ASSESSING THE POTENTIAL IMPACT OF ACID DEPOSITION ON HIGH ALTITUDE AQUATIC ECOSYSTEMS IN CALIFORNIA

INTEGRATING TEN YEARS OF INVESTIGATION

DRAFT FINAL REPORT

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ABSTRACT

The objective of the Aquatic Ecosystems Research Program of the CARB was to determine the effects of acidic deposition on water quality and biological populations in high elevation lakes and watersheds of the Sierra Nevada. Toward this end, the CARB funded ten years of research on the hydrochemistry and biology of high elevation sites in the Sierra Nevada. The resulting information is contained in 32 final reports and ca. 65 publications. Until now, an overall synthesis of this large body of survey, monitoring and expermental data was lacking. In this report, we integrate the findings of the Aquatic Ecosystems Research Program in order to evaluate (1) the chemistry of snow and rain that currently falls in the Sierra Nevada, (2) the current chemical status of high elevation surface waters, (3) long term trends in chemical and biological features of high elevation lakes, (4) the mechanisms of ANC generation and consumption in high elevation catchments, (5) the sources and fates of solutes over the course of the hydrological year, (6) the role of infrequent events on the hydrochemistry and biota of high elevation watersheds, (7) the potential use of bio-indicators in the Sierra Nevada, and (8) the use of models to predict the hydrochemistry of Sierra Nevada surface water.

Annual loading rates for hydrogen, sulfate, nitrate, ammonium, and calcium are low in the Sierra Nevada relative to the country as a whole. For most sites, hydrogen was the most concentrated ionic species in snow in the Sierra Nevada, and ammonium and nitrate were the second-ranked and third-ranked ions in snow, respectively. Nitrate and ammonium were the two most concentrated species in rain at all of the high elevation monitoring sites. Third- and fourth-ranked ions in rain were sulfate or hydrogen at most sites. In summer rainfall, NH_4^+:H^+ is always > 1 and NH_4^+ is strongly correlated with NO_3^- and SO_4^{-2}. Thus in the summer, NH_4^+ is an important neutralizer of the strong acid anions NO_3^-, SO_4^{-2}, and Cl^-. In the absence of NH_4^+, $[H^+]$ in rainfall would potentially be 11-fold higher.

In most respects, the chemical composition of 89 lakes surveyed under CARB support was similar to that of the Sierra Nevada lakes sampled during the EPA's Western Lake Survey (WLS) of 1985. Results of the CARB lake surveys indicate a somewhat higher sensitivity to acidification for high elevation lakes of the Sierra Nevada than was indicated by the WLS. For example, 65% of Sierra Nevada lakes in the WLS had ANC $\leq$

100 $\mu Eq\ L^{-1}$, whereas 74% of CARB sampled lakes had ANC $\leq 100\ \mu Eq\ L^{-1}$. Although none of the Sierra Nevada lakes sampled in the WLS had ANC ≤ 0, 4.5% of the CARB sampled lakes had ANC ≤ 0. In the WLS only one lake was sampled with $pH < 6.0$; in the CARB survey, 10 lakes had $pH < 6.0$. These differences are partly due to the inclusion in the CARB surveys of a number of naturally acidic lakes in the Mt. Pinchot area of Kings Canyon National Park in the southern Sierra Nevada, the presence of which has been tentatively ascribed to the oxidation of pyrite. In addition, generally higher concentrations of strong acid anions (nitrate, sulfate and chloride) were measured in the CARB survey lakes than in the WLS lakes. No inter-annual trends in the pH or ANC of lakewater or outflow streamwater were found during the period 1983 through 1994. Surface waters in high elevation regions of the Sierra Nevada have not undergone measurable acidification since 1983.

The majority of $[H^+]$ stored in the snowpack of Sierra Nevada watersheds is currently neutralized before reaching outflow streams. Buffering by formate and acetate in snow, reactions with particulate clay and dust from dry deposition, and neutralization by cation exchange in soils and talus may all contribute to this neutralization. All of the high elevation Sierra Nevada watersheds studied produced sufficient ANC to neutralize much of the acidity of precipitation and to be net exporters of ANC and base cations. Sierra Nevada watersheds are effective at retaining dissolved inorganic nitrogen delivered in wet deposition. Ammonium was almost completely retained by the headwater catchments studied. Net annual retention of nitrate was almost always observed, although the percentages of nitrate consumed by watershed processes were lower than for ammonium. Ammonium consumption appears to occur along the pathway of meltwater to the lakes, rather than in the lakes.

Rain in the Sierra Nevada in summer is acidic. Most of the annual deposition of nitrogen, sulfate and organic acids occurs during the non-winter months. Although the quantity of non-winter precipitation is much smaller than snowfall, solute concentrations in rain are much greater than in snow. Large summertime rainstorms have been observed to cause a drop in the pH and ANC of Emerald Lake. The chemistry of rain in the Sierra Nevada is greatly changed by passage through foliage (e.g. chinquapin, western white pine, and willow). Nitrate is almost doubled, and ammonium is almost completely retained, by foliage, thus lowering the ANC of precipitation.

The unusual events considered in this report include the melting of exceptionally deep snow packs, rain-on-snow events, avalanche, and large summer storms. The melting of exceptionally deep snow packs after wet winters does not currently pose a threat to stream or lake biota in terms of reduced pH or ANC of surface waters. Instead, it appears that the potential for deep snowpacks to harm aquatic biota lays in the impacts of high discharge rates on the physical characteristics of streams. These impacts include displacement of sand and gravel, replacement of small diameter gravel with larger gravel and cobbles, and stream bed scouring. These changes result in greatly higher mortality of the eggs and larvae of fall-spawning trout, and a decrease in suitable spawning substrate for spring-spawning trout. Winters of sufficiently high snowfall and sufficiently high snowmelt discharge to modify stream channels appear to occur less than once per decade. Rain-on-snow events also produce discharge rates high enough to affect trout recruitment. Rain-on-snow events occur at least once a year in the most catchments, and are probably responsible for more juvenile trout mortality in the Sierra Nevada than other kinds of winter floods.

Surface waters are not currently sufficiently acidic in the Sierra Nevada to threaten the juvenile or adult stages of Sierra Nevada amphibians, even during snowmelt. The most important factor governing the distribution of amphibians at high altitude in the Sierra Nevada is probably the presence/absence of introduced trout species; juvenile stages of amphibians will be excluded by fish predation. The most vulnerable lifestages of the spring- and fall-spawning trout occur at different times in streams or lakes, and are differentially at risk from episodic acidification. For example, the fertilized eggs of spring spawning trout (such as golden trout and rainbow trout) are susceptible to low pH in snowmelt water. Later in the year, the swim-up fry of spring-spawning trout could be damaged by episodic acidification due to runoff from summer storms. Episodic acidification of streams due to snowmelt or summer rains may temporarily decrease the benthic density of some species of stream invertebrates. Vulnerable species identified in experimental work in the Emerald Lake Watershed are the nymphs of mayflies of the genera *Baetis*, *Paraleptophlebia*, *Epeorus*, and chironomid fly larvae. Certain changes in zooplankton community structure are expected if Sierra Nevada lakes become subjected to chronic acid stress in the future. For example, *Daphnia rosea*, *Daphnia middendorffiana* and *Diaptomus signicauda* are likely to be removed if pH levels reach as low as 5.0.

The watershed modeling efforts sponsored by the CARB fall into two categories. In one category, relatively simple models were applied to a database of 150-200 Sierra Nevada lakes to predict the outcomes of various precipitation scenarios for Sierra Nevada lakes in general. In the other category, more complex models were developed using detailed hydrochemical data from the Emerald Lake Watershed. These models were calibrated with field data from particular years of study at Emerald Lake and used to simulate observed results from other years of study at Emerald Lake, or applied to other well-studied watersheds.

The modeling efforts of the first category suffer from oversimplification and flawed assumptions. For example, Nishida and Schnoor's (1989) model relied on the assumption that sulfate is a conservative ion in the watersheds and that sulfate is the only acid ion being delivered to the watershed. The Episodic Event Model (EEM) of Nikolaidis et al. (1989) assumed that there are no reactions in the watershed that neutralize the acidity of runoff from either snow of rain. In several respects, the hydrochemical model of Hooper et al. (1990), dubbed the Alpine Lake Forcaster (ALF), suffered from oversimplification. For example, a crude formula for chemical weathering was included in their model, but cation exchange processes in soils were excluded. In addition, the authors treat sulfate as a conservative ion. In contrast to the models above, the Alpine Hydrological Model (AHM), described by Sorooshian and Bales (1992), was extremely complex and densely parameterized. A myriad of hydrologic and biogeochemical processes were modeled, requiring a wide array of field data. Application of the AHM to the Emerald Lake Watershed proved to be labor intensive and problematic, despite the availability of data from several years of intensive hydrochemical research.

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DISCLAIMER

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SUMMARY AND CONCLUSIONS

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Loading rates for hydrogen, sulfate, nitrate, ammonium, and calcium are low in the Sierra Nevada relative to the country as a whole. Mean annual deposition rates for H^+ ranged from 27-63 eq ha^{-1} in the Sierra Nevada. Mean annual deposition rates for H^+ in the US and Ontario ranged from 337-407 eq ha^{-1}. Similarly, annual deposition rates for sulfate ranged from 18-57 eq ha^{-1} in the Sierra Nevada, and from 207-241 eq ha^{-1} in the US and Ontario. Annual deposition rates for nitrate ranged from 24-77 eq ha^{-1} in the Sierra Nevada, and from 214-236 eq ha^{-1} in the US and Ontario. Finally, annual deposition rates for ammonium ranged from 7-102 eq ha^{-1} in the Sierra Nevada, and from 160-175 eq ha^{-1} in the US and Ontario. In contrast, deposition rates for calcium were similar in magnitude for the Sierra Nevada (13-44 eq ha^{-1}) and the US and Ontario (40-51 eq ha^{-1}). Concentrations of sulfate in precipitation of the Sierra Nevada occupy a similar range to that provided for non-sea-salt sulfate along the northwestern coast of North America.

For most sites, hydrogen was the most concentrated ionic species in snow in the Sierra Nevada. In eight of the fourteen sites studied, ammonium was the second-ranked ion in snowfall. Nitrate was the most commonly observed third-ranked ion. In eleven of fourteen sites, hydrogen, ammonium, and nitrate were the three highest ranked ions in snow. Chloride was more concentrated than sodium in snow in all but two monitoring locations. Calcium ranked higher than all other base cations in the snowfall at every site except for Alpine Meadows. Potassium, magnesium, acetate and formate, in varying orders, were consistently the four lowest ranking species in the snow pack.

Nitrate and ammonium were the two most concentrated species in rain at all of the ten high elevation monitoring sites in the Sierra Nevada. Sulfate ranked third in six of the ten sites, and fourth in the remaining four sites. Hydrogen ranked either third or fourth in rain at every site except for Emerald Lake, where it ranked seventh. Magnesium and potassium, together with phosphate were consistently the lowest ranked ions measured in rain at all of the sites. As in snow, calcium was the highest ranked base cation in rain. In contrast to the results for snow, sodium was higher ranked than chloride in rain at the majority of sites (seven of ten sites). In summer rainfall, $NH_4^+:H^+$ is always > 1 and NH_4^+ is strongly correlated with NO_3^- and SO_4^{-2}. Thus in the summer, NH_4^+ is an important neutralizer of the strong acid anions NO_3^-, SO_4^{-2}, and Cl^-. In the absence of NH_4^+, $[H^+]$ in rainfall would potentially be 11-fold higher.

In California, NO_X emissions are generally three times higher than SO_2 emissions. Nevertheless, the range of values for nitrate:sulfate in wet deposition in high elevation regions of California does not differ much from the range of values observed in eastern North America. Nitrate:sulfate in snowfall among individual sites in the Sierra Nevada ranged from 0.53 to 4.30 over four years of study. The ratio for snow was lowest in years of normal or above normal snowfall and greatest in years of below normal snowfall. The ratio $NO_3^-:SO_4^{-2}$ in the Emerald Lake Watershed snowpack was highest in dry year snowpacks. A major source of ions in snow in dry years are air masses that originate over land from convective sources or from the mixing of weak fronts with air over the Central Valley.

The relationship between $[NH_4^+]$ and $[NO_3^- + SO_4^{2-}]$ was investigated via linear regression for rain and snow for high elevation sites in the Sierra Nevada. The slopes of the regressions were significant for all analyses except for rain in 1991, implying that ammonium-nitrate and ammonium-sulfate aerosols may be largely responsible for the wet deposition of nitrate and sulfate in these habitats. In most cases, however, the y-intercept of the regression lines were negative, suggesting that some portion of the combined deposition of sulfate and nitrate was due to other contaminants, including nitric and sulfuric acids.

Current status of high elevation surface waters in the Sierra Nevada

In most respects, the chemical composition of 89 lakes surveyed under CARB support was similar to that of the Sierra Nevada lakes sampled during the EPAS's Western Lake Survey (WLS) of 1985. Calcium was the the dominant cation in both surveys, followed by sodium. In general, sulfate was the dominant strong acid anion, followed by chloride. Nitrate was the least concentrated strong acid anion in both studies. Combined results of the CARB lake surveys indicate a somewhat higher sensitivity to acidification for high elevation lakes of the Sierra Nevada than was indicated by analysis of the Sierra Nevada lakes of the WLS. The median value for alkalinity (56 $\mu Eq\ L^{-1}$) for CARB lakes was lower than that reported for the Sierra Nevada lakes of the WLS (71 $\mu Eq\ L^{-1}$). Most of the Sierra Nevada lakes (65%) in the WLS had ANC values $\leq 100\ \mu Eq\ L^{-1}$. A somewhat higher percentage (74%) of CARB lakes had alkalinity values $\leq 100\ \mu Eq\ L^{-1}$. None of the Sierra Nevada lakes sampled in the WLS had ANC ≤ 0. However, a small number (4.5%)

of the CARB lakes had alkalinity values ≤ 0. In the WLS only one sampled lake had a pH < 6.0. However, the minimum pH measured in the CARB surveys was 4.71, and 10 lakes had pH < 6.0. Additionally, the median pH for CARB survey lakes (6.5) was lower than for WLS lakes (6.93). These differences are primarily due to the inclusion in one of the CARB surveys of a number of naturally acidic lakes in the Mt. Pinchot area of Kings Canyon National Park in the southern Sierra Nevada. Otherwise, the distribution of alkalinity values in the two studies are similar; only a few lakes (6 in the case of the CARB lakes) had alkalinity values higher than 200 μEq L^{-1}, and no lakes in either study had alkalinities greater than 400 μEq L^{-1}.

The somewhat higher acid sensitivity of the CARB lakes, relative to WLS lakes, cannot be explained by lower ionic strengths or by lower concentrations of base cations in CARB lakes. The median values for $\sum$ base cations, and for each of the individual base cations (Ca^{2+}, Mg^{2+}, N^{+}, and K^{+}) were higher for CARB lakes than the Sierra Nevada WLS lakes. Instead, it appears that generally higher concentrations of strong acid anions were measured in the CARB lakes than in the WLS lakes; median values for nitrate, sulfate, and chloride were higher for CARB lakes than the WLS lakes.

Long term trends in hydrochemistry and biological parameters

No inter-annual trends in the pH or ANC of lakewater or outflow streamwater were found during the period 1983 through 1994 . Surface waters in high elevation regions of the Sierra Nevada have not undergone measurable acidification since 1983. Time series of lake and outflow chemistry suggested inter-annual trends for other chemical parameters at only two study sites, Ruby Lake and Emerald Lake. Volume-weighted-mean sulfate and base cations increased over time in Ruby Lake. Sulfate concentrations increased from ca. 6 μEq L^{-1} to ca. 12 μEq L^{-1} in the lake and the lake outflow from October 1987 to April 1994. The upward trend in sulfate appeared to end in 1994 and may have been associated with the regional drought that occurred from water year 1987 to water year 1992. This temporary increase in sulfate of ca. 6 μEq L^{-1} was apparently balanced by an increase in base cations of approximately the same magnitude.

The only other observable trend in surface water chemistry during the CARB lake studies was a decline of nitrate in the Emerald Lake. Nitrate levels fell during 1988 and 1989. In the years prior to this period (1983 - 1987), peak concentrations of nitrate in Emerald Lake were above ca. 10 μEq L^{-1}. Later, from 1990 to 1994, peak concentrations of nitrate were less than 5 μEq L^{-1} in the lake. The pattern of the decline is unclear during water years 1988 and 1989 because sampling frequency was low at this time of the study.

Zooplankton data from the Emerald Lake was examined for long term trends in lake biota. Inspection of the 8 year zooplankton record for Emerald Lake failed to reveal any consistent trend spanning the sampling period. Rather, there appear to be a few years in which many species occurred at especially high or especially low densities. For example, several zooplankton species were especially abundant during the summer of 1985 and 1988. Especially low abundances were observed in 1986 for four species. Three of the crustacean species were least abundant in Emerald Lake during the last three years of record (1990-1992). Whether or not this reflects a recent downward trend in crustacean abundance, or an artifact of infrequent sampling during those years (once every two months) is unknown.

Mechanisms of ANC consumption and generation in high elevation watersheds of the Sierra Nevada, and analysis of the sources and fates of solutes over the course of the hydrological year

Autumn. In most of the high altitude watersheds studied in the Sierra Nevada, streamflow during the autumn months (Sept.-Nov.) is scanty or absent. Based on work at the Emerald Lake Watershed (ELW), during the period of low flow, from autumn through winter, streamflow consists of discharge from groundwater reservoirs which has been stored on the order of months, and whose composition is not controlled by contact with the soil zone. Streamwater at this time is in stoichiometric equilibrium with weathering products. Autumn snow can be important in terms of total annual ion flux to watersheds. In "normal" and "wet" years (such as 1985 and 1986, respectively) 30% of the annual nitrate and sulfate flux and 50% of NH_4^+ flux in the ELW came from autumn snow.

Winter. Most of the annual deposition of hydrogen, chloride, and base cations in the Sierra Nevada occurs during the winter months. Although the concentrations of these solutes are higher in rain than in snow, the quantity of snowfall exceeds the quantity of non-winter precipitation. 67% to 92% of H^+ deposition occurs as winter snowfall in most of the headwater catchments studied by the CARB. H^+ loading is directly related to snow quantity. In the Emerald Lake Watershed, the greatest deposition of H^+ occurred in 1986 and 1993, which were the years of highest snowfall during the period 1985 - 1994.

Snowmelt. Acidity derived from snowmelt is delivered to surface waters in the form of an ionic pulse. At any site of melting snow, the first 5-15 days of melt deliver the ionic pulse, which magnifies solute concentrations 5-10 fold. Where snowmelt is rapid, the ion pulse may last ca. 2 days. Where snowmelt is slow, the ion pulse may last ca. 10 days. The anion release sequence from snowpacks is generally SO_4^{-2}, $NO_3^- > Cl^-$.

Lake outflow chemistry does not exactly mirror the chemistry of melting snow in high elevation Sierra Nevada watersheds. Rather, lake outflow chemistry results from the interactions between snowmelt water and the soils, rock and vegetation upstream of the lake, and biological and chemical in-lake processes. The importance of in-lake processes will vary with the flushing rate of the lake during snowmelt; when flushing rates are high (such as during peak discharges), lake outflow chemistry should differ little from lake inflow chemistry.

pH was the most variable chemical parameter measured in lake outflows during snowmelt runoff in seven watersheds studied. The most common pattern for pH consisted of a decrease in pH as discharge increased, with lowest pHs occurring near the time of peak runoff. Changes in lake outflow pH over the course of snowmelt were not large. The typical pH change observed from before the onset of snowmelt to peak runoff was about 0.5 pH units. Minimum outflow pH ranged from 5.5 to 6.1 and was fairly consistent among years and among catchments.

Patterns of ANC in lake outflow were more consistent among years and among lakes than patterns in outflow pH. The most common pattern of ANC during snowmelt was an inverse relationship between ANC and discharge, with minimum ANC values occurring at or near peak runoff. ANC usually declined by about 50% from before the onset of snowmelt to peak snowmelt runoff; minimum values of ANC were typically in the range of 15 to 30 $\mu eq\ L^{-1}$.

Concentrations of nitrate in lake outflows during snowmelt runoff followed a consistent pattern consisting of two stages. In the first stage, nitrate concentrations in runoff increased from the start of snowmelt until 2-5 weeks before peak discharge occurs. In the second stage, nitrate concentrations decreased in runoff during the remainder of the rising limb of the hydrograph and into the falling limb of the hydrograph. Some of the initial increase in nitrate can be ascribed to the ion pulse occuring during the early stages of snowmelt. However, nitrate concentrations often increased in lake outflows more than could be explained by snowmelt alone, even allowing for preferential elution of nitrate during the ion pulse of snowmelt. The drop in nitrate during the second stage of the pattern is ascribed to biological consumption, presumably both in the watershed along the pathway of meltwater and in-lake.

In most cases, sulfate was diluted less during snowmelt than ANC, base cations or silica. Biogeochemical processes are probably regulating sulfate concentrations during snowmelt in the Sierra Nevada. Sulfate concentrations followed three general patterns during snowmelt in the watersheds studied. In some cases, sulfate decreased slightly during snowmelt, but increased after snowmelt discharge ended and base flow was reestablished. In other cases, sulfate also decreased only slightly during snowmelt, but failed to increase later after the end of snowmelt discharge. In still other cases, sulfate initially increased at the beginning of snowmelt, was subsequently diluted, and then increased up to pre-melt concentrations.

Hydrogen budgets. The majority of $[H^+]$ stored in the snowpack of Sierra Nevada watersheds is currently neutralized before reaching outflow streams. Several mechanisms may contribute to this buffering. Formate and acetate comprise 25-30% of anions in snow. The formate and acetate in the snowpack have pKs that would allow them to be dissociated at the pH of snowpack melt water and thus be able to buffer free acidity. Dry deposition may also play a role in the buffering of snowpack acidity. Particulate clay and dust may react with CO_2, yielding HCO_3^- and Ca^{+2} or Mg^{+2} in meltwater and decreasing $[H^+]$. Much of the acidity of snowpack runoff is apparently neutralized by cation exchange in soils and talus (the subsurface). The buffering occurs during contact of meltwater with the terrestrial watershed over only hours or days. Regardless of the mechanisms responsible, all of the high elevation Sierra Nevada watersheds studied produced sufficient ANC to neutralize most of the acidity of precipitation and to be net exporters of ANC and of base cations

Sulfate budgets. On an annual basis many cases of net export of sulfate from Sierra Nevada watersheds were observed. The watersheds which always exported sulfate are located in the eastern Sierra Nevada. The Emerald Lake watershed is the only watershed studied in the western Sierra Nevada that tended to export sulfate more often than retain sulfate. Sulfate export from these headwater catchments is indicative of the weathering of sulfur bearing minerals in the watersheds. Two major categories of sulfur bearing minerals comprise the probable parent rock for sulfate export; (1) sulfide bearing minerals containing reduced sulfur, and (2) sulfate bearing minerals containing oxidized sulfate molecules. The weathering of sulfide bearing rocks involves a redox reaction in which ferrous iron and sulfur are oxidized, and the ferric iron hydrolyzes to precipitate ferric hydroxide. This reaction is an internal watershed source of acid (sulfuric acid), and thus a process consuming ANC.

In some lakes a substantial quantity of Ca^{2+} is present which is not associated with ANC. The dissolution of calcite present in pyrite bearing rocks may explain this result. Some Sierran lakes belonging to the high sulfate category in the WLS occur in watersheds containing meta-sedimentary bedrock (such as marble). In these cases, such as in the Convict Lake area of the eastern Sierra Nevada, the weathering of gypsum is a likely source of sulfate and calcium.

The presence of naturally acidified lakes in the Mt. Pinchot region of the Sierra Nevada has been tentatively ascribed to the oxidation of pyrite. Pyritized granite occurs very locally in the Mt. Pinchot area; it is present in some headwater catchments, and not in other nearby or adjacent catchments. However, where it occurs, pyrite weathering is a potentially an important internal source of acidity (and a sink for ANC) in watersheds. For every equivalent of sulfate hypothetically produced by pyrite weathering, 2 equivalents of H^+ are produced. In a hypothetical scenario in which 100% of the sulfate exported by the Sierran watersheds resulted from the weathering of pyrite, the acidity produced would be of the same order of magnitude as the acidity currently entering the watersheds in wet deposition.

Nitrogen budgets. The watersheds studied by the CARB were effective at retaining dissolved inorganic nitrogen delivered in wet deposition. Ammonium was almost completely retained by the headwater catchments. Retention of ammonium was observed in every lake in every water year studied. Net retention of nitrate was almost always observed in the seven watersheds, although the percentages of nitrate consumed by watershed processes was lower than for ammonium. Ammonium consumption appears to occur along the pathway of meltwater to the lakes rather than in the lakes. For example, greater than 99% of the NH_4^+ from wet deposition is consumed by the watershed of Emerald Lake before reaching the lake itself.

Summer. During the summer transition period between snowpack runoff and low flow conditions, discharge from soil reservoirs is the primary source of stream flow in the ELW. Both the Na^+:Ca^{2+} ratio and Si content of soil water were similar to that of stream water during summer. The composition of stream flow at this time was congruent with the stoichiometry of plagioclase weathering. The residence time of this water is on the order of months and sufficient for mineral weathering reactions to reach completion. The H^+ retained in the soils during snowpack runoff may participate in mineral weathering in soils and talus during summer months.

Most of the annual deposition of nitrogen, sulfate and organic acids occurs during the non-winter months. Although the quantity of non-winter precipitation is much smaller than snowfall, the concentrations of these solutes in rain is much greater than in snow. One or more large rains in the summer or during snowmelt can cause a year to have higher than average solute loading. Low Cl^- and high NH_4^+ in rain suggest that localized convection storms are main source of ions. Without current levels of NH_4^+, $[H^+]$ in rainfall would be up to 11-fold higher in rain. Rain in the Sierra Nevada in summer is acidic. Large summertime rainstorms have been observed to cause a drop in the pH and ANC of Emerald Lake.

Based on work at the ELW, the N concentrations of incident rain are greatly changed by passage through foliage (chinquapin, western white pine, and willow). Nitrate was released by vegetation, either as a consequence of leaching or washoff of dry deposition, leading to almost a doubling of nitrate concentrations in incident rain. Almost all NH_4^+ in incident rain was retained by foliage. The net effect of foliage on rain was to greatly increase the concentration of the strong acid anion nitrate and to greatly reduce the concentration of a cation normally available to neutralize strong acid anions in precipitation, thus lowering the ANC of precipitation. The importance of this process in a particular watershed will vary with the areal extent of vegetation.

The effect of infrequent events on hydrochemistry and biota

The melting of exceptionally deep snow packs during wet winters appears not to pose a threat to stream or lake biota in terms of reduced pH or ANC of surface waters. The volume weighted mean ANC of lake outflows during the snowmelt period of wet winters is only slightly less than that during dry winters, and has not been observed to reach zero. In addition, the pH of lake outflows and the volume weighted mean pH of Sierran lakes were not observed to reach the pH critical for stream and lake biota ($pH \leq 5.5$) during the snowmelt periods of wet winters.

Instead, it appears that the potential for deep snowpacks to harm aquatic biota lays in the impacts of high discharge rates on the physical characterics of streams. These impacts include displacement of sand and gravel, replacement of small diameter gravel with larger gravel and cobbles, and stream bed scouring. These changes result in greatly higher mortality of the eggs and larvae of fall-spawning trout, and a decrease in suitable spawning substrate for spring-spawning trout. Discharge rates sufficiently high to affect trout recruitment have been recorded (1) after lake water displacement by avalanche onto an ice-covered lake, (2) during floods caused by rain-on-snow events, and (3) by snow melt discharge after wet winters. Winter floods caused by the first two mechanisms are likely to be more detrimental to fish because in these two cases the presence of snow banks confines unusually high flows to the stream channel, leading to higher shear stress and more stream bed disturbance than would occur later in the season.

Winters of sufficiently high snowfall and sufficiently high snowmelt discharge to modify stream channels appear to occur less than once per decade. Although avalanches in general are more common in wet winters, the probability that an avalanche will strike an ice-covered lake is unknown, and is probably very low. Notable rain-on-snow events occur at least once a year in the studies cited herein, and are probably responsible for more juvenile trout mortality in the Sierra Nevada than other kinds of winter floods. In addition, the warm storms that produce rain-on-snow events deliver precipitation with higher than average nitrate and sulfate concentrations, and thus potentially cause short term depressions in pH and ANC, in addition to stream bed alterations.

Use of models to predict hydrochemistry

The watershed modeling efforts sponsored by the CARB fall into two categories. In one category, relatively simple models were applied to a database of 150-200 Sierra Nevada lakes to predict the outcomes of various precipitation scenarios for Sierra Nevada lakes in general. In the other category, more complex models were developed using detailed hydrochemical data from the Emerald Lake Watershed. These models were calibrated with field data from particular years of study at Emerald Lake and used to simulate observed results from other years of study at Emerald Lake, or applied to other well-studied watersheds.

The objectives of the modeling by Nishida and Schnoor (1989) were twofold: (1) to calculate the net annual consumption or production rate of chemical species in a suite of high altitude Sierra Nevada watersheds, and (2) to determine the sensitivity of the same suite of lakes to hypothetical changes in loading rates of sulfate and nitrogen species. The second objective was approached in two different ways. First a graphical technique based on the Henriksen nomograph was used to identify acid sensitive lakes under different loading scenarios. Secondly, the principal of charge balance was used to develop equations (assuming steady state conditions) to predict the change in ANC (Δ ANC) that would result from changes in loadings of N and S species. Nishida and Schnoor did not consider the potential for episodic acidification during snowmelt and summer storm events in their models.

Nishida and Schnoor's approach toward the first objective relied on the estimation of evapoconcentration factors for each of the lakes in the data set. The calculation of these factors was based on the assumption that sulfate is a conservative ion in the watersheds, i.e. that the only process affecting the ratio of sufate deposition and its concentration in lake water is evaporation. Sulfate is a poor choice for such a calculation. On an annual basis, sulfate is retained in some catchments, and exported in other catchments. Out of 36 water years (among 7 watersheds) evaluated by the CARB, in only 3 cases did sulfate behave even close to conservatively ("close to conservatively" indicating that net watershed flux of sulfate was $\leq 10\%$ of total loading).

The second objective was not met by Nishida and Schnoor's application of Henriksen's nomograph. When the present condition of the database lakes was plotted as a nomograph, only 6 lakes fell into the region of the graph for acid-sensitive lakes. However, based on the criteria that ANC < 50 μeq/L confers acid-sensitivity, at least 38% of the database lakes (ca. 75 lakes) should have fallen into this category. The authors suggest that Henriksen's nomograph may not be applicable to the Sierra Nevada, in part perhaps because the lines dividing the graph into zones of acid sensitivity were achieved empirically using data from 700 Norwegian lakes. In addition, the model assumes that sulfate is the only acid ion being delivered to the watershed. It is well known that nitrate is a significant contributor to precipitation acidity in the Sierra Nevada.

The steady state model of Nishida and Schnoor was also flawed. The model employed a parameter dubbed the "watershed removal fraction" for nitrate. This parameter was estimated for each lake in the data base using the faulty evapoconcentration factors discussed above. The parameter also incorporated lake concentrations of nitrate obtained from one-time synoptic sampling of lake chemistry in the fall or late summer. This methodology ignores that fact that much of the nitrate delivered as snow passes through the watershed during the period of high discharge and high lake flushing rates associated with snowmelt. Nitrate measured in the lake in the fall or late summer fails to reflect the behavior of nitrate during the snowmelt season. Not surprisingly, estimates for nitrate removal based on year-round field measurements of lake outflow chemistry provide a different picture. Again, using the results of 35 water years of data obtained by the CARB in the high Sierra, the overall average watershed retention rate for nitrate is ca. 21 $eq{\cdot}ha^{-1}yr^{-1}$. Division by the average nitrate loading (ca. 46 $eq{\cdot}ha^{-1}yr^{-1}$) results in a removal fraction of 47%, much lower than the values used by Nishida and Schnoor.

Nikolaidis et al. (1989) attempted to predict the number of lakes that would lose ANC during snowmelt and large summer rain events using a Monte Carlo simulation technique. They developed a simple mixing model (Episodic Event Model, or EEM) which simulated the effects of snowmelt and summer rainstorms on lake chemistry by diluting epilimnetic water with runoff from snowmelt or summer rainstorms. Their model investigated the effect of changes in the timing, rather than the chemistry, of snowmelt. They investigated the consequences of an early thaw (late March to early April), and a late thaw (late May to early June). Their model assumes that there are no reactions in the watershed that neutralize the acidity of runoff from both kinds of events. As such, the model is a gross simplification of Sierra Nevada watersheds, however, the authors represent their model as a technique to predict the worst case scenarios for the region.

According to the EEM, lakes of the Central Sierra region appear to be most at risk from early snowmelt, although they do not have the lowest average initial ANC. The authors explain this result as a consequence of regional differences in the Watershed Area:Lake Area ratio (WLR). Lakes in the central Sierra region had somewhat higher average WLR than lakes in the southern Sierra Region or the northern region. The authors of the EEM contend that lakes with a high WLR are able to dilute the acidity of snowmelt runoff to a lesser extent than lakes with a low WLR. However, most of the modification of snowmelt chemistry (including the neutralization of acidity) occurs during its passage through the watershed before runoff enters the lake. Flushing rates are high during snowmelt discharge - the chemistry of the lake at this time will largely reflect the chemistry of snowmelt. Because the authors of the EEM used lake chemistry obtained in the late summer and autumn, the model fails to elucidate the true relationship between lake chemistry and snowmelt chemistry.

The EEM also fails to considers the seasonal patterns of the aquatic organisms that may be a risk in the future from increased acidity in surface waters. Small differences between the chemistry of a late or early thaw may be less consequential to the biota of high altitude Sierran lakes than the timing of snowmelt and the ionic pulse. Many zooplankton of high altitude Sierra lakes experience population increases only in late spring and summer. Even if a late thaw results in a less pronounced ANC depression during snowmelt (as the model suggested), the delivery of acidic meltwater into the epilimnion in June and July may have more negative consequences for a zooplankton population than an early thaw. In addition the eggs of spring-spawning trout (such as golden, cutthroat and rainbow trout) would be more susceptible to low pH episodes caused by a late thaw than an early thaw.

The hydrochemical model of Hooper et al. (1990), dubbed the Alpine Lake Forecaster (ALF), is a sparsely parameterized model, based on the hydrology and mineral weathering rates in the Emerald Lake watershed. Although data requirements to run the model are modest, the model suffers from oversimplification. These watershed processes controlling surface water chemistry were described by a series of nonlinear simultaneous equations in which there were four unknowns: [H^+], bicarbonate, silica, and sum of base cations (SBC). A grossly simplified formula for chemical weathering was included in the model, but cation exchange processes in soils were excluded. A simplified nitrogen cycle was described, specifying proportions of NH_4^+ and NO_3^- taken up by biota. In contrast, the hydrological component of the ALF was complex. The watershed was divided into several subunits, for each of which potential solar radiation per unit area was calculated using an algorithm using latitude, slope, aspect and day of year.

The first scenarios that were investigated with the ALF involved applying different elution rates for solutes in the snowpack. All solutes were eluted from the snowpack at the same rates, no allowances were made for preferential elution. The ALF failed to model observed solute dynamics during snowmelt in Emerald Lake. Sulfate dynamics were not well described by any of the elution rates tested. The poor results for sulfate are not surprising, because the authors treat sulfate as a conservative ion, and it is now known that sulfate rarely behaves conservatively in Sierra Nevada watersheds. The model underestimated silica and base cations in runoff during the two months of snowmelt, and overestimated them during the later months of snowmelt. This result may be related to the fact that cation exchange is not modeled by the ALF

The most complex model developed with CARB support is the compartmentalized algorithm, dubbed the Alpine Hydrological Model (AHM), described by Sorooshian and Bales (1992). In contrast to the other models developed with CARB support, the AHM was very complex and densely parameterized. A myriad of hydrologic and biogeochemical processes were modeled, requiring a wide array of field data. Application of the AHM to the Emerald Lake Watershed proved to be labor intensive and problematic, despite the availability of data from several years of intensive hydrochemical research. In order to apply the AHM to other high elevation watersheds in the Sierra Nevada (which must have similar geologic, soil, and hydrologic features) the minimum data required are (1) values of the state variables used for calibration and evaluation, (2) a general soil survey, (3) 3-5 snow-covered-area scenes or maps spanning the snowmelt season, (4) a general vegetation survey similar in detail to the soil survey, (5) record of precipitation, including timing, amount, and chemistry of events, (6) an estimate of dry deposition, (7) base saturation of the soil, and (8) values for sublimation and potential evapo-transpiration.

As a result of the complexity of the AHM, future users of the model will have to employ a number of assumptions concerning hydrologic and biogeochemical minutia in a particular watershed in order to assign input values and estimate the numerous parameters required to make the model run. The values chosen, and the assumptions taken in these cases are at the discretion of the user. However, there are a number of "assumptions" or simplifications of biogeochemical processes that are built into the AHM that may not be acceptable in all applications of the model.

Potential use of bio-indicators in the Sierra Nevada

Surface waters are not currently sufficiently acidic in the Sierra Nevada to threaten the juvenile or adult stages of Sierra Nevada amphibians, even during snowmelt. However, chemical factors related to low pH may be responsible for the observed absence of *Rana muscosa* tadpoles in survey lakes with pH < 6.0. The most important factor governing the distribution of amphibians at high altitude in the Sierra Nevada is likely to be the presence/absence of introduced trout species; juvenile stages of amphibians will be excluded by fish predation.

Of the five species of trout occurring at high elevation in the Sierra Nevada, the three species which spawn in the spring must be considered separately from the two species which are fall spawners. This is because the most vulnerable lifestages of the spring- and fall-spawning trout occur at different times in streams or lakes, and are differentially at risk from episodic acidification. The fertilized eggs of spring spawning trout (such as golden trout and rainbow trout) are susceptible to low pH in snowmelt water. However, surface water pH is currently well above the critical pH for this life stage of spring spawning trout during snowmelt in the Sierra watersheds studied. The swim-up fry of spring-spawning trout could be damaged by episodic acidification due to runoff from summer storms. The most sensitive life stages of the brook trout are larval stages, thus recruitment failure is probably responsible for the disappearance of this species from acid-stressed systems. In the Sierra, emerging brook trout larvae could be damaged by low pH runoff from summer rain storms. Sac fry of brook trout may be negatively impacted by snowmelt runoff.

Episodic acidification of streams due to snowmelt or summer rains may decrease the benthic density of some species of stream invertebrates. Vulnerable species identified in experimental work in the Emerald Lake Watershed study are the nymphs of mayflies of the genera *Baetis*, *Paraleptophlebia*, *Epeorus*, and chironomid fly larvae. When pH is lowered to 5.0 or below, for as little as 8 hours, the drift rates of vulnerable species increases, and much of the increased drift is is due to mortality (i.e. drifting insects are killed by low pH). Knowledge that acid pulses in streams can cause temporary increases in drift is useful for developing a list of macroinvertebrate species that are sensitive to low pH and that should be rare or absent in chronically acidified drainages. However, drift induced by episodic acidification may not lead to reduced benthic densities in a stream section being monitored, because if there are upstream sources of live drift, sites unoccupied by acid-killed invertebrates may be reoccupied, obscuring the effect of the acid pulse. Only if repeated acid pulses in a headwater stream cause a decrease in benthic densities over large stretches of a stream, will measurements of background drift rates and benthic densities be able to detect an impact of acidification on vulnerable stream invertebrates.

Based on the available descriptive and experimental information, certain changes in zooplankton community structure are expected if Sierra Nevada lakes become subjected to chronic acid stress in the future. *Daphnia rosea*, *Daphnia middendorffiana* and *Diaptomus signicauda* are likely to be removed if pH levels reach as low as 5.0. In the lakes in which the above species overlap seasonally with *Bosmina longirostris*, *Holopedium*, *Diaphanosoma*, *Keratella taurocephala*, or *Polyarthra vulgaris*, increases in the latter, more acid-tolerant, taxa are fairly certain. Regardless of the species involved, some increase in rotifer biomass can be expected at least temporarily after a collapse of the crustacean component of zooplankton in an acidified lake.

PART 1

CURRENT STATUS OF HIGH ELEVATION WET AND DRY DEPOSITION IN THE SIERRA NEVADA, CALIFORNIA

PART 1

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TABLES

1.1. INTRODUCTION

Chemical analysis of wet deposition for high-altitude sites in the Sierra Nevada was a focus of several CARB studies. Time series for a suite of chemical variables are available for wet deposition from the Emerald Lake watershed, conducted under contracts A3-106-32 and A6-147-32 by Jeff Dozier and John Melack, from the monitoring work by John Melack in the Lake Comparison Study (Contract A032-188), and at eleven additional sites in the High Sierra (Contract A932-081). Additional wet deposition data are forthcoming from the intensive study of two small catchments by Aaron Brown and John Melack (Contract A032-116) and from the two year study of 9 acid-sensitive lakes being conducted by John Stoddard (Contract A132-048). In addition, some data are available for six additional sites in the Sierra Nevada via the California Acid Deposition Monitoring Program (CADMP). In this chapter, information from these studies will be coalesced in order to provide a summary of the current status of high-elevation wet deposition.

1.2. DATA RESOURCES

CARB-supported studies that provide results of precipitation sampling at high elevation sites in the Sierra Nevada are listed below:

1. Blanchard C. and H. Michaels (1994) Regional estimates of acid deposition fluxes in California. Final Report to the California Air Resources Board, Contract A132-149.

2. Dozier J., J. Melack, D. Marks, K. Elder, R. Kattelmann and M. Williams (1987) Snow deposition, melt, runoff and chemistry in a small subalpine watershed, Emerald Lake Basin, Sequoia National Park. Final Report to the California Air Resources Board, Contract A3-106-32.

   The physical and chemical characteristics of snow deposition, melt and runoff were measured over the course of two field seasons in the Emerald Lake Basin. During the period of peak runoff, the loss of acid neutralizing capacity (ANC) and substantial amounts of sulfate and nitrate were observed in surface waters. A model of snowmelt chemistry was developed using energy transfer data for the watershed.

3. Dozier J., J. Melack, K. Elder, R. Kattelmann, D. Marks and M. Williams (1989) Snow, Snow Melt, Rain, Runoff and Chemistry in a Sierra Nevada Watershed. Final Report to the California Air Resources Board, Contract No. A6-147-32.

   Field work at the Emerald Lake watershed was continued in an effort to strengthen the data bases on hydrological processes in summer and snow deposition, melt and runoff in winter. The main focus of this project was to develop a statistically-based sampling regime for obtaining reliable estimates of parameters which influence snow accumulation in the watershed. On an annual basis, the mass of water that entered the basin closely matched the outputs determined from measurements of outflow through streams, evaporation and sublimation. Solutes from snowmelt pulses were also measured during intense sampling periods in 1987 and 1988. Many of the methods developed in this study have been incorporated into subsequent watershed monitoring projects.

4. Melack J., J. Sickman, F. Setaro and D. Engle (1993) Long-Term Studies of Lakes and Watersheds in the Sierra Nevada; Patterns and Processes of Surface-Water Acidification. Final Report to the California Air Resources Board, Contract No. A932-060.

   This project continued the monitoring of wet deposition and surface water discharge parameters for water years 1990 and 1991 at seven watersheds in the Sierra Nevada, to determine the interannual variability in wet deposition in regions where snowfall is the major atmospheric input. Surface water monitoring emphasized the detection of changes in ANC and pH during snowmelt. The results provide a basis for comparing the effects of acidic deposition at the Emerald Lake watershed to other high-elevation sites.

5. Melack J., J. Sickman, F. Setaro and D. Dawson (1997) Monitoring of Wet Deposition in Alpine Areas in the Sierra Nevada. Final Report to the California Air Resources Board, Contract No. A932-081.

   The purpose of this project was to initiate a long-term wet deposition monitoring program in the alpine zone of the Sierra Nevada (i.e. above elevation 2400 m). Snow volume and chemistry were measured at 11 sites by sampling the snowpack at maximum accumulation in spring. Summer rain samples were collected with Aerochem Metrics Wet/Dry collectors and tipping-bucket rain gauges. Four years of wet deposition data from the 11-site network (water years 1990, 1991, 1992, 1993) will provide the means for estimating rates of acidic material loading to high-elevation sites in the Sierra Nevada.

6. Melack J., J. Sickman, A. Leydecker and D. Marrett (1996) Comparative Analyses of High-Altitude Lakes and Catchments in the Sierra Nevada: Susceptibility to Acidification. Draft Final Report to the California Air Resources Board, Contract No. A032-188.

   This project continued the monitoring of temporal trends and patterns of wet deposition and surface-water chemistry in seven watersheds in the Sierra Nevada under Contract No. A932-060. By extending the monitoring effort for two years (water years 1992, 1993), better resolution of seasonal and long-term trends in water chemistry will be achieved.

Other CARB-supported studies included measurements of the quantity and chemistry of high elevation precipitation at sites in the Sierra Nevada, but the results were not available for inclusion in this report at the time of writing. Forthcoming Final Reports associated with these studies will expand the data set described in this report. These studies are listed below:

1. Watershed Biogeochemical Processes Affecting Surface Waters in the Sierra Nevada, with Emphasis on Snowmelt Episodes. Contract A032-116. Principal Investigators: Aaron Brown, John Melack.

   The objective of this project is to determine the extent to which snowmelt runoff reaching high-elevation lakes and streams is altered by watershed soils in the Sierra Nevada. Snowmelt runoff, soil water and surface water chemistry in two paired mini-catchments were monitored intensively during spring 1992 and 1993, in addition to special studies involving tracer compounds and manipulation of the watersheds during snowmelt.

2. Monitoring for Acidic Snowmelt Episodes in the Sierra Nevada. Contract No. A132-048. Principal Investigator: John Stoddard.

   This project is jointly sponsored by the CARB and the USEPA's Environmental Research Laboratory in Corvallis, Oregon. The purpose of this project is to determine the frequency, duration and magnitude of episodic acidification events during snowmelt in the spring. Nine of the most acid-sensitive lakes in the Sierra Nevada were selected for study, and they have been intensively sampled from March through May for two years. Samples of snowpack, snowmelt water, lake and stream water will be collected to determine if: (1) the lakes become snowmelt; and (2) levels of acidity become high enough to affect aquatic populations.

Publications. Several publications have summarized precipitation data from monitoring networks that include sites in the Sierra Nevada, or have analyzed precipitation data as part of the hydrochemical study of Emerald Lake Watershed. These are listed below:

Blanchard C.L. and K.A. Tonnesson (1993) Precipitation-chemistry measurements from the California Acid Deposition Monitoring Program, 1985-1990. Atmos. Environ. 27A: 1755-1763.

Melack J.M. and J.L. Stoddard (1991) Sierra Nevada, California. pp. 503-530. *In* Charles D.F. (ed) Acidic Deposition and Aquatic Ecosystems. Regional Case Studies. Springer-Verlag, New York.

Williams M.W. and J.M. Melack (1991) Precipitation chemistry in and ionic loading to an alpine basin, Sierra Nevada. Water Resourc. Res. 27:1563-1574.

Williams M.W., R.C. Bales, A.D. Brown and J.M. Melack (1995) Fluxes and transformations of nitrogen in a high-elevation catchment, Sierra Nevada. Biogeochemistry 28:1-31.

1.3. PRECIPITATION NETWORKS

CADMP Network Wet deposition was monitored by the CADMP at 34 sites in California. Six of these sites were located in the Sierra Nevada (Giant Forest, Lake Isabella, Quincy, S. Lake Tahoe, Soda Springs, Yosemite). Blanchard & Michaels (1994) reported results from the CADMP network of monitoring sites for wet deposition from July 1984 through June 1990, and dry deposition from early 1988 through September 1991. More recent data were not included in their analyses because they had not yet been validated by the CARB at the time of publication. Chemical data for longer time series for wet deposition at the six Sierra Nevada CADMP sites are as yet unpublished, except as listings of weekly values (Takemoto et al. 1985a, b). Unpublished volume-weighted mean concentrations and annual loadings for Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+ , NO_3^-, Cl^- and SO_4^{2-} in wet deposition at the six sites listed above for the years 1985 to 1994 were furnished to us in June 1996 by the CARB.

CARB Alpine Site Network The CARB high elevation network consisted of eleven stations: Alpine Meadows, Angora Lake, Sonora Pass, Tioga Pass, Mammoth Mountain, Eastern Brook Lake, Kaiser Pass, South Lake, Onion Valley, Emerald Lake, and Mineral King (Melack et al. 1997). The elevation of these stations ranged from ca. 2000 to 3000 m ASL. The stations spanned nearly the entire north-south extent of the Sierra Nevada from southern Sequoia National Park to the north shore of Lake Tahoe. These stations were also located on both the western and eastern slopes of the range. All of the sampling stations were located in National Forests or National Parks. Precipitation data is also available from four watersheds studied under CARB Contract No. A032-188 (Lake Comparison Study) which are not co-located with any of the eleven high elevation monitoring sites. These sites are Crystal Lake, Pear Lake, Ruby Lake, and Topaz Lake (Melack et al. 1996). Table 1 identifies the sources and types of chemical data available (rain, snow, catchment outflow) from precipitation studies carried out with CARB funding by UCSB.

1.4. IONIC LOADING FROM WET DEPOSITION

Melack & Stoddard (1991) coalesced values for annual wet deposition and volume-weighted mean concentrations of hydrogen, nitrate and sulfate from the two Sierra Nevada sites (Giant Forest, Yosemite) of the NADP program from 1981-1985, six Sierra Nevada sites of the CADMP network (Quincy, Soda Springs, S. Lake Tahoe, Yosemite, Giant Forest, Lake Isabella) from July 1985-June 1987, and CARB-supported monitoring of the Emerald Lake watershed during water years 1985-1987. Annual deposition (in meq m^{-2}) ranged from ca. 2-14 for hydrogen, 2-12 for nitrate, and 1.5-13 for sulfate. More recent data from the Emerald Lake Watershed allows us to report annual wet deposition values for a period of eight consecutive water years due to snow (Table 2). These data from the Emerald Lake

Watershed provide a wider range of values for ionic loading than previously reported (meq m^{-2}): 24-112 for hydrogen, 13-50 for nitrate and 8-55 for sulfate.

Annual wet deposition rates (rain + snow) for a suite of major ions are available for up to 4-5 consecutive water years for 20 Sierra Nevada sites (Table 3). Fourteen of these sites are over 2000 m in elevation and were monitored via CARB contract A032-188 (Lake Comparison Study) and contract A932-081 (Alpine Site Study). Data from these sites was reported for water years 1990-1993 (Melack et al. 1997). The other six sites were part of the CADMP wet deposition network (described in detail above) and are somewhat lower in elevation (only one site is above 2000 m ASL). Data from these CADMP sites was reported for water years 1985-1990 (Blanchard & Tonnessen 1993).

Sisterson et al. (1991) report mean annual wet deposition rates for major ions for each year from 1983- 1987 from 148 sampling sites representing most of the states of the continental USA and several sites in Ontario (Table 4). The eastern USA and Canada were sampled more densely than the western USA. Geographic coverage was as follows: 43 sites in southeast Canada (Ontario and Quebec); 24 sites in northeastern states (ME, NH, VT, MA, CN, RI, NY, PA, NJ); 25 sites in midwestern states (MN, WI, MI, OH, IL, IND); 12 sites in southeastern states (MD, VA, DE, NC, SC, FL); 18 sites in southern states (WV, KT, TN, GA, AL, MS, AR, TX, MO); 4 sites in central plains states (ND, SD, KS, OK, IO, NB); 8 sites in southwestern states (CO, NM, AZ, UT, NV); 6 sites in the northern Rockies (WY, MT, ID); and 7 sites along the West Coast (WA, OR, CA).

A comparison of the mean annual deposition rates for hydrogen, sulfate, nitrate, ammonium, and calcium in Table 4 with those reported for the same solutes at Sierra Nevada sites (Table 3) illustrates that loading rates for these species are low in the Sierra Nevada relative to the country as a whole. Multi-year means for annual deposition rates for H^+ ranged from 27-63 eq ha^{-1} in the Sierra Nevada (Table 3). Mean annual deposition rates for H^+ in the US and Ontario ranged from 337-407 eq ha^{-1} (Table 4). Similarly, annual deposition rates for sulfate ranged from 18-57 eq ha^{-1} in the Sierra Nevada, and from 207-241 eq ha^{-1} for the US and Ontario. Annual deposition rates for nitrate ranged from 24-77 eq ha^{-1} in the Sierra Nevada, and from 214-236 eq ha^{-1} in the US and Ontario. Finally, annual deposition rates for ammonium ranged from 7-102 eq ha^{-1} in the Sierra Nevada, and from 160-175 eq ha^{-1} in the US and Ontario. In contrast, deposition rates for calcium were similar in magnitude for the Sierra Nevada and the US and Ontario. Annual calcium deposition rates in the Sierra Nevada ranged from 13-44 eq ha^{-1}. The range for annual calcium deposition in the US and Canada was 40-51 eq ha^{-1}.

1.5. CHEMICAL COMPOSITION OF PRECIPITATION

The Global Precipitation Chemistry Project (GPCP) has provided the most complete and the largest quality-assured data set on precipitation chemistry for remote sites around the world. As of 1991, the GPCP network included six remote sites (Katherine, Australia; Cape Point, South Africa; Torres del Paine, Chile; Lijiang, China, Mauna Loa, Hawaii, and Amsterdam Island in the Indian Ocean). Discontinued sites for which data are available include San Carlos, Venezuela; St. Georges, Bermuda, and Poker Flat, Alaska. Among the criteria for inclusion in the GPCP were that sites had to be at least 1000 km from any large industrial or urban area, and removed from local volcanic influences.

The average pH and volume-weighted mean concentrations for major ions in wet precipitation at five GPCP sites is presented in Table 5. Sea salt is believed to contribute to the concentrations of SO_4^{2-}, Cl^-, Na^+, K^+, Mg^{2+}, and Ca^{2+}. The portion of K^+, Mg^{2+}, and Ca^{2+} that originates from sea salt is primarily associated with Cl^-, however the sea-salt related contribution of these cations is generally neglible in comparison to anthropogenic and soil sources (Sisterson et al. 1991). Naturally acidic, unpolluted precipitation has a pH of 5.6 (or $[H^+] = 2.5$ µeq L^{-1}) based on CO_2 dissolved in pure water. At the six GPCP sites, fewer than 10% of samples taken contained H^+ at concentrations less than 2.5 µeq L^{-1}, indicating that wet deposition in even remote sites is naturally acidic (Sisterson et al. 1991). pH at the remote sites of the GPCP ranged from 4.78 - 4.96. pH of wet deposition in the Sierra Nevada is somewhat higher - ranging from 5.22 - 5.42 over 5 water years at the Emerald Lake Watershed (Table 6). This range is not very different than that expected for other North American regions highly influenced by the Pacific Ocean. A pH value of ca. 5.1 - 5.2 is suggested for the extreme northwestern coast of North America (Sisterson et al. 1991). Hydrogen ions are less concentrated in Sierra Nevada precipitation than at the remote GPCP sites. $[H^+]$ at the Emerald Lake Watershed ranged from 3.1-6.0 µeq L^{-1} (Table 6); $[H^+]$ at the five GPCP sites was reported to range from 11.0-16.6 µeq L^{-1} (Table 5).

Melack & Stoddard (1991) reported ranges of volume-weighted mean concentrations for important ions in wet precipitation (rain + snow) for a suite of Sierra Nevada sites. Values were reported for hydrogen (3.2-6.6 µeq L^{-1}), for nitrate (2.8 -9.3 µeq L^{-1}), and for sulfate (2.3-12.1 µeq L^{-1}). An eight-year record available from the Emerald Lake Watershed

(Table 6) provides ranges for hydrogen (3.1-6.0 μeq L^{-1}), for nitrate (2.0-12 μeq L^{-1}), and for sulfate (2.5 -9.8 μeq L^{-1}) that are similar to those reported by Melack & Stoddard (1991). Concentrations of sulfate in precipitation of the Sierra Nevada occupy a similar range to that provided for non-sea salt sulfate along the northwestern coast of North America (ca. 6 - 10 μeq L^{-1}, Sisterson et al. 1991), and a narrower range than sulfate concentrations at the GPCP sites (2.9-30.6 μeq L^{-1}, Table 5). Nitrate, however is more concentrated in Sierra Nevada precipitation (see above) than in precipitation at the GPCP remote sites ($[NO_3^{-1}]$ = 1.7 - 5.5 μeq L^{-1}, Table 5).

Solute ranking in wet deposition

Solutes in snow and rain at the ten high elevation Sierra Nevada sites studied under CARB contract A932-081, and in snow at an additional four sites, were ranked according to their volume-weighted mean concentrations as described below. At each site, and for each year from 1990 to 1993, ions were ranked separately for snow and rain using data reported by Melack et al. (1995). The volume-weighted mean concentrations from pooled rain samples within a water year were used to rank ions in rain that year. The volume-weighted mean concentrations of ions in snow measured in snowpits at the time of maximum accumulation (ca. April-1) were used to rank ion species in snow for each water year. Chemical species were assigned a numerical score for each year based on their rank. A mean score for the four years was calculated for each ion, and used to derive the overall ranking for each site for snow (Table 7) and for rain (Table 8).

Snow. For every site except one (Crystal Lake), hydrogen was the most concentrated ion species in snow (Table 7). In eight of the fourteen sites, ammonium was the second-ranked ion in snowfall. Nitrate was the most commonly observed third- ranked ion. In eleven of fourteen sites, hydrogen, ammonium, and nitrate were the three highest ranked ions in snow. The exceptions were South Lake and Pear Lake, for which sulfate was third-ranked, and Sonora Pass, at which calcium was the second-ranked ion, and at which sulfate was tied with nitrate as the third most concentrated solute in snow. Chloride was more concentrated than sodium in all but two of the monitoring locations (Crystal and Ruby Lakes). Calcium ranked higher than all other base cations in the snowfall at every site except for Alpine Meadows. Potassium, magnesium, acetate and formate, in varying orders, were consistently the four lowest ranking species in the snow pack.

Rain. Nitrate and ammonium were the two most concentrated species in rain at all of the ten high elevation monitoring sites (Table 8). Sulfate ranked third in six of the ten sites, and fourth in the remaining four sites. Hydrogen ranked either third or fourth in rain at every site except for Emerald Lake, where it ranked seventh. Phosphate was the most dilute ion in rain at all of the sites. Magnesium and potassium, together with phosphate were consistently the lowest ranked ions measured in rain at all of the sites. As in snow, calcium was the highest ranked base cation. In contrast to the results for snow, sodium was higher ranked than chloride at the majority of sites (seven of ten sites).

These data illustrate the relative importance of H^+ and NH_4^+ in the charge balance of strong acid ions (SO_4^{2-}, NO_3^-, Cl^-) in wet deposition. Although, H^+ is always more concentrated in snow than NH_4^+, the neutralization of strong acid anions by NH_4^+ is reported to be higher in the snowpacks of relatively dry years than in wet years (Dozier et al. 1989). In summer rainfall, NH_4^+:H^+ is always > 1 and NH_4^+ is strongly correlated with NO_3^- and SO_4^{-2}. Thus in the summer, NH_4^+ is an important neutralizer of the strong acid anions NO_3^-, SO_4^{-2}, and Cl^-. In the absence of NH_4^+, $[H^+]$ in rainfall would potentially be 11-fold higher.

1.6. DRY DEPOSITION

Dry deposition was monitored by the CADMP at 10 sites in California and included measurements of gases (SO_2, NO_2, NH_3, O_3, HNO_3) and SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, Mg^{+2}, K^+ and Ca^{+2} in particulate dry deposition (Blanchard & Michaels 1994). Three of the sites in the dry deposition network were non-urban (Gasquet, Yosemite, Sequoia). Of these three non-urban sites, two sites (Yosemite and Sequoia) are located in the Sierra Nevada (Table 9). In general, at the three non-urban sites included in the dry deposition network of the CADMP, wet deposition of nitrate and sulfate was approximately equal to or slightly greater than dry deposition of oxidized nitrogen species (NO_2, HNO_3^-, and NO_3^-) and oxidized sulfur species (SO_4^{-2} and SO_2), respectively.

Williams & Melack (1991) concluded that dry deposition was not an important contributor of hydrogen, nitrate or sulfate to the winter snowpack of the Emerald Lake Basin. Their evidence was that the cumulative amount of these solutes (as eq m^{-2}) obtained by summing measurements from snowboard samples from single snow events was similar (in the case of H^+ and SO_4^{2-}) or greater than (ca. 20% in the case of NO_3^-) the accumulated deposition of these solutes measured in snowpits both at midwinter and later at the time of maximum snow accumulation (ca. April). Although dry deposition must have occurred onto the snowpack during winter, its contribution to snowpack totals was undetectable, or the loss of certain solutes from the snowpack over winter (in the case of nitrate) obscured contributions from dry deposition.

1.7. QUALITATIVE ANALYSES OF WET DEPOSITION

Many studies have examined relationships between chemical species in precipitation in order to make inferences about the sources of the solutes in rain and snow and the meteorological processes by which they are transported and deposited. Hooper & Peters (1989) evaluated relationships between the major solutes in wet deposition collected from 1980-1987 at 194 sites in the NADP/NTN network. They hypothesized three associations of solutes: 1) acidic solutes resulting from the combustion of fossil fuels (H^+, SO_4^{2-}, NO_3^-); 2) salt originating from sea salt or road salt (primarily Na^+ and Cl^-); 3) solutes arising from agriculture and soil (primarily base cations Ca^{2+}, Mg^{2+} and K^+ and/or the nitrogenous solutes NO_3^- and NH_4^+) arising from fertilizers, feed lots and dust particles. The review by Sisterson et al. (1991) categorizes solutes according to probable sources. Wind-blown soil and dust from the tilling of fields and from use of unpaved roadways are assumed to be the major contributors of Ca^{2+}, Mg^{2+} and K^+. Sea salt is the primary source of Na^+ and Cl^- in wet deposition. Anthropogenic emissions are assumed to be the primary sources of H^+, SO_4^{2-} and NO_3^-. Finally, NH_4^+ arises primarily from natural soil processes. In addition to these major associations, Sisterson et al. (1991) provide examples of more localized phenomena that can contribute solutes to precipitation. Wintertime road salting (such as with $CaCl_2$), cement plants and other industries can be sources of Ca^{2+}, Mg^{2+} and K^+. Na^+ and Cl^- can be locally increased by wintertime road salting with NaCl. Biogeochemical processes in wetlands such as swamps, bogs and marshes contribute SO_4^{2-}. Nitrate can originate from domestic woodburning, such as in fireplaces and wood stoves. Finally, feed lots and sludge ponds are alternative localized sources of NH_4^+.

One of the dominant relationships discovered for analytes in aerosols or precipitation of the eastern half of the United States is that $Na^+ = Cl^-$ (Sisterson et al. 1991). There are no known terrestrial sources of chloride near the Sierra Nevada, thus it is reasonable to assume that most chloride in precipitation in this region originates from sea salt aerosols. Deviations of the $Na^+:Cl^-$ ratio in precipitation from 1.0 can be indicative of the relative importance of sea salt aerosols in determining the ionic composition of precipitation. For each of the four years studied by Melack et al. (1997), the annual mean Na:Cl was higher in rainfall than in snow (Tables 10 - 11). In 1990-1992, the Na:Cl for rain was > 1.0, indicating that rainfall was depleted in Cl^- with respect to sea salt aerosol. In contrast, the annual mean Na:Cl for snow was < 1.0 for three of the four years studied (1990, 1991, 1993) and equal to 1.0 in 1992. Thus winter precipitation was enriched with chloride relative to summertime precipitation.

This result is consistent with seasonal differences in the meteorological sources of precipitation for the Sierra Nevada. Apparently, frontal systems that originate over the Pacific Ocean are not contaminated with strong acids (Williams & Melack 1991). Urban and agricultural activities in the San Joaquin valley are heavy contibutors of NH_4^+ and NO_3^-. In normal or wet years, higher relative Cl^- and lower strong acid anion concentrations (nitrate and sulfate) suggest that the oceanic frontal systems undergo only limited mixing with terrestrial air masses before depositing snow in the Sierra Nevada. In relatively dry winters, storms are produced closer to the Sierra Nevada. For example, in the dry years 1987 and 1988, concentrations of Cl^- and Na^+ in the snowpack of the Emerald Lake watershed were halved, and NO_3^- and NH_4^+ more than doubled, as compared to the snowpacks in the wet years 1985 and 1986 (Dozier et al. 1989). The resulting low ranking for Cl^- and Na^+, and high ranking of NO_3^- and NH_4^+, suggests that a major source of ions in snow in the two dry years was air masses that originated over land from convective sources or from the mixing of weak fronts with air over the Central Valley. Low Cl^- and high NH_4^+ in rain suggest that localized convective storms (e.g. San Joaquim Valley air masses that are pulled into the Sierra by upslope heating) are the main source of these ions in summertime.

Due to the differences in the meteorological sources of winter and summer precipitation, a seasonal difference in the chemistry of rainfall and snowfall may be expected in the Sierra Nevada. There was a pronounced difference in the NH_4^+:Cl^- ratio of snowfall and rainfall in the high elevation sites studied under CARB contract A932-188 (Alpine Site Study). Annual means for NH_4^+:Cl^- in rainfall for the four years 1990 - 1993 ranged from 4.90 to 8.40 (Table 12). Values in snowfall were much lower. Annual means for NH_4^+:Cl^- for 14 sites for the years 1990-1993 ranged from 1.46 to 2.80 (Table 13). This seasonal difference in NH_4^+:Cl^- reflects the greater influence of urban and agricultural pollutants in the air masses which ultimately produce wet deposition in the high Sierra Nevada in summer months.

Nitrate in wet deposition is as important, or more important, than sulfate as an acidifying agent in high elevation areas of California (Williams & Melack 1991). The nitrate:sulfate ratio in wet deposition is often used to evaluate geographical or temporal variation in the relative importance of these two strong acid anions in causing the acidity of precipitation. Seasonal and geographic variation in the molar nitrate:sulfate ratio of wet precipitation was investigated by Summers & Barrie (1986) using four years of precipitation chemistry data from eastern North America. The factors attributed by these authors to be responsible for variations in this ratio were the proportions of sulfate and nitrate in upwind emissions, the relative rates of oxidation of the gaseous oxides to secondary products, and the relative efficiencies of the dry and wet removal of the gaseous and particulate S and N compounds. Four distinctive patterns were observed in their study. In northeastern US and southeastern Canada, the ratio reached a strong summer minimum in rainfall (ca. 0.67) and a strong winter maximum in snowfall (ca. 2.0). Many other studies report a lower nitrate:sulfate ratio in rain than in snow (Williams & Melack 1991). This may be attributable to preferential scavenging by snow of nitrate over sulfate. However, seasonal variation in the nitrate:sulfate ratio does not always follow this pattern. In the southern states Texas, Louisiana and Mississippi, Summers & Barrie (1986) observed a winter minimum and a summer maximum in the nitrate:sulfate of precipitation. In the upper midwest and central states, two minima (spring and fall) and two maxima (summer and winter) in nitrate:sulfate were observed in wet deposition. Finally, in the southeastern US, no systematic minima or maxima in this ratio were observed. The lowest nitrate:sulfate ratio was observed in the Appalachian mountains (0.67).

In California, NO_X emissions can be three times higher than SO_2 emissions. Nevertheless, the range of values for nitrate:sulfate in wet deposition in high elevation regions of California does not differ greatly from the range of values observed in eastern North America. In the study of Williams & Melack (1991) the annual mean ratio of nitrate to sulfate in winter snow at the Emerald Lake Watershed varied from 0.77 to 1.75 on an equivalent basis during water years 1985-1988. The ratio was lowest in years of normal or above normal snowfall and greatest in years of below normal snowfall. The same ratio in rain at the Emerald Lake Watershed varied from 1.11 to 1.32. The nitrate to sulfate ratio was generally higher in autumn snow than in winter snow, ranging from 1.47 to 2.93. These results are consistent with the finding by Dozier et al. (1989) that the ratio $NO_3^-:SO_4^{-2}$ in the Emerald Lake Watershed snowpack was highest in dry year snowpacks. A major source of ions in snow in dry years are air masses that originate over land from convective sources or from the mixing of weak fronts with air over the Central Valley.

For the ten high altitude sites studied in water years 1990 to 1993 (Melack et al. 1997), the overall annual mean nitrate:sulfate ratios in rainfall (combining sites for each year) ranged from 1.25 to 1.48 (Table 14), and the overall annual mean nitrate:sulfate ratios in snowfall ranged from 0.87 to 1.87 (Table 15). Within each water year, values varied between sites. For example, in water year 1990, nitrate:sulfate in rain ranged from 1.13 to 1.83 and in snow from 0.87 to 2.28. In water year 1991, nitrate:sulfate in rain ranged from 1.22 to 1.88 and in snow from 0.53 to 3.14. In three of the four years studied, Onion Valley had the lowest ratio of nitrate:sulfate in rainfall. In the fourth year (1993) rain at Mammoth Mountain had the lowest nitrate:sulfate ratio. Rain at Alpine Meadows had consistently high-end values for nitrate:sulfate from 1990-1993. Otherwise, consistent spatial differences were not apparent. For example, although in 1993, Mammoth Mountain received rain with the lowest nitrate:sulfate, in the water year 1990, it received rain with the highest nitrate:sulfate of the ten sites studied. Annual means for nitrate:sulfate in rain among individual sites ranged from 0.92 to 2.06 over the course of all four years studied. Both the minimum and maximum values were obtained in the same water year (1993). Nitrate:sulfate in snowfall among individual sites ranged from 0.53 to 4.30 over the four years.

The statistical relationship between $[NH_4^+]$ and $[NO_3^- + SO_4^{2-}]$ in wet deposition was used as a tool by Williams & Melack (1991) to investigate possible sources of these two strong acid anions in precipitation at the Emerald Lake Watershed. When the two variables were significantly related to each other (via linear regression, $[NH_4^+]$ as the independent variable), the interpretation given by the authors was that ammonium salt aerosols were the source of the strong acid ions, rather than nitric or sulfuric acids. If y-intercepts were negative, the implication was that not all of the deposition of NO_3^- and SO_4^{2-} could be accounted for by salt aerosols. Ammonium was significantly related to the sum of nitrate and sulfate for a data set comprised of measurements for individual snowfalls in the Emerald Lake watershed (Williams & Melack 1991). In an analagous manner, the relationship between $[NH_4^+]$ and $[NO_3^- + SO_4^{2-}]$ was investigated for this report separately for rain and snow for other high elevation sites in the Sierra Nevada (Table 16). For each year from 1990 to 1993, annual mean volume-weighted concentrations of the three ion species were used for all sites for which data were available, and linear regression performed for each year. Sources included published values in Melack et al. (1997) and unpublished data for additional sites provided by Jim Sickman. The slopes of the regressions were significant for all analyses except for rain in 1991 ($p=0.08$, Table 16), implying that ammonium-nitrate and ammonium-sulfate aerosols may be largely responsible for the wet deposition of nitrate and sulfate in these habitats. In most cases, however, the y-intercept of the regression lines were negative, suggesting that some portion of the combined deposition of sulfate and nitrate was due to other contaminants, including nitric and sulfuric acids.

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Table 1. Availability of wet precipitation chemistry and outflow chemistry data from CARB sponsored research in the Sierra Nevada (UCSB Contracts). Letters refer to CARB Reports as follows: A--Melack et al. (1997) "Alpine Site Study"; B--Melack et al. (1996) "Lake Comparison Study"; C--Melack--unpublished data. Where more than one references is listed, values cited for that parameter are differ between references. "Solutes" refers to the following suite of measured species: H^+, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_2^-, $CH_2CO_2.^-$

	RAIN				SNOW				OUTFLOW			
SITE	Period	[solutes] Eq·L^{-1}	pH	solute loading Eq·ha^{-1}	Year	[solutes] Eq·L^{-1}	pH	solute loading Eq·ha^{-1}	Year	[solutes] Eq·L^{-1}	ANC Eq·L^{-1}	solute flux Eq·ha^{-1}
EMERALD LAKE	1990 Nov-Oct	A	A	A	1985	B	---	B	1985	B	B	B
	1991 Nov-Oct	A	A	A	1986	B	---	B	1986	B	B	B
	1992 Nov-Oct	A	A	A	1987	B	---	B	1987	B	B	B
	1993 Nov-Oct	A	A	A	1988	B	---	B	1988	B	B	B
					1989	B	---	B	1989	B	B	B
	1985 Oct-Sept	B	---	B	1990	A, B	A	A, B	1990	B	B	B
	1986 Oct-Sept	B	---	B	1991	A, B	A	A, B	1991	B	B	B
	1987 Oct-Sept	B	---	B	1992	A, B	A	A, B	1992	B	B	B
	1990 Oct-Sept	B	---	B	1993	A, B	A	A, B	1993	B	B	B
	1991 Oct-Sept	B	---	B	1994	B	---	B	1994	B	B	B
	1992 Oct-Sept	B	---	B								
	1993 Oct-Sept	B	---	B	1995	C	C	C				
	1994 Oct-Sept	B	---	B	1996	C	C	C				
	1995	C	C	C								
	1996	C	C	C								
PEAR LAKE	1990	(rain volume only)			1990	B	---	B	1990	B	B	B
	1991		"		1991	B	---	B	1991	B	B	B
	1992		"		1992	B	---	B	1992	B	B	B
	1993		"		1993	B	---	B	1993	B	B	B
TOPAZ LAKE	1990	(rain volume only)			1990	B	---	B	1990	B	B	B
	1991		"		1991	B	---	B	1991	B	B	B
	1992		"		1992	B	---	B	1992	B	B	B
	1993		"		1993	B	---	B	1993	B	B	B
					1994	C	C	C				
					1995	C	C	C				
					1996	C	C	C				

Table 1. (continued)

	RAIN				SNOW				OUTFLOW			
SITE	Period	[solutes] Eq·L^{-1}	pH	solute loading Eq·ha^{-1}	Year	[solutes] Eq·L^{-1}	pH	solute loading Eq·ha^{-1}	Year	[solutes] Eq·L^{-1}	ANC Eq·L^{-1}	solute flux Eq·ha^{-1}
CRYSTAL LAKE	1990		(rain volume only)		1990	B	---	B	1990	B	B	B
	1991		"		1991	B	---	B	1991	B	B	B
	1992		"		1992	B	---	B	1992	B	B	B
	1993		"		1993	B	---	B	1993	B	B	B
					1994	C	C	C				
RUBY LAKE	1990		(rain volume only)		1990	B	---	B	1990	B	B	B
	1991		"		1991	B	---	B	1991	B	B	B
	1992		"		1992	B	---	B	1992	B	B	B
	1993		"		1993	B	---	B	1993	B	B	B
	1994		"		1994	B	---	B	1994	B	B	B
					1995	C	C	C				
					1996	C	C	C				
SPULLER LAKE	1990		(rain volume only)		1990	B	---	B	1990	B	B	B
	1991		"		1991	B	---	B	1991	B	B	B
	1992		"		1992	B	---	B	1992	B	B	B
	1993		"		1993	B	---	B	1993	B	B	B
	1994		"		1994	B	---	B	1994	B	B	B
					1995	C	C	C				
					1996	C	C	C				
LOST LAKE	1990		(rain volume only)		1990	B	---	B	1990	B	B	B
	1991		"		1991	B	---	B	1991	B	B	B
	1992		"		1992	B	---	B	1992	B	B	B
	1993		"		1993	B	---	B	1993	B	B	B

Table 1. (continued)

		RAIN			SNOW				OUTFLOW			
SITE	Period	[solutes] Eq·L^{-1}	pH	solute loading Eq·ha^{-1}	Year	[solutes] Eq·L^{-1}	pH	solute loading Eq·ha^{-1}	Year	[solutes] Eq·L^{-1}	ANC Eq·L^{-1}	solute flux Eq·ha^{-1}
MAMMOTH MTN.	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				
reported as "Crystal L."	1990 Oct-Sept	B	---	B								
	1991 Oct-Sept	B	---	B								
	1992 Oct-Sept	B	---	B								
	1993 Oct-Sept	B	---	B								
	1994 Oct-Sept	B	---	B								
	1995	C	C	C								
TIOGA PASS	1990 Nov-Oct	A	A	A								
	1991 Nov-Oct	A	A	A								
	1992 Nov-Oct	A	A	A								
	1993 Nov-Oct	A	A	A								
reported as "Spuller L."	1990 Oct-Sept	B	---	B								
	1991 Oct-Sept	B	---	B								
	1992 Oct-Sept	B	---	B								
	1993 Oct-Sept	B	---	B								
	1994 Oct-Sept	B	---	B								
ANGORA LAKE	1990 Nov-Oct	A	A	A								
	1991 Nov-Oct	A	A	A								
	1992 Nov-Oct	A	A	A								
	1993 Nov-Oct	A	A	A								
reported as "Lost L."	1990 Oct-Sept	B	---	B								
	1991 Oct-Sept	B	---	B								
	1992 Oct-Sept	B	---	B								
	1993 Oct-Sept	B	---	B								
	1994 Oct-Sept	B	---	B								
	1995	C	C	C								

Table 1. (continued)

	RAIN			SNOW				OUTFLOW			
SITE	Period	[solutes] $Eq \cdot L^{-1}$	pH	solute loading $Eq \cdot ha^{-1}$	Year	[solutes] $Eq \cdot L^{-1}$	pH	solute loading $Eq \cdot ha^{-1}$	Year	[solutes] $Eq \cdot L^{-1}$	ANC $Eq \cdot L^{-1}$	solute flux $Eq \cdot ha^{-1}$
E. BROOK LAKE	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				
reported as "Ruby L."	1990 Oct-Sept	B	---	B								
	1991 Oct-Sept	B	---	B								
	1992 Oct-Sept	B	---	B								
	1993 Oct-Sept	B	---	B								
	1994 Oct-Sept	B	---	B								
ALP. MEADOWS	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				
SONORA PASS	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				
ONION VALLEY	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				
SOUTH LAKE	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				

Table 1. (continued)

	RAIN				SNOW				OUTFLOW			
SITE	Period	[solutes] Eq·L^{-1}	pH	solute loading Eq·ha^{-1}	Year	[solutes] Eq·L^{-1}	pH	solute loading Eq·ha^{-1}	Year	[solutes] Eq·L^{-1}	ANC Eq·L^{-1}	solute flux Eq·ha^{-1}
E. BROOK LAKE	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				
reported as "Ruby L."	1990 Oct-Sept	B	---	B								
	1991 Oct-Sept	B	---	B								
	1992 Oct-Sept	B	---	B								
	1993 Oct-Sept	B	---	B								
	1994 Oct-Sept	B	---	B								
ALP. MEADOWS	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				
SONORA PASS	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				
ONION VALLEY	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				
SOUTH LAKE	1990 Nov-Oct	A	A	A	1990	A	A	A				
	1991 Nov-Oct	A	A	A	1991	A	A	A				
	1992 Nov-Oct	A	A	A	1992	A	A	A				
	1993 Nov-Oct	A	A	A	1993	A	A	A				

Table 2. Ionic loading (eq ha^{-1}) of the Emerald Lake Basin snowpack at maximum snow accumulation.

Year	H^+	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NO_3^-	SO_4^{2-}	Cl^-	PO_4^{3-}	$CH_3CO_2^-$	HCO_2^-
1985[a]	53	9	23	7	19	9	23	31	41	na	na	na
1986[a]	95	49	18	7	31	17	50	41	63	na	na	na
1987[a]	31	25	11	7	4	3	28	19	10	na	3	2
1988[a]	24	12	9	3	6	2	13	8	9	na	13	4
1990[b]	28.2	27.6	7.6	3.5	10.9	2.9	15.4	15.6	12.9	na	6.2	2.6.
1991[b]	32.9	28.7	11.0	3.7	9.9	2.7	17.0	11.5	11.6	na	2.2	3.0
1992[b]	18.2	22.0	15.9	3.1	6.0	0.8	19.3	12.5	10.9	0.0	3.8	3.5
1993[b]	111.9	51.0	20.0	11.9	34.9	6.2	40.8	54.6	64.0	na	13.8	5.4
1994[c]	23	25	21	4	8	6	20	11	13	na	0	3

[a] Data from Williams & Melack (1991).

[b] Data from Melack et al. (1997).

[c] Data from Melack et al. (1996).

Table 3. Elevation (m) and mean annual solute loadings (eq $ha^{-1}yr^{-1}$, rain + snow) for sites in the Sierra Nevada.

Site	(m)	H^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
Alpine Meadows[a]	2164	57.7	44.3	21.4	47.6	33.0	25.2	7.0	17.9	8.3
Angora Lake[a]	2286	61.5	58.8	32.7	54.0	44.7	34.1	8.9	28.0	7.6
Crystal Lake[b]	2951	50.8	53.7	15.2	45.7	36.9	34.0	9.1	17.4	10.5
Eastern Brook Lake[a]	3170	26.9	23.2	7.1	24.1	18.2	16.0	5.1	5.0	3.9
Emerald Lake[a]	2824	57.8	59.6	29.4	46.2	40.7	22.9	8.2	21.1	7.7
Mammoth Mountain[a]	2940	63.1	55.5	18.1	48.6	42.4	25.4	5.8	17.1	6.1
Mineral King[a]	2694	33.2	57.0	14.7	45.7	30.8	23.1	7.3	12.1	8.2
Onion Valley[a]	2800	34.6	32.3	8.2	31.6	24.2	21.1	5.4	7.8	4.7
Pear Lake[b]	2904	45.7	59.3	22.1	45.5	39.3	21.7	7.4	19.8	7.6
Ruby Lake[b]	3426	49.7	35.7	10.5	37.1	31.1	28.1	5.2	10.4	3.3
Sonora Pass[a]	2937	40.5	30.5	10.2	31.6	27.6	22.5	8.1	11.1	6.9
South Lake[a]	3010	34.1	24.3	7.3	28.2	21.9	13.7	3.8	5.7	2.9
Tioga Pass[a]	2993	62.4	45.7	16.9	43.9	36.4	29.2	7.3	15.6	8.2
Topaz Lake[b]	3219	33.0	44.0	15.7	35.4	30.1	33.2	5.4	15.1	7.4
Giant Forest[c]	1865	------	106.0	19.2	79.6	46.3	54.5	19.7	20.2	6.5
Lake Isabella[c]	1200	------	19.8	25.5	25.6	16.9	28.6	11.5	25.6	4.7
Quincy[c]	1000	------	33.0	23.8	45.4	40.4	60.3	20.8	23.2	6.7
S. Lake Tahoe[c]	1880	------	21.3	9.8	26.5	20.8	19.2	7.0	10.1	3.9
Soda Springs[c]	2200	------	60.4	47.2	83.1	69.0	111.2	30.3	38.1	9.8
Yosemite[c]	1408	------	55.4	21.9	54.6	39.1	41.5	16.0	20.8	5.6

[a] Data from Melack et al. (1997). Values are means for water years 1990-1993 (water year defined Nov.1-Oct.31).

[b] Data from Melack et al. (1996). Values are means for water years 1990-1993 (water year defined Oct.1-Sep.30).

[c] Means were calculated using yearly solute loadings provided by the CARB (S. Brown, pers. comm.). Values are means for water years 1990-1993 (water year defined July-June).

Table 4. Mean annual solute loadings (eq ha^{-1}) in wet deposition at monitoring sites in the US and Canada[a]. For geographic distribution of sites see text.

Ion Species	year	N	mean eq/ha	SD eq/ha	range
H^+	1982	108	407	218	0 - 883
	1983	108	347	189	0 - 823
	1984	108	377	208	10 - 923
	1985	108	367	208	10 - 962
	1986	108	367	228	10 - 1012
	1987	108	337	189	10 - 933
SO_4^{2-}	1982	102	241	104	18 - 456
	1983	102	225	97	27 - 421
	1984	102	236	105	21 - 451
	1985	102	229	111	19 - 496
	1986	102	221	111	20 - 555
	1987	102	207	102	13 - 458
NO_3^-	1982	119	218	94	16 - 428
	1983	119	214	90	29 - 457
	1984	119	236	107	23 - 478
	1985	119	234	117	11 - 499
	1986	119	224	110	20 - 523
	1987	119	220	105	19 - 472
NH_4^+	1982	119	168	81	22 - 412
	1983	119	166	77	22 - 397
	1984	119	175	79	21 - 348
	1985	119	162	88	7 - 481
	1986	119	161	88	10 - 416
	1987	119	160	83	14 - 376
Ca^+	1982	114	47	28	8 - 157
	1983	114	51	30	13 - 169
	1984	114	51	28	8 - 197
	1985	114	45	29	9 - 133
	1986	114	40	26	8 - 149
	1987	114	41	32	7 - 218

[a] Data adapted from Sisterson et al. (1991).

Table 5. Average pH, and volume weighted mean concentrations (μeq L^{-1}) of solutes in precipitation at GPCP sites.[a]

Site	N	Avg. pH	H^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
Amsterdam Island	26	4.92	12.0	2.1	208	1.7	30.6	7.4	38.7	177	3.7
Poker Flat	16	4.96	11.0	1.1	2.6	1.9	7.2	0.1	0.2	1.0	0.6
Katherine	40	4.78	16.6	2.0	11.8	4.3	6.3	2.5	2.0	7.0	0.9
San Carlos	14	4.81	15.5	2.3	2.5	2.6	2.9	0.3	0.5	1.8	0.8
St. Georges	67	4.79	16.2	3.8	175	5.5	36.3	9.7	34.5	147	4.3

[a] Adapted from Sisterson et al. (1991).

Table 6. Volume weighted mean concentrations of solutes in annual wet deposition (rain + snow) for Emerald Lake Watershed. Units for solutes are $\mu eq\ L^{-1}$. Units for specific conductivity (S.C.) are $\mu S\ cm^{-1}$.

Water Year	pH	S.C.	H^+	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NO_3^-	SO_4^{2-}	Cl^-	CH_3CO_2	HCO_2
1985[a]	5.24	4.4	5.8	2.6	2.9	0.8	2.4	1.0	3.5	3.7	4.5	------	------
1986[a]	5.31	3.8	4.9	3.3	1.3	0.4	1.6	0.9	3.1	2.5	3.2	------	------
1987[a]	5.22	6.2	6.0	14.4	5.6	1.9	3.5	1.0	11.9	9.8	2.8	------	------
1990[b]	5.32	------	4.8	5.7	2.6	0.9	2.5	1.3	4.9	4.2	2.4	1.0	0.5
1991[b]	5.42	------	3.8	6.7	2.0	0.7	1.2	0.6	3.6	2.5	1.4	1.7	1.0
1992[c]	------	------	3.1	5.3	2.7	0.6	1.6	0.6	5.6	4.1	1.9	2.4	3.2
1993[c]	------	------	5.2	2.6	0.9	0.5	1.5	0.3	2.0	2.6	2.7	0.4	0.7
1994[d]	-----	-----	3.3	3.9	3.3	0.7	1.2	0.9	3.3	2.0	1.8	0.3	0.8

[a] Data from Williams & Melack (1991).

[b] Data from Melack et al. (1993).

[c] Adapted from Melack et al. (1997). Water year defined Nov.1 - Oct.30.

[d] Data from Melack et al. (1996). Water year defined Oct.1 - Sep.30.

Table 7. Solute rankings in snow at high elevation sites in the Sierra Nevada. Rankings were calculated using annual volume-weighted mean concentrations from snowpits dug at maximum accumulation during water years 1990-1993, reported in Melack et al. (1997). See text for details.

Alpine Meadows	H^+	>	NH_4^+	>	NO_3^-	>	SO_4^{-2}	>	Cl^-	>	Na^+	>	Ca^{+2}	>	K^+	>	Mg^{+2}	>	OAc	>	OFm
Angora Lake	H^+	>	NH_4^+	>	NO_3^-	>	SO_4^{-2}	>	Cl^-	>	Ca^{+2}	>	Na^+	>	OAc	>	OFm	>	Mg^{+2}	>	K^+
Eastern Brook	H^+	>	NO_3^-	>	NH_4^+	>	Ca^{+2}	>	SO_4^{-2}	>	Cl^-	>	Na^+	=	Mg^{+2}	>	K^+	>	OFm	>	OAc
Emerald Lake	H^+	>	NH_4^+	>	NO_3^-	>	SO_4^{-2}	>	Cl^-	>	Ca^{+2}	>	Na^+	>	Mg^{+2}	>	OAc	>	K^+	=	OFm
Mammoth Mtn.	H^+	>	NH_4^+	>	NO_3^-	>	SO_4^{-2}	>	Ca^{+2}	>	Cl^-	>	Na^+	>	OFm	>	K^+	>	OAc	=	Mg^{+2}
Mineral King	H^+	=	NH_4^+	>	NO_3^-	>	Ca^{+2}	>	SO_4^{-2}	>	Cl^-	>	Na^+	>	Mg^{+2}	>	K^+	=	OAc	=	OFm
Onion Valley	H^+	>	NO_3^-	>	NH_4^+	>	Ca^{+2}	>	SO_4^{-2}	>	Cl^-	>	Na^+	>	K^+	>	Mg^{+2}	>	OFm	>	OAc
Sonora Pass	H^+	>	Ca^{+2}	>	NO_3^-	=	SO_4^{-2}	>	NH_4^+	>	Cl^-	=	Na^+	>	K^+	=	Mg^{+2}	>	OFm	>	OAc
South Lake	H^+	>	NO_3^-	>	SO_4^{-2}	>	NH_4^+	>	Ca^{+2}	>	Cl^-	>	OAc	=	OFm	=	Na^+	>	Mg^{+2}	>	K^+
Tioga Pass	H^+	>	NH_4^+	>	NO_3^-	=	SO_4^{-2}	>	Ca^{+2}	>	Cl^-	>	Na^+	>	K^+	>	Mg^{+2}	>	OAc	>	OFm
Pear Lake	H^+	>	NH_4^+	>	SO_4^{-2}	>	NO_3^-	>	Cl^-	>	Ca^{+2}	>	Na^+	>	OFm	>	OAc	=	Mg^{+2}	>	K^+
Topaz Lake	H^+	>	NH_4^+	>	NO_3^-	>	SO_4^{-2}	>	Ca^{+2}	>	Cl^-	>	Na^+	>	OAc	>	OFm	>	K^+	>	Mg^{+2}
Crystal Lake	NH_4^+	>	H^+	>	NO_3^-	>	Ca^{+2}	>	SO_4^{-2}	>	Na^+	>	Cl^-	>	K^+	>	Mg^{+2}	>	OAc	=	OFm
Ruby Lake	H^+	>	NO_3^-	>	NH_4^+	=	SO_4^{-2}	=	Ca^{+2}	>	Na^+	=	Cl^-	>	OAc	=	OFm	>	Mg^{+2}	>	K^+

Table 8. Solute rankings in rain at high elevation sites in the Sierra Nevada. Rankings were calculated using annual volume-weighted mean concentrations for water years 1990-1993 reported in Melack et al. (1997). See text for details.

Alpine Meadows	NO_3^-	>	NH_4^+	>	H^+	>	Ca^{+2}	>	SO_4^{-2}	>	OAc	>	Na^+	>	Cl^-	>	OFm	>	K^+	>	Mg^{+2}	>	PO_4^{-3}
Angora Lake	NO_3^-	>	NH_4^+	>	SO_4^{-2}	>	H^+	>	Ca^{+2}	>	OAc	>	Na^+	>	OFm	>	Cl^-	>	K^+	=	Mg^{+2}	>	PO_4^{-3}
Eastern Brook	NO_3^-	>	NH_4^+	>	SO_4^{-2}	=	H^+	>	Ca^{+2}	>	OFm	>	OAc	>	Cl^-	>	Na^+	>	Mg^{+2}	>	K^+	>	PO_4^{-3}
Emerald Lake	NO_3^-	>	NH_4^+	>	SO_4^{-2}	>	OFm	>	Ca^{+2}	>	OAc	>	H^+	>	Na^+	>	Cl^-	>	K^+	>	Mg^{+2}	>	PO_4^{-3}
Mammoth Mtn.	NH_4^+	>	NO_3^-	>	SO_4^{-2}	>	H^+	>	OFm	>	Ca^{+2}	>	OAc	>	Na^+	>	Cl^-	>	Mg^{+2}	>	K^+	>	PO_4^{-3}
Mineral King	NO_3^-	=	NH_4^+	>	SO_4^{-2}	>	H^+	=	Ca^{+2}	>	OFm	>	Na^+	>	Cl^-	>	OAc	>	K^+	>	Mg^{+2}	>	PO_4^{-3}
Onion Valley	NO_3^-	=	NH_4^+	>	SO_4^{-2}	>	H^+	=	Ca^{+2}	>	OFm	>	OAc	>	Cl^-	>	Na^+	>	Mg^{+2}	>	K^+	>	PO_4^{-3}
Sonora Pass	NO_3^-	>	NH_4^+	>	H^+	>	SO_4^{-2}	>	OFm	>	Ca^{+2}	>	OAc	>	Na^+	>	Cl^-	>	Mg^{+2}	>	K^+	>	PO_4^{-3}
South Lake	NO_3^-	=	NH_4^+	>	H^+	>	SO_4^{-2}	>	Ca^{+2}	>	OFm	>	OAc	>	Cl^-	>	Na^+	>	Mg^{+2}	>	K^+	>	PO_4^{-3}
Tioga Pass	NH_4^+	>	NO_3^-	>	H^+	>	SO_4^{-2}	>	Ca^{+2}	=	OFm	>	OAc	>	Na^+	>	Cl^-	>	K^+	=	Mg^{+2}	>	PO_4^{-3}

Table 9. Mean annual deposition of total sulfur and total nitrogen (eq ha^{-1} yr^{-1}) from wet and dry deposition at two CADMP sites in the Sierra Nevada.[a]

Site	Elevation	Total Nitrogen		Total Sulfur	
		wet	dry	wet	dry
Giant Forest (Sequoia)	1,865 m	185	99	26	10
Yosemite	1,408 m	140	78	22	9

[a] Adapted from Blanchard & Michaels (1994).

Table 10. Sodium:chloride ratios in rain at high elevation sites in the Sierra Nevada. Ratios were calculated using the VWM concentrations of Na^+ and Cl^- reported in Melack et al. (1997).

			Na/Cl		
Site	1990	1991	1992	1993	1994
Alpine Meadows	0.85	1.37	1.49	0.63	
Angora Lake	1.05	1.48	1.35	1.18	
Eastern Brook Lake	0.87	0.70	1.34	0.92	
Emerald Lake	1.64	0.88	1.40	0.78	0.90[b]
Kaiser Pass	NA	1.08	1.38	0.92	
Mammoth Mountain[a]	1.05	1.85	1.51	0.77	
			1.45	0.86	
Mineral King	1.21	0.84	1.19	0.85	
Onion Valley[a]	0.99	0.89	1.07	0.76	
			1.07	0.93	
Sonora Pass	0.89	0.80	2.39	1.36	
South Lake	0.76	0.77	1.58	1.03	
Tioga Pass	1.76	0.75	1.10	1.01	1.27[b]
Mean	1.11	1.04	1.41	0.92	
(SD)	(0.34)	(0.37)	(0.34)	(0.19)	
N	10	11	13	13	

[a] For 1992 and 1993, values are reported for two co-located precipitation collectors.

[b] Data from Melack et al. (1996).

Table 11. Sodium:chloride ratios in snow at high elevation sites in the Sierra Nevada. Ratios for sites were calculated using volume weighted mean concentrations from duplicate snowpits (Melack et al. 1997). Except where noted, snowpits were dug at the time of maximum snow accumulation (ca. April 1). Annual means for each year were calculated using all cases.

			Na/Cl		
Site	1990	1991	1992	1993	1994
Alpine Meadows[a]	1.08	0.78	0.91	0.82	
	0.67	0.59	0.89	0.86	
Crystal Lake	1.21	1.02	0.97	1.21	
Eastern Brook Lake	0.30	0.57	1.04	0.41	
Emerald Lake[a]	0.93	0.78	0.75	0.59	0.42[d]
	0.85	0.85	0.55	0.55	
Kaiser Pass	NA	1.1	0.92	0.77	
Long Lake	0.79	0.66	1.15	0.78	
Mammoth Mountain[b]	0.62	0.96	1.12	0.58	
	0.80	0.75	1.27	0.90	
		0.73			
Mineral King	0.80	0.86	0.70	0.61	
Onion Valley[c]	1.01	0.80	1.85	0.75	
		0.61			
Pear Lake	0.80	0.91	0.94	0.75	
Ruby Lake	1.09	0.85	1.66	0.82	0.91[d]
Sonora Pass	0.63	1.75	1.22	0.74	
South Lake	0.35	0.78	0.78	0.82	
Spuller Lake	0.53	0.91	0.88	0.79	
Topaz Lake[c]	0.77	0.92	0.40	0.95	
		1.55			
Mean	0.78	0.90	1.00	0.76	
(SD)	(0.25)	(0.28)	(0.35)	(0.18)	
N	17	22	18	18	

[a] First value for each year is from snowpit dug in February or early March. For exact dates, refer to text.

[b] First value for each year is from snowpit dug in February or early March. In 1991, third value is from snowpit dug in early May.

[c] First value for 1991 is from snowpit dug in late-February.

[d] Data from Melack et al. (1996).

Table 12. Ammonium:chloride ratios in rain at high elevation sites in the Sierra Nevada. Individual ratios were calculated from volume-weighted mean values for ammonium and chloride from pooled precipitation collected from ca. May through October at each site (Melack et al. 1997).

Site	1990	1991	1992	1993	1994	Site Mean	SE
Angora Lake	3.64	4.28	2.92	8.45		4.82	1.24
Alpine Meadows	3.76	3.29	6.26	7.04		5.09	0.92
Eastern Brook Lake	4.30	7.85	7.79	4.59		6.14	0.98
Emerald Lake	2.94	12.61	4.09	5.04	4.46[b]	5.83	1.93
Kaiser Pass	NA	10.46	7.57	3.10			
Mammoth Mountain	5.56	6.27	17.98[a]	9.50[a]		9.83	2.85
Mineral King	8.01	5.51	7.60	8.11		7.31	0.61
Onion Valley	6.78	7.15	7.17[a]	4.84[a]		6.49	0.56
Sonora Pass	5.63	5.26	12.84	6.16		7.47	1.80
South Lake	4.68	5.48	10.76	5.34		6.57	1.41
Tioga Pass	3.73	5.82	6.57	11.64	6.76[b]	6.90	1.30
Annual Mean	4.90	6.73	8.32	6.71			
SD	1.59	2.72	4.20	2.51			

[a] Values are means for two co-located collectors.

[b] Data from Melack et al. (1996).

Table 13. Ammonium:chloride ratios in snow at high elevation sites in the Sierra Nevada. Individual ratios were calculated from volume-weighted mean values for ammonium and chloride from snow pit profiles collected at the time of maximum snow accumulation (Melack et al. 1997).

Site	1990	1991	1992	1993	1994	Site Mean	SE
Alpine Meadows	1.28	1.74	1.74	1.63		1.60	0.11
Crystal Lake	1.56	3.58	3.58	2.35		2.77	0.50
Eastern Brook Lake	1.60	2.23	2.23	0.82		1.72	0.34
Emerald Lake	2.14	3.76	2.02	0.80	1.88[a]	2.12	0.47
Kaiser Pass	NA	4.20	2.33	1.15		2.56	0.77
Lost Lake	1.12	1.51	1.51	1.59		1.43	0.10
Mammoth Mountain	2.91	3.02	3.02	1.72		2.67	0.32
Mineral King	2.06	3.72	3.72	1.04		2.64	0.66
Onion Valley	1.85	3.60	3.60	2.32		2.84	0.45
Pear Lake	1.91	3.32	3.32	1.04		2.40	0.56
Ruby Lake	1.92	3.19	3.19	1.40	3.64[a]	2.67	0.43
Sonora Pass	1.27	2.95	2.95	1.26		2.11	0.49
South Lake	1.46	1.97	1.97	1.81		1.81	0.12
Spuller Lake	1.20	2.74	2.74	1.49	2.50[a]	2.04	0.41
Topaz Lake	1.66	1.87	1.87	1.11		1.63	0.18
Annual Mean	1.71	2.89	2.65	1.44			
SD	0.48	0.85	0.74	0.48			

[a] Data from Melack et al. (1996).

Table 14. Nitrate:sulfate ratios from rain at high elevation sites in the Sierra Nevada. Ratios were calculated using annual volume weighted mean concentrations of nitrate and sulfate for rain reported in Melack et al. (1997).

			NO_3^-/SO_4^{2-}		
SITE	1990	1991	1992	1993	1994
Alpine Meadows	1.72	1.88	1.41	1.90	
Angora Lake	1.46	1.45	1.19	1.50	
Eastern Brook Lake	1.55	1.43	1.19	1.17	
Emerald Lake	1.36	1.48	1.29	1.09	1.32[b]
Kaiser Pass	NA	0.99	1.28	1.75	
Mammoth Mountain[a]	1.83	1.28	1.29 1.44	0.92 0.95	
Mineral King	1.25	1.43	1.36	2.06	
Onion Valley[a]	1.13	1.22	1.16 1.09	1.24 1.29	
Sonora Pass	1.46	1.45	1.16	1.45	
South Lake	1.37	1.31	1.27	1.58	
Tioga Pass	1.64	1.36	1.18	1.43	1.33[b]
Annual Mean	1.48	1.38	1.25	1.41	
SD	0.21	0.22	0.10	0.35	
N	10	11	13	13	

[a] For 1992 and 1993, values are reported for two co-located precipitation collectors.
[b] Data from Melack et al. (1996).

Table 15. Nitrate:sulfate ratios in alpine snowpits. Ratios for sites were calculated using volume weighted mean concentrations from duplicate snowpits reported in Melack et al. (1997). Except where noted, snowpits were dug at the time of maximum snow accumulation (ca. April 1).

	NO_3^-/SO_4^{2-}				
SITE	1990	1991	1992	1993	1994[d]
Alpine Meadows[a]	1.13	2.32	1.41	0.96	
	1.11	1.60	1.35	0.94	
Crystal Lake	1.32	1.90	1.05	0.78	
Eastern Brook Lake	2.28	1.14	1.53	0.84	
Emerald Lake[a]	0.69	3.87	1.43	0.79	1.85
	0.99	1.48	1.55	0.75	
Kaiser Pass	NA	1.93	1.77	0.69	
Lost Lake	1.37	1.30	1.26	1.00	
Mammoth Mountain[b]	1.47	1.88	1.25	0.73	
	1.38	1.36	1.39	0.76	
		1.98			
Mineral King	1.27	3.14	1.97	0.84	
Onion Valley[c]	1.15	2.55	1.17	1.45	
		1.92			
Pear Lake	0.83	1.50	1.54	0.78	
Ruby Lake	1.24	1.21	1.24	0.86	1.62
Sonora Pass	1.54	0.53	1.40	0.84	
South Lake	1.84	0.83	2.27	0.95	
Spuller Lake	1.20	1.22	1.38	0.81	1.68
Topaz Lake[c]	1.05	4.30	1.48	0.72	
		1.35			
Mean	1.29	1.87	1.47	0.86	
SD	0.37	0.94	0.29	0.17	
N	17	21	18	18	

[a] First value for each year is from snowpit dug in February or early March. For exact dates, refer to text.

[b] First value for each year is from snowpit dug in February or early March. In 1991, third value is from snowpit dug in early May.

[c] First value for 1991 is from snowpit dug in late-February.

[d] Data for 1994 is from Melack et al. (1996).

Table 16. Results of linear regression between ($[NO_3^-] + [SO_4^{2-}]$) and $[NH_4^+]$ measured in precipitation at alpine sites. Annual mean volume-weighted concentrations from all sites were pooled for each analysis.

Year		N	r^2	F	p	y	SE	b	SE
1990	Rain	10	0.89	63.2	5×10^{-5}	-12.8	5.3	0.92	0.12
1991	Rain	10	0.33	4.0	0.08	7.9	11.0	0.47	0.23
1992	Rain	13	0.80	44.8	3×10^{-5}	-3.7	4.3	0.65	0.09
1993	Rain	13	0.73	30.1	2×10^{-4}	2.0	2.8	0.47	0.09
1990	Snow	18	0.51	16.5	9×10^{-4}	-0.4	0.8	0.72	0.18
1991	Snow	21	0.82	86.5	2×10^{-8}	-1.3	0.8	0.98	0.11
1992	Snow	18	0.42	11.7	0.003	-0.2	1.1	0.68	0.20
1993	Snow	18	0.34	8.2	0.01	-0.1	0.7	0.51	0.18

PART 2

CURRENT STATUS OF HIGH ELEVATION SURFACE WATERS IN THE SIERRA NEVADA, CALIFORNIA

AND

LONG TERM TRENDS IN CHEMICAL AND BIOLOGICAL FEATURES OF HIGH ELEVATION SIERRA NEVADA LAKES

PART 2

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FIGURES (cont.)

2.1. INTRODUCTION

By 1996, several independent regional surveys of surface waters in the Sierra Nevada, and of those in other montane regions of California, were available. Among these are the survey of 50 lakes conducted by McCleneghan et al. (CARB Contracts A3-107-32, A3-107-32A), the survey of 23 lakes conducted by Melack and Setaro (CARB Contract A3-107-32B), the survey of 104 lakes conducted by Bradford et al. (CARB Contract A132-173), and Sierra Nevada sites sampled in the US EPA Western Lake Survey (Landers et al. 1987). In this report, the results of the above mentioned CARB-sponsored lake surveys have been pooled, where appropriate, and re-evaluated in order to provide a unified characterization of the current chemical condition of California's lake population, with an emphasis on chemical or physical features known to affect lake susceptibility to acidification. Component data sets have been considered in light of potential biases produced by the time of sampling in synoptic surveys, or by interannual variation in such variables as size of snowpack. The results of this evaluation are compared to Melack & Stoddard's (1991) analysis of the hydrochemistry of the Sierra Nevada lakes that were sampled as part of the Western Lake Survey.

Results of the CARB Emerald Lake Integrated Watershed Study and the complementary Lake Comparison Study have produced long term data sets (4 to 10 years) for a large array of hydrochemical and biological features of several intensively studied high altitude Sierra Nevada sites. Through existing Contract A032-188 much of this hydrochemical data will be analyzed in order to (1) identify temporal trends in hydrochemistry, and (2) evaluate the ability to identify trends due to the nature and magnitude of interannual varitiation. The conclusions currently available from the Draft Final Report for Contract A032-188 (Melack et al. 1996) are summarized herein. In addition, a description of long-term biological data (zooplankton) from the Emerald Lake watershed and the Lake Comparison Study is included. Consideration is given as to how the detection of long-term trends is affected by intra-annual variation in physicochemical or biological parameters.

2.2. HYDROCHEMICAL DATA SETS

2.2.1. McCleneghan Statewide Survey in 1985 and 1986.

With support from the CARB (Contracts A3-107-32 and A3-107-32A), McCleneghan surveyed 50 Sierra Nevada lakes in 1985 and 1986. Sites were located in major mountain ranges and varied in elevation from 73 m to 3462 m ASL. Sites were avoided that exhibited one or more of the following characteristics: (1) high recreational use, (2) cattle grazing in the immediate watershed, or (3) eutrophic appearance. Sites were sampled two times per year - once during spring run-off and once in late summer or fall. Water samples were collected 6.5 m offshore near the outlet of lakes, or mid-channel in streams. Samples were collected 0.5 m below the surface. Details of chemical procedures, and a report of results of the survey (raw data) are located in the following two publications (no data analysis was undertaken by the authors):

McCleneghan K., J Nelson, J. King and S. Baumbartner (1985) Statewide survey of aquatic ecosystem chemistry; 1985. Final Report to the C.A.R.B., Contract No. A3-107-32.

McCleneghan K., R. Imai, J. King and S. Boggs (1986) Statewide survey of aquatic ecosystem chemistry; 1986. Final Report to the C.A.R.B., Contract No. A5-178-32.

2.2.2. Lake Surveys of Melack & Setaro, 1985 and 1986.

Concurrent with the statewide survey of McCleneghan described above, synoptic surveys of an additional 23 Californian lakes were carried out in 1985 and 1986 with CARB support by Melack and Setaro at UCSB (Contract A3-107-32B). Sampling took place during two periods: (1) the autumn of 1985 (September to November), and spring or summer of 1986 (April to August). The second sampling period was intended to characterize the lakes under ice or soon after ice out. The autumn 1985 survey included 16 lakes in the Sierra Nevada. The spring 1986 survey included 15 lakes in the Sierra Nevada. The rest of the lakes were coastal or low elevation lakes (<1700 m) in Santa Barbara county. For the purposes of this report, only the Sierra Nevada sites will be considered. Criteria used for site selection included susceptibility to acidification as deduced from bedrock geology and proximity to sources of acidic materials, accessibility, extraneous influences on water quality, and prior sampling.

Chemical parameters measured in the surveys included pH, alkalinity, conductance, major cations, major anions, silica, ammonium, phosphate, total P, total N, total dissolved P, total dissolved N, aluminum, iron, manganese. Samples were taken at two depths (subsurface and near bottom) at 2 stations in the lakes. Samples were collected by peristaltic pumping from an inflatable boat. Details of chemical procedures, report of raw data, and some preliminary data analysis are contained in the following publication:

> Melack J. and F. Setaro (1986) Survey of sensitivity of southern Californian lakes to acid deposition. Final Report to the C.A.R.B., Contract No. A3-107-32B.

2.2.3. Lake survey of Bradford et al. (1994)

In 1992 the CARB funded a survey of 104 lakes in a 50 km^2 section of the BenchLake/Mt. Pinchot area in Kings Canyon National Park. This survey was motivated by the discovery in 1991 of several naturally acidic lakes (pH < 6.0) in this region of the Sierra Nevada. In this synoptic survey, the only chemical parameters measured were pH and conductivity. Subsequently, a more detailed chemical survey was conducted on a subset of 33 of these lakes (eight of which had pH < 6.0). The survey area was divided into 11 watersheds, six of which drain into the South Fork of the Kings River, and four of which drain into Woods Creek. One of the catchments was a closed basin. Acidic lakes were present in 3 of the 11 basins. Lakes were chosen so that the elevation, size and depths of non-acidic lakes (pH > 6.0) matched those for acidic lakes. Lakes were chosen so that a reasonable number of lakes containing and lacking fish and breeding amphibians were included.

The survey of 33 lakes took place in August and September 1992. Chemical variables measured included conductivity, pH, alkalinity, chloride, nitrate, sulfate, ammonium, calcium, magnesium, sodium, potassium, and aluminum. Water samples were collected by hand from lake outlets. Details of chemical procedures, and full report of results of the survey are contained in the following publication:

Bradford D., S. Cooper, A. Brown, T. Jenkins, K. Kratz and O. Sarnelle (1994) Distribution of aquatic animals relative naturally acidic waters in the Sierra Nevada. Final Report to the C.A.R.B., Contract No. A132-173.

2.2.4. Lake sampling in the Lake Comparison Study of Melack et al. (1996)

In the Lake Comparison Study (Melack et al., 1996; CARB Contract No. A032-188) lake chemistry was routinely sampled in seven high altitude Sierra Nevada lakes. Lakes were sampled more frequently (every 2 months) and at more depths (4 depths) in the Lake Comparison Study than in the synoptic studies described above. Melack et al. (1996) calculated lake-volume-weighted mean pH, alkalinity, conductivity, and concentrations of important solutes using the data from the four sampling depths and existing hypsographic curves for each of the lakes. For the purposes of this report, only the data from samples obtained at the same lake depths and at the same times of year used in the above-mentioned synoptic surveys were needed. Towards this end, chemical data from samples taken at discrete lake depths over the course of the Lake Comparison Study was provided by J. Sickman (UCSB). An explanation of the criteria used for choosing samples for inclusion with the results of the synoptic surveys is found below. Full site descriptions, and details of chemical procedures are contained in the following publication:

Melack J., J. Sickman, A. Leydecker, and D. Marrett (1996) Comparative Analyses of High-Altitude Lakes and Catchments in the Sierra Nevada: Susceptibility to Acidification. Draft Final Report to the California Air Resources Board, Contract No. A032-188.

2.2.5. EPA Western Lake Survey

In 1985, the USEPA conducted the National Surface Water Survey (NSWS) in an effort to characterize the chemical condition of the nation's lake and stream population in a statistically valid fashion. Seven regions were picked to survey streams and lakes based on existing alkalinity maps and physiographic characteristics. In all of these regions, most lakes and streams are likely to have ANC less than 400 $\mu eq \cdot L^{-1}$.

The seven regions were as follows:

Northeast
Upper Midwest
West
Mid-appalachians
Interior Southeast
Mid-Atlantic Coastal Plain
Southeastern Coastal Plain

In the NSWS, lake chemistry was sampled during fall turnover. Lake water samples were single, mid-lake samples just after fall turnover. In doing so, the EPA strove to characterize the "chronic" chemical condition of the lake population in each region as opposed to chemical conditions potentially produced by episodic acidification. In the NSWS, the lakes chosen for sampling in each region were selected based on a stratified random sampling process described in general terms below:

(1) All lakes in the region were identified that were visible on topographic maps at a particular scale (1:100,000 in the West).

(2) The total population of lakes was stratified into subpopulations based ranges of expected ANC (<100 µeq L^{-1}, 100-200 µeq L^{-1}, > 200 µeq L^{-1}).

(3) Lakes were selected from the substrata in a systematic fashion based on a random starting point.

(4) In order for the lake selection process to be statistically valid, it had to be possible to calculate the probability of a particular lake being selected based on the total possible lake population.

(5) Population statistics for chemical variables were not calculated directly from the data for the sampled lakes. Instead, the results for each lake were weighted by the probability of having picked that lake.

Western Lake Survey

The Western Lake Survey (WLS) included lakes in five subregions: California, Pacific Northwest, Northern Rockies, Central Rockies and Southern Rockies. The WLS identified 10,393 lakes as being within the total target population--of these 719 were sampled. Sierra Nevada lakes were included in the WLS in the California subregion (subregion "4a"). The total target population of lakes in the California subregion numbered 2401, of these 149 were sampled. The California lakes included in the survey were predominantly drainage lakes (~84%), as opposed to seepage or closed lakes. Within the NSWS, the WLS had the largest percentage of lakes with ANC $\leq$ 200 μeq L^{-1} (66%), but only 1 lake in the sample population was acidic (ANC = 0). Within the WLS, the California subregion had the lowest median ANC (67 μeq L^{-1}). Eighty-six percent of the subregion's lakes had ANC $\leq$ 200 μeq L^{-1}. No strong relationship between ANC and elevation was found. Base cations in the California subregion occurred in the order: $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$. The relative importance of Na^{+} reflects presence of sodium feldspar bedrock.

A detailed description of the methodology and results of the NSWS may be found in the following publication:

> Baker L., P. Kaufman, A. Herlihy, J. Eilers, D. Brakke, M. Mitch (1990) Current status of surface water acid-base chemistry. U.S. National Acid Precipitation Assessment Program, Report 9, Washington, D.C. 367 pp.

Melack and Stoddard (1991) performed qualitative analyses on the Sierra Nevada lakes included in the California subregion on the WLS. Many of their results will be discussed later in this chapter as a basis for comparison with analyses carried out on the pooled data set from the CARB synoptic lake surveys described above. A full description of their work is found in the following publication:

> Melack J. and J. Stoddard (1991) Sierra Nevada, California. Chapter 15. In: D.F. Charles (Ed.), Acidic Deposition and Aquatic Ecosystems: Regional Case Studies. Springer-Verlag, New York. pp. 503-530.

2.3 . ASSEMBLY OF JOINT DATA SET

2.3.1. Biases due to intra-annual variation in hydrochemistry

Intra-annual variation in surface water chemistry makes the choice of sampling times critical if the results of synoptic surveys are to be used to search for year to year differences. Changes in stream chemistry from the onset of snowmelt until the reestablishment of base flow conditions in the autumn was a focus of the Lake Comparison Study of Melack et al. (1996). Their results show that snowmelt discharge dilutes the concentration of solutes and lowers ANC from April until the end of snowmelt. In their study, snowmelt was complete by the beginning of August, except following wet winters, such as in 1986, when snowmelt discharge was prolonged by at least one month. Subsequently, from early autumn until the following snowmelt period, Melack et al. (1996) measured steady increases in lake ANC and in the concentrations of other solutes.

During the snowmelt period, volume-weighted-mean lake ANC can drop by as more than 50% (Melack et al. 1996). If the goal of a spring-time lake survey is to document the effect of snowmelt discharge, or to describe lakes when they are most vulnerable to acidification because of ANC minima, the timing of sampling must be carefully coordinated with snowmelt hydrographs. If visits to a suite of lakes during the snowmelt period are spread out over several weeks, investigators are guaranteed to sample lakes during different phases of solute dilution, rendering all but the coarsest comparisons between lakes and between years difficult. In McCleneghan's statewide survey of lakes in 1985 and 1986, lakes were visited twice each year, supposedly to characterize "spring" and "fall" conditions (Table 1). However, spring sampling over the two years of the study spanned the period April 8 to August 3. Such widespread sampling dates guarantee that lakes were sampled at different points along their snowmelt hydrographs, possibly yielding solute concentrations representing the full range from the high values of the early melt phase (perhaps further complicated by an ionic pulse, in the case of nitrate), to the minimum values observed during maximum discharge and dilution.

The timing of fall lake surveys is affected by the seasonal variation in surface water chemistry typical of high elevation lakes. Synoptic surveys designed to characterize fall lake chemistry, when base flow is reestablished in streams, should be planned for periods which are unlikely, even after wet winters, to coincide with the tail end of the snowmelt hydrograph. For the Sierra Nevada lakes studied in detail by Melack et al. (1996) this would appear to be at least after the beginning of September. However, if the sampling dates are spread out over a period of many weeks, samples will reflect solute concentrations during different phases of the characteristic "recovery" period, during which solute concentrations climb from late summer minima to the maxima sampled under ice prior to onset of snowmelt (for detailed time series plots of ANC, pH, nitrate, sulfate, chloride, specific conductivity, sum of base cations, and silicate for individual lakes, see Melack et al. 1996). In McCleneghan's Statewide Survey, fall lakes samples over the two year study spanned the period of August 5 to November 26 (Table 1). Because snowmelt of 1986 was prolonged into September, the August samples in that year did not reflect lake chemistry after base flow was reestablished. Samples obtained later during October and November in both years may have been biased toward higher solute concentrations related to their timing further along the "recovery" trajectory for lake solute concentrations.

Other, less predictable factors may influence the results of synoptic sampling of Sierra Nevada lakes. McCleneghan et al. (1985) state that in 1985, the "fall" samples in the Southern Sierra had lower conductivity and pH than the "spring" samples. They attribute this result to the fact that their "spring" samples were not collected at the time of maximum run-off (thus presumably missing the low points of conductivity and pH associated with snowmelt) and that the "fall" samples were collected soon after summer rain occurred in the southern Sierra. Thus the fall samples may have been affected by episodic acidification from summertime precipitation.

2.3.2. Use of synoptic survey data

An effort was made to produce a combined data set from the component synoptic surveys that could be legitimately compared to data from the Californian lakes sampled in the EPA's Western Lake Survey. Because the WLS sampled lakes during fall turnover, and because lake chemistry changes rapidly during the snowmelt season (as discussed above), samples were selected from the CARB surveys from dates after the snowmelt season (fall, or late summer) and during or as close as possible to fall homothermy. Although data from more than one lake depth was available in some of the surveys, data from near surface samples only were included in the joint data file.

The suite of chemical species measured differed among the various synoptic surveys. Parameters related to the nutrient or trophic status of lakes, such as chlorophyll, TP, TN, NH_4^+, PO_4^{3-}, were not measured in each of the component surveys, and were not included in the joint data file. Most of the species relevant to acid-base chemistry and weathering reactions were included in the joint data set. Organic acid anions (formate, acetate) were not measured in any of the synoptic surveys, thus, they were not included in the joint data file. In the end, the following suite of measurements was included: pH, alkalinity, conductivity, sum of base cations, calcium, magnesium, sodium, potassium, nitrate, sulfate, chloride, and silicate.

Field replicates were obtained for a small subset of lakes in McCleneghan's Statewide Survey in both 1985 and 1986. In only 4 of these cases were the lakes from the Sierra Nevada; Eureka Lake in fall-1985 and High Loch Leven, Serene and Pear Lakes in fall-1986. In these cases, replicate values for chemical parameters were averaged so that one value per sampling date was entered in the joint data file. When solutes were designated as "below detection" in survey results, a value of zero was entered in the joint data file. Silicate was measured by McCleneghan et al. in 1986, but not in 1985. Hume Lake and Oriole Lake, sampled in the Melack/Setaro surveys of 1985-1986, were omitted from the joint data file because of low elevation (< 2000 m) and high alkalinity values.

2.3.3. Use of data from the Lake Comparison Study (Melack et al. 1996)

A subset of lake chemistry data from the Lake Comparison Study (Melack et al. 1996) was included in the joint data set that satisfied the criteria used for selecting data from the component CARB synoptic surveys. Chemistry data from surface water samples were assembled from sampling dates that coincided with fall turnover. Dates were chosen on the basis of inspection of temperature plots in Melack et al. (1996) showing surface water temperature versus near-bottom temperature over the entire study period for each lake. Dates were selected when surface water temperature and near-bottom temperature were identical, or within 1° C of each other. With few exceptions, dates were selected after maximum summer surface temperatures were observed. In a few cases, the only sampling date in a given year that coincided with homothermy was also when the highest temperature was recorded. Surface water temperature was taken at 1 m in all of the lakes. Near bottom temperature was measured at the following depths: Crystal Lake - 12 m; Emerald Lake - 9 m; Lost Lake - 4.5 m; Pear Lake - 25 m; Ruby Lake - 34 m; Spuller Lake - 5 m; Topaz Lake - 4 m. The water samples from the Lake

Comparison Study that satisfied the above criteria, and thus that were included in the joint data set, are listed by lake and date in Appendix 2.1.

2.4. ANALYSIS OF JOINT DATA SET

Data from a total of 89 lakes was included in the joint data set, spanning the northern, central and southern Sierra Nevada and compiling information from 5 CARB sponsored studies. A complete listing of the lakes, their locations and elevations, and the sampling dates and data sources used for each lake is found in Appendix 2.2. Hereafter, these 89 lakes will be referred to as the "CARB Survey" lakes, or *CARBS* lakes.

2.4.1. Treatment of replicates

Three of the lakes included in the joint data set were sampled on more than one appropriate date in certain years by the same investigator(s). These cases were as follows: Topaz Lake in 1991 in the Lake Comparison Study, Pear Lake in 1985 in the Melack-Setaro survey, and Emerald Lake in several years from 1983 to 1994 in the "Lake Comparison" study (Table 2). In these cases, the results from all dates taken by the same investigators within a given year were averaged, providing one mean value per year per investigator for each chemical species.

For each lake in the data set, the resulting set of values (one/year/investigation) were averaged to provide a single average and error estimate (mean ± SE) for each chemical species. In six cases, two different investigations (McCleneghan et al. and Melack/Setaro) sampled the same lake in the same year. Same-year values produced by these two investigations were not averaged, but treated as independent estimates. The six cases were as follows: Gaylor Lake in 1985; McCloud Lake in 1985; Piute Lake in 1985; Golden Trout Lake in 1985; and Pear Lake in 1985 and 1986.

2.4.2. Chemical characteristics of the CARBS lakes

The CARBS lakes were located across a somewhat narrower range of elevation than the target population of 2119 lakes in the EPA's Western Lake Survey (WLS). CARBS lakes were located between 1866 m and 3672 m ASL (Fig. 13), whereas the WLS lakes were located between 1600 and 3800 m ASL (Melack and Stoddard 1991). However, the distribution of elevations were similar in both studies, with the majority of lakes occurring between ca. 3400 m and 3500 m (the CARBS median elevation was 3210 m; the WLS median elevation was 3008 m).

Frequency histograms were plotted for elevation and chemical parameters for the CARBS lakes (Fig. 1-13). With the exception of silica, the distributions of all the major chemical parameter were positively skewed. This property resulted in mean values that were higher than the median values for each of the chemical parameters (Table 2). Silica concentrations were more uniformly distributed in the CARBS than in the WLS (Fig. 12), and overall, values were lower. The maximum silica value obtained in the CARBS was 72 μmol L^{-1} and most lakes had silica concentrations below ca. 40 μmol L^{-1}, whereas silica concentrations were measured up to ca. 200 μmol L^{-1} in the WLS, and most lakes had silica concentrations between 50 to 150 μmol L^{-1} (Melack & Stoddard 1991). In other respects, the chemical composition of the CARBS lakes was similar to that of the WLS lakes. Calcium was the the dominant cation in both surveys, followed by sodium. In general, sulfate was the dominant strong acid anions, followed by chloride. Nitrate was the least concentrated strong acid anion in both studies.

The results of the CARBS indicate a somewhat higher sensitivity to acidification for high elevation lakes of the Sierra Nevada than was indicated by analysis of the Sierra Nevada lakes of the WLS (Melack and Stoddard 1991). The median value for alkalinity (56 μEq L^{-1}) for CARBS lakes was lower than that reported for the Sierra Nevada lakes of the Western Lake Survey (71 μEq L^{-1}, Melack and Stoddard 1991). Most of the Sierra Nevada lakes (65%) in the WLS had ANC values $\leq$ 100 μEq L^{-1} (Melack and Stoddard 1991). A somewhat higher percentage (74%) of CARBS lakes had alkalinity values $\leq$ 100 μEq L^{-1} (Table 3). None of the Sierra Nevada lakes sampled in the WLS had ANC $\leq$ 0. However, a small number (4.5%) of the CARBS lakes had alkalinity values ≤ 0. In the WLS only one sampled lake had a pH < 6.0 (closed system pH, the corresponding air-equilibrated value is 6.2, Melack and Stoddard 1991). However, the minimum pH measured in the CARBS was 4.71 (Table 3), and 10 lakes had pH < 6.0. Additionally, the median pH for CARBS lakes (6.5) was lower than for WLS lakes (6.93). These differences are primarily due to the inclusion in the CARBS of a number of naturally acidic lakes in the Mt. Pinchot area of Kings Canyon National Park in the southern Sierra Nevada sampled by Bradford et al. (1994). Otherwise, the distribution of alkalinity values in the two studies are similar; only a few lakes (6 in the case of the CARBS) had alkalinity values higher than 200 μEq L^{-1} (Fig. 2), and no lakes in either study had alkalinities greater than 400 μEq L^{-1}.

The somewhat higher acid sensitivity of the CARBS lakes, relative to WLS lakes, cannot be explained by lower ionic strengths or by lower concentrations of base cations in CARBS lakes. The median values for Σ base cations, and for each of the individual base cations (Ca^{2+}, Mg^{2+}, N^{+}, and K^{+}) were higher for CARBS lakes than the Sierra Nevada WLS lakes (Table 3). Instead, it appears that generally higher concentrations of strong acid anions were measured in the CARBS lakes than in the WLS lakes; median values for nitrate, sulfate, and chloride were higher for CARBS lakes than the WLS lakes (Table 3).

2.5. LONG TERM TRENDS IN HYDROCHEMICAL DATA

One of the objectives of the Lake Comparison Study (CARB Contract A032-188, Melack et al. 1996) was the characterization of long-term variability and trends of surface water chemistry in the Sierra Nevada. Toward this end, they analyzed time series of volume weighted mean lake chemistry and lake outflow chemistry for several Sierran lakes studied on an annual basis during the period 1982 to 1994. The longest series of measurements was available for Emerald Lake (1982-1994), while somewhat shorter series of measurements were available for Pear, Topaz, Crystal and Ruby Lakes (1989-1994). Detailed time series plots for these lakes are presented in Melack et al. (1996) for the following suite of measurements: pH, ANC, nitrate, sulfate, base cations, silicate.

No inter-annual trends in the pH or ANC of lakewater or outflow streamwater were found by these investigators at the above mentioned study sites during the period 1983 through 1994 (Melack et al. 1996). Based on these data, the authors conclude that surface waters in high elevation regions of the Sierra Nevada have not undergone measurable acidification since 1983.

The time series of lake and outflow chemistry suggested inter-annual trends for other chemical parameters at only two study sites, Ruby Lake and Emerald Lake. Volume-weighted-mean sulfate and base cations exhibited an increase over time in Ruby Lake (Melack et al. 1996). Sulfate concentrations increased from ca. 6 $\mu Eq\ L^{-1}$ to ca. 12 $\mu Eq\ L^{-1}$ in the lake and the lake outflow from October 1987 to April 1994. The upward trend in sulfate appeared to end in 1994. This temporary increase in sulfate of ca. 6 $\mu Eq\ L^{-1}$ was apparently balanced by an increase in base cations of approximately the same magnitude. Melack et al. (1996) suggest that this trend was associated with the regional drought that occurred from water year 1987 to water year 1992. Water years with below average precipitation were followed by increases in sulfate in Ruby Lake. The return of normal precipitation in water year 1993 was followed by a leveling off and decline of lake sulfate in water year 1994.

Although a mechanism by which drought conditions could affect sulfate concentrations in Ruby Lake is unknown, Melack et al. (1996) suggest that the storage and release of groundwater in the Ruby Lake watershed may be involved. Groundwater comprises a more important component in the water budget of Ruby Lake than in the budgets of the other lakes of the Lake Comparison Study. Both groundwater release and glacier meltwater provide alternative water supplies to Ruby Lake during times of below average precipitation, and these inputs may be enriched with sulfate compared to snowmelt discharge.

The only other observable trend in surface water chemistry during the Lake Comparison Study was a decline of nitrate in the Emerald Lake watershed. The reduction of nitrate in the Emerald Lake basin was greater in the lake than in the lake outflow stream. The decline in nitrate occurred during 1988 and 1989. In the years prior to this period (1983 - 1987), peak concentrations of nitrate in Emerald Lake were above ca. 10 $\mu Eq\ L^{-1}$. Later, from 1990 to 1994, peak concentrations of nitrate were less than 5 $\mu Eq\ L^{-1}$ in the lake. The pattern of the decline is unclear during water years 1988 and 1989 because sampling frequency was low at this time of the study. An ecological mechanism to explain these observations is unknown at this time, although analytical artifacts have been ruled out by the investigators (J. Sickman, personal communication).

2.6. LONG TERM TRENDS IN BIOLOGICAL DATA

2.6.1. Zooplankton data set

The longest-term zoological data generated by the CARB sponsored studies of the high elevation Sierra Nevada watersheds are of zooplankton abundances in the seven lakes of the Lake Comparison Study (Emerald, Pear, Topaz, Spuller, Ruby, Crystal, and Lost Lakes; Melack et al. 1987, 1989, 1993). Many features of the zooplankton record were described by Engle & Melack (1993).

Of these seven lakes, the longest record of zooplankton abundance exists for Emerald Lake. Although the density of sampling varied to some degree during the entire study period, mid-lake abundances of zooplankton are available from July 1984 until December 1992. A long term data set of zooplankton abundance for Emerald Lake was compiled using data on file at UCSB from sampling during studies supported by CARB contracts A3-096-32, A6-184-32, A932-060. Details of sampling procedures may be found in the corresponding Final Reports to the CARB. In brief, on every sampling occasion, duplicate mid-lake vertical tows were taken from an inflatable boat, except when the lake was ice-covered, in which case vertical tows were taken through a hole drilled mid-lake through the ice cover. Duplicates were averaged to provide one estimate of zooplankton density per sample date. The frequency of sampling varied among years depending on whether the years were ones in which field experiments were taking place in the Emerald Lake Watershed (such as the Emerald Lake bag experiments and stream channel experiments) or whether the years were ones of routine semi-monthly monitoring. The following thirteen zooplankton species were included in the data set: *Daphnia rosea*, *Diaptomus signicauda*, *Holopedium gibberum*, *Chydorus sphaericus*, *Ceriodaphnia affinis*, *Macrocyclops albidus*, *Bosmina longirostris*, *Tropocyclops prasinus*, *Conochilus unicornis*, *Keratella taurocephala*, *Keratella quadrata*, *Polyarthra vulgaris*, and *Trichocerca capucina.*

2.6.2. Intra-annual variation in zooplankton abundance

The sampling schedule of once per 60 days that was adhered to in most years provided only a coarse record of changes in zooplankton density. Indeed, sampling may have failed to coincide with the peak densities of individual species in any one particular year. In order to examine the "average" seasonal patterns of population density, the data from individual years for each species was pooled, and abundances from the whole time record plotted as a function of day-of-year (Fig. 14 - 26). Three of the crustacean species, *Daphnia rosea*, *Diaptomus signicauda*, and *Holopedium gibberum*, occur principally during the summer and early autumn months between July and late October (ca. 180 d to 300 d), and are scarce or absent otherwise (Fig. 14, 15, 16, respectively). A clear seasonal pattern for *Bosmina longirostris* is lacking; occasional peak abundances for this species were observed under ice between December and March, and somewhat higher than average abundances are observed in late summer months between July and October (Fig. 17). *Chydorus sphaericus* is more appropriately assigned to the benthos than the pelagic zone, but occurs in low numbers in net tows in Emerald Lake. This species increases in abundance from June to November (Fig. 18). *Ceriodaphnia affinis* was not counted in zooplankton samples until 1989, and occurred in only 5 samples between 1989 and 1992, (samples taken between late June and early October, Fig. 19). The two cyclopoid copepod species, *Macrocyclops albidus* and *Tropocyclops prasinus*, were also not counted in zooplankton samples until 1989. *T. prasinus* occurred in only 4 samples, each of which was a summertime sample (July -Sept, Fig. 20). *Macrocyclops albidus* occurred in samples more frequently, and at almost any time of the year (Fig. 21).

Seasonal patterns are apparent from the pooled data for most of the rotifer species of Emerald Lake. *Keratella taurocephala* occurred in every sample taken in Emerald Lake from 1984 to 1992. Although *K. taurocephala* occurs year-round in the water column, the peak abundances within the pooled data set occur from July to November (Fig. 22). *Keratella quadrata*, on the other hand, is scarce or absent in Emerald Lake except during May, June and July (Fig. 23). *Polyarthra vulgaris* also occurred in every sample taken from 1984 to 1992. Summertime increases in abundance for this species span the period of June to November (Fig. 24). *Conochilus unicornis* and *Trichocerca capucina* were scarce or absent except during the months of July through October (Fig. 25, 26).

The pooled abundance records for Emerald Lake zooplankton reveal that synoptic sampling of zooplankton (once per year) cannot yield much more than absence/presence data from one year to the next, even if the sampling takes place during the summer, when most of the species increase in abundance. There is no one particular month in which it can be guaranteed that you will always sample peak summertime abundance for even one species. Over a period of several years, a particular week during the summer can coincide with peak summertime abundances for a species, *or* a time when the species is scarce or absent.

2.6.3. Inter-annual variation in zooplankton abundance

The marked seasonality of zooplankton abundances, as well as the inherent variability of replicate zooplankton tows (note the large standard errors in Fig. 14 - 26), restricts the suitability of data collected once every two months for examination of long-term (multi-year) trends. In order to examine the 8 year zooplankton record for Emerald Lake for inter-annual trends, abundances over the course of individual years of sampling effort were plotted with respect to day of year and presented together to facilitate comparisons between years (Fig. 27 - 35). Inspection of these plots fails to reveal any consistent trend spanning the sampling period. Rather, there appear to be a few years in which many species occurred at especially high or especially low densities. Several zooplankton species were especially abundant during the summer of 1985 (*Daphnia rosea*, *Diaptomus signicauda*, *Holopedium gibberum*, *Keratella taurocephala*). Similarly, several species were especially abundant during 1988 (*Holopedium gibberum*, *Keratella taurocephala*, *Keratella quadrata*, *Trichocerca capucina*, *Conochilus unicornis*). Especially low abundances were observed in 1986 for four species (*Daphnia rosea*, *Diaptomus signicauda*, *Keratella quadrata* and *Polyarthra vulgaris*. The wet winter of 1985-1986 produced an exceptionally deep ice cover on Emerald Lake (6 m deep, as opposed to a normal range of 1-2 m; Melack et al. 1996). The lake remained ice-covered longer in 1986 than in other years. A delay in ice-out may have contributed to the low summertime abundances of these four species in 1986. Three of the crustacean species (*Daphnia rosea*, *Diaptomus signicauda*, and *Holopedium gibberum*) were least abundant in Emerald Lake during the last three years of record (1990-1992). Whether or not this reflects a recent downward trend in crustacean abundance, or an artifact of infrequent sampling during those years (once every two months) is unknown.

2.7. REFERERNCES

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Table 1. Ranges of dates for lake sampling by McCleneghan et al. (1985, 1986).

	Spring Surveys		Fall Surveys	
Range	1985	1986	1985	1986
Northwest Ranges	21-May - 3-Jun	13-May to 15-May	7-Oct to 9-Oct	26-Aug to 28-Aug
Northeast Ranges	4-Jun to 2-Jul	28-May to 18-Jun	13-Aug to 15-Aug	18-Aug to 21-Aug
Mendocino Ranges	13-May to 16-May	15-Apr to 27-May	22-Oct to 26-Nov	5-Aug to 7-Aug
Northern Sierra Nevada	13-Jun to 1-Jul	7-May to 2-Jul	16-Aug to 21-Aug	12-Aug to 14-Aug
Central Sierra Nevada	12-Jun to 16-Jul	2-Jun to 24-Jun	23-Aug to 1-Oct	2-Sep to 24-Oct
Southern Sierra Nevada	16-Jul to 3-Aug	25-Jun to 17-Jul	4-Sep to 1-Nov	9-Sep to 16-Oct
Southern California	23-Apr to 26-Apr	8-Apr to 10-Apr	4-Nov to 7-Nov	4-Nov to 5-Nov

Table 2. Chemical characteristics of high elevation Sierra Nevada lakes sampled with CARB support. Lakes were sampled during fall homothermy.

	pH	Alkalinity μEq L^{-1}	Conduct. μS cm^{-2}	Ca^{2+} μEq L^{-1}	Mg^{2+} μEq L^{-1}	Na^{+} μEq L^{-1}	K^{+} μEq L^{-1}	Base Cations μEq L^{-1}	NO$_3^-$ μEq L^{-1}	SO$_4^{2-}$ μEq L^{-1}	Cl$^-$ μEq L^{-1}	Si μM
Mean + SE	6.49 ± 0.06	70.8 ± 7.0	21.3 ± 2.8	113.4 ± 13.7	24.3 ± 3.7	27.7 ± 3.6	7.3 ± 0.6	172.3 ± 18.1	3.02 ± 0.61	105.3 ± 19.8	4.1 ± 0.3	31.2 ± 2.4
N	87	87	87	89	89	89	89	89	89	89	89	57
Minimum	4.71	-12.0	2.8	9.0	2.4	5.3	1.1	19.6	0.00	2.9	0.0	3.7
Maximum	7.65	341.0	159.3	787	186.0	316.0	28.0	1012.0	26.24	920.0	23.5	71.8
Median	6.5	56	9.5	56.9	11.0	21.1	5.3	95.1	0.47	25.0	3.9	29.0
WLS median*	6.93	60	—	43	6	19	—	76	0.4	7	2	—

*Median of the target population (N = 2119) of Sierra Nevada lakes from the EPA Western Lake Survey (Melack & Stoddard 1991).

Table 3. Numbers of high elevation Sierra Nevada lakes in ANC categories. Data set included 89 lakes sampled in autumn.

ANC range (μEq L^{-1})	Number of Lakes	Percentage of Lakes
<0	4	4.5 %
0 - 50	36	40.4 %
51 - 100	34	38.2 %
101 - 150	7	7.8 %
151 - 200	2	2.2 %
201 - 250	3	3.3 %
251 - 300	1	1.1 %
301 - 350	2	2.2 %

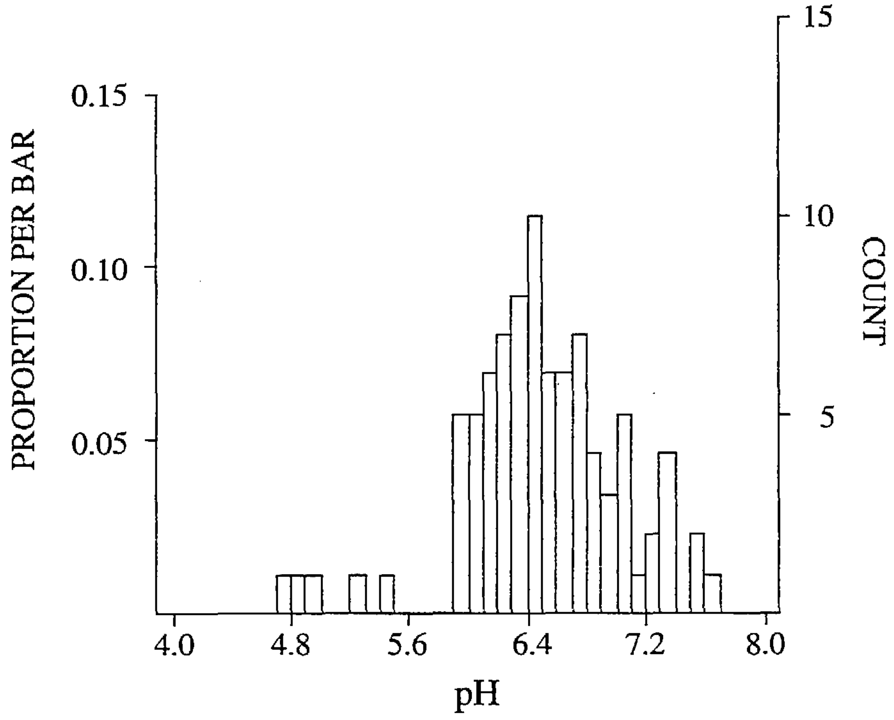

Figure 1. Frequency histogram of surface pH for 87 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.

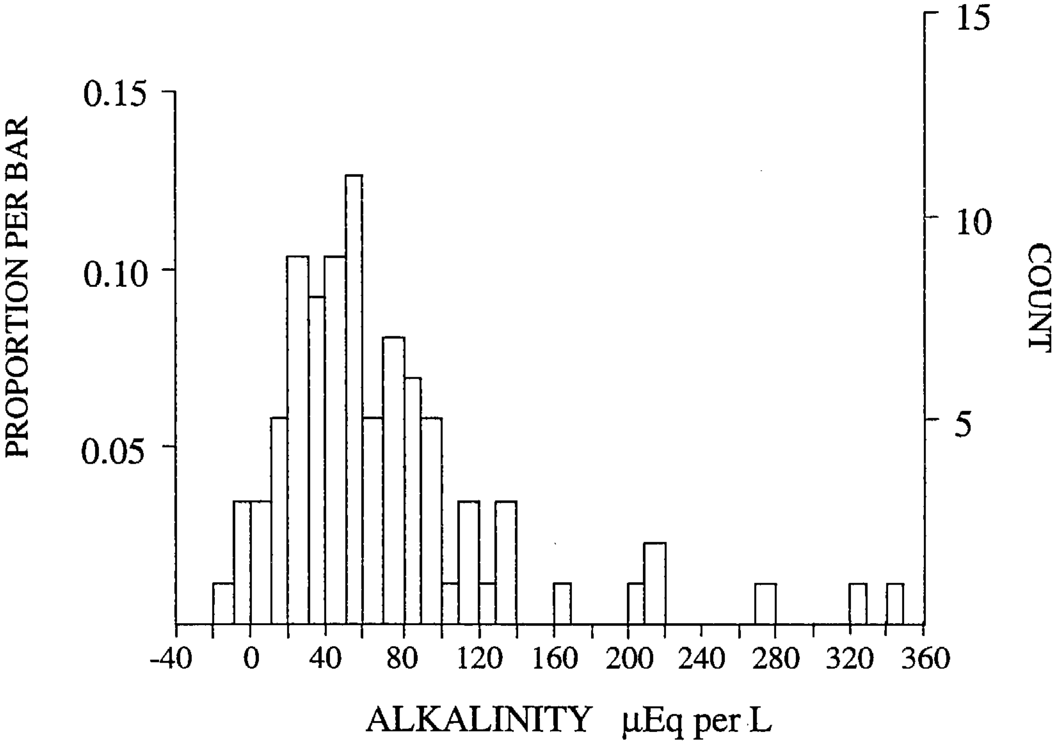

Figure 2. Frequency histogram of surface alkalinity for 87 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.

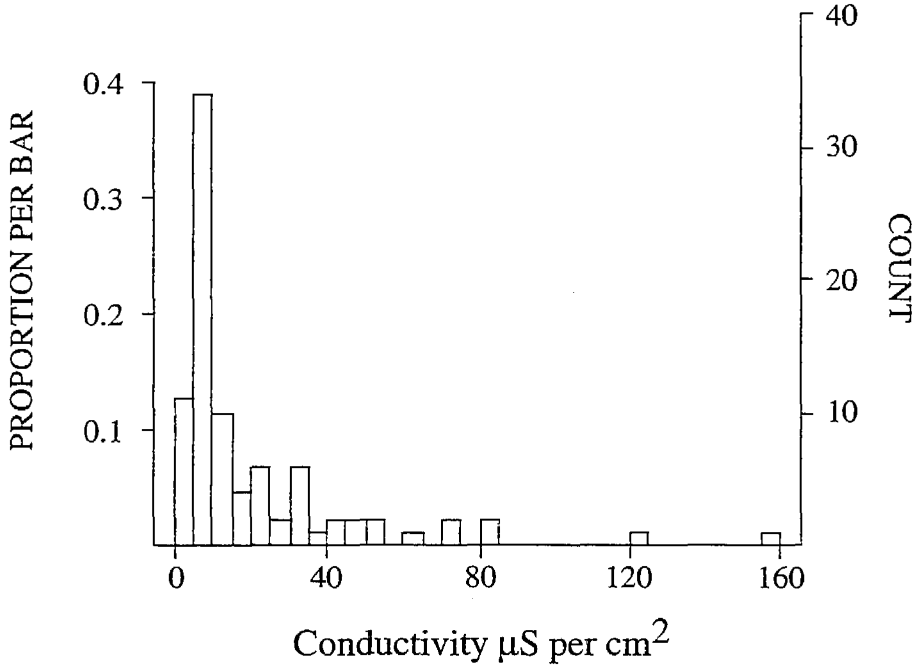

Figure 3. Frequency histogram of surface conductivity for 87 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.

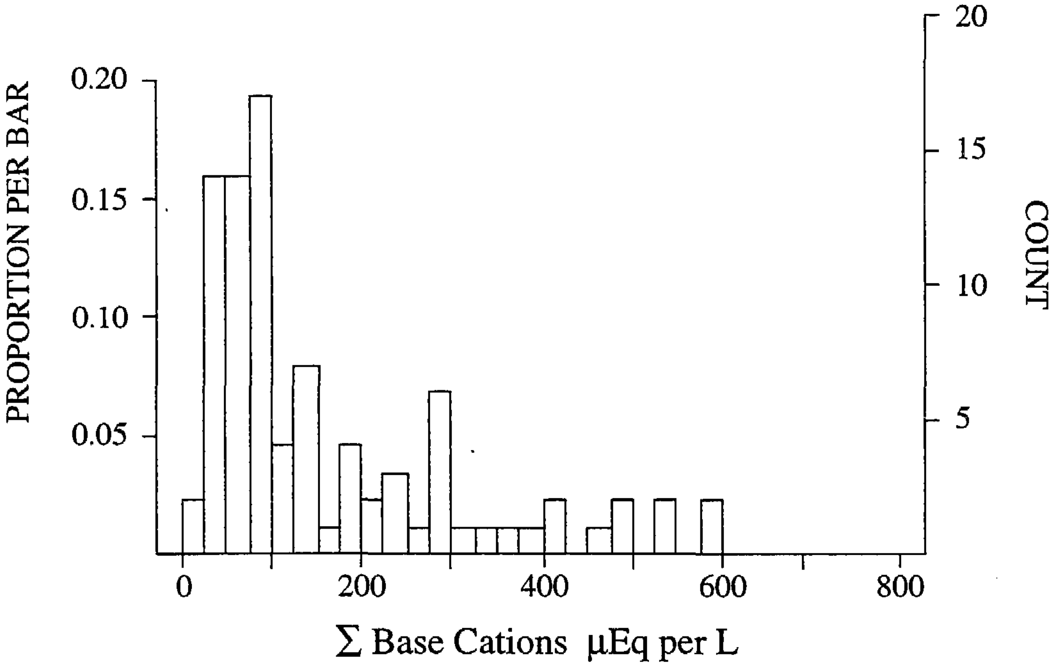

Figure 4. Frequency histogram of ∑ base cations in surface water for 89 high elevation Sierra Nevada lakes in sampled in autumn between 1981 and 1993. Omitted from the figure is a single outlier with the value 1012 μEq per L.

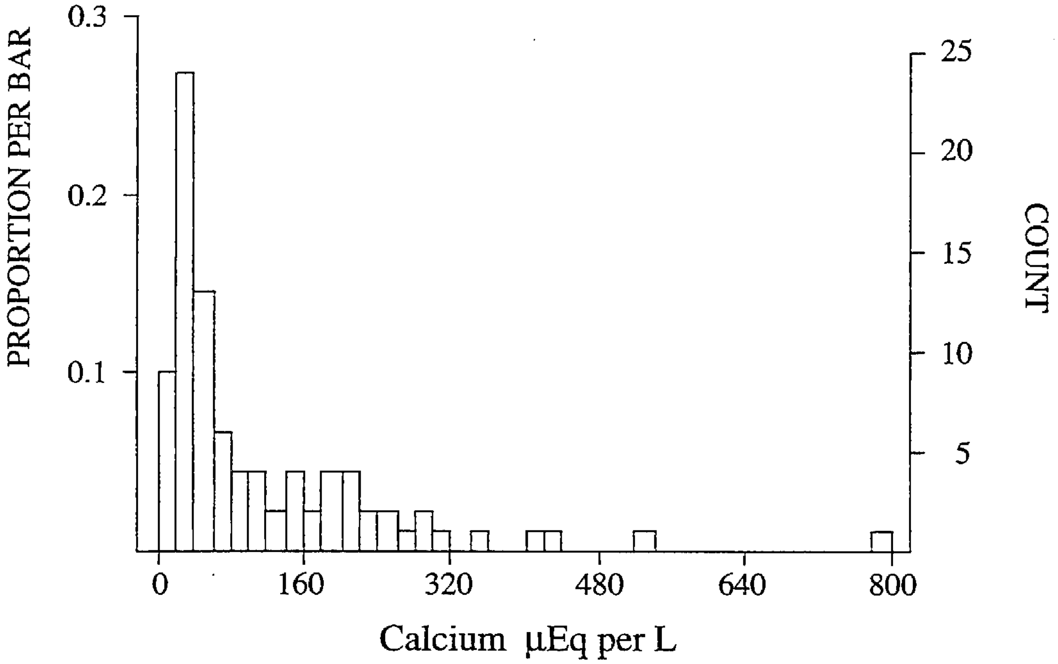

Figure 5. Frequency histogram of surface calcium for 89 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.

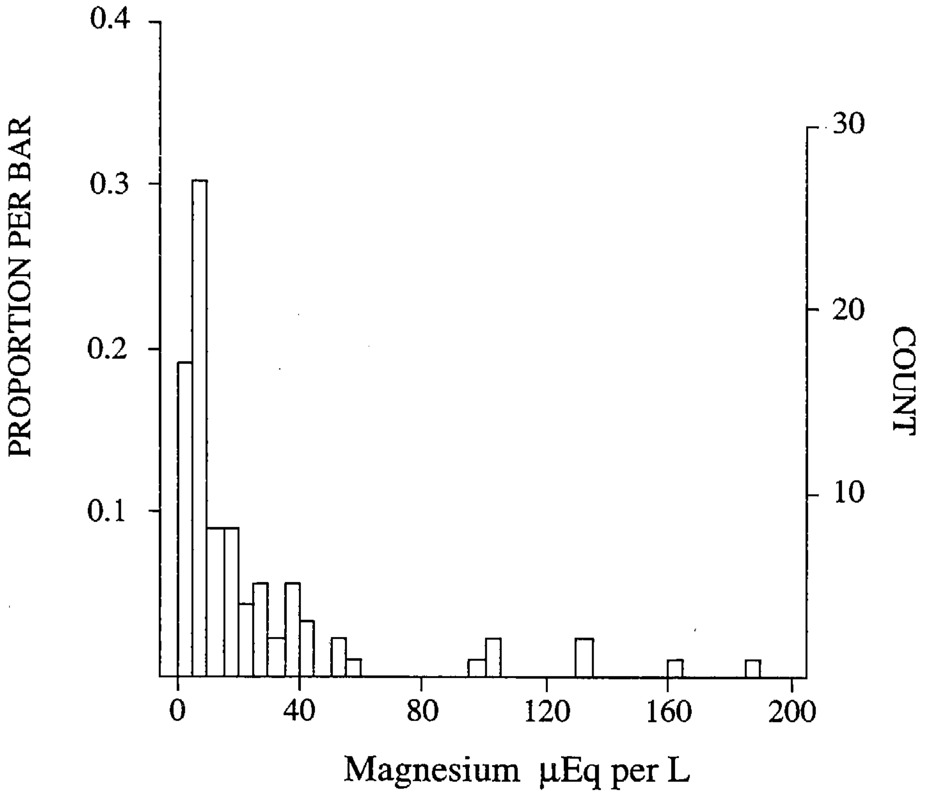

Figure 6. Frequency histogram of surface magnesium for 89 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.`

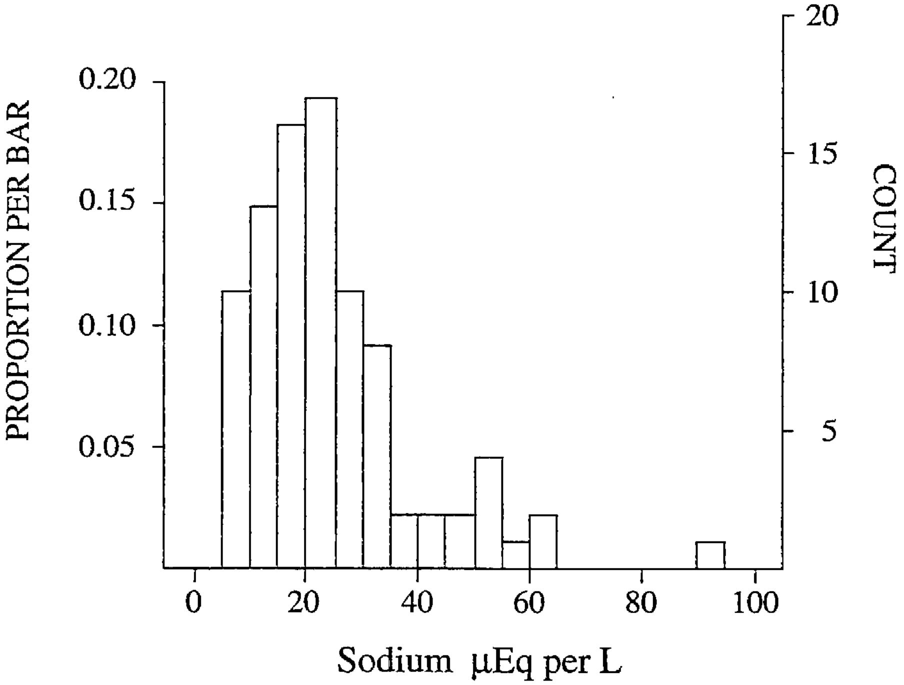

Figure 7. Frequency histogram of surface sodium for 89 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.

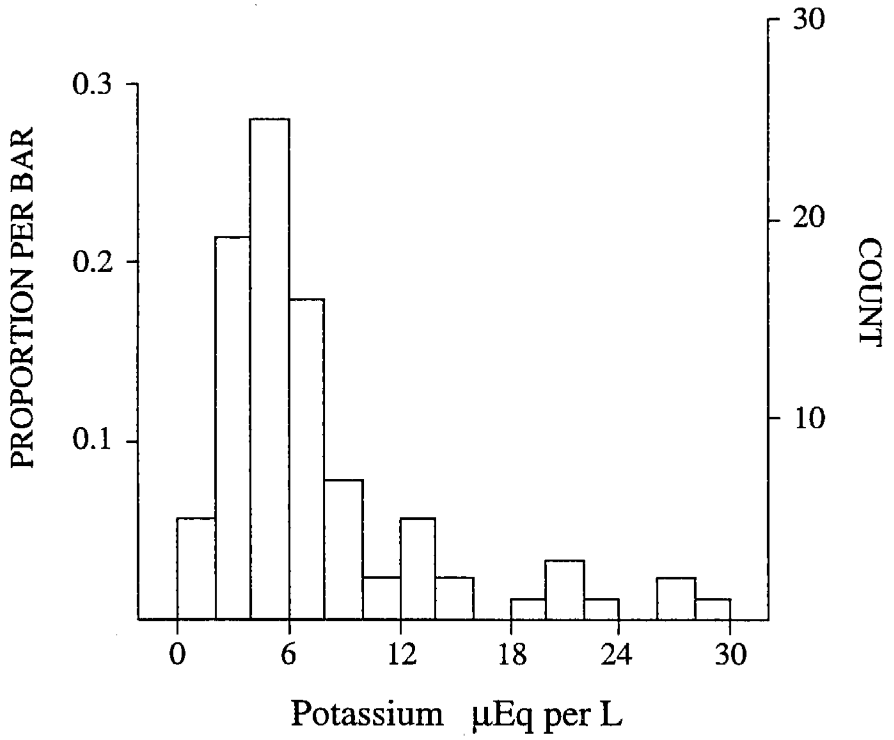

Figure 8. Frequency histogram of surface potassium for 89 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.

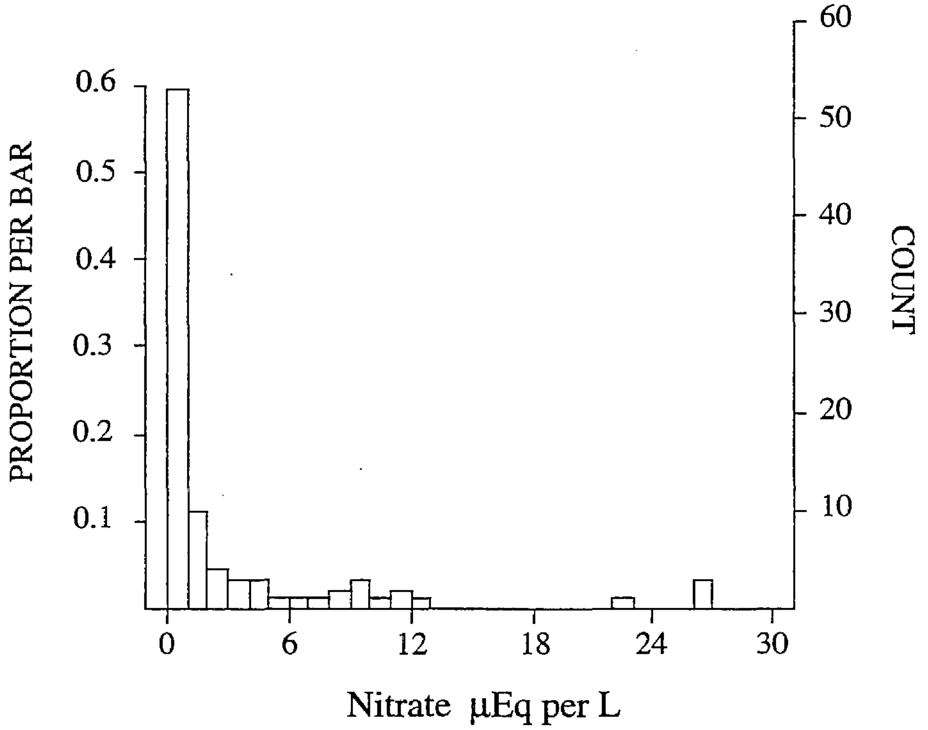

Figure 9. Frequency histogram of surface nitrate for 89 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.

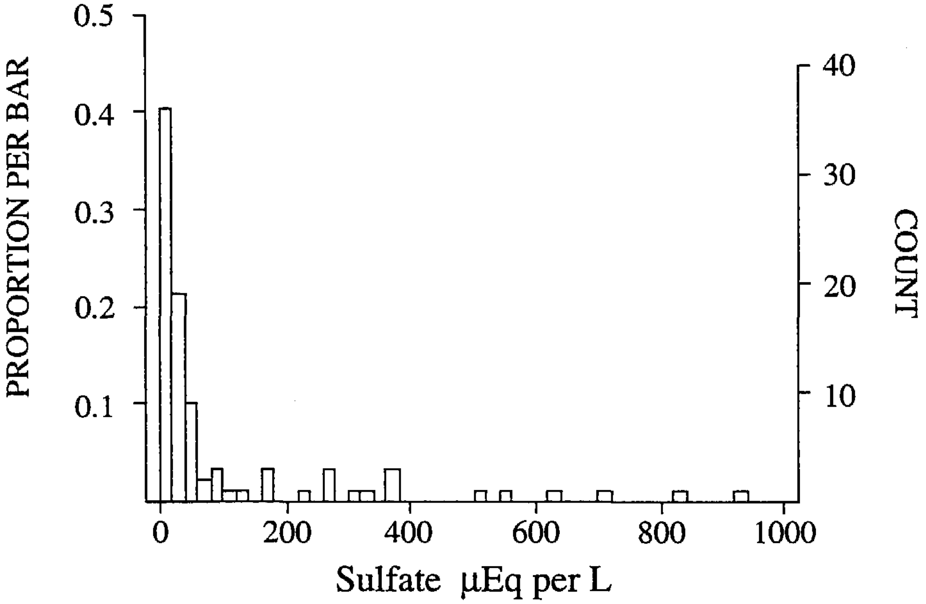

Figure 10. Frequency histogram of surface sulfate for 89 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.

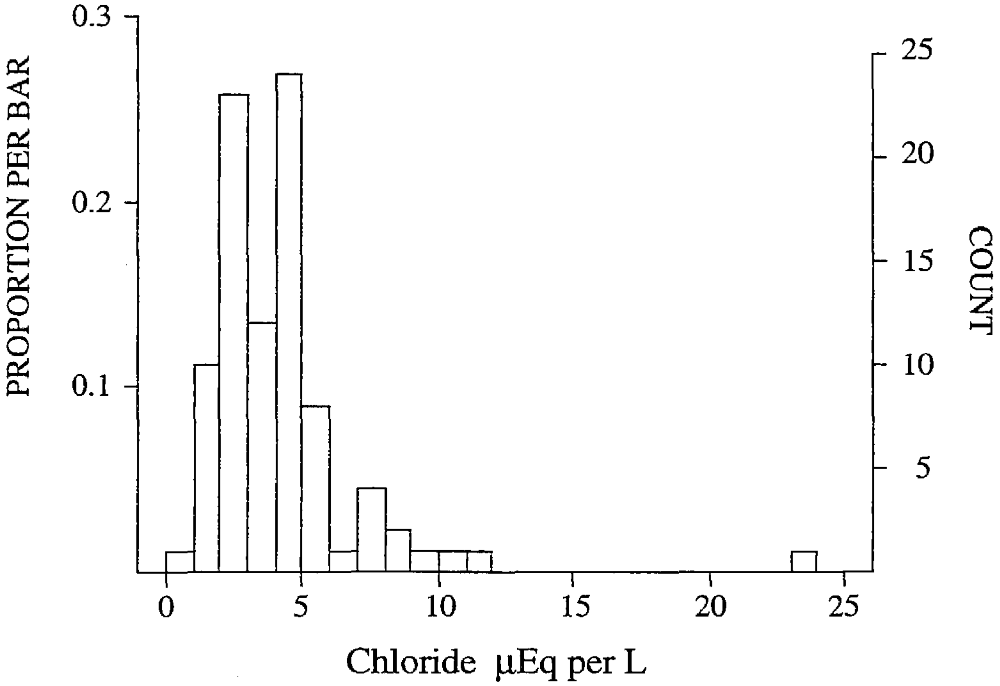

Figure 11. Frequency histogram of surface chloride for 89 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.

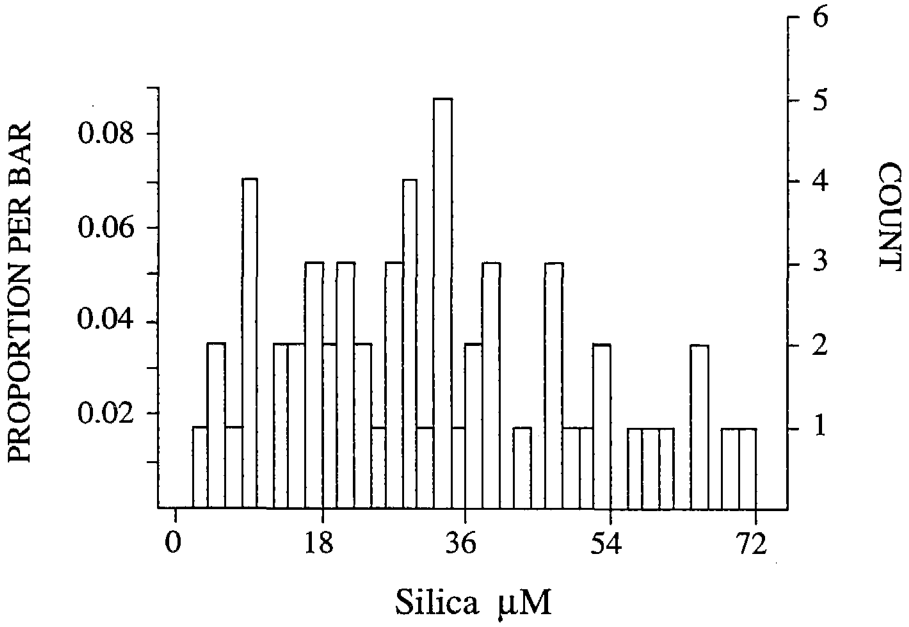

Figure 12. Frequency histogram of surface silica for 89 high elevation Sierra Nevada lakes sampled in autumn between 1981 and 1993.

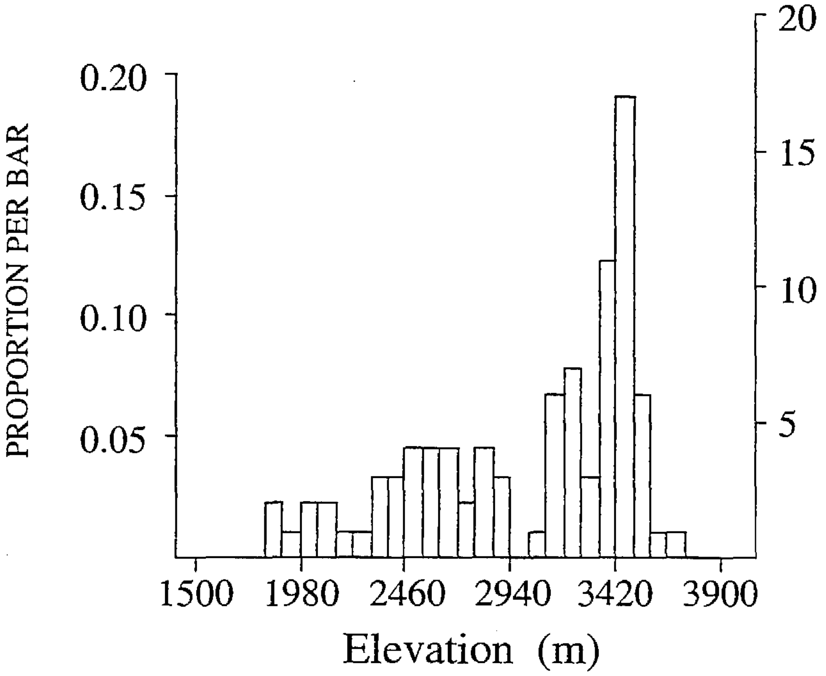

Figure 13. Frequency histogram of elevation for 89 high elevation Sierra Nevada lakes sampled between 1981 and 1993.

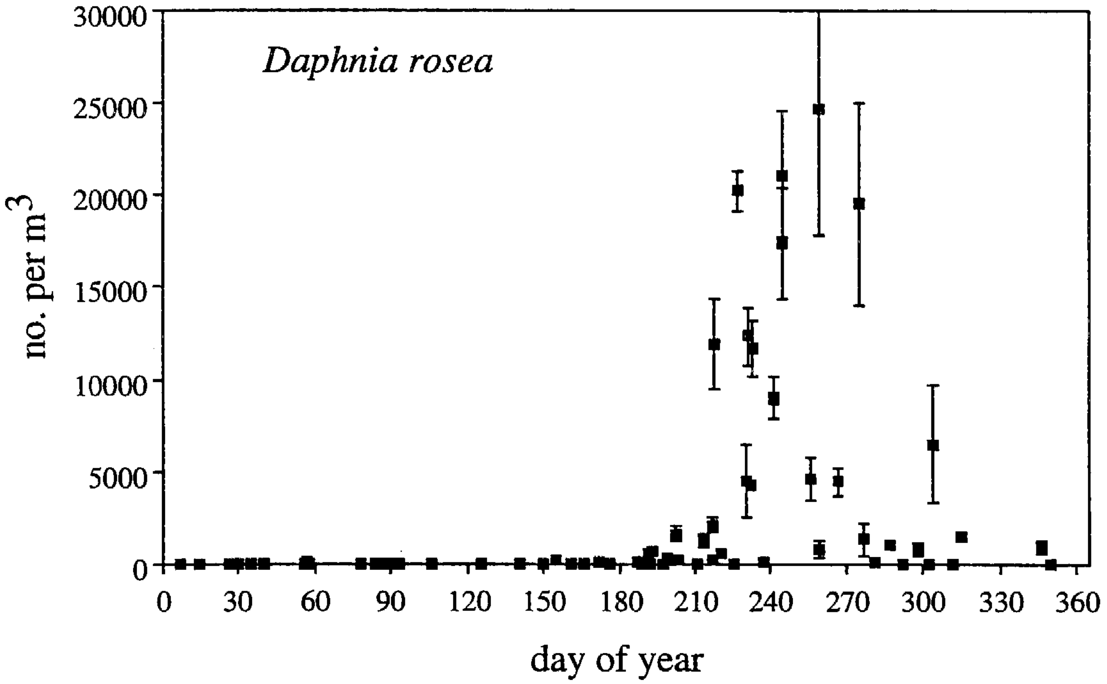

Figure 14. Mean abundance of *Daphnia rosea* in Emerald Lake by day of year. Data are combined results of sampling from July 1984 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

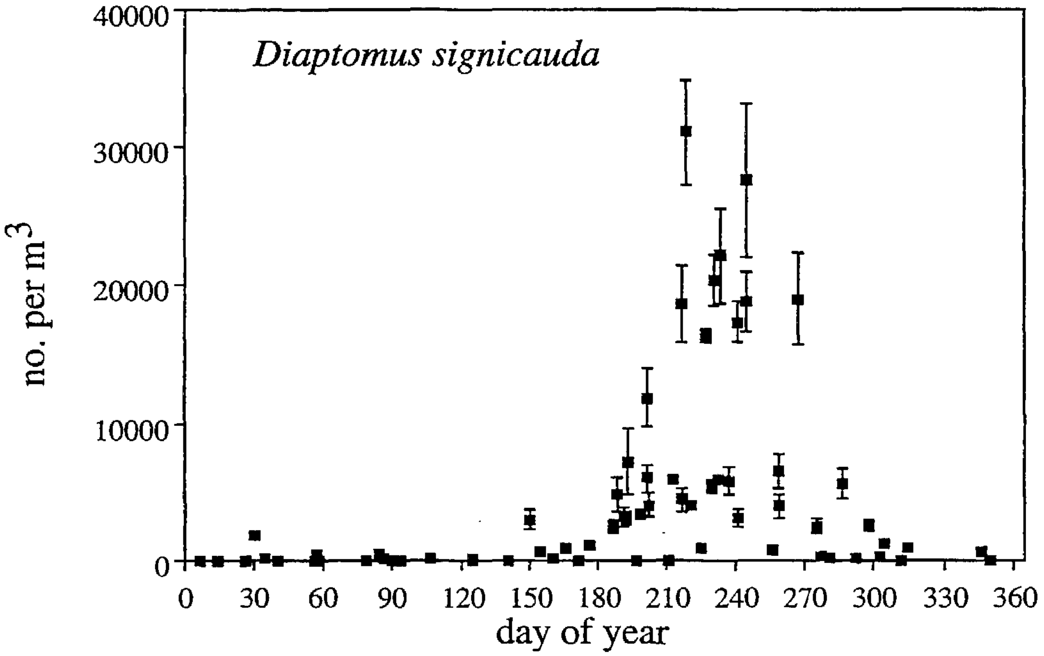

Figure 15. Mean abundance of *Diaptomus signicauda* in Emerald Lake by day of year. Data are combined results of sampling from July 1984 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

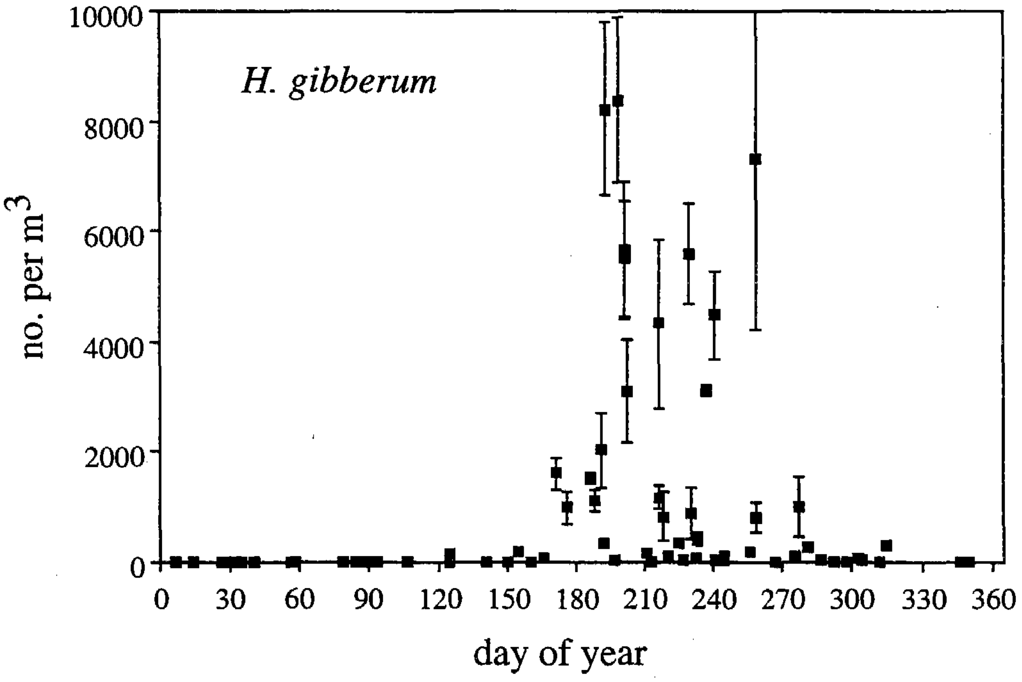

Figure 16. Mean abundance of *Holopedium gibberum* in Emerald Lake by day of year. Data are combined results of sampling from July 1984 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

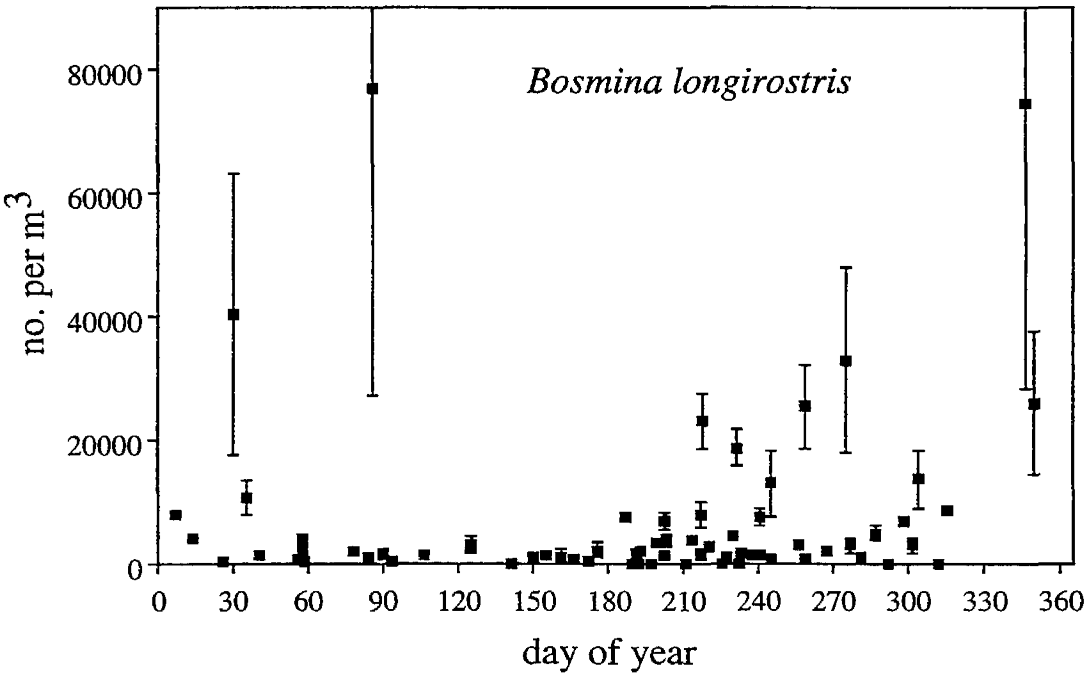

Figure 17. Mean abundance of *Bosmina longirostris* in Emerald Lake by day of year. Data are combined results of sampling from July 1984 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

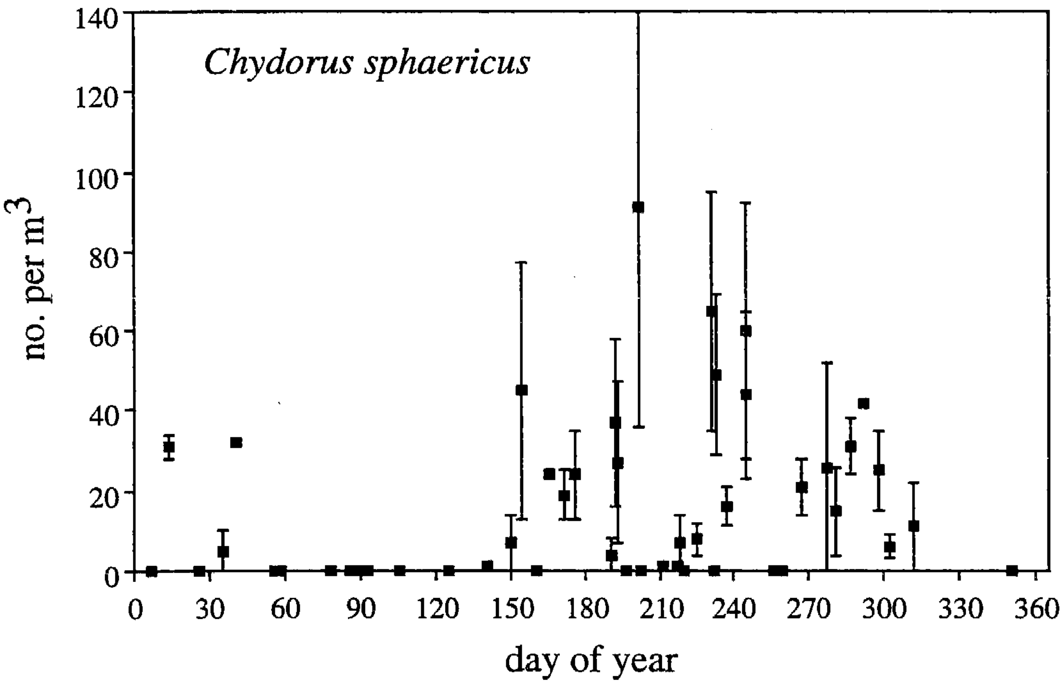

Figure 18. Mean abundance of *Chydorus sphaericus* in Emerald Lake by day of year. Data are combined results of sampling from July 1984 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

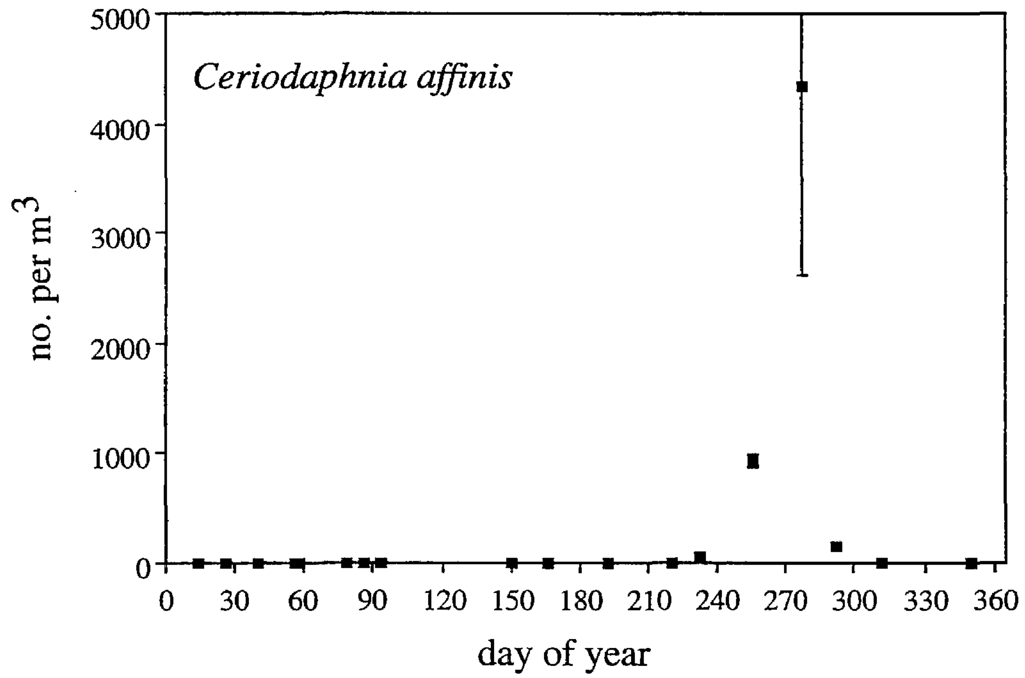

Figure 19. Mean abundance of *Ceriodaphnia affinis* in Emerald Lake by day of year. Data are combined results of sampling from February 1989 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

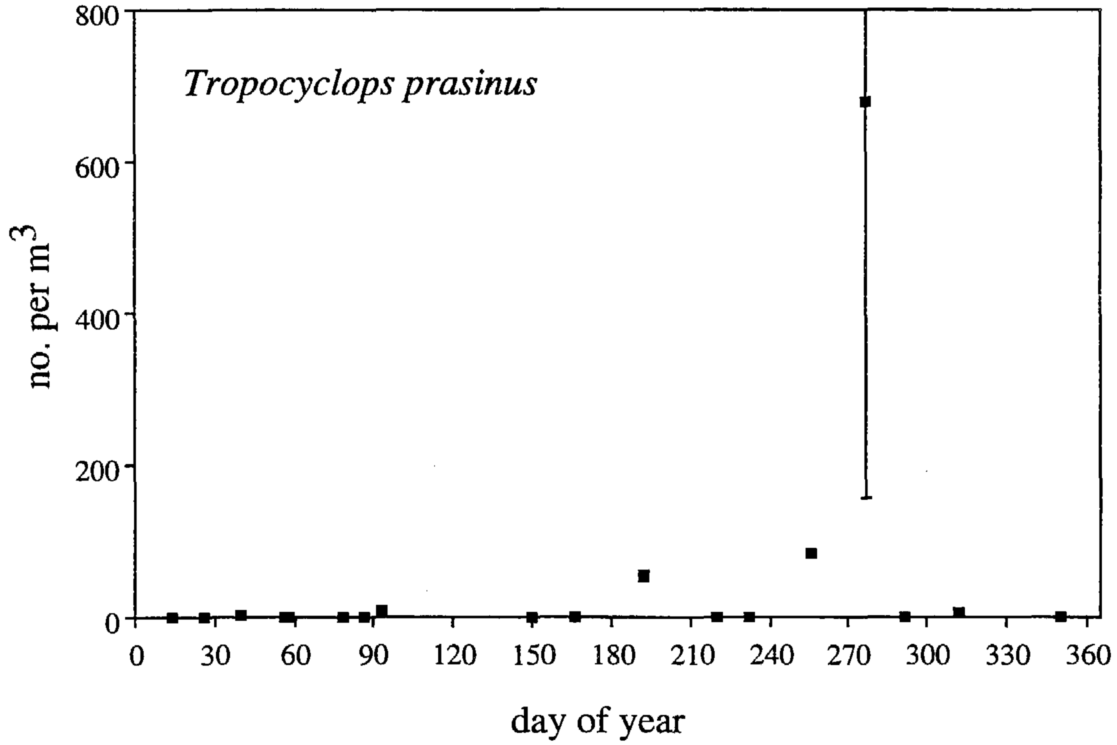

Figure 20. Mean abundance of *Tropocyclops prasinus* in Emerald Lake by day of year. Data are combined results of sampling from February 1989 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

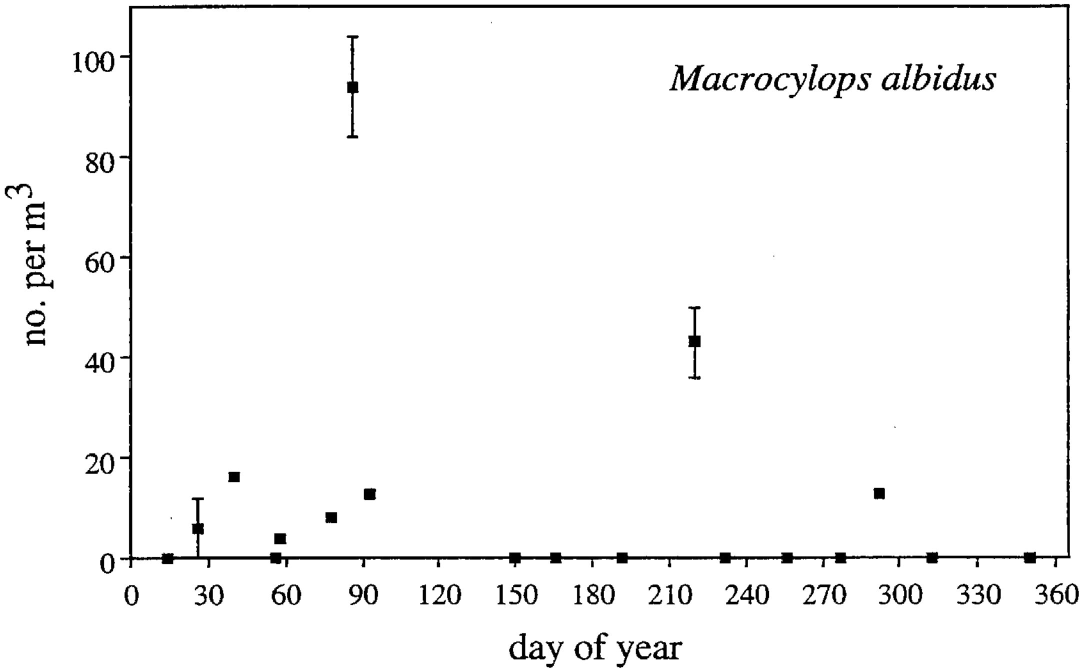

Figure 21. Mean abundance of *Macrocyclops albidus* in Emerald Lake by day of year. Data are combined results of sampling from February 1989 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

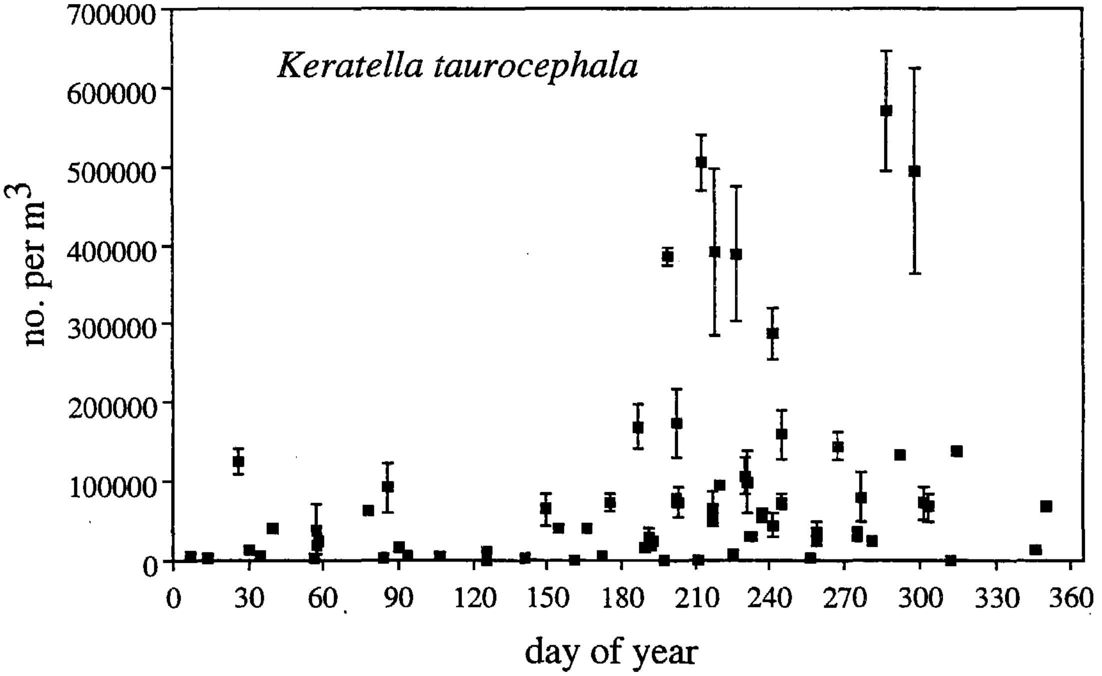

Figure 22. Mean abundance of *Keratella taurocephala* in Emerald Lake by day of year. Data are combined results of sampling from July 1984 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

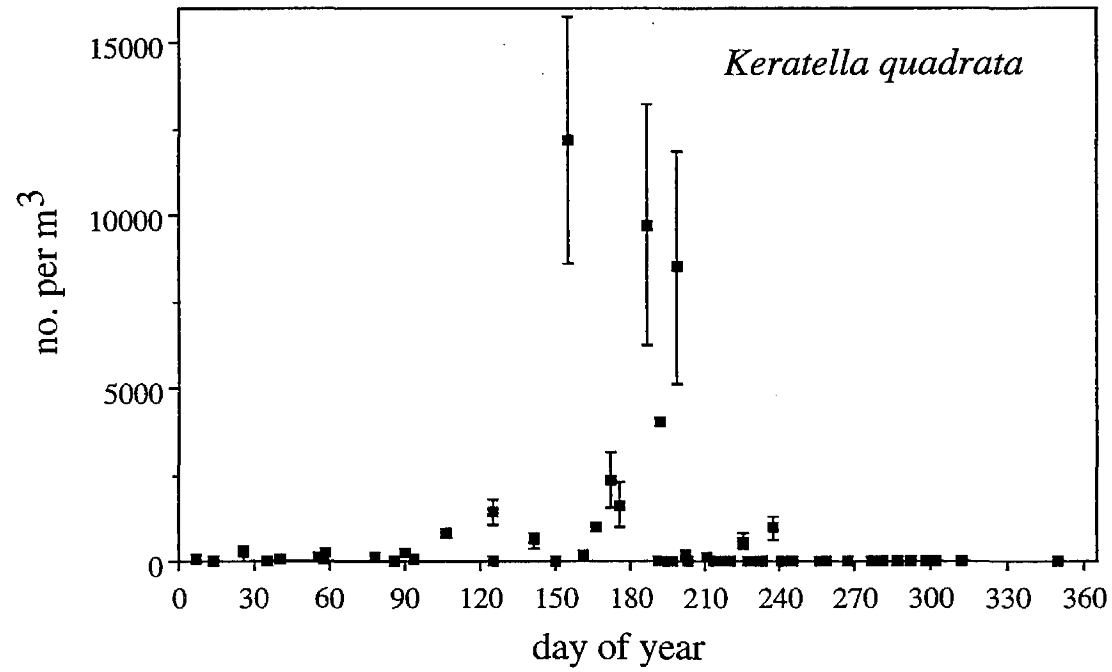

Figure 23. Mean abundance of *Keratella quadrata* in Emerald Lake by day of year. Data are combined results of sampling from July 1984 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

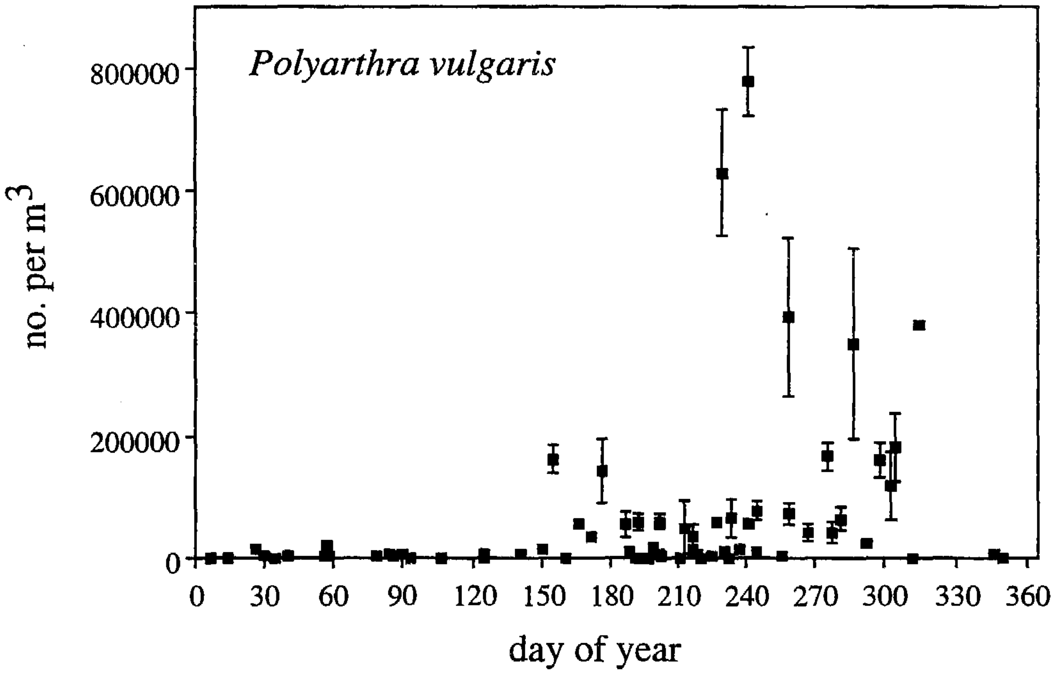

Figure 24. Mean abundance of *Polyarthra vulgaris* in Emerald Lake by day of year. Data are combined results of sampling from July 1984 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

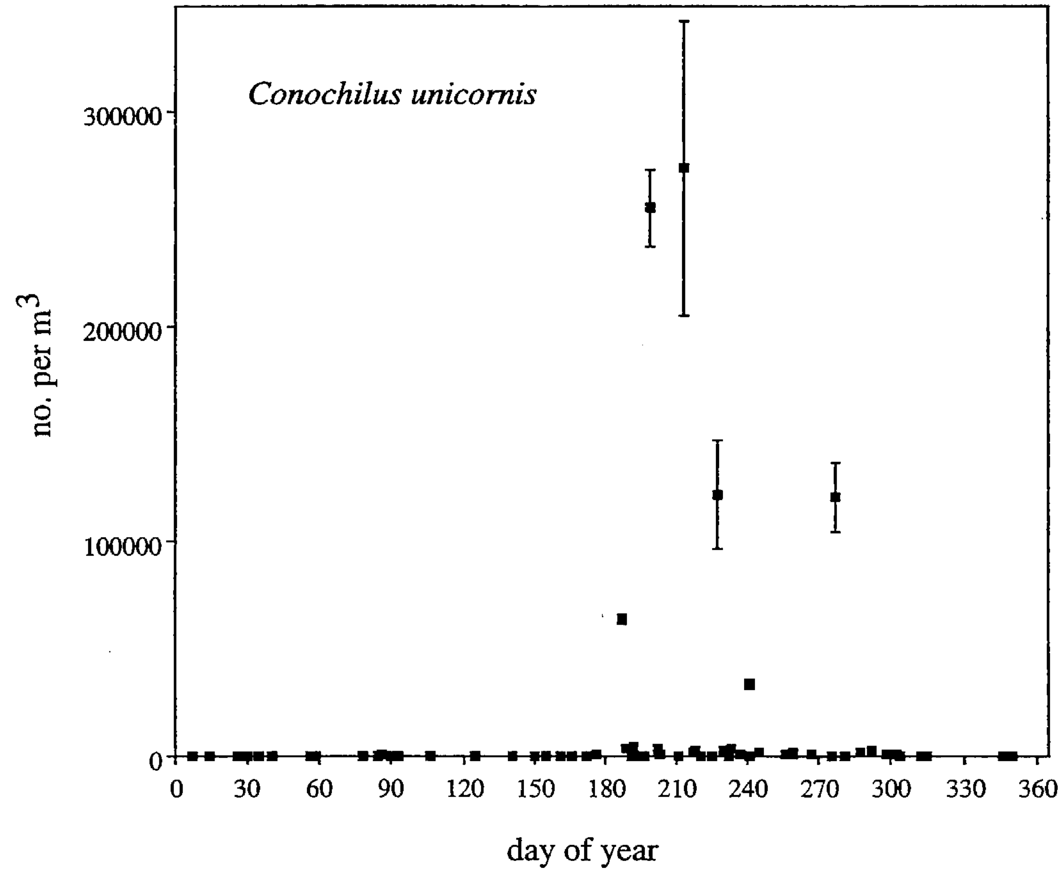

Figure 25. Mean abundance of *Conochilus unicornis* in Emerald Lake by day of year. Data are combined results of sampling from July 1984 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

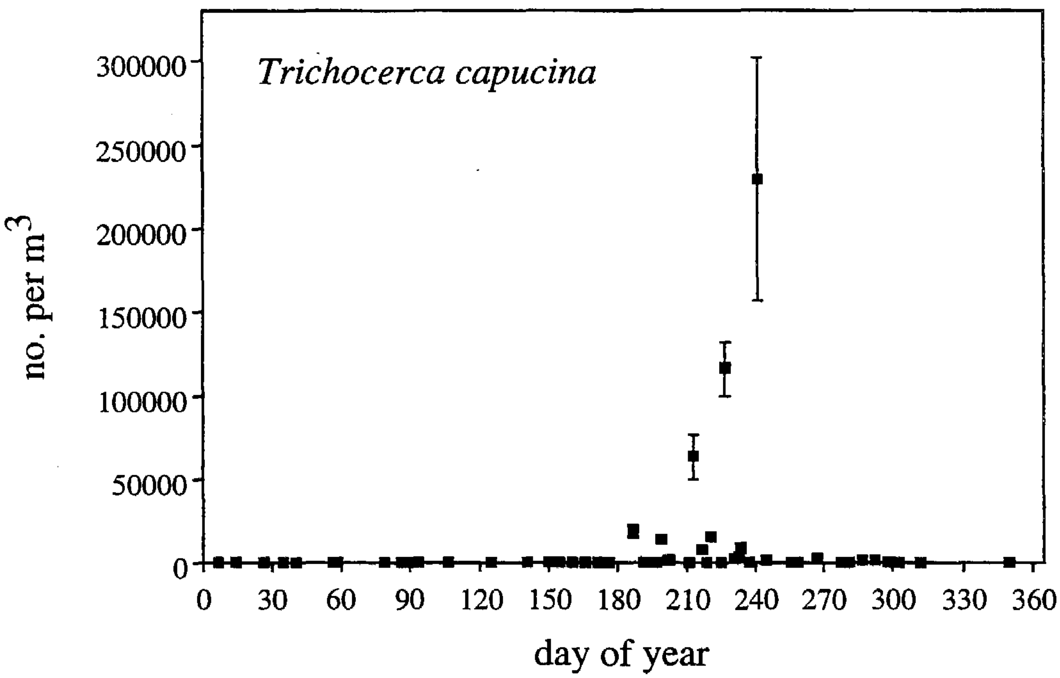

Figure 26. Mean abundance of *Trichocerca capucina* in Emerald Lake by day of year. Data are combined results of sampling from July 1984 to December 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

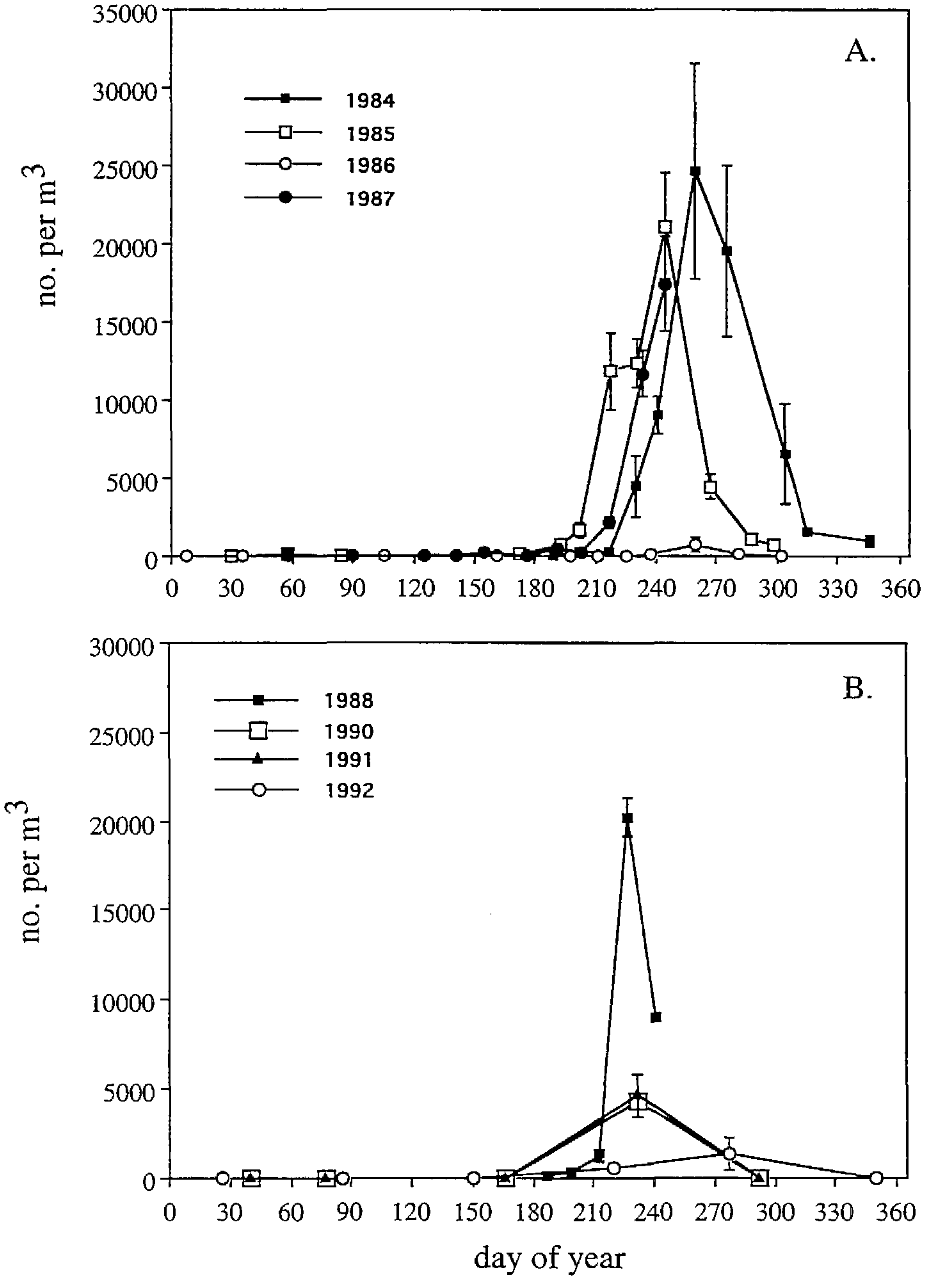

Figure 27. Mean abundance of *Daphnia rosea* in Emerald Lake by day of year. A. Abundances in 1984, 1985, 1986 and 1987. B. Abundances in 1988, 1990, 1991 and 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

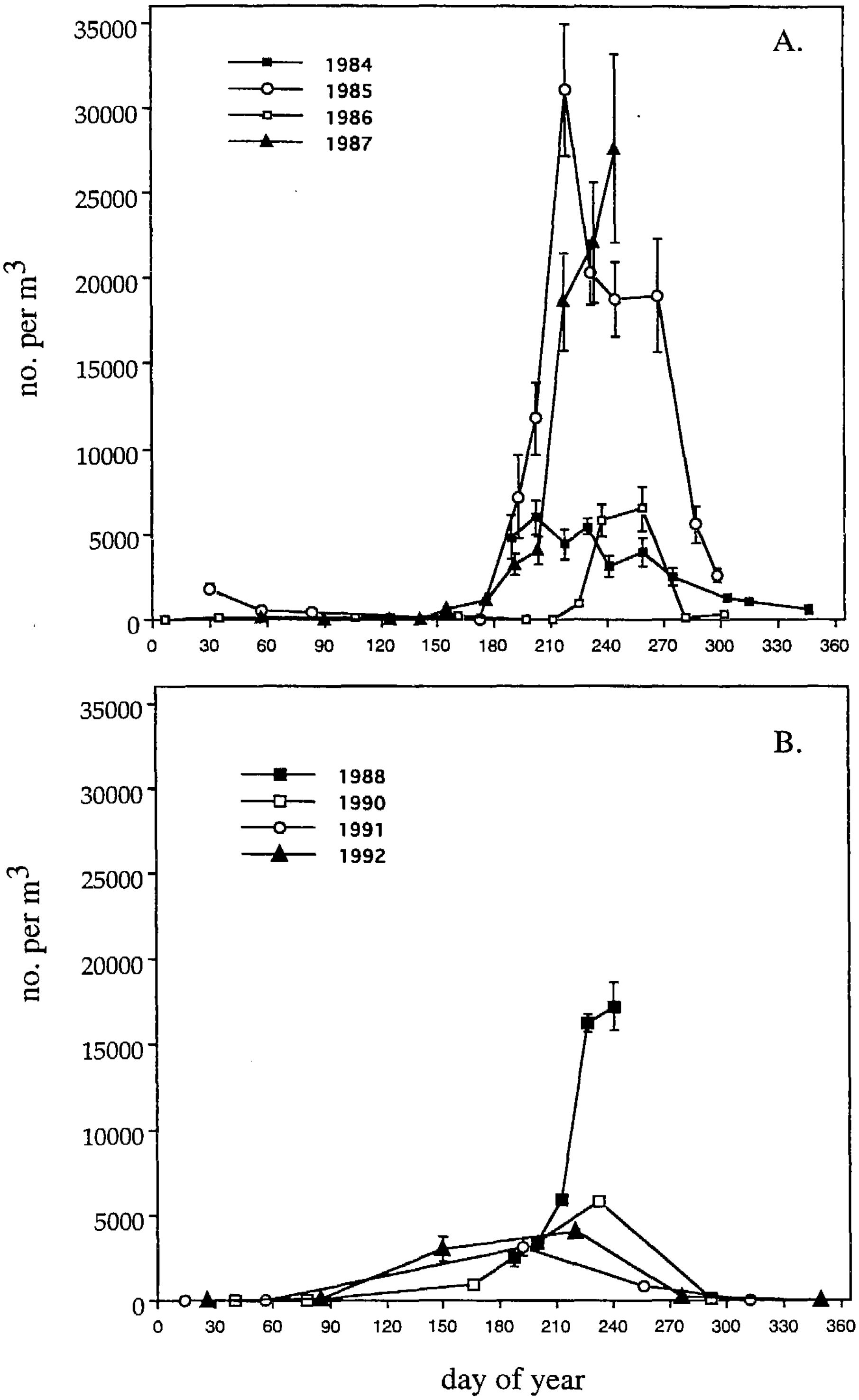

Figure 28. Mean abundance of *Diaptomus signicauda* in Emerald Lake by day of year. A. Abundances in 1984, 1985, 1986 and 1987. B. Abundances in 1988, 1990, 1991 and 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

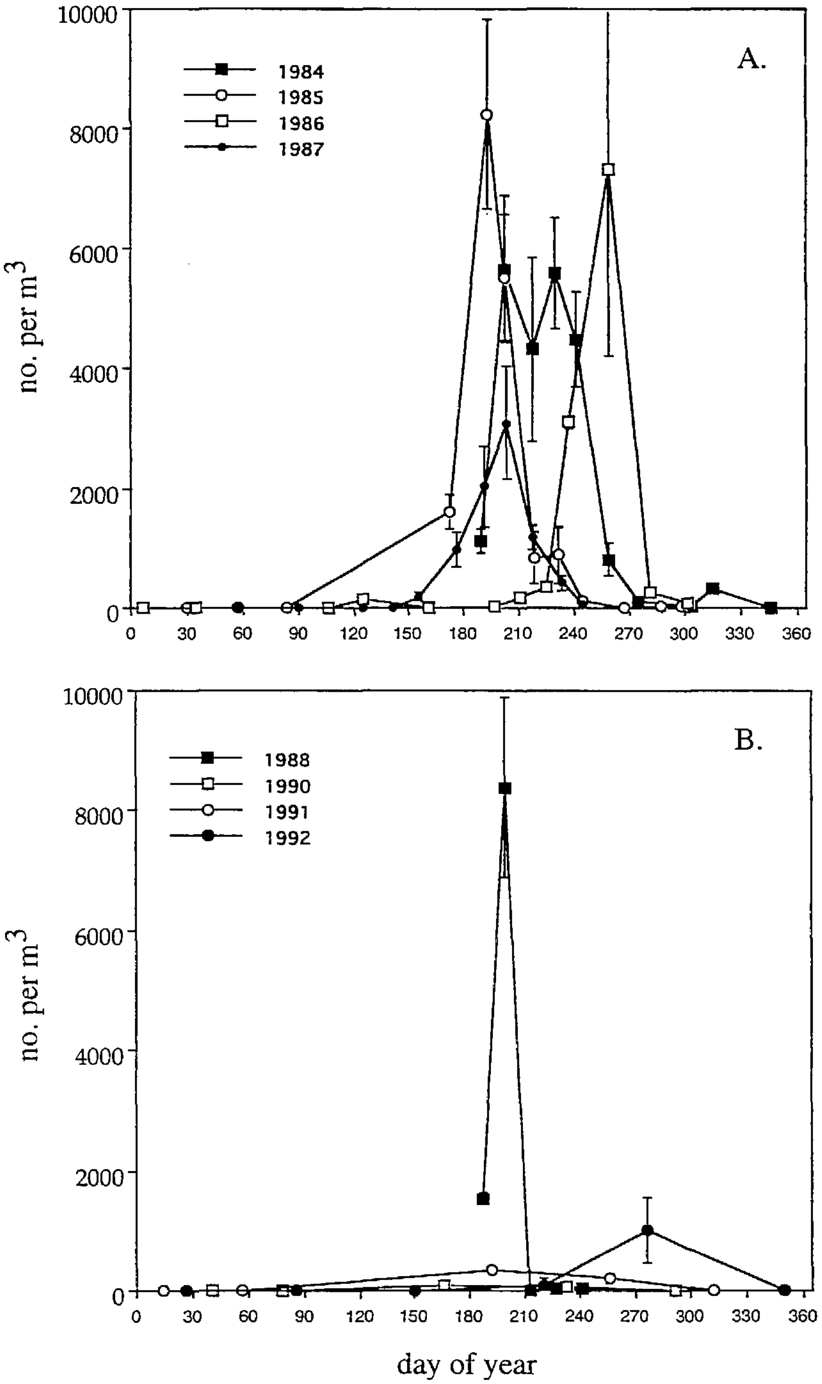

Figure 29. Mean abundance of *Holopedium gibberum* in Emerald Lake by day of year. A. Abundances in 1984, 1985, 1986 and 1987. B. Abundances in 1988, 1990, 1991 and 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

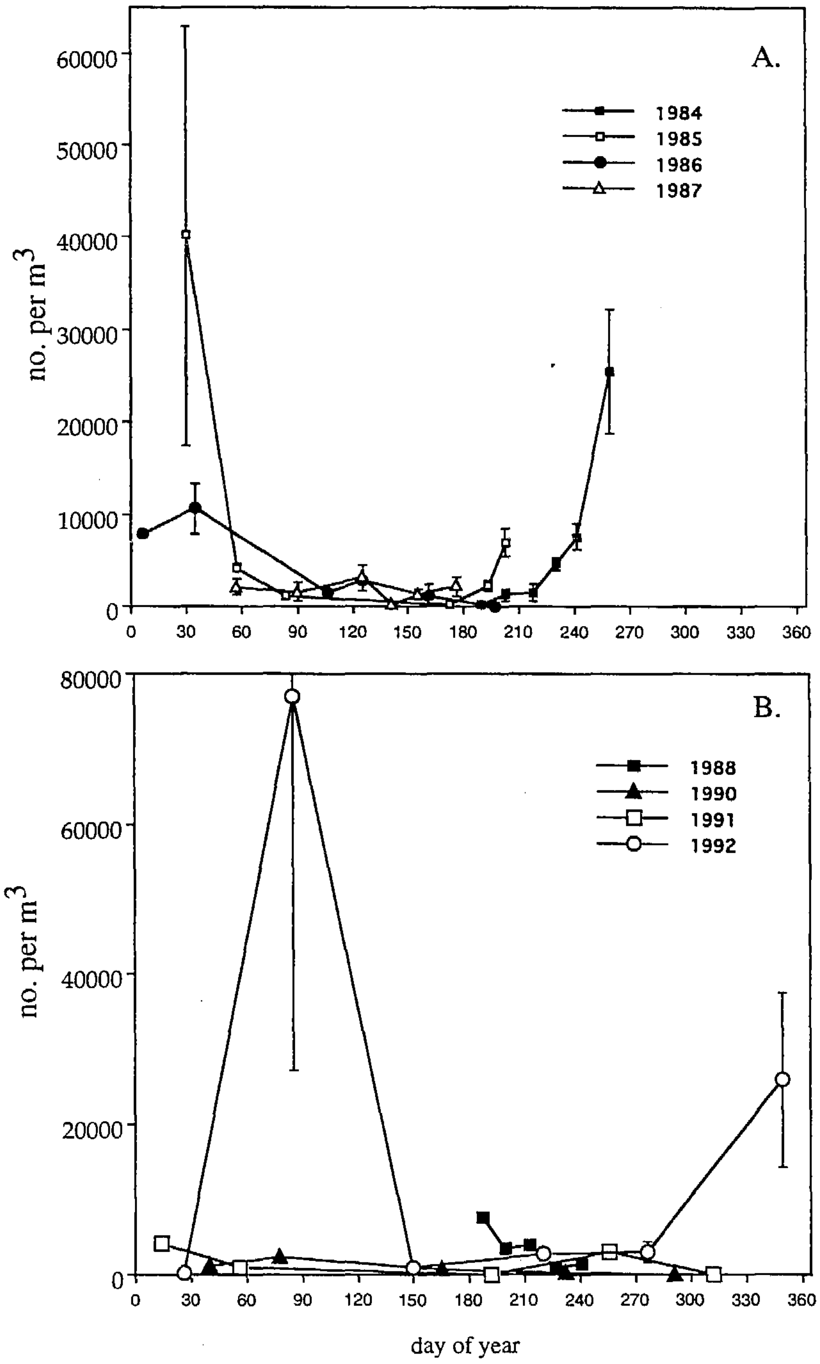

Figure 30. Mean abundance of *Bosmina longirostris* in Emerald Lake by day of year. A. Abundances in 1984, 1985, 1986 and 1987. B. Abundances in 1988, 1990, 1991 and 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

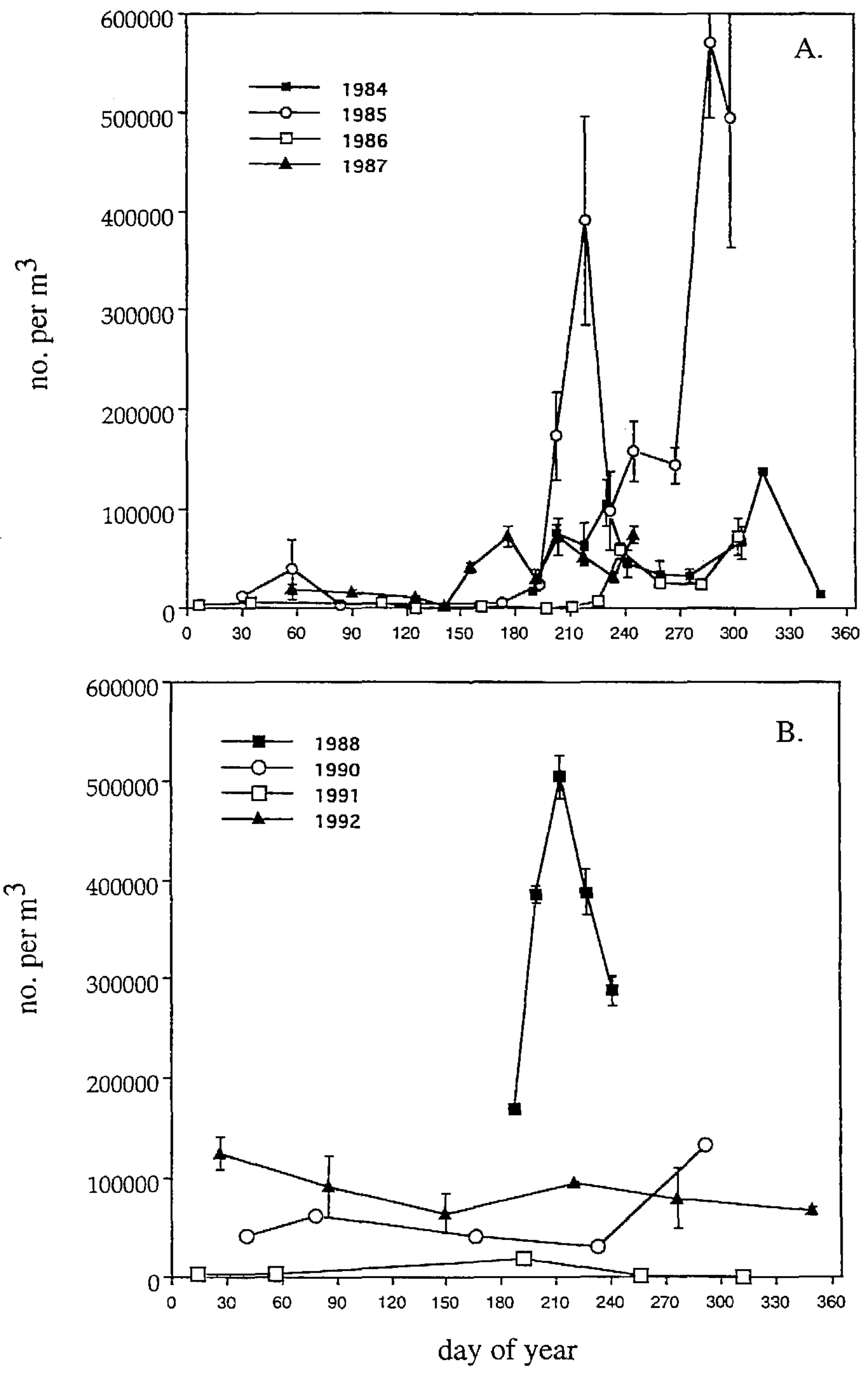

Figure 31. Mean abundance of *Keratella taurocephala* in Emerald Lake by day of year. A. Abundances in 1984, 1985, 1986 and 1987. B. Abundances in 1988, 1990, 1991 and 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

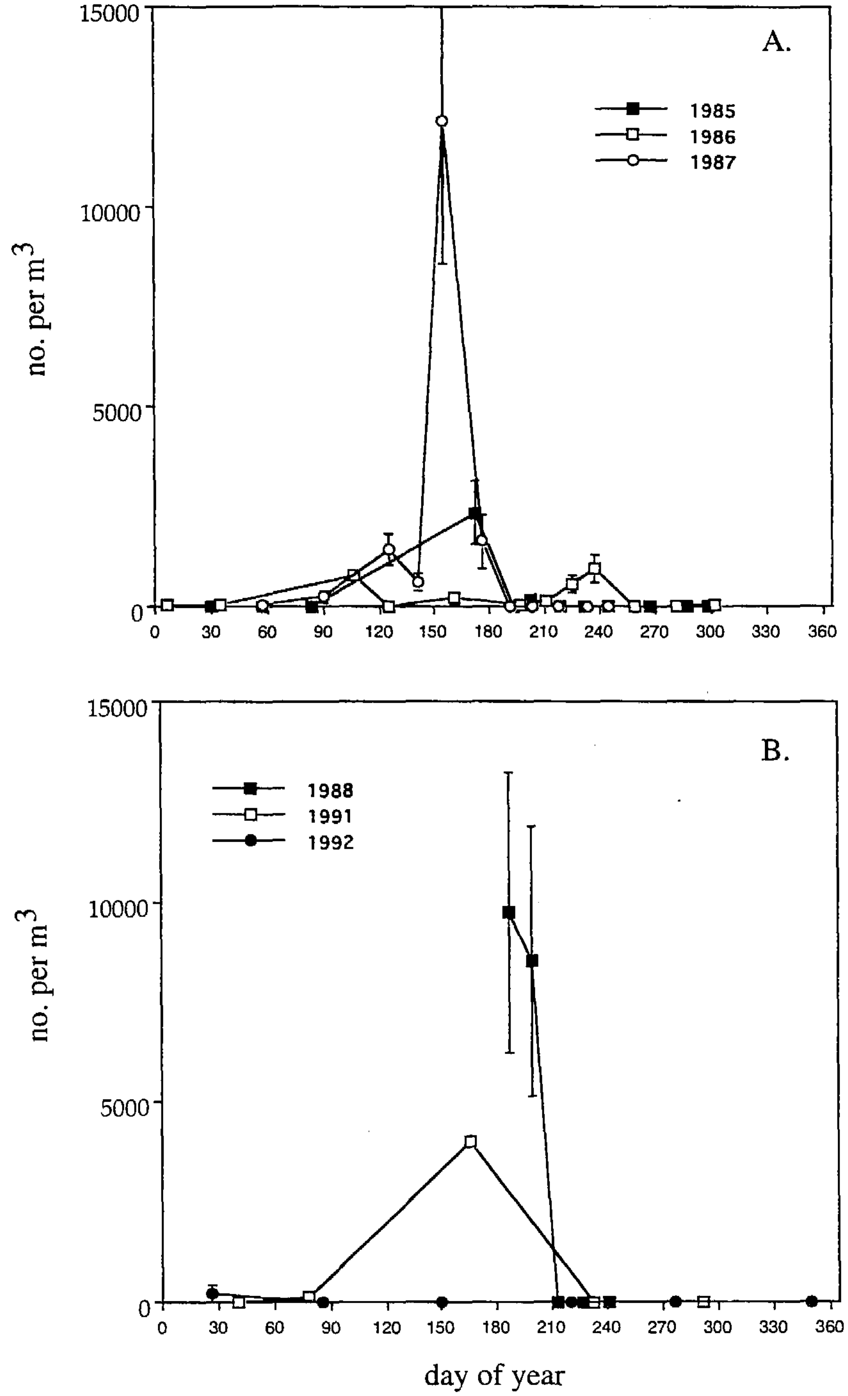

Figure 32. Mean abundance of *Keratella quadrata* in Emerald Lake by day of year. A. Abundances in 1984, 1985, 1986 and 1987. B. Abundances in 1988, 1991 and 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

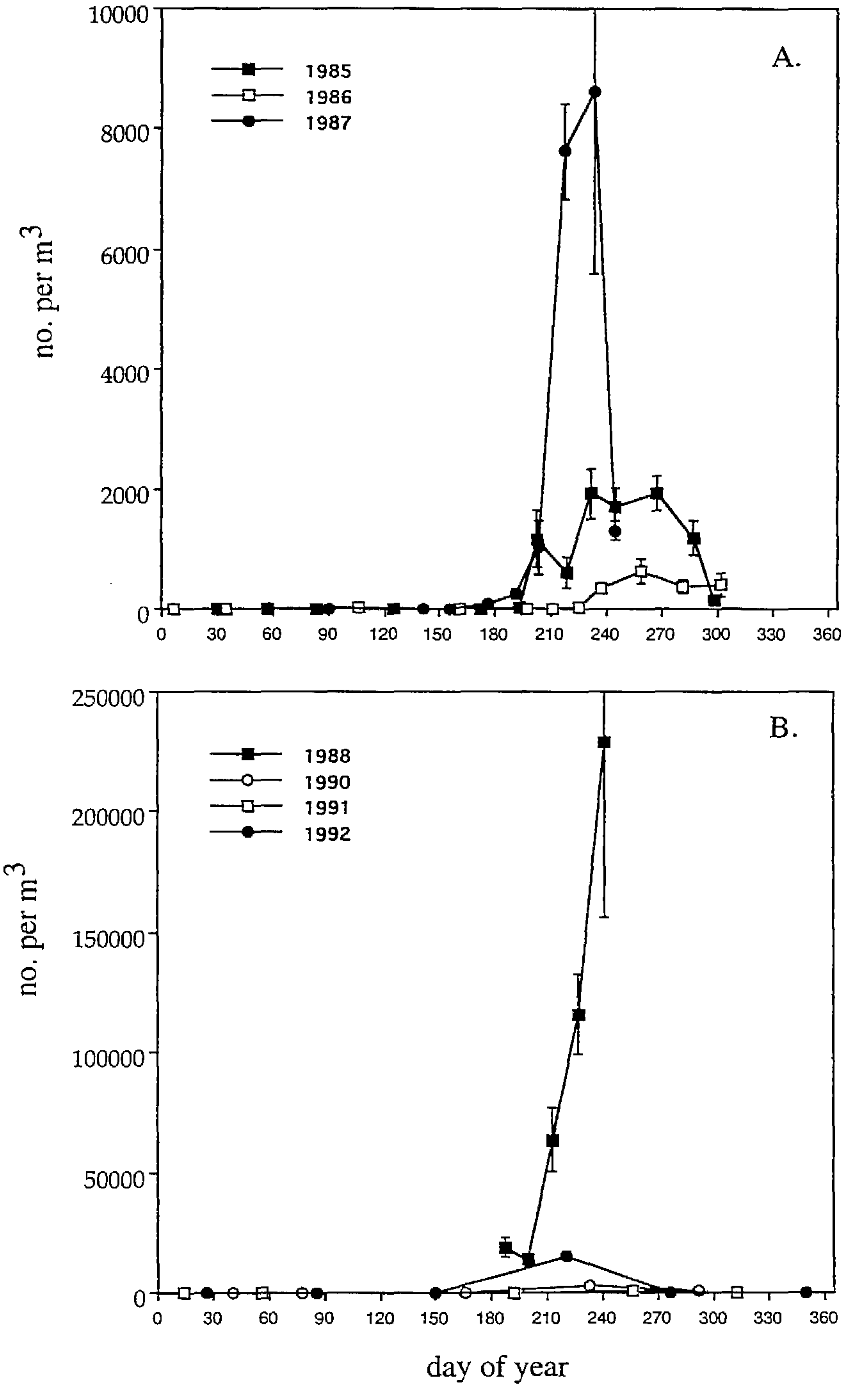

Figure 33. Mean abundance of *Trichocerca capucina* in Emerald Lake by day of year. A. Abundances in 1985, 1986 and 1987. B. Abundances in 1988, 1990, 1991 and 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

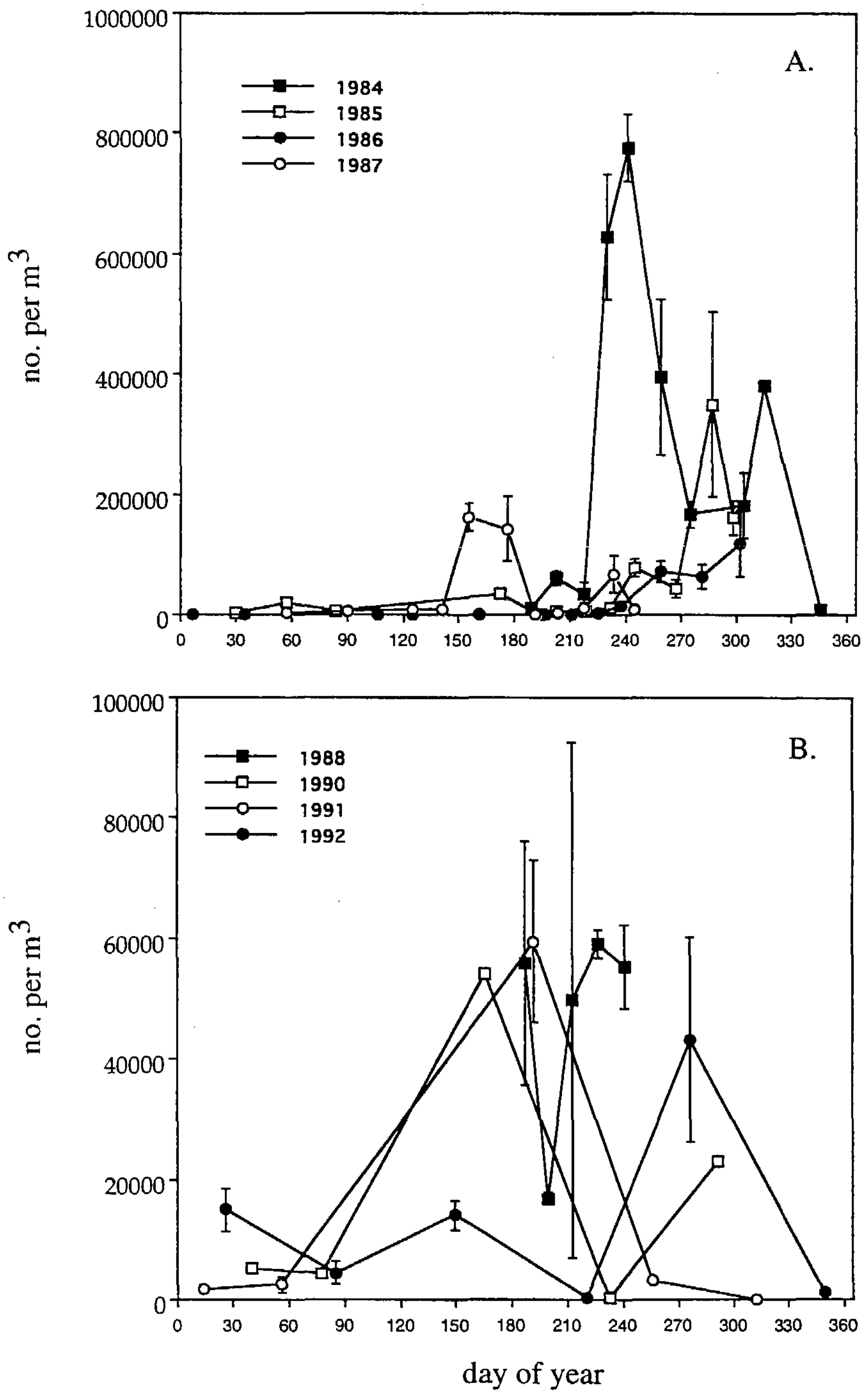

Figure 34. Mean abundance of *Polyarthrus vulgaris* in Emerald Lake by day of year. A. Abundances in 1984, 1985, 1986 and 1987. B. Abundances in 1988, 1990, 1991 and 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

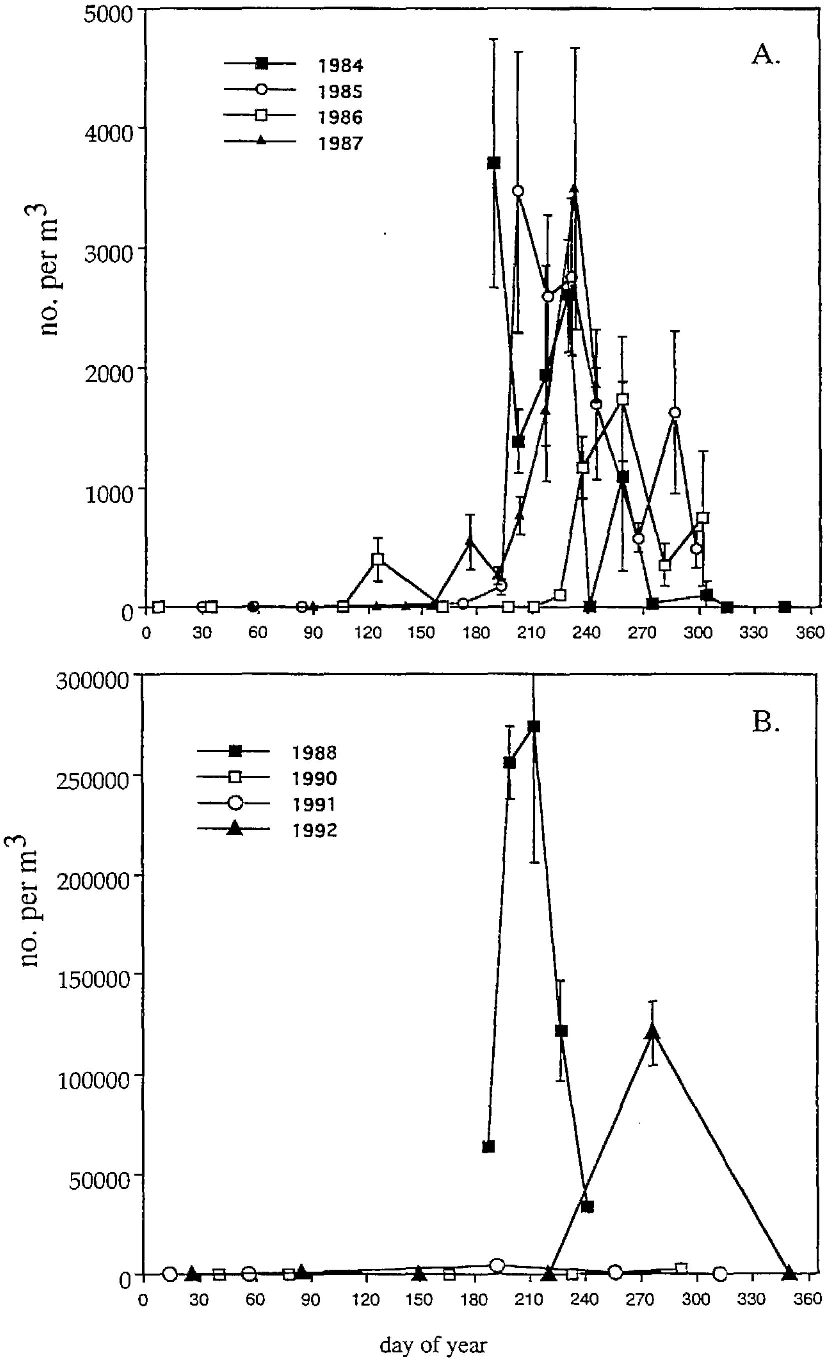

Figure 35. Mean abundance of *Conochilus unicornis* in Emerald Lake by day of year. A. Abundances in 1984, 1985, 1986 and 1987. B. Abundances in 1988, 1990, 1991 and 1992. Errors shown are standard errors for duplicate mid-lake vertical tows.

APPENDIX 2.1

Water samples taken in the Lake Comparison Study that satisfied the criteria for inclusion in the joint hydrochemical data set.

Emerald Lake

1983: 28-Sep, 14-Oct., 30-Oct, 8-Nov
1984: 6-Oct, 23-Oct,
1985: 10-Oct, 25-Oct, 20-Nov
1986: 16-Sep, 8-Oct, 29-Oct
1987: 1-Oct, 12-Oct, 25-Oct
1988: 1-Oct, 12-Oct, 25-Oct
1989: 3-Oct
1990: 19-Oct
1991: 13-Sep
1992: 3-Oct, 15-Dec
1993: 17-Oct
1994: 23-Sep

Crystal Lake

1986: 11-Oct
1987: 14-Oct
1988: 10-Nov
1989: 18-Oct
1990: 30-Oct
1991: 6-Sep
1992: 13-Aug
1993: 10-Oct

Lost Lake

1989: 20-Nov
1990: 17-Oct
1991: 15-Nov
1992: 29-Aug
1993: 26-Oct

Pear Lake

1986: 19-Oct
1987: 8-Dec
1988: 14-Dec
1989: 3-Oct
1990: 19-Oct
1991: 8-Nov
1992: none
1993: none

APPENDIX 2.1 (cont.)

Topaz Lake

1986: 18-Oct
1987: 30-Sep
1988: none
1989: 20-Oct*
1991: 14-Sep, 9-Nov
1992: 4-Oct
1993: 11-Oct

*5-Oct-89 satisfied the criteria for inclusion as a sampling date for Topaz Lake. However, abnormally high values for Ca^{2+}, Na^{+}, NO_3^- and Cl^- were observed on this date, and the data were omitted.

Spuller Lake

1989: 17-Oct
1990: 28-Oct
1991: none
1992: 9-Oct
1993: 27-Oct

Ruby Lake

1986: 12-Oct
1987: 12-Oct
1988: 9-Nov
1989: none
1990: 4-Jan
1990: 29-Oct
1991: 19-Nov
1992: none
1993: 8-Nov

Appendix 2.2. Sampling locations and dates for all fall lake samples from the Sierra Nevada used to prepare the joint data set for statistical analysis. Refer to the text for treatment of intra-annual and inter-annual replicates. Data sources are coded as follows: McClen = McCleneghan et al. (1985, 1986); Lake Comp = Melack et al. (1996); Mel/Set = Melack & Setaro (1986); Brad = Bradford et al. (1994); Sickman = J. Sickman (UCSB, unpublished data). See text for details on component data sets.

	REGION	LAKE	N. Longitude	W. Latitude	Elev. m	DATE	DATA SOURCE
1	No. Sierra	Taylor Lake	40°09'	120°43'	2061	16-Aug-85	McClen
						14-Aug-86	McClen
2	No. Sierra	Crystal Lake	40°03'	120°53'	2037	20-Aug-85	McClen
						14-Aug-86	McClen
3	No. Sierra	Three Lakes	39°58'	121°12'	1866	20-Aug-85	McClen
						13-Aug-86	McClen
4	No. Sierra	Eureka Lake	39°46'	120°43'	1884	21-Aug-85	McClen
						12-Aug-86	McClen
5	No. Sierra	Haven Lake	39°39'	120°38'	2049	19-Aug-85	McClen
						12-Aug-86	McClen
6	Cen. Sierra	Secret Lake	39°27'	120°32'	1951	23-Aug-85	McClen
						20-Oct-86	McClen
7	Cen. Sierra	Warren Lake	39°21'	120°24'	2195	22-Aug-85	McClen
						21-Oct-86	McClen
8	Cen. Sierra	High Loch Leven Lake	39°17'	120°30'	2073	23-Aug-85	McClen
						24-Oct-86	McClen
9	Cen. Sierra	Five Lakes	39°10'	120°15'	2585	27-Aug-85	McClen
						22-Oct-86	McClen
10	Cen. Sierra	Lost Lake	39°01'	120°11'	2341	27-Aug-85	McClen
						23-Oct-86	McClen
11	Cen. Sierra	Lois Lake	38°55'	120°12'	2585	10-Oct-91	Sickman
						8-Sep-92	Sickman
						18-Sep-93	Sickman
12	Cen. Sierra	Dicks Lake	38°55'	120°08'	2561	17-Oct-91	Sickman
						17-Sep-92	Sickman

Appendix 2.2. continued

13	Cen. Sierra	Leconte Lake	38°52'	120°07'30"	2500	15-Sep-92	Sickman
						28-Sep-93	Sickman
14	Cen. Sierra	Azure Lake	38°55'	120°07'30"	2293	17-Oct-91	Sickman
						17-Sep-92	Sickman
15	Cen. Sierra	Waca Lake	38°51'30"	120°08'	2500	16-Sep-92	Sickman
						29-Sep-93	Sickman
16	Cen. Sierra	Smith Lake	38°51'	120°11'	2659	30-Sep-85	McClen
						4-Sep-86	McClen
17	Cen. Sierra	Lost Lake	38°51'37"	120°05'48"	2475	20-Nov-89	Lake Comp
						17-Oct-90	Lake Comp
						15-Nov-91	Lake Comp
						29-Aug-92	Lake Comp
						26-Oct-93	Lake Comp
18	Cen. Sierra	Ralston Lake	38°50'	120°05'	2384	28-Aug-85	McClen
						6-Jun-86	McClen
19	Cen. Sierra	Triangle Lake	38°51'	120°05'	2439	15-Sep-92	Sickman
						28-Sep-93	Sickman
20	Cen. Sierra	Winnemucca Lake	38°40'	120°00'	2756	29-Aug-85	McClen
						13-Jun-86	McClen
						21-Sep-92	Sickman
21	Cen. Sierra	Cup Lake	38°49'	120°05'	2660	23-Sep-92	Sickman
22	Cen. Sierra	Forni Lake	38°48'	120°10'	2329	4-Sep-92	Sickman
23	Cen. Sierra	Saucer Lake	38°50'	120°04'	2622	23-Sep-92	Sickman
24	Cen. Sierra	Emigrant Lake	38°39'30"	120°02'30"	2622	29-Sep-92	Sickman
						20-Sep-93	Sickman
25	Cen. Sierra	Granite Lake	38°39'	120°05'	2341	29-Aug-85	McClen
						12-Jun-86	McClen
26	Cen. Sierra	Twin Lake	38°36'	119°57'	2488	1-Oct-85	McClen
						24-Jun-86	McClen
27	Cen. Sierra	Beebe Lake	38°33'	120°03'	2561	22-Sep-92	Sickman
						21-Sep-93	Sickman
28	Cen. Sierra	Highland Lake	38°29'	119°47'	2665	1-Oct-85	McClen
						3-Sep-86	McClen

Appendix 2.2. continued

29	Cen. Sierra	Spuller Lake	37°56'55"	119°17'02"	3131	17-Oct-89	Lake Comp
						28-Oct-90	Lake Comp
						9-Oct-92	Lake Comp
						27-Oct-93	Lake Comp
30	So. Sierra	Gaylor Lake	37°55'	119°16'	3171	27-Sep-81	Sickman
						1-Oct-85	McClen
						24-Sep-85	Mel/Set
						30-Sep-86	McClen
						22-Aug-87	Sickman
						28-Oct-90	Sickman
						5-Oct-91	Sickman
						10-Nov-92	Sickman
						7-Nov-93	Sickman
31	So. Sierra	Granite Lake	37°55'	119°16'	3170	27-Sep-81	Sickman
						24-Sep-85	Mel/Set
						28-Oct-90	Sickman
						5-Oct-91	Sickman
						10-Nov-92	Sickman
						22-Oct-93	Sickman
						20-Oct-94	Sickman
32	So. Sierra	McCloud Lake	37°36'29"	119°01'47"	2829	16-Sep-85	McClen
						1-Oct-86	McClen
						22-Sep-85	Mel/Set
33	So. Sierra	Crystal Lake	37°35'41"	119°01'04"	2902	22-Sep-85	Mel/Set
						11-Oct-86	Lake Comp
						14-Oct-87	Lake Comp
						10-Nov-88	Lake Comp
						18-Oct-89	Lake Comp
						30-Oct-90	Lake Comp
						6-Sep-91	Lake Comp
						13-Aug-92	Lake Comp
34	So. Sierra	Serene Lake	37°27'	118°45'	3146	17-Sep-85	McClen
						1-Oct-86	McClen
35	So. Sierra	Devil's Bathtub	37°26'	119°00'	2795	10-Sep-85	McClen
						15-Oct-86	McClen

Appendix 2.2. continued

36	So. Sierra	Ruby Lake	37°24'50"	118°46'15"	3365	23-Sep-85	Mel/Set
						12-Oct-86	Lake Comp
						12-Oct-87	Lake Comp
						9-Nov-88	Lake Comp
						4-Jan-90	Lake Comp
						19-Nov-91	Lake Comp
						8-Nov-93	Lake Comp
37	So. Sierra	Upper Treasure Lake	37°23'13"	118°46'00	3389	23-Sep-85	Mel/Set
						1-Nov-90	Sickman
						6-Oct-91	Sickman
						14-Nov-92	Sickman
						28-Sep-93	Sickman
						1-Nov-94	Sickman
38	So. Sierra	Gem Lake	37°23'05"	118°39'57	3330	23-Sep-85	Mel/Set
						24-Oct-87	Sickman
						1-Nov-90	Sickman
						6-Oct-91	Sickman
						14-Nov-92	Sickman
						28-Sep-93	Sickman
						1-Nov-94	Sickman
39	So. Sierra	Long Lake	37°18'	119°04'	2451	2-Oct-85	McClen
						16-Oct-86	McClen
40	So. Sierra	Crater Lake	37°15'	119°00'	2878	3-Oct-85	McClen
						16-Sep-86	McClen
41	So. Sierra	Piute Lake	37°14'04"	118°40'12"	3342	20-Sep-85	McClen
						7-Oct-86	McClen
						25-Sep-85	Mel/Set
42	So. Sierra	Summit Lake	37°14'	118°41'	3415	20-Sep-85	McClen
						7-Oct-86	McClen
43	So. Sierra	Emerson Lake	37°13'49"	118°39'57"	3413	25-Sep-85	Mel/Set
44	So. Sierra	Chocolate Lake	37°06'	118°33'	3201	17-Sep-85	McClen
						6-Oct-86	McClen
45	So. Sierra	B1	36°56'	118°26'	3470	15-Aug-92	Brad
						15-Aug-92	Brad
46	So. Sierra	B5	36°56'	118°26'	3500	15-Aug-92	Brad

Appendix 2.2. continued

47	So. Sierra	C10	36°56'	118°26'	3600	13-Aug-92	Brad
48	So. Sierra	C17	36°56'	118°26'	3550	13-Aug-92	Brad
49	So. Sierra	C2	36°56'	118°26'	3350	4-Jul-92 12-Aug-92 26-Sep-92	Brad Brad Brad
50	So. Sierra	C21	36°56'	118°26'	3393	29-Jun-92 11-Aug-92 26-Sep-92	Brad Brad Brad
51	So. Sierra	C22	36°56'	118°26'	3425	3-Jul-92 12-Aug-92 26-Sep-92	Brad Brad Brad
52	So. Sierra	C23	36°56'	118°26'	3430	12-Aug-92	Brad
53	So. Sierra	C24	36°56'	118°26'	3485	29-Jun-92 12-Aug-92 26-Sep-92	Brad Brad Brad
54	So. Sierra	C4	36°56'	118°26'	3370	11-Aug-92	Brad
55	So. Sierra	C5	36°56'	118°26'	3515	13-Aug-92	Brad
56	So. Sierra	D4	36°56'	118°26'	3275	20-Aug-92	Brad
57	So. Sierra	D5	36°56'	118°26'	3470	20-Aug-92	Brad
58	So. Sierra	E1	36°56'	118°26'	3218	30-Jun-92 19-Aug-92 25-Sep-92	Brad Brad Brad
59	So. Sierra	E4	36°56'	118°26'	3230	20-Aug-92	Brad
60	So. Sierra	F1	36°56'	118°26'	3130	30-Jun-92 21-Aug-92 25-Sep-92	Brad Brad Brad
61	So. Sierra	F11	36°56'	118°26'	3475	30-Jun-92 22-Aug-92 25-Sep-92	Brad Brad Brad
62	So. Sierra	F12	36°56'	118°26'	3478	23-Aug-92	Brad
63	So. Sierra	F13	36°56'	118°26'	3480	23-Aug-92 23-Aug-92 23-Aug-92	Brad Brad Brad

Appendix 2.2. continued

64	So. Sierra	F14	36°56'	118°26'	3520	30-Jun-92	Brad
						23-Aug-92	Brad
						25-Sep-92	Brad
65	So. Sierra	F2	36°56'	118°26'	3210	30-Jun-92	Brad
						21-Aug-92	Brad
						25-Sep-92	Brad
66	So. Sierra	F4	36°56'	118°26'	3470	1-Jul-92	Brad
						22-Aug-92	Brad
						25-Sep-92	Brad
67	So. Sierra	L11	36°56'	118°26'	3535	30-Aug-92	Brad
68	So. Sierra	L1	36°56'	118°26'	3388	30-Aug-92	Brad
						30-Aug-92	Brad
69	So. Sierra	L7	36°56'	118°26'	3470	2-Jul-92	Brad
						30-Aug-92	Brad
70	So. Sierra	L8	36°56'	118°26'	3495	30-Aug-92	Brad
71	So. Sierra	L9	36°56'	118°26'	3530	30-Aug-92	Brad
72	So. Sierra	N3	36°56'	118°26'	3490	24-Aug-92	Brad
73	So. Sierra	O21	36°56'	118°26'	3450	24-Aug-92	Brad
74	So. Sierra	O7	36°56'	118°26'	3428	1-Sep-92	Brad
75	So. Sierra	O8	36°56'	118°26'	3430	24-Aug-92	Brad
76	So. Sierra	P3	36o56'	118°26'	3672	1-Sep-92	Brad
77	So. Sierra	Golden Trout Lake	36°46'50"	112°2'04"	3463	18-Sep-85	McClen
						8-Oct-86	McClen
						26-Sep-85	Mel/Set
78	So. Sierra	Unnamed	36°47'18"	112°1'55"	3488	26-Sep-85	Mel/Set
79	So. Sierra	Monarch Lake	36°27"	118°33'	3232	24-Oct-90	Sickman
						9-Oct-92	Sickman
						5-Oct-92	Sickman
						26-Oct-94	Sickman
80	So. Sierra	Aster Lake	36°36'	118°40'	2756	10-Nov-91	Sickman
						8-Oct-92	Sickman
						16-Oct-93	Sickman
						19-Oct-94	Sickman

Appendix 2.2. continued

81	So. Sierra	Topaz Lake	36°37'30"	118°38'11"	3218	18-Oct-86	Lake Comp
						30-Sep-87	Lake Comp
						5-Oct-89	Lake Comp
						20-Oct-90	Lake Comp
						14-Sep-91	Lake Comp
						9-Nov-91	Lake Comp
						4-Oct-92	Lake Comp
						11-Oct-93	Lake Comp
82	So. Sierra	Pear Lake	36°36'02"	118°40'00"	2899	6-Sep-85	McClen
						11-Sep-86	McClen
						6-Sep-85	Mel/Set
						14-Oct-85	Mel/Set
						19-Oct-86	Lake Comp
						8-Dec-87	Lake Comp
						14-Dec-88	Lake Comp
						8-Nov-91	Lake Comp
83	So. Sierra	Emerald Lake	36°35'49"	118°40'29"	2800	28-Sep-83	Lake Comp
						14-Oct-83	Lake Comp
						30-Oct-83	Lake Comp
						8-Nov-83	Lake Comp
						6-Oct-84	Lake Comp
						23-Oct-84	Lake Comp
						10-Oct-85	Lake Comp
						25-Oct-85	Lake Comp
						20-Nov-85	Lake Comp
						16-Sep-86	Lake Comp
						8-Oct-86	Lake Comp
						29-Oct-86	Lake Comp
						1-Oct-87	Lake Comp
						12-Oct-87	Lake Comp
						25-Oct-87	Lake Comp
						3-Oct-89	Lake Comp
						19-Oct-90	Lake Comp
						13-Sep-91	Lake Comp
						8-Nov-91	Lake Comp
						3-Oct-92	Lake Comp

Appendix 2.2. continued

83	So. Sierra	Emerald Lake	36°35'49"	118°40'29"	2800	15-Dec-92	Lake Comp
						17-Oct-93	Lake Comp
						23-Sep-94	Lake Comp
84	So. Sierra	Heather Lake	36°36'02"	118°41'15"	2804	5-Sep-85	Mel/Set
						21-Oct-90	Sickman
						10-Nov-91	Sickman
						8-Oct-92	Sickman
						8-Oct-93	Sickman
						17-Oct-94	Sickman
85	So. Sierra	Cottonwood Lake 5	36°28'	118°14'	3355	19-Sep-85	McClen
						9-Oct-86	McClen
86	So. Sierra	Crystal Lake	36°26'30"	118°34'11"	3267	29-Oct-85	Mel/Set
						10-Aug-86	Mel/Set
						9-Oct-91	Sickman
						6-Oct-92	Sickman
87	So. Sierra	Franklin Lake	36°25'	118°31'	3146	5-Sep-85	McClen
						10-Sep-86	McClen
88	So. Sierra	Bullfrog Lake	36°24'	118°31'	3366	4-Sep-85	McClen
						9-Sep-86	McClen
89	So. Sierra	Upper Mosquito Lake	36°24'53"	118°37'35"	3048	29-Oct-85	Mel/Set
						25-Oct-90	Sickman
						10-Oct-91	Sickman
						4-Oct-92	Sickman
						6-Oct-93	Sickman
						21-Oct-94	Sickman

PART 3

MECHANISMS OF ANC CONSUMPTION AND GENERATION IN HIGH ELEVATION WATERSHEDS OF THE SIERRA NEVADA

AND

ANALYSIS OF THE SOURCES AND FATES OF SOLUTES OVER THE COURSE OF THE HYDROLOGICAL YEAR

PART 3

TABLE OF CONTENTS

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TABLES

3.1. INTRODUCTION

Assessment of watershed ANC generation. It is now known that the interaction of snowmelt run-off with the bedrock, soils, and vegetation of a watershed significantly modifies the ionic composition of snowmelt before it enters streams and lakes. The consequences of acid deposition are therefore substantially related to the capacity of the watersheds to generate ANC. Mineral weathering and cation exchange, to a major extent, and nitrate consumption, to a minor extent, appear to be the principal mechanisms generating ANC in high-altitude watersheds of the Sierra Nevada. Biogeochemical mechanisms responsible for H^+ buffering by watersheds have been directly or indirectly studied in several CARB-funded studies, including those supervised by Jeff Dozier and John Melack (Contracts A3-106-32, A6-147-32), by Ron Admundson (Contract A4-042-32), by Lanny Lund (Contracts A5-204-32, and A3-105-32) and by Aaron Brown and John Melack (Contract A032-116). The results of these studies will be integrated to provide a summary of the watershed processes responsible for ANC generation and consumption and the ability of Sierran high-altitude watersheds to neutralize acid deposition.

3.2. RELEVANT CARB STUDIES AND PUBLICATIONS

3.2.1. Reports to the CARB addressing watershed ANC generation.

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Admunson R., Harte J., Michaels H. and Pendall E. 1988. The Role of Sediments in Controlling the Chemistry of Subalpine Lakes in the Sierra Nevada, California. Final Report No. A4-042-32.

Soil Processes

Brown A., Lund. L. and Lueking M. 1990. Integrated Soil Processes Studies at Emerald Lake Watershed. Final Report No. A5-204-32.

Lund L., Brown A., Lueking M., Nodvin S., Page A. and Sposito G. 1987. Soil Processes at Emerald Lake Watershed. Final Report No. A3-105-32.

Reilly T. 1990. Survey of Soil Map Sensitivity to Acid Deposition in the Sierra Nevada. Final Report No. A733-037.

EXPECTED 1997. (P.I.s Aaron Brown, John Melack) Watershed Biogeochemical Processes Affecting Surface Waters in the Sierra Nevada, with Emphasis on Snowmelt Episodes. Contract No. A032-116.

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Dozier J., Melack J., Marks D., Elder K., Kattelmann R. and Williams M. 1987. Snow Deposition, Melt, Runoff and Chemistry in a Small Subalpine Watershed, Emerald Lake Basin, Sequoia National Park. Final Report No. A3-106-32.

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Rundel P., St. John T., and Berry W. 1988. Integrated Watershed Study: Vegetation Process Studies. Final Report No. A4-121-32.

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3.2.2. Publications directly related to CARB-funded research on Sierra Nevada hydrochemistry and biogeochemistry.

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Brown A. (1991) Hydrology of Eastern Brook Lakes Watershed, Acidity and Alkalinity Generation in a Subalpine Sierra Nevada Lake. In: G. Taylor and L. Piehl (Eds.), The Eastern Brook Lakes Watershed Study. Desert Research Inst. Reno, NV.

Brown A. and D. Johnson (1991) Biochemical modifications of snowpack runoff in an alpine basin. In: G. Taylor and L. Piehl (Eds.), The Eastern Brook Lakes Watershed Study. Desert Research Inst. Reno, NV.

Brown A. and L. Lund (1991) Kinetics of weathering of some Sierra Nevada soils. Soil Sci. Soc. Am. J. 55: 1767-1773.

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Whiting M., D. Whitehead, R. Holmes and S. Norton (1989) Paleolimnological reconstruction of recent acidity changes in four Sierra Nevada lakes. J. Paleolimnol. 2: 285-304.

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3.3. AUTUMN STREAMFLOW

In most of the high altitude watersheds studied in the Sierra Nevada, streamflow during the autumn months (Sept.-Nov.) is scanty or absent (Melack et al. 1996). In the Lake Comparison Study conducted by Melack et al. (1996), Ruby Lake watershed was the only one of seven headwater catchments studied in which streamflow is observed year-round. Drainage from soil and groundwater reservoirs is presumably responsible for this flow, and the recharging of subsurface reservoirs is believed to take place during spring snowmelt. The Spuller Lake watershed also produces streamflow during periods without snowmelt, indicating that groundwater is an important component of streamflow in that catchment as well (Melack et al. 1996).

Based on work at the Emerald Lake Watershed (ELW), during the period of low flow, from autumn through winter, streamflow consists of discharge from groundwater reservoirs which has been stored on the order of months, and whose composition is not controlled by contact with the soil zone. Streamwater at this time is in stoichiometric equilibrium with weathering products (Williams et al. 1993). More specifically, the chemical composition of autumn stream water is congruent with the preferential weathering of the anorthite component of plagioclase in subsurface rock and further weathering of kaolinite to gibbsite (Williams et al. 1993). Stream chemistry suggests that kaolinite in the watershed undergoes further weathering to gibbsite until stream waters are saturated with Si at a concentration of ~60 μmol L^{-1}. As additional evidence that autumn streamflow is hydrologically distinct from the soil solution, the Na^{+1}:Ca^{+2} ratio simultaneously reaches an annual maximum in soils during autumn and an annual minimum in stream flow. Later in the hydrologic year, base cations, silica, and HCO_3^- in streamwater are diluted by snowmelt, indicating that weathering and leaching from the watershed are the dominant processes supplying these solutes instead of snowmelt. Williams et al. (1993) showed that the ratio of calculated to measured HCO_3^- remained near 1.0 during the period of low flow from July to March in both 1986 and 1987 in streamflow in the Emerald Lake watershed, indicating that no acidification was occurring at that time, or that mineral weathering was the source of alkalinity.

3.4. AUTUMN SNOWFALL

Autumn snow was defined by Melack et al. (1995) as *wet snow* or combined *rain and snow* that occurs in September and October, and which does not accumulate in the watershed. Winter snowfall, on the other hand, is defined as snowfall that accumulates. Melack et al. (1996) defined winter precipitation as any precipitation occuring from December through May with the following two exceptions: (1) large snow storms in November were counted as winter snow, (2) rain in May was classified as non-winter precipitation. The reason for the first exception is that the chemistry of large snow storms in November is more similar to the chemistry of snow from December onward. Smaller snow storms occuring in November are unlikely to accumulate, and are chemicallly similar to autumn rain.

Autumn snow can be important in terms of total annual ion flux to watersheds. In "normal" and "wet" years (such as 1985 and 1986, respectively) 30% of the annual nitrate and sulfate flux and 50% of NH_4^+ flux in the ELW came from autumn snow. Solute concentrations in stream water were elevated in October and November of these years. It is possible that the melt water from autumn snow may rinse the summer's accumulation of dry deposition off of soil and rock surfaces and wash some of the products of microbial activity out of soils into surface water.

3.5. WINTER SNOWFALL

3.5.1. Contribution of winter snowfall to annual solute budgets.

Most of the annual deposition of hydrogen, chloride, and base cations in the Sierra Nevada occurs during the winter months. Although the concentrations of these solutes are higher in rain than in snow (grand means of VWM concentrations, in μeq L^{-1}, for 36 water years (8 sites) rain vs. snow: for H^+, 11.7 vs. 3.8; for Cl^-, 4.1 vs. 1.7) the quantity of snowfall greatly exceeds the quantity of non-winter precipitation. Melack et al. (1996) report that 67% to 92% of H+ deposition occurs as winter snowfall in seven headwater catchments. H^+ loading is directly related to snow quantity. In the Emerald Lake Watershed, the greatest deposition of H^+ occurred in 1986 (128 Eq ha^{-1}) and in 1993

(123 Eq ha^{-1}), which were the years of highest snowfall during the period 1985 - 1994 (Melack et al. 1996).

3.5.2. Sources of winter storm fronts.

The chemistry of winter snow varies interannually. In normal or wet years, winter air masses arrive in strong fronts that originate over the Pacific Ocean, resulting in higher relative Cl^- and lower strong acid anion concentrations (nitrate and sulfate) in snow. Also, generally low levels of ammonium in Sierra snow indicate that the oceanic frontal systems undergo only limited mixing with terrestrial air masses before depositing snow in the Sierra Nevada.

In the dry years 1987 and 1988, concentrations of Cl^- and Na^+ were halved, and NO_3^- and NH_4^+ more than doubled in the ELW snowpack, as compared to the 1985 and 1986 snowpacks (Dozier et al. 1989). The resulting low ranking for Cl^- and Na^+, and high ranking of NO_3^- and NH_4^+, suggests that a major source of ions in snow in these two years was air masses that originated over land from convective sources or from the mixing of weak fronts with air over the Central Valley. Also, the ratio $NO_3^-:SO_4^{-2}$ in the snowpack was highest in dry year snowpacks. Although, in every year, H^+ neutralizes more strong acid anions in snow than NH_4^+, the relative neutralization of strong acid anions by NH_4^+ was highest in the dry years.

3.5.3. Winter temperature regime.

Another factor that differs between wet and dry years is the winter temperature regime. Wet years are relatively warmer than dry years. For example, in 1986, soil temperature beneath the snowpack in the ELW did not stay below 0° C. Soils were well insulated by snow cover and air temperature was relatively higher. Dry years are relatively colder. For example, in the dry years 1987 and 1988, the soil surface beneath the snowpack in the ELW froze at all five sites (pine stand, inlet, bench, cirque and ridge) monitored with thermistors (Brown et al. 1990) and there was ice over the soil (Williams et al. 1993).

If the ground surface does freeze prior to the development of the snowpack, overland flow can be high during snowmelt. Increased overland flow relative to subsurface flow of melt water could result in decreased buffering of snowpack acidity because cation exchange in soil and talus is an important mechanism for neutralizing acidity of snowpack runoff (see below). However, as is stated in Williams et al. (1993), even in 1987 as much as 62% of snowpack runoff infiltrated soils and talus at ELW. This was apparently because the soil temperature under the snowpack increased to 0° C in midwinter.

3.5.4. Solute storage in the snowpack.

Data from the ELW indicated that in the water year 1985-1986, loadings calculated for hydrogen, sulfate, and chloride using snowpits dug prior to melt were within 10% of those calculated from cumulative event sampling with snow boards. However, evidence was obtained that nitrate can migrate through the snowpack to underlying soils even in the absence of significant melting (Williams & Melack 1991b). In early January, 1986, nitrate loading in the snowpack of ELW was about 80% of cumulative nitrate deposition. Thus ca. 20% of NO_3^- was lost from the snowpack during winter.

3.6. SNOWMELT

3.6.1. Snowpack ripening.

Snowpack ripening is synonymous with removal of the cold content of the snowpack. Melt water production takes place at a site in the snowpack when the pack becomes locally isothermal at 0° C. Surface melt water may percolate down into the snowpack to an "unripe" portion and refreeze. If this occurs, and an ice lens is formed, the pack temperature is raised by an amount corresponding to the latent heat of fusion. Melting and refreezing, and thus the formation of ice lenses, is a common mechanism for snowpack ripening in the the Sierra (Dozier et al. 1989). Wind crusts formed between snowfalls become ice layers after melt water percolates down to their level and freezes. During snowmelt, the snowpack can be melting during the day and then the surface of the snowpack can refreeze at night to a depth of 5-20 cm due to radiative cooling (Kattelmann & Elder 1993). An important side effect of melt-freeze cycles is an increase in the ionic concentration of melt water. Accompanying the ripening process is an increase in the density of the snow. A common pattern observed is for the density of the snow to remain relatively low (300-350 kg m^{-3}) until energy inputs are sufficient to cause a rapid warming of the snowpack and a rapid increase in density to about 500-550 kg m^{-3}. After this point, further increases in snow density are slow and asymptotic.

3.6.2. Onset of snowmelt.

The onset of snowmelt varies to some extent between watersheds and between years. Elevation and the aspect of the basin contribute to differences between watersheds. For example, the onset of snowmelt in Ruby Lake tends to occur in May, a few weeks later than in the other six watersheds studied by Melack et al. (1996). Cool springtime weather and deep snowpacks retard the onset of snowmelt, and can contribute to interannual variation in the timing of snowmelt. For example, in dry years, ice and snow on top of Emerald Lake, in the western Sierra Nevada, can be up to 1 m deep, and can last until early May. In wet years, ice and snow on top of Emerald Lake can be up to 6 m deep and can last until July. In general, however, June and July are typically the months of greatest streamflow in the high Sierra Nevada (Melack et al. 1996). Streamflow in the Emerald Lake basin during May and June accounted for one half of annual water flux in each of the 5 water years 1983-1987 (Melack et al. 1993). April through July bracket ca. 75% of annual runoff in the same catchment.

3.6.3. Speed of snowmelt.

Local terrain has a number of influences on the speed of snowmelt. In the Sierra Nevada, net radiation is the dominant influence on snowmelt. The exposure of each slope to solar radiation largely determines the energy balance of the snow cover. Melt rates may range from 0 on the north side of a ridge to several mm h^{-1} on the south side. Once rocks are exposed, snowmelt is locally accelerated because reradiation from sun-warmed rocks melts snow much faster than direct insolation (Kattelmann & Berg 1987). In a dry year, the snowpack is more rapidly depleted than in a normal year. The CCSS statewide snow survey showed that in the dry year 1987, by April 1, SWE was 50% of normal for that date, but by May 1, SWE was only 20% of normal for that date. Thus the already low SWE in the snowpack of a dry year becomes exacerbated as the melt season progresses. Spring snowfall can retard the melt rate by restoring the high albedo of the snowpack (Kattelmann & Elder 1993).

3.6.4. Role of pre-event groundwater during snowmelt.

Empirical studies based on division of stream hydrographs into "base flow" and "quick flow" suggest that new rainwater or meltwater contributes a large portion of storm runoff. However, isotopic and hydrochemical studies show that the bulk of water in storm or snowmelt runoff can be old water that has resided a significant period in soil or groundwater. Relative proportions of "new" water from snowmelt vs "old" water from groundwater have been studied in other systems using oxygen isotopes. Pre-event groundwater can make up the largest fraction of streamflow during snowmelt and precipitation events in some Swedish, Norweigan and Canadian watersheds (Turner et al. 1990). In these cases, snowmelt in the spring *displaces* old water stored in the soil. Apparently, water held in storage in groundwater reservoirs contributes only a small fraction of stream flow during snowpack runoff in the Emerald Lake Watershed (see below), which contrasts in this way with more highly forested montane areas of eastern North America. Groundwater may contribute somewhat more to streamflow during snowmelt in the Ruby Lake and Spuller Lake watersheds, in the eastern Sierra Nevada, because these watersheds exhibit streamflow during periods without snowmelt (autumn and winter, Melack et al. 1996).

3.6.5. Ionic pulse

Acidity derived from snowmelt is delivered to surface waters in the form of an ionic pulse. At any site of melting snow, the first 5-15 days of melt deliver the ionic pulse, which magnifies solute concentrations 5-10 fold. Where snowmelt is rapid, the ion pulse may last ca. 2 days. Where snowmelt is slow, the ion pulse may last ca. 10 days. The ion release sequence from snowpacks is generally SO_4^{-2}, $NO_3^- > Cl^-$. In the ELW, the ion release sequence for strong acid anions is generally $SO_4^{-2} > NO_3^- > Cl^-$. Ionic pulses are assumed to be delivered within the first 20% of snowmelt runoff volume (Kattelmann & Elder 1993). The duration of the first 20% of snowmelt runoff ranged from 20 to 60 days over five years of study in the Emerald Lake Watershed (Kattelmann & Elder 1993). The duration of the ion pulse at lake inflows does vary between years, but not in a manner that necessarily corresponds to the first 20% of snowmelt runoff. During the wet year 1986, the first 20% of snowmelt runoff occurred in 60 days (Kattelmann & Elder 1993), however, nitrate was elevated in lake inflow water at Emerald Lake above the bulk winter precipitation average of 5 μeq L^{-1} for only 20 days

(Williams & Melack 1991b). During the dry year 1987, the first 20% of snowmelt runoff occurred in 20-25 days, however, nitrate was elevated (above bulk precipitation average) in Inflows 1 and 2 of Emerald Lake for 110 days and 60 days, respectively (Williams & Melack 1991b).

3.6.6. Solute concentrations in lake outflows during snowmelt.

Melack et al. (1996) present time-series plots of solute chemistry (pH, ANC, nitrate, sulfate, base cations, and dissolved silica) in the lake outflows of seven Sierra Nevada lakes studied from 1990 to 1994 under CARB contract A032-188. Lake outflow chemistry does not exactly mirror the chemistry of melting snow in the watershed. Rather, lake outflow chemistry results from the interactions between snowmelt water and the soils, rock and vegetation upstream of the lake, *and* biological and chemical in-lake processes. The importance of in-lake processes will vary with the flushing rate of the lake during snowmelt; when flushing rates are high (such as during peak discharges), lake outflow chemistry should differ little from lake inflow chemistry.

pH. pH was the most variable chemical parameter measured in lake outflows during snowmelt runoff in the seven watersheds studied. Melack et al. (1996) described five patterns observed for outflow pH during snowmelt months (April through September). The most common pattern (occuring in 10/32 cases) consisted of a decrease in pH as discharge increases, with lowest pH's occurring near the time of peak runoff. Changes in lake outflow pH over the course of snowmelt were not large. The typical pH change observed from before the onset of snowmelt to peak runoff was about 0.5 pH units (Melack et al. 1996). Minimum outflow pH ranged from 5.5 to 6.1 among the seven lakes studied, and were fairly consistent among years and among catchments.

ANC. Patterns of ANC in lake outflow were more consistent among years and among lakes than patterns in outflow pH. The most common pattern of ANC during snowmelt was an inverse relationship between ANC and discharge, with minimum ANC values occurring at or near peak runoff. ANC usually declined by about 50% from before the onset of snowmelt to peak snowmelt runoff; minimum values of ANC were typically in the range of 15 to 30 μeq L^{-1}. The extent to which outflow ANC changed during snowmelt varied among lakes. The largest changes observed during snowmelt consisted of drops in ANC of about 70 to 90 μeq L^{-1} (Spuller Lake), whereas the smallest changes observed were drops in ANC on the order of ca. 20 μeq L^{-1} (Crystal Lake).

Nitrate. Concentrations of nitrate in lake outflows during snowmelt runoff followed a consistent pattern in the seven watersheds studied by Melack et al. (1996). The pattern, referred to by Melack et al. (1996) as *Pulse/Depletion* , consists of two stages. In the first stage, nitrate concentrations in runoff increase from the start of snowmelt until 2-5 weeks before peak discharge occurs. In the second stage, nitrate concentrations decrease in runoff during the remainder of the rising limb of the hydrograph and into the falling limb of the hydrograph. Some of the initial increase in nitrate can be ascribed to the ion pulse occuring during the early stages of snowmelt. However, in the Lake Comparison Study, nitrate concentrations often increased in lake outflows more than could be explained by snowmelt alone, even allowing for preferential elution of nitrate during the ion pulse of snowmelt (Melack et al. 1996, see section 7.4 below).

The drop in nitrate during the second stage of the pattern is ascribed to biological consumption, presumably both in the watershed along the pathway of meltwater and in-lake. Evidence for in-lake consumption of nitrate was provided for by comparisons of nitrate concentrations in lake inflows with nitrate concentrations in lake outflows. In Ruby, Spuller, Emerald, Pear and Topaz Lakes the initial pulse of nitrate during the early portion of snowmelt was detected in both the inflows and the outflows for the lakes. Thus in these catchments, in-lake processes did not obscure the nitrate pulse in lake outflows. Lost and Crystal Lakes apparently consumed more of the nitrate delivered from their watersheds. The nitrate pulses in the catchments of these two lakes were observed in lake *inflows*, but not in the *outflows*, indicating uptake of nitrate by lake biota (J. Sickman, pers. comm.).

Sulfate. In most cases, sulfate was diluted less during snowmelt than ANC, base cations or silica. This finding leads Melack et al. (1996) to suggest that some biogeochemical process(es) are regulating sulfate concentrations during snowmelt. Sulfate concentrations followed many patterns during snowmelt in the Lake Comparison Study (Melack et al. 1996). Several of the catchments displayed similar patterns of sulfate concentrations in each of the years they were studied. In the Marble Fork (1993 - 1994) sulfate decreased slightly during snowmelt, but increased after snowmelt discharge ended and base flow was reestablished. In the Emerald Lake watershed (1990 - 1994), sulfate also decreased only slightly during snowmelt, but failed to increase later after the end of snowmelt discharge. In Lost Lake (1990 - 1993), sulfate concentrations were strongly diluted during snowmelt (ca. 50% or more), but no subsequent increase in sulfate was observed during the summer. In the Spuller Lake watershed (1990-1993), sulfate was strongly diluted initially during snowmelt, but increased later in runoff before the end of the falling limb of the hydrograph. Data from the Ruby Lake watershed (1990-1993) showed an initial increase in sulfate at the beginning of snowmelt, followed by dilution, and followed in turn by a recovery of sulfate to pre-melt concentrations.

Base cations and silica. Dilution of base cations and silica during snowmelt, followed by at least partial recovery of pre-melt concentrations, was the dominant pattern observed in most cases by Melack et al. (1996) for seven Sierran lakes. One notable exception to this pattern was Crystal Lake in 1993. In this year, silica concentrations were quite stable during both the rising and falling limbs of the hydrograph, despite very high snowmelt discharge. Sulfate was only weakly diluted in Crystal Lake outflow in 1993 as well. Melack et al. (1996) suggest that a mechanism may be operating to regulate these solutes in Crystal Lake.

3.7. FATE OF SOLUTES IN SNOWPACK RUNOFF

3.7.1 Retention of H^+ from snowmelt by watershed.

It is clear from the Lake Comparison Study (Melack et al. 1996), as well as the longer term study of the Emerald Lake Watershed, that currently the majority of $[H^+]$ stored in the snowpack of Sierra Nevada watersheds is neutralized before reaching outflow streams. All seven of the headwater catchments studied in the Lake Comparison Study, and the higher order Marble Fork, neutralized most of the acid deposition from both winter and non-winter precipitation (Melack et al. 1996). The two headwater catchments best able to neutralize H^+ were the Ruby Lake and Crystal Lake watersheds (Table 1). The mean percentage of H^+ consumed by these two watersheds was 94%. The other watersheds neutralized 80-90% of the H^+ delivered by precipitation. The neutralizing capacity of the watersheds was not greatly affected by interannual variations in the amount of snowfall. In the ELW in 1986, 80% of H^+ and in 1987, 90% of H^+ was removed from snowpack meltwater before reaching the lake - despite the huge disparity in SWE in those years.

Several mechanisms may contribute to this buffering. Formate and acetate comprise 25-30% of anions in snow. The formate and acetate in the snowpack have pKs that would allow them to be dissociated at the pH of snowpack melt water and thus be able to buffer free acidity. Dry deposition may also play a role in the buffering of snowpack acidity. Particulate clay and dust may react with CO_2, yielding HCO_3^- and Ca^{+2} or Mg^{+2} in meltwater and decreasing $[H^+]$. There is some evidence for this process. On April 23, 1987, $[Ca^{+2}]$ increased 5-fold and $[H^+]$ decreased 5-fold in lake inlet meltwater at the ELW. However, according to Dozier et al. (1989), titration of HCO_3^- accounts for little of overall snowpack buffering.

Results from Emerald Lake suggest that much of the snowpack runoff in the ELW infiltrates soils and unconsolidated materials (talus), undergoes reactions with soil water and soil exchangers, and is subsequently discharged to stream flow (Williams et al. 1993). The areal extent of unconsolidated sand, gravel and talus in the ELW is 23% of the watershed. Massive rock outcrops cover 33% of the watershed, and only ~ 20% of the watershed is classified as soils. In general, during snowpack runoff, ~ 50% of streamflow is from direct surface runoff and ~ 50% is return flow from subsurface reservoirs. For example, in 1987, as much as 62% of discharge was from the subsurface and 38% of discharge was from surface runoff. The residence time of water in subsurface reservoirs at this time of year is on the order of hours to days; LiBr tracer studies provide another estimate of 9-20 hours (Williams et al. 1993).

According to Williams et al. (1993), the acidity of snowpack runoff at ELW is neutralized by cation exchange in soils and talus (the subsurface). The buffering occurs during contact of meltwater with the terrestrial watershed over only hours or days. Cation exchange reactions are completed on the order of seconds to minutes, while silicate mineral weathering reactions take place on the order of months to years. Thus cation exchange reactions, and not mineral weathering, would appear to be the primary source of buffering for snowpack runoff.

More evidence that cation exchange by H^+ in snowmelt was occurring in the ELW comes from plots of "calculated alkalinity" ($[Ca^{+2} + Mg^{+2} + Na^+ + K^+]$, which should equal HCO_3^- released by the weathering of granodiorites) and measured HCO_3^-. During low flow of 1987, this relationship yielded a slope close to 1, but during snowpack runoff, there was an excess of cations. Also, $Na^+:Ca^{+2}$ increases in soil solution during snowpack runoff. Because divalent cations are retained over monovalent cations in soils of the ELW, this also provides evidence of cation exchange (Williams et al. 1991).

The capacity of soils and talus to provide exchangeable cations at the time of snowmelt is an important element in the overall capacity of Sierran watersheds to generate ANC. However, there is evidence from other studies that rapid weathering of granitic rock in contact with meltwater can provide an additional source of buffering. Clow and Mast (1995) compared the chemistry of wet and bulk precipitation with runoff from a 30 m^2 granite outcrop in the Loch Vale watershed. Base cations, chloride, sulfate and nitrate were elevated in the runoff after rain events in relation to both wet and bulk precipitation. Silica, which was below detection in bulk deposition, was present in runoff from the rock face at a concentration of ca. 11 μmol L^{-1}. In addition, ANC was elevated and pH increased as precipitation flowed over the exposed rock. They conclude that rapid weathering reactions, either of the exposed rock, or of mineral dry deposition, is the only reasonable source of the silica. It remains unknown whether a similar mechanism generates ANC during rainfall or snowmelt runoff in the granite-rich Sierra Nevada watersheds. The weathering of silicate minerals certainly supplies alkalinity to Sierran lakes on an *annual* basis. However, water held in storage in groundwater reservoirs contributes only a small fraction of stream flow *during snowpack runoff* in the ELW. Thus the ANC produced by weathering reactions that accumulates in groundwater can not be responsible for buffering of snowmelt runoff.

Regardless of the mechanisms responsible, all of the high elevation Sierra Nevada watersheds studied by Melack et al. (1996) produced sufficient ANC to neutralize much of the acidity of precipitation (Table 1) and to be net exporters of ANC and of base cations [Ca^{2+}, Mg^{2+}, Na^+, K^+]. The quantity of base cations produced by the watersheds was considerable in relation to the quantity delivered via precipitation: 62% - 92% of the sum of base cations that left the catchments was produced by within thewatersheds, and ultimately by the weathering of bedrock (Table 2). In every case, Ca^{2+} was the cation exported in greatest quantity. The ranking of base cations by the magnitude of their annual net yields from the studied watersheds was as follows: $Ca^{2+} > Na^+ > Mg^{2+} > K^+$.

3.7.2. Watershed processes affecting sulfate in surface waters.

3.7.2.1. Sulfate regulation in Sierra Nevada watersheds.

There is evidence from the Lake Comparison Study (Melack et al. 1996) that the concentration of sulfate in surface waters is regulated to some degree *during snowmelt* in

Sierra Nevada watersheds. Increases in sulfate concentration in lake outfows during the first stage of snowmelt (when the ionic pulse is expected) were low in magnitude, if observed at all (increases of 1 to 3 μEq L^{-1}, Melack et al. 1996). In most cases, however, sulfate was diluted relative to base flow concentrations during the rising limb of the hydrograph during snowmelt (see above). Sulfate was diluted less than ANC, base cations and silicate in most catchments in most years during snowmelt. These observations suggest that sulfate is initially sequestered by the watershed (removed along the pathway taken by meltwater to the lakes) during the first stages of snowmelt, and then released back into surface water - mitigating the dilution effect while discharge remains high.

Sulfate adsorption in soil is one of the mechanisms by which sulfate anions can be removed from snowmelt. When sulfate contacts soil particles, sulfate anions can displace OH or OH^{2+} from the surfaces of hydrous Fe- or Al-oxides. If OH is displaced, an OH^- anion is released, neutralizes H^+, and the adsorption of sulfate onto the oxide will create a cation exchange site. If OH^{2+} is displaced, water is released, and the charge of the site is changed from positive to negative (thus changing the original anion exchange site to a cation exchange site). Sulfate adsorption is enhanced when soil pH is low because Fe- and Al-oxide surfaces are protonated and have increased positive charge. However, if soil acidification procedes too far, Fe- and Al-oxides surface coatings can dissolve and sulfate adsorption will be disrupted. Organic ligands can reduce sulfate adsorption even when Fe- and Al-oxide contents are high (Turner et al. 1990).

Sulfate precipitation in soil solution is another mechanism for sulfate retention by watersheds. Sulfate precipitation with Al requires especially low pH in soil solutions, otherwise Al concentrations are not high enough to allow precipitation. Minerals produced by sulfate precipitation include basaluminite ($Al_4OH_{10}SO_4$), alunite ($KAl_3OH(SO_4)_2$), and jurbanite ($AlOHSO_4$). These minerals may be produced when there are alternating accumulations and releases of both sulfate and Al due to increased soil acidification via nitrification. Whether or not sulfate adsorption is reversible will depend in part on whether the sulfate is held to soil by only electrostatic attraction, or whether it is held by a stronger molecular bond, with Fe or Al oxides forming a direct double bond with S atom. Sulfate reduction, followed by volatilization of H_2S is not likely to be important in soils, unless waterlogged, but can play a role in within-lake ANC production in lake sediments.

Evidence that soils retain sulfate in the Emerald Lake watershed, at least on a seasonal basis, is provided by the constancy of sulfate concentrations in *stream water* in 1987 (7.1 to 7.6 μeq L^{-1} in outflow) following rain events with maximum concentrations of up to 74 μeq L^{-1} (Williams et al. 1991). Whether or not the watershed retains the sulfate in snowmelt may be related to the size of the snowpack. In the *wet* year 1986, more sulfate flowed into Emerald Lake than was present in the snowpack (stream loading/snowpack loading = 1.87). In contrast, in the *dry* year 1987, more sulfate melted out of the snowpack than reached the inflows to Emerald Lake. Thus sulfate retention occurred in the soil shed (stream loading/snowpack loading = 0.49).

Uptake of sulfate by plants or microbes contributes to sulfate retention in watersheds. When S uptake by plants exceeds S requirements, SO_4^{-2}-S is stored in foliage. N limitation will reduce SO_4^{-2} uptake by plants and the extent to which it (S) is incorporated into organic compounds instead of easily leachable SO_4^{-2} in litter. Microbial immobilization of sulfate (into C-bonded S and ester-SO_4) can be a net sink of atmospheric deposited SO_4^{-2}. It appears that ester-SO_4 is more indicative of microbial transformation than C-bonded S (which can come from fine root mortality and litter). Microbial-S retention in a watershed will require sufficient carbon supplies. S immobilization by biota is generally a low percentage of total ecosystem S retention - most retention occurs in the soil (Turner et al. 1990).

3.7.2.2. Sulfate export from Sierra Nevada watersheds.

Although Sierran watersheds appear capable of retaining sulfate on a short time scale (see above), on an *annual* basis many cases of net export of sulfate from watersheds were observed in the Lake Comparison Study (Melack et al. 1996). The watersheds of Pear, Topaz and Crystal Lakes retained sulfate in all of the study years except for 1993, which was a high snowpack year (Table 3). The watersheds of Ruby, Spuller and Lost Lakes always exported sulfate, and the largest export values were observed in 1993. Sulfate retention was only observed in two water years (1985, 1987) in the Emerald Lake watershed. During the years 1990-1994, the Emerald Lake Watershed either exported sulfate, or loading balanced outflow (1992). As in all of the other catchments, the largest net export of sulfate from the Emerald Lake Watershed took place in 1993.

The watersheds which *always* exported sulfate are located in the eastern Sierra Nevada (Ruby, Spuller and Lost Lake watersheds). The Emerald Lake watershed is the only watershed studied in the western Sierra Nevada that tended to export sulfate more often than retain sulfate. In addition, two of the three eastern Sierra catchments consistently had the highest VWM concentrations of sulfate in lake outflow. Ranges of VWM sulfate (μeq L^{-1}) in lake outflows in the Lake Comparison Study were as follows: Ruby Lake 9.3-12.1; Spuller Lake 8.3-12.0; Lost Lake 5.3-6.9; Crystal Lake 6.0-6.4; Emerald Lake 5.3-7.0; Pear Lake 5.5-6.5; Topaz Lake 4.6-6.0 (Melack et al. 1996). VWM sulfate in the second order stream Marble Fork ranged 7.2-8.8.

Sulfate export from these headwater catchments is indicative of the weathering of sulfur bearing minerals in the watersheds. Two major categories of sulfur bearing minerals comprise the probable parent rock for sulfate export; (1) sulfide bearing minerals containing reduced sulfur, and (2) sulfate bearing minerals containing oxidized sulfate molecules. Important sulfide bearing minerals include pyrite (FeS_2), marcasite (FeS_2), pyrrhotite (FeS) and galena (PbS). Important sulfate bearing minerals include baryte ($BaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) (Stumm & Morgan 1981). The weathering of sulfide bearing rocks involves a redox reaction in which ferrous iron and sulfur are oxidized, and the ferric iron hydrolyzes to precipitate ferric hydroxide:

$$2\ FeS_2 + 15/2O_2 + 7\ H_2O = 2\ Fe(OH)_3 + 8\ H^+ + 4\ SO_4^{2-}$$

This reaction is an internal watershed source of acid (sulfuric acid), and thus a process consuming ANC. Weathering reactions of this type are responsible for acid mine drainage in locations where oxygenated meteoric waters contact sulfide minerals through mining activities (Turner et al. 1990). When the weathering products of the above reaction contact calcite crystals, a secondary weathering reaction occurs, liberating Ca^{2+}. Export rates of sulfate and Ca^{2+} can thus be related whether the source of sulfur was the weathering of gypsum or or the weathering of pyrite (Melack & Stoddard 1991).

Major ion data from the Western Lake Study (Sierra Nevada sites) was subjected to R-mode factor analysis by Melack & Stoddard (1991) in order to examine whether geochemical processes other than plagioclase weathering are responsible for the chemistry of some Sierran lakes. Ninety percent of the variance in major ion composition was explained by a factor highly related to ANC, cations and silica, and can be explained by the weathering of minerals in granitic bedrocks (plagioclase, K-feldspars, hornblende, biotite). The next most important factor in the anaysis was associated with SO_4^{2-} and

Ca^{2+}. This result was due to the lakes in the data set with high relative proportions of Ca^{2+} and sulfate, and is interpreted as evidence of weathering of small amounts of gypsum or pyrite. In these lakes a substantial quantity of Ca^{2+} is present which is *not associated with ANC*. Melack & Stoddard (1991) ascribe this result to the dissolution of calcite present in pyrite bearing rocks (as described above). Some Sierran lakes belonging to the high sulfate category in the WLS occur in watersheds containing meta-sedimentary bedrock (such as marble). In these cases, such as in the Convict Lake area of the eastern Sierra Nevada, the weathering of gypsum is a likely source of sulfate and calcium.

Mahood et al. (1994) attribute the presence of naturally acidified lakes in the Mt. Pinchot region of the Sierra Nevada to the oxidation of pyrite. However, the presence of pyrite in a catchment will not necessarily lead to the acidification of surface waters. Processes that promote mechanical grain size reduction of pyrite-bearing rocks (e.g. crushing in a fault zone or a rock glacier) enhance the probability that weathering of pyrite will produce acidified waters. Other processes that result in the exposure of pyrite-free rock surfaces will promote acid-neutralizing weathering reactions (Mahood et al. 1994). Examples of such processes are rock falls and talus slopes in glacially produced landscape.

The occurrence of pyrite is generally restricted to lithologies containing hydrothermally altered metamorphic rocks or small pods of leucocratic granite (leucocratic granite is a light colored granite containing < 30% mafic minerals). The Mt. Pinchot area in the central Sierra Nevada is underlain by granitic plutons (plutons refer to igneous rock formed at depth) of Jurassic and Cretaceaous age separated by roof pendants of metasedimentary rock (such as biotite schist, calc-hornfels, pelitic hornfels, quartzite, and minor marble (Mahood & Gansecki 1994). The Mt. Pinchot area is one of the few in the Sierra Nevada where the metasedimentary roof pendants are abundantly exposed.

Pyrite can be formed in metamorphic rock (and perhaps in granite) that is hydrothermally altered. It also occurs as widely scattered small mm-sized cubes in true granite. It is apparently the former type of pyrite-bearing rock that is responsible for the acidification of surface waters in the Mt. Pinchot area within Kings Canyon National Park (Mahood & Gansecki 1994). Lakes in the Mt. Pinchot area which receive drainage from hydrothermally altered rocks of the correct geology include the naturally acidic lakes surveyed by Bradford et al. (1994). Whether or not the metamorphic rock was hydrothermally altered appears related to its age. Granitic plutons and metamorphic rock belonging to the period before the Independence dike swarm was produced (therefore called "Pre-Independence-dike-swarm" plutons) were pyritized. This process would have occurred at least 148 mya, within the Jurassic Period. However, granitic plutons belonging to the "Post-Independence-dike-swarm" period (more recent than ca. 148 mya) were apparently not exposed to heated groundwater, and thus were not pyritized (Mahood & Gansecki 1994). As a result of this geology, pyritized granite occurs very locally in the Mt. Pinchot area-- it is present in some headwater catchments, and not in other nearby or adjacent catchments. For example, the drainages designated "L" and "F" in the Bradford et al. (1994) study coincide with Pre-Independence-dike-swarm granite, and thus contain lakes and streams naturally acidified due to the weathering of pyrite. However, adjacent drainages, designated "D", "E" and "C", do not have exposed Pre-Independence-dike-swarm rock, and lack acidified surface water (Mahood & Gansecki 1994).

The presence of pyrite-bearing rock in the South Sierra Nevada catchments studied by Melack et al. (1996) was not specifically addressed. Thus it cannot yet be confirmed that the consistent net export of sulfate from some of the Sierra Nevada watersheds studied is due to the weathering of pyrite-bearing rocks. The *potential* importance of pyrite weathering as an internal watershed source of acidity (and as a sink for ANC) is illustrated in Table 4. For every equivalent of sulfate hypothetically produced by pyrite weathering, 2 equivalents of H^+ are produced. In a scenario in which 100% of the sulfate exported by the Sierran watersheds is produced by the weathering of pyrite, the acidity produced would be of the same order of magnitude as the acidity currently entering the watersheds in wet deposition.

Some relationship appears to exist between sulfate loading from wet precipitation and sulfate yield from catchments. The year in which the greatest total sulfate loading occurred for each catchment in the Lake Comparison Study was generally a year of sulfate export (Table 3). The exception was the Crystal Lake watershed, which received its highest total sulfate load in 1992, but retained sulfate in the same water year. However, the one year in which Crystal Lake watershed exported sulfate (1993) was a year in which 97% of sulfate loading came from the snowpack. The years in which the highest export of sulfate was observed in eastern Sierra catchments were not necessarily years with higher than average total sulfate loading, but tended to be years in which a high percentage of sulfate loading came from the snowpack. For these catchments

(Crystal, Ruby, Spuller, Lost), 89% or more of sulfate came from snow in such years (as opposed to other years, in which snow contributed generally 30% -55% of annual sulfate). This result suggests that these catchments are more efficient at regulating sulfate that arrives as non-winter precipitation.

3.7.3. Watershed processes affecting N in surface waters.

The watersheds studied in the Lake Comparison Study were effective at retaining dissolved inorganic nitrogen delivered in wet deposition (Table 5). Ammonium was almost completely retained by the headwater catchments. Retention of ammonium was observed in every lake in every water year studied. Net retention of nitrate was almost always observed in the seven watersheds also, although the percentages of nitrate consumed by watershed processes was lower than for ammonium. There were only five cases in which more nitrate left the catchments than was deposited in precipitation: Emerald Lake in 1986, 1993, and 1994; Ruby Lake in 1993; and Spuller Lake in 1993. The majority of these cases occured in 1993, which was a large snow year. This suggests that in years of very high discharge, mechanisms for nitrate retention may be overwhelmed during snowmelt.

Ammonium consumption appears to occur along the pathway of meltwater to the lakes rather than in the lakes. Williams & Melack (1991b) reported that >99% of the NH_4^+ from wet deposition was consumed by the watershed of Emerald Lake before reaching the lake itself. Ammonium concentrations in stream waters in the ELW were always near or below detection limits and showed no seasonal or interannual trends (Williams et al. 1995). NH_4^+ infiltrating soils during snowmelt may be retained by ion exchangers, and subsequently used by biota. Microbial assimilation or ion exchange may take place in talus and rock fractures when soils are saturated and overland flow is occurs (Williams et al. 1993).

The biological assimilation of NH_4^+ leads to production of H^+ and subsequent leaching of base cations (on an annual basis). Using data from the Emerald Lake Watershed, Williams et al. (1993) demonstrated that if all of the base cations in stream water are backreacted with secondary minerals to produce bedrock minerals in the basin, the sum of the weathering reactions accounts for only ~75% of the annual alkalinity in stream flow. The excess alkalinity measured in stream flow can be almost balanced by net production of H^+ if the assumption is made that all NH_4^+ retained in the basin was retained by biological assimilation (producing H^+ on a molar basis) and that all nitrate retained was converted to organic N (producing OH^- on a molar basis). In 1987, less than 1% of the NH_4^+ in deposition was exported from the basin (Williams et al. 1995).

Nitrification is especially influential on soil solution pH and ANC. When NH_4^+ is nitrified to NO_3^-, two H^+ are released. Thus, the process of nitrification consumes ANC. In addition, the nitrate produced is particularly mobile in soil - facilitating the downward leaching of base cations displaced by H^+. This process may result in a significant reduction in soil base saturation and an increase in soil acidity. If base cations are reduced sufficiently in the soil, Al can be mobilized in their place, leading to potential toxicity. If N-supplies in a watershed gradually overcome N-demand, atmospheric N deposition may cause a site to become N-saturated so that nitrate leaching begins. Thus, both nitrification and atmospheric nitrate inputs can set into motion nitrate-mediated cation leaching from the soil.

In 1987, soil lysimeter data from the ELW showed that nitrate was lacking in soil solution at the onset of snowpack runoff. Because concentrations of nitrate in the soil solution at the initiation of snowmelt were so low, it is doubtful that nitrification processes under the snowpack supplied the nitrate in surface waters during early snowmelt (Williams et al. 1995). Later in the snowmelt period, nitrate in soil solution increased more than can could be accounted for by snowmelt concentrations and snow-rain concentrations. At the same time, NH_4^+ in soil solution remained low and static, and lower than NH_4^+ in melt plus rain. Other evidence that nitrification was taking place in soils after the initiation of snowmelt is provided by lake inflow chemistry. Overall ELW snowpack release of NO_3^- plus NH_4^+ from 5 May to 27 June 1986 (4800 Eq) was similar to the overall yield of NO_3^- in all inflowing streams of the basin (4631 Eq, Williams et al. 1991).

Melack et al. (1996) compared solute export from Emerald Lake during the rising and the falling limbs of the snowmelt hydrograph with the amounts of each solute expected from melted snow. They showed that more nitrate leaves the catchment during the rising limb of the hydrograph than is contained in the entire snowpack. They suggest that nitrification of ammonium can account for the excess nitrate in surface waters.

Fate of nitrate. The fate of nitrate delivered to the Sierran watersheds in snowfall apparently varies interannually. In the wet year 1986, about 20% of the nitrate that fell as snow failed to accumulate in the snowpack. Later, streams carried more nitrate than was stored in the snowpack (stream loading/snowpack loading = 1.21). If one assumes that the nitrate that was 'lost' from the snowpack (and presumably held in soil over winter) moved into streamwater along with the nitrate of meltwater, the disparity between streamflow and snowpack nitrate is reduced (stream loading/snowpack loading = 0.98). In other words, in 1986, essentially all of the nitrate delivered by snow was removed from the watershed and delivered to surface water. In contrast, in the dry year 1987, only ca. 60% of the nitrate in wet plus dry deposition was exported from the basin as nitrate in stream waters (Williams et al. 1995).

The ELW is apparently not N-saturated during the growing season. Net mineralization rates (obtained in soil-bag experiments) were often low or negative during the growing season, suggesting that available N was utilized by vegetation or immobilized in microbial biomass. Nitrate concentrations in surface waters declined to detection limits during the growing season, but increased to a mean of 5 μeq L^{-1} when vegetation activity was reduced in the fall and winter months (Williams et al. 1995). However, this means that the basin is assimilating all atmospheric sources of N delivered during the growing season. If NO_3^- is retained in the basin and converted to organic nitrogen, OH^- is produced on a molar basis, and contributes to ANC. Organic N accounted or about 60% of all N loss from the Emerald Lake watershed in 1986 (Williams et al. 1995).

Denitrification is another process that can consume nitrate from wet deposition. Denitrification will not take place if soils are frozen or if soils become dry. In situ estimates of denitrification were done by Brown et al. (1990) in two entisols of the ELW using acetylene block. Maximum rates occurred immediately after rain. Denitrification losses amounted to an estimated minimum of only ~10 eq ha^{-1} in 1987, which is about 5% of deposition inputs of nitrate (Williams et al. 1995). However, this estimate ignores denitrification losses under the snowpack, which are potentially as high as N_2O emissions during the snow-free season (Sommerfeld et al. 1993). However, the combined losses of NH_4^+ in stream water and of N_2 and N_2O through denitrification in the ELW are estimated to be less than 2% of the export of N in stream water as NO_3^- and organic N (Williams et al. 1995).

3.8. HYDROLOGIC COMPOSITION OF SUMMER STREAMFLOW

During the summer transition period between snowpack runoff and low flow conditions, discharge from soil reservoirs is the primary source of stream flow in the ELW. Both the Na^{+}:Ca^{+2} ratio and Si content of soil water were similar to that of stream water during summer. The composition of stream flow at this time was congruent with the stoichiometry of plagioclase weathering. The residence time of this water is on the order of months and sufficient for mineral weathering reactions to reach completion (Williams et al. 1993). The H^{+} retained in the soils during snowpack runoff may participate in mineral weathering in the soils and talus during summer months.

3.9. SUMMER RAIN.

Contribution of summer rain to the annual water budget. Most of the annual deposition of nitrogen, sulfate and organic acids occurs during the non-winter months. Although the quantity of non-winter precipitation is much smaller than snowfall, the concentrations of these solutes in rain is much greater than in snow (Table 6). The importance of summer precipitation to annual solute laoding varies greatly from year to year in the Sierra Nevada. One or more large rains in the summer or during snowmelt can cause a year to have higher than average solute loading. For example, in the summers of normal water year 1985 and the wet year 1986, rain provided 1% of water flux and 10% of ion flux in the Emerald Lake Watershed. In the dry year 1987, rain was much more important- accounting 17% of water flux and 66% of solute flux- -however, 85% of the rain solute flux occurred in spring as rain-on-snow. Western slope basins receive more summer rain than eastern slope basins in the Sierra Nevada (Sickman & Melack 1989).

Ionic composition of summer rain. Low Cl^{-} and high NH_4^{+} in rain suggest that localized convection storms are main source of ions (see Part 1, this report). In summer rainfall, NH_4^{+}/H^{+} is always > 1 (whereas in winter snow, NH_4^{+}/H^{+} is always < 1), and NH_4^{+} is strongly correlated with NO_3^{-} and SO_4^{-2}. NH_4^{+} is an important neutralizer of the strong acid anions NO_3^{-}, SO_4^{-2}, and Cl^{-}. Without NH_4^{+}, $[H^{+}]$ in rainfall could be 11-fold higher. Rain in the Sierra Nevada in summer is acidic. Example ranges of annual VWM pH for non-winter precipitation are as follows: Crystal Lake, pH 4.7-5.2; Emerald Lake, pH 4.7 to 5.5; Eastern Brook Lake, pH 4.7 -5.2; Tioga Pass, pH 4.4 -4.7; Angora Lake, pH 4.8 - 5.7 (Melack et al. 1996). Large summertime rainstorms have been observed to cause a drop in the pH and ANC of Emerald Lake (Melack et al. 1987). Episodic acidification from summer rain is discussed more thoroughly in Part 4 of this report.

3.10. VEGETATION-MEDIATED PROCESSES AFFECTING ANC

In the ELW, vegetation (all types) covers 20% of the 120 ha basin, and within that 20%, 3% consists of scattered trees (Williams et al. 1993). Approximately 75% of the vegetation in the watershed is accounted for by three plant communities, each roughly corresponding to a soil map unit: *Pinus monticola* on typic cryorthod-rock outcrop, *Salix orestera* on entic cryumbrept, and wet meadow on lithic cryumbrept-rock outcrop.

Throughfall. Based on work at the ELW, the N concentrations of incident rain are greatly changed by passage through foliage (chinquapin, western white pine, and willow; Williams et al. 1995). Nitrate was released by vegetation, either as a consequence of leaching or washoff of dry deposition, leading to almost a doubling of nitrate concentrations in incident rain (1.51 vs 0.7 meq m^{-2}). Almost all NH_4^+ in incident rain was retained by foliage (0.77 meq m^{-2} vs 0.8 meq m^{-2}). Because the total area covered by vegetation in the Emerald Lake watershed is small, the overall effect of throughfall on loadings of N species is low. However, the effect of foliage on rain was to greatly increase the concentration of the strong acid anion nitrate and to greatly reduce the concentration of a cation normally available to neutralize strong acid anions in precipitation, thus lowering the ANC of precipitation. The importance of this process in a particular watershed will vary with the areal extent of vegetation.

3.11. IN-LAKE BUFFERING MECHANISMS

In-lake processes that can produce alkalinity include nitrate assimilation, denitrification, ammonification, dissimilatory sulfate reduction, sulfate assimilation (ester sulfate formation, reduction to organic sulfides), ferrous (FeIII) oxidation, mineral weathering, and cation exchange on minerals and organic sediments. In some studies it has been found that ANC production by a lake is greater than ANC production in its terrestrial watershed per unit area (Schindler et al. 1986, Brezonik et al. 1987, Lin et al. 1987), however, studies distinguishing ANC production by a lake versus its watershed are few.

3.11.1 Water column sources and sinks of ANC.

The assimilation of sulfate and nitrate by algae and bacteria in the water column, and the subsequent sedimentation of this S is a source of ANC in lakes. However, because S levels are usually above limiting in lakes, the biotic assimilation of sulfate may not increase substantially with increasing sulfate inputs. As a result, whereas sedimentation of organic S can be as high as 50-60% for oligotrophic, unacidified lakes (Baker et al. 1989), it is likely to be a minor term in overall lake retention of S for S-polluted lakes (e.g. < 3% in Cook & Schindler 1983). Annual peaks in the outflow flux of sulfate associated with snowpack runoff are observed in all seven lakes studied by Melack et al. (1993), with peak fluxes generally occuring in May or June. On a molar basis, the sulfate outflow flux is greater than the nitrate outflow flux. However, values for lake *inflow* fluxes of solutes are lacking for these lakes, thus we are unable to evaluate the net effect of solely in-lake processes on sulfate retention or yield.

Biological assimilation of NH_4^+ produces acidity. If net retention of NH_4^+ can be demonstrated in a lake, a net loss of ANC has occurred. Use of NH_4^+ by biota can cause acidification in two ways. First, if phytoplankton are not otherwise nutrient limited (e.g. if provided sufficient P) uptake of NH_4^+ can acidify the water column. Secondly, if phytoplankton are nutrient limited, NH_4^+ will be in excess. If NH_4^+ builds up in the water column and nitrifiying bacteria increase, the nitrification of NH_4^+ to NO_3^- can acidify the water column. If NH_4^+ and NO_3^- are supplied and retained at similar rates the net effect on ANC is balanced.

Base cations. The removal of base cations from the water column by macrophytes or algae, and their subsequent sedimentation, represent a sink of ANC in the water column because when a base cation is taken up by a macrophyte or an alga, either an OH^- is also taken up or a proton is released to preserve electroneutrality. According to the Turner et al. (1990), detailed water column ANC budgets are lacking, but plant stoichiometry indicates that if NH_4^+ is the dominant N source, overall cation removal from the water column (base cations + NH_4^+) will exceed anion removal, and cause a loss of ANC. Regional differences in precipitation chemistry suggest that NH_4^+ is a relatively greater component of TDN in the lakes of the eastern US than in the western US, and that in the West, NH_4^+ is generally undetectable in the water column of lakes, or lower than NO_3^- (Landers et al. 1987).

3.11.2. Lake sediment influences on ANC.

There are three categories of reactions by which lake sediments can yield alkalinity to the water column of a lake: (1) nitrate and sulfate reduction, (2) NH_4^+ and base cation production from decomposition, and (3) proton consumption and cation release by mineral weathering. The reduction of Mn, Fe and sulfate under anaerobic conditions will produce ANC, but once the reduced species difuse out of the hypolimnion, or are mixed at spring overturn, the following oxidation cancels the effect, and net change in ANC = 0. However, if bacterial reduction of SO_4^{-2} is followed by precipitation of Fe_2S, a *permanent input of ANC results.* Similarly, contributions to lake ANC via the production of NH_4^+ in decomposition may be only temporary, as the reduced species can be assimilated after transport into oxygenated strata of the water column (a process which consumes alkalinity). However, fluxes of base cations out of sediments represent a permanent contribution of alkalinity.

Nitrate and sulfate reduction. Denitrification can lead to permanent increases in ANC due to the permanent loss of NO_3^- via production of N_2 (1 equiv. NO_3^- denitrified = 1 equiv. ANC produced). A consequence of the high NO_3^-/SO_4^{-2} ratio in Californian acidic deposition is an increase in the potential importance of denitrification. When sulfate reduction takes place, (SO_4^{-2}----> H_2S), 1 eq of ANC is produced per eq SO_4^{-2} used. However, if the H_2S is subsequently re-oxidized, ANC is reconsumed and net effect is zero. Thus, in order for sulfate reduction to result in permanent contribution of ANC, the H_2S must (1) react with metals to form insoluble metal sulfides (FeS, FeS_2), (2) react with organic matter to form C-bonded S compounds such as thiols, mercaptans, thioethers, or (3) be released to the atmosphere as reduced gas.

Decomposition and release of base cations. HCO_3^- and base cation flux out of the sediments are not subject to redox reactions, and thus represent a permanent source of alkalinity. The production of organic acids via decomposition can have variable effects on ANC. Weak organic acids can serve as a source of ANC if the organic anions react with protons. The production of strong organic acids can lower ANC by introducing into the water column non-protonated anions that fail to react with H^+. Cation release from sediments may be attributed to both cation exchange or mineral dissolution. For lakes of the Eastern Lake Survey, with mean depth of 3 m and residence times of 1 year, Ca^{+2} release from sediments can amount to as much as 7-10 μeq L^{-1} (Turner et al. 1990).

Weathering evidence from Sierran lakes. The sediments of three sub-alpine lakes were studied by Admunson et al. (1988). The three lakes were chosen to represent the western slope (Emerald Lake), the summit (Mosquito Lake), and the eastern slope (Eastern Brook Lake) of the Sierra Nevada. All lakes have alkalinitiy $< 150\ \mu eq\ L^{-1}$. The upper 25 cm of sediment represents several hundred years of sedimentation in these lakes. Two predominant patterns in sediment chemistry were observed with depth: (1) a decrease in organic matter with depth, (2) a decrease in iron hydroxides with depth. Silica was present in the pore waters of the sediment, which suggest that some mineral weathering of mineral particles is taking place over time in the sediments, and/or that diatoms are dissolving. However, the weathering of silicate-clay minerals apparently did not occur rapidly enough to be detectable by X-ray diffraction. In the clay size fraction, there were clay size quartz crystals, which would have undergone physical weathering from larger quartz crystals in the intrusive igneous bedrock. Smectite was another dominant mineral in the sediments, and is a weathering product of plagioclases and primary micas.

Admundson et al. (1988) used pore water analysis in Emerald Lake to show the flux of base cations, Si, and NH_4^+ out of the sediment and flux of sulfate into the sediments. Although there is a net production of Ca^{2+} during the winter in Emerald Lake, there is not a net production of Si. Because the Ca^{2+} must be due to weathering of Ca-aluminosilicate minerals, there must be a process consuming Si, such as uptake by diatoms or formation of secondary aluminosilicate minerals (such as kaolinite).

In Eastern Brook Lake, there is a consistent pattern of solute build up during the winter months under ice cover. This process coincides with the period of minimum surface water flows - thus the source of the solutes and the ANC must be from in-lake processes or groundwater inputs, instead of stream inflow. In Eastern Brook Lake, the seasonal pattern of Ca^{2+} mirrors the seasonal pattern of ANC, suggesting that the weathering of Ca-containing minerals such as anorthite or hornblende is generating the ANC. Table 6 summarizes evidence for over-winter hypolimnetic ANC build-up in the lakes of the Lake Comparison Study. From the limited evidence available, it appears that ANC build up in high altitude lakes is a common phenomenon, but not one that occurs every year.

3.11.3. Role of CO_2.

When soil or groundwater with positive ANC emerges into a stream or lake, it will be supersaturated with CO_2, and degassing after emergence will cause its pH to rise. Piezometers, seepage meters, and temperature measurements show no discernible direct seepage of groundwater into lake sediments at Emerald Lake (Melack et al. 1989, Williams et al. 1990). In Emerald Lake, mean water column CO_2 levels in the summer are not different than one would expect from atmospheric equilibrium, but the mean concentration in winter water columns (March, April, May) are significantly larger than atmospheric concentrations (Amundson et al. 1988). CO_2 was present in high concentrations in the sediments of Mosquito, Eastern Brook and Emerald Lakes (and is likely a byproduct of methanogenesis). This pool of CO_2 serves as a potential source to the water column. A build-up of pCO_2 under ice cover during winter can decrease pH in the water column without a corresponding change in water column ANC. This occurs because as the production of CO_2 drives the following reaction to the right,

$$H_2CO_3^* \text{ -------> } H^+ + HCO_3^-$$

both cations (protons) and anions (bicarbonate) are produced in equimolar proportions, cancelling out any numerical effect on ANC. However, at the same time, $[H^+]$ increases, lowering pH in the water column.

In Eastern Brook Lake, DIC storage and H^+ storage in the water column track each other. Minimum values for both occur in the early fall. And springtime peaks in both parameters occur at the same time. The acidity of the lake thus appears to be dominated by CO_2 production. The rate of H_2CO_3 production in the winter was greater than the rate of ANC production, resulting in net acidification during winter. Thus peak DIC and minimum pH occurs in early spring at the onset of snowmelt. Input of acidic anions in snowmelt runoff consistently, but only slightly, influences this acidification pattern in Eastern Brook Lake (Brown & Lund 1991).

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Table. 1. Details of annual mass balances for hydrogen ion in seven high altitude Sierra Nevada watersheds. Water years refer to the period Oct. 1 - Sept 30. H^+ loading is from winter and non-winter preciptation. Units for loading and retention are $eq \cdot ha^{-1} \cdot yr^{-1}$. Data obtained from Melack et al. (1996).

Watershed	water year	H^+ load	H^+ retention	% exported
Emerald Lake	1985	65	61	6
	1986	128	105	18
	1987	58	52	10
	1990	34	30	13
	1991	38	24	37
	1992	22	19	14
	1993	123	112	9
	1994	29	25	14
Pear Lake	1990	37	33	11
	1991	38	31	18
	1992	25	21	16
	1993	76	54	29
Topaz Lake	1990	29	26	10
	1991	37	32	14
	1992	23	20	13
	1993	50	43	13
Crystal Lake	1990	53	51	4
	1991	37	33	11
	1992	49	48	2
	1993	63	57	10
Ruby Lake	1990	60	57	5
	1991	37	32	14
	1992	44	42	5
	1993	53	50	6
	1994	29	28	3
Spuller Lake	1990	57	53	7
	1991	56	44	21
	1992	68	65	4
	1993	63	47	25
	1994	39	38	3
Lost Lake	1990	54	44	19
	1991	46	26	43
	1992	53	33	38
	1993	80	54	33

Table 2. Details of annual mass balance for base cations [$Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}$] for seven high altitude watershed in the Sierra Nevada.

yield = [amount in outflow] -[amount delivered by precipitation]

Yield/outflow indicates the % of base cations exported that originated from weathering processes or cation exchange rather than from precipitation. Water year refers to the period Oct. 1-Sept. 30. Yield and outflow data obtained from Melack et al. (1996).

Watershed	water year	yield $Eq \cdot ha^{-1}$	outflow $Eq \cdot ha^{-1}$	Yield/Outflow (%)
Emerald Lake	1985	132	212	62
	1986	551	658	84
	1987	199	314	63
	1990	155	211	73
	1991	252	304	83
	1992	178	225	79
	1993	467	542	86
	1994	193	247	78
Pear Lake	1990	97	153	63
	1991	101	156	65
	1992	106	147	72
	1993	308	376	82
Topaz Lake	1990	139	187	74
	1991	147	207	71
	1992	177	218	81
	1993	406	465	87
Crystal Lake	1990	135	193	70
	1991	169	248	68
	1992	96	179	54
	1993	596	653	91
Ruby Lake	1990	227	299	76
	1991	255	293	87
	1992	277	320	87
	1993	475	514	92
	1994	271	308	88
Spuller Lake	1990	262	312	84
	1991	363	422	86
	1992	315	371	85
	1993	597	669	89
	1994	305	343	89
Lost Lake	1990	197	256	77
	1991	202	258	78
	1992	352	404	87
	1993	520	655	79

Table 3. Details of sulfate budgets for seven Sierra Nevada headwater catchments. Bold face indicates the highest values obtained for selected parameters for each catchment between the years 1990-1994. Water years refer to the period Oct. 1-Sept. 30. Data are from Melack et al. (1996).

		SO_4^{2-} Loading					VWM SO_4^{2-}
	Water	Total	Snow only		Catchment Yield		Outflow
	Year	$\mu Eq \cdot ha^{-1}$	$\mu Eq \cdot ha^{-1}$	% total	$Eq \cdot ha^{-1}$		$\mu Eq \cdot L^{-1}$
Emerald	1985	45	32	71	-13	sink	5.7
	1986	64	38	59	32	export	5.3
	1987	95	23	24	-47	sink	7.0
	1990	36	14	40	2	export	6.9
	1991	32	11	34	24	export	6.8
	1992	33	11	33	0	balance	5.8
	1993	**61**	**52**	**85**	**37**	export	6.0
	1994	18	11	61	26	export	6.1
Pear	1990	39	18	46	-9	sink	6.6
	1991	35	14	40	-5	sink	6.6
	1992	32	11	34	-8	sink	5.6
	1993	**48**	**40**	**83**	**32**	export	5.5
Topaz	1990	33	12	36	-11	sink	5.7
	1991	30	9	30	-3	sink	6.0
	1992	30	9	30	-10	sink	4.8
	1993	**35**	**27**	**77**	**18**	export	4.6
Crystal	1990	32	14	44	-17	sink	6.1
	1991	31	17	55	-10	sink	6.4
	1992	**43**	24	56	-28	sink	6.1
	1993	32	**31**	**97**	**20**	export	6.0
Ruby	1990	**38**	14	37	6	export	9.3
	1991	28	8	29	15	export	9.5
	1992	35	11	31	19	export	12.1
	1993	28	**25**	**89**	**60**	export	11.8
	1994	28	15	53	21	export	11.4
Spuller	1990	27	9	33	27	export	9.7
	1991	33	15	45	40	export	9.1
	1992	**47**	15	32	22	export	12.0
	1993	35	**33**	**94**	**76**	export	8.3
	1994	28	19	68	49	export	11.5
Lost	1990	37	20	54	15	export	6.7
	1991	32	18	56	14	export	5.6
	1992	31	11	35	46	export	6.9
	1993	**72**	**69**	**96**	**54**	export	5.3

Table 4. Relationship between measured H^+ loading from wet deposition and hypothetical H^+ production from sulfide oxidation, based on measured sulfate yield. Net sulfate yield indicates sulfate exported from the watersheds in excess of sulfate loading from precipitation. The assumption is made that 100% of the net sulfate leaving the watersheds was produced by the oxidation of sulfide (such as occurs in the weathering of pyrite). H^+ loadings and sulfate yields were obtained from Melack et al. (1996).

Watershed	Water Year	H^+ from Precip. Eq·ha^{-1}·yr^{-1}	Net Sulfate Yield Eq·ha^{-1}·yr^{-1}	Hypothetical H^+ from sulfide oxidation Eq·ha^{-1}·yr^{-1}	$\frac{H+(Sulfide)}{H^+(precip)}$
Emerald Lake	1986	128	32	64	0.50
	1990	34	2	4	0.12
	1991	38	24	48	1.26
	1993	123	37	74	0.60
	1994	29	26	52	1.79
Pear Lake	1993	76	32	64	0.84
Topaz Lake	1993	50	18	36	0.72
Marble Fork	1993	123	63	126	1.02
	1994	26	52	104	4.00
Crystal Lake	1993	63	20	40	0.63
Ruby Lake	1990	60	6	12	0.20
	1991	37	15	30	0.81
	1992	44	19	38	0.86
	1993	53	60	120	2.26
	1994	29	21	42	1.45
Spuller Lake	1990	57	27	54	0.95
	1991	56	40	80	1.43
	1992	68	22	44	0.65
	1993	63	76	152	2.41
	1994	39	49	98	2.51
Lost Lake	1990	54	15	30	0.56
	1991	46	14	28	0.61
	1992	53	46	92	1.74
	1993	88	54	108	1.23

Table 5. Details of annual mass balances for ammonium and nitrate in seven high altitude Sierra Nevada watersheds. Water years refer to the period Oct. 1 - Sept. 30. Solute loading is from winter plus non-winter preciptation. Units for loading and yield are eq ha^{-1} yr^{-1}. Negative yields indicate net retention by the watershed. Data obtained from Melack et al. (1996).

	water	NH_4^+		NO_3^-	
Watershed	year	loading	yield	loading	yield
Emerald Lake	1985	35	-34	43	-5
	1986	85	-83	80	10
	1987	141	-140	116	-62
	1990	44	-42	41	-16
	1991	86	-85	47	-1
	1992	40	-39	42	-21
	1993	60	-52	50	25
	1994	35	-34	29	5
Pear Lake	1990	46	-44	41	-22
	1991	93	-92	54	-26
	1992	41	-39	40	-27
	1993	50	-41	43	-4
Topaz Lake	1990	35	-35	39	-32
	1991	75	-74	45	-32
	1992	33	-29	37	-26
	1993	38	-34	30	-21
Crystal Lake	1990	50	-49	51	-51
	1991	60	-60	52	-49
	1992	61	-61	50	-49
	1993	33	-33	27	-23
Ruby Lake	1990	47	-46	54	-39
	1991	50	-49	38	-14
	1992	39	-39	42	-19
	1993	19	-15	24	15
	1994	45	-44	38	-31
Spuller Lake	1990	38	-37	40	-15
	1991	47	-47	44	-1
	1992	57	-57	58	-27
	1993	35	-35	30	14
	1994	40	-38	45	-27
Lost Lake	1990	43	-41	52	-47
	1991	53	-53	44	-39
	1992	28	-27	38	-32
	1993	103	-97	73	-57

Table 6. Comparison of volume weighted mean chemistry of non-winter precipitation (April through November) and snow (December through March). Values were obtained from Melack et al. (1996) and are arithmetic means of 36 water years of record combining eight study sites during the period 1985-1994.

	VWM µEq L^{-1}			
	non-winter precipitation		snow	
Solute	mean	SE	mean	SE
Hydrogen	11.1	0.61	3.8	0.21
Ammonium	23.6	0.70	2.7	0.38
Chloride	4.1	0.51	1.7	0.51
Nitrate	20.8	0.46	2.4	0.33
Sulfate	15.3	0.44	2.0	0.26
Calcium	10.4	0.59	1.7	0.46
Magnesium	2.4	0.60	0.5	0.43
Sodium	4.5	0.66	1.3	0.48
Potassium	2.4	0.67	0.5	0.90
Acetate	7.6	0.60	0.6	0.68
Formate	9.1	0.58	0.5	0.66
Deposition (mm)	115	0.52	1037	0.60

Table 7. Interannual variation in over-winter hypolimnetic ANC build-up. Where ranges are given, values represent increases in the ANC of hypolimnetic water from fall turnover to time of peak vertical stratification mid-winter. Values werw derived from time-depth diagrams for ANC in Melack et al. (1993).

	Winter			
Lake	1986-1987	1987-1988	1989-1990	1990-1991
Pear Lake	no build up	100-600 $\mu eq \cdot L^{-1}$	40-120 $\mu eq \cdot L^{-1}$	no build up
Ruby Lake	surface (z=1m) ANC greater than ANC near sediment	no build up	60-100 $\mu eq \cdot L^{-1}$	no build up
Topaz Lake	at z = 1 m, ANC $\approx$ 60 $\mu eq \cdot L^{-1}$ at z = 4 m, ANC $\approx$ 80 $\mu eq \cdot L^{-1}$	at z = 1 m, ANC $\approx$60 $\mu eq \cdot L^{-1}$ at z = 4 m, ANC $\approx$80 $\mu eq \cdot L^{-1}$	no build-up	no build-up
Crystal Lake	at z = 1 m, ANC $\approx$ 25 $\mu eq \cdot L^{-1}$ less than ANC near bottom	at z = 1 m, ANC $\approx$ 25 $\mu eq \cdot L^{-1}$ less than ANC near bottom	no build-up	no build-up
Emerald Lake	N.A.	N.A.	no build-up	no build-up
Spuller Lake	N.A.	N.A>	$\approx$ 80 - 140 $\mu eq \cdot L^{-1}$	N.A.