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Watershed management and underlying geology in three lakes control divergent responses to decreasing acid precipitation

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ABSTRACT

In northeastern North America, acidification of precipitation and freshwater ecosystems is due to increased anthropogenic emissions of sulfate (SO_4^{2-}) and nitrogen oxides (NO_x). Legislative changes (e.g., the 1990 Clean Air Act Amendment) have resulted in decreasing emissions and increasing precipitation pH. We hypothesized that precipitation pH increased and regional improvements in acid precipitation resulted in increasing pH levels in our study lakes – Lake Minnewaska, Lake Awosting, and Mohonk Lake, on the Shawangunk Ridge, New York, USA – but the rates of change would be dependent on underlying geology and watershed management. Precipitation pH increased from 4 in 1976 to >5 in 2015. Our 3 study lakes had increasing pH, although at different rates from changes in precipitation pH and compared to each other. Several factors likely control the differences in lake acidity improvements. Mohonk has remained neutral because of an exposed shale inlier in the lake that buffers the acidic precipitation. The bedrock under Awosting and Minnewaska is quartz-conglomerate with little buffering capacity. Changes in Awosting seem to be closely linked to precipitation pH recovery; however, the pH in Minnewaska has increased above biologically meaningful levels because of eroding shale recreational trails around the lake, a finding supported by water chemistry trends. Across this region and around the world, the rate of recovery from acid precipitation and decrease in lake acidity in this region can affect the return of acid-sensitive freshwater ecological communities.

KEYWORDS

acid precipitation;
lake acidification; lake
ecosystems; recovery

Introduction

Acidification of precipitation has historically been a problem in northeastern North America, areas of Europe, and, recognized more recently, in eastern Asia because of anthropogenic sulfur and nitrogen emissions from the burning of fossil fuels and agricultural activity (Likens et al. 1972, Cogbill and Likens 1974, Schindler et al. 1989, Driscoll et al. 2001, Duan et al. 2016). Acid precipitation is caused by emissions of sulfate (SO_4^{2-}) and nitrogen oxides (NO_x) from stationary and mobile sources such as fossil-fuel driven power production, smelters, other industry, and vehicles (Menz and Seip 2004). Awareness of the contributions of fossil fuel burning to local air and precipitation quality spans several centuries (Cowling 1982). Acid precipitation was first identified as an environmental problem across eastern North America and Europe in the 1970s, however, with records of increase in precipitation acidity dating back to the 1950s (Likens et al. 1972, Bolin

and Persson 1975). Northeastern North America is downwind of coal fired power plants in Midwestern USA and receives deposition laden with sulfuric and nitric acids (Raynor and Hayes 1981, Menz and Seip 2004) because of the Prevailing Westerlies, west to east winds at high altitude.

Acid precipitation has led to the acidification of some freshwater ecosystems with major ramifications for food webs; however, the magnitude of the effect can be controlled by underlying geology (Jeffries et al. 2003). Lakes with underlying limestone or shale bedrock will increase the acid-neutralizing capacity of the lake through slow release of solutes and mute the effects of acid precipitation (Kirby et al. 2008). Alternatively, lakes with shallower soils in their watershed and underlying lithology with poor buffering capacity (e.g., quartz or granite) can be more susceptible to increased surface water acidity, changes in chemistry, and subsequent losses of sensitive taxa including fish and macroinvertebrates (Schindler et al. 1989).

These lakes can experience ecological regime shifts from fish-dominated food webs to alternate states where few or no fish species remain (Beamish 1974, Driscoll et al. 2001). Further, lakes undergoing acidification can experience the loss of phytoplankton species along with a shift in phytoplankton community dominance to acid tolerant species (Findlay 2003).

Following the recognition in the scientific community and general public of acid precipitation as an environmental problem, policy changes were enacted by national governments. For example, the US Federal legislature passed Title IV of the Clean Air Act amendment (CAAA) of 1990 and implemented the amendment in January 1995 to limit sulfur dioxide emissions from coal-fired power plants upwind of northeastern North America (Lynch et al. 2000). This successful regulation led to decreased precipitation acidity in northeastern North America, largely due to decreases in sulfur emissions (Greaver et al. 2012). Following implementation of the CAAA, annual precipitation pH increased from 4.3 in 1994 to 5.1 in 2015 as measured at the New York Catskill Mountains National Atmospheric Deposition Program site (NTN Site NY68: <http://nadp.isws.illinois.edu/>); however, lake chemistry recovery has varied (Driscoll et al. 2003, Clair et al. 2011). Models suggest that biological recovery and regime shifts back to prior states could take decades or longer and depend on many factors, including geology, regional biological species pools, species dispersion, and management interventions (Driscoll et al. 2001, Johnson and Angeler 2010, Layer et al. 2010).

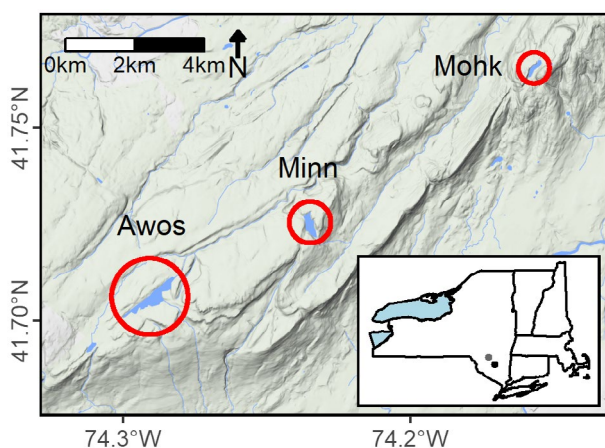


Figure 1. The Sky Lakes on the Shawangunk Ridge (circled: Awos = Awosting, Minn = Minnewaska, and Mohk = Mohonk). Map from Google Earth, accessed 7 Dec 2017, and figure created using R packages *ggplot2* and *ggmap* (Wickham 2009; Kahle and Wickham 2013). Study lakes were in southeastern New York State, USA (inset, black point). Precipitation depth and pH was taken at the northern edge of Mohonk; precipitation chemistry was from National Atmospheric Deposition Program site (NY68, inset gray point), < 40 km from the study lakes.

In the absence of management, recovery of acid-sensitive lakes (i.e., increasing pH and alkalinity) is nonexistent (Clair et al. 2011) or slow (Futter et al. 2014), driven by regional decreases in deposition of SO_4^{2-} and NO_x ; however, directed human intervention can facilitate recovery. One management strategy is to add base cations, typically in the form of calcium carbonate (lime; CaCO_3) to facilitate lake recovery to pre-acidification pH (Clair and Hindar 2005). Liming is labor intensive and expensive, however, and may have to be conducted for more than 50 years to reach pre-acidification conditions (Bengtsson et al. 1980, Clair and Hindar 2005). Anthropogenic activities that do not actually target recovery from acid precipitation, such as importing gravel for transportation and treating roads with dust suppressants or deicing agents, can increase base cation concentrations or slow calcium decline in lakes (Yao et al. 2011). The dissolution effect of gravel is significantly lower than that of powdered limestone (Watt et al. 1984). Over a longer time period, these modifications to the landscape, especially occurring near lake shores, could facilitate recovery from the effects of acid precipitation through direct contribution of calcium to the lake or by replacing soil calcium reserves depleted by acid precipitation (Yao et al. 2016).

Aquatic ecosystems on the Shawangunk Ridge in the Hudson River Valley, eastern New York State, USA (Fig. 1), have experienced acid precipitation. The Shawangunk Ridge is downwind of the coal-fired power plants in the Midwest and has a history of local industry with smelting and charcoal production (Josephson and Larsen 2013). Further, the Shawangunk Ridge has thin soils with erosion-resistant underlying bedrock (Caine et al. 1991). The susceptibility of the lakes to deleterious effects of acid precipitation could vary across multiple lakes in geologic transition zones, however, and are similar to other locations with varying geology (e.g., Chen and Hung 1987, Futter et al. 2014). Here, we asked 3 major questions: (1) How has acid precipitation changed over time, especially following the CAAA amendments? (2) Does lake acidity on the Shawangunk Ridge reflect changing acid precipitation? (3) How does recovery from acidification differ in lakes close in proximity as a result of watershed management and underlying geology? We used long-term precipitation and lake chemistry records to test if the Shawangunk Ridge experienced acidification of precipitation and freshwater ecosystems followed by more recent recovery. We predicted decreasing acidity of precipitation following anthropogenic reductions in emissions. We predicted that lake pH would increase with improvements in acid precipitation, but the magnitude of effect and recovery would be dependent on underlying geology. Finally, we hypothesized that application of shale and other gravel to lakeside trails could decrease acidity in lake water.

Methods

Study site descriptions

The Shawangunk Ridge, New York, USA, is composed of erosion-resistant quartz-pebble conglomerates and quartz sandstones. Retreating glaciers gouged out depressions in the hard bedrock ~16 000 years ago forming “Sky Lakes” on the Shawangunk Ridge (Peteet et al. 2009); these waterbodies are clear mountain (379–683 m a.s.l.) lakes with small watersheds relative to lake surface area (Table 1). Mohonk, Minnewaska, and Awosting are the focal lakes of this study and are within 13 km of each other (Fig. 1). These lakes have no perennial inflows and minimal outflows; the bedrock is solid with little groundwater exchange (Caine et al. 1991). The erosion-resistant quartz conglomerate results in shallow acidic soils with little buffering capacity within the watershed. The one exception is Mohonk, which has an inlier of the older Martinsburg shale covering a portion of the lake bed that buffers the lake water (Menking et al. 2012). The small watersheds, combined with the lack of surficial and groundwater inflows, result in predominantly ombrotrophic (rain-fed) lakes. The lakes reside within state park lands, private preserves, or protected resorts (Richardson et al. 2016) and are minimally affected by land use change and anthropogenic influence in the watershed outside of past and current land use for hotels and maintained hiking trails.

Precipitation

Precipitation depth has been measured since 1 January 1896 at the same location (41.767842°N, -74.155586°W; Fig. 1 at Mohonk Lake) using a US Weather Bureau/National Weather Service rain gauge, and the precipitation acidity has been measured at a National Weather Service station (index no. 30-5426-05) since 3 January 1976 by members of the Mohonk Preserve. Multiple pH readings were often recorded close together (<12 h) without indication of one or multiple precipitation events. We defined a single precipitation event as all events occurring <24 h after the previous collection. We applied this definition iteratively across the entire dataset, and all rainfall measurements for a single event were summed over all readings for that event. We averaged pH for a single event by transforming pH to H⁺ concentration (molarity), taking the arithmetic

mean, and back-transforming to pH units. This calculation occurred for all pH means, but for other subsequent statistical analyses we used pH values as a log-transformed variable. In total, 1984 precipitation events were recorded, and of those, 1966 had a pH value recorded. Data for precipitation pH analysis end 31 December 2015.

Precipitation water chemistry was not available at the same location as precipitation pH; therefore, we used cation and anion data from the US National Atmospheric Deposition Program/National Trends Network (NADP/NTN) at the Biscuit Brook site (NY68; 41.9942°N, 74.5036°W; Fig. 1 inset) in the nearby Catskill Mountains, ~40 km from our 3 lakes, to examine trends in precipitation chemistry. We downloaded monthly cation and anion wet deposition data over 2 time periods: 1983–1986, the earliest complete years on record, and 2013–2016. We used a 2-sample *t*-test to compare the 2 time periods of each cation or anion concentration. All statistical analyses for this and subsequent analyses were conducted using the R statistical package (R Core Team 2016).

Lakes

For Awosting, sample water was measured for pH at the outflow starting monthly in 1977; however, ~1 pH measurement for Awosting was recorded each August from 1972 to 1974. For Minnewaska, regular sampling every 2 to 4 weeks started in 1987; prior to 1987, one sample was recorded per year for 1972, 1977, 1983, 1984, and 1986. For Mohonk, daily or every other day sampling began 1 November 1977. All data used for lake pH analysis end 31 December 2015.

From 1977 to 1991, pH was measured using a Sargent-Welch analog pH meter. Beginning 13 December 1991, pH was measured with a Fisher Accumet digital pH meter with higher resolution, and probes were replaced every 6 months. In 2002, the meter was replaced with a new Fisher Accumet pH meter. We split each dataset into pre- and post-13 December 1991 because the upgrade in pH meter resulted in more consistent readings with finer resolution. We examined data prior to and following that date separately. Pre-1991 precipitation data however, were in close agreement with the pre-1991 data from the National Atmospheric Deposition Program NTN site NY68. For the pre-December 1991 data, we compared the

Table 1. Characteristics of study lakes, Shawangunk Ridge, NY. Lat. = latitude, Long. = longitude, Max depth = the maximum measured depth, SA = surface area of the lake, and SA:WA = percentage of the lake surface area out of the total watershed area. Shale refers to Martinsburg shale formation and QC refers to quartz conglomerate.

Lake	Lat. (°N)	Long. (°W)	Max depth(m)	SA(ha)	SA:WA (%)	Bedrock
Mohonk	41.766	-74.158	18.5	6.9	40	Shale-QC
Minnewaska	41.726	-74.235	23.4	13.8	45	QC
Awosting	41.706	-74.290	28.5	37.6	34	QC

pH of precipitation and the 3 lakes using a nonparametric Kruskal-Wallis test with comparison of multiple samples using the Nemenyi *post hoc* test (Tukey and Kramer approach) in the PMCMR R package (Pohlert 2014).

The post-December 1991 precipitation dataset and all 3 lake datasets were analyzed using time series. The autocorrelation (ACF) and partial autocorrelation (PACF) functions for all 3 lake pH time series indicated significant autocorrelation. We calculated autoregressive models for each lake using the `auto.arima()` function in the *R forecast* package that fits a time series model based on the Akaike information criterion adjusted for the number of parameters fit (AICc; Hyndman and Khandakar 2008). We calculated the slope of the time series by using a regression that fit days since the first day of the record (13 Dec 1991) and then modeled the residuals as an ARIMA process (Hyndman and Athanasopoulos 2012). Following model selection for each time series, we recorded the best-fit model, the regression slope, and its standard error. We present ARIMA results as ARIMA(p,d,q), where p is the number of autoregressive terms, d is the number of non-seasonal differences for stationarity, and q is the number of moving average terms as selected for the best-fit model.

We collected water samples from the epilimnion (<1 m) of Minnewaska, Awosting, and Mohonk between 2 and 5 times per summer from 2013 to 2016. We analyzed all samples for cation and anion concentrations (in $\mu\text{Eq/L}$), including chloride (Cl^-), sulfate (SO_4^{2-}), calcium (Ca^{2+}), and magnesium (Mg^{2+}) using ion chromatography (Dionex ICS-3000, Sunnyvale, CA, USA). No temporal trends emerged over this shorter time period in any cation and anion data, so we aggregated temporal data for comparison across lakes (hereafter: 2013–2016). For historical reference, we compiled cation and anion concentrations from 1972 to 1988 (hereafter: 1972–1988) for the lakes from published and unpublished literature (Pearson et al. 1976, Rubin 1981, Schiff 1986, Friedman et al. 1990). We ran 2-way ANOVAs for each cation and anion with lake (Awosting, Minnewaska, and Mohonk) and time period (1972–1988 and 2013–2016) as the 2 factors. Following significant interaction or main effects, we made *post hoc* pairwise comparisons with Šidák adjustment for means comparisons (family $\alpha = 0.05$).

The Henrikson nomograph, based on empirical relationships, separates lakes into bicarbonate ($\text{pH} > 5.3$), acidic ($\text{pH} < 4.7$), and transition ($5.3 > \text{pH} > 4.7$) lakes based on their relative concentrations of major cations (Ca^{2+} and Mg^{2+}) relative to SO_4^{2-} and their susceptibility to acid precipitation (Henriksen 1980). Schiff (1986) created the Henrikson nomograph for the Sky Lakes for data from 1984 (see figure 5.2 in Schiff 1986). We used median Ca^{2+} , Mg^{2+} , and SO_4^{2-} from our 2 time periods to recreate this figure and examine if our 3 study lakes

continued to fall into the same categories. We corrected concentrations for marine sea salt contribution (Wright and Cosby 2003) and included $\text{pH} = 5.3$ and $\text{pH} = 4.7$ boundary lines on the Henrikson nomograph per Schiff (1986). We also calculated the breakdown of sources for the median SO_4^{2-} concentration in Minnewaska water for each time period. We calculated precipitation marine (discussed earlier) and nonmarine sources, including natural sources and anthropogenic pollution. Watershed contributions (including soils and geologic sources) were assumed similar to Awosting given their close proximity and geology. The remaining portion, by difference, was calculated as anthropogenically imported trail gravel.

Trail gravel experiment

Four types of gravel were identified by the Minnewaska State Park Preserve management as commonly applied to trails in the State Park Preserve. The trail surrounding Minnewaska is between 7 and 170 m of the lake edge. Some trails extend into the Awosting watershed, but the trails are predominantly native bedrock and soil substrate. For Minnewaska State Park Preserve, 4 types of gravel were used for trails: 3 purchased from external suppliers and one mined locally on site (Minnewaska State Park Preserve, pers. comm.). A gravel mix (R1) was used by an outside contractor when modifying the trails. Item 4 (R2) was a silty shale gravel from the Mt. Marion formation (A. Bartholomew, Geology Department, SUNY New Paltz, 2013, pers. comm.). Shale (R3) was mined about 2.4 km from Minnewaska and was from the Pen Argyl member of the Martinsburg formation also exposed under Mohonk. This shale has been used to line trails around Minnewaska for >50 years. A mix purchased from offsite (R4) contained several types of rock, including limestone as indicated by bubbles released during a simple acid test for carbonate rocks via application of hydrochloric acid. All 4 types combined represented a mixture used on the 3.2 km trail loop around Minnewaska, the parking lot, and elsewhere in the park in 2013. We collected all gravel from the park's onsite storage areas prior to their application on the trails.

In spring 2013, we conducted 2 experiments to test the ability of different trail gravel types to decrease lake water acidity. For each experiment, we added the same 4 types of rock mixtures collected to acidic Awosting lake water (conductivity $< 10 \mu\text{S cm}^{-1}$ and $\text{pH} \sim 5$) in a ratio of 0.1 grams of rock per milliliter. We included 5 replicates per treatment as well as 1 gravel-free control with 5 replicates. The first experiment included unsorted materials of all size fractions; the second experiment included only rocks in the 2–4 mm size range to examine if the rocks themselves, independent of fine-grained particulates that

might dissolve more readily, were capable of decreasing lake acidity water. Following incubation at room temperature, the final pH measurements were taken using a benchtop pH meter (Mettler Toledo FE-20, Columbus, OH, USA). Final measurements of specific conductivity ($\mu\text{S cm}^{-1}$) were taken using a hand-held multimeter (Hanna HI 98129, Woonsocket, RI, USA) after the increase in pH stabilized, with measurements occurring every 2–7 d prior to stabilization. This plateau occurred at 22 d for the unsorted experiment and 28 d for the 2–4 mm size range. We analyzed data for each parameter (pH and specific conductivity) and experiment (unsorted and 2–4 mm) using a one-way ANOVA across the 5 treatments. Following significant ANOVA results, we applied *post hoc* means comparisons with Tukey's honestly significant difference (HSD) tests.

Results

Precipitation

Prior to December 1991, the precipitation was acidic with a median pH of 4.0 (Fig. 2). From December 1991 to December 2015, the median pH was 4.6 ± 0.4 (\pm quartiles). Over that time, precipitation pH increased (Fig. 3a). The time series model was selected as a second-order autoregressive model with 2 moving average terms (ARIMA(1,1,2), $\sigma^2 = 0.284$) with an increasing slope of 0.56 (SE 0.005) pH units per decade (Fig. 3a).

Precipitation SO_4^{2-} and nitrate (NO_3^-) concentrations have decreased over the past 25 years in this study area. In 2016, annual median SO_4^{2-} concentrations (8 $\mu\text{Eq/L}$) were 21% of 1991 concentrations (39 $\mu\text{Eq/L}$); similarly, in 2016, annual median NO_3^- concentrations (12 $\mu\text{Eq/L}$) were 44% of 1991 concentrations (27 $\mu\text{Eq/L}$). From the mid-1980s to mid-2010s, precipitation SO_4^{2-} ($t_{49} = 11.6$; $p < 0.001$), Cl^- ($t_{75} = 3.7$; $p < 0.001$), and Mg^{2+} ($t_{58} = 5.3$;

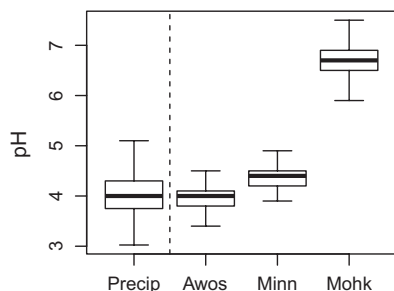


Figure 2. The median pH (± 25 th and 75th quartiles; whiskers are 1.5 \times interquartile range) of precipitation events (Precip) and each lake (Awos = Awosting; Minn = Minnewaska; Mohk = Mohonk) prior to 13 Dec 1991 on the Shawangunk Ridge, NY. The precipitation record begins 3 Jan 1976, Awosting's record begins 16 Aug 1972, Minnewaska's record begins 13 Aug 1972, and Mohonk's record begins 1 Nov 1977.

$p < 0.001$) concentrations all significantly decreased (Fig. 4). Precipitation Ca^{2+} concentrations did not significantly change over the 30-year time span ($t_{62} = 1.6$; $p = 0.13$; Fig. 4).

Lakes

Prior to 1991, Minnewaska and Awosting were both acidic, with median pH values of 4.4 and 4 respectively; Mohonk was generally neutral with a median pH of 6.7 (Fig. 2). Prior to 1991, Mohonk was significantly different than Awosting and Minnewaska (overall comparison: $\chi^2 = 3824$, $df = 3$, $p < 0.001$; Fig. 2); however, Awosting and Minnewaska pH were indistinguishable from precipitation pH ($p > 0.05$ for pairwise comparisons). For each lake from 1991 to 2015, the selected time series model included one or more autoregressive terms and a linear regression with increasing but varying slopes across the lakes (Fig. 3). The Awosting time series was selected as a first-order autoregressive model with one nonseasonal difference term and one moving average term (ARIMA(1,1,1), $\sigma^2 = 0.008$; Fig. 3b). The Minnewaska time series was selected as a second-order autoregressive model (ARIMA(2,0,0), $\sigma^2 = 0.047$; Fig. 3c). The Mohonk time series was selected as a first-order autoregressive model with a moving average term (ARIMA(1,0,1), $\sigma^2 = 0.012$; Fig. 3d).

From the time series slopes, Minnewaska had the largest rate of change in pH (0.72 [SE 0.008] pH units per decade) over the time investigated period; Awosting had an intermediate slope of pH (0.31 [SE 0.01] pH units per decade), and Mohonk had little change in pH over time (0.03 [SE 0.0005] pH units per decade). The precipitation slope was 50% greater than the Awosting slope but 35% smaller than the Minnewaska slope. Between 1991 and 2015, the precipitation H^+ concentration decreased by 95 μM , similar to a 82 μM decrease in Awosting over the same time period. Minnewaska had a decrease in H^+ concentration by 39 μM ; Mohonk had only a slight decrease of 0.03 μM . Annual mean precipitation pH was significantly correlated with Awosting ($r = 0.92$; $p < 0.001$), Minnewaska ($r = 0.93$; $p < 0.001$), and Mohonk ($r = 0.56$; $p < 0.001$) annual average pH (Fig. 5); however, only Awosting's annual pH followed a close match to precipitation pH (Fig. 5).

In general, Mohonk had the highest anions and cations concentrations relative to the other lakes, with differing temporal responses except for SO_4^{2-} (Fig. 4). Concentrations of SO_4^{2-} have decreased significantly over time ($F_{1,45} = 125$; $p < 0.001$; time main effect; Fig. 4) and were highest in Mohonk and Minnewaska and lowest in Awosting ($F_{2,45} = 77$; $p < 0.001$; lake main effect; Fig. 4). An interaction between lake and time was noted for Cl^- concentrations ($F_{2,38} = 43$; $p < 0.001$; Fig. 4), driven by the increase in Cl^- concentrations in Mohonk in the 2013–2016

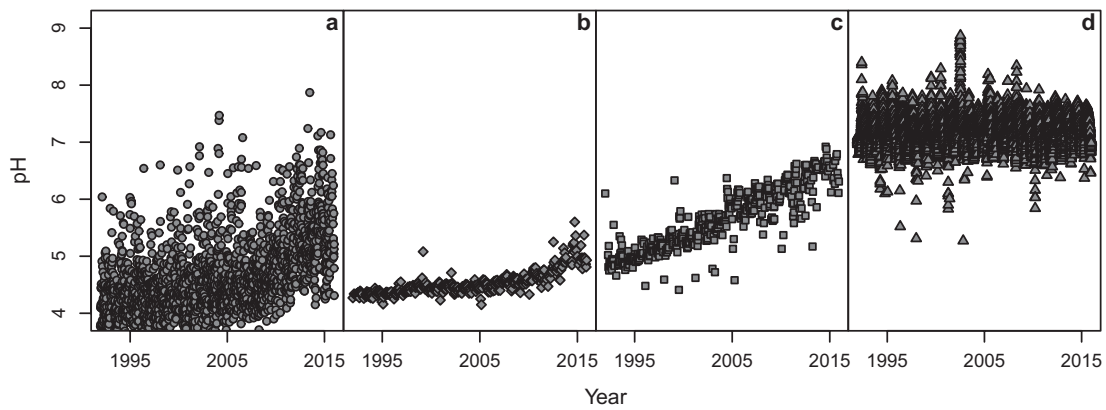


Figure 3. (a) pH of precipitation for every measured storm on the Shawangunk Ridge and time series of pH from (b) Awosting (diamonds), (c) Minnewaska (squares), and (d) Mohonk (triangles) from 13 Dec 1991 to 31 Dec 2015.

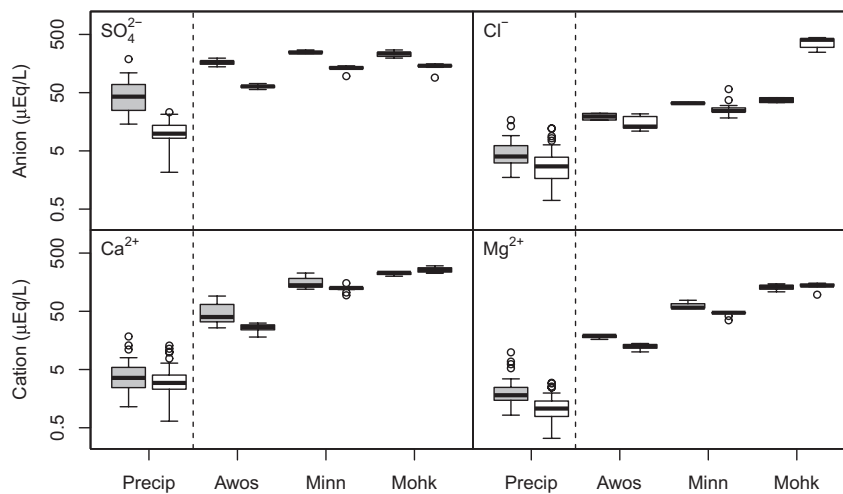


Figure 4. Concentrations of major anions in top row (sulfate [SO_4^{2-}] and chloride [Cl^-]) and cations in bottom row (calcium [Ca^{2+}] and magnesium [Mg^{2+}]) for US National Atmospheric Deposition Program/National Trends Network (NADP/NTN) site NY68 (Precip), Awosting (Awos), Minnewaska (Minn), and Mohonk (Mohk) for 1972–1988 (left gray boxes) and 2013–2016 (right white boxes). Boxes span the first through third quartiles with the median trend represented by the thick center line with whiskers adding ± 1.5 interquartile range to the boxes. Open circles are individual points that fall outside that span.

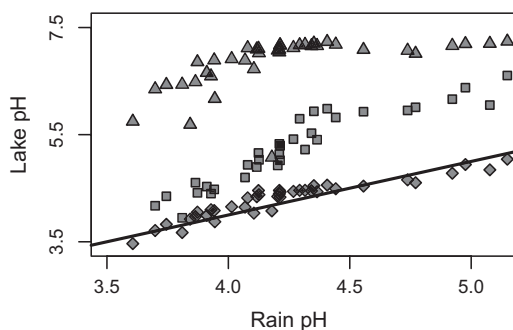


Figure 5. Annual mean precipitation pH compared to annual mean lake pH for Mohonk (triangles), Minnewaska (squares), and Awosting (diamonds) from 1977 to 2015. The solid line represents the 1:1 line.

time period. A weak but significant interaction between lake and time was recorded for both Ca^{2+} ($F_{2,41} = 8.5$; $p < 0.001$) and Mg^{2+} ($F_{2,41} = 8.5$; $p = 0.017$). *Post hoc* mean

comparisons of all interaction levels indicated cation concentrations increasing across lakes from Awosting to Minnewaska to Mohonk (Fig. 4).

Minnewaska had similar concentrations of SO_4^{2-} relative to Mohonk (103% in 1972–1988 and 92% in 2013–2016) but approximately half the Ca^{2+} (Fig. 6). Mohonk is a bicarbonate-buffered lake and has not changed from that category over time (Fig. 6). Awosting has remained an acidic lake, although it is approaching the transition boundary (Fig. 6). Despite little change in cation concentration, Minnewaska has shifted from a transition lake to a bicarbonate lake because of decreasing SO_4^{2-} concentrations (Fig. 6). A small percentage of that SO_4^{2-} is from precipitation, including marine, natural, and anthropogenic pollution sources (Table 2); however, the SO_4^{2-} from pollution dropped between the 2 time periods. In 1972–1988, 52% was from watershed sources (i.e., soils and geology) and the remaining 31% was from trail gravel (Table 2).

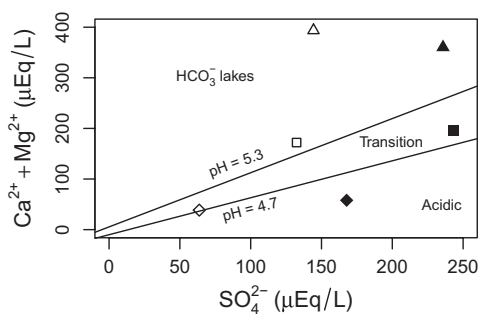


Figure 6. Henriksen nomograph of Mohonk (triangles), Minnewaska (squares), and Awosting (diamonds) where closed symbols are the median values for 1972–1988 and open symbols are median values for 2013–2016. Cations and anions are corrected for sea salt contribution.

Table 2. Lake Minnewaska sulfate (SO_4^{2-}) in $\mu\text{Eq/L}$ (percentage) origins during 1972–1988 and 2013–2016 time periods. The type indicates the source of SO_4^{2-} , including marine and nonmarine origins in precipitation (precip.), watershed sources (Watershed), and trail gravel. Note, precipitation data are from 1983 to 1986.

Type	1972–1988	2013–2016
Precip. (marine)	0.4 (0.2%)	0.3 (0.2%)
Precip. (non-marine)	42.3 (17.4%)	9.6 (7.2%)
Watershed	125.5 (51.6%)	54.3 (40.9%)
Trail gravel	75.2 (30.9%)	68.7 (51.7%)
Lake total	243.4 (100.0%)	132.8 (100.0%)

In 2013–2016, 41% of SO_4^{2-} was from watershed sources and the remaining 52% was from trail gravel (Table 2).

Trail gravel experiment

After 22 d in the unsorted shale experiment, the pH of the control water had changed minimally but the water pH in all treatments increased ($F_{4,20} = 1114$, $p < 0.001$; Fig. 7a). Similarly, after 28 d in the 2–4 mm experiment, the pH of the control had not changed, but the pH had increased in the treatment groups ($F_{4,20} = 795$, $p < 0.001$; Fig. 7b). For both experiments, the trail mixtures, regardless of the source, decreased acidity in lake water within 5 d. The final specific conductivity was more variable for both the unsorted ($F_{4,20} = 205$, $p < 0.001$; Fig. 7c) and the 2–4 mm experiments ($F_{4,20} = 58$, $p < 0.001$; Fig. 7d) but still increased relative to the control. In both experiments, R2 generated the highest specific conductivity (Fig. 7).

Discussion

Acid precipitation has been an acknowledged environmental problem for almost 50 years in northeastern North America and has been a key environmental issue on the Shawangunk Ridge in the past. Scientific research and advocacy led to United States federal policy changes (Weathers and Lovett 1998, Likens 2010) and increasingly

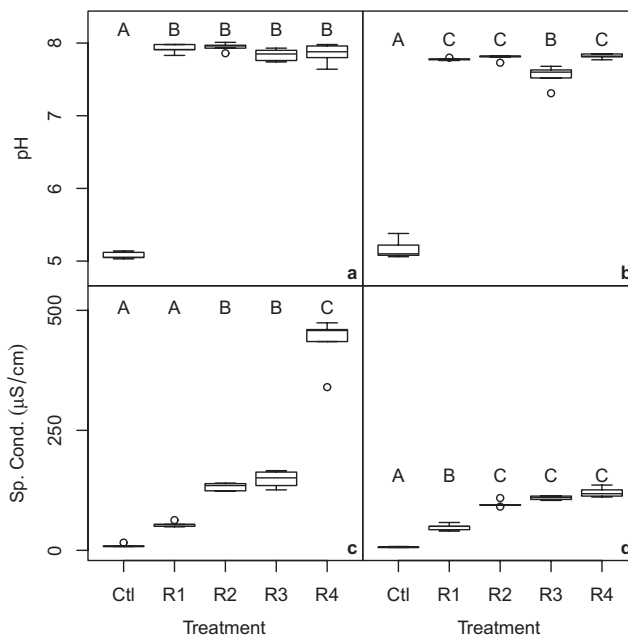


Figure 7. The median pH and specific conductivity (Sp. Cond.; ± 25 th and 75th quartiles; whiskers are $1.5 \times$ interquartile range) from the trail gravel experiments where Ctl = control, R1 = contractor's mix, R2 = Item 4, R3 = locally mined shale, and R4 = a purchased mix. The unsorted experiment (a and c) had an initial pH of 4.96 and specific conductivity of $7 \mu\text{S cm}^{-1}$ in all treatments. The 2–4 mm experiment (b and d) had an initial pH of 5.10 and specific conductivity of $5 \mu\text{S cm}^{-1}$ in all treatments. Final measurements were taken after 22 d for the unsorted experiment and 28 d for the 2–4 mm experiment. Similar capital letters above the boxplots indicate nonsignificant differences of means (adjusted $p < 0.05$) from *post hoc* comparisons.

strict emissions standards imposed through governmental regulation. Globally, precipitation acidity has decreased (Likens et al. 2001, Garmo et al. 2014, Strock et al. 2014; Fig. 3a); however, the improvements to surface water chemistry are much more varied and context-dependent (Stoddard et al. 1999, Driscoll et al. 2001, Kahl et al. 2004, Greaver et al. 2012). In this study, the 3 Sky Lakes are close in proximity yet show different trends in susceptibility to and recovery from acid precipitation (Fig. 3 and 6). We discuss the trends in acid precipitation, possible reasons for differential lake recovery, and implications for freshwater ecosystem structure and function.

Causes of acid precipitation trends

Precipitation pH on the Shawangunk Ridge has increased dramatically, but nonlinearly (Fig. 3a), as a response to the regulation of emissions of both SO_4^{2-} and NO_x and advances in technology. The 1990 CAAA focused on regulation of SO_4^{2-} emissions from stationary sources (Lee 1991); shortly after the amendment implementation in 1994, SO_4^{2-} emissions and SO_4 in precipitation decreased (Likens et al. 2001). Precipitation has experienced a 77% reduction in SO_4^{2-} (Table 2), reflecting decreased national SO_4^{2-} emissions (Likens et al. 2001, Strock et al. 2014). Federal regulations were revised for NO_x emissions, resulting in the NO_x Budget Trading Program initiated in 2003 (US EPA 2005), leading to a decline in NO_x emissions from stationary sources in northeastern United States (Butler et al. 2011, He et al. 2013). Mobile sources of NO_x have decreased because of national emission standards and improving exhaust after-treatment systems such as 3-way catalytic converters (Dallmann and Harley 2010, McDonald et al. 2012). Regionally, nitrate concentrations in precipitation have decreased by 50% between early 1980s and 2016 (Strock et al. 2014). Overall, the trend in NO_x emissions and deposition is nonlinear (Lloret and Valiela 2016), with more rapid decreases in the 2000s (Strock et al. 2014), consistent with increasing trends in precipitation pH at our location (Fig. 3a).

Geologic controls on lake acidity

Geologic and soil features of each lake and watershed can control lake sensitivity to and recovery from acid precipitation. Soil thickness, lake turnover time, and internal acid neutralizing capacity can all affect the vulnerability of lakes to acidification and recovery (Jeffries et al. 2003). Watersheds with soils and geology containing calcite or thick glacial till have lakes insensitive to acid deposition (Driscoll et al. 2003). Mohonk can be grouped with insensitive lakes because the high calcite composition within the exposed Martinsburg shale beneath the lake buffers

acid precipitation (Drake and Epstein 1967). Lakes most sensitive to acid precipitation have thin till covering most of their watersheds (Driscoll et al. 2003). The Awosting watershed has a lake that covers a large proportion (34%) of the total watershed (Table 1) and shallow soils, making direct rainfall important. We identified Awosting as an acid-sensitive lake, as evidenced by the closely related changes in precipitation and lake pH (Fig. 5) and low major cation and anion concentrations (Fig. 4). Awosting seems to be slowly recovering, especially since 2010 (Fig. 3c). Regionally, surface water quality has improved, but, depending on characteristics within and surrounding each lake, up to a decade or more could still pass before shifting back to pre-industrial conditions, matching observations in other regions worldwide, including northern Europe and Asia (Skjelkvåle et al. 2005, Futter et al. 2014, Duan et al. 2016).

Trends in lake acidity

Given the underlying geology, low acid neutralizing capacity, and high lake area to watershed ratio (Table 1), Minnewaska pH has increased well above Awosting water and precipitation pH (Fig. 5). Concentrations of SO_4^{2-} can be used to explain the divergent trends of pH by tracking precipitation, geologic, and anthropogenic sources of ions to the lake. Decreasing precipitation SO_4^{2-} accounts for some of the decreases in SO_4^{2-} in Minnewaska (Table 2); however, additional reductions can be explained by reduced weathering of bedrock. Both Minnewaska and Awosting have sulfur-rich sphalerite, galena, and chalcopyrite veins in the bedrock that contribute to geologic sources of SO_4^{2-} (Friedman et al. 1990); however, these minerals are low in base cations (Ca^{2+} and Mg^{2+}) that would buffer lake water and explain cross-lake differences in cation concentrations (Fig. 4). Minnewaska still has concentrations of SO_4^{2-} comparable to those in Mohonk and intermediate concentrations of Ca^{2+} and Mg^{2+} (Fig. 6), indicating an additional source of sulfate and base cations (Table 2). Mohonk, with an exposed shale inlier, currently has a $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio of 1.88. In Minnewaska, the remaining SO_4^{2-} , after accounting for other sources (Table 2), yields a $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio of 1.86 (1972–1988) and 1.83 (2013–2016), indicating that SO_4^{2-} likely comes from shale. In the Minnewaska watershed, locally and regionally mined shale has been applied long-term for transportation and recreational use.

Minnewaska differs from Awosting in that the gravel trails around Minnewaska start at the State Park parking lot, are wider, and experience more recreational traffic requiring frequent maintenance and repair (Nepal and Way 2007). The trails that encircle Minnewaska have been well maintained for >50 years and make acidic lake water

neutral (Fig. 7). In other impacted freshwater ecosystems, managers have applied lime to counteract acidity and have effectively raised pH and acid neutralizing capacity (e.g., Angeler and Goedkoop 2010, Holmgren et al. 2016), resulting in conditions appropriate for the recovery of acid-sensitive species (Shapiera et al. 2011). To reverse surface water acidification, managers and researchers have applied ~5 metric tons of lime (CaCO_3) per watershed hectare to buffer the pH and sustain populations of sensitive species, especially in the Adirondack region (NY DEC 1990, Driscoll et al. 1996). Minnewaska, at 30 ha, would require 150 metric tons of lime. The 3.2 km trail that surrounds Minnewaska is 3 m wide and 5 cm deep (NYS OPRHP 2010) with ~1400 metric tons (500 m^3) of trail gravel composed of a mix of the 4 gravel types (Fig. 7). This estimate is conservative for the total trail gravel within the watershed, not accounting for additional trails, parking lots, material storage within the watershed and regular replacement of eroded trail gravel. Water running over or through this trail gravel or direct erosion of the gravel into the lake could be equivalent to liming the lake over a >50 year period. Certain portions of the trail system are especially prone to storm damage and overland flow and are replaced with additional gravel more than once a year. Erosion of the trail material has been progressively worse as short, strong summer storms increase in frequency (Westra et al. 2014) and more extreme storms like tropical cyclones (e.g., Klug et al. 2012) occur in this region.

In addition to trail materials decreasing Minnewaska acidity, alternate, but not mutually exclusive, explanations are possible for the 30 year increase in pH. Because of the clarity and acidic conditions, the lake was home to a rare mat of trinity sphagnum moss (*Sphagnum trinitense*) present at depths ranging from 4.5 to >10 m. *Sphagnum* species can also generate organic acids and create acidic conditions themselves (Clymo et al. 1984). Minnewaska was the only place in New York where this rare underwater peat bog occurred (Bahret 1996, NY NHP 2014). Since documentation in the 1990s, the lake bryophytes have been infrequently surveyed, but recreational divers that complete SCUBA certification in Minnewaska have indicated that the cover may be changing over time, and no *S. trinitense* was found during multiple SCUBA surveys in 2012 and 2013 (L.A. Townley, New York State Parks, Recreation, and Historic Preservation Environmental Management Bureau, 2013, pers. comm.). *S. trinitense* cover has likely decreased because of lower water transparency (Richardson et al. 2016) combined with decreased acidity in the lake water (Fig. 3c). For example, Walker and Everett (1987) found that gravel road dust on a northern Alaskan road decreased acidophilous bryophytes, including *Sphagnum* at the edge of the road. The loss of

S. trinitense may have led to a feedback loop by decreasing in organic acids generation near the lake sediments, further raising the pH of the lake.

Ecological implications of recovery

Lake acidification from acid precipitation has resulted in major ecosystem and ecological community changes that have lasted for years (Schindler et al. 1989, Driscoll et al. 1991, Josephson et al. 2014). Many lakes were acidified and suffered severe biological impairment as a result of acid precipitation (Driscoll et al. 2003). Minnewaska and Awosting have historically been fishless dating back to at least the 1920s as a result of acidic water (Charifson et al. 2015). The decreasing acidity in Minnewaska (Fig. 3c), however, resulted in conditions amenable to fish survival and reproduction (pH > 6; e.g., Eaton et al. 1992). In 2008, without the State Park manager's knowledge or permission, a small minnow (*Notemigonus crysoleucas*) was introduced and caused a trophic cascade that modified the food web (Richardson et al. 2016), resulting in a reduction in water clarity to below state limits and consequent closure of the swimming beach for the first time in the Park's history (Minnewaska State Park Preserve, pers. comm.). Fish survival would not have been possible under pH conditions observed prior to 2005 (Mount 1973, Eaton et al. 1992); unsuccessful introductions may have been attempted earlier. Because Awosting's acidity is decreasing at a much slower rate, it may also be susceptible to biological introductions, but only in the future.

Conclusions

Regions with the most acid precipitation have human population clusters with high energy demand and fossil fuel combustion. Northeastern North America, northern Europe, and eastern Asia are located downwind of major fossil fuel emissions, resulting in acid precipitation (Strock et al. 2014, Yu et al. 2016). Scientific recognition of acid precipitation, advocacy, and broader policy responses have led to widespread reductions in acid precipitation in North American and European regions (Fig. 3a; Strock et al. 2014); however, in eastern Asia, acid precipitation was recognized as problem decades later and is more slowly recovering (Duan et al. 2016, Yu et al. 2016).

In regions with acid precipitation, watershed characteristics can control surface water susceptibility to acidification. In Mohonk, the exposed bedrock buffers lake pH, superseding environmental harm and recovery from acid precipitation (Fig. 3d), similar to other lakes with calcareous geology (Tao and Feng 2000, Jeffries et al. 2003). Small lakes that have watersheds with shallow soils and catchment geology with little alkalinity-producing materials

(e.g., granite, quartz, or igneous rock) fall into the acidic or transition category, like Awosting and Minnewaska from this study (Fig. 6). In these lakes, recovery from acidification is slow, even with improving air quality (Fig. 3b; Driscoll et al. 2001, Futter et al. 2014, Garmo et al. 2014, Duan et al. 2016).

Management may be necessary to accelerate lake recovery from acidification, especially if improved biological conditions is desired. For example, Sweden implemented a national effort to increase lake pH and improve fisheries by applying lime to watersheds and lakes (Holmgren et al. 2016) as a direct management approach. Alternatively, this study details a more indirect and unintentional approach through long-term gravel trail maintenance that has resulted in decreases in lake acidity (Fig. 3b). This approach serves multiple purposes of transportation, recreation, and buffering incoming water and could be used in locations with many small, susceptible lakes (e.g., eastern China; Duan et al. 2016) that are slow to improve relative to decreases in acid precipitation.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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