Use of regression-based models to map sensitivity of aquatic resources to atmospheric deposition in Yosemite National Park, USA

David W. Clow,[1] Leora Nanus,[2] and Brian Huggett[3]

Received 21 June 2009; revised 26 April 2010; accepted 30 April 2010; published 24 September 2010.

[1] An abundance of exposed bedrock, sparse soil and vegetation, and fast hydrologic flushing rates make aquatic ecosystems in Yosemite National Park susceptible to nutrient enrichment and episodic acidification due to atmospheric deposition of nitrogen (N) and sulfur (S). In this study, multiple linear regression (MLR) models were created to estimate fall-season nitrate and acid neutralizing capacity (ANC) in surface water in Yosemite wilderness. Input data included estimated winter N deposition, fall-season surface-water chemistry measurements at 52 sites, and basin characteristics derived from geographic information system layers of topography, geology, and vegetation. The MLR models accounted for 84% and 70% of the variance in surface-water nitrate and ANC, respectively. Explanatory variables (and the sign of their coefficients) for nitrate included elevation (positive) and the abundance of neoglacial and talus deposits (positive), unvegetated terrain (positive), alluvium (negative), and riparian (negative) areas in the basins. Explanatory variables for ANC included basin area (positive) and the abundance of metamorphic rocks (positive), unvegetated terrain (negative), water (negative), and winter N deposition (negative) in the basins. The MLR equations were applied to 1407 stream reaches delineated in the National Hydrography Data Set for Yosemite, and maps of predicted surface-water nitrate and ANC concentrations were created. Predicted surface-water nitrate concentrations were highest in small, high-elevation cirques, and concentrations declined downstream. Predicted ANC concentrations showed the opposite pattern, except in high-elevation areas underlain by metamorphic rocks along the Sierran Crest, which had relatively high predicted ANC (>200 μeq L^{-1}). Maps were created to show where basin characteristics predispose aquatic resources to nutrient enrichment and acidification effects from N and S deposition. The maps can be used to help guide development of water-quality programs designed to monitor and protect natural resources in national parks.

Citation: Clow, D. W., L. Nanus, and B. Huggett (2010), Use of regression-based models to map sensitivity of aquatic resources to atmospheric deposition in Yosemite National Park, USA, *Water Resour. Res.*, *46*, W09529, doi:10.1029/2009WR008316.

1. Introduction

[2] Many high-elevation, glaciated basins in the western United States (U.S.) have basin characteristics that may make them susceptible to nutrient enrichment or episodic acidification from atmospheric deposition of nitrogen (N) and sulfur (S) [*Melack and Stoddard*, 1991]. This "sensitivity" to atmospheric deposition of N and S is due to a combination of factors. Deep seasonal snowpacks melt quickly during the spring, with much of the meltwater running off over exposed bedrock or through highly porous talus fields [*Kattlemann and Elder*, 1991]. The spring snowmelt releases acidity (HNO_3 and H_2SO_4) and nutrients (NO_3 and NH_4) in a pulse that has little opportunity for interaction with soils and vegetation, where most acid-neutralizing and nutrient uptake processes occur [*Berg*, 1992]. In alpine areas, vegetation is sparse and soils are thin, rocky, and have limited water storage capacity [*Clow et al.*, 2003a]. Granitic bedrock, which is common in the western U.S., weathers slowly and provides little acid neutralizing capacity to streams and lakes [*Bricker and Rice*, 1989]. Alpine ecosystems may be particularly sensitive to atmospheric deposition of N and S because the sparseness of vegetation and soil at high elevations limits the ability of alpine ecosystems to assimilate nutrients or neutralize acids that are deposited in rain, snow, and dry deposition. High rates of atmospheric deposition at high elevation may compound the risk of nutrient enrichment or acidification for alpine ecosystems.

[1]U.S. Geological Survey, Denver, Colorado, USA.
[2]Department of Geosciences, San Francisco State University, San Francisco, California, USA.
[3]Department of Forestry and Wildland Resources, Humboldt State University, Arcata, California, USA.

Published in 2010 by the American Geophysical Union.

[3] Conceptual models suggest that the sensitivity of aquatic ecosystems to deposition of N and S depends on basin physical characteristics [*Clow and Sueker*, 2000; *Sickman and Melack*, 2002; *Berg et al.*, 2005]. Bedrock type and the amount of vegetation and soil development in a basin influence rates of biogeochemical reactions that govern N assimilation and acid neutralization [*Bricker and Rice*, 1989; *Sickman and Melack*, 2002]. Average basin slope and elevation, and the depth, permeability, and distribution of soils influence hydrologic characteristics, and thus, help determine the degree of interaction between atmospheric deposition and soil and vegetation. Thus, basin characteristics often are surrogates for processes that vary spatially in importance. High-resolution digital maps of topography (elevation), geology, and vegetation are increasingly available, especially for national parks, and geographic information system (GIS) tools are becoming more powerful and easier to use. This makes statistical analyses of relations between basin characteristics and surface-water chemistry feasible for more places than ever before.

[4] Many studies have used GIS tools to relate basin characteristics to the sensitivity of aquatic resources to acidic deposition [e.g., *Billett et al.*, 1996; *Cooper et al.*, 2000; *Ito et al.*, 2005b; *Deviney et al.*, 2006; *Evans et al.*, 2006; *Sullivan et al.*, 2007; *Nanus et al.*, 2009], but relatively few have examined how basin characteristics influence N-assimilation capacity. One measure of the sensitivity of basins to acidic deposition is the acid neutralizing capacity (ANC) of surface water in the basin. In an analysis of factors influencing stream chemistry in northeast Scotland, *Billett et al.* [1996] documented marked changes in ANC as water flowed over different bedrock lithologies. *Cooper et al.* [2000] used a geostatistical approach to evaluate mixing of solutes from various landscapes in Wales; fluxes from each landscape were summed to produce a mean annual ANC estimate for all streams within a basin. Landscape types were defined as areas with relatively homogenous elevation, soils, land use, and surface-water chemistry. *Evans et al.* [2006] developed the landscape-based mixing approach further by linking it to MAGIC, a process-based model that simulates soil-water and surface-water chemistry at annual time scale in response to changing S and N deposition. This allowed them to predict future ANC for streams throughout their study area on the basis of landscape type and sulfur emission scenarios. *Sullivan et al.* [2004] used a similar approach for the southern Appalachian Mountains of the eastern U.S.

[5] In the western U.S., multiple linear regression (MLR) models have been used to relate ANC to topography, bedrock and surface geology, and vegetation [*Melack et al.*, 1985; *Clow and Sueker*, 2000; *Berg et al.*, 2005]. *Nanus et al.* [2009] used logistic regression to estimate the probability of lakes having ANC less than 100 μeq L^{-1} in the Rocky Mountains based on elevation, aspect, and bedrock geology. In general, these studies documented that ANC often strongly correlates with elevation (negative) [*Turk and Spahr*, 1991; *Drever and Zorbrist*, 1992; *Nanus et al.*, 2009], presence of calcareous bedrock (positive) [*Melack et al.*, 1985; *Bricker and Rice*, 1989], abundance of glacial till (positive) [*Driscoll et al.*, 1987; *Peters and Driscoll*, 1987], and amount of unvegetated terrain (negative) [*Clow and Sueker*, 2000; *Berg et al.*, 2005].

[6] Although most of these studies focused on ANC, a few studies have evaluated relations between basin characteristics and surface-water nitrate concentrations. Surface-water nitrate concentration can be a useful indicator of sensitivity to nutrient enrichment effects of N deposition because nitrate leaching is one of the first easily observable symptoms of N saturation of ecosystems [*Fenn et al.*, 1998]. In a study of nine basins in the Rocky Mountains, annual volume-weighted mean streamwater nitrate was positively correlated with basin slope (r^2 = 0.85), and amount of talus (r^2 = 0.90) and unvegetated terrain (r^2 = 0.96) within the basins [*Clow and Sueker*, 2000]. A study in the southern Sierra Nevada and southern Rocky Mountains determined that N yield was positively correlated with surface roughness and negatively correlated with percent soil cover in the basins [*Sickman and Melack*, 2002]. In the Adirondack region of New York, nitrogen export was strongly related to elevation [*Ito et al.*, 2005a]. The relations observed in these studies support the hypothesis that high-elevation areas with steep slopes, talus, and exposed bedrock are highly sensitive to N deposition.

[7] To better understand the spatial extent and location of sensitive resources, maps showing the distribution of basin characteristics that predispose aquatic ecosystems to nutrient enrichment effects of N and acidification effects of N and S deposition are needed. This information will be useful to federal land managers who are required by the Clean Air Act to protect air-quality related values (AQRVs) in Class I wilderness areas, including many national parks in the western U.S. [*Berg et al.*, 2005]. To protect sensitive resources from degradation caused by excess N and S deposition, federal agencies in the U.S. have adopted the critical loads approach, which involves identifying the amount of deposition of a given pollutant that an ecosystem can receive below which ecological effects are thought not to occur [*Porter et al.*, 2005]. The threshold value at which ecological effects occur is likely to vary spatially because of variations in basin characteristics; thus, the critical loads approach would benefit from improved understanding of how basin characteristics influence sensitivity of aquatic ecosystems to N and S deposition.

1.1. Objectives and Scope

[8] The objectives of this study were to (1) identify the dominant sources of solutes in surface water in Yosemite National Park (Yosemite), (2) identify basin characteristics that predispose aquatic ecosystems to nutrient enrichment effects of N and acidification effects of N and S deposition, (3) create maps depicting the spatial distribution of sensitive aquatic resources with respect to atmospheric deposition of N and S in the park, and (4) develop regression-based models to predict surface-water nitrate and ANC, using basin characteristics as explanatory variables. Although the geographic scope of this study is limited to Yosemite, the methods developed for mapping sensitivity to N and S deposition and for creating predictive models of surface-water chemistry should have broad applicability in other undeveloped, mountainous areas worldwide.

1.2. Site Description

[9] Yosemite is located in the central Sierra Nevada of California, and 95% of the park is managed as wilderness, where point sources of pollution and water diversions are minimal (Figure 1a). The park is 3080 km^2 in area, and

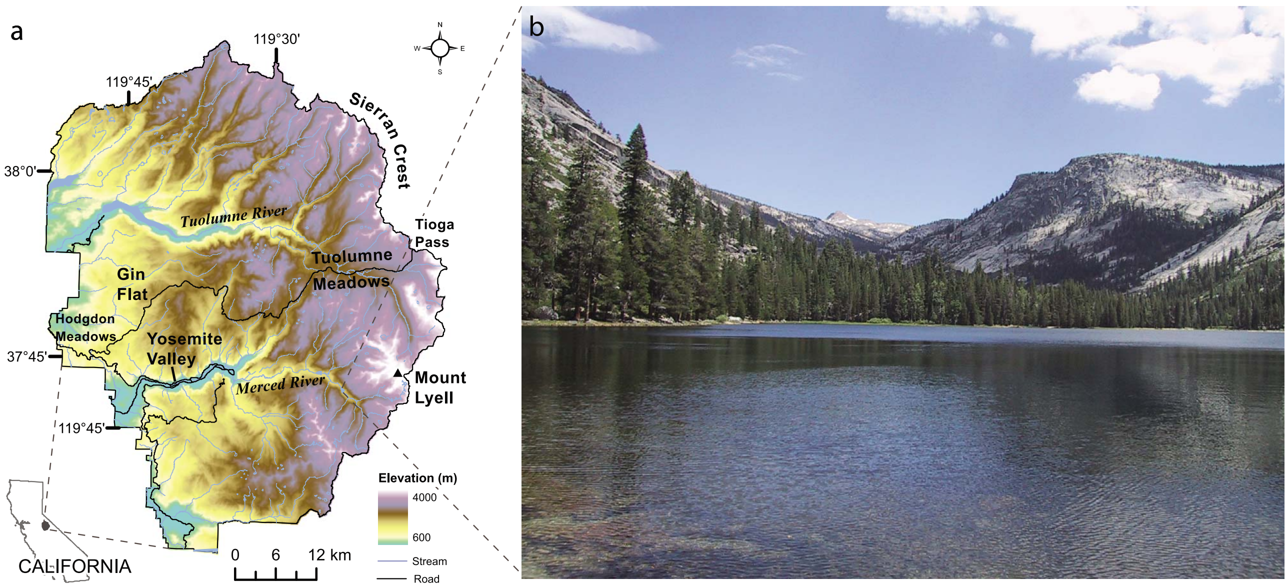

Figure 1. (a) Location map showing Yosemite National Park, and (b) photograph of Washburn Lake looking southeast from outlet.

ranges in elevation from 610 m on the western boundary to 3997 m on the eastern boundary, which follows the Sierran Crest. Numerous high-elevation lakes occur in glacial cirques in the eastern part of the park; these are drained by small, high-gradient streams that coalesce and flow to the west in deep, glacially formed river canyons of the Tuolumne and Merced Rivers. High elevations have large expanses of exposed bedrock and talus with sparse lichen, grasses, and shrubs, middle elevations have extensive conifer forests, and low elevations are dominated by foothill woodland vegetation (Figure 1b). Lakes in Yosemite are among the most dilute in the western U.S., reflecting the abundance of exposed granitic bedrock and the paucity of soil and vegetation at high elevations in the park [*Melack and Stoddard*, 1991; *Clow et al.*, 2002b]. The park is downwind (east) of substantial sources of nitrogen emissions, including agriculture, natural gas fired power plants, vehicles, and industry in the Central Valley and the San Francisco Bay Area [*Fenn et al.*, 2003]. Usually, 80%–90% of annual precipitation falls as snow, which accumulates in seasonal snowpacks from October through April, and melts in a large pulse during May and June.

2. Methods

[10] Development of the maps and models created in this study required several steps, including: (1) characterization of spatial patterns in winter deposition of N and S and in surface-water chemistry in the park, (2) examination of interrelations among surface-water solutes to identify possible solute sources, (3) analysis of relations between surface-water chemistry (nitrate and ANC) and basin characteristics, (4) development of multiple linear regression (MLR) models to estimate surface-water nitrate and ANC concentrations using basin characteristics (topography, geology, and vegetation) and winter N and S deposition as explanatory variables, and (5) application of the MLR models to unsampled basins in the park to show spatial variations in predicted surface-water nitrate and ANC.

2.1. Atmospheric Deposition of Nitrogen and Sulfur

[11] Atmospheric deposition of N and S can be an important influence on surface-water concentrations of nitrate and ANC [*Stoddard*, 1994; *Fenn et al.*, 1998; *Sickman and Melack*, 2002]. Thus, estimates of N and S deposition were developed, and were used as input to the MLR models that simulated fall-season nitrate and ANC in surface waters. Atmospheric deposition of N and S has been well characterized at one site in the park, Hodgdon Meadows (elevation 1393 m), where the National Park Service (NPS) has operated a National Atmospheric Deposition Program (NADP) site since 1981. Although these data are useful for characterizing N and S deposition in the montane forest zone in Yosemite, little or no data on N and S deposition are available for higher-elevation areas of Yosemite, which comprise most of the park; this information is essential for characterizing water-quality responses to N and S deposition. Conducting year-round atmospheric deposition measurements in high-elevation wilderness areas is logistically challenging because of the remoteness of sites. In the Rocky Mountains, winter deposition and annual deposition of N and S are strongly correlated [*Clow et al.*, 2002a; *Nanus et al.*, 2003]. This indicates that in areas not subject to midwinter melting of snow (typically above 2500 m in Yosemite), winter deposition of N and S can be used as an index of annual deposition.

[12] In the present study, winter deposition of N and S was estimated using a combination of snowpack chemistry, NADP, and snow course data. The snowpack chemistry and NADP data were used to characterize N and S concentrations in winter precipitation, and the snow course data were used to characterize winter precipitation amounts (snow courses are areas where snowpack water content, or SWE, is routinely measured by state hydrologists). Winter deposition of N and S is the product of concentrations of N and S in precipitation and precipitation amount; thus, each of these parameters must be measured in order to calculate winter N and

S deposition. N and S concentrations in snowpack samples from high-elevation sites and volume-weighted winter concentrations in NADP samples from Hodgdon Meadows were regressed against elevation to derive an equation for predicting N and S concentrations throughout the park. The regression equation was applied to each grid cell in a 30 m resolution DEM for the park to obtain gridded winter N and S concentration estimates. Combining the snowpack and NADP data was deemed reasonable based on work in the Rocky Mountains, which demonstrated that for N and S, snowpack and NADP chemistry data are comparable [*Clow et al.*, 2002a; *Nanus et al.*, 2003].

[13] Snowpack samples were collected just prior to the beginning of snowmelt at nine locations in the upper Tuolumne and upper Merced River basins, at elevations ranging from 2530 to 3536 m. The procedure involved digging snow pits from the snow surface to the ground and collecting integrated snow samples of the entire snowpack for chemical analyses, as described by *Ingersoll et al.* [2002]. Snow samples were placed in clean Teflon bags and kept frozen until just prior to analyses.

[14] Gridded estimates of winter precipitation amount were developed using long-term average (1951–2000) April 1 snow-water equivalent (SWE) data, which are available for 29 snow courses in Yosemite from the California Department of Water Resources (http://cdec.water.ca.gov/cgi-progs/snow/COURSES). The snow courses range in elevation from 1981 to 2987 m. April 1 SWE also was measured at one higher elevation site (3353 m) as part of the present study to extend the range of available data to higher elevations. SWE was regressed against elevation to develop a predictive equation, which was applied to grid cells in the 30 m DEM to develop preliminary gridded estimates of SWE across the park. Residuals from the preliminary SWE model were kriged to create a grid showing where SWE tended to be over- or under-predicted; kriging is a geostatistical interpolation method that uses weighted averages of data to predict values between data points [*Webster and Oliver*, 2001]. The residuals grid was added to the preliminary SWE grid to obtain the final gridded SWE estimates.

[15] As an independent check on the adjusted SWE estimates, moderate resolution imaging spectroradiometer (MODIS) snow-covered area (SCA) images for the winter of 2002–2003 were obtained from the National Snow and Ice Data Center (http://www-nsidc.colorado.edu/data/nisdc-0321.html), and a snow-duration map was created by summing the SCA grids for the winter period. The remotely sensed MODIS images represent 8 d maximum SCA with a resolution of 0.5 km^2 [*Hall et al.*, 2002].

[16] Final gridded estimates of winter N and S deposition were calculated by multiplying the gridded estimates of N and S concentrations in winter precipitation by the gridded SWE estimates described above.

2.2. Surface-Water Sampling

[17] Surface-water samples were collected at 52 wilderness sites under base-flow conditions during September 2003 (“base-flow” refers to periods of low streamflow and dry antecedent conditions). Sites included streams ($n = 21$) and the outlets of small lakes ($n = 31$; typically <10 ha). In Yosemite, these features usually have similar chemistry because the surface-water systems typically consist of chains of small lakes connected by high-gradient streams [*Clow et al.*, 2002b; *Clow et al.*, 2003b]. Sites were selected to provide good geographic distribution across the park, with emphasis on sites at high elevations, which were expected to be relatively sensitive to atmospheric deposition of N and S. Although random site selection sometimes is preferred because it allows extrapolation from a sample of sites to a population of sites, doing so in this study would have greatly reduced the number of lakes and streams that could have been sampled with available resources because of the difficulty of access in remote wilderness areas. Water samples were collected during fall base-flow conditions to minimize the effect of temporal variability in hydrologic conditions, such as snowmelt and summer storms, on surface-water chemistry. These conditions and time of year are useful because nitrate concentrations typically are near their annual minima and ANC concentrations are near their annual maxima, thus representing biogeochemically relevant indices. Fall is the end of the growing season, so the minima in surface-water nitrate concentrations reflects the capacity of biota in a basin to assimilate nitrogen. ANC concentrations tend to be near their annual maxima because the ratio of groundwater inputs to precipitation inputs typically is greatest during fall.

[18] Water samples were collected along well-mixed reaches using standard grab-sampling methods [*Wilde et al.*, 1998]. Samples were filtered through 0.45 μm polysulfone-ester cartridge filters within 1 h of collection, and were kept cool and in the dark while being transported from the field.

2.3. Analytical Methods and Quality Assurance

[19] All sampling equipment was cleaned, rinsed, and soaked using 18 megaohm deionized water prior to use. Snowpack and surface-water samples were analyzed using methods developed for low-ionic-strength waters in an approved U.S. Geological Survey (USGS) laboratory [*Fishman et al.*, 1994]. Analytes and methods included ANC by Gran titration; calcium (Ca), magnesium (Mg), silica (SiO_2), sodium (Na), and potassium (K) by inductively coupled plasma-atomic emission spectroscopy (ICP-AES); ammonium (NH_4), chloride (Cl), sulfate (SO_4), and nitrate (NO_3) by ion chromatography; dissolved organic carbon (DOC) by ultraviolet promoted persulfate oxidation with infrared detection, pH using a low-ionic-strength electrode, and specific conductance by Wheatstone bridge [*Fishman et al.*, 1994]. Blanks and replicates comprised at least 5% of the total number of samples. Solute concentrations in the blanks were less than the detection limit for all constituents (≤ 1 μmol L^{-1}), and median differences between replicates were ≤ 2 μmol L^{-1}.

2.4. Quantification of Basin Characteristics

[20] Basin characteristics were quantified in ArcGIS using a 10 m resolution digital elevation model (DEM), geologic and vegetation layers obtained from the NPS (http://www.nps.gov/gis/data_info/park_gisdata/ca.htm), and a hydrologic layer obtained from the USGS (http://nhd.usgs.gov/). The geology layer was a digitized version of the 1:125,000 scale compilation geologic map by *Huber et al.* [1989]. The vegetation layer was developed by the NPS using photo interpretation of 1:24,000 scale orthophotos with ground-based validation. The hydrology layer was the 1:24,000 scale

Table 1. Basin Characteristics and Spearman Correlations, Grouped by Data Layers[a]

	ANC		NO_3	
	Correlation	*p*-value	Correlation	*p*-value
	Topography			
Basin area (km^2)	*0.71*	*0.0000*	0.08	0.5555
Min Elevation (m)	*−0.63*	*0.0000*	0.11	0.4369
Average Elevation (m)	−0.37	0.0063	*0.48*	*0.0003*
Max Elevation (m)	0.39	0.0039	*0.65*	*0.0000*
Average Slope (%)	−0.14	0.3380	*0.43*	*0.0014*
Slope > 30° (%)	−0.13	0.3662	*0.47*	*0.0005*
	Geology			
Alluvium (%)	*0.59*	*0.0000*	−0.15	0.2794
Pleistocene glacial till (%)	*0.53*	*0.0001*	−0.18	0.1981
Neoglacial and talus (%)	0.23	0.0965	*0.58*	*0.0000*
Granite (%)	0.15	0.2944	−0.29	0.0338
Granodiorite (%)	−0.04	0.7544	0.20	0.1471
Diorite (%)	0.25	0.0732	−0.19	0.1727
Mafic Intrusive (%)	0.12	0.3997	−0.11	0.4237
Metamorphic (%)	*0.65*	*0.0000*	−0.17	0.2268
	Vegetation			
Mixed Conifer (%)	*0.56*	*0.0000*	*−0.44*	*0.0010*
Deciduous (%)	*0.64*	*0.0000*	0.11	0.4516
Foothill Woodland (%)	*0.51*	*0.0001*	−0.32	0.0214
Juniper/Cedar (%)	*0.50*	*0.0001*	−0.08	0.5817
Unvegetated (%)	*−0.51*	*0.0001*	*0.44*	*0.0010*
Snow (%)	−0.02	0.8759	*0.48*	*0.0003*
Water (%)	*−0.65*	*0.0000*	−0.21	0.1380
Riparian (%)	−0.11	0.4543	−0.25	0.0762
	Snow			
Winter N deposition	*−0.50*	*0.0002*	−0.14	0.3338
MODIS Snow Duration	*−0.44*	*0.0010*	0.19	0.1833

[a]Statistically significant correlations ($p \leq 0.003$) are italicized.

National Hydrography Data set (NHD+), which is a digital representation of surface water in the United States. In Yosemite, the NHD+ includes 1407 stream reaches joined by nodes, which occur at stream junctions or lakes.

[21] A variety of indices of basin area, elevation, and slope were calculated using the DEM and the basin boundaries (Table 1). Mapped units on the geologic map included bedrock and surficial debris units, as well as minor nongeologic features such as snow and open water [*Huber et al.*, 1989]. Units with similar geochemical characteristics were combined to obtain a simplified classification scheme, resulting in eight geology classes (Table 1); intrusive rocks covered the largest area, but metamorphic rocks were locally important. Neoglacial and talus deposits, which are young surficial deposits of Holocene age with minimal soil development, were combined as in previous studies in the Colorado Front Range due to their similar age and hydrogeochemical characteristics [*Clow and Sueker*, 2000; *Williams et al.*, 2006]. Neoglacial deposits include rock glaciers and cirque moraines. Talus is coarse-grained rock waste material deposited at the base of cliffs [*Huber et al.*, 1989]. Vegetation units were grouped into eight classes on the basis of major vegetation or land cover types (Table 1); the most important classes by area were unvegetated, mixed conifer, juniper and cedar, and foothill woodland.

[22] Characteristics were quantified for the 52 basins above the sites sampled in this study, as well as for the 1407 basins delineated in the NHD+. For nested basins in the NHD+, basin characteristics were calculated for the entire basin area above each node.

2.5. Statistical Tests and Creation of Sensitivity Maps

2.5.1. Principal Components Analysis

[23] To identify the dominant sources of solutes in surface water, a principal components analysis (PCA) was performed on surface-water concentrations in the samples collected during September 2003. PCA is a nonparametric statistical technique that tests for interrelations between variables (e.g., solutes) in complex data sets [*Lins*, 1986]. It is useful for reducing a large number of intercorrelated variables to a smaller number of "components." In a PCA on natural waters, the components may be interpreted as representing solute sources [*Drever*, 1997]. The first component explains the most variance in a data set, while the second explains the next most variance, and so on. Individual solutes "load" on components, and the magnitude of those loadings reflect the strength of association between solutes and components [*Puckett and Bricker*, 1992].

2.5.2. Correlation Analysis

[24] Associations between basin characteristics and surface-water concentrations of nitrate and ANC were analyzed using the nonparametric Spearman's rho test, which is suitable for water quality data because it is resistant to the influence of outliers and skewness in data [*Helsel and Hirsch*, 1992]. All tests for significance were evaluated at $p \leq 0.003$ unless otherwise stated.

2.5.3. Development of Maps Showing Distribution of Sensitive Resources

[25] To illustrate the distribution of sensitive resources with respect to atmospheric deposition of N and S in the park, grid-based maps were created at 30 m resolution based on interpretation of results from the correlation analyses. These "sensitivity maps" depict the distribution of basin characteristics that correlated strongly (either positively or negatively) with surface-water nitrate or ANC concentrations. In contrast with the MLR analyses, which provide quantitative predictions of nitrate and ANC concentrations in surface water, the maps depicting sensitivity of aquatic resources to N and S deposition are qualitative. They are useful, however, as an aid to visualizing where sensitive resources are likely to occur. Two aquatic sensitivity maps were created, one pertaining to nutrient enrichment effects of N deposition and the other for acidification effects of N and S deposition.

2.5.4. Multiple Regression Modeling

[26] To create predictive models of surface-water nitrate and ANC, concentrations of these variables were regressed against basin characteristics for the 52 sampled basins using stepwise MLR, with a threshold for acceptance into the model set at $p \leq 0.1$. The basin characteristic that explained the most variance in the chemical variable entered the model first. The variances explained by the remaining explanatory variables were recalculated, and the variable that explained the next greatest amount of variance entered the model next. This iterative process was repeated until no additional variables showed statistically significant correlations to the chemical variable at $p \leq 0.1$. Multicollinearity among explanatory variables was evaluated using the variance inflation factor ($1/1-r^2$) [*Hair et al.*, 2005], with a threshold for exclusion of 0.2. The resulting beta coefficients (partial regression coefficients) for the explanatory variables represent independent contributions of each explanatory variable [*Kachigan*, 1986]. Residuals plots were used to identify and screen outliers. Residuals plots and normal probability plots

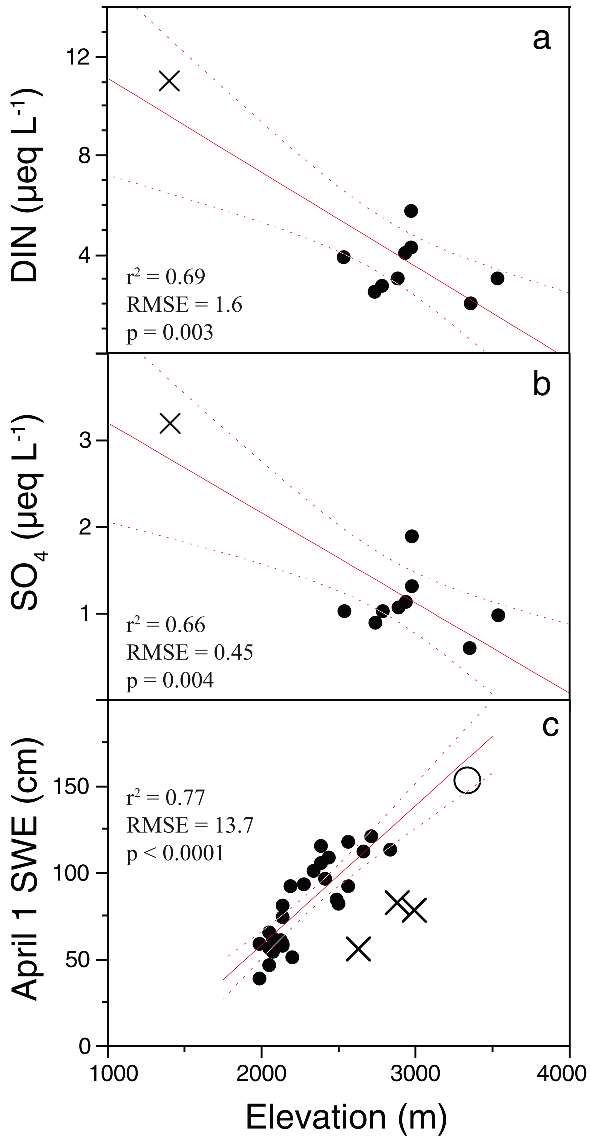

Figure 2. Relations between elevation and (a) DIN (dissolved inorganic nitrogen) in winter precipitation, (b) SO_4 (sulfate) in winter precipitation, and (c) snow water equivalent (SWE). In Figures 2a and 2b, Xs represent Hodgdon Meadow NADP site and dots represent samples from snow pits. In Figure 2c, Xs are Tuolumne Meadows area snow courses, which plot off of the regression line, indicating that SWE at those sites is lower than would be predicted by the regression equation; dots are for other snow courses in Yosemite, and the circle represents SWE in the upper Lyell Fork of the Merced basin. In Figure 2c, the regression line was created using data from all sites except those in the Tuolumne Meadows area. In all plots, the solid line represents the regression equation, and dashed lines represent 95% confidence intervals for the equation.

were used to check for violation of assumptions of normality, linearity, and homoscedasticity [*Kachigan*, 1986]. Separate MLR models were developed using concentrations and log concentrations of nitrate and ANC as the dependent variables, and the best model was chosen on the basis of the percentage of variance explained (r-square), the root mean square error (RMSE), the linearity of the model equation, and the homoscedasticity of model residuals [*Helsel and Hirsch*, 1992].

[27] After developing the MLR models using data from the 52 sampled basins, the resulting MLR equations were applied to 1407 basins delineated in NHD+ for Yosemite to predict fall-season nitrate and ANC concentrations at the downstream nodes of each stream reach in the park.

3. Results and Discussion

3.1. Atmospheric Deposition of Nitrogen and Sulfur

[28] N and S concentrations in winter precipitation showed a strong, inverse relation with elevation (Figures 2a and 2b), and the two solutes were highly correlated (r^2 = 0.96). The inverse relation may reflect greater distance of high elevation sites from emissions sources, increased dilution of N and S at high elevation due to greater precipitation amounts, or a decreasing rain:snow ratio at higher elevations (rain tends to have higher solute concentrations than snow). Further research is needed to ascertain the relative importance of these potential causes.

[29] SWE showed a strong, positive relation with elevation, except for several sites in the Tuolumne Meadows area that plotted well below the regression line (Figure 2c). Kriged residuals from the preliminary SWE model for the Tuolumne Meadows area were negative, indicating that the model overpredicted SWE in that area. Kriged residuals were positive in the Gin Flat area, located 40 km to the west of Tuolumne Meadows (Figure 1), indicating that the preliminary SWE model under-predicted snowfall in that area. Gin Flat is on a prominent ridge on the west side of the park, where snowfall tends to be relatively heavy compared to similar elevations elsewhere in the park. The prevailing wind direction during winter storms is from west to east, and the snowfall pattern at Gin Flat and Tuolumne Meadows is consistent with preferential deposition of precipitation on the windward (west) side of the mountain range and a precipitation shadow to the east. Adjustments to the preliminary SWE values on the basis of the kriged residuals ranged from −9% to +13%. The adjusted SWE map shows that estimated SWE had a wide range, with low values in the valleys of the major basins and high values along the Sierran Crest, particularly near Mount Lyell (Figure 3a). Spatial patterns in adjusted SWE estimates generally were consistent with those of snow-cover duration derived from the MODIS SCA data (Figure 3b), and the two variables were positively correlated (r = 0.43; p = 0.002).

[30] Estimated winter N deposition in snow ranged from 0.19 to 1.22 kg ha^{-1} (Figure 4). Estimated winter S deposition ranged from 0.08 to 0.52 kg ha^{-1} (not shown for brevity, but spatial patterns were very similar to those of N deposition, as expected due to their high positive correlation). Estimated winter N deposition was greatest in the western part of the park because of high snowfall amounts and relatively high N concentrations. The high-elevation area near Mount Lyell, in the eastern part of the park, also had high estimated winter N deposition (Figure 4), primarily because of the abundant snowfall the area receives. Some areas with low estimated winter N deposition, such as the Tuolumne and Merced River canyons, receive a portion of their winter deposition as rain and may experience high rates of dry

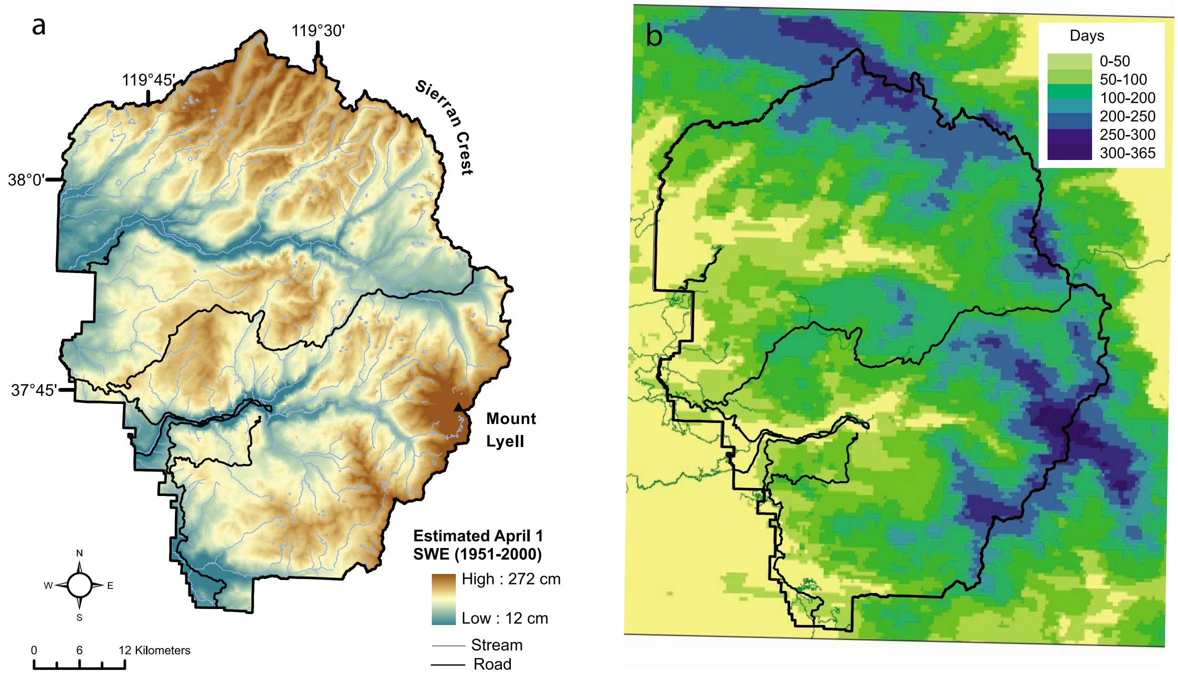

Figure 3. Maps of (a) estimated average April 1 snow water equivalent (SWE) in Yosemite National Park for 1951–2000 (http://cdec.water.ca.gov/cgiprogs/snow/COURSES), and (b) duration of snow cover in Yosemite during winter 2002–2003 from MODIS imagery.

deposition of N during summer. Thus, although Figure 4 indicates very large spatial differences in winter N deposition between high and low elevations, spatial differences in total annual N deposition might be smaller than indicated by Figure 4.

3.2. Spatial Patterns in Surface-Water Chemistry

[31] Surface-water nitrate concentrations ranged from ≤1 to 14 μeq L^{-1} and were greatest in small, high-elevation basins in the eastern part of Yosemite (Figure 5a). Surface-water ANC concentrations showed the opposite pattern, with low concentrations at high elevation and increasing concentrations downstream; concentrations ranged from 11 to 370 μeq L^{-1} (Figure 5b). An exception to the general ANC pattern occurred in the vicinity of the Sierran Crest north of Tioga Pass; this area is underlain by metamorphic bedrock that contains carbonate and sulfide minerals, which weather rapidly [*Huber*, 1987; *Huber et al.*, 1989]. The carbonate minerals provide substantial acid neutralizing capacity to surface water due to their rapid weathering rate; ANC in surface waters in this area often exceeded 200 μeq L^{-1} (Figure 5b). Surface water concentrations of calcium (not shown) and sulfate (Figure 5c) also were high along the Sierran Crest, suggesting that weathering of metamorphic rocks affected those solutes as well; calcium is released during weathering of carbonate minerals, and sulfate is released by weathering of sulfide minerals.

3.3. Sources of Solutes in Surface Water

[32] The initial PCA on surface-water chemistry was strongly affected by two small groups of samples with relatively high solute concentrations. One group, near the Sierran

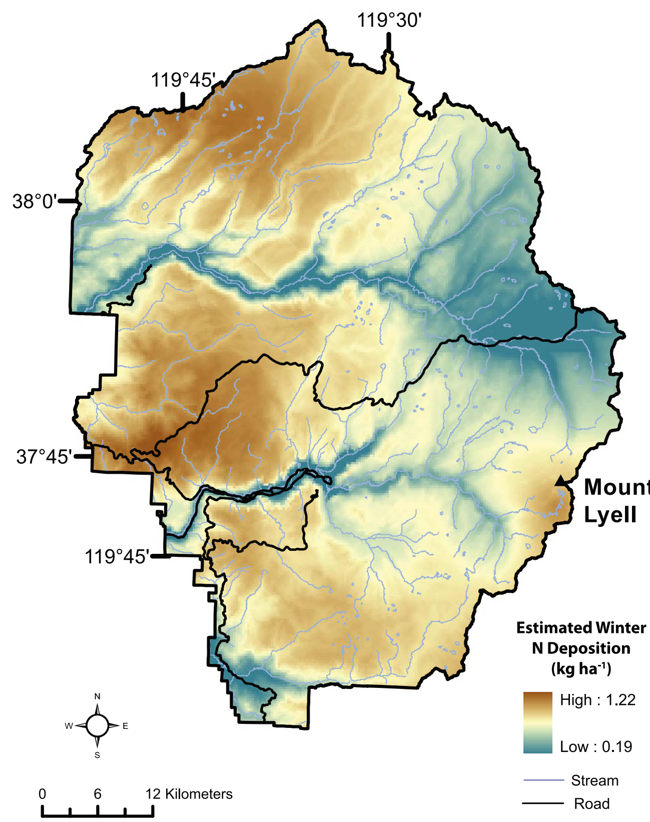

Figure 4. Map showing estimated nitrogen (N) deposition in snow in Yosemite National Park during November 2003–March 2004.

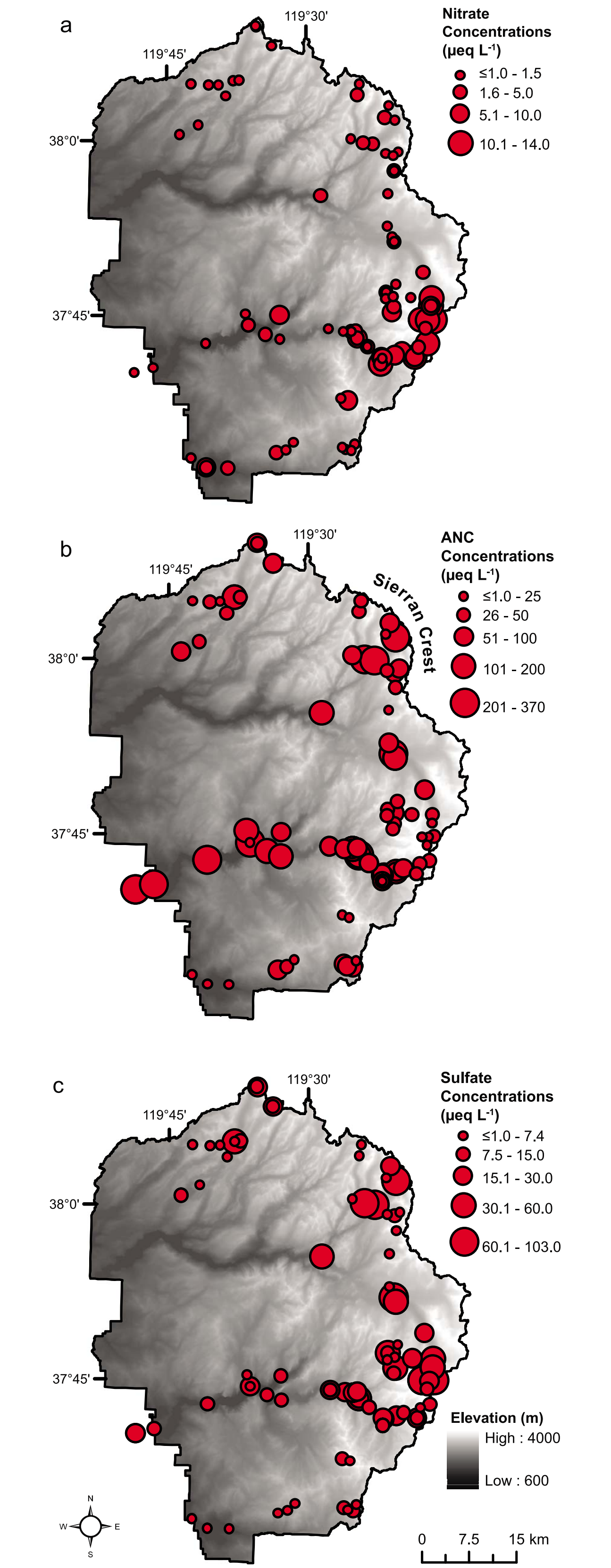

Figure 5. Plots showing surface-water concentrations of (a) nitrate, (b) ANC, and (c) sulfate in Yosemite National Park during September 2003.

Table 2. Results From PCA on Water Samples With Specific Conductance <20 μS cm^{-1} [a]

Solute	Component 1: Granitic Weathering	Component 2: Saline Springs	Component 3: Atmospheric Deposition + Soil Processes	Total
ANC	*0.83*	0.50	−0.08	
pH	*0.83*	0.28	0.00	
Ca	0.49	*0.65*	0.50	
Mg	0.31	*0.83*	0.23	
Na	*0.81*	0.27	−0.30	
K	0.20	0.60	0.05	
Si	*0.87*	−0.08	−0.07	
Cl	−0.02	*0.79*	−0.22	
SO_4	−0.18	0.23	*0.84*	
NO_3	−0.19	0.09	*0.81*	
DOC	−0.05	0.25	*−0.76*	
% Variance Explained	29	24	22	75

[a] Loadings ≥0.65 or ≤−0.65 are italicized.

Crest, had high ANC, calcium, and sulfate concentrations, and the other group, which occurred at middle elevations, had high chloride, magnesium, sodium, and potassium concentrations. These two groups reflect localized influences of metamorphic rock weathering and saline spring water, respectively, which have been previously noted by *Feth et al.* [1964] and *Clow et al.* [1996]. Although of interest geochemically, these solute sources can have such a dominating influence on surface-water chemistry that they obscure other biogeochemical sources and processes in the PCA. To investigate other potential sources of solutes, the PCA was rerun on surface-water samples with specific conductivity <20 μS cm^{-1} (n = 40) to reduce the effect of metamorphic rock weathering and saline springs on the PCA results.

[33] In the PCA on samples with specific conductivity <20 μS cm^{-1}, three primary components were identified (Table 2). ANC, pH, silica, and sodium had high positive loadings on the first component, which accounted for 29% of the variation in the data set; this component is indicative of the influence of weathering of granitic bedrock. Chloride, magnesium, and calcium had high positive loadings on component 2, which accounted for 24% of the variance in the data set; this component is interpreted to reflect inputs from saline springs, which we were only partly able to control for (Table 2). The third component had high positive loadings for nitrate and sulfate and a high negative loading for DOC, and accounted for 22% of variation in the data. The opposite sign for nitrate and sulfate compared to DOC indicates that nitrate and sulfate varied inversely with DOC. This component reflects the importance of spatially varying soil processes in consuming atmospherically deposited N and S and producing DOC. Processes in organic-rich soil, such as N assimilation and sulfate adsorption, consume atmospheric N and S, while other processes, such as organic matter decomposition, produce DOC [*Charles*, 1991].

[34] The PCA results provide insight into the relative importance of processes controlling surface-water chemistry. This aided the interpretation of correlations between basin characteristics and surface-water chemistry, which are described in section 3.4.

3.4. Relations Between Basin Characteristics and Surface-Water Chemistry

3.4.1. Nitrate

[35] The correlation analysis indicated that nitrate concentrations were positively correlated with average elevation, maximum elevation, basin slope, and the percentage of the basin covered by neoglacial and talus material (percent neoglacial/talus), unvegetated terrain (percent unvegetated terrain), and snow (percent snow) (Table 1). The positive correlation between surface-water nitrate and elevation probably reflects cold temperatures and short growing seasons at high elevations, which limit uptake of atmospherically deposited nitrogen by vegetation and aquatic biota in those areas. Similarly, the positive correlations between nitrate and (1) steep slopes, (2) neoglacial till and talus, and (3) percent unvegetated terrain may be explained by fast hydrologic flow rates and a lack of vegetation and well-developed soil in these areas, which limit nitrogen assimilation. The positive correlation between surface-water nitrate and percent snow reflects the N content of snow and the lack of N assimilation capacity of snow-covered terrain. Nitrate concentrations were negatively correlated with the percentage of mixed conifer forest in the basin due to the substantial N assimilate capacity of these forests (Table 1). These results are consistent with those of *Sickman and Melack* [2002], who documented a negative relation between annual volume weighted mean nitrate concentrations and percent soil cover in basins in the Sierra Nevada.

[36] It is noteworthy that estimated winter N deposition was not significantly correlated with surface-water nitrate concentrations (Table 1). This is consistent with results of *Sickman and Melack* [2002], who found no relation between dissolved inorganic N loading and N yield within regions similar in size to Yosemite in the southern Sierra and southern Rocky Mountains. Relations between DIN and N yield only became apparent at larger scale, when they analyzed the Sierran and Rocky Mountain data together [*Sickman and Melack*, 2002]. Large-scale national assessments of controls on background concentrations of nutrients also have documented strong relations between DIN loading and surface-water nitrate concentrations in relatively undisturbed watersheds of the United States [*Smith et al.*, 2003].

3.4.2. ANC

[37] Surface-water ANC concentrations were positively correlated with basin area and with the percentage of the basin underlain by alluvium (percent alluvium), Pleistocene glacial till (percent till), and metamorphic bedrock (percent metamorphic; Table 1). The positive correlation between ANC and basin area reflects increasing residence time and water-rock interaction as basin size increases. Alluvium and Pleistocene glacial till have a similar effect; areas with alluvium and Pleistocene till tend to have deep soils, allowing extensive interaction between soil minerals and infiltrating water. As previously mentioned, carbonate minerals in the metamorphic rocks in Yosemite contribute substantial ANC due to their rapid weathering rates. ANC also was positively correlated with all of the forest classes, reflecting extensive mineral weathering in forest soils (Table 1). In contrast, ANC was negatively correlated with percent unvegetated terrain and percent water due to minimal mineral weathering in these environments. ANC concentrations were negatively correlated to winter N and S deposition and MODIS snow duration, reflecting the influence of acidic deposition associated with snow. ANC also was negatively correlated with minimum basin elevation (elevation at the sampling site) due to decreasing basin size, water-rock interaction, and temperatures as elevation increased.

3.5. Distribution of Sensitive Resources

[38] Maps showing the distribution of basin characteristics that predispose aquatic ecosystems to nutrient enrichment effects of N and acidification effects of N and S deposition were developed based on interpretation of the correlation analysis results. Surface water nitrate and ANC correlated with many basin characteristics, and it is not possible to show all of the predisposing characteristics on a single paper map; thus, only some of the strongest predictors of surface-water nitrate and ANC are depicted in the sensitivity maps.

[39] Elevation, neoglacial till and talus, and unvegetated terrain, which were positively correlated with surface-water nitrate concentrations, are shown in Figure 6a. These basin characteristics were derived from separate GIS layers (topography, geology, and vegetation, respectively), and thus, overlap can occur. Neoglacial till and talus, for example, typically occur in areas mapped as unvegetated in the vegetation data layer. Talus deposits and unvegetated terrain can occur at any elevation in Yosemite, but are particularly common at high elevations; neoglacial till is confined strictly to high elevations. The amount of talus shown on Figure 6a is an underestimate because only especially extensive areas were indicated on the compilation geologic map of Yosemite due to its coarse scale [*Huber et al.*, 1989]. Most high-elevation basins in Yosemite contain extensive talus deposits. High-elevation areas that are unvegetated, and especially where neoglacial till or talus occur, are expected to be particularly susceptible to nutrient enrichment effects from N deposition (Figure 6a). Low elevation, vegetated areas should be relatively insensitive to nutrient enrichment effects from N deposition.

[40] The map in Figure 6b shows relative sensitivity to acidic deposition, which is the inverse of geologic materials' ability to neutralize acid deposition. The geologic materials listed in Table 1 were grouped into four classes, ranked in order of sensitivity from very high to low: (1) neoglacial and talus, (2) felsic intrusive rocks (granite, granodiorite, diorite), (3) mafic intrusive rocks, and (4) metamorphic rocks, alluvium, and Pleistocene glacial till. This simplified geologic classification scheme was developed on the basis of results from the correlation analysis and on previous studies that related surface-water ANC to bedrock type [*Melack et al.*, 1985; *Clow and Sueker*, 2000; *Sullivan et al.*, 2004; *Nanus et al.*, 2005]. The estimated relative neutralization abilities of the geologic classes are functions of relative chemical weathering rates and hydraulic conductivity of bedrock and soil. High-elevations and unvegetated terrain (Figure 6a) are additional factors that would be expected to make aquatic ecosystems susceptible to acidic deposition. On the basis of the geologic classification scheme, most of Yosemite's surface waters would be considered highly sensitive to acidic deposition (Figure 6b). This is consistent with the relatively low ionic strength of surface water in Yosemite compared to other regions of the western U.S. [*Clow et al.*, 2002b]. Areas of relatively low sensitivity to acidic deposition are scattered throughout the park; most of these areas are asso-

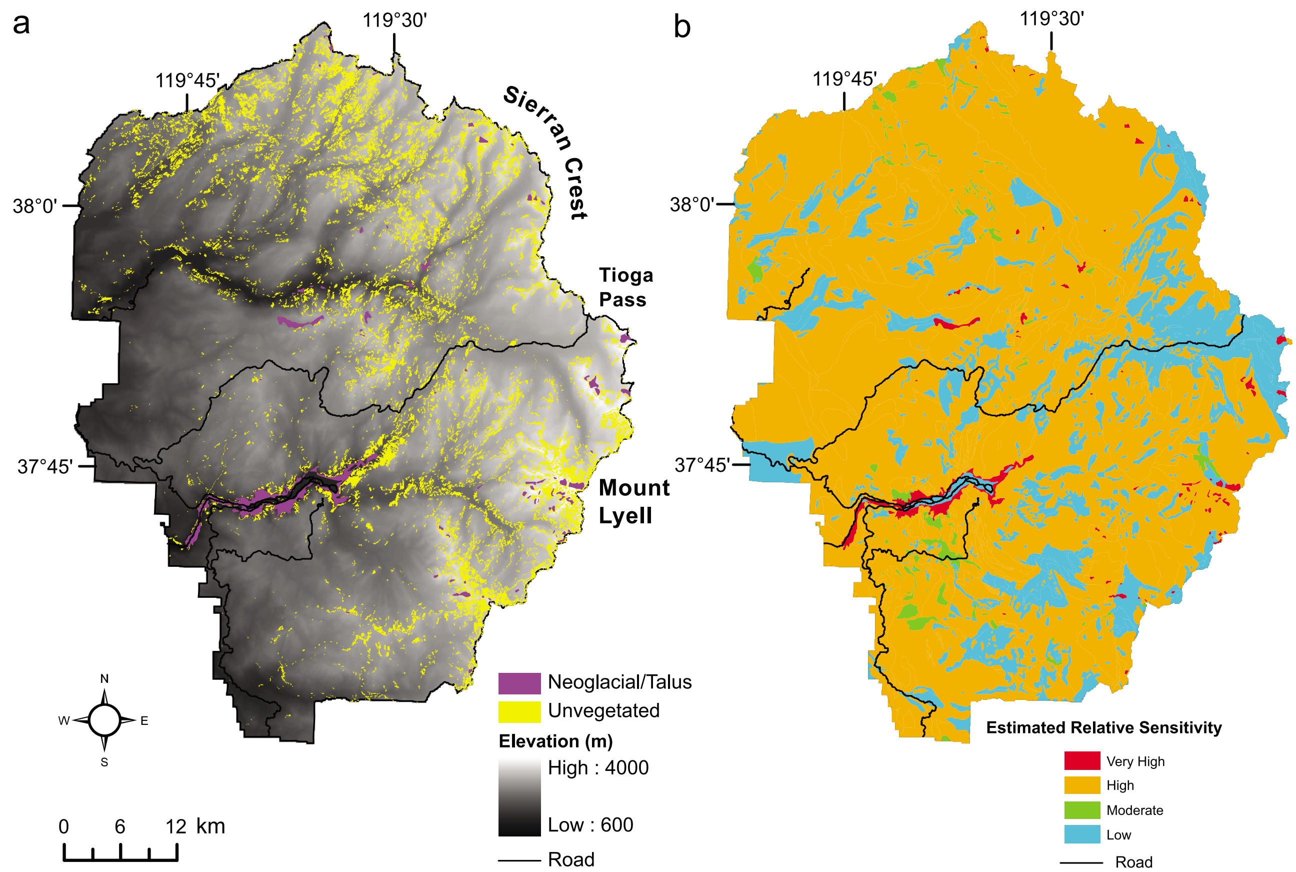

Figure 6. Map of (a) distribution of basin characteristics associated with probable sensitivity to nutrient enrichment effects of nitrogen deposition, and (b) estimated relative sensitivities to acid deposition on the basis of surficial and bedrock geology. Geologic data are from *Huber et al.* [1989].

ciated with alluvium and Pleistocene glacial till, although some areas occur along in the eastern part of the park near the Sierran Crest, where metamorphic rocks crop out (Figure 6b).

3.6. Multiple Regression Modeling

3.6.1. Nitrate

[41] The MLR models for surface-water nitrate concentrations included maximum elevation, percent alluvium, percent neoglacial/talus, percent unvegetated terrain, and percent riparian as explanatory variables (Figures 7a and 7b). The nitrate model performed substantially better than the log nitrate model, on the basis of a higher r^2 (0.84 versus 0.61) and lower RMSE (1.4 versus 2.9 μeq L^{-1}), and because the variance of residuals exhibited less heteroscedasticity. Scaled coefficients, which are beta coefficients centered by the mean and scaled by range/2, show the relative influence of factors in the regression equation; the explanatory variable with the most predictive power was percent neoglacial/talus. Scaled coefficients for maximum elevation, percent neoglacial/talus, and percent unvegetated terrain were positive, indicating a positive association with surface-water nitrate concentrations (Figure 7a). Scaled coefficients for percent alluvium and percent riparian were negative (Figure 7a), indicating that they had an inverse relation with nitrate.

[42] The MLR model for nitrate was applied to the 1407 stream reaches in the NHD+ for Yosemite; it yielded predicted nitrate concentrations ranging from $\leq$1 to 25 μeq L^{-1}, with relatively high values in the eastern part of Yosemite and relatively low values in the west (Figure 8a). This spatial pattern reflects variations in elevation, which tend to be higher in the east than in the western part of the park, as well as the distribution of alluvium, neoglacial and talus deposits, unvegetated terrain, and riparian areas, which are locally important.

[43] Previous research in the central Rocky Mountains suggests that threshold values for surface-water nitrate at which shifts in diatom species abundance occur may be as low as 0.5 μeq L^{-1} based on in situ growth bioassays [*Michel et al.*, 2006]. Results from the present study indicate that 43% of total stream reach length in Yosemite is estimated to have fall-season nitrate concentrations $\geq$0.5 μeq L^{-1}. Additional research is needed to evaluate threshold values at which diatom species shifts might occur in the Sierra Nevada.

3.6.2. ANC

[44] The MLR models for surface-water ANC concentrations included basin area, percent metamorphics, percent unvegetated terrain, percent water, and winter N deposition as explanatory variables (Figures 7c and 7d). The ANC model performed slightly better than the log ANC model; the r^2 value was higher (0.87 versus 0.70), the RMSE was lower (28 versus 40 μeq L^{-1}), and residuals from both models exhibited moderate heteroscedasticity (Figure 7d). Scaled coefficients were positive for basin area and percent metamorphics and were negative for percent unvegetated terrain, percent water, and winter N deposition (Figure 7d).

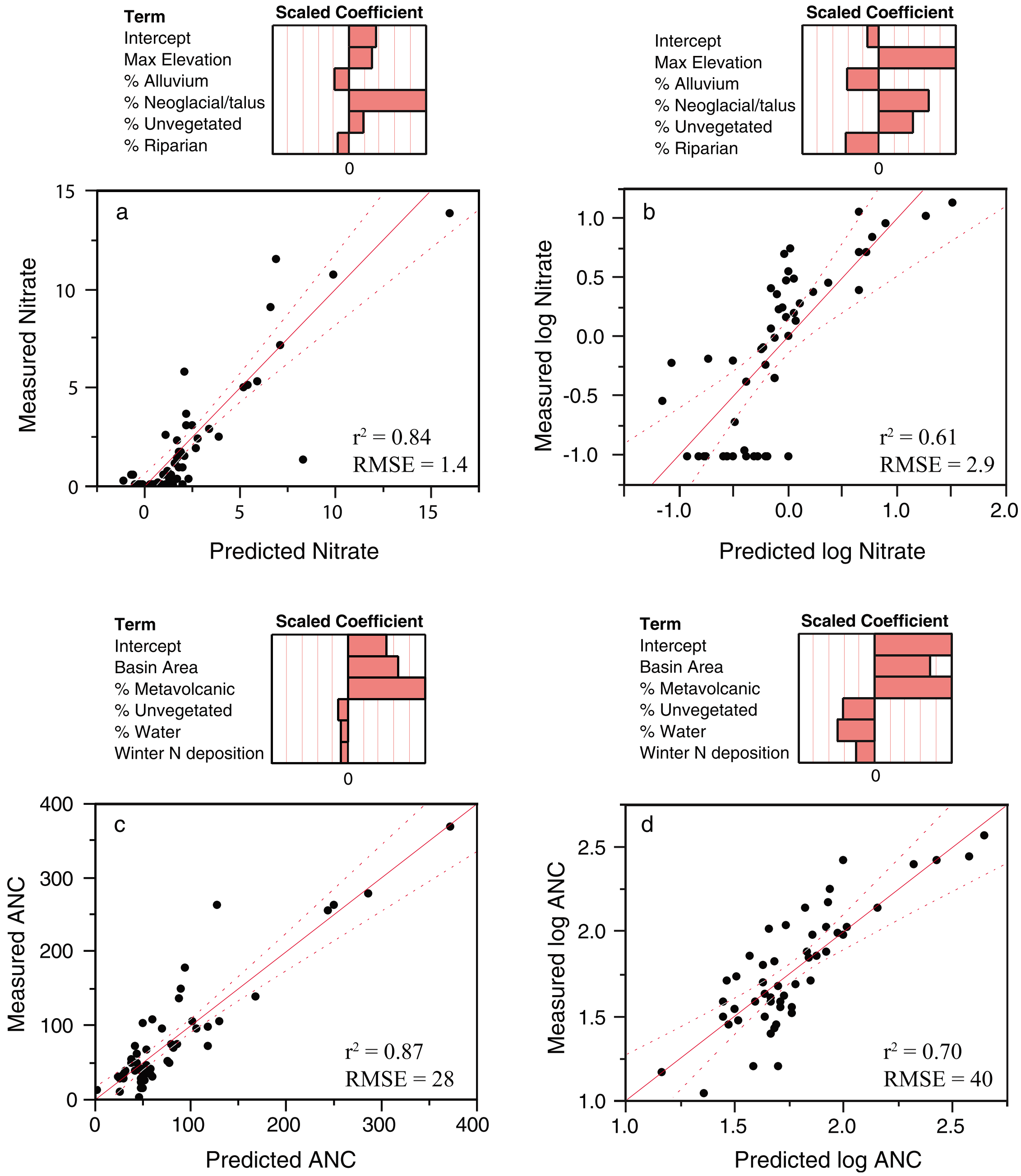

Figure 7. Scatterplot showing predicted versus measured (a) nitrate, (b) log nitrate, (c) ANC, and (d) log ANC for surface-water samples collected during September 2003. Units are μeq L^{-1}. Solid red line represents the regression equation. Dashed lines represent 95% confidence intervals for the regression equations. Scaled coefficients are beta coefficients centered by mean, scaled by range/2, and show the relative influence of factors in the regression equation. RMSE is root mean square error, and is expressed as μeq L^{-1}.

[45] Predicted fall-season surface-water ANC concentrations for the 1407 stream reaches in the NHD+ calculated using the log ANC model ranged from 15 μeq L^{-1} near Mount Lyell in the southeast part of the park, to approximately 800 μeq L^{-1} along areas of the Sierran Crest north of Tioga Pass (Figure 8b). Predicted ANC concentrations tended to increase downstream, reflecting the importance of increasing basin area (and by implication, water-rock interaction) for surface-water ANC. Of the total stream length in the park, 82% had predicted fall-season surface-water ANC concentrations ≤100 μeq L^{-1} (Figure 8b), indicating that most surface water in the park has limited buffering capacity. Many small, high-elevation surface waters had predicted surface-water alkalinities ≤50 μeq L^{-1} (Figure 8b), which has been identified as a threshold for surface water at risk from episodic acidification during snowmelt and storm events [*Sullivan et al.*, 2007]. Areas underlain by metamorphic rocks had relatively high predicted surface-water ANC concentrations, as expected given the

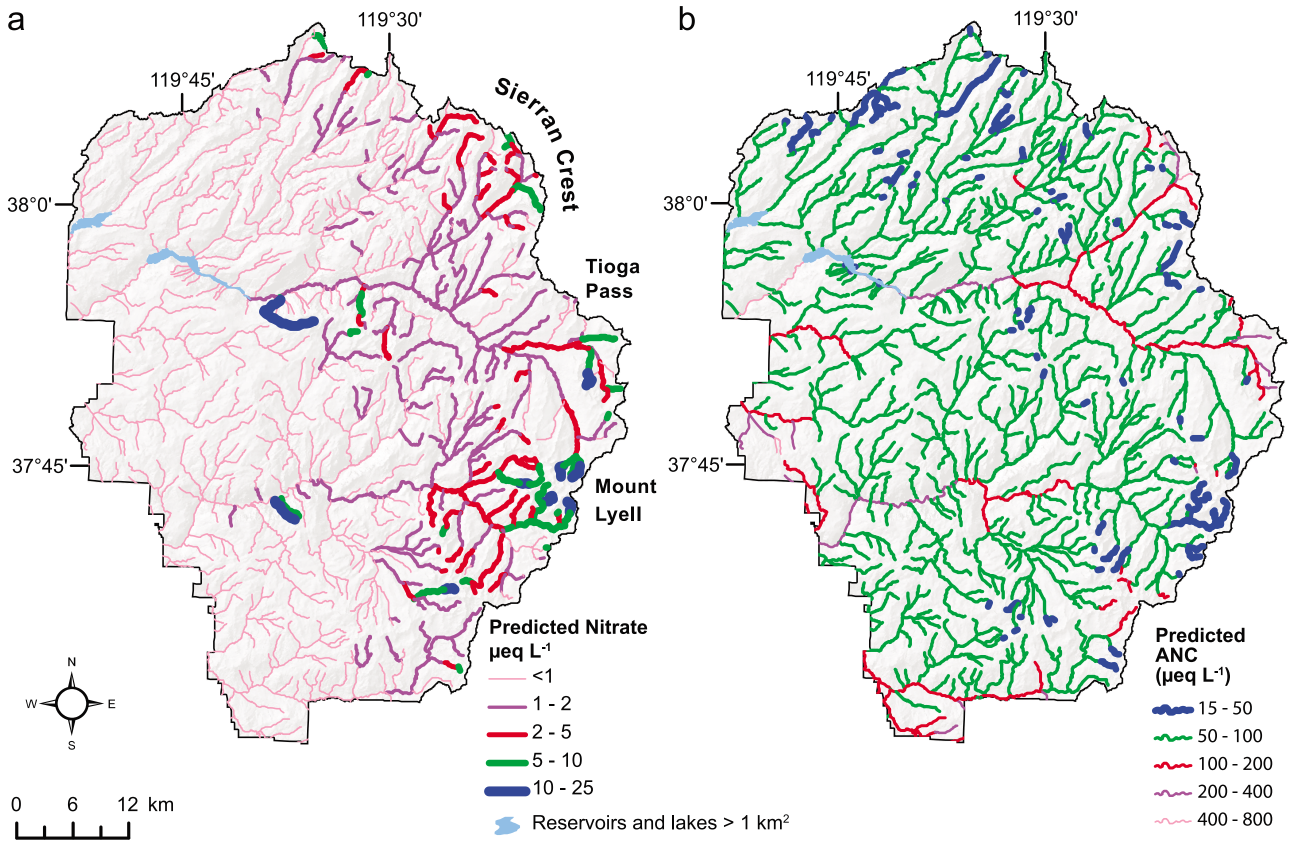

Figure 8. Maps of (a) predicted fall-season surface-water nitrate concentrations, and (b) predicted fall-season surface-water ANC concentrations.

positive correlation between ANC and abundance of metamorphic rocks in the basins (Figure 8b).

3.7. Comparison With Previous Studies in Mountains of the Western United States

[46] Comparison of results from this study to others in the western U.S. allow some generalizations to be made about the sensitivity of high-elevation aquatic ecosystems to atmospheric deposition of N and S. A number of studies, including this one, have documented the importance of bedrock type as one of the strongest controls on surface-water ANC [*Melack et al.*, 1985; *Drever and Hurcomb*, 1986; *Bricker and Rice*, 1989; *Berg et al.*, 2005; *Sullivan et al.*, 2007]. The prevalence of alluvium and Pleistocene glacial till in basins also is an important influence on a basin's acid neutralization and N assimilation capacity [*Sullivan et al.*, 1999; *Clow and Sueker*, 2000; *Ito et al.*, 2005b]. The age and type of glacial and periglacial deposits is important, however, in determining acid buffering and N assimilation capacities in alpine basins. In contrast with Pleistocene till, Holocene neoglacial till and talus deposits have been found in this and other studies to be negatively correlated with ANC and positively correlated with nitrate [*Clow and Sueker*, 2000; *Williams et al.*, 2006]. The difference in geochemical behavior of different ages of glacial deposits is related to greater soil development and more vegetation in areas with older deposits, which promotes N uptake and ANC generation through weathering. Neoglacial and talus deposits have high porosity and little soil development, so hydrologic flushing rates in these areas are fast and N assimilation and weathering reactions are minimal.

[47] Strong correlations between basin slope and surface-water nitrate (positive) and ANC (negative) have been documented in the Colorado Front Range [*Clow and Sueker*, 2000]. A positive correlation between basin slope and nitrate was identified in the present study; however, no correlation was found between slope and surface-water ANC, nor was one documented by *Berg et al.* [2005] in their study of Sierra Nevada wilderness lakes. The hypothesis by *Clow and Sueker* [2000] was that steep slopes promote fast hydrologic flushing rates and preclude extensive interaction between percolating water and soil or vegetation, thus limiting N assimilation and acid neutralization. The lack of correlation between basin slope and ANC concentrations in Sierran basins might be due to the confounding effect of bedrock lithology on ANC. Metamorphic rocks, which can produce substantial ANC due to high weathering rates, are common in steeply sloping basins along the Sierran Crest, obscuring possible correlations between basin slope and surface-water ANC.

3.8. Limitations

[48] There are several limitations to this study that must be recognized. Each of the regression equations that were developed has an uncertainty, as depicted by dashed lines on either side of the regression lines in Figures 2 and 7, which represent 95% confidence limits on the regression slopes. Uncertainty is greatest at the limits of the range of each variable; this is particularly important when modeling solute

concentrations near thresholds of interest (e.g., high nitrate or low ANC concentrations). Use of the regression equations to estimate values beyond the range of measurements has even larger uncertainty. The estimates for SWE and winter N deposition between 3500 m and 4000 m, for example, could be substantially in error, which would strongly affect the spatial patterns depicted in Figures 3 and 4.

[49] Several of the regression equations are highly leveraged (Figures 2a, 2b, and 7a). Thus, the slopes of the regression lines are strongly dependent on sparse values at one end of the range of measurements. In some cases, the leveraging effect could be reduced by transforming the data to obtain a normal distribution (e.g., log ANC in Figure 7d); however, additional data are needed where they currently are sparse to reduce the uncertainty of these regression equations.

4. Conclusions

[50] In Yosemite, the most sensitive aquatic ecosystems with respect to nutrient enrichment effects of N and acidification effects of N and S deposition are in small, alpine basins, which have little soil or vegetation and abundant neoglacial and talus deposits. Susceptibility to nutrient enrichment and acidification decreases downstream due to increasing amounts of soil and vegetation and increasing water residence time. Bedrock geology is an additional influence affecting sensitivity to acidic deposition in Yosemite. Areas underlain by metamorphic rocks, primarily along the Sierran Crest, are relatively insensitive to acidic deposition because of the buffering effects of carbonate mineral weathering.

[51] The maps of predicted surface-water nitrate and ANC can be used to identify sensitive aquatic resources that would be appropriate for long-term monitoring for effects of climate change, atmospheric deposition of N and S, or other stressors. By analyzing relations between N and S deposition and surface-water chemistry, this study provided the foundation required to begin quantifying critical loads of N and S in the park. Future research needs include refinement of N and S deposition estimates, characterizing seasonal variations in surface-water chemistry at high elevation, and identifying relations between surface-water chemistry and biological indices.

[52] **Acknowledgments.** This research was supported by the National Park Service through the Water Quality and Assessment program. Snowcourse data were provided by the California Department of Water Resources. Thanks go to Jim Roche for help with sample collection, Jennifer Flynn for help with the GIS analysis and figures, and Jessica Lundquist for processing the MODIS imagery. Constructive suggestions for improving the manuscript were provided by Jim Sickman, Charles Driscoll, Natalie Latysh, and an anonymous reviewer.

References

Berg, N. H. (1992), Ion elution and release sequence from deep snowpacks in the central Sierra Nevada, California, *Water Air Soil Pollut.*, *61*, 139–168.

Berg, N. H., A. Gallegos, T. Dell, J. Frazier, T. Proctor, J. O. Sickman, S. Grant, T. Blett, and M. Arbaugh (2005), A screening procedure for identifying acid-sensitive lakes from catchment characteristics, *Environ. Mon. Assess.*, *105*, 285–307.

Billett, M. F., J. A. H. Lowe, K. E. Black, and M. S. Cresser (1996), The influence of parent material on small-scale spatial changes in streamwater chemistry in Scottish upland catchments, *J. Hydrol.*, *187*, 311–331.

Bricker, O. P., and K. C. Rice (1989), Acidic deposition to streams: A geology-based method predicts their sensitivity, *Environ. Sci. Technol.*, *23*(4), 379–385.

Charles, D. F. (Ed.) (1991), *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, 747 pp., Spring-Verlag, New York.

Clow, D. W., and J. K. Sueker (2000), Relations between basin characteristics and stream-water chemistry in alpine/subalpine basins in Rocky Mountain National Park, Colorado, *Water Resour. Res.*, *36*(1), 49–61.

Clow, D. W., M. A. Mast, and D. H. Campbell (1996), Controls on surface water chemistry in the upper Merced River basin, Yosemite National Park, California, *Hydrol. Process.*, *10*, 727–746.

Clow, D. W., G. P. Ingersoll, M. A. Mast, J. T. Turk, and D. H. Campbell (2002a), Comparison of snowpack and winter wet-deposition chemistry in the Rocky Mountains, USA: Implications for winter dry deposition, *Atmos. Environ.*, *36*, 2337–2348.

Clow, D. W., R. Striegl, L. Nanus, M. A. Mast, D. H. Campbell, and D. P. Krabbenhoft (2002b), Chemistry of selected high-elevation lakes in seven national parks in the Western United States, *Water Air Soil Pollut.*, *2*, 139–164.

Clow, D. W., L. Schrott, R. M. Webb, D. H. Campbell, and M. M. Dornblaser (2003a), Groundwater occurrence and contributions to streamflow in an alpine catchment, Colorado Front Range, USA, *Ground Water*, *41*(7), 937–950.

Clow, D. W., J. O. Sickman, R. G. Striegl, D. P. Krabbenhoft, J. G. Elliott, M. M. Dornblaser, D. A. Roth, and D. H. Campbell (2003b), Changes in the chemistry of lakes and precipitation in high-elevation National Parks in the Western United States, 1985–99, *Water Resour. Res.*, *39*(6), 1171, doi:10.1029/2002WR001533.

Cooper, D. M., A. Jenkins, R. Skeffington, and B. Gannon (2000), Catchment-scale simulation of stream water chemistry by spatial mixing: theory and application, *J. Hydrol.*, *233*, 121–137.

Deviney, F. A., K. C. Rice, and G. M. Hornberger (2006), Time series and recurrence interval models to predict the vulnerability of streams to episodic acidification in Shenandoah National Park, Virginia, *Water Resour. Res.*, *42*, W09405, doi:10.1029/2005WR004740.

Drever, J. I. (1997), *Geochemistry of Natural Waters: Surface and Groundwater Environments*, 3rd ed., 436 pp., Prentice-Hall, Englewood Cliffs, New Jersey.

Drever, J. I., and D. R. Hurcomb (1986), Neutralization of atmospheric acidity by chemical weathering in an alpine drainage in the North Cascade Mountains, *Geology*, *14*, 221–224.

Drever, J. I., and J. Zorbrist (1992), Chemical weathering of silicate rocks as a function of elevation in the southern Swiss Alps, *Geochim. Cosmochim. Acta*, *56*, 3209–3216.

Driscoll, C. T., C. P. Yatsko, and F. J. Unangst (1987), Longitudinal and temporal trends in the water chemistry of the North Branch of the Moose River, *Biogeochem.*, *3*, 37–61.

Evans, C. D., D. M. Cooper, S. Juggins, A. Jenkins, and D. Norris (2006), A linked spatial and temporal model of the chemical and biological status of a large, acid-sensitive river network, *Sci. Tot. Environ.*, *365*, 167–185.

Fenn, M. E., B. T. Bormann, D. W. Johnson, A. D. Lemly, S. G. McNulty, D. F. Ryan, R. Stottlemeyer, M. Poth, J. D. Aber, and J. S. Baron (1998), Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses, and management strategies, *Ecol. App.*, *8*(3), 706–733.

Fenn, M. E., et al. (2003), Nitrogen emissions, deposition, and monitoring in the Western United States, *Bioscience*, *53*(4), 391–403.

Feth, J. H., C. E. Roberson, and W. L. Polzer (1964), Sources of mineral constituents in water from granitic rocks, Sierra Nevada, California and Nevada, *Water-Supply Paper Rep. 1535-I*, 70 pp., U.S. Geological Survey.

Fishman, M. J., J. W. Raese, C. N. Gerlitz, and R. A. Husband (1994), U.S. Geological Survey approved inorganic and organic methods for the analysis of water and fluvial sediment, 1954–94, *Open-File Report Rep. 94-351*, 55 pp., U.S. Geological Survey.

Hair, J. F., W. C. Black, B. Babin, R. Anderson, and R. L. Tatham (2005), *Multivariate Data Analysis*, 6th ed., 928 pp., Prentice Hall, Upper Saddle River, New Jersey.

Hall, D. K., G. A. Riggs, V. V. Salomonson, N. E. DiGirolamo, and K. J. Bayr (2002), MODIS snow-cover products, *Remote Sens. Environ.*, *83*, 181–194.

Helsel, D. R., and R. M. Hirsch (1992), *Statistical Methods in Water Resources*, 522 pp., Elsevier, Amsterdam, The Netherlands.

Huber, N. K. (1987), The Geologic Story of Yosemite National Park *Rep.*, 64 pp.

Huber, N. K., P. C. Bateman, and C. Wahrhaftig (1989), Geologic Map of Yosemite National Park and Vicinity, California, U.S. Geological Survey, Denver, Colorado.

Ingersoll, G. P., J. T. Turk, M. A. Mast, D. W. Clow, D. H. Campbell, and Z. C. Bailey (2002), Rocky Mountain Snowpack chemistry network: history, methods, and the importance of monitoring mountain ecosystems, *Open-file report Rep. 01-466*, 14 pp., U.S. Geological Survey, Denver, Colorado.

Ito, M., M. J. Mitchell, C. T. Driscoll, and K. Roy (2005a), Nitrogen input-output budgets for lake-containing watersheds in the Adirondack region of New York, *Biogeochemistry*, *72*, 283–314.

Ito, M., M. J. Mitchell, C. T. Driscoll, and K. M. Roy (2005b), Factors affecting acid neutralizing capacity in the Adirondack region of New York: A solute mass balance approach, *Environ. Sci. Technol.*, *39*, 4076–4081.

Kachigan, S. K. (1986), *Statistical Analysis*, 589 pp., Radius Press, New York.

Kattlemann, R., and K. Elder (1991), Hydrologic characteristics and water balance of an alpine basin in the Sierra Nevada, *Water Resour. Res.*, *27*(7), 1553–1562.

Lins, H. F. (1986), Recent patterns of sulfate variability in pristine streams, *Atmos. Environ.*, *20*, 367–375.

Melack, J. M., and J. L. Stoddard (1991), Sierra Nevada, California, in *Acidic Deposition and Aquatic Ecosystems*, edited by D. F. Charles, pp. 503–530, Springer-Verlag, New York.

Melack, J. M., J. L. Stoddard, and C. A. Ochs (1985), Major ion chemistry and sensitivity to acid precipitation of Sierra Nevada Lakes, *Water Resour. Res.*, *21*(1), 27–32.

Michel, T. J., J. E. Saros, S. J. Interlandi, and A. P. Wolfe (2006), Resource requirements of four freshwater diatom taxa determined by in situ growth bioassays using natural populations from alpine lakes, *Hydrobiology*, *568*, 235–243.

Nanus, L., D. H. Campbell, G. P. Ingersoll, D. W. Clow, and M. A. Mast (2003), Atmospheric deposition maps for the Rocky Mountains, *Atmos. Environ.*, *37*, 4881–4892.

Nanus, L., D. H. Campbell, and M. W. Williams (2005), Sensitivity of alpine and subalpine lakes to acidification from atmospheric deposition in Grand Teton National Park and Yellowstone National Park, Wyoming, *Sci. Invest. Report Rep. 2005-5023*, 37 pp., U.S. Geological Survey, Denver, Colorado.

Nanus, L., M. W. Williams, D. H. Campbell, K. A. Tonnessen, T. Blett, and D. W. Clow (2009), Assessment of lake sensitivity to acidic deposition in national parks of the Rocky Mountains, *Ecol. App.*, *19*(4), 961–973.

Peters, N. E., and C. T. Driscoll (1987), Hydrogeologic controls of surface-water chemistry in the Adirondack region of New York State, *Biogeochemistry*, *3*, 163–180.

Porter, E., T. F. Blett, D. U. Potter, and C. Huber (2005), Protecting resources on federal lands: implications of critical loads for atmospheric deposition of nitrogen and sulfur, *BioScience*, *55*(7), 603–612.

Puckett, L. J., and O. P. Bricker (1992), Factors controlling the major ion chemistry of streams in the Blue Ridge and Valley and Ridge physiographic provinces of Virginia and Maryland, *Hydrol. Process.*, *6*, 79–98.

Sickman, J. O., and J. M. Melack (2002), Regional analysis of nitrogen yield and retention in high-elevation ecosystems of the western United States, *Biogeochemistry*, *57/58*, 341–374.

Smith, R. A., R. B. Alexander, and G. E. Schwarz (2003), Natural background concentrations of nutrients in streams and rivers of the conterminous United States, *Environ. Sci. Technol.*, *37*(14), 3039–3047.

Stoddard, J. L. (1994), Long-term changes in watershed retention of nitrogen, in *Environmental Chemistry of Lakes and Reservoirs*, edited by L. A. Baker, pp. 223–284, American Chemical Society, Washington, D.C.

Sullivan, T. J., J. R. Webb, K. U. Snyder, A. T. Herlihy, and B. J. Cosby (2007), Spatial distribution of acid-sensitive and acid-impacted streams in relation to watershed features in the southern Appalachian Mountains, *Water Air Soil Pollut.*, *182*, 57–71.

Sullivan, T. J., D. F. Charles, J. A. Bernert, B. McMartin, K. B. Vache, and J. Zehr (1999), Relationship between landscape characteristics, history, and lakewater acidification in the Adirondack Mountains, New York, *Water Air Soil Pollut.*, *112*(3–4), 407–427.

Sullivan, T. J., B. J. Cosby, A. T. Herlihy, J. R. Webb, A. J. Bulger, K. U. Snyder, P. F. Brewer, E. H. Gilbert, and D. L. Moore (2004), Regional model projections of future effects of sulfur and nitrogen deposition on streams in the southern Appalachian Mountains, *Water Resour. Res.*, *40*, W01102, doi:10.1029/2003WR002511.

Turk, J. T., and N. E. Spahr (1991), Rocky Mountains, in *Acidic Deposition and Aquatic Ecosystems*, edited by D. F. Charles, pp. 471–499, Springer-Verlag, New York.

Webster, R., and M. Oliver (2001), *Geostatistics for Environmental Scientists*, 271 pp., John Wiley, West Sussex, England.

Wilde, F. D., D. B. Radtke, J. Gibs, and R. T. Iwatsubo (Eds.) (1998), *National Field Manual for the Collection of Water-Quality Data*, U.S. Geological Survey, Denver, Colo.

Williams, M. W., M. Knauf, R. Cory, N. Caine, and F. Liu (2006), Nitrate content and potential microbial signature of rock glacier outflow, Colorado Front Range, *Earth Surf. Processes Landforms*, *32*(7), 1032–1047.

D. W. Clow, U.S. Geological Survey, MS 415 Federal Center, Denver, CO 80225, USA. (dwclow@usgs.gov)

B. Huggett, Department of Forestry and Wildland Resources, Humboldt State University, Arcata, CA 95521, USA.

L. Nanus, Department of Geosciences, San Francisco State University, 1600 Holloway Ave., San Francisco, CA 94132, USA.