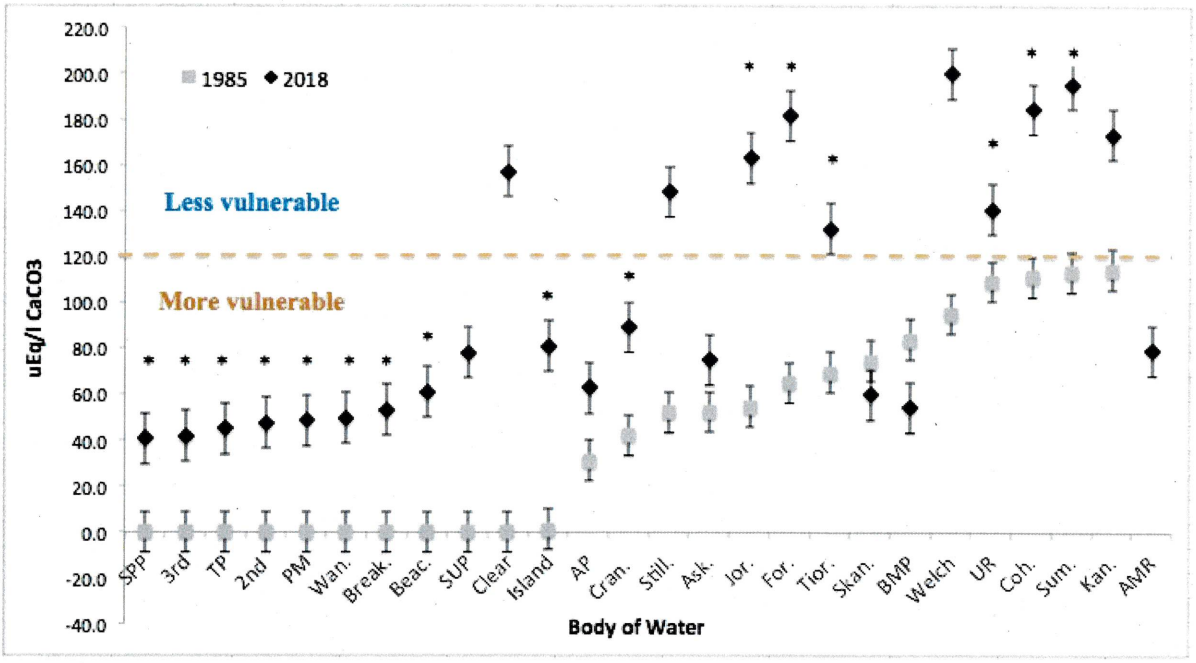

Figure 13: Distribution of surface alkalinity values for 25 lakes in 1985 and 26 lakes in 2018. The gray squares represent the surface alkalinity values for 25 lakes sampled in 1985, ordered from lowest alkalinity (Sphagnum Pond [SPP]) to highest alkalinity (Lake Kanawauke [Kan.]). The black diamonds show the surface alkalinity values for the same 25 lakes in 2018, plus Aleck Meadow Reservoir (AMR), which was not included in the 1985 list of the 25 most vulnerable lakes in the Hudson Highlands because its alkalinity was higher than 120 μEq/L at 132.6 μEq/L. The dotted orange line marks the boundary between "vulnerable" and "less vulnerable" to acid deposition at 120 μEq/L. The single asterisks indicate the lakes with statistically significantly higher alkalinity values in 2018 (p<0.05). Both plots have error bars of +/- 1 standard error.

To compare the alkalinity values in 1985 and 2018, 2-sample t-tests were also performed. Of the 26 bodies of water, 16 of them have alkalinity values in 2018 that are statistically significantly higher than the alkalinity values in 1985 ($p < 0.05$; Appendix C, Table C1). These lakes include Upper Reservoir ($p = 0.002$), Tamarack Pond ($p = 0.03$), Sphagnum Pond ($p = 0.01$), Lake Tiorati ($p = 0.02$), Breakneck Pond ($p < 0.01$), Lake Wanoksink ($p = 0.02$), Pine Meadow Lake ($p = 0.04$), Second Reservoir ($p = 0.02$), Third Reservoir ($p = 0.003$), Island Pond ($p = 0.002$), Summit Lake ($p = 0.025$), Forest Lake ($p = 0.03$), Cranberry Pond ($p = 0.03$), Beacon Reservoir ($p = 0.02$), Jordan Pond ($p = 0.02$), and Lower Cohasset ($p = 0.03$). Of these

ponds, nine had 0.0 μEq/L alkalinity in 1985 (Figure 13). One lake, Clear Lake, does not have enough historical alkalinity data to be tested for statistical significance (Appendix C, Table C1). Out of the 26 lakes, one pond, Aleck Meadow Reservoir, has alkalinity that is statistically significantly lower in 2018 than in 1985 ($p = 0.02$), but this is the one pond that was not included in the 1985 list of the 25 "most vulnerable" lakes because it already had an alkalinity higher than 120 μEq/L at 132.6 μEq/L. However, in 2018, its alkalinity is now lower than 120 μEq/L at 79.2 μEq/L (Figure 13). This result was unexpected, but could be because in 1998, Aleck Meadow's average alkalinity decreased drastically down to only 52.2 μEq/L. Even though the current alkalinity value is not statistically significantly higher than this extremely low 1998 value ($p = 0.07$), this historical trend could suggest that Aleck Meadow Reservoir suffered from its peak acidification after 1985 and is currently experiencing a slow recovery process. The remaining eight ponds do not have statistically significantly different alkalinity in 2018 than in 1985.

The distribution of the 2018 alkalinity values suggests the presence of two different "populations" of ponds - those with alkalinity lower than 90 μEq/L and those with alkalinity higher than 120 μEq/L. For the 2018 values, the histogram depicting the number of lakes in each "population" reveals a fairly bimodal trend, with 16 ponds in the "low alkalinity" population and 10 in the "high alkalinity" population (Figure 14). The low alkalinity population includes: Tamarack Pond, Sphagnum Pond, Sutherland Pond, Arthur's Pond, Aleck Meadow Reservoir, Bog Meadow Pond, Cranberry Pond, Lake Askoti, Lake Skannatati, Breakneck Pond, Lake Wanoksink, Pine Meadow Lake, Island Pond, Beacon Reservoir, 2nd Reservoir, and 3rd Reservoir. Meanwhile, the high alkalinity population includes: Upper Reservoir, Lake Tiorati,

Lake Kanawauke, Lake Welch, Forest Lake, Summit Lake, Jordan Pond, Stillwater Pond, Clear Lake, and Lower Cohasset.

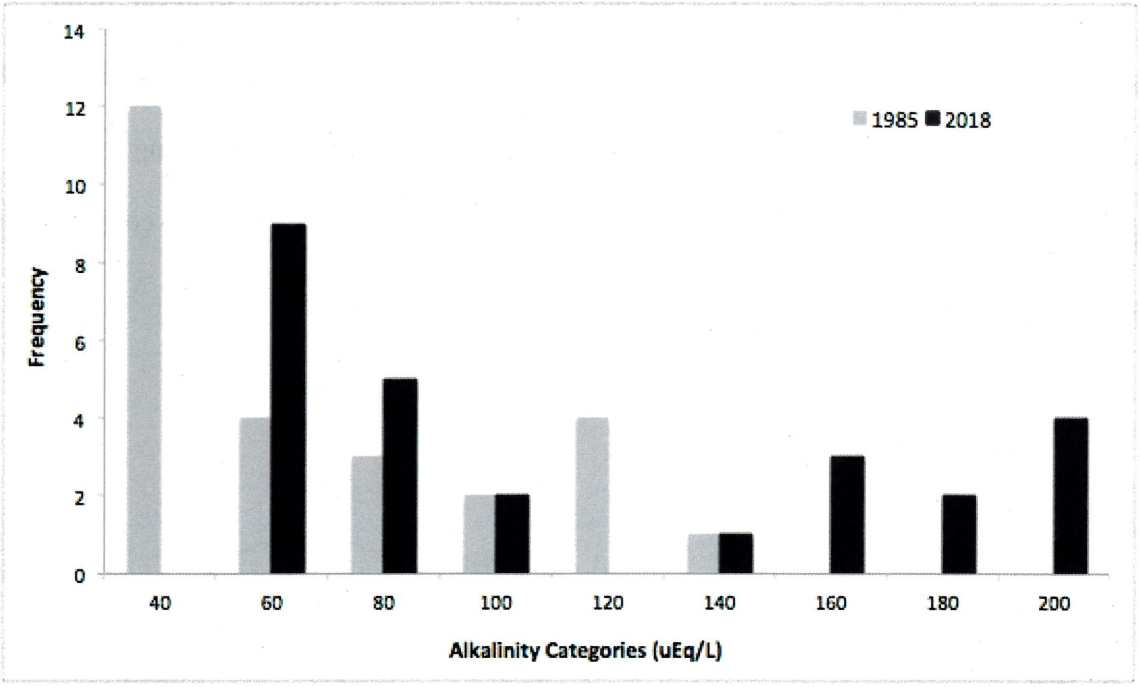

Figure 14: Histogram of alkalinity values in 1985 vs. 2018. The light gray bars show alkalinity values for 1985, including Aleck Meadow Reservoir, while the black bars show alkalinity values for 2018. The x-axis shows categories of alkalinity, in which "40" represents alkalinities between 0 and 40 μEq/L, "60" represents alkalinities between 40 and 60 μEq/L, "80" represents alkalinities between 60 and 80 μEq/L, etc. For 2018, the histogram shows a fairly bimodal trend from 60 μEq/L to 200 μEq/L.

In contrast, a bimodal trend for the 1985 alkalinity values is less clear, with 12 ponds - nearly half of the total - containing alkalinities less than 40 μEq/L (Figure 14). Except for the "120 μEq/L" category, the number of ponds within each increasing alkalinity category rapidly declines (Figure 14). This could mean that alkalinity values in 1985 were similarly depleted for both low and high alkalinity ponds, but that as the lakes gradually recover, the difference between the two populations becomes more obvious.

In addition to having a statistically significant but non-linear increase in pH, Breakneck Pond is also an example of a statistically significant increase in alkalinity, though this trend is

less clear. From 1982 to 2008, Breakneck Pond experienced a non-linear increase in alkalinity that appears to almost mirror the pattern of pH increase (Figure 15, Figure 11). Though limited by the gaps in historical data, it is clear that the alkalinity increases from <120 µEq/L in the 1980s to >120 µEq/L in the 1990s and 2000s (Figure 15). However, between 2008 and 2018, the alkalinity dropped back down to 53.2 µEq/L, deviating from the previous increasing pattern (Figure 15). The accuracy of both the past and current alkalinity data is a factor to consider when discussing the possible reasons for this trend.

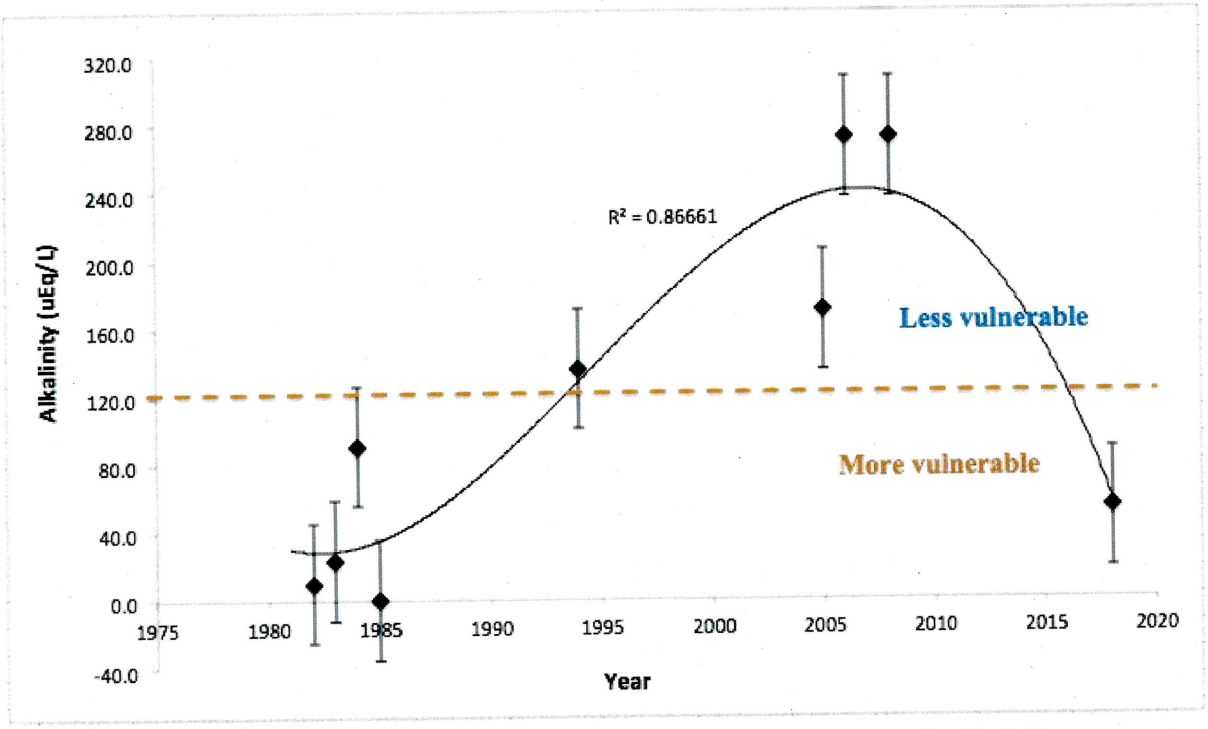

Figure 15: Variability in alkalinity for Breakneck Pond from 1982 to 2018. The black line represents a third-order polynomial with an R^2 of 0.86661. The dotted orange line marks 120 µEq/L, below which is considered an alkalinity that is very vulnerable to acid precipitation. The errors bars are +/- 1 standard error.

4.3. Surface Water Ion Concentrations

4.3.1. Anion Concentrations

Analyzing the anion concentrations for the 26 lakes over time can reveal possible recovery from acid rain, as well as effects from other anthropogenic activities. Though six anions - chloride, nitrite, bromide, nitrate, sulfate, and phosphate - were tested in 2018, the lack of historical data for the bodies of water only allows sulfate concentrations, and to a lesser extent nitrate and chloride, to be analyzed over time. After conducting 2-sample t-tests comparing past and present sulfate (SO_4^{2-}), 15 bodies of water were found to have significantly lower sulfate concentrations in 2018 ($p < 0.05$; Appendix C, Table C2). These ponds include Upper Reservoir ($p = 0.035$), Lake Tiorati ($p = 0.025$), Lake Askoti ($p = 0.01$), Lake Kanawauke ($p = 0.035$), Breakneck Pond ($p = 0.049$), Lake Wanoksink ($p = 0.009$), Pine Meadow Lake ($p = 0.03$), Second Reservoir ($p = 0.006$), Summit Lake ($p = 0.001$), Forest Lake ($p = 0.005$), Beacon Reservoir ($p = 0.02$), Jordan Pond ($p = 0.003$), Stillwater Pond ($p = 0.02$), Clear Lake ($p < 0.001$), and Lower Cohasset ($p = 0.006$). One pond, Bog Meadow Pond, does not have enough historical anion data to be tested for statistical significance. The remaining 10 lakes do not have statistically significantly different sulfate concentrations in 2018 than in the 1980s.

Of the 26 bodies of water, only 16 have enough historical nitrate (NO_3^-) concentration data to be tested for statistically significant differences. Of these 16, only Stillwater Pond has NO_3^- concentrations that are statistically significantly lower in 2018 ($p = 0.04$; Appendix C, Table C2). Meanwhile, three lakes - Lake Askoti, Breakneck Pond, and Cranberry Pond - have statistically significantly higher nitrate concentrations in 2018 ($p = 0.004$, $p = 0.04$, and $p = 0.03$,

respectively). Of the 16 testable ponds, there are 12 bodies of water that do not have statistically significantly different nitrate concentrations in 2018 than in the 1980s (Appendix C, Table C2).

When testing to see if chloride (Cl^-) concentrations were statistically significantly different in 2018, there were only 6 ponds that had enough historical data. Of these six, two bodies of water - Upper Reservoir and Breakneck Pond - have statistically significantly higher chloride concentrations in 2018 than in 1985 ($p = 0.007$ and $p = 0.02$, respectively; Appendix C, Table C2). The remaining four lakes do not have statistically significantly different chloride concentrations in 2018 than in 1985 (Appendix C, Table C2).

4.3.2. Cation Concentrations

Similar to the anions, analyzing cation concentrations can reveal possible alkalinity depletion and therefore increased susceptibility to acid deposition. Though four cations - calcium, potassium, magnesium, and sodium - were tested in 2018, the lack of historical data for the bodies of water only allows limited analysis for calcium, magnesium, and sodium concentrations over a shorter period of time. Only three bodies of water had sufficient historical cation concentration data to conduct 2-sample t-tests: Aleck Meadow Reservoir, Upper Reservoir, and Sutherland Pond. Instead of 1985, the earliest data available for comparison was from 1987 for Aleck Meadow and Upper Reservoir, and from 1992 for Sutherland Pond. Of these three ponds, only Sutherland Pond has statistically significantly different (higher) calcium concentrations in 2018 than in 1992 ($p = 0.03$; Appendix C, Table C3). Only Upper Reservoir has statistically significantly different (lower) magnesium concentrations in 2018 than in 1987 ($p = 0.049$; Appendix C, Table C3), while both Upper Reservoir and Aleck Meadow have

statistically significantly higher sodium concentrations in 2018 than in 1987 ($p = 0.03$ and $p = 0.02$, respectively; Appendix C, Table C3).

4.3.3. Charge Balance

After measuring the cation and anion concentrations, the charge balance and charge balance error could be calculated (Appendix D, Table D1). Because natural systems must maintain electroneutrality, theoretically the sum of the base cations and the sum of the acid anions should be equal and subtract to zero, also expressed as a zero percent difference (Anderson, 2018). Thus, a perfect analysis would lead to a charge balance error of 0%, though of course this is rare when multiple instruments are used for analyses (Andersen, 2015). The charge balance is represented by the percent difference between the cations and anions relative to the cations. The percent charge differences for the 26 bodies of water in 2018 at both surface and depth range from -30.7% to 53.3%, with an average of 21.2% (stdev = 18.7). These charge balance values correspond to a CBE range of -13.3% to 36.3%, with an average error 13.1% (stdev = 11.2). Typically, a CBE greater than +/-10% indicates some error associated with the determination of anion and cation concentrations or the omission of an important component in the analyses (Andersen, 2015). Notably, the percent difference and the CBE ranges reveal significant variability within the 26 bodies of water. For example, the overall lowest magnitude of percent difference and CBE is in the surface water of Stillwater Pond (1.7% difference, 0.88% CBE). In contrast, the greatest positive percent difference and CBE is in the 17.5-meter water of Island Pond, while the greatest negative percent difference and CBE is in the surface water of Third Reservoir (Appendix D, Table D1).

4.4. Comparison with Precipitation

Comparing the pH levels of the bodies of water with that of the precipitation can help clarify the relationship between the atmosphere and the studied ecosystems. In order to use the largest datasets over time, only the six Black Rock Forest ponds have been compared to the historical precipitation data. This study found that the median pond water pH increases as the elevation of the ponds decreases. Precipitation has the lowest median pH of 4.49 from 1983 through 2017, while Tamarack Pond has a slightly higher median pH of 5.00 from 1985 to 2018, correlating to the highest elevation of 390 meters (Figure 16). The next highest median pH of 5.10 is in Sphagnum Pond, which has a slightly lower elevation than TP of 381 meters (Figure 16). Sutherland Pond (elevation = 380 meters) has the next highest median pH from 1985 to 2018 of 5.51, followed by Arthur's Pond (elevation = 375 meters) with a median pH of 6.02 (Figure 16). Aleck Meadow Reservoir has the second highest median pH of 6.41, correlating to the second lowest elevation (314 meters), while Upper Reservoir has the highest median pH of 6.69 and lowest elevation of 298 meters (Figure 16).

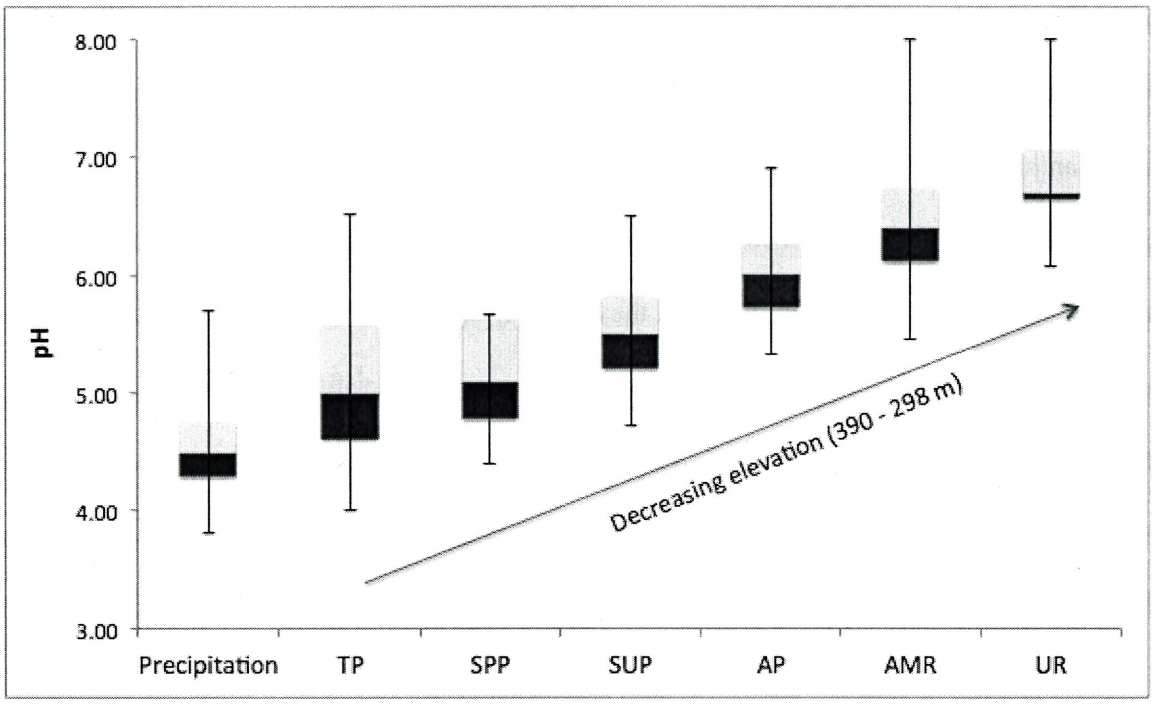

Figure 16: The median pH of precipitation and six BRF ponds. ±25th and 75th quartile are shown, with interquartile range whiskers. TP = Tamarack Pond; SPP = Sphagnum Pond; SUP = Sutherland Pond; AP = Arthur's Pond; AMR = Aleck Meadow Res.; UR = Upper Res. The ponds are ordered from highest elevation (TP) to lowest elevation (UR). The precipitation record is September 1983 to December 2017, while the BRF pond records are August 1985 to June 2018.

In order to further investigate the roles of atmospheric deposition and any other possible sources of the components in the lake waters, the amount of precipitation and marine contribution to the ponds can be determined. This is especially relevant at Black Rock Forest, which is located such that it receives a mix of marine and continental-type rain (Anderson, 2018). Tamarack Pond was found to generally have the largest precipitation and sea salt contributions for each ion except for chloride, which is expected based on the pond's high elevation (Table 3). Upper Reservoir generally has the smallest precipitation and sea salt contributions for each ion except for calcium, which is expected based on the pond's low elevation (Table 3). For all the ponds, chloride and magnesium have the largest marine contributions, while sulfate and calcium have the lowest. With that said, the percent of

precipitation chloride and sea salt chloride for the Upper Reservoir are surprisingly low at 0.93% and 0.90% respectively (Table 3), indicating the dominance of other chloride sources, either natural or anthropogenic. Among the six ponds and four different ions, the BRF waters have a maximum of 18.82% precipitation contribution (Table 3), which indicates that even though many of the ponds are thought to be ombrotrophic, they actually appear to obtain more ions from non-precipitation, non-marine sources. This conclusion may help clarify the amount of anthropogenic influence over these ponds and could also help explain any patterns of recovery from acid rain.

Table 3: Percent precipitation and sea salt contribution of sulfate, chloride, calcium, and magnesium concentrations in the six BRF ponds. The most current precipitation data from the NADP was from 2017. Ion concentrations were averaged for that year and compared to the 2018 ion concentrations for the six BRF ponds. Ion to sodium ratios in Table 2 were used to calculate the amounts of sea salt in mg/L, later converted to μEq/L, in the precipitation and then in each pond for each ion.

	Percent Precipitation Contribution (%)				**Percent Sea Salt Contribution (%)**			
Pond	**SO_4^{2-}**	**Cl^-**	**Ca^{2+}**	**Mg^{2+}**	**SO_4^{2-}**	**Cl^-**	**Ca^{2+}**	**Mg^{2+}**
TP	11.32	17.06	11.47	11.35	1.00	16.54	0.69	6.76
SPP	7.32	18.30	7.92	9.37	0.64	17.75	0.48	5.58
SUP	6.58	7.28	8.11	9.81	0.58	7.06	0.49	5.84
AP	7.00	18.03	4.22	6.23	0.62	17.49	0.25	3.71
AMR	7.27	18.82	2.04	4.12	0.64	18.25	0.12	2.45
UR	6.22	0.93	2.19	3.44	0.55	0.90	0.13	2.05

With these precipitation and marine contributions in mind, the median ion concentrations over time for each pond can be compared to those in the precipitation. The median sulfate, chloride, calcium, and magnesium concentrations of the six BRF ponds are all greater than the concentrations in the precipitation, but are less correlated with elevation. Arthur's Pond has the

highest median sulfate concentration of 235.3 μEq/L, followed by Upper Reservoir with 229.0 μEq/L, then Sutherland Pond with 168.6 μEq/L, Sphagnum Pond with 149.9 μEq/L, Aleck Meadow with 137.1 μEq/L, then Tamarack Pond with 131.2 μEq/L, and then finally the precipitation with only 29.7 μEq/L (Figure 17a). Upper Reservoir has by far the greatest median chloride concentration at 473.4 μEq/L, while the precipitation only has a median chloride concentration of 7.3 μEq/L (Figure 17b). The remaining ponds range from 33.2 μEq/L (AMR) to 114.6 μEq/L (SUP) (Figure 17b). Upper Reservoir also has the greatest median calcium concentration of 226.6 μEq/L, followed by Aleck Meadow Reservoir with 134.1 μEq/L, while the precipitation only has a median calcium concentration of 3.8 μEq/L (Figure 17c). The remaining ponds all have median calcium concentrations between 30 and 60 μEq/L (Figure 17c). Finally, the median magnesium concentrations generally increase with decreasing elevation, excluding Tamarack Pond, with precipitation having the lowest median magnesium concentration of 2.1 μEq/L and Upper Reservoir having the greatest of 80.2 μEq/L (Figure 17d). Of all four ions, the amount of sulfate and calcium in each pond are perhaps the most important for investigating potential biological recovery.

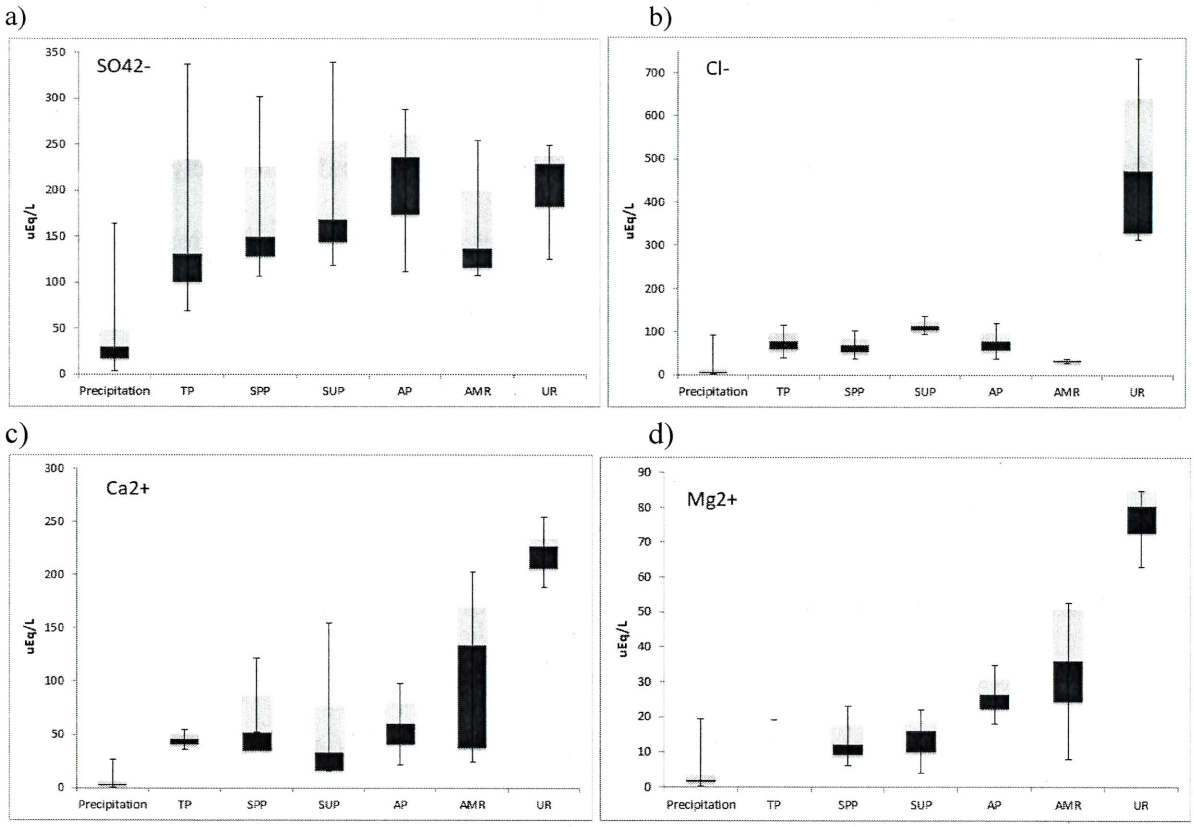

Figure 17: The median sulfate, chloride, calcium, and magnesium concentrations of precipitation and six BRF ponds. ±25th and 75th quartile are shown, with interquartile range whiskers. TP = Tamarack Pond; SPP = Sphagnum Pond; SUP = Sutherland Pond; AP = Arthur's Pond; AMR = Aleck Meadow Res.; UR = Upper Res. The ponds are ordered from highest elevation (TP) to lowest elevation (UR). The precipitation record is September 1983 to December 2017, while the BRF pond records are July 1987 to June 2018, except for SUP and AP, which begin August 1992.

4.5. Recovery of Fish Populations

After evaluating the possible chemical recovery of the bodies of water from acid deposition, any potential changes in biological health could be investigated. Due to limited time available for this study, new data on the fish populations in the sampled bodies of water could not be collected. Instead, historical and pre-existing data, albeit limited, has been compiled and analyzed. In 2018 compared to 1987, there were both additions and eliminations of species from some of the ponds. In Sphagnum Pond (SPP), pumpkinseed are currently thought to be present, but had not been observed in 1987 (Table 4). Aleck Meadow Reservoir (AMR) is currently

thought to contain yellow perch and smallmouth bass (*Micropterus dolomieu*), which were absent in 1987 (Table 4). Additionally, Upper Reservoir (UR) is currently thought to contain smallmouth bass and banded killifish (*Fundulus diaphanus*), which were absent from all the ponds in 1987 (Table 4). Though smallmouth bass appear to have been added to Arthur's Pond (AP) after 1987, the golden shiner and banded sunfish are no longer observed despite being caught in 1987 (Table 4). Furthermore, the species richness in 2018 generally appears to correlate with the relative pH and calcium levels, both of which are known influencers of fish abundance (Driscoll et al., 2001). As expected, the lower pH, lower calcium ponds like TP contain fewer species, while higher pH, higher calcium ponds like AMR and UR contain a wider range of species (Table 4). The lower pH and calcium ponds still contain mostly acid-tolerant species like brown bullhead and chain pickerel, while the higher pH and calcium ponds have begun to support more acid-sensitive species like smallmouth bass (Table 4).

Table 4: Major ponds in Black Rock Forest and associated fish species in 2018 vs. 1987. The "X" indicates the presence of the fish species in that reservoir in 2018. The shaded blue cells indicate the addition of a species in 2018 compared to 1987, while the shaded red cells without Xs indicate the loss of a species in 2018 vs. 1987. Unshaded cells mean the species was found in that reservoir both in 2018 and in 1987. The 2018 data was preliminarily determined by the Black Rock Forest forest manager, Matthew Brady.

Pond name	Elevation (m)	Mean pH	$[Ca^{2+}]$ (μEq/L)	Brown Bullhead	Chain Pickerel	Pumpkinseed	Yellow Perch	Golden Shiner	Banded Sunfish	Smallmouth Bass	Banded Killifish
TP	390	5.59	35.9	X	X	X					
SPP	381	5.64	52.1	X	X	X	X				
SUP	380	5.88	50.8	X	X	X	X				
AP	375	6.27	97.6	X						X	
AMR	314	6.43	202.4	X	X	X	X	X	X	X	
UR	298	6.77	188.4	X				X		X	X

Only seven bodies of water outside of Black Rock Forest had available fishery data for the current fish species found in each pond. The lack of historical data prevents preliminary comparisons such as those done for BRF, but the data does show a similar correlation between pH, calcium, and species richness, in which the lower pH, lower calcium lakes have lower species richness, and the higher pH, higher calcium lakes have greater species richness. For example, Pine Meadow Lake has the lowest pH of 5.84 and lowest calcium concentration of 47.0 μEq/L, and only contained largemouth bass (*Micropterus salmoides*) and panfish (Table 5). In contrast, Lake Welch has the highest pH of 7.29 and the second-highest calcium concentration of 192.3 μEq/L, correlating with the greatest species richness: panfish, chain pickerel, smallmouth bass, and largemouth bass (Table 5).

Table 5: Current fish species associated with seven ponds throughout the Hudson Highlands. The "X" indicates the presence of the fish species in that lake/pond. These seven bodies of water were the only ones of the non-BRF ponds with available fishery data (New York State Department of Environmental Conservation, 2019). Note that "panfish" is not a specific species, but rather a category for several types of small game fish.

Pond name	Elevation (m)	Mean pH	$[Ca^{2+}]$ (μEq/L)	Brook Trout	Rainbow Trout	Brown Trout	Pan-fish	Chain Pickerel	Yellow Perch	Small-Mouth Bass	Large-Mouth Bass
Tior.	269.0	6.84	167.8				X	X	X		X
Ask.	230.0	6.51	124.4			X	X				X
Skan.	231.0	6.47	117.9	X			X				X
Welch	269.0	7.29	192.3				X	X		X	X
PM	266.0	5.84	47.0				X				X
Still.	242.0	6.63	326.9	X	X		X				
Coh.	203.0	6.59	175.8				X	X			X

Overall, of the 13 total ponds that had available fish data in BRF and Harriman, four ponds had pH values less than 6.0 in 2018, and of those four ponds, two contained three or fewer fish species (Tables 4 & 5). Of the remaining nine bodies of water with pH values 6.0 or greater in 2018, eight contained three or more fish species (Tables 4 & 5). Of those eight, four ponds had four or greater fish species in 2018 (Tables 4 & 5). Due to the small number of samples, however, the power of these results are very limited.

4.6. General Characteristics of Recovery

Despite observing general improvement in water quality for a majority of the 26 bodies of water, discrete response patterns of recovery could not clearly be identified. That is, each lake's trajectory for recovery could not necessarily be correlated with consistent characteristics like depth or elevation, but rather was mostly influenced by unmeasured differences in local geology, soils, and ecology throughout the study region. With that said, there were a few key characteristics that the most-recovered lakes appeared to share.

The most recovered bodies of water were decidedly defined as having statistically significantly higher pH and alkalinity, as well as statistically significantly lower sulfate, in 2018 vs. 1985. Four bodies of water fulfilled this criteria: Lake Tiorati, Breakneck Pond, Summit Lake, and Beacon Reservoir. Of these four ponds, three (Tiorati, Breakneck, and Summit) are in Harriman State Park. Additionally, two of them - Breakneck and Beacon - had endangered or critical pH levels and 0 μEq/L alkalinity in 1985, and now have satisfactory pHs and 40-60 μEq/L alkalinity. The other two - Tiorati and Summit - already had satisfactory pH levels and higher alkalinity values in 1985, and remain this way.

The second-most recovered bodies of water were decidedly defined as fulfilling two out of three of the same criteria. There were 15 bodies of water in this category: Upper Reservoir, Tamarack Pond, Sutherland Pond, Sphagnum Pond, Lake Kanawauke, Lake Wanoksink, Pine Meadow Lake, Second Reservoir, Third Reservoir, Island Pond, Forest Lake, Cranberry Pond, Jordan Pond, Clear Lake, and Lower Cohasset. Again, over half (8/15) of these ponds are in or adjacent to Harriman, while four are in BRF. Ten of the ponds had critical or endangered pH levels in 1985 and now have either endangered or satisfactory levels, while the remaining five already had satisfactory pHs in 1985 and are still satisfactory in 2018. Additionally, nine had 0.0 μEq/L alkalinity in 1985 and now have 40-60 μEq/L, while five of the remaining six had above-zero alkalinity in 1985 and now have alkalinities above 120 μEq/L.

There are seven ponds that either fulfill one out of the three criteria or none at all: Arthur's Pond, Aleck Meadow Reservoir, Stillwater Pond, Lake Askoti, Lake Skannatati, Lake Welch, and Bog Meadow Pond. Three of the seven are in Harriman, two are in BRF, one is in West Point, and one is near Clarence Fahnestock. All seven had some of the highest pHs and alkalinities in 1985 and have remained that way, though one has experienced a statistically significant drop in pH and one has had a statistically significant drop in alkalinity.

These patterns suggest that the two factors that may predominantly influence the trajectory for recovery in this region are location and the degree of past acidification. For example, most of the considerably recovered bodies of water are clustered together in Harriman State Park, with a smaller cluster also in Black Rock Forest. Furthermore, a majority of the most-recovered lakes according to the chosen definition generally seem to have been the most acidic and alkalinity-depleted in 1985. Relative to their severely acidified status in 1985, these

ponds have clearly chemically improved the most over time and are continuing to do so. The comparatively less acidic ponds in 1985 that are also in the "most-recovered" category have continued to become even more satisfactory for aquatic life. In contrast, the ponds that did not meet the defined criteria were all some of the least acidic and least vulnerable ponds in 1985. Thus, they have either not changed significantly since 1985 but remain satisfactory, or have actually become more chemically similar to the rest of the ponds by experiencing slight decreases in pH or alkalinity.

5. DISCUSSION

The recovery of the 26 most vulnerable bodies of water in the Hudson Highlands on the basis of surface pH and alkalinity has been examined. It was hypothesized that as a result of the post-Clean Air Act increase in precipitation pH, 26 lakes in Black Rock Forest and the surrounding Hudson Highlands would exhibit increased pH and alkalinity to healthy levels, as well as more viable aquatic ecosystem populations since 1985. However, the rate and extent of such recovery was expected to depend on each lake's underlying geology and surrounding environment. This hypothesis was mostly supported by the results of the study.

5.1. Surface Water pH and Alkalinity

This study finds that more bodies of water in 2018 have improved water quality than in 1985. Four more ponds that were previously classified as endangered or even critical in 1985 are now considered satisfactory for aquatic life, according to the New York State Department of Environmental Conservation (Figure 9; Becker & Boyle, 1986). The results also show that ten ponds that had previously been deemed vulnerable to acid deposition in 1985 have since become less vulnerable to acid deposition in 2018 (Figure 12). Additionally, 13 ponds had statistically

significantly higher pHs in 2018 than in 1985, while 16 had statistically significantly higher alkalinities (Figures 10 & 13). Of the half that showed this pH improvement, three were critical and seven were endangered in 1985, but are now either endangered or satisfactory (Figure 10). Of the 16 ponds that increased in alkalinity, nine had 0.0 μEq/L alkalinity in 1985 and now have greater than 0 μEq/L alkalinity (Figure 13). Unlike in 1985, the 2018 alkalinity values appear to follow a bimodal trend that separates the ponds into "low alkalinity" ponds that have ≤90 μEq/L alkalinity, or "high alkalinity" ponds with ≥120 μEq/L (Figure 14). This could mean that the alkalinity values in 1985 were so depleted for all of the ponds that the two categories could not be distinguished. But, as the lakes gradually recover and return to their natural states, the differences between the two populations become more obvious. Furthermore, the degree of scatter for the 2018 alkalinity values has increased from that in 1985, with the ponds in the "higher alkalinity" population exhibiting more scatter than those in the "lower alkalinity" population (Figure 13). This increase in scatter could be attributed to the location of the higher alkalinity bodies of water, which are generally closer to roads and therefore human influence, such as those in the middle of Harriman State Park. This trend suggests that each lake's surrounding environment, and especially the degree of isolation from humans, influences the rate of recovery from acidification. Overall, most of the lakes that were the most acidic and vulnerable to acid rain in 1985 experienced statistically significant increases in both pH and alkalinity in 2018. Similarly, many of the lakes that had been the least acidic and vulnerable to acid deposition in 1985 have either become more satisfactory for aquatic life or have not significantly changed.

Breakneck Pond not only exemplifies the statistically significant increases in pH and alkalinity, but also represents the nonlinearity of the recovery process (Figures 11 & 15). The pond's pH and alkalinity values did not steadily increase after 1985, but rather more closely follow a second-order polynomial trendline for pH and a third-order polynomial trendline for alkalinity (Figures 11 & 15). More important than the specific type of trendline is how that nonlinearity likely results from the influence of other variables like geology and soil on lake sensitivity to and recovery from acid precipitation. Variables like soil thickness and lake turnover time have all been known to affect lake vulnerability and rates of recovery (Richardson et al., 2018). For example, bodies of water in watersheds with calcite-containing soil or thick glacial till may be able to better resist acidification or more quickly recover, while those surrounded by thin, calcite-lacking till and soil may remain vulnerable for longer and struggle to chemically recover from acidification (Driscoll et al., 2003). Ultimately, surface water quality appears to have locally improved since 1985, but the length of time it may take to return to pre-industrial levels depends on the individual lakes' intrinsic and surrounding characteristics, as well as the continued reduction of sulfate and nitrate emissions (Richardson et al., 2018).

A significant limitation of this study is the accuracy and precision of the historical and current alkalinity values. The alkalinity values measured in the 1990s and 2000s for various water bodies seem much too high for the pHs during that time - especially considering that at a pH between 5.0 and 6.0, the dominant species in the carbonate system is free carbon dioxide rather than the bicarbonate and carbonate ions that generate alkalinity (Kalff, 2002). One possible reason for such discrepancies between past and current alkalinity data is the lack of standardized methodology for measuring alkalinity even within government and research

organizations. For example, in some cases where the pH of water is at 4.5 or lower, the alkalinity is just assumed to be zero without performing any titration (Neal, 2001). Based on how many ponds were recorded as having zero alkalinity by Becker and Boyle in 1985, these types of assumptions may have been made. As a result, researchers' methods and data are presented without explanation, leading to rampant confusion over the measurements and assumptions made, particularly in acidic systems (Neal, 2001). Another possible reason for inaccurate alkalinity data both in the past and in 2018 is the difference between on-site and laboratory alkalinity measurements. In 1994, it was found that measuring alkalinity in the laboratory rather than in the field introduced significant errors (Trick et al., 2008). But because *in situ* measurements are difficult and therefore may also generate significant error, it is recommended that alkalinity be determined both in the field and back in the laboratory (Trick et al., 2008). This thesis only measured alkalinity in the laboratory and not the field, so significant error is certainly possible. It is completely unknown whether the historical alkalinity values were measured in the field, lab, or both. With that said, one possible reason for the overestimation of those past alkalinity values is the promulgation of errors from the pH endpoint indicators used in alkalinity titrations (Haines et al., 1983). If the pH measurement during the alkalinity titration is incorrect because of indicator interference, then the amount of acid needed to reach the endpoint will be skewed, which thereby alters the experimentally-determined alkalinity value (Haines et al., 1983). For example, if a specific pH endpoint indicator overestimates the pH measured during the titration, then there is the possibility that more acid will be added to lower the pH to the necessary level, which corresponds to an overestimated alkalinity value (Haines et al., 1983).

5.2. Surface Water Ion Concentrations

Though most of the anion and cation analysis was limited due to a lack of historical data, a complete analysis over time for sulfate was possible. It was found that 15 of the 26 bodies of water have significantly lower sulfate concentrations in 2018 than in 1985 ($p < 0.05$; Appendix C, Table C2). These decreases are at least partly due to the statistically significant decrease in precipitation sulfate (Figure 5), but additional factors - such as any reduction in the weathering of sulfur-containing bedrock - may also contribute to further decreases in sulfate concentrations (Richardson et al., 2018). However, a lack of decrease in sulfate for the remaining 11 lakes does not necessarily indicate a failure to recover from acid rain, but rather could mean that those lakes predominantly obtain sulfate from sources other than precipitation. These concepts will be further explored in section 5.3. Measuring the concentrations of the major cations and anions is valuable for evaluating general water quality as well as recovery from acidification. For example, measuring Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+} over time can reveal any alkalinity and ANC depletion, and therefore possible increased vulnerability to acidification. Analyzing SO_4^{2-} and NO_3^{-} as proxies for SO_2 and NO_χ emissions can further reveal how acid deposition affects bodies of water. Sulfate in particular is important to monitor because US federal water quality guidelines for sulfate have not been developed as of 2011, despite evidence that elevated concentrations can be toxic for fish (Elphick et al., 2011).

Though time-series analyses for cations and anions were limited, the 2018 charge balance and charge balance error could be calculated to reveal the extent to which the ecosystem obeys electroneutrality, as well as the degree of sampling precision and accuracy. The results of this study found that the average percent charge difference for the 26 bodies of water in 2018 at both

surface and depth was 21.2%, ranging from -30.7% to 53.3%. This large variability results from the unique characteristics of each ecosystem, emphasizing the need to factor in any specific geologic parameters. The average charge balance error was 13.1%, ranging from -13.3% to 36.3%. A CBE greater than +/-10% typically represents some error with the determination of anion and cation concentrations, or the omission of an important component in the analyses (Andersen, 2015). Though the seven major ions - sodium, potassium, magnesium, calcium, bicarbonate, chloride, and sulfate - are usually sufficient to calculate a charge balance, a thorough understanding of the specific system is crucial for determining the most relevant ions for the calculation (Andersen, 2015). Because the majority of the charge balances are positive, it is possible that an important anion was excluded from the analyses. However, it is thought that most errors in charge balance determinations originate from errors in alkalinity titrations, which is also possible for this study (Andersen, 2015). The likelihood of various errors in these analyses highlights the importance of understanding the basics like pH, conductivity, surrounding land use, geology of the region, and potential sources of pollution when attempting data interpretation (Andersen, 2015).

5.3. Comparison with Precipitation

The relationship between the Black Rock Forest ponds and the atmosphere was illustrated by comparing the pond water pHs with that of the precipitation. This study found that the precipitation had the lowest median pH of 4.49 over the study period, while the median pond water pH increased from 5.00 at Tamarack Pond to 6.69 at the Upper Reservoir as the elevation of the ponds decreased from 390 meters to 298 meters (Figure 16). This trend is expected because as elevation decreases, the precipitation runoff interacts more with neutralizing factors

in the environment, such as limestone that was glacially-deposited as till. Processes like weathering, cation exchange, and biological uptake all increasingly neutralize protons in the water as it moves from pond to pond, especially as the streams connecting the ponds increase in length from Tamarack to Sphagnum to Aleck Meadow (Lawrence et al., 1999). As a separate system that receives relatively more groundwater, the Upper Reservoir exhibits even higher pH levels in comparison to the connected, less stream-fed ponds.

Because Black Rock Forest receives a mixture of marine and continental-type rain, it is important to further clarify the possible sources of ions in the ponds by calculating the overall precipitation and marine contributions. At the highest elevation, Tamarack Pond generally has the largest precipitation contribution, and therefore the largest sea salt contribution, for all ions except chloride (Table 3). At the lowest elevation, Upper Reservoir generally has the smallest precipitation and sea salt contributions, aside from calcium (Table 3). For all the ponds, chloride and magnesium have the largest marine contributions, while sulfate and calcium have the lowest. However, Upper Reservoir has surprisingly low precipitation and sea salt chloride at 0.93% and 0.90% respectively (Table 3). Though many of these ponds are thought to be ombrotrophic, all six ponds generally receive 18.82% or less of their ions from precipitation, and therefore even less from marine sources, depending on the specific ion (Table 3). Furthermore, the median sulfate, chloride, calcium, and magnesium concentrations of the six BRF ponds are all greater than the concentrations in the precipitation, but are less correlated with elevation (Figure 17). This trend is mostly because of evapotranspiration from the ecosystem, which concentrates ions in the surface waters (William Schuster, personal communication). In addition to

evapotranspiration, however, it appears that these ponds obtain a large amount of ions from non-precipitation, non-marine sources, both natural and anthropogenic.

Chloride has the largest sea salt contribution in both precipitation and therefore the ponds because it partially makes up sea salt (NaCl). However, concentrations of chloride in rain rapidly decline further inland due to the combined effects of rainout, washout, and enhanced vertical mixing of the air over the continent (Berner & Berner, 2012). While Black Rock Forest is known to receive a mix of both marine and continental rain, the surprisingly small amounts of chloride reaching these ponds, especially the Upper Reservoir, may indicate that the primary sources of chloride in these ponds are not from precipitation. A major natural source may actually be from the underlying biotite that is known to contain high amounts of chloride (Léger et al., 1996). However, a possible anthropogenic source of chloride specifically for the Upper Reservoir could be road salt pollution because it has the closest proximity to the main gravel trail in the forest.

In contrast, the small amounts of marine and precipitation sulfate and calcium that reach these ponds are expected considering the significant continental and non-precipitation sources of both ions. While calcium primarily results from continental dust in the form of calcium carbonate, one natural source of sulfate could be sulfur-rich minerals, such as sphalerite, galena, and chalcopyrite, within the bedrock (Berner & Berner, 2012; Richardson et al., 2018). As seen in the Sky Lakes in the Shawangunk Mountains, weathering of these types of minerals provide additional geologic sources of sulfate to the nearby waters (Richardson et al., 2018). In addition to bedrock weathering, another possible natural source of sulfate to these ponds is the decomposition of organic material (Berner & Berner, 2012). As a result, sulfate concentrations are useful for tracking precipitation, geologic, and anthropogenic sources of ions into an

ecosystem (Richardson et al., 2018). Understanding the various non-precipitation sources of ions is especially valuable for explaining complicated pH trends and the nuances of acid rain recovery. Monitoring the calcium and sulfate concentrations and their possible sources in particular is perhaps most important for evaluating possible aquatic ecosystem recovery.

5.4. Recovery of Fish Populations

Total ecosystem recovery from acidification can only occur if both aquatic chemistry and biology recover. Biological recovery, however, depends directly on that of the water chemistry (Baldigo et al., 2016). In particular, fish species presence and community structure are often controlled by tolerance for changing habitats, climate, and water chemistry such as acidity. For example, in the 1970s, 46% of lakes in the New York Adirondacks and Catskills had critically low pHs and nonexistent fish populations. Since then, however, the proportion of acidified and fishless lakes in this region has substantially dropped in correlation to increased pH, alkalinity, and acid neutralization capacity (Charifson et al., 2015). In addition to higher pH and alkalinity, increased calcium concentrations have also been shown to reduce any toxic stress on fish caused by acidification because of its direct contribution to alkalinity and ANC. As a result, lakes with higher calcium are more hospitable to fish (Driscoll et al., 2001).

With the Adirondacks and Catskills as a model, the comparison of Black Rock Forest's fish survey data from 1987 to the current anecdotal data revealed that three ponds gained fish species over time, while one both gained and lost species. Between 1987 and 2018, Sphagnum Pond gained pumpkinseed, Aleck Meadow Reservoir gained yellow perch and smallmouth bass, and Upper Reservoir (UR) gained smallmouth bass and banded killifish (Table 4). Though Arthur's Pond gained a population of smallmouth bass, it appears to have lost golden shiner and

banded sunfish (Table 4). It was observed that in 2018, the lower pH ponds like Tamarack still contain mostly acid-tolerant species, while the higher pH ponds like Upper Reservoir have begun to support more acid-sensitive species like smallmouth bass. After analyzing the current available fishery data for seven ponds in Harriman, it was found that both the Harriman ponds and the BRF ponds generally have a similar positive correlation between pH, calcium concentrations, and species richness, with the lower pH, lower calcium ponds overall containing three or fewer species, and the higher pH, higher calcium ponds generally supporting more than three species (Tables 4 & 5). These results suggest that water chemistry parameters like pH, alkalinity, and calcium concentrations have recovered enough only in some of the ponds to support acid-sensitive fish like bass, meaning the most common species in all of the ponds are still acid-tolerant fish like brown bullhead and yellow perch. However, the power of these conclusions is limited due to the small number of samples with available fish data.

Along with changes in water chemistry, varying fish species abundance is also affected by human introduction, fishing, and geographic barriers (Charifson et al., 2015). The addition of smallmouth bass in Arthur's Pond, Aleck Meadow, and Upper Reservoir - along with the banded killifish gain in Upper Reservoir - could have resulted from deliberate stocking after 1987. However, it is also possible that the populations did exist in these ponds in 1987, but had gotten so small that the Adirondack Lakes Survey did not catch any individuals. The sustained satisfactory pH levels and relatively higher alkalinity values in these ponds since the 1980s could have allowed these populations to substantially increase. Furthermore, the new population of pumpkinseed in Sphagnum Pond could have simply traveled downstream from Tamarack Pond if there were no geographic barriers, while the population of yellow perch in Aleck Meadow could

have similarly traveled down from Sphagnum. Meanwhile, the loss of golden shiner and banded sunfish in Arthur's Pond could have resulted from the continued acidification of the pond after 1987 before the 1990 Clean Air Act Amendment was implemented. Additionally, even if the pH, alkalinity, and other water chemistry parameters improved over time, any fish populations that completely died out would have no way of being re-established without human intervention methods such as stocking.

Regardless of the specific mechanisms by which species were gained or lost, such changes in species abundance can have widespread effects on the entire ecosystem. Fish communities in general are integral components of most aquatic ecosystems because they link trophic levels and provide ecosystem services. This means that any loss of a species impacts the whole-lake community structure (Charifson et al., 2015). Golden shiners, for example, are zooplanktivorous, and therefore control the zooplankton population in ponds. Because zooplankton are predators of phytoplankton, the golden shiner indirectly increases the phytoplankton population and biomass by consuming zooplankton (Charifson et al., 2015). If the entire golden shiner population were to be eliminated, as it appears to have been in Arthur's Pond, then there may be a correlated increase in zooplankton population and therefore a decrease in producer biomass. The result of these combined effects would be a massive decrease in pond productivity, marked by an increase in water transparency (Charifson et al., 2015). Thus, even though some of the BRF ponds have chemically recovered enough to support the addition of more acid-sensitive species, the apparent loss of two species in Arthur's Pond suggests the need for continued monitoring, especially since one of those species is golden shiner.

6. CONCLUSION

Due to its downwind location from major fossil fuel emissions, the Hudson Highlands region of New York state is particularly vulnerable to acid deposition, and has historically suffered from such pollution. Despite effective recognition and political mitigation of acid precipitation, the corresponding chemical and biological recovery of certain vulnerable bodies of water since 1985 has been relatively unknown. Overall regional improvement of surface water has been shown in 2018 compared to the 1980s, but still the rate and extent of chemical and biological recovery of the 26 most vulnerable bodies of water is undoubtedly influenced by specific watershed characteristics and underlying geology. In comparison to the direct increase in rain pH between 1983 and 2018, the increases in lake pH follow expected trends for decreasing pond elevation, but still are generally less universal or consistent over time. Additionally, in comparison to the direct decrease in rain sulfate concentrations between 1983 and 2018, the corresponding decreases in lake sulfate are much less significant and also less universal. However, this lack of decrease does not necessarily mean recovery is not occurring, but rather could signify that the ponds obtain most of their sulfate from non-precipitation, non-marine sources, as they appear to do for their other ions as well. Regarding subsequent biological recovery, analyses of fish species in the six BRF ponds from 1987 to 2018 show that some of the ponds are now able to support more acid-sensitive species like smallmouth bass, but that the most abundant fish in all the ponds are still the most acid-tolerant. Additionally, the apparent loss of golden shiner and banded sunfish in Arthur's Pond between 1987 and 2018 is concerning if it is accurate. Finally, analysis of the current fish species in correlation to pH and calcium concentrations for the six BRF ponds and seven of the Harriman ponds suggests that lakes with

higher pHs and calcium concentrations can indeed support a greater range of species, though data supporting this conclusion are limited.

Other lake studies have been conducted in nearby regions, such as the Catskills, Adirondacks, and Shawangunk mountains. With comparable bedrock and soil compositions, the Hudson Highlands lakes have been similarly sensitive to historic acidification. In terms of recovery, compared to the lakes in the Adirondacks and Catskills, the water bodies in the Hudson Highlands appear to be experiencing more successful and faster recovery from acidification. While significant increases in both pH and alkalinity have been observed for a majority of these 26 bodies of water, no such increases in alkalinity or ANC have been observed in the Catskills or Adirondacks (Driscoll et al., 2001). This lack of recovery of Adirondack and Catskill surface waters is likely because of the historically greater inputs of acid deposition in these higher-elevation areas, which has resulted in a greater depletion of base cations (Driscoll et al., 2001). Compared to the Sky Lakes in the nearby Shawangunk Mountains, however, the Hudson Highlands lakes have experienced analogous increases in pH since the 1980s (Richardson et al., 2018). With that said, the recovery of the Sky Lakes has been facilitated by humans in the form of trail gravel experimentation to increase the amount of base cations, while no such management has occurred in these 26 bodies of water (Richardson et al., 2018). In the context of these similar lake acidification studies, the results for the Hudson Highlands appear to be more optimistic, yet also generally comparable.

7. RECOMMENDATIONS

The results of this study have assessed the overall health and degree of recovery of the 26 most vulnerable bodies of water in the Hudson Highlands. This is especially important because

some of these 26 lakes have not been consistently studied from 1985 to 2018, resulting in gaps in compiled historical water chemistry data. Due to the inconsistency of water chemistry collection from these vulnerable surface waters over the last three decades, it is highly recommended that researchers and scientists begin regularly surveying the health of these waters. In the complete absence of historical data for some of the ponds, these results can serve as a baseline. Similarly, it has been discovered that Black Rock Forest lacks both historical and current data on the fish populations in the BRF reservoirs. Upon noticing such gaps in knowledge, Dr. Schuster and the BRF staff are now dedicated to maintaining a more updated record of their fish species, population sizes, and overall health.

Though it has been concluded that the Clean Air Act has been successful in promoting recovery from acidification in these 26 bodies of water, the term "recovery" itself can be interpreted differently. If "recovery" is interpreted as a gradual process of improving pH, alkalinity, and biological health, then these 26 lakes can be considered to be currently recovering. But, if "recovery" is instead taken as a return to pre-industrial conditions, then most of these ponds have not recovered from acidification (Futter et al., 2014). Under this latter definition, full recovery of these bodies of water will likely be very slow or even nonexistent. As a result, human management may be necessary to accelerate such recovery from acidification and improve the health of biological communities, particularly for the most acid-sensitive lakes. For instance, Sweden has implemented a national effort to apply lime to watersheds and lakes, thereby increasing the amount of base cations and facilitating lake and fishery recovery to pre-acidification status. Liming, however, is labor-intensive, expensive, and may take over 50

years to establish desired recovery (Richardson et al., 2018). Thus, liming is not recommended at this time for any of the studied ponds.

On a larger scale, these results have quantified the success and importance of the Clean Air Act Amendment and similar emissions controls, which is especially important in this hostile political climate in which efforts have been made to limit such regulatory policies. Limitations on these successful policies would likely lead to a resurgence of SO_4^{2-} and NO_χ emissions, and thus an increase in acid deposition that would once again damage the health of these aquatic ecosystems. In addition to serving as an example for how to reduce acid precipitation in similarly acidified areas like Canada, Northern Europe, and China, the Clean Air Act can also be used to model regulations against other anthropogenic harms to water quality. Ultimately, though the rates and degrees of recovery are quite variable, these 26 lakes in the NY Hudson Highlands have undoubtedly improved in water quality as a result of the Clean Air Act, making it an essential policy to preserve and even expand.

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10. APPENDICES

10.1. Appendix A: Descriptions of Sampled Lakes

Table A1: Basic descriptions of 26 lakes sampled in the Hudson Highlands. Table is adapted from the December 1995 table called "Basic descriptions of ponds in the immediate Black Rock Forest Vicinity" (Adirondack Lakes Survey, 1987; Greeson & Robinson, 1970). Non-BRF data comes from New York State DEC, Division of Fish, Wildlife and Marine Resources Lake Map Series (New York State Department of Environmental Conservation, 2019).

Name (Abbrev.)	GPS; Elevation (m)	Area (ha)	Max Depth (m)	Flushing Rate	Notes
Arthur's Pond (AP)	41.40050763 -74.02140565; 375.0	5.8	5.5	1.8 times/yr	1920-1922; man-made; dammed
Aleck Meadow Reservoir (AMR)	41.40616816 -74.01501521; 314.0	3	7	10.5 times/yr	1910-1915; man-made; dammed
Upper Reservoir (UR)	41.41130445 -74.0063821; 298.0	6.1	7.2	4.9 times/yr	man-made; dammed
Tamarack Pond (TP)	41.39498391 -74.02531259; 390.0	7.3	2.5	2 times/yr	man-made; dammed
Sutherland Pond (SUP)	41.39345645 -74.0366712; 380.0	4.1	2.75	2.1 times/yr	Pleistocene; natural; dammed
Sphagnum Pond (SPP)	41.39819479 -74.02959064; 381.0	6	4.25	2.4 times/yr	man-made; dammed
Bog Meadow Pond (BMP)	41.38549281 -74.01272218; 308.0		5.75		man-made; dammed
Lake Tiorati (Tior.)	41.26846839 -74.08733141; 269.0	119	10		man-made; dammed
Lake Askoti (Ask.)	41.23957777 -74.10549984; 231.0	17.4	6		man-made; dammed
Lake Skannatati (Skan.)	41.24246182 -74.10094963; 230.0	14.7	7		man-made; dammed
Lake Kanawauke (Kan.)	41.23095968 -74.11754169; 243.0		4.5		man-made; dammed

Breakneck Pond (Break.)	41.20625944 -74.09663524; 289.0		3.5		natural; dammed
Lake Welch (Welch)	41.23024987 -74.07237094; 269.0	83	9.25		man-made; dammed
Lake Wanoksink (Wan.)	41.1824069 -74.12334336; 274.0		6.25		man-made; dammed
Pine Meadow Lake (PM)	41.17447997 -74.1240046; 266.0	29.7	4.25		man-made; dammed
Second Reservoir (2nd)	41.20853048 -74.07204766; 246.0		5.6		man-made; dammed
Third Reservoir (3rd)	41.20792031 -74.08329588; 298.0		5.5		man-made; dammed
Island Pond (Isl.)	41.2590522 -74.13966821; 260.0	21.5	36.6		natural; NOT dammed
Summit Lake (Sum.)	41.31083422 -74.09465109; 285.0		7.6		man-made; dammed
Forest Lake (For.)	41.29788996 -74.1029881; 292.0		17.25		man-made; dammed
Cranberry Pond (Cran.)	41.34946161 -74.0044974; 229.0	9.7	7.5		man-made; dammed
Beacon Reservoir (Beac.)	41.4880876 -73.94103993; 361.0		8.5		man-made; dammed
Jordan Pond (Jor.)	41.45104942 -73.8661448; 247.0		2		man-made; dammed
Stillwater Pond (Still.	41.44066973 -73.82165132; 242.0	22.4	7		man-made; dammed
Clear Lake (Clear)	41.43025376 -73.84073606; 245.0		>>18		man-made; dammed
Lower Cohasset (Coh.)	41.27586981 -74.1192408; 203.0	4.5	4.25		man-made; dammed

10.2. Appendix B: Marine Contributions to Precipitation Ions

Table B1: Sea salt contribution of Black Rock Forest precipitation. The average 2017 ion concentrations in the precipitation were retrieved from NADP station NY99 operated by Black Rock Forest. Ratios to sodium in Table 2 were used for the calculation of sea salt contribution (National Atmospheric Deposition Program, 2019).

Ion	Total Concentration (μEq/L)	Sea Salt (μEq/L)	Excess (μEq/L)	Percent sea salt to total (%)
SO_4^{2-}	7.79	0.69	7.11	8.79
Cl^-	6.63	6.62	0.21	97.00
Ca^{2+}	4.12	0.25	3.87	6.01
Mg^{2+}	2.17	1.29	0.88	59.54

10.3. Appendix C: T-Test *p* Values

Table C1: Calculated *p* values from paired one-tailed t-tests comparing pH between 1985 and 2018 and alkalinity between 1985 and 2018. The critical p value is set as 0.05. Analyses were conducted in Microsoft Excel.

Name	pH *p* values	Alkalinity *p* values
AP	0.265291586	0.137357897
AMR	0.311543217	0.023169092 (lower)
UR	0.259625597	0.00216534
TP	0.030194899	0.017998335
SUP	0.010006	0.050723203
SPP	0.033735869	0.013901869
BMP	0.143316196	0.243548656
Tior.	0.002936883	0.017708409
Ask.	0.014125425 (lower)	0.247493675
Skan.	0.046790268	0.402406126
Kan.	0.000823789 (lower)	0.087621934
Break.	5.86838E-05	0.011783869

Welch	0.012453479	0.151853013
Wan.	0.17803763	0.020950572
PM	0.121731945	0.037007231
2nd Res	0.17543425	0.018437559
3rd Res	1.25997E-05	0.00309029
Island	0.001263628	0.002253718
Sum.	0.001466258	0.024924834
For.	0.131265797	0.034233598
Cran.	0.007668634	0.028178516
Beac.	0.00091206	0.020476333
Jor.	0.176609794	0.024311669
Still.	0.412976126	0.057635854
Clear	8.13852E-05	Not enough data
Coh.	0.480489578	0.03109952

Table C2: Calculated *p* values from paired one-tailed t-tests comparing anion concentrations pre-2018 vs. 2018. The pre-2018 time periods of comparison depend on the historical data available for each body of water. The critical p value is set as 0.05. Analyses were conducted in Microsoft Excel.

Name	Cl- One-tailed T-test P value	SO42- One-tailed T-test P value	NO3- One-tailed T-test P value	PO43- One-tailed T-test P value
AP		0.053107365		
AMR	0.256117323	0.136135717	0.222060653	
UR	0.007089329	0.034877867	0.063320842	
TP		0.177853732	0.206735867	
SUP		0.192371415	0.400622528	
SPP		0.180738028		
BMP				

Tior.		0.024592394	0.083239663	
Ask.		0.012615006	0.004133662	
Skan.		0.074566889		
Kan.		0.034948003		
Break.	0.021453888	0.049362067	0.043292265	0.238075759
Welch		0.08623351	0.060161433	
Wan.		0.009010784	0.101424508	0.094261415
PM		0.032351928	0.14135661	0.249901978
2nd Res		0.006016885		
3rd Res	0.210071029	0.051263588	0.121134909	
Island	0.10352878	0.052178765	0.100481174	
Sum.		0.001305657		
For.		0.005116774		
Cran.	0.201059953	0.144684796	0.026705177	
Beac.		0.020522716	0.076270154	
Jor.		0.003005304		
Still.		0.016757271	0.042583948	0.029093294
Clear		0.009726715		
Coh.		0.005728597	0.095418457	

Table C3: Calculated *p* values from paired one-tailed t-tests comparing cation concentrations pre-2018 vs. 2018. The pre-2018 time periods of comparison depend on the historical data available for each body of water. The critical p value is set as 0.05. Analyses were conducted in Microsoft Excel.

Name	Ca2+ One-tailed T-test P value	K+ One-tailed T-test P value	Mg2+ One-tailed T-test P value	Na+ One-tailed T-test P value
AMR	0.215982925	0.267548841	0.441812437	0.033054097 (H)
UR	0.085357375	0.06282624	0.049780907 (L)	0.024684437 (H)
SUP	0.027283928 (H)		0.156869313	

10.4. Appendix D: Charge Balance and Error Values

Table D1: Calculated charge balance and charge balance error for 26 bodies of water at surface and at depth. The charge balance is expressed as percent charge difference between anions and cations. A charge balance error less than +/-10% is considered precise and accurate.

Name (Depth)	Charge Balance (percent charge difference)	Charge Balance Error (CBE) (%)
AP (0.5 m); (5.0 m)	44.45342495; 49.21616614	28.57885166; 32.64021406
AMR (0.5 m); (6.5 m)	31.07738846; 40.51944269	18.3974118; 25.40713637
UR (0.5 m); (7.0 m)	15.92081074; 12.07332386	8.648892252; 6.424486461
TP (0.5 m); (2.0 m)	44.89507474; 50.92364707	28.94497042; 34.15943982
SUP (0.5 m); (2.5 m)	21.18811341; 50.55966231	11.84938754; 33.83267403
SPP (0.5 m); (4.0 m)	36.16798738; 36.98576033	22.07626385; 22.68866843
BMP (0.5 m); (5.5 m)	35.34273159; 31.06506726	21.46442239; 18.38877653
Tior. (0.5 m); (9.75 m)	14.99627673; 20.00802419	8.105932394; 11.11606454
Ask. (0.5 m); (6.75 m)	15.948888; 15.64348303	8.665466797; 8.485451608
Skan. (0.5 m); (5.75 m)	16.9483343; 13.91773467	9.258770867; 7.479345034
Kan. (0.5 m); (4.0 m)	6.65818181; 10.25692563	3.443736007; 5.405691703
Break. (0.5 m); (3.5 m)	36.83509061; 42.75406768	22.57537527; 27.18929962

Welch (0.5 m); (9.25 m)	16.02690337; 6.580430034	8.711547321; 3.402153171
Wan. (0.5 m); (6.0 m)	16.79295152; 12.15670535	9.166105591; 6.471727073
PM (0.5 m); (4.0 m)	12.68278626; 17.88664658	6.77075321; 9.821710623
2nd Res (0.5 m); (5.25 m)	20.4812018; 45.16583715	11.40894547; 29.17045975
3rd Res (0.5 m); (5.25 m)	-30.72953388; 20.73277495	-13.31842238; 11.56529028
Island (0.5 m); (>17.5 m)	48.76056303; 53.29206607	32.24064041; 36.32527884
Sum. (0.5 m); (7.5 m)	34.69444408; 28.51230563	20.98806896; 16.62644409
For. (0.5 m); (17.0 m)	33.28834531; 24.83707714	19.96761737; 14.17941464
Cran. (0.5 m); (7.0 m)	-11.05609686; -13.98721313	-5.238463625; -6.536471469
Beac. (0.5 m); (8.25 m)	14.62954365; 14.92940324	7.892057851; 8.066869347
Jor. (0.5 m); (1.5 m)	21.84004423; 14.6389382	12.25867179; 7.897526082
Still. (0.5 m); (6.75 m)	1.735387266; -5.712077482	0.875288455; -2.776734138
Clear (0.5 m); (>17.5 m)	-10.85473775; -12.13704956	-5.147969578; -5.721324771
Coh. (0.5 m); (4.0 m)	19.42023843; 14.72988268	10.75438258; 7.950490288