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20th Century Atmospheric Deposition and Acidification Trends in Lakes of the Sierra Nevada, California, USA

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Supporting Information

ABSTRACT: We investigated multiple lines of evidence to determine if observed and paleo-reconstructed changes in acid neutralizing capacity (ANC) in Sierra Nevada lakes were the result of changes in 20th century atmospheric deposition. Spheroidal carbonaceous particles (SCPs) (indicator of anthropogenic atmospheric deposition) and biogenic silica and $\delta^{13}C$ (productivity proxies) in lake sediments, nitrogen and sulfur emission inventories, climate variables, and long-term hydrochemistry records were compared to reconstructed ANC trends in Moat Lake. The initial decline in ANC at Moat Lake occurred between 1920 and 1930, when hydrogen ion deposition was approximately 74 eq ha^{-1} yr^{-1}, and ANC recovered between 1970 and 2005. Reconstructed ANC in Moat Lake was negatively correlated with SCPs and sulfur dioxide emissions ($p = 0.031$ and $p = 0.009$). Reconstructed ANC patterns were not correlated with climate, productivity, or nitrogen oxide emissions. Late 20th century recovery of ANC at Moat Lake is supported by increasing ANC and decreasing sulfate in Emerald Lake between 1983 and 2011 ($p < 0.0001$). We conclude that ANC depletion at Moat and Emerald lakes was principally caused by acid deposition, and recovery in ANC after 1970 can be attributed to the United States Clean Air Act.

INTRODUCTION

Mountain lakes are sensitive indicators of environmental change and are especially useful for detecting changes from regional-scale stressors including air pollution. Sensitivity of aquatic ecosystems to atmospheric deposition of sulfate and nitrate is well documented throughout the northern hemisphere.[1−3] Adverse effects from acidification include chronic or episodic depression of acid neutralizing capacity (ANC) and changes in the structure of biotic communities.[4,5] Associated nutrient inputs are contributing to long-term eutrophication and shifts in nutrient limitation and phytoplankton communities.[6−8] At the same time, climate change is altering hydrologic and water temperature regimes, which may further contribute to variability in productivity and algal community shifts.[9,10]

The Clean Air Act and Amendments (CAAA) is the primary policy for improving air quality and reducing atmospheric deposition in the United States (US). The legislation targets decreases in acid deposition and the recovery of surface waters from acidification and prohibits deterioration of air quality in national parks and wilderness areas, where a large proportion of western mountain lakes occur. Chemical recovery of lakes from acid deposition has been attributed to the CAAA, although most of the published research and success stories have been in the northeastern US where negative ecological effects have been most notable and acid deposition has received the most attention.[11,12] Recently, western land management agencies have been adopting the critical load (CL) as a policy approach to further protect mountain lakes from air pollution.[13] A CL is a quantitative estimate of an input or exposure to a pollutant at which unacceptable impacts occur to sensitive ecosystem components.[14]

Paleolimnological research suggests that Sierra Nevada lakes may have been affected by acid deposition as early as 1920. Sickman et al.[15] reconstructed the last 1600 years of ANC using diatom inference models in Moat Lake, a subalpine lake located in the Sierra Nevada, and observed a decrease in ANC from 1920 to 1970. ANC increased after 1970 and returned to pre-1920 levels by 2005. The causes underlying Moat Lake ANC patterns are uncertain, but it is possible that the CL for acid

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deposition was exceeded well before regular monitoring in the 1980s. Sierra Nevada lakes have been affected by other stressors during the 20th century such as nutrient inputs, climate change, and non-native fish species so additional information is needed to understand the primary drivers of ANC change.

Multiproxy approaches can aid interpretation of the Moat Lake ANC reconstruction.[16] Spheroidal carbonaceous particles (SCPs) found in lake sediments have been used to investigate historic atmospheric deposition.[17] SCPs are porous spheroids composed primarily of elemental carbon that are chemically resistant and well-preserved.[18] They are unambiguous indicators of anthropogenic atmospheric deposition because they are produced only by industrial combustion of fossil fuels; there are no natural sources. Biogenic silica (BSi) and $\delta^{13}C$ are proxies for algal productivity and are used to assess effects of nutrient inputs and climate change on aquatic ecosystems.[19,20] Paleolimnological studies are further strengthened by comparison with long-term climate and lake chemistry data.

The primary goal of our research was to determine if the ANC changes observed in Moat Lake[15] are a result of acid deposition. In our study we synthesize multiple lines of evidence, including measurements of SCPs, BSi, and $\delta^{13}C$ in lake sediments, emission inventories for oxides of sulfur (S) and nitrogen (N), climate, and long-term hydrochemistry records to test the hypothesis that high elevation lakes in the Sierra Nevada were affected by atmospheric deposition early in the 20th century. Using these analyses we evaluate the effectiveness of the CAAA in protecting Sierra Nevada lakes and contribute to the development of air pollution standards, including CLs.

METHODS

We analyzed SCPs, BSi, and $\delta^{13}C$ in Moat Lake sediments from the same core where Sickman et al.[15] reconstructed ANC. Moat Lake is located on the eastern slope of the Sierra Nevada, California, United States of America on Humboldt-Toiyabe National Forest at 3224 m (Figure S1). It has a maximum depth of 7 m, lake surface area of 2.8 ha, and watershed area of 59 ha. The bedrock geology of the watershed is dominated by metasedimentary rocks including quartzite and argillite. To increase our spatial understanding of atmospheric deposition and ANC chemistry in the Sierra Nevada, we also investigated SCP patterns at Pear and Emerald lakes and hydrochemistry trends at Emerald Lake. Pear and Emerald lakes are located in adjacent watersheds on the western side of the Sierra Nevada in Sequoia National Park at 2904 and 2800 m, respectively. Pear Lake has a maximum depth of 24 m, lake surface area of 7.3 ha, and watershed area of 136 ha. Emerald Lake has a maximum depth of 10 m, lake surface area of 2.7 ha, and watershed area of 120 ha. The bedrock geology of both watersheds is dominated by granite and granodiorite. Less than 10% of the three watersheds are vegetated.

At Moat Lake we used a rod-corer to collect a 210 cm core in September 2008 and field sectioned the core at 1 cm intervals.[15] The Pear and Emerald cores were collected in the summer of 2003 as part of the Western Airborne Contaminants Assessment Project (WACAP) using a gravity corer fitted with a Plexiglas tube and field sectioned at 0.5 cm intervals.[21] The chronology of the Moat Lake core was established with ^{210}Pb and ^{14}C dating[15] and the Pear and Emerald lake cores using ^{210}Pb dating.[21]

SCPs (gDM^{-1}) were analyzed in the Moat, Pear, and Emerald cores per methods in Rose,[22] and diatom BSi ($mg\ g^{-1}$) and $\delta^{13}C$ (‰) of bulk organic matter were analyzed in the Moat core per methods in Conley and Schelske[23] and Sickman.[15] Methods are described in the SI.

Sickman et al.[15] described the methods and results for the Moat Lake ANC reconstruction based on a diatom inference model. In this paper we compare the Moat Lake ANC reconstruction to SCP sediment profiles (Moat, Emerald, and Pear lakes) and 20th century sulfur dioxide (SO_2) and nitrogen oxide (NO_x) emissions estimated by the EPA[24] and Smith et al.[25] National emissions (1900–2012) were used as regional data were only available back to 1990, and we have provided a Kendall correlation analysis of national and regional emissions in the SI to demonstrate that national emissions provide a good proxy for understanding multidecadal trends. ANC variations are strongly influenced by precipitation and snow water equivalent (SWE) and to a lesser extent by temperature which affects snowpack dynamics and watershed weathering rates.[26] Using available long-term records, we compared ANC changes to mean annual air temperature and precipitation, and April 1st SWE. Temperature and precipitation data were obtained for the Sierra climate region, as defined by Abatzoglou et al.,[27] from the Western Regional Climate Center's California Climate Tracker (http://www.wrcc.dri.edu/monitor/cal-mon/).[27] SWE data were examined from two snow courses: (i) Donner Summit located near Lake Tahoe (39.3100 N, 120.3380 W) (1910–2011) and (ii) Virginia Lakes located near Moat Lake (38.0570 N, 119.2470 W) (1947–2011) (http://cdec.water.ca.gov). Climate data were analyzed using the Mann-Kendall (MK) test for trend[28] with Theil-Sen slope estimator.[29,30] Correlations among variables were tested using Pearson and principal component analysis (PCA).

We investigated trends for 30 years (1982–2012) of sulfate chemistry and 28 years (1983–2011) of fall ANC and base cation (BC) chemistry from Emerald Lake. Sampling and laboratory methods are described in Melack et al.[31] Sulfate trends were analyzed using the Seasonal Kendall test (SKT)[32] with Theil-Sen slope estimator[29,30] and compared to sulfate deposition trends from the National Atmospheric Deposition Program site CA75 in Sequoia National Park (http://nadp.sws.uiuc.edu/). Deposition trends were analyzed using the MK[28] test with Theil-Sen slope estimator,[29,30] and correlations between lake chemistry and deposition were analyzed using a Kendall tau. We used two approaches to test for ANC and BC trends that control for the effect of SWE as the correlation between these variables and SWE coupled with the high annual variability of SWE makes it challenging to detect temporal trends. Method (i) is computing the residuals for the SWE-ANC linear regression, plotting them in chronological order, and computing a linear regression between residuals and year and (ii) is using multiple linear regression (MLR) to predict ANC using year and SWE as explanatory variables.[33] We used the residuals approach (i) to test for BC trends.

We calculated a CL for acid deposition by hindcasting deposition rates back to the time period when changes in diatom communities and reconstructed ANC were initially observed by Sickman et al.[15] We assumed acid deposition to be the sum of nitrate and sulfate, estimated deposition rates for these constituents separately, and then summed them. Hindcasting methods are based on Baron[34] and described in the SI section.

RESULTS

SCPs were first consistently detected in 1869 ± 96 in Moat Lake, 1842 ± 33 in Pear Lake, and 1932 ± 10 in Emerald Lake

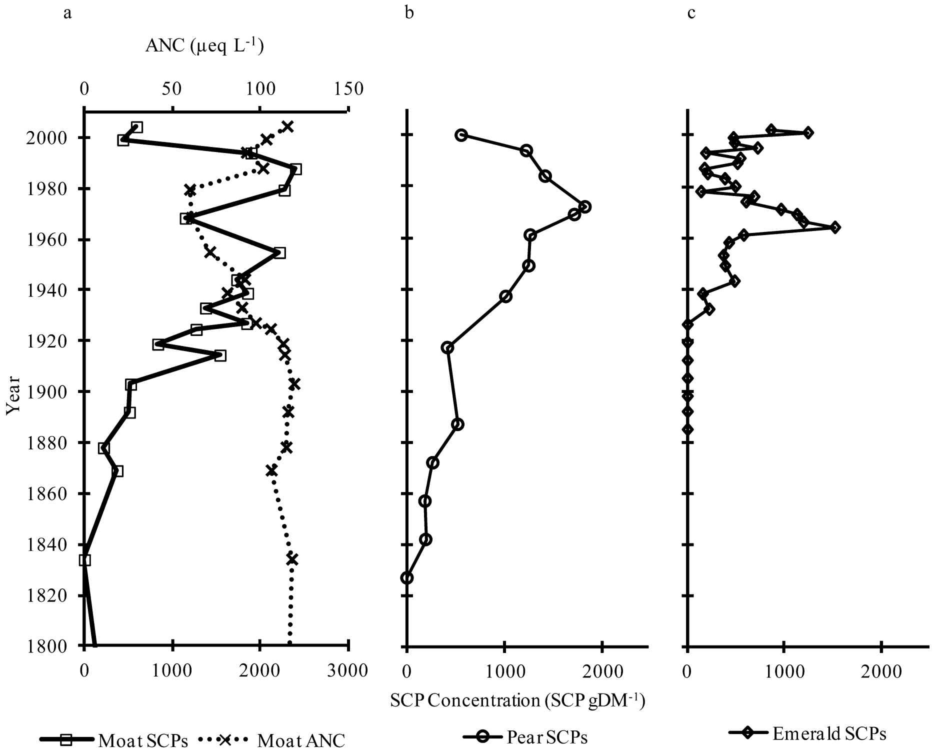

Figure 1. a) Moat Lake SCP concentrations and reconstructed ANC, b) Pear Lake SCP concentrations, and c) Emerald Lake SCP concentrations.

(Figure 1). In Moat Lake a few SCPs were detectable prior to industrial fossil fuel combustion. These SCPs may be contamination-derived, although the core chronology suggests limited contamination overtime. Following initial detection, SCPs show an increasing trend at all three sites until maximum SCP concentrations were reached in 1964 ± 6 at Emerald Lake (1,500 gDM^{-1}, 90% CI [910, 2100]), 1972 ± 9 at Pear Lake (1,800 gDM^{-1}, 90% CI[1200, 2400]), and 1988 ± 4 at Moat Lake (2,400 gDM^{-1}, 90% CI [1700, 3100]). A decreasing trend in SCP concentrations was then observed through ca. 2000, with the exception of Emerald Lake where SCPs decrease but then increase again after 1999 ± 2. SCP concentrations measured in surface sediments are 560 gDM^{-1}, 90% CI [240, 870] in Pear, 590 gDM^{-1}, 90% CI [260, 900] in Moat, and 860 gDM^{-1}, 90% CI [480,1200] in Emerald.

Moat Lake BSi ranged from 175.1 to 227.9 mg g^{-1} from 1834 ± 277 to 2004 ± 3 (Figure 2). We observed an initial increase between 1920 and 1930 and a second increase between 1980 and 2000. Sediment δ^{13}C ranged from −22.3 to −21.4‰ from ca. 1830 to ca. 1900 with no notable trend (Figure 2). We observed an increasing trend in δ^{13}C between 1900 and 2000 where δ^{13}C ranged from −21.9 to −19.2‰. By 1990, δ^{13}C had increased from the most depleted value of −22.2‰ in 1903 ± 36 to −20.20‰. In the analysis we focus on δ^{13}C trends from before 1990 as sediment diagenesis complicates interpretation of the most recent 10 years of sediment accumulation.[35]

The PCA identified three principal components, which together account for about 80% of the variance (Figure 3 and Table S1). The first axis was positively correlated with air quality indices (NO$_x$ and SO$_2$ emissions) and temperature and negatively correlated with ANC and precipitation indices. The second axis positively correlated with phytoplankton productivity indices and negatively correlated with SCP and SO$_2$ emissions. The third axis was positively correlated with precipitation indices.

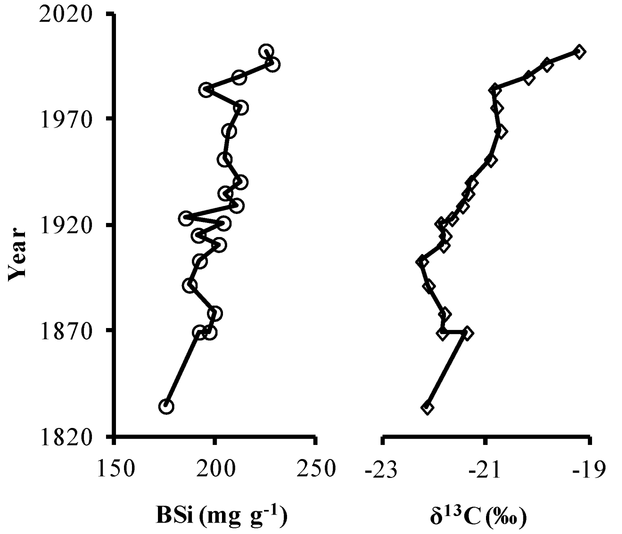

Figure 2. BSi and δ^{13}C profiles for Moat Lake.

The PCA and Pearson correlation demonstrated negative correlations between ANC and SCPs ($p = 0.031$) and ANC and SO$_2$ emissions ($p = 0.009$) (Figure 3 and Table S2). Relatively low levels of SCPs were observed in Moat Lake prior to any notable change in ANC (Figure 1). A decreasing trend in ANC began after 1920 and continued until the late 1970s. The ANC decrease coincides with increasing concentrations of SCPs between 1920 and 1980 and rising SO$_2$ emissions between 1920 and 1970. ANC in Moat switches to an increasing trend within the same decade that SCPs and SO$_2$ emissions switch to a decreasing trend. Pear and Emerald SCPs showed similar declines between 1970 and 2000. Moat ANC patterns correlate less with NO$_x$ emissions ($p = 0.185$), although the time series suggests a stronger correlation after 1950 (Figure 4).

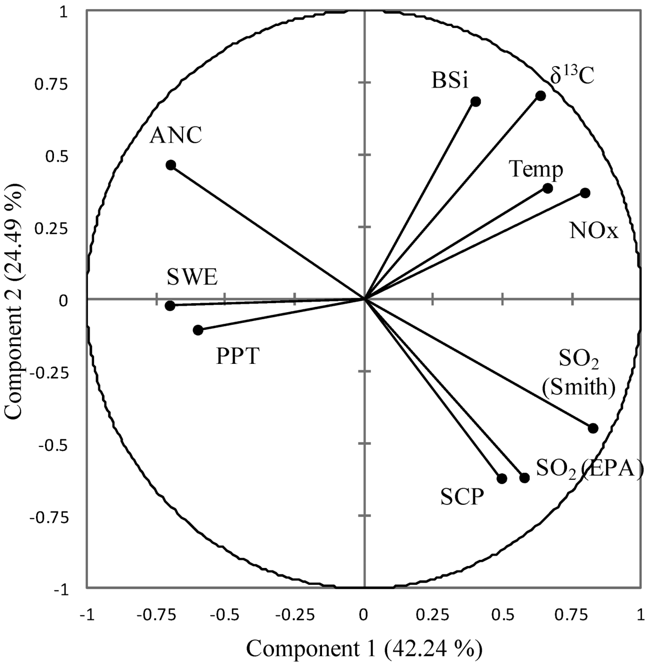

Figure 3. PCA plot for Moat Lake sediment, emissions, and climate variables.

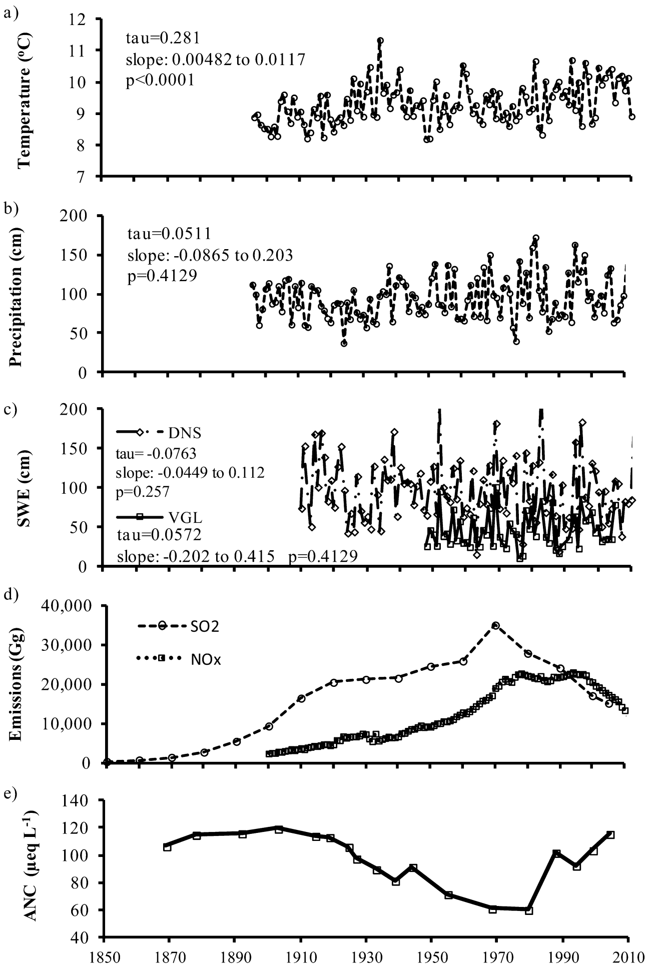

Figure 4. Time series graphs for a) Sierra Nevada mean annual air temperature, b) Sierra Nevada mean annual precipitation, c) April 1st SWE at Donner Summit (DNS) and Virginia Lakes (VGL), d) national NO_x and SO_2 emissions, and e) diatom reconstructed ANC at Moat Lake. The slopes are reported as the 95% CI range.

The PCA and Pearson correlation indicate no direct correlation between Moat Lake ANC and the climate variables considered (Figure 3 and Table S2). Sierra Nevada air temperature records demonstrate a 20th century warming trend of 0.1 °C decade^{-1} ($p < 0.0001$) (Figure 4). The ca. 1920 decrease in ANC coincided with a slight warming trend observed during the same period. However, temperature continued to rise through 2010, whereas the ANC trend in Moat Lake reversed after 1980. There were no statistically significant trends in precipitation (p = 0.4129) or SWE (Donner Summit: p = 0.257;Virginia Lakes: p = 0.4129), nor were these variables correlated with ANC. Temperature was more closely correlated with productivity (δ^{13}C p = 0.007) and NO_x emissions (p = 0.021). Temperature, δ^{13}C, and BSi increased throughout the 20th century. Temperature and NO_x emissions both increased throughout the 20th century but diverge after 2000 when NO_x begins to decline as temperature continues to increase.

Emerald Lake sulfate significantly declined over the 30 year monitoring period (Sen slope 95% CI: −0.080 to −0.053; $p <$ 0.0001) as did annual sulfate deposition concentration (Sen slope 95% CI: −0.273 to −0.088; p = 0001) and loading (Sen slope 95% CI: −0.077 to −0.003; p = 0.0338) (Figure S2). Emerald Lake sulfate concentrations were positively correlated with deposition concentrations (tau = 0 .519; $p < 0.0001$) and loading (tau = 0.262; p-value = 0.0470). The residuals from the Emerald Lake SWE-ANC linear regression demonstrate a concurrent increasing trend in ANC between 1983 and 2011 (slope = 0.139 μeq L^{-1} yr^{-1}; p = 0.006) (Figure 5). The 95% confidence interval for the slope fell between 0.042 and 0.236 further supporting a nonzero change in the residuals through time. Over the 28 year record, ANC increased approximately 4 μeq L^{-1}. MLR results confirm that Year (p = 0.005) and SWE (p < 0.001) are both significant predictors of ANC (R^2 = 0.89) and the coefficient for Year is positive:

$$\text{ANC} = -245 + [(0.142)(\text{Year})] - [(0.00814)(\text{SWE})] \qquad (1)$$

The variable inflation factor for the MLR was 1.002 indicating no significant covariance between SWE and YEAR. We expect SWE to be a significant predictor as it controls ANC concentrations through dilution when the snowpack melts. The significance of YEAR as a copredictor suggests an ANC trend overtime. The residuals from the SWE-BC linear regression indicate no significant trend in base cations between 1983 and 2011 (p-value = 0.16 and 95% CI slope: −005 to 0.29) (Figure S3).

Mean nitrate and sulfate deposition from 1985−1999 at Emerald Lake was 99 ± 17 eq ha^{-1} yr^{-1} and 52 ± 15 eq ha^{-1} yr^{-1}, respectively, and the sum of acid anions was 150 ± 30 eq ha^{-1} yr^{-1} (Table S3). The resulting hindcast model equation used to compute historical nitrate deposition was

$$\text{Nitrate Deposition} = (8 \times 10^{-19})(e^{0.0232\text{Year}}) \qquad (2)$$

Hindcasted sulfate deposition was modeled to match US emissions records. We estimate that annual deposition varied from 13 to 76 eq ha^{-1} yr^{-1} over the 20th century (Figure S4).

The CL was defined as the rate of nitrate and sulfate deposition during 1920−1930 as estimated from hindcasting

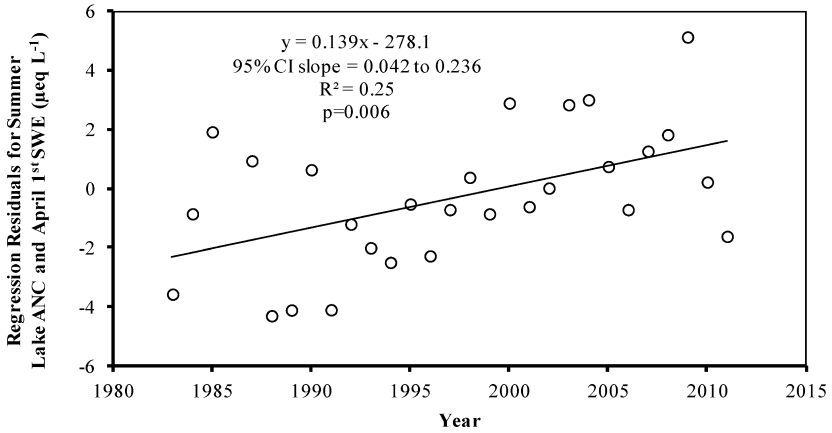

Figure 5. Residuals for regression between April 1st SWE and fall ANC at Emerald Lake graphed against year.

analysis. This decade coincides with the timing of initial ANC decrease at Moat Lake and was characterized by increasing SO_2 emissions and rising SCP concentrations in lake sediment cores. Mean nitrate deposition during 1920−1930 was 20 eq ha^{-1} yr^{-1} (90% CI: 18 to 21), and mean sulfate deposition was 54 eq ha^{-1} yr^{-1} (90% CI: 47 to 61) (Figure S4). The CL, expressed as the sum of acid anions, was 74 eq ha^{-1} yr^{-1} (90% CI: 66 to 82) (Table 1).

Table 1. Mean Critical Load Results Presented with 90% Upper and Lower Confidence Intervals[a]

	mean deposition from 1920 to 1930		critical load
	nitrate ($eq\ ha^{-1}\ yr^{-1}$)	sulfate ($eq\ ha^{-1}\ yr^{-1}$)	sum acid anions ($eq\ ha^{-1}\ yr^{-1}$)
mean	20	54	74
lower	18	47	66
upper	21	61	82

[a] Mean deposition from 1920−1930 are the hindcasted deposition estimates during the period of initial ANC decrease.

■ DISCUSSION

SCP profiles in Moat and Pear lakes have similar patterns. SCP concentrations gradually increased in the mid to late 19th century and then rose faster in the early part of the 20th century. In contrast, SCPs were not detected until the early 1930s in Emerald Lake, although, once detected, they increased rapidly through the mid-1960s, matching the trends in Moat and Pear. The difference in Emerald SCP patterns is likely explained by the higher mean sedimentation rate in Emerald Lake (0.047 g cm^{-2} yr^{-1}) compared to Pear (0.008 g cm^{-2} yr^{-1}) and Moat (0.030 g cm^{-2} yr^{-1}) lakes. SCP detection limits are sensitive to sedimentation rates, especially in remote lakes that have relatively low SCP inputs. Increased sediment fluxes decrease the already low concentration of SCPs making it less likely that an SCP will be detected in a sample. Hence, the detection limit for SCPs in Emerald Lake may be higher than at Moat and Pear lakes, possibly resulting in a later first detection.

SCPs at our study sites reached maximum concentrations during the decades of the 1960s to 1980s which is consistent with sites in the northwestern US and Rocky Mountains[21] (Table S4). Our maximum SCP concentrations are similar to other sites in the western US, which range from 1,100 gDM^{-1} (Glacier National Park) to 3,700 gDM^{-1} (Mt. Rainer National Park) (unpublished concentration data; flux data in Landers et al. 2008). Maximum SCP concentrations in Moat and Pear are greater than remote sites, such as Svalbard or the Canadian Athabasca Oil Sands,[36] suggesting a regional source of SCPs in the Sierra Nevada above global background levels.

SCPs in Pear and Moat lakes began to decline ca. 1970 and ca. 1985, respectively (Figure 1), in response to declining atmospheric inputs from industrial fossil fuel burning. The pattern for Emerald is similar except SCP concentrations rose again after 2000. We are not certain what this SCP increase means but offer two explanations. It could reflect a change in atmospheric deposition that has not yet been detected in Pear and Moat. Higher sedimentation rates in Emerald provide higher temporal resolution, and thus Emerald Lake may contain a more sensitive sediment profile, when SCPs are above detection. Alternatively, it may be due to differences in watershed and lake characteristics as SCP profiles can be consistent across regions, but high variation between lakes that are in close proximity can still occur.[37]

Surface sediment SCPs in Moat and Pear lakes are now similar to concentrations measured in remote sites lacking local and regional sources (500−1000 gDM^{-1}).[38] Emerald Lake was below 1000 gDM^{-1} in the 1980s and 1990s; however, after 2000 Emerald again exceeded 1000 gDM^{-1}. SCP concentrations in surface sediments at our three study sites are in the low to midrange of values measured in a larger set of Sierra Nevada lakes (n = 42),[39] where concentrations ranged from below detection to 5,900 gDM^{-1}.

We compared reconstructed ANC to SCPs, climate, and emissions and concluded that changes in 20th century ANC were primarily caused by acid deposition. We also considered the influence of climate as diatoms, and ANC can be sensitive to climate variables.[15,40] The increasing temperature trends we noted for the Sierra Nevada are consistent with increasing temperature trends, especially post-1940, observed for mountainous regions of the western US.[41] Temperature can affect watershed weathering rates and snowpack dynamics, which in turn could alter ANC concentrations.[42] The time series and correlation analysis indicate limited effects of temperature on 20th century ANC trends. If weathering rates were increasing we would expect to see increases in Emerald Lake sulfate and BC as observed in other studies.[43] In contrast, we observed a declining trend in sulfate concentration and no trend in BC (Figure S3). Thus, it is unlikely that weathering rate changes are significantly contributing to ANC recovery.

Precipitation and Donner Summit SWE varied throughout the 20th century but exhibited no monotonic trend overall.

Precipitation slightly increased and SWE slightly decreased, although trends are weak (tau <0.08) and the 95% confidence intervals for the slopes include zero. There was limited to no correlation between precipitation and ANC, and there was no correlation between SWE and reconstructed ANC. This is in contrast to the Emerald Lake chemistry where SWE was a predictor of ANC in the MLR. Annual ANC variation in the lake chemistry data is well explained by SWE and is consistent with our understanding of processes that regulate ANC.[15] Increased SWE, and the subsequent melting of the snowpack, results in greater dilution of ANC during the spring and summer months. This annual SWE driven variability is not observed in the Moat Lake reconstruction because the diatom communities measured in each 1 cm sample integrate multiple years, allowing us to examine ANC trends with less annual "noise". When we tested the reconstructed ANC-SWE relationship we did not detect a correlation (p = 0.286), suggesting that other factors better explained ANC patterns over the 20th century time scale. While some studies have shown that SWE has been decreasing over parts of the western US due to increased warming, increasing SWE has been observed in the higher elevations of the Sierra Nevada due to moderate increasing trends in precipitation and lower sensitivity to temperature changes.[44] The Virginia Lakes snow course, located near Moat Lake, indicates no local trends in SWE suggesting minimal effects on Moat Lake ANC in the later 20th century when ANC trends were strongest. The strong coherence between ANC, SCPs, and SO_2 emissions and late 20th century NO_x emissions, coupled with the lack of coherence between ANC and climate, support our conclusion that changes in 20th century ANC are primarily driven by atmospheric deposition.

We attribute the early 20th century decrease in ANC primarily to sulfate deposition as SO_2 was negatively correlated with ANC in the PCA. The initial increase in SCPs in Moat and Pear (mid 19th century) coincides with increased settlement and energy use during the California gold rush.[45] We observed the initial decrease in ANC in the early 20th century when SCP concentrations begin to accelerate. These trends are consistent with SO_2 emission increases prior to the Great Depression (Figure 4). Sulfate deposition accounted for 69% of acid deposition in 1900; however, the percentage has decreased over time as nitrate deposition has increased and sulfur emissions curtailed (Table S3). The nitrate deposition increase over the 20th century is largely attributed to rapid population growth in the western US after 1950, the Haber-Bosch process substantially increasing reactive nitrogen in the environment, and shifts in fossil fuel types.[45,46] We considered the decision to use national emissions given the lack of long-term regional data and concluded this was a reasonable approach given (i) 1990–2012 national and regional emissions were significantly correlated (SO_2 p-value = 0.0007; tau = 0.524; NO_2 p-value < 0.0001; tau = 0.846) (Figure S5) and (ii) national SO_2 emissions were correlated with SCP profiles (indicator of local deposition patterns) (Table S2).

We attribute the recovery of ANC in Moat Lake and decrease in SCPs to emission reductions resulting from air quality regulations. The CAAA have been effective in reducing SO_2 and NO_x emissions and sulfate deposition across the US.[11,47] Reductions in nitrogen deposition are harder to quantify due to a lack of monitoring data for all nitrogen species and smaller changes that are harder to detect.[11] Many studies have shown that the CAAA have yielded improvements in surface water ANC in the northeastern US.[11,12] Our study suggests that the CAAA have also reduced the effects of acid deposition on Sierra Nevada aquatic ecosystems.

The increasing ANC trend in Emerald Lake observed over the last three decades is consistent with the late 20th century recovery of ANC in Moat Lake and suggests recovery of acid sensitive lakes in the Sierra Nevada is ongoing. The increase in Emerald ANC was accompanied by a statistically significant decline in lake sulfate ($p < 0.0001$) and sulfate deposition (p = 0.0338) we observed in the Emerald watershed between 1983 and 2011 (Figure S2) and has been observed more broadly throughout the western US.[48] Declining sulfate concentrations and rising ANC further suggests that the CAAA have benefited aquatic ecosystems in the Sierra Nevada.

The recovery of Moat Lake ANC is a positive result that further contributes to the already noted successes of the CAAA. However, we must build on these successes in order to continue protecting sensitive high-elevation lakes. Despite the recovery observed in Moat, results from research we are conducting at a larger spatial scale (n = 42 lakes) show a negative correlation between present day ANC and SCP concentrations in surface sediments, suggesting that Sierra Nevada lakes are still affected by acid deposition.[39] In addition, late 20th century acid anion deposition at Emerald Lake (mean = 150 eq ha^{-1} yr^{-1}) (Table S3) consistently exceeds the Sierra Nevada acidification CL of 74 eq ha^{-1} yr^{-1} computed in this paper and a less conservative CL estimate of 149 eq^{-1} ha^{-1} yr^{-1} computed previously by Shaw et al.[49] This confirms the findings of Burns et al.[11] that current emission reductions are not adequate to allow for full recovery of more sensitive lakes. The CAAA have been effective at reducing sulfur emissions and deposition,[25,50] but effects on NO_x emissions and nitrogen deposition have been less pronounced, especially in the western US where mobile and agricultural sources are significant contributors.

The Moat Lake BSi and $\delta^{13}C$ reconstructions indicated that phytoplankton productivity increased during the 20th century suggesting that multiple stressors are acting on and changing the Moat Lake ecosystem; therefore, we considered the connections between these stressors and ANC. Productivity effects on ANC vary depending on the driver. Nitrate inputs and subsequent biological uptake is an alkalizing lake process, while assimilation of ammonium is acidifying. The lack of correlation between ANC and productivity proxies suggests eutrophication is not the primary driver; however, we cannot rule out subtle effects. Temperature driven eutrophication can lead to late summer drawdown of dissolved inorganic carbon; however, we do not observe this phenomenon in Emerald Lake (Sickman unpublished data), suggesting that temperature driven productivity effects on ANC are negligible.

Moat Lake surface water temperatures increased in the late 20th century,[51] and NO_x emissions were correlated with BSi and $\delta^{13}C$. Increases in BSi and $\delta^{13}C$ have been attributed to increased productivity from climate warming[19,52] and eutrophication.[20,53]When interpreting the $\delta^{13}C$ data we considered if the carbon source was terrestrial or aquatic by examining sediment C:N ratios. Cellulose-poor and nutrient-rich algae C:N molar ratios range between 4 and 10 and are lower than terrestrial vegetation, which are typically greater than 20.[54] Moat C:N ratios ranged from 5.4 to 9.7, with one exception (a 13.3 ratio at 1.5 cm depth) indicating variations in sediment $\delta^{13}C$ are mostly driven by algal productivity. Bioassay experiments in Moat Lake have demonstrated phytoplankton response to nitrogen additions,[39] and diatom analyses from sediment cores show 20th century increases in *Fragilaria crotonensis*, an N sensitive indicator species.[15] Many Sierra Nevada lakes are N-limited for part of the growing season.[55] Ammonium and total dissolved N deposition are increasing in the western US, which could further drive lake eutrophication. Thus, increased N-deposition tied to greater NO_x emissions has the potential to alter lake productivity leading to higher abundances of diatoms (as measured by Bsi) and alteration of $\delta^{13}C$.

Our research suggests that, although atmospheric deposition is the dominant driver of 20th century ANC trends, aquatic communities in the Sierra Nevada are responding to combined effects from acidification, climate change, and eutrophication. Early in the 20th century the primary stressor effecting Sierra Nevada lakes was acid deposition driven by SO_2 emissions. As the century and industrialization progressed, NO_x levels increased adding a eutrophication stressor while simultaneously contributing to acidification. Effects are further complicated by a warming climate in the late 20th century, as warmer temperatures may have contributed to the recovery of ANC in lakes via increased weathering rates, while simultaneously enhancing eutrophication effects. There is a need for further research to understand eutrophication effects and how acidification, eutrophication, and a warming climate are interacting in these fragile ecosystems.

Our research highlights the complexities associated with developing CLs on landscapes that have been altered well before research and monitoring programs were in place. Recent paleolimnological investigations have altered our perception of the effects of global change on Sierra Nevada lakes from waiting to detect changes to observing the recovery of the lakes from much earlier perturbations. The CL at Moat Lake was surpassed in 1920 and the recovery started in 1970. Both of these milestones occurred well before monitoring was initiated at Moat Lake in 2006 and Emerald Lake in 1983. Paleolimnology studies can play an important role in more fully understanding pre- and postindustrial conditions in the absence of long-term monitoring data. It also underscores the importance of long-term environmental monitoring in evaluating the effectiveness of environmental policies such as the CAAA and disentangling the effects of multiple anthropogenic stressors from natural variability.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional methodology and graphics summarizing site locations, reconstructed deposition, Emerald chemistry trends, and emissions and SCP comparisons. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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