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A SCREENING PROCEDURE FOR IDENTIFYING ACID-SENSITIVE LAKES FROM CATCHMENT CHARACTERISTICS

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Abstract. Monitoring of Wilderness lakes for potential acidification requires information on lake sensitivity to acidification. Catchment properties can be used to estimate the acid neutralizing capacity (ANC) of lakes. Conceptual and general linear models were developed to predict the ANC of lakes in high-elevation (≥2170 m) Wilderness Areas in California's Sierra Nevada mountains. Catchment-to-lake area ratio, lake perimeter-to-area ratio, bedrock lithology, vegetation cover, and lake headwater location are significant variables explaining ANC. The general linear models were validated against independently collected water chemistry data and were used as part of a first stage screen to identify Wilderness lakes with low ANC. Expanded monitoring of atmospheric deposition is essential for improving the predictability of lake ANC.

Keywords: atmospheric deposition, California, lake ANC, model, Sierra Nevada, water quality, watershed

1. Introduction

Amendments to the United States Clear Air Act in 1977 and 1990 give federal land managers in the United States "affirmative responsibility" for protecting Air Quality Related Values (AQRVs) of "Class I" Wilderness Areas (Wilderness Areas existing prior to 1977 and with areas greater than either 2025 ha for USDA Forest Service Areas, or 2430 ha for USDI National Park Service or Fish and Wildlife Service Areas) from adverse air pollution impacts from new and modified pollution sources. Federal land managers consider specific agency and Class I area legislative mandates in their decisions and, in cases of doubt, "err on the side of protecting AQRVs for future generations" (US Senate, 1977). Federal land managers must provide timely, effective and credible recommendations to regulatory agencies for permit decisions in the Prevention of Significant Deterioration (PSD) process required by the Clean Air Act (Peterson *et al.*, 1992). Only a small increment of additional pollution is allowed in these Wilderness “clean air areas.”

AQRV’s are characterized as resource elements that may be degraded by air pollution and include flora, fauna, soils, water, cultural resources, geologic features, and visibility. Sensitive receptor components of AQRV’s are often targeted for monitoring. Monitoring focuses on very specific indicators that are measurable elements of injury or change. AQRV’s in federally administered Class I areas typically include a water component described as “lakes with low acid neutralizing capacity (ANC).” Monitoring of lake chemistry over time provides essential information on the status and change of lake resources and is a primary method for executing the legislative mandate to protect aquatic AQRV’s in Class I areas. Unfortunately, because Class I areas in the western United States contain lakes of varying degree of sensitivity to atmospheric deposition, resource managers commonly do not know which lakes to select for long-term monitoring. Lake selection is complicated further by a lack of detailed knowledge on pollutant transmission pathways and on deposition levels in remote Wilderness Areas. Land managers often want to focus limited resources on monitoring the lakes of highest sensitivity to acidic deposition (lowest ANC), because these lakes will respond first to acidic deposition. However, no standardized quantitative methods are currently available to pre-select lakes likely to fit this criteria. Efficient and cost-effective screening procedures are needed for managers to determine which of potentially thousands of lakes to sample.

This paper describes a multi-stage procedure for screening a population of lakes within Wilderness Areas to identify a subset of lakes for long-term monitoring that are potentially vulnerable to acidification. The general linear models that are the core of the screening procedure are intended to aid land managers in lake selection in Wilderness Areas of the Sierra Nevada mountains in California. Lakes in the Sierra Nevada were described by Eilers *et al.* (1989) as the most chemically dilute group of lakes sampled in US EPA’s 1985 nationwide lake survey.

2. Methods

A premise of the screening procedure is that ANC is the best single indicator of lake sensitivity to potential acidification. Sullivan *et al.* (2001) identified ANC values of 25 and 50 μEq L^{-1} as probably protecting Sierra Nevada lakes from foreseeable chronic acidification and episodic acidification, respectively. Furthermore, ANCs $\leq$50 μEq L^{-1} represent “low” ANC water bodies that have some buffering capacity but have been shown to demonstrate decreases in ANC during snowmelt (Landers *et al.*, 1987). The modeling and field procedures in our study therefore focused on lake ANCs $\leq$50 μEq L^{-1}.

Development of the screening procedure had five components:

1. Develop a conceptual model for lake sensitivity to acidification.
2. Translate the conceptual model into a quantitative model(s), using Geographical Information System (GIS) techniques and based on analysis of a comprehensive existing lakes dataset.
3. Validate the quantitative model(s) with independent data from two Wilderness Areas.
4. Sample lakes at other Wilderness Areas anticipated from the model results to have low ANC.
5. Select lakes for long-term monitoring based on results of the field sampling.

Steps (1)–(3) are described in detail here.

Data from a subset of lakes sampled in the 1985 Western Lake Survey (WLS), a probabilistic survey of hundreds of lakes in the Western United States (Landers *et al.*, 1987; Eilers *et al.*, 1987), were the basis for general linear models incorporating the variables identified in the conceptual model anticipated to be influential determinants of lake ANC. The models were evaluated by applying them to lake chemistry measured in the Emigrant and Kaiser Class I areas in 2000.

2.1. Conceptual model-controlling variables

Sensitivity of a surface water system to potential acidification depends on the ability of the system to neutralize acidic compounds from atmospheric deposition. Factors increasing sensitivity to acidification minimize the contribution of geologic weathering products that could neutralize acidic compounds from atmospheric deposition. These include:

- Large ratio of surface area of lake or stream to catchment area (Turk, 2001).
- Periods of high inflow from snowmelt, rain on snow, or rain that reduce hydrologic residence times and push atmospherically derived chemicals quickly through or over the catchment materials into lakes (Landers *et al.*, 1987; Turk, 2001; Clow *et al.*, 2002).
- Little exposed soil in the catchment or near the lake or stream (Henriksen *et al.*, 1998; Turk, 2001; Clow *et al.*, 2002; Henriksen *et al.*, 2002; Sickman *et al.*, 2002).
- Areas with high percentage of rock outcrop, talus, and scree (Clow and Sueker, 2000).
- Coarse-textured soils and soils with low base saturation or soils derived from bedrock types (e.g., granitic) that weather slowly and produce few acid neutralizing compounds (Gibson *et al.*, 1983; Clayton *et al.*, 1991; Bilaletdin *et al.*, 2001; Clow *et al.*, 2002; Henriksen *et al.*, 2002).

In Sierra Nevada Wilderness Areas, acid-sensitive waters are commonly found at moderate to high elevation, in areas of high relief, coniferous vegetation (or above treeline), with large amounts of precipitation and flashy hydrology. Sensitive lakes are generally either small drainage systems or small seepage systems that derive much of their hydrologic input as direct precipitation to the lake surface and/or have short hydraulic residence times that reduce the relative importance of in-lake alkalinity generation processes (Gibson *et al.*, 1983; Stoddard, 1987; Sullivan, 2000).

In our conceptual model ANC is minimized in headwater catchments having little or no vegetation or soil cover, and granitic bedrock. Catchment to lake area is small, and lakes have small surface area compared to their perimeter – as a further indicator of rapid movement of water and solids from the hillslope into the lake. ANC can also be reduced in locations receiving high loading of acidic solutes from the atmosphere. Bedrock lithology, catchment vegetation, amount and chemistry of soil cover, and headwater status are the primary catchment determinants of ANC in this conceptualization. The other variables influence the rapidity of movement of watershed materials to lakes, and therefore control the duration of ANC-producing processes for resident water.

2.2. General linear model of lake ANC

We used a general linear model (GLM) to predict lake ANC. The GLM procedure allows inclusion of continuous, categorical and binomial variables and consideration of different theoretical approaches to the analysis of variance by computing up to four types of sums of squares and their related statistics. SAS routines (GLM procedure) were used in defining the GLMs (SAS, 1986).

2.2.1. *Definition of GLM Variables*

Variables identified as important in the conceptual model were characterized using the WLS dataset (see below). WLS lakes were operationally defined as water bodies shown on 1:100,000 US Geological Survey topographic maps in terrain anticipated to contain an abundance of lakes with ANC <400 μEq L^{-1}. This sample frame constrained minimum lake surface area to approximately 1 ha. The WLS is the only probabilistic survey of lake chemistry spanning the breadth of the Sierra Nevada and therefore allowing potential inference to a population of over 2000 Sierra Nevada lakes $\geq$1 ha in area.

The WLS quantified several variables (e.g., catchment and lake area, lake elevation) relevant to the conceptual model using 1:100,000 or smaller scale maps. Because data of finer resolution are now available and because of our desire to apply the GLM to hundreds or thousands of lakes in the Sierra Nevada, we used GIS procedures whenever possible to characterize the variables for the GLM. Nevertheless, finer scale mapping of bedrock geology in the Sierra Nevada is not generally available digitally, and quantification of the geology variables was manually undertaken. Only the ANC values were taken directly from the WLS; all other variables were re-quantified in the development of the models.

We used WLS operational definitions of variables as precedents in the GLM. ANC is the continuous dependent variable. The independent variables are defined as:

- *Lake elevation*: Higher elevation indicates elevated sensitivity – as a surrogate for availability of potential acid neutralizing materials.
- *Catchment-to-lake area ratio*: Lake area excludes islands and fringing wetlands. Catchment area includes the area of any islands and lakes within the catchment. Low ratios indicate elevated sensitivity – as a surrogate for short travel time taken by catchment materials to reach the lake (and consequently less time for interaction of atmospherically derived water with acid neutralizers like soil and vegetation).
- *Lake perimeter-to-lake area ratio*: Lake perimeter includes the perimeter of any islands within lakes. Higher ratios indicate slower movement of catchment materials to the lake and an elevated opportunity for acid neutralization.
- *Mean catchment slope*: Higher slopes indicate elevated sensitivity – as a surrogate for time available for water to interact with acid neutralizers within the catchment.
- *Catchment vegetation cover*: Vegetation is defined as at least 10% vegetation cover, otherwise the GIS polygon is considered barren. Non-vegetated land includes rock outcrop, water or alpine dwarf scrub vegetation. Vegetation is forest vegetation, shrubs or meadows. Vegetation typing was based on Landsat imagery for Forest Service lands and air photographs for National Park Service lands. Lower cover indicates potential elevated sensitivity to acidification – as a direct measure of vegetative acid neutralizing processes and as an indirect measure of soil acid neutralization processes. Vegetation is quantified as percent of catchment non-vegetated.
- *Catchment bedrock lithology class*: Bedrock information was derived from the highest resolution geologic maps available. Most of these were 1:62,500 scale US Geology Survey maps. Some 1:250,000 scale Geologic Maps of California were used when higher resolution maps were not available. Catchment bedrock types were categorized into five lithology classes based on sensitivity to acidic waters based upon Peper *et al.* (1996), Melack *et al.* (1985), Landers *et al.* (1987) and Clow *et al.* (1996):

Class 1	Felsic	Aplite, granite, alaskite, rhyolite, quartzite, fine-grained metaclastics, slate
Class 2	Intermediate intrusive	Granodiorite, diorite, tonalite, syenite, monzonite, felsic gneiss and schist
Class 3	Intermediate extrusive	Dacite, trachyte, latite, andesite, tuff
Class 4	Mafic/carbonate	Gabbro, diabase, basalt, anorthosite, ultramafics, mafic paragneiss and schist, hornfels, limestone, marble, dolomite, marlstone, calcareous slate
Class 5	Unconsolidated material	Alluvium, landslide deposits (talus), glacial deposits

Lower classes (e.g., Class 1) are associated with lower ANC, except for Class 5, which has indeterminate lithology. Per the WLS, this classification is based upon the "dominant bedrock class in which the lake was located" (Landers *et al.*, 1987). It also synthesizes the major bedrock classes within each catchment. This lithology classification is tailored to the geology of the Sierra Nevada. It does not necessarily apply in its details to other regions.

- *Carbonate presence*: Some lake catchments have minor amounts of carbonates within other rock types that resulted in an overall lithology classification for the catchment that did not reflect carbonate presence. Because carbonates are a critical control of ANC, presence of carbonates was incorporated as a separate variable. Carbonate presence elevates ANC.
- *Presence of major geologic contacts or faults*: Some lakes could be affected by groundwater from other catchments where carbonates and/or bedrock with high ANC are located. Presence of geologic contacts or faults was derived from the aforementioned geologic maps. Contact or fault presence influences ANC to an unknown degree because of the uncertainty of the chemistry of water potentially brought into the catchment via the contact or fault.
- *Headwater location*: A "headwater" lake has no water body greater than 1 ha in area observable upstream of the lake on 1:24,000 topographic maps. Headwater location indicates elevated sensitivity versus lakes lower down in a catchment because of the reduced likelihood of confounding of acid neutralizing processes by inputs from other catchments.

To assure correct catchment delineation, a critical component of several of the predictor variables, manual checks of the GIS-generated delineations using aerial photography and 1:24,000 scale topographic maps were done for each WLS lake and all Wilderness lakes sampled in 2000.

2.2.2. *Western Lake Survey Data*

One hundred and thirty lakes, the vast majority of the lakes included in the "California Cascades" and "Sierra Nevada" geomorphic units of the California sub-region of the WLS, were included in the GLMs (Table I). The Sierra Nevada is composed largely of granitic and volcanic rocks. It experiences a Mediterranean climate with cool, wet winters and warm, dry summers. Several thousand lakes and ponds support a diverse aquatic fauna in this sub-region. Lake Almanor, over 22 times larger than the next largest lake, strongly biases mean lake perimeter and area, and catchment area in Table I. Lake Almanor was included in the model. Three other WLS lakes were not included because their elevation was considerably below the lower border of the forested zone (one lake), or because vegetation cover information was not available for their catchments (two lakes). The WLS lakes included 84 lakes in Wilderness Areas under National Park Service or Forest Service jurisdiction. All of these lakes were included in the database for the model. Forty-one percent of the WLS lakes are headwater lakes.

TABLE I
Selected physical and chemical characteristics of 130 WLS lakes used in model development

Statistic	ANC (μEq L^{-1})	Elevation (m)	Perimeter (m)	Catchment area (ha)	Area (ha)	Sum base cations (Ca^{2+} + Mg^{2+} +Na^{+}+ K^{+}) (μ Eq L^{-1})	Sum acid anions (Cl^{-} + NO_3^{-} + SO_4^{2-} + F^{-}) (μ EqL^{-1})	F^{-} (μEqL^{-1})
Mean	150	2557	3015	2321	102	173	22	0.9
Median	73	2535	1123	124	4.9	88	11	0.6
90th percentile	305	3379	4941	2127	47	364	45	1.8
Minimum	13	859	490	8.5	1.1	21	2.9	0.1
Maximum	1260	3715	77540	129402	10077	1328	394	5.7

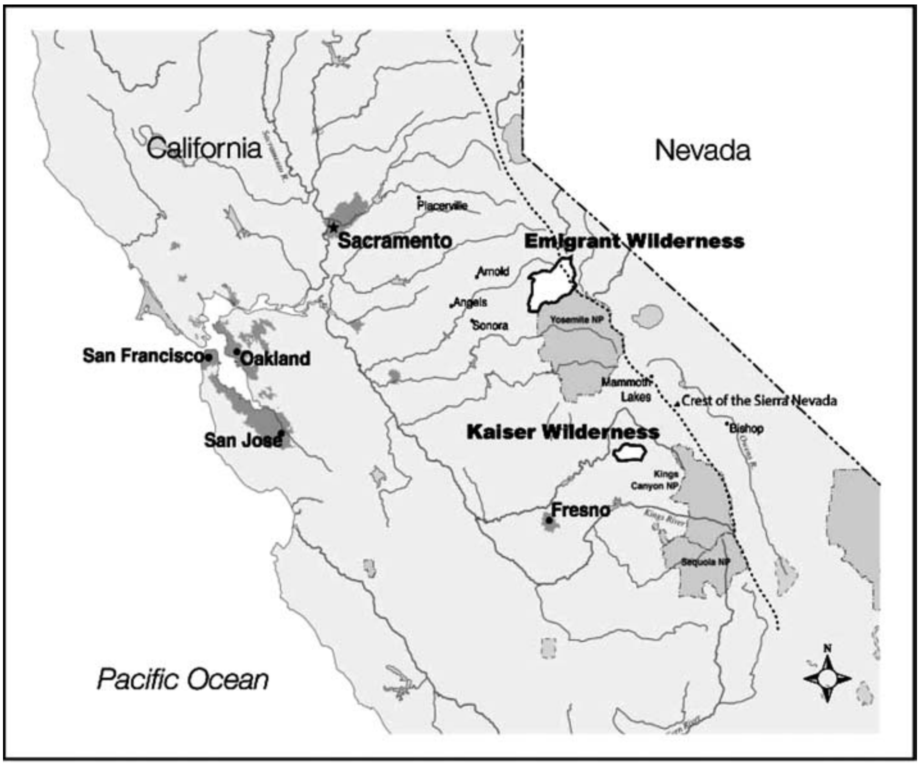

Figure 1. Location of Emigrant and Kaiser Class I Wilderness Areas in the Sierra Nevada of Central California.

2.2.3. *Sierra Nevada Lake Data*

Ninety-five water bodies (lakes ≥1 ha surface area and ponds <1 ha surface area) were sampled in June and July 2000, when lake ANC is typically at the annual minimum (Melack *et al*., 1998), in two Sierra Nevada Class I Wilderness Areas, Emigrant (56 water bodies) and Kaiser (39 water bodies) (Figure 1). These Class I

Wildernesses, plus eight others together totaling 5% of the area of the greater Sierra Nevada, contain almost 43% of the lakes in the greater Sierra Nevada. Emigrant Wilderness borders the western edge of the crest of the south-central Sierra Nevada and ranges in elevation from 1810 to 2870 m. Kaiser Wilderness is farther south and west of the Sierran crest between Yosemite and Sequoia-Kings Canyon National Parks. There are over 100 lakes in these two Wildernesses. Lakes in both Wilderness Areas are at high elevation, and have snowmelt-dominated hydrology, thin and poorly developed soils, patchy vegetation, and granitic or volcanic bedrock.

Atmospheric deposition patterns in these two Wildernesses are poorly known because no deposition monitoring sites exist in either Wilderness. Emigrant Wilderness is the potential receptor of air-borne pollutants from three inter-air basin pathways roughly associated with sources in the San Francisco Bay Area, the broader Sacramento area, and the San Joaquin Valley (Sullivan *et al.*, 2001). The Fresno Eddy affects Kaiser Wilderness, with daytime winds carrying polluted air masses into the foothills and higher elevations of the Sierra Nevada (Sullivan *et al.*, 2001).

Because of the relatively small number of water bodies in Kaiser Wilderness, all lakes and ponds in Kaiser were sampled. Water bodies in Emigrant Wilderness were selected on the basis of the conceptual model of low-ANC lakes. Over 78% of the Emigrant samples were from headwater water bodies in granitic terrain with minimal soil development and a range of catchment:lake area ratios, although several Emigrant water bodies in volcanic terrain were sampled.

The usefulness of the GLMs for ponds is of interest so the Kaiser Wilderness census included ponds <1 ha in area comprising 30 of the 39 water bodies sampled. Eight of the 56 Emigrant Wilderness water bodies sampled were ponds.

Grab samples were collected at the outlet of each water body, in moving water, or along the shore in well-mixed water approximately 30 cm deep if surface outlets did not exist. Elbow-length, powder-free gloves were used for each sample collection, and they were not re-used. Field blanks and duplicate samples were collected at approximately 10% of the localities. No preservatives were added to the samples nor were the samples filtered in the field. Samples were placed in coolers with refrigerant immediately after collection and a courier system transported samples to the analytical laboratory quickly from remote sites.

Samples were filtered at the laboratory and analyzed for cations (sodium, Na^{+}; ammonium, NH_4^+; potassium, K^+; magnesium, Mg^{+2}; calcium, Ca^{+2}), and anions (chloride, Cl^-; nitrate, NO_3^-; and sulfate, SO_2^4) by ion chromatography. The laboratory QA was evaluated with outlier and duplicate evaluation, anion–cation charge balance comparison, computed conductivity versus measured conductivity comparisons, and comparison of results either with data previously collected from the same lakes, or less satisfactorily, with other lakes in the Sierra Nevada. Subsets of the filtered samples were analyzed for cations at two other laboratories using atomic absorption spectrophotometry and inductively coupled plasma.

ANC, pH, and electrical conductivity were also quantified at the primary analytical laboratory, a USDA Forest Service facility in Ft. Collins, Colorado. Chemical attributes of the 95 sampled water bodies are summarized in Table II. Constituent concentrations are similar to those sampled in 1999 by Clow *et al*. (2002) for Wilderness lakes in nearby Yosemite and Sequoia-Kings Canyon National Parks.

3. Results

3.1. Assessment of the conceptual model

The model was evaluated by calculating statistics associated with the GLM's fit to the input WLS data and by validation of the GLM with respect to independent lake chemistry data collected in 2000.

3.1.1. *Statistical Analysis*

The statistical analysis generally supported the conceptual model; all elements of the conceptual model were statistically significant in the general linear modeling except mean slope and elevation. We used a single formulation for mean slope, and did not calculate mean slope, or other indices of terrain steepness by alternative methods. Therefore we cannot confirm that an artifact of the slope calculation, rather than slope itself, caused the non-significance. In one of the three models described below elevation correlated negatively with percent of non-vegetated catchment and was nearly as strong an independent variable as percent of catchment non-vegetated, but we selected percent of catchment non-vegetated over elevation because we believe vegetation cover more intrinsically represents catchment processes controlling ANC.

3.1.1.1. Number of Models. The conceptual model defined headwater location as a binary variable. After experimentation with a single model, with headwater location included, we determined that variables controlling ANC differed between the headwater and non-headwater situations. Consequently two models, "headwater yes" ($n = 77$) and "headwater no" ($n = 53$) were explored. Further assessment of the "headwater yes" model identified a sub-model incorporating one class of the five-category bedrock lithology variable – intermediate intrusive – as explaining appreciably more variation in ANC than a single consolidated "headwater yes" model. Fortunately, 32 lakes in the WLS dataset had intermediate intrusive bedrock lithology, an adequate sample size for model development. Three GLM models were therefore developed for:

1. lakes in non-headwater catchments;
2. lakes in headwater catchments having intermediate intrusive bedrock lithology;
3. all lakes in headwater catchments.

3.1.1.2. Model Specification. We identified one two-variable interaction term, lithology by percent of catchment non-vegetated, as a candidate variable for the

TABLE II

Descriptive statistics of chemical constituents from lakes and ponds sampled in June and July, 2000 at Emigrant ($n = 56$) and Kaiser ($n = 39$) Wildernesses, Sierra Nevada, California

	ANC (μEq L^{-1})	Conductivity (uS cm^{-1})	H^+ (μEq L^{-1})	Ca^{2+} (μEq L^{-1})	Mg^{2+} (μEq L^{-1})	Na^+ (μEq L^{-1})	K^+ (μEq L^{-1})	NH_4^+ (μEq L^{-1})	Cl^- (μEq L^{-1})	NO_3^- (μEq L^{-1})	SO_4^{-2} (μEq L^{-1})
Mean											
Emigrant	46 (46)	5.6 (5.7)	1.0 (1.0)	35 (35)	7.9 (8.1)	11.5 (11.7)	2.7 (3.0)	0.7 (0.7)	1.8 (1.9)	0.4 (0.5)	2.4 (2.4)
Kaiser	66 (66)	7.8 (7.0)	1.0 (0.6)	47 (49)	10.4 (8.4)	22 (18)	5.4 (3.8)	1.2 (1)	1.5 (1.3)	0.7 (0)	2.6 (2.7)
Median											
Emigrant	27 (26)	3.7 (3.7)	1.0 (1.0)	18 (18)	5.9 (5.8)	10.0 (9.9)	2.1 (2.3)	0.6 (0.6)	1.5 (1.6)	0 (0)	1.9 (1.8)
Kaiser	56 (44)	6.7 (5.4)	0.6 (0.6)	37 (33)	8.9 (6.3)	19 (16)	4.4 (3.8)	0.9 (0.8)	1.4 (1.3)	0 (0)	2.1 (2.6)
Max											
Emigrant	356 (356)	38 (38)	2.5 (2.4)	327 (327)	33 (33)	36 (36)	17 (17)	1.9 (1.9)	4.7 (4.7)	8.0 (8.0)	13.1 (0.8)
Kaiser	252 (158)	28 (14)	7.1 (1.0)	152 (137)	36 (18)	74 (32)	21 (4.4)	5.9 (1.7)	3.1 (1.7)	14.4 (0)	8.1 (3.8)
Min											
Emigrant	8.9 (10.6)	1.8 (2.0)	0.1 (0.1)	6.1 (6.1)	2.6 (2.7)	2.1 (4.4)	1.3 (1.5)	0 (0)	0.8 (0.8)	0 (0)	0.8 (0.8)
Kaiser	8.2 (25)	2.0 (3.8)	0.2 (0.2)	5.8 (16)	1.8 (4.1)	4.7 (11.3)	2.0 (2.6)	0 (0.5)	0.7 (0.8)	0 (0)	0 (1.9)

Statistics for lakes only ($\geq$1 ha) are listed parenthetically.

models. No other interaction terms were considered to be conceptually relevant. The emphasis in this modeling was on improved prediction for low ANC lakes. A transformation of the dependent variable, ANC, more effectively addressed this objective. After experimentation with several candidate transformations, $\log_{10}$ ANC was selected as the form of the dependent variable. The transformation also assisted in complying with the assumption of constant error variance.

The GLM models were:

1. *Headwater no*: $\log_{10}$ ANC = 3.17149 − b_{cp} − b_{geo} + 0.00060620 × catchment-to-lake area ratio − 19.172 × lake perimeter-to-area ratio + error, where b_{cp} and b_{geo} are:

Bedrock lithology	b_{cp}		b_{geo}
	Carbonate present	Carbonate absent	
Felsic	0	0.463	0.603
Intermediate intrusive	0	0.463	0.455
Intermediate extrusive	0	0.463	0.365
Mafic/carbonate	0	0.463	0.104
Unconsolidated	0	0.463	0

2. *Headwater yes, intermediate intrusive lithology (Class 2)*: $\log_{10}$ ANC = 2.12774 + 0.00276471 × catchment-to-lake area ratio − 6.09034 × lake perimeter-to-area ratio − 0.00509021 × percent of catchment non-vegetated + error
3. *Headwater yes, all lithologies*: $\log_{10}$ ANC = 1.82717 + 0.00273543 × catchment-to-lake area ratio − 7.513476 × lake perimeter-to-area ratio − 0.000966533 × percent of catchment non-vegetated + b_{geo} + b_{inter} + error, where b_{geo} is defined below and b_{inter} = percent of catchment non-vegetated × b_{lith}, with b_{lith} varying with lithology as:

Bedrock lithology	b_{geo}	b_{lith}
Felsic	0	0
Intermediate intrusive	0.3420	−0.00414
Intermediate extrusive	0.2805	−0.00424
Mafic/carbonate	0.0840	−0.00880
Unconsolidated	0.6915	−0.00845

Each of the variables in these models was significant ($\alpha = 0.05$) by the *F* test with the appropriate type of analysis. Most of the coefficients were also reasonable in that their signs and magnitudes matched anticipations from the conceptual model. For instance, predicted ANC declined as bedrock lithology became more felsic and vegetation cover decreased. The least squares means for the different levels of the classification factors also expressed trends that were consistent with the anticipations of the conceptual model. In terms of the SAS GLM procedure the type III analysis was appropriate for all models except the last listed above. This model was the only one with an interaction term and the type I analysis was utilized.

In the conceptual model, we hypothesized that lakes with small surface area compared to their perimeter would have lower ANCs. This was not borne out statistically. The lake perimeter:area values were skewed significantly to larger values, which may influence the GLMs, but otherwise we have no explanation for the unexpected relationship.

Coefficients of determination (R^2) and root mean square errors of the models were:

Model	Coefficient of determination	Root mean square error
Headwater no	0.51	0.341
Headwater yes: intermediate intrusive lithology	0.76	0.177
Headwater yes: all lithologies	0.60	0.276

Root mean square error values are for the predicted $\log_{10}$ of ANC; there is no valid way of un-transforming measures of dispersion to calculate root mean square error for ANC.

The headwater yes/lithology Class 2 model visually showed a closer fit between observed and predicted ANC than the other two models (Figure 2). The conceptual model inferred lower lake ANCs in headwater catchments with felsic lithologies. The lower observed ANCs for the headwater yes/lithology Class 2 model supported this inference.

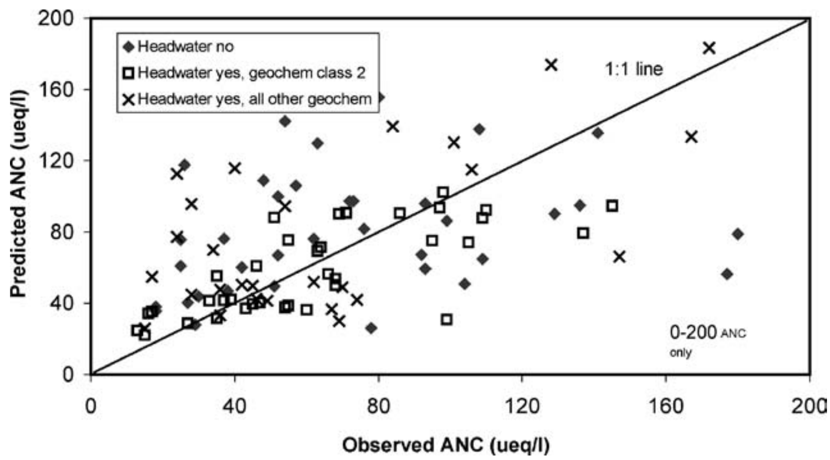

Figure 2. Observed and predicted ANC, by model type, WLS lakes.

TABLE III
Correlations (R) between observed ANC and continuous variables characterizing the Western Lake Survey dataset

Lake area	Catchment area	Catchment-to-lake area ratio	Lake perimeter-to-lake area ratio	Lake elevation	Catchment mean slope	Percent non-vegetated
0.37	0.42	0.33	−0.20	−0.28	−0.07	−0.30

TABLE IV
Mean and median observed ANC for categorical variables, WLS dataset

Variable and variable category	Mean observed ANC (μEq L^{-1})	Median observed ANC (μEq L^{-1})
	Bedrock lithology class	
1. Felsic	55	49
2. Intermediate intrusive	107	66
3. Intermediate extrusive	215	166
4. Mafic/carbonate	216	165
5. Unconsolidated	357	106
	Headwater catchment?	
No	189	93
Yes	123	67
	Carbonate in catchment?	
No evidence	141	71
Evidence	306	279

Although correlations between observed ANC and the lake and catchment characteristics were relatively low (Table III), mean and median values of observed ANC for the categorical variables in the models followed anticipated patterns (e.g., lower ANC in catchments with no evidence of carbonate minerals) (Table IV).

3.1.1.3. Residuals Analysis. Residuals (observed-predicted values) for ANC were plotted against all variables included in the models. No bias or trend in ANC residuals was observed in the plots for catchment area:lake area ratio, mean slope, elevation, lake perimeter:lake area ratio, or percent of non-vegetated catchment. Residual ANC was less for the more felsic bedrock lithology classes (Classes 1 and 2) than for the other classes (Figure 3).

ANC residuals plotted against observed ANC by headwater class (Figure 4) illustrated a slight bias to over-prediction of ANC for lakes with observed ANC less than approximately 100 μEq L^{-1} and a bias to under-prediction for ANC $\geq$ 200

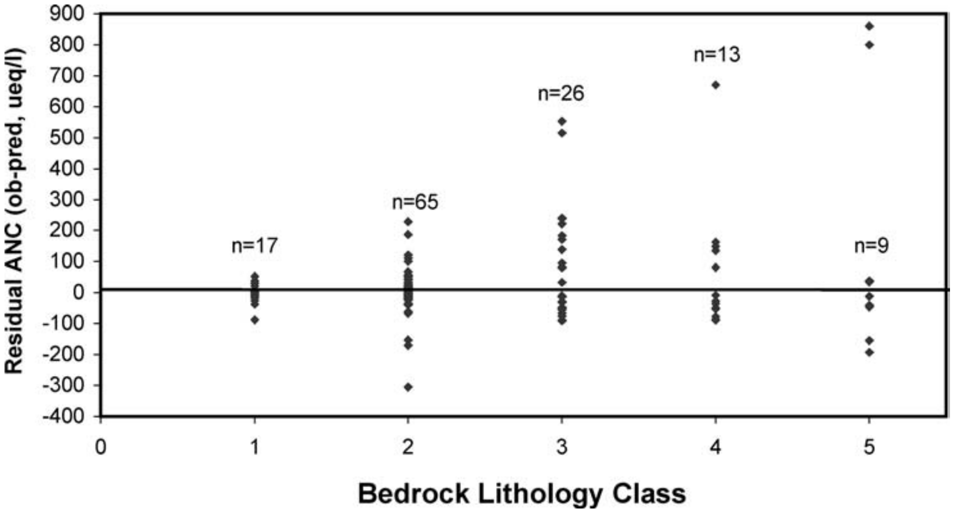

Figure 3. ANC residuals by bedrock lithology class, WLS lakes with ANC 0–200 μEq L^{-1}.

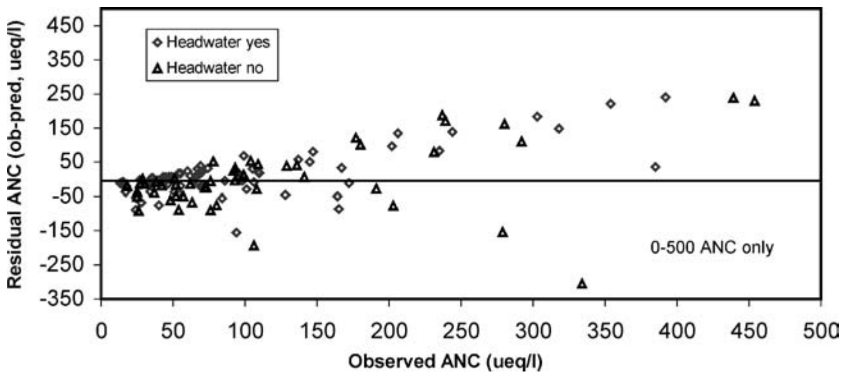

Figure 4. ANC residuals by observed ANC and headwater status, WLS lakes with observed ANC 0–500 μEq L^{-1}.

μEq L^{-1}. At low observed ANC, residuals were near 0 for predicted ANC for the "headwater-yes" lakes, while the "headwater-no" lakes were over-predicted. Above 200 μEq L^{-1}, the reverse occurred (Figure 4). Figure 4 includes only observed ANC $\leq$500 μEq L^{-1} to provide better resolution for the more sensitive low-ANC lakes.

3.1.1.4. Model Validation Using Independent Data. The 95 water bodies sampled in Emigrant and Kaiser Wildernesses in 2000 provided an independent dataset for assessment of the models. The three GLMs explained 51% of the variation in observed lake ANC with most of the lake ANCs over-predicted (Figure 5). Although the models were not developed for water bodies smaller than 1 ha in surface area, "ponds" in this size range are important habitat for biota in the Sierra Nevada and

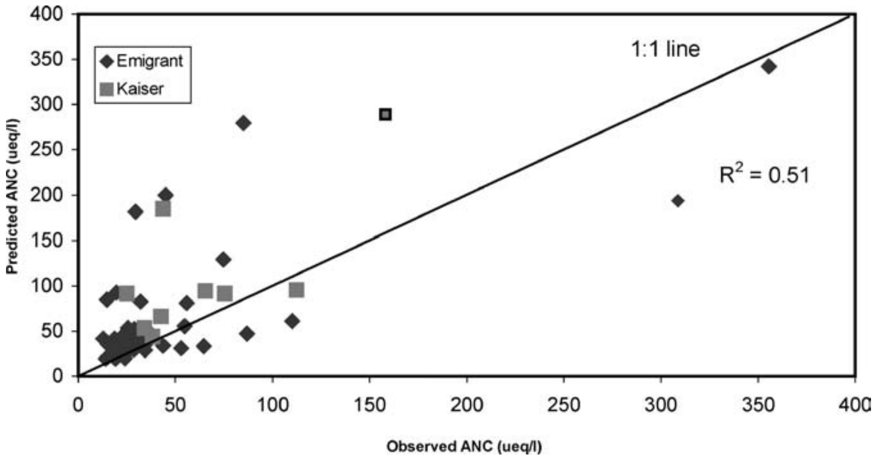

Figure 5. Observed and predicted lake ANC, Kaiser and Emigrant Wildernesses.

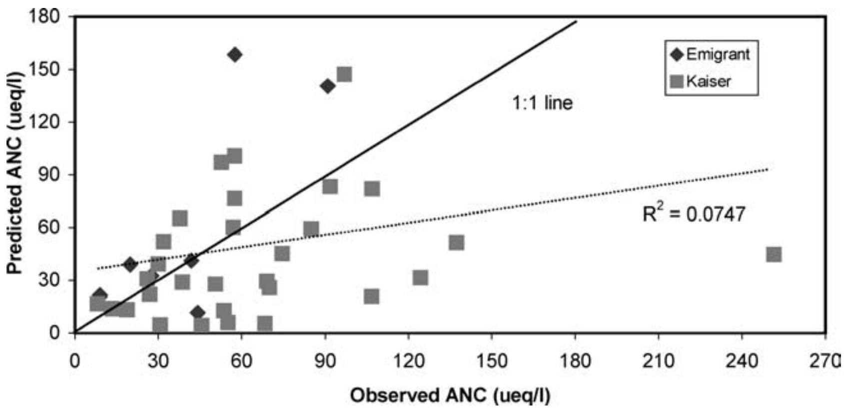

Figure 6. Observed and predicted ANC, Emigrant and Kaiser ponds.

the GLMs explained much less of the variation in observed pond ANC ($R^2 = 0.07$) (Figure 6).

Because of our interest in low-ANC lakes, we calculated residual ANC for lakes with observed ANC $\leq$50 μEq L^{-1}. The median residual ANC for these lakes was 14.3 μEq L^{-1} and 65% of the lakes had residual ANCs $\leq\pm$20 μEq L^{-1} (Figure 7). Over 79% of the 43 lakes with observed ANC $\leq$50 μEq L^{-1} were predicted to have ANC $\leq$50 μEq L^{-1}.

3.2. Applying the models to identify lakes for long-term-monitoring

An objective of the Air Resources program of the California region of the USDA Forest Service is monitoring of one or a few lakes with low ANC in each Class I

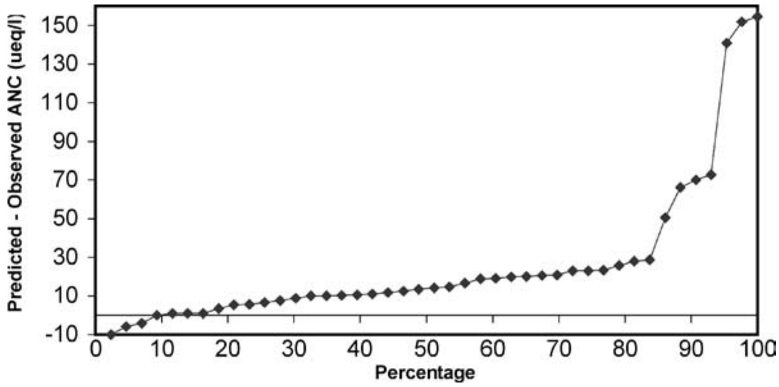

Figure 7. Cumulative frequency plot of lake ANC residuals (observed ANC $\leq$50 μEq L^{-1} only).

Wilderness. Field sampling of all lakes in each Wilderness is not a cost-effective means of identifying low-ANC lakes, and a method is needed to screen out lakes with high ANC. To identify candidate low-ANC lakes for long-term monitoring, we collected field samples from lakes predicted by the models to have low ANC, in anticipation that lakes with low predicted ANC will have low field-verified ANC.

We identified all water bodies meeting the 1-ha size criterion within the target area (e.g., Class I Wilderness Area) and ran the GLM models with GIS data for all lakes in each Wilderness. We then ranked the lakes by predicted ANC, manually checked values of all GIS input variables for the 10–30 lakes in each Wilderness with the lowest predicted ANC, corrected the values of the input variables as needed for these lakes, re-ran the models for the lakes in each Wilderness with the lowest predicted ANC using the corrected input values, and sampled the 10–30 lakes in each Wilderness with the lowest predicted ANC from the second model application. Last, we selected for monitoring the lakes with the lowest ANC that are adequately deep for monitoring (i.e., $\geq$1.5 m depth).

3.2.1. *Assessment of the GLMs for Long-Term Monitoring Lake Selection*

For long-term monitoring, we are less concerned about absolute errors (in ANC prediction) as long as the relative prediction of ANC is robust within each Wilderness. A relevant question is how many lakes need to be field-sampled to assure that the truly low ANC lakes (determined from the field sampling) are identified? If the GLMs are precise to the extent that few lakes need to be field-sampled to assure identification of low-ANC lakes, then the GLMs are operationally useful.

We assessed the utility of the GLMs by calculating from the Emigrant and Kaiser independent datasets the number of field observations needed to identify low-ANC lakes. The four lakes with the lowest observed ANC for Kaiser Wilderness were the four lakes predicted as having the lowest ANC (Figure 5). The nine lakes with lowest predicted ANC included four of the nine lakes with the lowest observed ANCs in Emigrant Wilderness (Figure 5). Sampling nine lakes in each of these Wildernesses would include the lowest observed ANC lake in Kaiser and the second-lowest observed ANC lake in Emigrant. Sample collection from nine lakes per Wilderness is cost-effective.

Observed lake ANCs in Emigrant Wilderness clustered tightly, with the lowest 11 observed ANCs ranging from 14 to 19 μEq L^{-1}. These are all low ANC lakes that from a management perspective would be good candidate lakes for long-term monitoring. The nine lakes with the lowest predicted ANC in Emigrant included four lakes with observed ANC under 20 μEq L^{-1}, further supporting the conclusion that the models meet management needs. As a prudent operational rule, for identification of low-ANC lakes in moderate-sized Class I Wilderness Areas, we will field sample 10–15 lakes with lowest predicted ANC. For larger areas, like John Muir Wilderness, which has over 500 lakes, we will sample proportionally more lakes, but we believe that no more than 10% of the lakes need to be sampled; they will be those with the lowest predicted ANC.

4. Discussion

Candidate causes for imperfect prediction by the GLMs include inadequate conceptualization of critical variables controlling ANC and spatial variability at the sub-catchment scale. Imprecise quantification of the predictor variables could increase variability in the ANC predictions. The influence of antecedent conditions may also influence the veracity of the predictive models. Last, variation in atmospheric deposition may explain some of the unexplained variance in the models.

4.1. Variable conceptualizations and scale considerations

The conceptual model is a meso-scale conceptualization of ANC dynamics at the scale of individual lake catchments. At the broader scale, Rutkowski *et al.* (2001) focused on lithology and lake presence to assess acidification risk at the scale of entire Wildernesses. At finer scales, other variables become relevant, variables that are not readily quantifiable with adequate resolution for operational use in land management. For instance, the supply of weathering products, and therefore ANC, may be influenced by variation in surficial geology within a single class of bedrock geology that is not discernable without examination of the site in the field (Don Campbell, personal communication, USGS 8/10/01). Similarly, the role of till, as a reservoir of groundwater and supply of weathering products (Turk and Campbell, 1987; Clow and Sueker, 2000), is not quantifiable from readily available geological mapping at the meso-scale. Another local-scale determinant of ANC may be topographic-driven differences in the magnitude and function of hydrologic flowpaths; ponds situated in topographic lows or at the toe of hillslopes theoretically receive elevated inputs of groundwater, and therefore weathering products, as neutralizers of acidic deposition (Don Campbell, personal communication, USGS 8/10/01). Campbell

(2001, unpublished data on file at USGS) quantified substantial ANC differences among ponds tens of meters apart having similar vegetation and geological parent material. These fine-scale phenomena are not incorporated into the conceptual model and may be causes in ANC variability that are not picked up in the meso-scale GLMs.

Leydecker *et al.* (2001) examined snow depth and stream chemistry variation in alpine and subalpine watersheds in the central and southern Sierra Nevada and determined that the "representative elementary area" (REA) concept may apply to these hydrologic attributes. Depending on the spatial extent and magnitude of various physical processes (e.g., preferential avalanche deposition or wind re-location of fallen snow in different areas within a catchment), spatial variability in hydrologic attributes can vary with scale. The REA addresses this phenomenon. It can be considered the smallest measurement area associated with the spatial variation of a parameter and ". . . as the sub-divisions of a drainage basin increase in size the variation in sub-catchment response decreases, reaching a minimum at the REA" (Leydecker *et al.*, 2001).

Leydecker *et al.* (2001) determined that the REA for snow depth, and outflow concentrations and annual export of nitrate, base cations and silica was between 35 and 70 ha for a 1900 ha headwater watershed in Sequoia National Park. These authors concluded that 35–70 ha ". . . should be the minimum size for catchment studies where results will be interpreted to apply over broader areas" (Leydecker *et al.*, 2001). Over 25% of the WLS catchments, and 68% of the Emigrant and Kaiser Wilderness catchments, are less than 50 ha in area. The common occurrence of catchments smaller in size than the proposed REA suggests that variability in hydrologic processes relevant to lake ANC (e.g., snow depth) may be relatively high, and therefore a cause of imperfect model prediction of ANC.

4.2. Quantification Deficiencies

A variety of sources of elevated variability in several of the predictor variables may contribute to reduced explanatory power of the models. Although laboratory analyses may be in error, procedures used for these activities followed generally accepted protocols, and ANC values probably have low error. Similarly, quantification of elevation, lake area and perimeter, and headwater status should have minimal error, although the 1 ha size criterion for headwater lakes may be too large – smaller upstream lentic water bodies not incorporated into the GLMs could influence ANC dynamics. Error sources may be greater in the other variables. In particular, geologic mapping was described by Sullivan (2003), in a GIS-based study of aquatic systems in the southern United States, as the "most problematic" of several explanatory variables.

Catchment area was poorly determined by GIS routines in areas of low slope. This problem was overcome by manual review of automated catchment area determinations. Although topographic slope intuitively is a control of ANC, as a determinant of the time available for atmospherically derived water to interact with bio-geologic materials in each catchment, the slope formulation used in the GLMs may be inappropriate. Rather than mean slope, Clow and Sueker (2000) used percentage of watershed area greater than 30° slope as a predictor. Quantifications of both the vegetation cover and geology variables may have low resolution relative to the size of some catchments because of limitations in operationally available information at proper scales. Source maps and imagery for geology and vegetation cover are relatively coarse with respect to the smaller catchments in the WLS that are incorporated into the GLM models. Ten percent of the WLS catchments used in developing the GLMs have areas under 25 ha. Errors in determination of vegetation cover and the geology variables are probably greater for these catchments than larger ones.

4.3. Antecedent conditions

Two differences in conditions antecedent to the 2000 Emigrant and Kaiser Wilderness sample collection and the 1985 WLS sampling may add variability to biogeochemical processes controlling lake water chemistry. Clow *et al.* (2003) describe increases in nitrate, dissolved organic carbon and aluminum concentrations with discharge during rainfall from the flushing of shallow organic soils. This phenomenon is more effective with short duration and relatively less intense storms that do not foster mixing and dilution of groundwater by event water (Clow *et al.*, 2003). Localized, often intense but short-lived thunderstorms are common in the summer in the Sierra Nevada. Some unknown portion of both the 1985 and 2000 catchments could have experienced increases in nitrate from thunderstorms affecting part of the catchments. Because of the lack of precipitation gages at these high-elevation sites, in combination with the localized nature of the storms, quantifying this potential effect would be difficult and would probably incur appreciable uncertainty. Because the WLS lakes were spread over the entire Sierra Nevada, as opposed to the higher density of lakes sampled in the two Wildernesses in 2000, potential flushing events could affect the 1985 lake chemistries differently than the 2000 chemistries.

A second, related difference in antecedent conditions stems from different dates of sample collection. The year 2000 samples were collected in June and July, when ANC is at an annual minimum in high-elevation Sierra Nevada lakes (Melack *et al.*, 1998). Snowmelt inflow to lakes is just ending at this time. The WLS samples were collected in late-September and October, during baseflow conditions when groundwater is the primary source of inflow to the lakes after a typically dry summer, and ANC would have started to rise after the early summer low. Melack *et al.* (1998) regressed September/October lake chemistries against June/July chemistries and calculated early June/July lake ANCs as approximately 88% of September/October ANCs. Five lakes were sampled in both the WLS and in 2000. The ANCs for these lakes were on average 7.4 μEq L^{-1} (86%) lower in 2000 than in the WLS (for WLS lake ANCs ranging from 15 to 164 μEq L^{-1} and averaging 63 μEq L^{-1}).

4.4. Atmospheric deposition

Lake ANC is a function of catchment properties and atmospheric deposition. We focus here on catchment characteristics and do not include atmospheric deposition of sulfate and nitrate in the models because of the scarcity of data applicable to modeling of ANC for individual lakes. Wet deposition monitoring data exist for four locations in the Sierra Nevada and northeastern California, although only two of these sites have data of sufficient quality and duration to allow trend determination (NADP, 2004). Dry deposition data are available from three of these sites (CASTNET, 2004). Variations in deposition, stemming from differences in the dynamics of the atmospheric drivers of deposition, and differences in the location and magnitude of upwind pollutant sources, may explain some of the variance in the GLMs. However, the limited NADP wet deposition data available does not show trends for either sulfate or nitrate from 1990–2000. We also believe that lake sulfate is largely determined by bedrock composition rather than S deposition. Given the paucity of monitoring data, expanded monitoring of deposition is essential for improving predictions of lake ANC and for developing next-generation screening tools.

Although deposition information for the Sierra Nevada is sparse (Fenn *et al.*, 2003a), nitrate concentrations appear variable across the Sierra Nevada, with elevated nitrate evident in some southern Sierra lakes, reportedly from nitrogen deposition (Fenn *et al.*, 2003b). Lower elevation locations in the southwestern Sierra Nevada exhibit high nitrate concentrations in streamwater from high rates of N deposition resulting from their proximity to N emission sources and from atmospheric inversions that concentrate pollutants below 1000–2000 m elevation (Fenn *et al.*, 2003a). The Chamise Creek catchment, a small, chaparral catchment in the southern Sierra Nevada, receives annual N deposition ranging from 10 to 15 kg ha^{-1} yr^{-1}, with the majority of the loading occurring as dry deposition (Takemoto *et al.*, 2001; Fenn *et al.*, 2003a). Annual volume-weighted mean nitrate concentrations range from 24 to 180 μEq L^{-1} in Chamise Creek with levels as high as 500–600 μEq L^{-1} measured during first-flush, autumn storms. Clarity of Lake Tahoe has also been degraded from auto and industrial emissions and winter biomass burning (Cahill *et al.*, 1996). Nevertheless, low nitrate concentrations in most high-elevation Sierran lakes, and the limited deposition data from high-elevation sites, suggest low N deposition (Sickman *et al.*, 2001).

5. Conclusions

Lake ANC can be estimated from information on catchment characteristics. The general linear models developed for estimating ANC for Sierra Nevada Wilderness lakes identified catcchment lithology, catchment:lake area ratio, vegetation cover, headwater location, and lake perimeter:area ratio as significant predictor variables. Although the models do not explain all variation in lake ANC, they are the basis for a screening procedure that allows cost-effective identification of lakes with low ANC. For Wilderness Areas with hundreds of lakes, finding one or a few lakes with low ANC for long-term monitoring is not straightforward, and could require an extremely expensive lake chemistry survey. The GIS-based screening procedure offers an alternative decision-making tool for selecting Wilderness lakes in the Sierra Nevada for long-term monitoring of sensitivity to acidification. We believe this tool is quicker, less expensive, more standardized and more repeatable than approaches based primarily on professional judgment. Expanded monitoring of atmospheric deposition at high elevation sites is the single most important gap in improving the predictability of lake ANC in the Sierra Nevada.

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