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Critical Loads of Acid Deposition for Wilderness Lakes in the Sierra Nevada (California) Estimated by the Steady-State Water Chemistry Model

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Abstract Major ion chemistry (2000–2009) from 208 lakes (342 sample dates and 600 samples) in class I and II wilderness areas of the Sierra Nevada was used in the Steady-State Water Chemistry (SSWC) model to estimate critical loads for acid deposition and investigate the current vulnerability of high elevation lakes to acid deposition. The majority of the lakes were dilute (mean specific conductance=8.0 μS cm^{-1}) and characterized by low acid neutralizing capacity (ANC; mean=56.8 μeq L^{-1}). Two variants of the SSWC model were employed: (1) one model used the *F*-factor and (2) the alternate model used empirical estimates of atmospheric deposition and mineral weathering rates. A comparison between the results from both model variants resulted in a nearly 1:1 slope and an R^2 value of 0.98, suggesting that the deposition and mineral weathering rates used were appropriate. Using an ANC_{limit} of 10 μeq L^{-1}, both models predicted a median critical load value of 149 eq ha^{-1} $year^{-1}$ of H^+ for granitic catchments. Median exceedances for the empirical approach and *F*-factor approach were −81 and −77 eq ha^{-1} $year^{-1}$, respectively. Based on the *F*-factor and empirical models, 36 (17 %) and 34 (16 %) lakes exceeded their critical loads for acid deposition. Our analyses suggest that high elevation lakes in the Sierra Nevada have not fully recovered from the effects of acid deposition despite substantial improvement in air quality since the 1970s.

Keywords Lake acidification · Sierra Nevada · Critical loads · Nitrogen deposition · Class I wilderness areas · Lake monitoring

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1 Introduction

High elevation lakes in the Sierra Nevada are sensitive to acid deposition (Melack et al. 1985; Stoddard 1987;

Stauffer 1990). These lakes have acid neutralizing capacity (ANC) typically less than 100 μeq $L^{-1}$and are located in small catchments with deep snowpacks, steep slopes, sparse soil, and vegetation cover and are predominantly underlain by granitic bedrock resistant to weathering (Stauffer 1990; Melack and Stoddard 1991). Recent paleolimnological investigations suggest that some Sierra Nevada lakes have experienced depression of acid neutralizing capacity in the mid-twentieth century in response to acid deposition (Sickman et al. 2013; Heard 2013), and episodic acidification occurs in most Sierran lakes during snowmelt and infrequent large rain events (Stoddard 1995; Leydecker et al. 1999). Episodic acidification of catchments and lakes in the Sierra Nevada primarily occurs from the large pulse of snowmelt in the springtime with low concentrations of base cations and elevated concentrations of acid anions. The primary acid anion in atmospheric deposition in the Sierra Nevada is NO_3^- which along with NH_4^+ deposition could cause eutrophication in high elevation lakes and streams (Fenn et al. 2003; Fenn et al. 2008; Fenn et al. 2010).

The concept of the "critical load" is useful for assessing the current status of lakes in relation to atmospheric deposition and is defined as the maximum rate of atmospheric deposition that will not lead to negative impacts on ecosystem function (Skokloster Critical Load Workshop; Nilsson and Grennfelt 1988; Sverdrup and De Vries 1994). Once critical loads have been established, lake conditions can be assessed by comparing the critical load to the estimated atmospheric deposition rate of varying substances (acids, nutrient, heavy metals, etc.). This approach is especially effective if the sources of pollution can be determined and emission controls can be implemented (Hindar et al. 1998; Porter et al. 2005; Burns et al. 2008).

Critical loads for lakes and watersheds can be based upon either eutrophication or acidification endpoints and have been estimated using biological indicators or water chemistry. Endpoint examples include lichens, phytoplankton species composition, and changes in terrestrial vegetation. The nitrogen content and changes in community composition of lichens (Fenn et al. 2010; Geiser et al. 2010) and terrestrial plants (Fenn et al. 2011) have been used as the basis for eutrophication critical loads. Fossil diatom assemblages have been used to infer critical loads for acidification (Holmes et al. 1989) and eutrophication in mountain lakes (Saros et al. 2010), but this approach relies upon very detailed studies of only a few individual lakes. For large regional assessments of lake status, simpler methods are often employed which rely on trends in concentrations of ANC, base cations, NO_3^-, and SO_4^{2-} in surface waters (Baron 2006; Baron et al. 2011).

Critical loads have been determined by using mass balance models for lakes and their catchments (Sverdrup et al. 1990; Ouimet et al. 2001; Henriksen and Posch 2001). Mass balance modeling is an effective assessment approach for regional studies looking at hundreds of lakes (Henriksen and Posch 2001) because input data can be derived from synoptic lake surveys, knowledge of bedrock geology, and estimates of acid deposition rates. These models compare the steady-state production of base cations and ANC from weathering to rates of acid anion deposition (principally NO_3^- and SO_4^{2-}). Subtracting acid anion deposition from base cation production yields an estimate of surplus ANC in a waterbody; when the difference is 0 (base cation production−acid anion deposition=0) or falls below a threshold level, then the critical load has been reached.

The last large-scale effort to assess the status of US high elevation lakes was the 1985 Western Lake Survey (WLS) conducted by the United States Environmental Protection Agency (EPA) (Landers et al. 1987). The WLS consisted of synoptic sampling of hundreds of lakes throughout the western USA including several dozen in the Sierra Nevada. The WLS study determined that Sierra Nevada lakes are the most dilute and lowest ANC waters in the USA and are highly sensitive to acid deposition. The United States Forest Service (USFS) Region 5 began investigating the status of high elevation Sierran lakes in class I and class II wilderness areas in the early 2000s (Berg and Grant 2002; Berg et al. 2005). During the past decade, the USFS has conducted annual synoptic surveys involving hundreds of lakes to determine the current condition and trends in lake chemistry with an emphasis on effects of acid deposition (Berg and Grant 2004).

It has been 28 years since the EPA Western Lake Survey assessed the status of high elevation lakes in the Sierra Nevada (Landers et al. 1987). New datasets on high elevation lake chemistry and atmospheric deposition have been collected, and there is a need to use these data in the context of critical loads development to improve understanding of how air quality is affecting wilderness lakes. We used water chemistry results from the USFS Region 5 lake monitoring study with the Steady-State Water Chemistry model (Henriksen and

Posch 2001) to estimate the critical load for acidification [CL(A)] in wilderness areas in the Sierra Nevada. This model incorporates a mass balance approach utilizing deposition and weathering of base cations, deposition of acid anions, and the acid neutralizing capacity of lakes within this region. Using hydrochemistry from 208 high elevation lakes in the Sierra Nevada we: (1) estimated the CL(A) using two variations of the Steady-State Water Chemistry model (SSWC) and (2) used the CL(A) from the models and water chemistry from synoptic surveys to estimate the number of lakes where the critical load for acidification is currently being exceeded. Our assessment is valuable to Federal Agencies who manage wilderness areas in the Sierra Nevada and could aid development of air quality standards by the State of California.

2 Methods

2.1 Study Area

Lakes sampled in this study are predominantly located in USFS wilderness areas in the Sierra Nevada of California (Fig. 1). These regions receive about 90 % of their precipitation as snow during November through April with the balance falling as rain during the spring and autumn (Sickman et al. 2003). Snowmelt is the dominant hydrologic event and typically occurs from April through June, but in winters with deep snowpack, high runoff can continue into July and August (Sickman et al. 2003).

The geology of the high Sierra Nevada consists of a complex network of fractures and faults throughout the system where multiple uplifts have occurred (Bateman and Wahrhaftig 1966; Clow et al. 1996; Wakabayashi and Sawyer 2001). The majority of the region is underlain by 70 to 210 Ma granitic intrusions from the Sierra Nevada batholith, but there are outcrops of metasedimentary, metavolcanic, and metamorphic rocks as well (Bateman 1992). Fractures are numerous and range from microscopic to kilometers in length (Bateman and Wahrhaftig 1966; Segall et al. 1990; Wakabayashi and Sawyer 2001; Ericson et al. 2005). Although much of the region consists of exposed basement rock, there are numerous surficial deposits, in the form of talus and scree, with lesser amounts of poorly developed soil (Jahns 1943; Warhaftig 1965).

2.2 Field and Analytical Methods

Six hundred water samples were collected from 208 lakes during synoptic surveys conducted between June 2000 and September 2009 (Electronic Supplementary

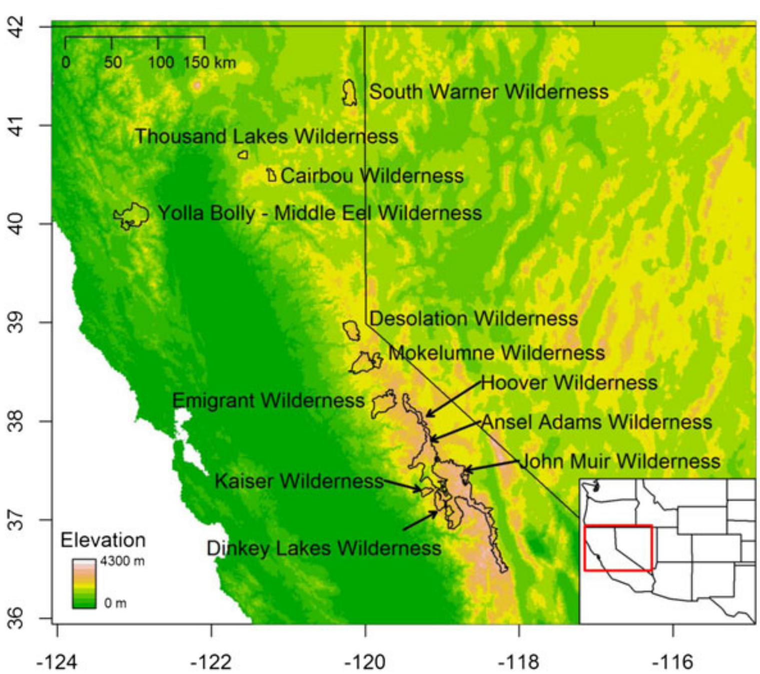

Fig. 1 Class I and II wilderness areas and lakes sampled as part of this study

Materials (ESM) Tables 1 and 2). Lakes were sampled in the months of June, July, and August depending on when the snowpack had melted enough to allow access to the lake by foot. Autumn samples were collected for selected lakes in late September and early October of some years. One hundred eighty-one lakes were visited one time, 10 lakes were visited two to five times, and 17 lakes were visited six or more times (Fig. 1; ESM Table 3). Epilimnion samples were taken from an inflatable raft above the point of maximum lake depth (hypolimnion samples were taken when the lake was stratified), and/or from the shoreline or at the lake outlet (ESM Table 2).

Sample bottles were triple rinsed with filtered (0.45 μm) lake water prior to sample collection. Water samples were kept cool and in the dark while in transit to the laboratory. In the laboratory, samples were kept at 4 °C until they were analyzed. Base cation concentrations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) were determined by ICP-MS. Ammonium (NH_4^+) was determined by the phenol hypochlorite method. Major anions (Cl^-, NO_3^-, and SO_4^{2-}) were determined by ion chromatography (NO_2^- is typically undetectable in Sierra Nevada lakes). Specific conductance was measured using a 1.0-cm^{-1} cell constant electrode and conductivity meter. pH was measured using a combination electrode and pH meter. ANC was determined by Gran titration. Chemical analysis was performed by the USDA Forest Service Rocky Mountain Station Analytical Laboratory in Fort Collins, Colorado which employed rigorous quality control and assurance protocols (Musselman and Slauson 2004; http://www.fs.fed.us/waterlab/).

2.3 Modeling Theory

Lake chemistry was used to derive the critical load of acidity using the Steady-State Water Chemistry (SSWC) model (Henriksen et al. 1992; Henriksen and Posch 2001). In our regional assessment, the lake is the sensitive resource and ANC is the indicator or the measurable endpoint of adverse effects from acid deposition. Equations for establishing critical loads and exceedances are described below and summarized in Table 3.

The critical load of acidity [CL(A)] is defined as:

$$\mathrm{CL(A)} = \mathrm{BC_w} + \mathrm{BC^*_{dep}} - \mathrm{BC_u} - \mathrm{ANC_{limit}} \tag{1}$$

(Henriksen and Posch 2001)

where BC_w is the production (e.g., equivalents per hectare per year) of base cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) from weathering; BC^*_{dep} is the sea salt-corrected, atmospheric deposition of base cations; BC_u is the net long-term average uptake of base cations by the catchment biomass; and ANC_{limit} is the specified level of lake ANC. To get sea salt-corrected values, all chloride deposition was assumed to come from sea salt (Henriksen and Posch 2001). The ANC_{limit} is defined as the threshold at which any additional H^+ loading will reduce ANC to a level where undesirable impacts occur in aquatic ecosystems. Based on previous studies and current ANC levels in the Sierra Nevada, we varied the ANC_{limit} between 0 and 20 μeq L^{-1}.

Critical loads were established for each sampling date at each lake by averaging the chemistry from duplicate samples (epilimnion, hypolimnion, shore, and outlet) if more than one sample was collected per visit. This resulted in a total of 342 critical load estimates. We also separately estimated critical load for granitic and nongranitic catchments. Thus, there were a total of 329 critical load estimates for granitic catchments and 13 critical load estimates for nongranitic catchments.

Exceedances of the critical load of acidity (Ex(A)) were computed from the difference between acid input rate to lakes and the critical load. Traditionally, inputs of acid to lakes have been computed as the sum of sulfur in atmospheric deposition and the net transport rate of N to the lake, which was approximated using the inorganic N concentration in runoff:

$$\mathrm{Ex(A)} = S_{\mathrm{dep}} + N_{\mathrm{leach}} - \mathrm{CL(A)} \tag{2}$$

where S_{dep} is the atmospheric deposition rate of S (in the form of SO_4^{2-}), and N_{leach} is the flux of nitrate and ammonium in catchment runoff (Henriksen and Posch 2001). Positive values of Ex(A) indicate the degree to which the critical load is exceeded. Negative values of Ex(A) are an estimate of the excess base cation production available in a catchment.

Equation 2 was developed in regions where the predominant form of atmospheric acidity was SO_4^{2-} and catchment N retention was relatively high. However, in the Sierra Nevada, acid deposition is dominated by N rather than S (Table 2), and environmental conditions (high elevation, sparse vegetation, and short growing seasons) can constrain the assimilation of atmospheric N in some catchments. Therefore, we suspect that using

Eq. 2 slightly underestimates the true number of lakes exceeding the critical load.

We used two approaches for parameterizing the SSWC model. In the first, all parameters in Eq. 1 were empirically estimated from lake and atmospheric deposition monitoring programs. The empirical approach to parameterizing the SSWC model allows for ranges of critical loads to be estimated under varying deposition scenarios. In the second approach, we used the *F*-factor (Henriksen and Posch 2001; Bishop et al. 2008), as described below, to estimate the model parameters. The *F*-factor is commonly used in critical load modeling because of the uncertainty in determining steady-state mineral weathering rates and deposition values from sparse field measurements. In this study, we primarily used the *F*-factor approach to validate the empirically based model.

2.4 SSWC Model—Empirical Parameterization

Critical loads and exceedances were determined by making direct estimates of each parameter in Eqs. 1 and 2 from field data. The net uptake of base cations (BC_u) was assumed to be 0, because there is no tree harvesting in these catchments (therefore no long-term net gain or loss in uptake) and no reason to suspect that plant biomass has changed substantially in the last 100 years. Setting BC_u to 0 implies that base cation uptake by growing vegetation is offset by base cation release during decomposition of dead vegetation.

Atmospheric deposition of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH_4^+) and anions (Cl^-, NO_3^-, and SO_4^{2-}) were derived from detailed wet and dry deposition measurements made at the Emerald Lake watershed in Sequoia and Kings Canyon National Parks (lake elevation=2,800 m; Tables 1 and 2). While deposition data from the National Trends Network (NTN) was available for 2000–2009 at a few locations in the Sierra Nevada, the Emerald Lake data provide a more accurate estimate of atmospheric deposition for critical loads modeling in high elevation lakes. There are only four NTN stations in the Sierra Nevada and all are located below 2,000 m elevation in mixed conifer forest (the transition zone between rain and snow in the Sierra Nevada). In contrast, the median lake elevation in our study was 2,725 m (mean 2,737 m, s.d. 407 m, max. 2,725 m, min. 1,817 m), and the study catchments extended up to 4,000 m elevation; in this elevation, zone precipitation is dominated by snowfall. More importantly, the NTN stations underestimate atmospheric deposition rates in the subalpine and alpine zones of the Sierra because they do not account for dry deposition. For example, dry deposition contributes 44, 41, and 12 % of annual atmospheric deposition of H^+, NO_3^-, and SO_4^{2-} deposition

Table 1 Precipitation depth and percentage of annual atmospheric deposition contributed by dry deposition at the Emerald Lake watershed (Melack and Sickman 1997 and J.O. Sickman and J.M. Melack, unpublished data)

Water year	Rain+snow (mm)	H^+ (%)	NH_4^+ (%)	Cl^- (%)	NO_3^- (%)	SO_4^{2-} (%)	Ca^{2+} (%)	Mg^{2+} (%)	Na^+ (%)	K^+ (%)
1985	1,156	38.4	6.8	0.9	48.7	11.2	1.1	2.6	1.7	2.5
1986	2,624	22.4	3.5	0.5	31.9	9.7	1.2	2.1	1.0	0.8
1987	959	41.1	3.4	1.6	32.8	10.0	0.7	0.8	2.5	2.4
1988	896	47.9	3.7	2.6	43.8	14.2	1.4	3.3	3.6	4.9
1989	684	70.0	8.9	2.2	63.8	25.0	3.8	7.1	2.6	10.5
1990	727	66.2	6.6	3.0	62.7	15.9	2.1	3.9	3.3	2.6
1991	1,058	59.2	3.1	3.0	54.6	14.3	2.2	3.3	3.5	2.9
1992	787	71.3	8.3	3.3	57.8	19.4	2.3	5.8	3.9	5.8
1993	2,384	22.4	3.6	0.7	42.0	7.6	1.5	1.5	1.5	2.6
1994	935	36.7	1.9	0.4	30.0	9.7	0.4	0.9	0.6	0.6
1995	2,891	12.2	0.9	0.2	12.8	2.8	0.1	0.3	0.3	0.5
1996	1,812	60.2	4.0	2.1	48.8	15.2	0.9	3.1	2.4	6.9
1997	1,862	49.4	3.6	2.4	32.0	11.4	0.7	1.3	2.8	3.0
1998	2,403	22.5	3.4	0.5	24.6	7.7	0.4	0.5	0.5	1.2
1999	1,277	42.2	2.3	1.2	29.1	7.6	1.3	1.8	1.6	2.6
Average	1497	44.1	4.3	1.7	41.0	12.1	1.3	2.6	2.1	3.3

at the Emerald Lake watershed (Table 1). The deposition rates for Emerald Lake account for all forms of atmospheric deposition (rain, snow, and dry deposition) and are representative of deposition throughout the high Sierra Nevada (Melack and Sickman 1997). The mean deposition values for Emerald Lake (Table 2) were used to estimate the following model parameters: BC^*_{dep} and S_{dep}.

Long-term mineral weathering rates within a catchment (BC_w) are difficult to directly measure (Lokke et al. 1996). A detailed study of mineral weathering at the Emerald Lake watershed has shown that base cation weathering rates can be estimated by subtracting annual atmospheric deposition of base cations from annual watershed base cation export and multiplying by catchment runoff (Williams et al. 1993). Since we do not have total export values of major cations at the USFS lakes, we instead used the lake base cation concentrations as a surrogate for average export of base cations. Weathering rates for base cations were computed as the difference between lake concentrations and the average concentrations in atmospheric deposition multiplied by annual catchment discharge. Average base cation concentrations in deposition were computed from loading rates in Table 2 divided by the volume of liquid precipitation.

In order to express units in Eq. 1 as fluxes and to estimate base cation production from weathering, the annual catchment discharge (Q) was required. Catchment discharge was approximated from streamflow measurements made at nearby gauging stations obtained from the USGS National Water Information System (http://waterdata.usgs.gov/nwis). We divided annual runoff at these stations (cubic meters per year) by the watershed contributing area (hectares) to create maps of stream flux per unit area (cubic meter per year per hectare) for regions of the Sierra Nevada that encompassed the wilderness lakes we sampled. Annual discharge through a lake was then computed from the area of the lake catchment times the stream flux per unit area for that region during the year of interest.

We computed N_{leach} from the sum of NO_3^- and NH_4^+ in lake water (epilimnion, hypolimnion, or outflow) and annual discharge (described above). For lakes where multiple samples were collected per sample visit, the concentrations were averaged. The value of N_{leach} was used in Eq. 2 with CL(A) results from both the empirical parameterization and F-factor methods.

Table 2 Annual atmospheric deposition of ions (rain+snow+dry deposition) at the Emerald Lake watershed (Melack and Sickman 1997 and J.O. Sickman and J.M. Melack, unpublished data). Units are equivalents per hectare per year

Water year	H^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	Ca^+	Mg^{2+}	Na^+	K^+
1985	105.0	37.4	48.7	83.5	50.3	34.3	9.2	25.5	11.8
1986	165.1	88.4	84.9	116.9	70.9	34.1	10.5	41.5	22.8
1987	85.3	79.0	28.9	108.3	64.7	41.1	14.3	19.0	9.2
1988	81.0	75.2	18.7	89.4	45.8	27.2	6.7	13.2	4.5
1989	84.1	40.9	25.0	93.1	31.2	12.3	4.2	21.8	2.8
1990	103.3	48.0	18.4	110.0	43.1	23.0	7.7	17.0	10.3
1991	97.5	90.4	16.8	106.6	38.1	24.0	9.1	14.2	8.6
1992	80.9	44.4	17.1	100.8	41.1	24.9	5.6	14.5	5.2
1993	157.6	61.7	43.6	84.8	64.3	21.2	11.6	22.0	6.9
1994	47.0	48.3	26.2	57.9	25.6	30.2	6.5	19.1	9.1
1995	116.4	105.4	39.2	112.1	72.7	84.1	19.9	28.6	12.8
1996	65.6	64.8	32.5	81.8	36.3	53.7	14.2	28.0	11.4
1997	76.3	78.7	27.4	119.0	65.6	72.6	31.8	24.0	23.0
1998	104.2	64.4	41.7	96.1	59.6	49.5	26.9	44.4	24.1
1999	81.6	90.6	31.3	119.4	64.0	21.2	11.2	22.5	10.6
Average	96.7	67.8	33.4	98.6	51.5	36.9	12.6	23.7	11.5

2.5 SSWC Model—F-factor Parameterization

The *F*-factor is defined as "a measure of catchment base cation response to changes in acidic deposition, that is, how many base cation equivalents will be produced for each additional equivalent of depositional acidity" (Leydecker et al. 1999). The *F*-factor was calculated using the methods described by Bishop et al. (2008), Henriksen and Posch (2001), and Wilander (1994). When using the *F*-factor to parameterize the SSWC model, all equation terms in Table 3 that have an * are sea salt-corrected, $_{dep}$ is deposition, $_{leach}$ is the runoff flux, $_{t}$ is present time, and $_{o}$ is the pre-industrial or non-anthropogenic time period. Pre-industrial atmospheric deposition of NO_3^- was assumed to be 0. In the *F*-factor approach, Eq. 3 defines the present-day production of sea salt-corrected base cations (BC_t^*):

$$BC_t^* = BC_w + BC_{dep}^* - BC_u + BC_i \tag{3}$$

(Henriksen and Posch 2001)

where BC_i is the release of base cations from soil ion exchange. Equations 1 and 3 can be rearranged (Eq. 4) and used to calculate critical loads of acidity for the lakes:

$$CL(A) = BC_t^* - BC_i - ANC_{limit} \tag{4}$$

and BC_i is estimated using the *F*-factor:

$$BC_i = F\Delta AN^* = F\left(\Delta SO_4^* + \Delta NO_3\right) \tag{5}$$

(Henriksen and Posch 2001)

In Eq. 5, ΔAN^* is the long-term change in inputs of nonmarine acid anions, and $\vartriangle \Delta SO_4^*$ and ΔNO_3 are the long-term change in inputs of SO_4^{2-} and NO_3^-, where SO_4^{2-} is sea salt-corrected. The *F*-factor is defined as:

$$F = \sin\left[\left(\frac{\pi BC_t^*}{2 \times [S]}\right)\right] \tag{6}$$

(Bishop et al. 2008)

where *S* is the base cation flux at which $F=1$. In our model, we used the commonly cited value of 400 meq L^{-1} for *S* (Brakke et al. 1990; Henriksen et al. 2002; Aherne et al. 2002). Since most of the Sierra Nevada lakes were sampled only once per year, computing an accurate lake-specific *S* value was problematic. However, using the mean lake-specific *S* value in our study (73 meq L^{-1}) yields only a 1 % decrease in the number of lakes exceeding the critical load, demonstrating that our models are relatively insensitive to *S* (Henriksen 1995).

Inserting Eq. 5 into Eq. 4 provides the final form of the CL(A) equation:

$$CL(A) = BC_t^* - F\left(\Delta SO_4^* + \Delta NO_3\right) - ANC_{limit} \tag{7}$$

The *F*-factor for all samples was calculated using Eq. 6. The pre-acidification deposition of SO_4^{2-} ($SO_{4,o}^{2-*}$) was estimated using the following equation:

$$SO_{4,o}^* = 5 + (0.10 \times BC^*) \tag{8}$$

(Wilander 1994)

We used a value of 0.10 for the constant in Eq. 8. Both higher and lower values of the constant have been used in other studies. Wilander (1994) discussed the differences when using constants of 0.005, 0.05, and 0.10 and found that a value of 0.10 gives the closest agreement with critical load estimates made with the MAGIC model (Model for Acidification of Groundwater In Catchments; Jenkins et al. 1997). Henriksen and Posch (2001) present multiple average constant values calculated from previous studies ranging from 0.05 to 0.17 (individual lakes ranged from 0.08 to 0.17). Although the true constants may vary from lake to lake, causing some uncertainty in the calculation of the pre-acidification SO_4^{2-} concentrations, Henriksen and Posch (2001) show that there was no significant impact on estimation of pre-industrial acidity within the constant range described above. Furthermore, Bishop et al. (2008) used a value of 0.10 and showed insignificant changes in *F*-factor values when the constant from Eq. 8 was varied from 0.05 to 0.15. We are confident that a constant of 0.10 provides a reasonable estimate of pre-industrial SO_4^{2-} deposition in the Sierra Nevada.

3 Results

3.1 Lake Chemistry

High elevation lakes in the Sierra Nevada are dilute and characterized by relatively low concentrations of ANC and base cations (Table 4 and Fig. 2). Specific conductance averaged 8.0±9.5 μS cm^{-1} and values ranged between 1.8 and 94.2 μS cm^{-1}, with a median value of 5.1 μS cm^{-1}. pH values were typical of lakes in predominantly granitic watersheds, with a mean of 6.4±0.6. pH values ranged between 5.2 and 8.9, with a median value of 6.3. Average

Table 3 Equations used in estimating critical loads and exceedances of acidification

Equation	Equation number
$CL(A)=BC_w+BC^*_{dep}-BC_u-ANC_{limit}$	Eq. 1
$Ex(A)=S^*_{dep}+N_{leach}-CL(A)$	Eq. 2
$BC^*_t=BC_w+BC^*_{dep}-BC_u+BC_i$	Eq. 3
$CL(A)=BC^*_t-BC_i-ANC_{limit}$	Eq. 4
$BC_i=F\Delta AN^*=F(\Delta SO^*_4+\Delta NO_3)$	Eq. 5
$F=\sin((\pi^* BC^*_t)/(2\times[S]))$	Eq. 6
$CL(A)=BC^*_t-F(\Delta SO^*_4+\Delta NO_3^-)-ANC_{limit}$	Eq. 7
$SO_{4,o}^{2-*}=5+0.10^*\ [BC^*]$	Eq. 8

Explanation of variables (all units are in equivalents per hectare per year except the dimensionless *F* factor): *CL(A)* critical load of acidification, BC_w base cation weathering rate, BC^*_{dep} sea salt-corrected base cation deposition rate, BC_u uptake rate of base cations, ANC_{limit} critical ANC value, *Ex(A)* exceedances of CL(A), S^*_{dep} deposition rate of sulfur, N_{leach} loading rate of inorganic nitrogen, BC^*_t total base cation flux, BC_i release of base cations from ion exchange, *F* *F*-factor, $SO^*_{4,o}$ pre-industrial sulfate, ΔSO^*_4 *and* ΔNO_3 changes in sulfate and nitrate

ANC was 56.8±74.3 μeq L^{-1}, with values ranging between −1.5 and 695.5 μeq L^{-1}. The median ANC was 33.3 μeq L^{-1}. Calcium, Mg^{2+}, Na^+, and K^+ concentrations averaged 46.5±80.3, 11.4±14.6, 18.2±16.1, and 4.8±4.3 μeq L^{-1}, respectively. Ammonium, NO_3^-, and SO_4^{2-} concentrations averaged 0.9±0.7, 1.4±3.2, and 9.9±34.2 mg L^{-1}, respectively. Ammonium ranged between 0.0 and 5.9 μeq L^{-1}, NO_3^- ranged between 0.0 and 23.6 μeq L^{-1}, and SO_4^{2-} ranged between 0.2 and 408.1 μeq L^{-1} (Fig. 2). Lakes with high SO_4^{2-} concentrations were located in predominantly volcanic and metasedimentary (nongranitic) geology.

3.2 Critical Load Estimates Based on Empirical Data

Average atmospheric deposition rates were derived from Table 2 and summary statistics for mineral weathering rates used in the SSWC modeling are shown in Table 5. Critical loads were estimated using ANC_{limit} values of 0, 5, 10, and 20 μeq L^{-1}, which span the range of minimum ANC values that have been observed previously in Sierra Nevada lakes and proposed as water quality criteria by the National Park Service (Stoddard 1995). Critical loads were computed using the four levels for ANC_{limit} for each lake for each date that the lake was sampled yielding several thousand values for CL(A) which are summarized in Table 6.

For all lakes, the median critical loads for ANC_{limit} 0, 5, 10, and 20 μeq L^{-1} were 217±575, 186±569, 157±565, and 101±557 eq ha^{-1} $year^{-1}$, respectively (Table 6). Median exceedances using Eq. 2 for ANC_{limit} 0, 5, 10, and 20 μeq L^{-1} were −152±565, −123±560, −92±555, and −42±548 eq ha^{-1} $year^{-1}$, respectively. Lakes within predominantly granitic catchments had median critical loads for ANC_{limit} 0, 5, 10, and 20 μeq L^{-1} of 200±321, 179±314, 149±309, and 93±302 eq ha^{-1} $year^{-1}$, respectively. Median exceedances for granitic watersheds using Eq. 2 for ANC_{limit} 0, 5, 10, and 20 μeq L^{-1} were −140±313, −114±307, −81±301, and −35±295 eq ha^{-1} $year^{-1}$, respectively.

Median critical loads of catchments underlain by nongranitic bedrock for ANC_{limit} 0, 5, 10, and 20 μeq L^{-1} were 1,127±1,954, 1,084±1,948, 1,042±1,942, and 956±1.930 eq ha^{-1} $year^{-1}$, respectively. Median exceedances for these lakes at ANC_{limit} 0, 5, 10, and 20 μeq L^{-1} were −886±1,770, −850±1,764, −807±1,758, and −725±1,746 eq ha^{-1} $year^{-1}$, respectively.

3.3 Critical Load Estimates Based on the F-factor

The mean *F*-factor calculated using all lake samples was 0.24 (median=0.18) which is near the low end of the range reported by Henriksen and Posch (2001). Using an *F*-factor of 0.2 and ANC_{limit} values of 0, 5, 10, and

Table 4 Descriptive statistics for the major ion chemistry of the synoptic survey lakes. SC is laboratory measured specific conductance

	Ca^{2+} (μeq L^{-1})	Mg^{2+} (μeq L^{-1})	Na^+ (μeq L^{-1})	K^+ (μeq L^{-1})	NH_4^+ (μeq L^{-1})	NO_3^- (μeq L^{-1})	SO_4^{2-} (μeq L^{-1})	ANC (μeq L^{-1})	SC (μS cm^{-1})
Average	46.5	11.4	18.2	4.8	0.9	1.4	9.9	56.8	8.0
Median	21.6	5.5	15.5	3.8	0.6	0.2	2.7	33.3	5.1
Standard deviation	80.3	14.6	16.1	4.3	0.7	3.2	34.2	74.3	9.5
Maximum	848.3	116.8	189.6	73.4	5.9	23.6	408.1	695.5	94.2
Minimum	0.4	0.3	0.4	0.5	0.0	0.0	0.2	−1.5	1.8

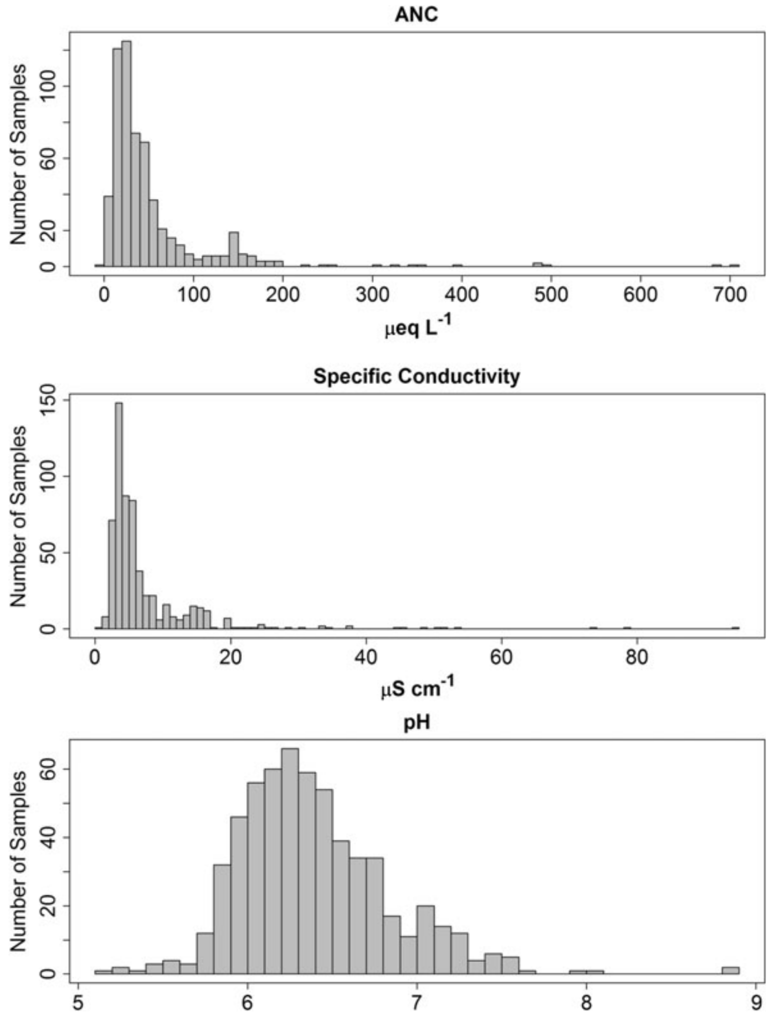

Fig. 2 Frequency histograms of ANC (microequivalent per liter), specific conductivity (microsiemens per centimeter), and pH (pH units) for lakes sampled in this study

20 μeq L^{-1} yielded median CL(A) values of 213±525, 185±519, 155±515, and 99±507 eq ha^{-1} year^{-1}, respectively, for all lakes (Table 6). Median exceedances for the same ANC_{limit} values were −149±515, −119±510, −86±506, and −40±498 eq ha^{-1} year^{-1}, respectively (Table 6).

For lakes in predominantly granitic catchments, median critical loads (ANC_{limit} of 0, 5, 10, and 20 μeq L^{-1}) were 198±320, 179±314, 149±308, and 93±300 eq ha^{-1} year^{-1}, respectively, Median exceedances were −139±312, −112±306, −77±301, and −33±294 eq ha^{-1} year^{-1}, respectively. For lakes in nongranitic

Table 5 Descriptive statistics for mineral weathering rates used in the critical loads modeling

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}
	(eq ha^{-1} year^{-1})	(eq ha^{-1} year^{-1})	(eq ha^{-1} year^{-1})	(eq ha^{-1} year^{-1})
Average	154.5	25.8	44.7	12.2
Median	56.9	13.6	25.1	4.4
Standard deviation	406.9	40.0	64.4	47.5
Maximum	6,925.2	310.1	365.7	1,064.5
Minimum	−36.2	−97.7	−559.1	−11.1

Table 6 Critical loads for acid deposition and exceedances at four ANC cutoffs (ANC_{limit}=0, 5, 10, and 20 μeq L^{-1}) under current acid deposition rates

	Critical loads				Exceedances			
ANC_{limit} (μeq L^{-1})	0	5	10	20	0	5	10	20
SSWC (empirical approach)								
Critical loads and exceedances for all lakes								
Mean (eq ha^{-1} $year^{-1}$)	356	329	302	249	−291	−264	−237	−184
Median (eq ha^{-1} $year^{-1}$)	217	186	157	101	−152	−123	−92	−42
St. dev. (eq ha^{-1} $year^{-1}$)	575	569	565	557	565	560	555	548
Max. (eq ha^{-1} $year^{-1}$)	7,367	7,326	7,285	7,203	46	46	74	255
Min. (eq ha^{-1} $year^{-1}$)	6	5	−13	−153	−7,213	−7,172	−7,131	−7,048
Critical loads and exceedances for granitic bedrock								
Mean (eq ha^{-1} $year^{-1}$)	294	268	242	189	−231	−205	−178	−126
Median (eq ha^{-1} $year^{-1}$)	200	179	149	93	−140	−113	−81	−35
St. dev. (eq ha^{-1} $year^{-1}$)	321	315	309	302	313	306	301	295
Max. (eq ha^{-1} $year^{-1}$)	2,419	2,368	2,317	2,216	46	46	74	255
Min. (eq ha^{-1} $year^{-1}$)	6	5	−13	−153	−2,349	−2,299	−2,248	−2,146
Critical loads and exceedances for nongranitic bedrock								
Mean (eq ha^{-1} $year^{-1}$)	1,918	1,882	1,845	1,771	−1,801	−1,764	−1,727	−1,653
Median (eq ha^{-1} $year^{-1}$)	1,127	1,084	1,041	956	−951	−917	−876	−790
St. dev. (eq ha^{-1} $year^{-1}$)	1,954	1,948	1,942	1,930	1,956	1,950	1,944	1,932
Max. (eq ha^{-1} $year^{-1}$)	7,367	7,326	7,285	7,203	−457	−431	−405	−353
Min. (eq ha^{-1} $year^{-1}$)	565	539	513	461	−7,213	−7,172	−7,131	−7,048
SSWC (F-factor approach)								
Critical loads and exceedances for all lakes								
Mean (eq ha^{-1} $year^{-1}$)	344	318	291	237	−279	−252	−226	−172
Median (eq ha^{-1} $year^{-1}$)	213	185	154	99	−149	−119	−85	−40
St. dev. (eq ha^{-1} $year^{-1}$)	525	519	515	507	515	510	506	498
Max. (eq ha^{-1} $year^{-1}$)	6,571	6,530	6,489	6,406	46	46	74	257
Min. (eq ha^{-1} $year^{-1}$)	6	5	−14	−155	−6,416	−6,375	−6,334	−6,252
Critical loads and exceedances for granitic bedrock								
Mean (eq ha^{-1} $year^{-1}$)	293	267	240	188	−230	−203	−177	−124
Median (eq ha^{-1} $year^{-1}$)	198	179	149	93	−139	−112	−77	−33
St. dev. (eq ha^{-1} $year^{-1}$)	320	314	308	300	312	306	301	294
Max. (eq ha^{-1} $year^{-1}$)	2,415	2,365	2,314	2,212	46	46	74	257
Min. (eq ha^{-1} $year^{-1}$)	6	5	−14	−155	−2,346	−2,295	−2,244	−2,142
Critical loads and exceedances for nongranitic bedrock								
Mean (eq ha^{-1} $year^{-1}$)	1,643	1,606	1,569	1,495	−1,526	−1,489	−1,452	−1,378
Median (eq ha^{-1} $year^{-1}$)	886	850	807	725	−706	−684	−642	−567
St. dev. (eq ha^{-1} $year^{-1}$)	1,770	1,764	1,758	1,746	1,772	1,766	1,760	1,749
Max. (eq ha^{-1} $year^{-1}$)	6,571	6,530	6,489	6,406	−350	−324	−298	−246
Min. (eq ha^{-1} $year^{-1}$)	458	432	406	354	−6,416	−6,375	−6,334	−6,252

catchments, median critical loads and exceedances (ANC_{limit} of 0, 5, 10, and 20 μeq L^{-1}) were 886±1,770, 850±1,764, 807±1,758, and 725±1,746 eq ha^{-1} $year^{-1}$, respectively, and −706±1,772,

$-684 \pm 1{,}766$, $-642 \pm 1{,}760$, and $-567 \pm 1{,}749$ eq ha^{-1} $year^{-1}$, respectively.

3.4 Model Uncertainty and Sensitivity

We lacked detailed and spatially distributed estimates for atmospheric deposition for the majority of the study lakes. While some attempts for mapping of atmospheric deposition in the Sierra Nevada have been attempted (Fenn et al. 2010), the resolution of these maps was insufficient to be useful in our modeling study and not all of the base cations and acid anions of interest have been mapped. Instead, we used deposition rates derived from 15 years of detailed measurements made at the Emerald Lake watershed in Sequoia National Park (http://ccb.ucr.edu/emeraldlake/). This is the only high elevation site in the Sierra Nevada where both wet and dry deposition rates have been routinely measured. While the use of the Emerald Lake deposition rates likely introduced error into computations of the critical loads and exceedances, wet deposition rates at Emerald Lake were demonstrated to be highly similar to rates measured at 11 other high elevation sites measured in the mid-1990s (Melack and Sickman 1997). Use of NTN data was considered, but dry deposition makes up a large proportion of the deposition of acid anions in the Sierra Nevada, so NTN-based models would have underestimated the true extent of exceedances of the critical load.

Using the range of annual base cation deposition reported by Melack and Sickman (1997) in the SSWC model produced critical load estimates very similar to those obtained with the Emerald Lake deposition data. Furthermore, the SSWC model was relatively insensitive to base cation deposition for determining the CL(A), demonstrating that mineral weathering rates and ANC_{limit} exert greater control on the value of CL(A). We would note that CL(A) and exceedance values estimated using the well-established *F*-factor approach were very similar to those obtained through empirical parameterization of Eq. 1, suggesting that our methodology for estimating mineral weathering rates was reasonable and unbiased (Table 6). When CL(A) values from both parameterization methods are plotted against each other, it results in a nearly 1:1 line with an R^2 value of 0.98 illustrating the close correlation between the two modeling approaches.

4 Discussion

4.1 Selection of ANC_{limit}

Selecting an appropriate ANC_{limit} is a function of the geologic materials and the tolerance of biotic species within the region of interest (Nilsson and Grennfelt 1988; Sverdrup et al. 1990). In Norway, Sweden, and Ontario, Canada, ANC_{limit} values of 20 μeq L^{-1} were used to estimate critical loads using the SSWC model and in the UK an ANC_{limit} of 0 μeq L^{-1} has been used (CLAG 1995; lien et al. 1996; Hindar et al. 1998; Henriksen et al. 2002). The US Environmental Protection Agency has defined four aquatic ecosystem status categories based on lake ANC for the Adirondack Mountains of New York: *Acute*<0 μeq L^{-1}; *Elevated* 0–50 μeq L^{-1}; *Moderate* 50–100 μeq L^{-1}; and *Low*> 100 μeq L^{-1} (http://www.epa.gov/airmarkets/progress/ARP_3.html Table 4 as viewed 05/24/2013). Using the EPA classification system, 71 % of the lakes in our study would be classified as having *Elevated* risk for negative ecological effects including reduced fish species richness.

In the Sierra Nevada, the large intra-annual variability of ANC caused by snowmelt runoff complicates the selection of the best ANC_{limit} to use in critical loads analyses. Many Sierra Nevada lakes experience episodic acidification (ANC≤0) during snowmelt (Leydecker et al. 1999) and have ANC levels of <20 μeq L^{-1} in the late summer and autumn (Fig. 2). To empirically establish ANC_{limit} for the Sierra Nevada, we varied ANC_{limit} from 0 to 200 μeq L^{-1} and plotted ANC_{limit} against the percentage of negative CL(A) values derived from Eq. 1. We noted an obvious break in slope from very few negative CL(A) values to steeply rising abundance of negative CL(A) at an ANC_{limit} of 10 μeq L^{-1} (Fig. 3).

4.2 Critical Loads for Acid Deposition in the Sierra Nevada

In the remainder of the discussion, we highlight the results obtained for an ANC_{limit} of 10 μeq L^{-1} when assessing the current status of wilderness lakes in the Sierra Nevada. Similarly, because lakes in nongranitic bedrock have high SO_4^{2-} concentrations not derived from atmospheric sulfur deposition, we emphasize the critical loads and exceedances computed for lakes found in predominantly granitic catchments. The CL(A) values derived for nongranitic lakes are so high that it

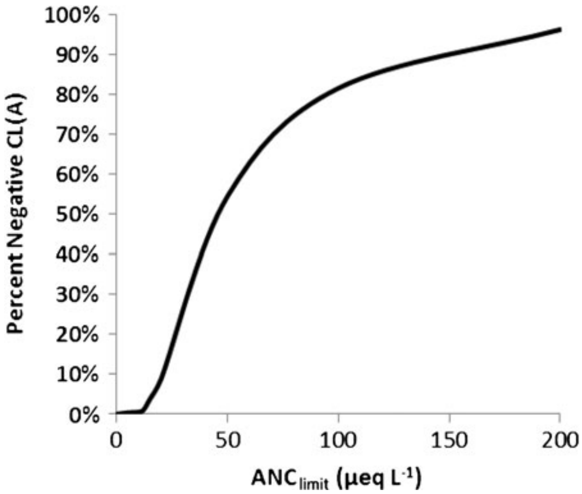

Fig. 3 Relationship between ANC_{limit} values and the percentage of lakes not exceeding the critical load for acid deposition (negative exceedance) under current deposition conditions

is very unlikely that they will ever be negatively impacted by acid deposition.

In the largely granitic catchments throughout the Sierra Nevada, the bedrock consists of slow weathering minerals, such a quartz and K-feldspar. For lakes in these types of catchments, the median critical load for acid deposition was 149 eq ha^{-1} year^{-1}. Most regions with granitic geology have critical loads for acid deposition less than 200 eq ha^{-1} year^{-1} (Nilsson and Grennfelt 1988), and Sverdrup et al. (1990) proposed that very slow weathering bedrock can produce CL(A) values less than 100 eq ha^{-1} year^{-1}. In 30 % of the Sierra Nevada lakes we investigated, CL(A) was less than 100 eq ha^{-1} year^{-1}, while 33 % were between 100 and 200 eq ha^{-1} year^{-1}.

For all Sierra Nevada lakes in granitic catchments, CL(A) ranged from −14 and 2,314 eq ha^{-1} year^{-1}. Sullivan et al. (2012) report that streams in Virginia and West Virginia generally have CL(A) values less than 500 eq ha^{-1} year^{-1}. While 90 % of our samples were below 500 eq ha^{-1} year^{-1}, 72 % of the samples were below 250 eq ha^{-1} year^{-1} showing less buffering capacity in the Sierra Nevada compared to these eastern US lakes. Harris and Juggins (2011) estimated CL(A) values between 0 and 26,400 eq ha^{-1} year^{-1} and Curtis et al. (1995) estimated CL(A) for S of 188 eq ha^{-1} year^{-1} in UK freshwaters ecosystems. Moiseenko and Gashkina (2011) estimated that 75 % of 323 small lakes in arctic European Russia have CL(A) less than 0.5 eq ha^{-1} year^{-1}. De Vries (1994) estimated a CL(A) of 300–500 mol ha^{-1} year^{-1} for phreatic groundwater and surface water in the Netherlands. Henriksen et al. (2002) examined 1,469 lakes in Ontario, Canada and estimated a CL(A) less than 1,000 eq ha^{-1} year^{-1}. Dupont et al. (2005) used the SSWC *F*-factor model to estimate CL(A) of 978 and 1,393 eq ha^{-1} year^{-1}, respectively, for over 2,000 lakes in Northeastern Canada and USA. Based on these studies, values of CL(A) for the lakes in our study appear to be among the lowest in the world.

4.3 Exceedances of Critical Loads of Acidity in the Sierra Nevada

About 80 % of the wilderness lakes in the Sierra Nevada we sampled did not exceed the CL(A). Mean Ex(A) for the empirical and *F*-factor approaches were −178 and −177 eq ha^{-1} year^{-1}, respectively, with median values of −81 and −77 eq ha^{-1} year^{-1}. Out of the 208 lakes studied, 34 and 35 exceeded their CL(A) at least one time, which corresponds to 16.3 and 16.8 % of all lakes sampled. The individual lakes exceeding the critical load using both parameterization approaches are nearly identical except that Moat Lake and Waca Lake each had one additional exceedance and Shallow Lake exceeded the CL(A) using the *F*-factor approach. While our study did not incorporate a sampling design that would allow us to make robust statistical inferences for all Sierra Nevada lakes, we conclude that hundreds of wilderness lakes and catchments are likely receiving acid loading in excess of their buffering capacity in at least some years.

No statistical relationship was found among Ex(A), elevation, or sample date. Mean and median elevation for all lakes was 2,737 and 2,725 m, while the mean and median lake elevations for exceeded lakes was 2,726 and 2,799 m. Of the lakes that exceeded the CL(A), 50 and 26 % are located in Sierra and Stanislaus National Forests, respectively. In particular, the Emigrant and Kaiser Wilderness areas had 26 and 24 % exceedances, respectively. Eldorado and Lassen National Forests each had 10 % of the lakes exceeding the critical load and Toiyabe National Forest had 4 % of the total exceedances. The most vulnerable lakes in the study appear to be located in the Sierra and Stanislaus National Forests located in the southern Sierra Nevada where N deposition is highest (Fenn et al. 2008, 2010).

One lake of particular interest in our study was Moat Lake in Hoover Wilderness (Humboldt-Toiyabe National Forest). The mean and median CL(A) at Moat Lake were 54 and 44 eq ha^{-1} year^{-1}, respectively, which are similar to the value of 73.9 eq ha^{-1} year^{-1} proposed by Heard (2013), based on paleolimnological reconstructions of ANC conducted at Moat Lake. Importantly, the critical load estimates for Moat Lake are low relative to acid deposition rates typical of the high Sierra Nevada (Table 2; mean H^+ deposition=96.7 eq ha^{-1} year^{-1}). Moat Lake was sampled six times between 2005 and 2009 and exceeded the CL(A) four and five times for the empirical and *F*-factor modeling approaches, respectively. Sickman et al. (2013) conducted paleolimnological reconstruction of ANC values in Moat Lake that showed that ANC began declining in the 1920s and reached a minimum in the 1960s and 1970s. The paleoreconstruction also suggested that ANC had largely recovered to pre-acidification levels by the end of the twentieth century owing to improvements in air quality driven by the US Clean Air Act (Heard 2013). Our modeling suggests that Moat Lake has not fully recovered from the effects of acid deposition and demonstrates that current levels of acid deposition in the Sierra Nevada exceed the critical load for some lakes despite substantial improvements in air quality in California (Cox et al. 2008).

4.4 Management Implications

Our regional assessment highlights the need for continued monitoring and study of the recovery of high elevation Sierran lakes from acid deposition. The high elevation lakes sampled in this study had exceptionally low ANC illustrating the minimal buffering capacity of these lakes. For lakes in granitic catchments, the majority of the critical loads of acidity would be exceeded if S deposition were >2.5 kg S ha^{-1} year^{-1}; peak S deposition rates in the Sierra Nevada (Table 2) are currently 1.2 kg S ha^{-1} year^{-1}. Current H^+ deposition rates exceed the critical load for a substantial number of high elevation lakes, emphasizing the need for continued reductions in NO_x, NH_3, and SO_x emissions.

Currently, the majority of critical loads research in the Sierra Nevada is focused on the effects of N deposition on forest soils and lakes (Fenn et al. 2010; and Saros et al. 2010). Critical load values of 3 kg ha^{-1} year^{-1} (Fenn et al. 2010; Pardo et al. 2011) and 1.4 kg ha^{-1} year^{-1} (Saros et al. 2010) have been proposed. Baron et al. (2011) considered eutrophication and acidification risks and estimated that high elevation lakes in the Sierra Nevada have critical loads of 1 to 3 kg N ha^{-1} year^{-1}. For the granitic catchments in our study, we estimated a median CL(A) value of 149 eq ha^{-1} year^{-1} which corresponds to 2.1 kg N ha^{-1} year^{-1}. However, in the future, if oxidized nitrogen deposition continues to decline while reduced nitrogen deposition (NH_4^+) stabilizes or rises, then the ratio of catchment NH_4^+ retention to catchment NO_3^- could increase above 1.0 such that biological N assimilation would result in net acidification (Dillon and Molot 1990). With the potential of generating four H^+ ions for every NH_4^+ molecule assimilated in lakes, this could result in lower critical loads for N deposition than currently proposed.

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