PART 4

THE EFFECT OF INFREQUENT EVENTS ON THE HYDROCHEMISTRY AND BIOTA OF HIGH ALTITUDE SIERRA NEVADA WATERSHEDS

PART 4

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TABLES

4.1. INTRODUCTION

Research conducted to date has shown that infrequent events can strongly affect the hydrochemical and biological features of high-altitude lakes and streams. For example, years of exceptionally high snowpack will have extended snowmelt periods, increased avalanche activity, shortened ice-free seasons, and may produce stronger ionic pulses and lower ANC during snowmelt. Other infrequent events, such as rain on snow, and large summertime rains may lead to the most severe episodic acidification. These events, although rare, may have disproportionate repercussions for lake biota. The consequences of unusual events will be summarized and discussed in light of their likelihood based on precipitation records for the region.

4.2. RAIN-ON-SNOW

In mountainous areas of the Pacific coast, rain-on-snow usually produces greater peak flows than either rain or snowmelt alone (Harr 1981). Rain-on-snow causes the only significant outflow from these high elevation watersheds between December and March (Berg et al. 1991). Rainfall on the snowpack at high elevations in British Colombia, Washington, Oregon and California is the most common factor leading to the largest flood flows, and is a major determinant of changes in channel morphology (Berg et al. 1991). In addition, in some areas (e.g. Oregon Cascades), the occurrence of landslides is largely coincident with rain-on-snow events (Harr 1981).

Large rains occur at elevations up to 2500 m at least once per year in the Sierra Nevada, causing serious flooding and erosion. Largely because of the effect of warm winter storms, Sierra Nevada reservoirs are planned with large flood reservations (Kattelmann 1987). Rain-on-snow produces the highest peak flows in the Sierra Nevada. All of the highest flows in this century in the Sierra Nevada were produced by mid-winter rain-on-snow events. Large magnitude warm storms in the Sierra Nevada tend to occur in mid-winter, rather than during springtime snowmelt (Kattelmann 1990). In the past 60 years, six large magnitude floods have occurred in almost all rivers draining the snow zone of the Sierra Nevada (Kattelmann 1990). Snow was absent in only one of these events. Widespread rain-on-snow in early January of 1997 produced significant flooding in rivers draining the Sierra Nevada. For example, 100-year flood stages were obtained or surpassed in the Tuolumne River at Modesto, CA, and the South Fork of the American River at Placerville, CA. The 50-year flood stage was reached on the Truckee River at

Farad, CA (Furniss 1997). The discharge produced in the Merced River from the same warm storm was among the five highest discharge leveles recorded since 1910 (Furniss 1997), and led to closure of the Yosemite National Park. The impact of rain-on-snow varies with elevation; the freezing level of winter storms tends to fluctuate between 1000 m and 2500 m. Even the warmest mid-winter storms rarely produce melting temperatures above 2500 m (Kattelmann 1990).

Kattelmann (1987) describes results of a study at the Central Sierra Environmental Studies Laboratory (CSESL) at 2100 m just west of the Sierran crest. The study site is near Lake Tahoe, 1 km east of Soda Springs, California. One or two major rain-on-snow events occur yearly at this site. Fourteen rain-on-snow events were monitored between 1972 and 1983. In general, snowpack water content differs little before and after a rain-on-snow event (Berg et al. 1991). In Kattelmann's study, little rainfall was stored or detained by the snowpack. At CSESL, generally less than 2 cm of rain fell before release of water occurred at the base of the snowpack (Kattelmann 1987). The exception to this occurred when rain fell on 60 cm of new snow; 3-4 cm of rain was held in the snow before outflow began. Comparisons of snowpack water content before and after rain-on-snow are similar in the central Sierra Nevada (Bergman 1983).

Data from the same site (CSESL) for 20 rain-on-snow events between March 1984 and January 1990 was analysed by Berg et al. (1991). A wide range of snowpack conditions and precipitation amounts (3-247 mm) were included in the study. Only four of the twenty rain-on-snow events occurred late enough in the season to coincide with snowpack ablation, and the rest occurred during periods of snowpack accumulation. The average duration of these storms was 32 h; the two longest single storms occurred in early March 1989 (150 h) and late Dec. 1985 (53 h). During 3 days in mid February, 1986, rain-on-snow events delivered a total of 320 mm. On average, more outflow occurred in both open and forested areas (86 mm, 72 mm respectively), than fell as precipitation (63 mm). In some storms, more outflow occurred than could be accounted for by precipitation. In unforested sites, 12 of the 20 rain-on-snow events produced more outflow than precipitation, and in forested sites, 8 of the 20 events produced more outflow than precipitation (Berg et al. 1991).

Forest is suspected to reduce the potential of snowmelt during rainfall because the presence of forest reduces windspeed, and thus reduces the turbulent exchange processes, such as sensible and latent heat exchanges, which are responsible for most of the snowmelt during rainfall (Kattelman 1987). In addition, outflow amount is expected to be less in the forest after rain-on-snow than in open areas because some of the precipitation intercepted by the forest canopy will be lost by evapotranspiration or re-routed to the ground through stemflow, and thus will fail to infiltrate the underlying snowpack (Berg et al. 1991). Data from the central Sierra Nevada supports this expectation. When outflow began after rain-on-snow events at CSESL, outflow in forested sites began ca. 2 hours after outflow at open sites (Kattelmann 1987).

Some cases have been observed in which outflow began before a rain-on-snow event occurred. In one third of the studied cases at Soda Springs, outflow began in forested sites before rainfall (Kattelman 1987). In these cases, snow fell before rainfall began. When snow occurs right before a wintertime rain, snow is present in the crowns of forested sites. When this intercepted snow melts as the temperature of the storm increases, its meltwater can produce measurable initial outflow from forested sites several hours before neighboring open sites.

Rain-on-snow can contribute substantially to solute flux. A series of unusually large rain storms occurred at Emerald Lake during the spring of 1987. Eighty-seven percent of all rain in 1987 occurred in May, delivering ca. 66% of the solute flux for that year in one month (Dozier et al. 1989). These storms had especially high concentrations of solutes. The enriched nature of this precipitation can be illustrated by comparing the solute loading values for rain in 1987 versus other years of record (Melack et al. 1996). For example, in 1987 ammonium loading per cm of non-winter precipitation in the Emerald Lake watershed was 1.47 $eq \cdot ha^{-1}cm^{-1}$, whereas average loading for the remaining 35 years of record (7 lakes combined) was 0.46 $eq \cdot ha^{-1}cm^{-1}$. Similarly, 1987 loading for nitrate was 1.21 $eq \cdot ha^{-1}cm^{-1}$, versus 0.52 $eq \cdot ha^{-1}cm^{-1}$ for the remaining years of record, and 1987 loading for sulfate was 0.99 $eq \cdot ha^{-1}cm^{-1}$, versus 0.37 $eq \cdot ha^{-1}cm^{-1}$ for the remaining years of record. The acidifying capacity of such a series of spring storms is high, due to the high delivery of acid anions and the unbuffered condition of streams and lakes at this time due to snowmelt runoff.

4.3. EXCEPTIONALLY LARGE SNOW YEARS

The vast majority of wet deposition occurs as snow during the winter every year in the Sierra Nevada. From 80 to 90% of annual water flux occurs as snow during the months December to April (Melack et al. 1996). Wet winters are infrequent in the Sierra

Nevada, but when they occur, an even greater percentage of annual water flux occurs as snow, as high as 95% or more. Thus a wet year is not one in which precipitation is higher year-round, but one in which snowfall is very high.

Kattelmann (1990) identifies five years in which especially large snowmelt floods occurred in this century: 1906, 1938, 1952, 1969, 1983. In each of these years, snowfall was greater than two times the average, and snowfall persisted into April or May. During snowmelt discharge in these years, stream channels were unable to accommodate the high flows, resulting in overbank flow, bed load movement and extensive channel alteration (Kattelmann 1990).

Dry winters were not uncommon in the Sierra Nevada during the decade of research sponsored by the CARB (1985 to 1994). At the Emerald Lake Watershed, for example, dry winters occurred 6 years out of 10 years, and only two years received near-average snowfall (1985 and 1991, Melack et al. 1996). Two wet winters occurred, in 1986 and 1993. Annual snow deposition during dry winters was typically 500 to 700 mm SWE in the high elevation watersheds studied by Melack et al. (1996). In contrast, wet winters delivered 1200 to 2000 mm SWE.

4.3.1. Wet winter solute concentrations

In wet winters, the concentrations of solutes in snow are not appreciably different than the concentrations in snow during dry or normal (averaage) winters (Table 1). For example, concentrations of H^+ in the snowpack of the Emerald Lake watershed in the year of greatest snowfall between 1985 and 1994 (4.6 $\mu eq \cdot L^{-1}$, 1986) were almost equal to concentrations in the year of least snowfall (4.7 $\mu eq \cdot L^{-1}$, 1990). Similarly, concentrations of sulfate in the Emerald Lake snowpack in 1993 (year of second greatest snowfall) were similar to concentrations of sulfate in 1990 (year of least snowfall). However, the quantity of snow is so much greater in wet winters than in dry or normal winters that annual loading values for individual solutes are much higher in wet winters. Table 2 compares the percent of loading of major solutes due to snow each year during the period 1990-1993. Very high percentages of total annual loadings for H^+ (92%), Cl^- (94%), nitrate (77%), and sulfate (84%) occured in snow in the high snowfall year of 1993 (2185 mm of SWE), as opposed to in 1990 (553 mm SWE) during which snow contributed 67% of H^+, 64% of Cl^-, 38% of nitrate and 41% of sulfate.

Although the snowpacks in high snow years contain the highest total masses of precipitation-delivered contaminants, the concentrations of acidulating solutes in meltwater are not necessarily higher during the snowmelt periods of wet winters. Melack et al. (1996) plot detailed time series plots for a suite of solutes measured in lake outflows during the snowmelt periods of water years 1990-1993 for seven high elevation lakes. From these plots, we estimated the lowest pH measured in the lake outflow streams of each lake in every year for which plots are available (Table 3). This time period included two very dry winters (1991 and 1992) and the exceptionally wet winter of 1993. An examination of the table shows that the pH of lake outflows is not lower during the melting of wet winter snowpacks than during the melting of dry winter snowpacks.

The potential impact of wet winters on stream chemistry, and thus on lake or stream biota, is not proportional to snowfall amount. VWM nitrate in Emerald Lake outflows for 1993 and 1994 (which were the years with the best data) were nearly identical (4.6 vs 4.8 μeqL^{-1}) despite the fact that almost 3 times as much snow fell in 1993. Similar VWM concentrations of ANC, Cl, sulfate, base cations and silica were also observed in 1993 and 1994. Time series plots of ANC during snowmelt are provided by Melack et al. (1996) for Emerald Lake outflow. During peak discharge in the snowmelt of 1993, ANC reached a minimum of ca. 10 $\mu eq.L^{-1}$, which is somewhat lower than the minimum ANC recorded during the snowmelt of 1994 (ca. 15 $\mu eq\ L^{-1}$). However, during snowmelt of 1991, the minimum ANC recorded was almost as low as in 1993 (ca. 12 $\mu eq\ L^{-1}$).

The minimum volume-weighted-mean lake pH values recorded in the 7 lakes of the lake comparison study are presented in Table 4. For every lake except Pear Lake the lowest recorded lake pH did not occur in a wet-winter year. The majority of the minimum pH values observed occurred in April or May. The minimum pH values were generally between 5.5 and 6.0. pH values below 5.5 were observed in Lost lake (5.46, April 1991) and in Pear Lake (5.29 , April 1993). For most of the lakes, the minimum observed VWM lake pH (Table 4) was nearly equivalent or somewhat higher than the minimum observed lake outflow pH (Table 3).

4.3.2. Stream discharge during winter months

Normally, stream discharge is minimal or absent during winter months in the high Sierra. However, during wet winters, when large snowstorms deposited much snow on ice-covered lakes, lake water displacement can produce streamflow in winter. Crystal

Lake, in the eastern Sierra, usually releases water to its outflow stream only during the snowmelt season. During the autumn and winter, the outlet stream is ordinarily dry, flowing only during large autumn storms before low temperature allows winter precipitation to accumulate (Melack et al. 1996). However, after very large snowfalls, lake water is displaced by depression of the ice cover and forced into the outlet of Crystal Lake. Winter stream flow has been recorded after large snowfalls in other headwater catchments, such as Emerald Lake and Lost Lake, in which stream discharge during the winter is negligible or absent (Melack et al. 1996). Although large snowfalls can occur in any year, they are more common during especially wet winters.

An extreme version of lake water displacement can take place when an avalanche deposits snow and ice onto an ice covered lake. Avalanche activity is higher in years of above average snowfall. Williams and Clow (1990) documented the effects of an avalanche in the Emerald Lake watershed on the lake and outlet stream morphology, winter stream flow, and on the overwintering embryonic and juvenile stages of a resident brook trout (*Salvelinus fontinalis*) population. The avalanche occurred after a series of snow storms deposited ca. 2 m of new wet snow in the catchment. Strong winds enabled snow to accumulate on steep cliffs above the lake that normally slough snow during storms. The avalanche deposited 3.7 m of debris over 850 m^2 of lake surface. Patterns of fracture in the lake ice indicated that the ice cover of the lake acted as plunger, remaining intact as it was forced downward at the southeast end of the lake and pushing lake water up onto the lake shores and out into the outlet stream. The avalanche caused the ice thickness of the lake to increase from 1.7 m to 6 m, the increase being a combination of snowfall, lake slush and avalanche debris. The net result of the avalanche was that 90,000 m^3 of unfrozen lake water (which was 70% of the unfrozen lake volume at that time) was pushed out of the lake and into the outlet stream.

The flood caused by the avalanche caused an increase in stage height in the outlet stream from the winter baseflow level of 20 cm to >89 cm for several hours. The return to baseflow conditions took ca. 26 hours. The resultant discharge rate (ca. 90,000 $m^3 \cdot d^{-1}$) was several-fold greater than the peak discharge rates observed later in the same year during maximum snowmelt runoff (ca. 30,000 $m^3 \cdot d^{-1}$, Williams & Clow 1990). The volume of water passing through the outlet stream removed 3.5 m of snow out of the 4 m wide stream channel for a distance of 94 m. Fractures were observed in the snow covering the stream for another 700 m downstream. The scouring force of the flood was sufficient to move logs up to 3.5 m in length and 60 cm in diameter. Sand and gravel were redistributed throughout the channel.

The observation of the avalanche occurred in a year in which a study of the population dynamics of a resident population of brook trout was underway (Cooper et al. 1988). Egg baskets (15 cm deep) and emergence traps had been placed in the lake and in the outlet stream during the 1985 fall spawning season for the fish. All of the baskets and traps were disturbed by the avalanche flood, and were either filled with sand and fine sediments or crushed. Uncaged nests suffered the same fate, or were washed out of the study area. The survival rate of the brook trout from hatching to emergence was only 2.5% after the flood, contrasting with a survival rate of ca. 90% prior to the avalanche.

Trout mortality has also been documented after winter floods due to rain-on-snow events. Erman et al. (1988) compared historical population densities (1952 to 1961) of Paiute sculpin and brook trout in Sagehen Creek to their densities after a winter flood in February 1982. Their censusing took place in August, 1982, and revealed decreased survival of YOY brook trout. YOY rainbow trout in Sagehen Creek were not reduced by the winter flood, presumably because they are spring spawners and thus the embryonic and juvenile stages were not present in the stream substrate at the time of the flood. Erman et al. (1988) emphasize that because snowbanks confine flow during winter floods (whether produced by rain-on-snow or avalanche displacement) they increase flood stage in the stream channel and thus the shear stress associated with a given discharge rate. In contrast, during snow melt later in the year, snow banks are reduced or absent, allowing overbank flow to accommodate some of the discharge volume. Therefore, although similar discharge rates may occur during winter floods and peak snowmelt discharge, the shear stress produced in the stream channel is lower later in the year, and thus has less potential to damage trout eggs or fry.

Kondolf et al. (1991) studied the consequences of snowmelt during a wet year (1986) and a dry year (1987) on the distribution of spawning-suitable substrate in seven high-gradient stream reaches in the eastern Sierra Nevada. During snowmelt runoff in 1986, stream channels were altered in ways that reduced the availablity of spawning gravel, replacing small diameter gravel with larger gravel and cobbles. In the snowmelt after the dry winter of 1987, smaller gravels were able to re-accumulate in the lee of boulders. Their study implies that precipitation extremes may have a greater effect on trout spawning habitat in high-gradient reaches than in lower altitude, lower gradient alluvial channels. In high gradient reaches, the accumulation of gravels is highly dependent on the stability of boulders, which move infrequently (once every 30-50 years), whereas in alluvial channels, the longitudinal profile is controlled primarily by particles which move every year or two. Scouring of gravel beds and channel modification occur only periodically in high gradient stream reaches. The unusually wet year of 1986 produced sufficient shear stress to scour gravel beds in the lee of stable boulders.

4.4. SUMMER RAIN

Non-winter precipitation is enriched with solutes in comparison to snow (see Table 6, Part 3 of this report). Ammonium and nitrate concentrations were found to be 8-9 times higher in non-winter precipitation than in winter snowfall in the Lake Comparison Study (Melack et al. 1996). Organic anions are also more abundant in rainfall than snow. Chloride, however, is only slightly higher in rainfall than in snowfall. As a consequence, most of the annual deposition of nitrogen, sulfate and organic acids occurs during non-winter periods. Non-winter precipitation is also more acidic than snowfall. When the 36 water years on record by Melack et al. (1996) are pooled, annual VWM pH the of non-winter precipitation ranged from 4.7 to 5.5, and of winter precipitation 5.3 to 5.6.

Although they are infrequent, large summer rain storms may produce sufficient runoff to alter the chemistry of high elevation lakes. In July of 1984, two relatively large storms occurred within one week in the Emerald Lake Watershed (Melack et al. 1991). The first storm delivered 4.5 cm of rain. Four days later a second storm delivered 1.1 cm of rain. The pH of the rain the the first storm was 4.3. No pH measurement was obtained during the second event. Lake chemistry was sampled the day following the second rain event. Thermal stratification was disrupted during the storm; the water column had mixed completely. Surface pH had decreased from 6.25 to 5.85 and ANC had dropped from 13 to 0 $\mu eq\ L^{-1}$. Over several weeks, thermal stratification was re-established and pH and ANC returned to prior levels. The rain storms also increased inorganic turbidity in the lake, which may have temporarily affected the growth of phytoplankton and benthic algae.

In the last week of September, 1994, two rain events occurred in the basin of the Marble Fork (a second order stream) of the Kaweah River (Emerald Lake Basin being a headwater catchment within the Marble Fork basin). During the increased discharge following the rainstorms, pH, ANC, sulfate, base cations declined precipitously in stream water, but nitrate increased. Peak nitrate measured in the Marble Fork was 55 $\mu eq\ L^{-1}$ (a level which occurred nearly 24 hours after the first rain). However, the highest nitrate level measured in the precipitation itself was < 30 $\mu eq\ L^{-1}$ (Melack et al. 1996). These values suggest that nitrate was liberated from the watershed from storm runoff - perhaps nitrate present in the soil, or on surfaces due to dry deposition. These storms occurred after a very dry summer (Melack et al. 1996). The effect of large rain in late summer (in terms of increasing solute concentration in stream flow) may be greater in a year receiving low summer precipitation. On this occasion, pH declined from ca. 7.5 before rain to ca. 6.5 after the second rainstorm. About one week after the second storm (Oct 2), a snowfall occurred, which upon melting increased stream discharge for over a week. A further decline in pH accompanied the discharge of the meltwater from this early autumn storm, from 6.5, reached after the initial rain events, to ca. 6.0. However, after neither rain nor snow did pH reach a value in stream water threatening to stream or lake biota (in general pH < 5.5 becomes threatening to aquatic biota, see Part 6 of this report for detail).

4.5. CONCLUSIONS

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 ≤ 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 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. Discharge rates sufficiently high to affect trout recruitment have been recorded (1) after lake water displacement by avalanche onto an ice-covered lake (Cooper et al. 1988), (2) during floods caused by rain-on-snow events (Erman et al. 1988), and (3) by snow melt discharge after wet winters (Kondolf et al. 1991). 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 (Kattelmann 1990). Although avalanches in general are more common in wet winters, the probability that an avalanche will strike an ice-covered lake is unknown to these authors, 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 (Dozier et al. 1989), and thus potentially cause short term depressions in pH and ANC, in addition to stream bed alterations.

REFERENCES

Berg N.H., Osterhuber R. and Bergman J. (1991) Rain-induced outflow from deep snowpacks in the central Sierra Nevada, California. Hydrol. Sci. J. 36, 611-629.

Bergman J.A. (1983) Hydrologic response of central Sierra Nevada snowpacks to rainfall. Proc. 51st Western Snow Conf. pp. 141-144.

Erman D.C., Andrews E.D. and Yoder-Williams M. (1988) Effects of winter floods on fishes in the Sierra Nevada. Can. J. Fish Res. Man. 45, 2195-2200.

Furniss M.J. (1997) Happy New Years: Yikes! Watershed Management Council Networker, Vol. 7, No. 1 , p. 23.

Harr, R.D. (1981) Some characteristics and consequences of snowmelt during rainfall in western Oregon. J. Hydrol. 53, 277-304.

Kattelmann R. (1987) Water release from a forested snowpack during rainfall. Forest Hydrology and Watershed Management, IAHS Pub. No. 167. pp. 265-272.

Kattelmann R. (1991) Peak flows from snowmelt runoff in the Sierra Nevada, USA. In: Bergmann H., H. Lang, W. Frey, D. Issler, and B. Salm (Eds.) Snow Hydrology and Forests in High Alpine Areas, IAHS Pub. No. 205. pp. 203-211.

Kattelmann R. (1992) Historical floods in the eastern Sierra Nevada. In: Hall C., Doyle-Jones V., and Widawski B. (Eds.) The History of Water in the Eastern Sierra Nevada, Owens Valley and White-Inyo Mountains. U.C. Press, Los Angeles.

Kattelmann R.C., Berg N.H. and B. McGurk. (1991) A history of rain-on-snow floods in the Sierra Nevada. Proc. 59th Western Snow Conference. pp. 138-141.

Kattelmann R. (1991) Floods in the high Sierra Nevada, California, USA. In: Sinniger R. and Monbaron M. (Eds.) Hydrology in Mountainous Regions II. IAHS Pub. No. 194. pp. 31-317.

Kondolf G.M., Cada G.F., Sale M.J. and T. Felando. (1991) Distribution and stability of potential salmonid spawning gravels in steep boulder-bed streams of the eastern Sierra Nevada. Trans. Am. Fish. Soc. 120, 177-186.

Melack J. M., S.K. Hamilton, K.W. Kratz and M.W. Williams. (1991) Ecological consequences of acidic deposition in the Sierra Nevada. pp. 47-53, In: DeVries J. and S. Conard (Eds.) Proc. Third Biennial Watershed Conference, California Water Resources Center, Report No. 75.

Williams M.W. and D.W. Clow (1990) Hydrologic and biologic consequences of an avalanche striking an ice-covered lake. Proc. 58th Western Snow Conference, Sacramento, CA. pp. 51-60.

Table 1. Volume-weighted mean concentrations of solutes in snow for the Emerald Lake Watershed, water years 1985 through 1994. Years are listed in descending order of the equivalent water depth of snowfall in mm. Data are from Melack et al. (1996).

Year	Snowfall mm	H^+ $\mu eq \cdot L^{-1}$	Cl^- $\mu eq \cdot L^{-1}$	NO_3^- $\mu eq \cdot L^{-1}$	SO_4^{2-} $\mu eq \cdot L^{-1}$
1986	2388	4.6	3.1	1.8	1.6
1993	2185	5.2	2.8	1.8	2.4
1985	1052	5.3	4.0	2.3	3.0
1991	916	3.3	1.2	1.7	1.2
1987	777	4.6	1.5	4.2	2.9
1994	765	2.8	1.6	2.4	1.3
1989	658	3.2	4.4	1.2	2.6
1988	630	3.8	1.4	2.1	1.2
1992	591	2.8	1.7	3.0	1.9
1990	553	4.7	2.1	2.6	2.6

Table 2. Percentage of annual solute loading contributed by snow (as opposed to non-winter precipitation). Values are averages for 15 sites*. Data adapted from Melack et al. (1996).

Winter	H^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	HCO_2^-	$CH_2CO_2^-$
1989-1990	67.2	42.0	63.6	38.4	41.4	38.1	21.5
1990-1991	65.4	44.8	68.7	44.7	44.3	35.4	40.0
1991-1992	57.7	40.2	64.7	39.4	36.4	20.0	23.9
1992-1993	92.0	78.1	93.8	77.1	83.7	82.4	60.2

*Sites included: Alpine Meadows, Crystal Lake, Eastern Brook Lake, Emerald Lake, Kaiser Pass, Lost Lake, Mineral King, Mammoth Mountain, Onion Valley, Pear lake, Ruby Lake, South Lake, Sonora Pass, Tioga Pass, Topaz Lake.

Table 3. Lowest pH values measured in lake outflows during snowmelt periods (April to September) from 1990 to 1993 for seven high altitude lakes in the Sierra Nevada. pH was estimated from time series plots in Melack et al. (1996).

Lake	Year	pH
Crystal Lake	1990	6.10
	1991	5.55
	1992	5.85
	1993	5.67
Emerald Lake	1990	5.90
	1991	5.60
	1992	6.10
	1993	5.75
	1994	6.00
Lost Lake	1990	5.75
	1991	5.40
	1992	5.60
	1993	5.60
Pear Lake	1990	5.80
	1991	5.60
	1992	5.85
	1993	5.60
Ruby Lake	1990	6.20
	1991	5.75
	1992	6.30
	1993	6.00
Spuller Lake	1990	5.95
	1991	5.70
	1992	6.20
	1993	5.65
Topaz Lake	1990	6.10
	1991	5.65
	1992	6.00
	1993	5.95

Table 4. Minimum volume-weighted-mean lake pH values recorded in seven high altitude lakes of the Sierra Nevada. Volume weighted mean lake pH was calculated from measurements at 4-5 depths, and use of hypographic curves for each lake (Melack et al. 1996). 1993 and 1986 were the years of highest snow deposition in the Sierra Nevada during the period 1985 to 1994 (see Table 1 for snowfall quantity). Study periods varied among lakes.* pH data were provided by J. Sickman.

Lake	overall minimum pH during study	minimum pH in years with wet winters 1993	1986
Crystal Lake	5.84 (7-Feb-92)	6.24 (13-Apr-93)	6.10 (14-May-86)
Emerald Lake	5.59 (3-Apr-89)	6.01 (30-Jul-93)	5.61 (25-May-86)
Lost Lake	5.46 (22-Apr-91)	5.75 (30-Mar-93)	NA
Pear Lake	5.29 (8-Apr-93)	5.29 (8-Apr-93)	5.78 (15-Apr-86)
Ruby Lake	5.80 (18-Apr-91)	6.43 (13-Apr-93))	6.08 (15-May-86)
Spuller Lake	5.80 (16-Jul-91)	6.32 (15-Apr-93)	NA
Topaz Lake	5.65 (10-Apr-91)	5.80 (8-Apr-93)	NA

*Study periods were as follows: Crystal Lake 9/85-1/94; Emerald Lake 8/82-1/95; Lost Lake 11/89-10/93; Pear Lake 9/85-10/93; Ruby Lake 9/85-9/94; Spuller Lake 10/89-10/93; Topaz Lake 10/86-10/93.

PART 5

USE OF MODELS TO PREDICT THE HYDROCHEMISTRY OF HIGH ELEVATION WATERSHEDS OF THE SIERRA NEVADA, CALIFORNIA

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5.1. INTRODUCTION

CARB contracts were awarded to several investigators to develop or refine models of hydrological and hydrochemical processes in high-Sierran watersheds. Two of the efforts applied relatively simple models to a group of 150-200 Sierra Nevada lakes, to predict the outcomes of various precipitation scenarios for Sierra Nevada lakes in general. The objectives of the modeling by Nishida and Schnoor, 1989, (Contract A732-036A) were to (1) evaluate the consumption or production rates of chemical species by Sierran watersheds assuming steady state conditions and using the results of synoptic lake surveys and a limited number of precipitation stations, and (2) predict the number of lakes that would be chronically acidified under theoretical loadings, without regard to episodic acidification from snowmelt or summer rain events. In contrast, Nikolaidis et al., 1989, (Contract A732-036B) predict the number of lakes that would lose ANC during snowmelt and large summer rain events using a Monte Carlo simulation technique. Other efforts have focused on modeling the responses of the Emerald Lake watershed to acid deposition. The most complex model developed with CARB support is the compartmentalized algorithm, dubbed the Alpine Hydrological Model (AHM), described by Sorooshian and Bales, 1992, (Contract A732-035). Hooper et al., 1990, (Contract A732-034) developed a much simpler watershed-acidification model, called the Alpine Lake Forecaster Model (ALF), based on the hydrology and mineral weathering rates in the Emerald Lake watershed. Hooper et al. (1993) tested the applicability of the ALF to four other watersheds Sierra Nevada (Contract A932-076). Herein, we summarize the structure and results of these models, including a description of how such models were used to predict effects of increased and decreased acid deposition to the Sierra Nevada.

5.2. STEADY STATE MODELS OF NISHIDA & SCHNOOR (1989)

The objectives of this project 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 to identify acid sensitive lakes under different loading scenarios. Secondly, the principal of charge balance was used to develop equations that predict changes in ANC. The models of Nishida and Schnoor do not consider the potential for episodic acidification during snowmelt and summer storm events. They use annual average precipitation chemistry and summer or fall lake chemistry to assess the potential for chronic acidification. The authors' description of the model and results of its application may be found in the following Final Report:

Nishida, A. and J. Schnoor (1989) Steady State Model to Determine Lake Resources at Risk to Acid Deposition in the Sierra Nevada, California. Final Report to the C.A.R.B., Contract No. A732-036A.

5.2.1. General Modeling Approach

The modeling efforts of Nishida and Schnoor were threefold. First, they developed equations, assuming steady state conditions, which calculated the consumption or production rate of chemical species for lakes given the following information for each lake:

(1) deposition flux (wet + dry)
(2) an evapoconcentration factor
(3) lake concentrations

Nishida and Schnoor coined the term "Reaction Term" or "RXN" as the parameter for this rate of consumption or production, and results of the model are presented as histograms of the values of RXN for the lakes included in their data base.

Secondly, they employed a graphical procedure called the "Henrikren's nomograph" to evaluate the sensitivity of the lakes in their data base to changes in sulfate loading. The hypothetical changes in loading that they investigated were twice (+100%) and one half (-50%) of existing lake sulfate.

Thirdly, they developed equations (again, assuming steady state conditions) to calculate the change in ANC (Δ ANC) that would result from changes in loadings of N and S species. This approach is referred to as the "Steady State Charge-Balance Model". Three different cases were evaluated, each resulting in a different equation to calculate Δ ANC: (1) changes in sulfate loading, (2) changes in ammonium-nitrate loadings, (3) changes in both sulfate and ammonium-nitrate loadings.

5.2.2. Data Base

All three of the modeling efforts employed a data base of information for 198 high elevation lakes in the Sierra Nevada, referred to by Nishida & Schnoor (1989) as the University of Iowa (UI) Database. In simple terms, the data base consisted of measured values or estimates of the following parameters for each lake:

1. concentration of chemical species in lake water
2. precipitation amount
3. concentration of chemical species in precipitation
4. evapoconcentration factor

Lake Chemistry. Data from a total of 198 lakes were combined into a single data base referred to by Nishida & Schnoor (1989) as the University of Iowa (UI) database. The majority of the data (102 lakes) was obtained from the Western Lake Survey of the U.S. E.P.A. (Landers et al. 1987). These data were combined with data for a subset of 28 lakes sampled in the McCleneghan et al. (1987) Statewide Survey of Aquatic Ecosystem Chemistry. Data for an additional 68 lakes from the study of Melack et al. (1985) completes the UI lake database.

The lake chemistry data used in the steady state model was obtained from the results of three synoptic surveys: 1) the Western Lake Survey, conducted by the U.S.E.P.A. (Landers et al. 1987); 2) the Statewide Survey of Aquatic Ecosystem Chemistry, conducted by the California Dept. of Fish and Game and the CARB (McCleneghan et al. 1985), and a survey conducted by the University of California, Santa Barbara (Melack et al. 1985). The lakes included in the Western Lake Survey and the Statewide Survey were sampled in the fall of 1985. The lakes in the survey of Melack et al. (1985) were sampled in the summers of 1981 and 1982. Only one of the three lake surveys used employed random sampling (Western Lake Survey). More detail about these three lake surveys can be found in Part 2 of this report.

Precipitation chemistry. Precipitation chemistry was obtained for seven of the wet deposition stations operated by the CARB in the Sierra Nevada (Mammoth, Quincy, Emerald Lake, Giant Forest, Soda Springs, S. Lake Tahoe, Yosemite - see Part 1 of this report for more detail on this network). The data used were the volume-weighted mean concentrations of solutes in wet deposition for the period 1984-1987. Elevation of these precipitation stations ranged from 1061 to 2926 m.

Dry deposition was added to wet precipitation in the following manner. Ionic concentrations from needle washings of lodgepole and western white pine from the Emerald Lake watershed were extrapolated assuming the dry deposition thus measured had occurred over a four month exposure during the dry summer months. This estimate of dry deposition rate assumes (1) dry deposition occurs principally during the summer (2) that dry deposition rates to forest canopy are the same as to other watershed surfaces, and (3) that dry deposition in the Emerald Lake watershed is representative of that in other regions of the Sierra Nevada. This procedure resulted in dry deposition flux for sulfate that was 6% of the total sulfate deposition and dry deposition fluxes for nitrate and ammonium that were 20% and 5% of total deposition, respectively.

Precipitation amount. In order to assign precipitation amounts to each lake in the data base, maps from the Department of Water Resources of yearly (1985) and percent normal precipitation were used. Lake locations were overlaid on the precipitation maps, and precipitation values assigned. The 1985 precipitation values were corrected to represent "normal" values (normal based on precipitation recorded from 1931-1980).

Evapoconcentration factors. Evapoconcentration factors (E) were calculated for each lake in the data base that came from the WLS as I/Q, with I equal to the annual precipitation amount, and Q as the annual discharge. Lakes which yielded a value for I/Q that was not between 1.0 and 3.5 were assigned a value of 2.0 (see below). The rest of the lakes in the data base (which were not in the WLS) were assigned an evapoconcentration factor of 2.0. This value was obtained as the average value of the following parameter calculated for the 102 lakes in the data base from the WLS:

$$E = [\text{sulfate}]_{\text{lake}} / [\text{sulfate}]_{\text{precip}}$$

5.2.3. Reactions (RXN) Model

In the Reactions Model, a parameter called the "reaction term" or RXN was calculated for each chemical species of interest for each lake using the following equation:

$$RXN = C_{lake} - E * C_{precip}$$

where C_{lake} equals the concentration of a species in the lake in $\mu eq\ L^{-1}$ (see details on data base), C_{precip} equals the concentration of a species in precipitation in $\mu eq\ L^{-1}$ (wet + dry). E, the evapoconcentration factor, is equal to I/Q, where I = annual precipitation amount in L/yr and Q = annual surface water runoff in L/yr.

The use of this equation assumes that all outflow from the watershed goes through the lake. A positive value for RXN indicates a net production of the chemical species by some process in the watershed at steady state, and a negative RXN indicates a net consumption of the chemical species by some process in the watershed.

Nishida and Schnoor (1989) applied the above equation to the University of Illinois database for the following chemical species: SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, ANC. Their results were presented as frequency histograms showing the number of lakes exhibiting ranges of RXN values, and are summarized below.

Sulfate: Approximately 30 lakes exhibited consumption of sulfate in the range of -10 to -5 $\mu eq\ L^{-1}$. The most frequent RXN term for sulfate was in the range -5 to 5 $\mu eq\ L^{-1}$.

Nitrate: All of the RXN terms for the database lakes were negative, the most common value in the range of -14 to -18 $\mu eq\ L^{-1}$. Thus, according to the model, all of the watersheds are net consumers of nitrate.

Ammonium: Results for ammonium were similar to the results for nitrate, in that almost all of the RXN terms were negative, and most common range for values was between -15 and -21 $\mu eq\ L^{-1}$.

Calcium, magnesium, and sodium: The results for these three species were similar, with most RXN terms near zero, with the remainder of the terms positive and declining rapidly with magnitude. Thus the model predicts near conservative behavior for these species in the watersheds of the database lakes, to modest net yields by the watershed.

Chloride: The majority of the RXN terms for chloride were between 0 and -8 $\mu eq\ L^{-1}$, indicating a small net consumption of chloride by the majority of database lakes.

ANC: A few ANC RXN terms (for ca. 20 lakes) were centered around 0, and all of the rest of the lakes had positive RXN terms, indicating net production of ANC by the watershed. The majority of the values were in the range of 30 to 90 μeq L^{-1}.

A secondary step within the reactions model was a calculation of watershed "removal fractions" for nitrate. This procedure first involved a calculation of a reaction rate (k) for nitrate for each lake as:

$$k = \frac{-Q * \dfrac{QC_{lake} - IC_{precip}}{Q}}{C_{lake} * V_{lake}}$$

where V_{lake} = lake volume.

Next, for a subset of the database lakes, the quantities C_{lake}/EC_{precip} were plotted against the quantity $k * r$, where r = residence time for the lake. Sufficient data were available to perform this for the 102 lakes of the Western Lake Survey. The ordinate value for each lake thus analyzed is the fraction remaining in the lake at steady state. 1 minus this quantity gives the *removal fraction* (R). Removal fractions for nitrate were used as components in the third modeling approach (steady state charge balance model).

RXN Model Weaknesses. The calculation of the evapoconcentration factor is 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. Melack et al. (1996) have shown that 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 Melack et al. (1996) in only 3 cases did sulfate behave even close to conservatively (net watershed flux within 10% of total loading).

5.2.4. Application of Henriksen's Nomograph

Henriksen's nomograph consists of a plot of lake sulfate versus the sum of calcium and magnesium for a suite of lakes. Two lines drawn on the graph divide the 2-dimensional space into zones of non-acidified lakes, acid sensitive lakes, and acidified lakes. The lines dividing the graph into zones of acid sensitivity were achieved empirically using data from 700 Norwegian lakes. The region in which the point for a given lake occurs in this graph indicates the extent to which the lake is acid sensitive. The technique is based upon the assumption that inputs of sulfate will be offset to varying degrees by mineral weathering and cation exchange in the watershed.

Wright and Henriksen (1983) defined a parameter, the F factor, as the change in base cation concentrations in lakewater due to a change in acid anion concentration in lakewater.

$$F = \frac{\Delta\,[Ca^{2+} + Mg^{2+}]}{\Delta\,[SO_4^{2-}]}$$

The F factor for a lake will vary depending on the extent to which a particular catchment is able to compensate for changes in acid loading through mineral weathering and ion exchange. The lower the F factor, the more acid sensitive the catchment is, because fewer cations are available for exchange with protons delivered in precipitation. Once an F factor is known for (or assigned to) a lake, hypothetical changes in sulfate concentrations can be used to predict the sum of Ca^{2+} and Mg^{2+}. Once the results are plotted, lakes can be assigned levels of acid sensitivity.

Use of the nomograph assumes that sulfate is the major anion associated with acid deposition. In Nishida & Schnoor's (1989) application of the nomograph, hypothetical doubling of lake sulfate and hypothetical halving of lake sulfate were investigated. F factors were used to calculate for each lake the changes in lake Ca and Mg expected from the changes in sulfate loading. In the absence of detailed geologic data for the database lakes, and assuming that granitic bedrock is characteristic of most of the Sierra Nevada watersheds, F-factors of 0.2, 0.4, and 0.6 were used when applying the database to Henriksen's nomograph. Nishida and Schnoor (1989) present the results graphically in the form of nomographs for each combination of loading rate and F factor.

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 $\mu eq\ L^{-1}$ 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. Because these flaws are serious, and the current conditions of the database lakes are not described by the nomograph, the rest of the results of the application of the nomograph will not be discussed in this report. We refer the reader to Nishida & Schnoor (1989) for further details on this portion of the steady state modeling effort.

5.2.5. Steady State Charge-Balance Model

The foundation of the steady state charge-balance model is the premise that changes in ANC can be determined by evaluating the net changes in the concentrations of cations and anions produced by changes in loadings, and by making some simplistic assumptions about watershed processes affecting the ions in question. Simply put,

$$\Delta\,[\mathrm{ANC}] = \Delta \sum[\text{base cations}] - \Delta \sum[\text{acid anions}]$$

The changes in ANC are intended to be the final values reached once sufficient reaction time in the watershed has elapsed, which is generally on the order of one hydraulic retention time. The model does not consider the potential for episodic acidification during snowmelt and summer storm events. It uses annual average precipitation chemistry and summer or fall lake chemistry to assess the potential for chronic acidification.

Equations were developed to predict Δ ANC under three loading scenarios. The first scenario hypothesized changes in loading rates of sulfuric acid. The second scenario hypothesized changes in the loading rates of ammonium nitrate. The third scenario hypothesized changes in the loading rates of both sulfate and ammonium nitrate. The magnitude of the changes were a doubling of loading (+100%) and a decrease by one half (-50%). Changes in loading rates were affected by changing the annual average concentrations of the chemical species in precipitation. The timing of delivery to the watershed was not considered. Wet and dry years were simulated by assigning the precipitation amount of 3.0 m yr^{-1} and 1.0 m yr^{-1}, respectively. Evapoconcentration factors of 2.5 and 1.5 were assigned for dry years and wet years, respectively.

In the first scenario, the change in cations is due to the change in base cation concentration caused by chemical weathering and ion exchange in the watershed. These geochemical processes were described by using the F-factor 0.4 (see Henriksen nomograph above) in the following equation:

$$\Delta\,[\mathrm{ANC}] = \Delta\,[\text{base cations in lake}] - \Delta[\text{sulfate in lake}] \quad \text{or,}$$

$$\Delta\,[\mathrm{ANC}] = \mathbf{0.4} * E * \Delta[\text{sulfate in precip}] - E * \Delta[\text{sulfate in precip}]$$

In the second scenario, the change in precipitation chemistry that is modeled is a change in the deposition of ammonium and nitrate. Several assumptions were involved in the formulation of the equation for this scenario. First it is assumed that the ratio of delivery of $NH_4/NO_3 = 1.1$. Second it is assumed that the ammonium delivered in precipitation is entirely consumed by plant uptake (thus no nitrification is assumed). Thirdly, the fraction of nitrate consumed by the watershed for each lake was either (1) the "nitrate removal fraction" (R) calculated as described above, or (2) the average value for the nitrate removal fractions calculated for the 102 lakes in the data base that came from the Western Lake Survey. Note that the biological uptake of ammonium has an acidifying effect (subtracts from ANC) and that the removal of nitrate (by either denitrification or plant uptake) has an alkalizing effect (adds to ANC). The equation for scenario #2 is as follows:

$$\Delta\,[\mathrm{ANC}] = E * \Delta[NH_4^+ \text{ in precip}] - E*R * \Delta[NO_3^- \text{ in precip}]$$

The third scenario involved changes in both the deposition rate of sulfate and ammonium nitrate. An assumption involved in generating the equation for scenario #3 is that the effects of sulfate and ammonium nitrate loading on ANC are additive. The equation for scenario #3 is as follows:

$$\Delta\,[\mathrm{ANC}] = (-0.6*E*\Delta[SO_4^{2-}]_{precip}) + (E*\Delta[NH_4^+]_{precip} - E*R*\Delta[NO_3^-]_{precip})$$

The results of this model were presented by Nishida & Schnoor (1989) as plots of the cumulative proportion of lakes in the data set versus predicted ANC. Lakes were considered to be acid sensitive if $0 < \mathrm{ANC} < 40\ \mu\mathrm{eq\ L^{-1}}$. Lakes were considered to be acidic if $\mathrm{ANC} < 0$. The initial number of sensitive lakes in the UI database according to this definition was 29%.

Scenario #1. A doubling of sulfate loading caused 35% of the lakes in the database to fall into the acid sensitive category, and 1% to become acidic. For a wet year, this changes to 33%. The halving of sulfate loading caused a decrease to 26% for a normal precipitation year. Varying the amount of precipitation had little effect on the results of the model for the case in which sulfate loading was halved.

Scenario #2. A doubling of amonium-nitrate loading (at 1:1 ratio) led to 31% acid sensitive lakes in a normal precipitation year, and 31% and 30% sensitive lakes in dry and wet years, respectively. In addition, in the dry year, 1% of the database lakes became acidic. A halving of ammonium nitrate loading led to 27% sensitive lakes in a normal precipitation year and 28% in a wet year.

Scenario #3. A doubling of both sulfate loading and ammonium-nitrate loading resulted in 37% acid sensitive lakes plus 3% acidic lakes. In a dry year, the model predicted 39% sensitive and 3% acidic lakes. In a wet year, 34% of the database lakes became acid sensitive. A halving of both sulfate loading and ammonium-nitrate loading resulted in 22% acid sensitive lakes in a normal precipitation year. Both wet and dry years resulted in 23% sensitive lakes.

<u>Validity of model assumptions.</u> Below are listed some of the important assumptions made by the authors of the steady state charge balance model, with comments as to their validity.

(1) The authors assumed that ammonium and nitrate were delivered in precipitation in a 1:1 ratio. This assumption is reasonable. Melack et al. (1996) provide the overall means for ammonium loading (52.1 eq $ha^{-1}yr^{-1}$) and nitrate loading (45.9 eq $ha^{-1}yr^{-1}$) obtained from 35 water years of field measurements in 8 Sierra Nevada catchments. The resulting loading ratio for NH_4^+:NO_3^- is 1.14.

(2) The authors estimate watershed removal fractions for nitrate using the estimated evapoconcentration factors, estimated precipitation loading, and lake concentrations of nitrate obtained from one-time synoptic sampling of lake chemistry in the fall or late summer. Although the authors do not provide the individual removal fractions thus obtained for the individual lakes of the database, they do state that the average removal rate was 93 ± 11%. Their methodology ignores that fact that much of the nitrate

delivered as snow passes through the watershed during the period 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 Melack et al. (1996) in the high Sierra, the overall average watershed retention rate for nitrate is 21.4 $eq \cdot ha^{-1} yr^{-1}$. Division by the average nitrate loading (45.9 $eq \cdot ha^{-1} yr^{-1}$) results in a removal fraction of 47%, much lower than the values used by Nishida and Schnoor.

(3) The authors assumed that the ammonium delivered to the watershed was entirely consumed by biological uptake. This assumption is reasonable. Using the overall average of ammonium retention in Melack et al. (1996) of 50.4 $eq \cdot ha^{-1} yr^{-1}$, and the ammonium loading average of 52.1$eq \cdot ha^{-1} yr^{-1}$, the removal fraction for ammonium is 97%.

5.3. EPISODIC EVENT MODEL (EEM) OF NIKOLAIDIS ET AL. (1989)

5.3.1. Modeling Approach

Nikolaidis et al. (1989) developed a simple mixing model 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 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. The model takes advantage of the fact that during the period of maxiumum discharge due to snowmelt, and in the late summer when large acidic storms occur periodically, the lakes are thermally stratified. For this reason, runoff can be modeled as mixing only within the top strata of the lake.

The EEM employed the Monte Carlo simulation technique to estimate the effect of episodic acidifying events on lake chemistry. In simple terms, the modeling approach can be described as follows:

(1) An equation was derived to predict lake alkalinity

(2) The equation contains some variables for which there are values for each lake in the database and other variables for which probability functions were developed using regional data.
(3) Hypothetical scenarios were chosen affecting the timing and/or chemistry of snowmelt and rainfall
(4) For each scenario, Monte Carlo simulations were performed for each lake. A simulation consisted of 250 model runs.
(5) For each run of the model, a value for each of the probabilistic variables was selected by random sampling of the normal or uniform distribution assigned to that variable. A model run consisted of repeated iterations of the equation on time steps of one day.
(6) The results for a given scenario consisted of the mean + SD for each lake, and were typically presented as cumulative distribution functions for the whole set of lakes with error estimates.

A description of the EEM and the results of its applications may be found in the following Final Report:

> Nikolaidis N., J. Schnoor and V. Nikolaidis (1989) Assessment of Episodic Acidification in the Sierra Nevada of California. Final Report to the C.A.R.B., Contract No. A732-036B.

Unless stated otherwise, the reference material for the following summary of the EEM is the above mentioned report.

5.3.2. Data Base

The database utilized by Nikolaidis et al. (1989) was the same database used by Nishida & Schnoor (1989) for the Steady State Models, i.e. the University of Iowa (UI) Database. As described above in the preceding section, this database was constructed by combining the results of three prior synoptic surveys of lake chemistry in the high Sierra Nevada - the Western Lake Survey of the US EPA, the statewide survey of McCleneghan et al. (1987), and the UCSB survey of Melack et al. (1985).

A limited number of parameters are needed for each lake to run the mixing model. These parameters are Q_C (critical flow), V_C (critical lake volume), L_{acy} (incoming lake acidity), and A_{LO} (initial lake alkalinity). Some of the variables used in the equations for these four parameters were available from the field surveys. In the case of other variables, separate values for individual lakes were not available. For this reason, the lakes of the database were assigned to one of three regions, North Sierra (36 lakes), Central Sierra (105 lakes), and South Sierra (28 lakes). Parameters describing the probability distributions (normal or uniform) for lake-unspecific variables were developed for the three regions using a variety of data sources.

5.3.3. Model Structure

The four parameters listed above were combined into the following equation to predict final lake alkalinity (A_L):

$$A_L = A_{LO} * e^{-Qc*t/Vc} - L_{acy} * [1-e^{-Qc*t/Vc}]$$

A brief description of the procedures used to estimate these parameters follows:

Critical Flow (Qc)

The critical flow is equal to the volume of water per unit time (eg. $m^3 \cdot d^{-1}$) that enters a lake from its watershed. In this model, critical flow measurements were not available for the individual lakes comprising the database.

Critical flow during snowmelt was estimated as:

$$Qc = (\text{Average Melt Rate})(\text{Watershed surface area})$$

Normal distribution parameters for melt rates (MR) for each of the three Sierra subregions were calculated using snow survey data from the California Cooperative Snow Survey (CCSS). Watershed areas were available for individual lakes in the lake database.

Critical flow during summer rainstorms was estimated as:

$$Qc = (\text{Precipitation event rate})(\text{Watershed surface area})$$

Data for precipitation event rates were obtained from precipitation records from 1983 to 1987 at eight meteorological stations in the Sierra Nevada (Grant Grove, Lodgepole, Gem Lake, Ellery Lake, Twin Lake, Tahoe City, Truckee Ranger and Sagehen). Rain events were included in the data set (1) if the number of days between rainfall events was greater than or equal to ten days, or (2) when the amount of rainfall was greater than or equal to 1 cm. Distribution parameters were then calculated for both (1) precipitation event rate (PPT, normal distribution) and (2) interval time between events (T, uniform distribution, see below for further use of these variables).

Critical lake volume (V_c)

Critical lake volume was calculated as (lake area) * (critical depth of stratification). Lake areas were available from the database. A range of values for depth of stratification was determined from published temperature profiles from 13 Sierra Nevada lakes. For early spring (relevant to snowmelt period) the critical depth ranged from 1.5 to 2.5 m. For late spring the critical depth ranged from 3 to 7.5 m. For summer, the critical depth was calculated as a percent of the maximum depth of the lake (D_{pc}). The database lakes from the Western Lake Survey were the only lakes for which maximum depth was provided. Thus the model simulations for summer rainstorms were performed only for these 101 lakes.

Incoming lake acidity (L_{acy})

During snowmelt, L_{acy} was estimated as:

$$L_{acy} = [H^+]_0 * [1 - (MR*t)/ d_s]^n$$

where $[H^+]_0$ = initial snowpack H^+ concentration in meq/m^3

MR = average snowmelt rate (described above)

d_s = initial snowpack water content in m

n = a constant indicating the proportion of snowpack acidity that is delivered per unit SWE (see "scenarios")

t = time step = 1 day

For summer rainstorms, L_{acy} was estimated as:

$$L_{acy} = [(H^+_{dry} * T)/ PPT] + H^+_{wet}$$

where: H^+_{dry} = H^+ in dry deposition in $meq \cdot m^{-2} d^{-1}$

T = interval between rain events, in days (described above)

PPT = precipitation event rate in $m \cdot d^{-1}$ (described above)

H^+_{wet} = H^+ concentration in rainfall in $meq \cdot m^{-3}$

$[H^+]_0$ was described by a normal distribution using data from CARB wet depositions stations. Each of the three regions (northern, central and southern Sierra) had its own normal distribution. Data on dry deposition of H^+ to lodgepole and western white pine was used to derive a uniform distribution for H^+_{dry}. H^+_{wet} was assigned to a normal distribution using all of the July and August data from wet deposition stations. Two variables were required to estimate d_s; snow depth and SWE. April 1 CCSS data was used to compute an average SWE for each of the three regions. Initial snow depth was assigned in each model run using a normal distribution based on 1930-1975 data collected at CCSS stations.

Initial lake alkalinity (A_{LO})

A value for this variable was obtained for each lake from the lake database (see above).

5.3.4. Variable Summary

Below are listed the variables that were used to run the EEM, and the categories to which they belonged. For the mean, SD, or ranges for the regionally based variables (those that were randomly sampled for model runs), the reader is referred to Nikolaidis et al. (1989).

Watershed specific variables:

Watershed Area

Lake Area

A_{LO} (initial lake ANC)

Randomly sampled variables:

Snowmelt simulations:

Normally distributed variables:

$[H^+]_0$

MR

ds

Uniformally distributed variables:

Dc

n

Rainstorm simulations:

Normally distributed variables:

PPT

H^+_{wet}

Uniformally distributed variables:

H^+_{dry}

T

D_{pc}

5.3.5. Scenarios and results

Snowmelt Scenarios. Different types of scenarios were examined for snowmelt and for summer rain events. Two scenarios affecting snowmelt were studied with the EEM. These scenarios involved the timing, rather than the chemistry, of snowmelt. The first scenario, called the "early-spring" scenario, assumes an early thaw (late March to early April), and occurs when the epilimnion is shallow. The second scenario, called the "late spring" scenario, assumes a late thaw (late May to early June), and occurs when the epilimnion is deeper. The authors explain this choice of scenarios as representing conditions under which snowmelt would have the most severe (early thaw) and the least severe (late thaw) consequences on lake chemistry, because the volume of lake water into which the runoff is mixing is lower early in the spring and greater later in the spring. The critical depth of stratification was chosen during model runs from separate uniform distributions for early spring and late spring, as described above. The model was iterated 20 times each run (representing 20 days of snowmelt). A Monte Carlo simulation of 250 runs was performed on each lake to give a probabilistic result for the lake. Below are summarized the average results from the whole database for each scenario.

Northern Sierra:

Initial ANC: ANC = $151 \pm 194\ \mu eq\ L^{-1}$

Early Thaw: ANC = $70 \pm 81\ \mu eq\ L^{-1}$

Late Thaw: ANC = $107 \pm 129\ \mu eq\ L^{-1}$

Central Sierra:

Initial ANC: ANC = $138 \pm 240\ \mu eq\ L^{-1}$

Early Thaw: ANC = $21 \pm 44\ \mu eq\ L^{-1}$

Late Thaw: ANC = $45 \pm 86\ \mu eq\ L^{-1}$

Southern Sierra:

Initial ANC: ANC = $60 \pm 38\ \mu eq\ L^{-1}$

Early Thaw: ANC = $16 \pm 17\ \mu eq\ L^{-1}$

Late Thaw: ANC = $30 \pm 22\ \mu eq\ L^{-1}$

Overall Database:

Annual average conditions: 29% of lakes have ANC < $40\ \mu eq\ L^{-1}$

After 20 days of early thaw: 79% of lakes have ANC < $40\ \mu eq\ L^{-1}$

After 20 days of late thaw: 65% of lakes have ANC < $40\ \mu eq\ L^{-1}$

Lakes of the Central Sierra region appear to be most at risk from early snowmelt according to the EEM, 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 an average WLR = 18. Lakes in the Southern Sierra Region had an average WLR = 14, and in the Northern Region, an average WLR = 8. Lakes with a high WLR are able to dilute the acidity of snowmelt runoff to a lesser extent than lakes with a low WLR.

Model Weaknesses. The model considers only the differences in the values of ANC resulting from the mixing of lake epilimnia with snowmelt runoff at different times of the year, but not the seasonal patterns of the aquatic organisms that may be a risk in the future from increased acidity in surface waters. The small differences in 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 (see Melack et al., 1993, for details). Although a late thaw may result in a less pronounced ANC depression after 20 days of snowmelt, 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, spring-spawning trout such as golden, cutthroat and rainbow trout) begin spawning during late May and early June. The eggs of these trout would be more susceptible to low pH episodes caused by a late thaw than an early thaw (see Part 6 of this report).

Summer Rainfall Scenarios. The scenarios investigated for the summer season hypothesized changes in the chemistry, rather than the timing, of rainfall. The EEM was run to predict the effects of halving (-50%), and doubling (+100%) current H^+ loadings in rainfall. (Note that the database for summertime model runs consisted of 101 lakes rather than 168, as explained above). Using the summertime database, 24% lakes with ANC < 40 μeq L^{-1} under current average annual conditions. At 0.5 X current loadings, the EEM predicted that 27% of database lakes would experience short term ANC < 40 μeq L^{-1}. At 2X current loadings, the EEM predicted that 29% of database lakes would experience short term ANC < 40 μeq L^{-1}.

5.4. HYDROCHEMICAL MODEL OF HOOPER ET AL. (1990)

Under the Kapiloff Acid Deposition Program, the USGS developed the Alpine Lake Forecaster Model to simulate the impact of snowmelt and rain-on-snow events on surface water quality in streams in the Emerald Lake Basin. The objective of this project was to develop a watershed-acidification model based on the hydrology and mineral weathering rates in the Emerald Lake watershed. The model was calibrated using data from water year 1986 to used to simulate stream chemistry in water year 1987. The authors recommended that additional work was needed to improve existing data bases for rates of mineral weathering and soil processes, for the timing and magnitude of snowmelt episodes, and to measure rates of sulfate adsorption by watershed soils. The model identified acidic rain storms during snowmelt as the period of greatest acidic stress to Emerald Lake. Details about the model are available in the following publication:

Hooper R., C. West and N. Peters. 1990. Assessing the Response of Emerald Lake, an Alpine Watershed in Sequoia National Park, California, to Acidification During Snowmelt Using a Simple Hydrochemical Model. Final Report, Contract A732-034.

Unless otherwise stated, the reference for the following summary is the above mentioned Final Report.

5.4.1. Model Structure

The hydrochemical model of Hooper et al. (1990), dubbed the Alpine Lake Forcaster (ALF), is a sparsely parameterized model, consisting of a hydrologic component and a chemical component. Data requirements to run the model are modest, and the authors avoid much of the need to use existing data to estimate or optimize values for model parameters. Model output consisted of plots of the concentrations of individual solutes over time during the snowmelt season. The output for various scenarios is compared to observations made in field studies of the Emerald Lake Watershed. At the time this model was developed there were field data from Emerald Lake for only water years 1986 and 1987. Field data from water year 1986 was used to design and callibrate the ALF. Observations from water year 1987 were used to validate the model.

Hydrological model.

The hydrologic model has two primary functions. First, it determines the quantity of discharge from a number of terrestrial subbasins to the lake. Secondly, it determines for each time step the volume of the lake epilimnion into which watershed runoff mixes. As a simplification, snowmelt was assumed to equal catchment discharge on a daily basis. This assumes not only that groundwater storage and lake volume are stable during the snowmelt season, but also that seepage and groundwater losses not accounted for by the gauged outflow stream are negligible. These assumptions are reasonable for Emerald Lake, but may be less so for other Sierra Nevada watersheds, as has been shown by Melack et al. (1996).

In order to simulate snowmelt from different parts of the watershed, the watershed was divided into 7 subbasins, each with a measured area, slope and aspect. The daily proportion of total snowmelt discharge arising from each subbasin was determined by an equation incorporating the potential solar radiation per unit area. Potential solar radiation per unit area was calculated using an algorithm using latitude, slope, aspect and day of year. Although in reality, each subbasin of the Emerald Lake watershed does not have equal snow covered area, for the purposes of the model, each subbasin was assigned a portion of the total seasonal discharge proportional to its area.

The volume of the epilimnion over the course of the snowmelt season was calculated in a straightforward manner using field data on ice depth, thermocline depth, and lake bathymetry. In the Emerald Lake watershed, measurements of ice depth and thermocline depth were available monthly or bi-weekly. Linear extrapolation was used to estimate values for dates between sampling events. Lake ice cover was assumed to displace epilimnetic water, decreasing the volume of the epilimnion.

Chemical model.

The chemical model calculates the equilibrium concentrations of key solutes in lake water and lake outflow based on primary mineral weathering and the dissolution of carbon dioxide. 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). Only a few watershed processes were described by the equations. Chemical weathering was described, but cation exchange processes in soils were not included. A simplified nitrogen cycle was described, including proportions of NH_4^+ and NO_3^- taken up by biota, and nitrification. Finally, in-lake carbonate buffering was described. More detail on these three compartments of the chemical model follows:

Weathering reaction

First, an equation was constructed that describes a greatly simplified stoichiometry for mineral weathering:

$$\text{Rock} + 1.2\,H^+ \Longrightarrow 1.2*[Na^+ + K^+ + Ca^{2+} + Mg^{2+}] + SiO_2(aq) + \text{secondary mineral.}$$

Secondly, the reaction constant (k) for the weathering process was described by the following weathering raio:

$$K = \frac{[Na^+ + K^+ + Ca^{2+} + Mg^{2+}]^{1.2}\,[SiO_2]^{1.2}}{[H^+]^{1.2}}$$

The parameter K was found by regressing the log of the weathering ratio on the 10-day average discharge (all from field measurements).

Nitrogen cycle

A very simple representation of the nitrogen cycle was included in the ALF by taking the following steps:

1. A date is chosen, before which the biota are inactive, and after which the biota are active.
2. When the biota are active, 100% of ammonium, and a fraction **v** of nitrate, are taken up by biota.
3. When the biota are inactive, 100% of ammonium is nitrified, and the resulting nitrate leaves the watershed. All other nitrate leaves the watershed also.
4. The appropriate quantities of H^+ are added or subtracted from the system depending on whether the N processes are alkalizing or acidifying.

Carbonate buffering system

The effects of carbonate equilibria on lake chemistry were incorporated using standard equations. The terrestrial portion of the watershed, and the lake when ice-free, were assumed to be at equilibrium with the atmosphere. P_{CO_2} in the lake under ice was not measured in the Emerald Lake Study, and thus became one of the few model parameters that was subject to callibration.

In summary, five parameters occur in the chemical model which must be callibrated.

1, 2. upper and lower bounds of the weathering reaction regression coefficients (K)
3. the fraction of nitrate retained by the biota
4. the date at which biota become active
5. the partial pressure of CO_2 in the lake under ice

5.4.2. Data Requirements

As stated before, the data requirements for the ALF are modest. Variables for which the model requires input are listed below:

Hydrologic variables:

- Daily discharge from lake
- Thermocline depth
- Ice thickness
- Temperature of inflows
- Temperature of epilimnion

Chemical variables:

- Mass of solutes at maximum snowpack accumulation
- Rainwater chemistry
- Initial lake water chemistry
- Initial chemical composition of ice on lake

5.4.3. Scenarios

Elution rates. The first scenarios that were investigated with the model 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. What was investigated in separate model runs was the percentage of the total mass of solutes in the snowpack at maximum accumulations that were eluted in the first 20% of snowmelt. Three percentages were used: 20% (referred to as uniform), 40%, and 80%.

The results of these runs were presented by the authors for chloride, nitrate, sulfate, alkalinity, H+, sum of base cations, and silica. The elution rate of 80/20 (signifying that 80% of a solute was lost from the snowpack in the first 20% of snowmelt) showed the best match for observed nitrate in water year 1986. However, the elution rate of 40/20 (signifying that 40% of a solute was lost from the snowpack in the first 20% of snowmelt) provided the best fit for observed nitrate in water year 1987. Sulfate was not well described by any of the elution rates tested. The model tended to underestimate both silica and sum of base cations in runoff during the two months of snowmelt (by ca. 5-10 $\mu eq\ L^{-1}$), and to overestimate them (by ca. 10 $\mu eq\ L^{-1}$) during the later months of snowmelt. Results for other solutes were ambiguous. The authors suggest that cation exchange, which was not modeled, may be elevating base cations, ANC, and silica concentrations during the early phases snowmelt above model predictions. The poor results for sulfate are not surprising, because the authors treat sulfate as a conservative ion, and the studies of Melack et al. (1996) show that sulfate rarely behaves conservatively in Sierra Nevada watersheds (see Part 3 of this report).

Hypothetical loadings. Two hypothetical loading scenarios were investigated with the ALF, a doubling of both sulfuric acid and ammonium nitrate deposition, and a halving of both sulfuric acid and ammonium nitrate. The authors conclude that minimum alkalinity will drop by only ca. 2-5 $\mu eq\ L^{-1}$ if loadings are doubled. However, the failure of the model to adequately describe nitrate and sulfate dynamics during the early part of snowmelt renders this prediction invalid. When simulations were run for "reactive" solutes (silica, base cations, hydrogen ion) only the uniform and the 40/20 elution rates were employed. Using current loadings, the model underpredicts nitrate by up to 5 $\mu eq\ L^{-1}$, and sulfate by ca. 2-5 $\mu eq\ L^{-1}$, when the uniform and 40/20 elution rates. If the model correctly simulated nitrate and sulfate concentrations, the predicted ANC would be lower under current or increased loadings.

5.5. APPLICATIONS OF THE ALPINE LAKE FORECASTER (ALF)

This project was an extension of the work carried out under Contract A932-075 (Hooper et al. 1990, see section 5.4 above). First, the Alpine Lake Forecaster (ALF) was applied to three more watersheds in the Sierra Nevada that were studied with CARB support. Secondly, a sensitivity analysis of the ALF was performed using streamwater chemistry data from Emerald Lake. Thirdly, principal components analysis (PCA) was used to explore the contributions of soil solutions to the chemical makeup of streamwater in the Emerald Lake watershed. The detailed description of this work may be found in the following publication:

> Hooper R.and J. Peters (1993) The Application of the Alpine Lake Forecaster (ALF) to Watersheds in the Sierra Nevada. Final Report to the CARB, Contract No. A932-076. (USGS, Water Resources Investigations Report 93-4030).

Unless otherwise stated, the reference for the following summary is the above mentioned Final Report.

5.5.1. Application of the ALF to four Sierran lakes.

As described in Part 5.4 of this report, the initial callibration and validation steps for the ALF were carried out using data from the Emerald Lake watershed. Subsequently, sufficient data were available from four other Sierra Nevada watersheds to test the suitability of the ALF to catchments other than the Emerald Lake watershed. For the purposes of this study, data from bi-monthly sampling of lake and outlet chemistry from October 1986 to June 1988 from Pear, Ruby, Topaz and Crystal Lake watersheds were used.

The suitability of the ALF to these four watersheds was investigated by applying the weathering reaction of the ALF to field data from the four catchments. As described in Part 5.4, the reaction constant (K) for the weathering process was described by the following weathering ratio:

$$K = \frac{[Na^{+} + K^{+} + Ca^{2+} + Mg^{2+}]^{1.2}\,[SiO_2]^{1.2}}{[H^{+}]^{1.2}}$$

The upper and lower limits for K for model simulations were obtained for Emerald lake by regressing the weathering ratio to the 10-day average discharge and taking values above and below the y-intercept of the relationship that bracket most of the scatter about the line. For this approach to be valid for other catchments, SBC must be related in a linear fashion to ANC and to silica. Therefore, individual regression models relating SBC to ANC and silica were developed for Ruby, Topaz and Crystal lakes. The results for each lake are briefly summarized below:

<u>Crystal Lake</u>

SBC in the lake was highly correlated with ANC, but not with silica. This suggested to the authors that in-lake processes other than mineral weathering were affecting silica concentration. When inlet chemistry was tested instead of lake chemistry, the results were more consistent with the weathering model of the ALF.

<u>Ruby Lake</u>

The results of the regressions for Ruby Lake showed a linear relationship between SBC and both ANC and silica. However, the strength of the correlations were highly dependent on the result of samples from 4 dates from one of the lake inlets in which SBC was relatively high.

Topaz Lake

The regression analyses for Topaz lake were consistent with the weathering formulation of the ALF, although the correlation between SBC and ANC was much stronger than between SBC and silica.

Pear Lake

The regression analyses for Pear Lake revealed that ANC is not controlled by SBC, rendering the ALF unsuitable to this catchment. The relationship between SBC and ANC was weak. The authors suggest that in-lake biological processes may be responsible for the failure of ANC to be linearly related to SBC in this catchment.

5.5.2. Sensitivity analysis

Sensitivity analysis for the ALF was restricted to the stoichiometric coefficient (c) of the generalized weathering reaction

$$\text{Rock} + \mathbf{c} * H^+ \Longrightarrow \mathbf{c} * [Na^+ + K^+ + Ca^{2+} + Mg^{2+}] + SiO_2(aq) + \text{secondary mineral.}$$

In the original formulation of the ALF, the coefficient was set equal to 1.2 (see section 5.4 above). This value (1.2) was obtained originally as the slope of the regression of SBC and silica for Emerald Lake sampled over a wide range of discharge rates during the snowmelt season. The authors interpret the coefficient as a reflection of the proportion of easily weathered minerals in the parent rock (the higher the coefficient, the higher the amounts of easily weathered minerals). In the sensitivity analysis, Hooper and Peters used the ALF to predict ANC in Emerald Lake from April to Sept., 1986, using 5 different values for c (1.2, 1.0, 0.5, 0.1, 0.0). The results were similar for c = 1.2 and c = 1.0. Predicted alkalinity was successively lower for lower values of c. The two lowest values of c (0.1 and 0.0) produced predictions of negative ANC (thus predicting lake acidification during snowmelt). The authors suggest that the potential sensitivity of a watershed can be analyzed by regressing SBC with silica over a wide range of discharge values. If the slope of the regression, *c*, is near 1.0 (as it was for Emerald Lake) the watershed should have about the same sensitivity to acidification as Emerald

Lake. If the resulting coefficient is less than 1.0, the watershed should be more susceptible to acidificiation.

5.5.3. Multivariate soil-solution mixing model

In order to determine whether or not soil solutions can be used as end members in a mixing model for stream chemistry in the Emerald Lake watershed, an evaluation of the chemical composition of soil solutions (from lysimeter samples) was carried out using mixing diagrams. One mixing diagram was constructed for every pairwise combination of the following nine solutes: ANC, chloride, nitrate, sulfate, calcium, magnesium, sodium, potassium and silica. On each mixing diagram, the median values and error bars for the 25th and 75th quartiles were plotted for each of the following six soil types from the Emerald Lake watershed: inlet meadow -shallow, inlet meadow-deep, bench meadow-shallow, bench meadow-deep, ridge-shallow, ridge-deep. Superimposed on these 2-dimensioanl plots were data points for samples of stream water from the inlet of Emerald Lake.

The purpose of the mixing diagrams was to determine which group of soil solutions were potential end members for a mixing model to describe stream chemistry. In order for a group of soil solutions to be qualifed, a triangle or quadrilateral drawn in the 2-dimensional space of mixing diagram (using the median values of three or four soil solutions, respectively, as vertices) must enclose the data points describing the stream water samples. In addition, these conditions must be met for all of the pairwise combinations of solutes under consideration. The result of this exercise for the Emerald Lake watershed data revealed:

(1) Soil solution chemistry is more variable than stream water chemistry
(2) The median concentrations of the soil solutions generally do not enclose the concentrations in the stream
(3) Calcium concentrations in soil solutions are generally too low to explain calcium concentrations in streamwater samples.
(4) Deep and shallow soil solutions differed little from eachother

Because the results of the mixing diagrams were ambiguous, and rather complicated (36 separate mixing diagrams), the authors tried another related approach. They performed principal components analysis (PCA) on the correlation matrix for the same suite of nine solutes and the same six soil solutions. The first two principal components explained 73% of the variation in the data (the authors did not list the loadings of the individual solutes in the principal components). The orthogonal projections of the 2 PCs for the six soil solutions were plotted in a 2-dimensional graph with the first and second principal components as the X and Y axes. The orthogonal projections of the stream water samples were superimposed on the same graph. The resulting diagram is essentially a mixing diagram using the first two principal components in the place of a pair of solutes. The diagram shows that the stream chemistry samples can be explained fairly well as a mixture of (1) bench site soil solution (shallow *or* deep) and (2) inlet soil solution *or* ridge site soil solution (although inlet-shallow appears to enclose the data better than ridge-deep or -shallow or inlet-deep).

5.5.4. Summary

The ALF was only reasonably suitable for three out of four of the watersheds tested (Crystal, Ruby and Topaz), and unsuitable for the fourth (Pear). The attempts to relate SBC and silica as a result of mineral weathering were less successful than the attempts to relate SBC and ANC. There are fewer watershed processes unrelated to weathering likely to affect silica once it enters surface waters, than there are that could alter ANC (such as N reactions, cation exchange, strong acid anion release from the snowpack). The soil solution mixing model shows some promise in elucidating the soil compartments most associated with stream chemistry - however, lysimeter data is not widely available from Sierra Nevada watersheds, so a wider application is not possible at this time.

5.6. UNIVERSITY OF ARIZONA ALPINE HYDROGEOCHEMICAL MODEL (AHM)

5.6.1. Purpose of the AHM

The Alpine Hydrochemical Model (AHM) was created by researchers at the University of Arizona, initially with support from the CARB. The development of the AHM constituted part of the CARB's Sierra Watershed Modeling Project. The AHM is a compartmental model, that was calibrated and tested using data from the intensive field study of the Emerald Lake Watershed from 1985 to 1987. The AHM computes integrated water and chemical balances for multiple terrestrial, stream, and lake subunits within a watershed, each of which can have a unique and variable snow-covered area (Wolford et al. 1996). Following Sorooshian et al. (1992), the primary objectives of the modeling effort were:

(1) To develop a process to identify the most important parameters, inputs, and chemical processes that influence lake/stream composition.

(2) To provide a better understanding of the physical interactions between the various subprocesses of the watershed.

(3) To propose a model structure of the Emerald Lake watershed that will facilitate future interpretation and prediction of the response to changes in atmospheric inputs to the watershed.

Publications describing the model and its application to Sierra Nevada catchments:

Ohte N. and R. Bales. 1994. Multi-parametric sensitivity analysis and optimatiztion of the Alpine Hydrochemical Model, Tech. Rep. 94-020, Dep. Hydrol. and Water Resourc., Univ. of Ariz., Tucson.

Sorooshian S., Bales R., Gupta V., Noppe P. and Wolford R. 1992. Development of Watershed Models for Emerald Lake Watershed in Sequoia National Park and for Other Lakes of the Sierra Nevada. Final Report to the C.A.R.B, Contract No. A732-035.

Wolford R., R. Bales and S. Sorooshian. 1996. Development of a hydrochemical model for seasonally snow-covered alpine watersheds: Application to Emerald Lake watershed, Sierra Nevada, California. Water Resources Res. 32: 1061-1074.

Wolford R. and R. Bales. 1996. Hydrochemical modeling of Emerald Lake Watershed, Sierra Nevada, California: Sensitivity of stream chemistry to changes in fluxes and model parameters. Limnol. Oceanogr. 41: 947-954.

5.6.2. Comparison between AHM and other similar watershed models.

Before the development of the AHM, there was only one other model of similar complexity and purpose, ILWAS, created by the Integrated Lake-Watershed Acidification Study in the Adirondack mountains of New York (Chen et al. 1983). The AHM differs from this earlier model in several ways that are intended to make the AHM more suitable to modeling high elevation watersheds with hydrological characteristics such as those found in the Sierra Nevada. ILWAS was not designed with snow-dominated mountainous regions in mind. As a result, it suffers from the following shortcomings (Sorooshian et al. 1992):

(1) Snowmelt is modeled on the basis of air temperature.

(2) A given watershed unit is presumed to be either 100% or 0% snow covered.

(3) Sublimation from the snowpack surface is improperly modeled, or optionally, ignored.

(4) Snowfall interception is not accounted for.

Design features which render the AHM more suitable to snow-dominated, moderate to high elevation watersheds include procedures or routines external to the model to determine such factors as potential snowmelt and potential sublimation from the snow-covered area (SCA). This allows the user to employ the methods for determining snowmelt, snow-covered area (SCA), sublimation, and potential evapotranspiration which are most appropriate to the region under consideration. SCA is an essential element in the AHM. On the basis of SCA, the AHM uses user-provided parameters for potential snowmelt, sublimation and evapotranspiration to predict actual values of the same hydrologic processes. Many other less significant computational differences exist between the AHM and ILWAS. For a more complete listing of these differences, the reader is referred to Sorooshian et al. (1992). In addition to the preceding characteristics, the AHM possesses the following unique attributes:

1. Ability to partition outputs from one subunit to several receiving subunits
2. Ability to automatically sequence subunit computations
3. Ability to treat stream segments as separate watershed subunits
4. Ability to handle any number of streams and lakes
5. Ability to extract streamflow to maintain a minimum soil-water content in riparian areas
6. Ability to automatically estimate subunit snowmelt rates, given snow-covered area and watershed outflow data

5.6.3. User Specified Input

There are two categories of information that the AHM requires as user input. First are a variety of parameters, or constants, related to snowpack hydrology, watershed subunit characteristics and soil chemistry and hydrology. Second are a suite of variables for which values must be provided on a daily basis (the computational time step of the AHM is one day). When field data are not available from the watershed on a daily basis (as is usually the case), linear extrapolation between values from intermittent dates can be used, or constants can be assigned to portions of the year, accounting for seasonal variation on a broad scale.

Daily input:

(1) Amounts and chemistry of rain or snow (at least the base elevation)
(2) Dry deposition values for chemical species for each subunit
(3) SCA for each subunit
(4) Potential evaporation and potential sublimation rates for each subunit on up to a daily basis (what are the input variables here--the model calculates "ET")
(5) A user defined fraction of NH_4^+ and NO_3^- to become organic-N (for each soil horizon)
(6) A user defined fraction of NH_4^+ to be nitrified to NO_3^- (for each soil horizon)

Daily input for lake subunits:

(1) Hypolimnion depth
(2) Lake ice thickness
(3) Lake snow covered area
(4) Volume of water reaching lake as baseflow
(5) Lake evaporation rate

The watershed parameters used by the AHM can be divided up into three categories. These are (following Sorooshian et al. 1992) (1) those that apply to the entire basin being modeled, (2) those applicable to an entire subunit of that basin, and (3) those applicable to a given soil layer. The parameters for each category are listed below.

Parameters applying to the entire watershed:

(1) Snowpack free water holding capacity, a constant
(2) Date when stream surfaces freeze
(3) Date when stream surfaces thaw
(4) Maximum water holding capacity of the snowpack (a fractional value of SWE)
(5) Date that lake subunits freeze and thaw

Parameters applying to an entire subunit:

(1) Number of soil (or talus) layers
(2) Subunit type (soil, rock, stream, lake, etc.)
(3) Subunit area
(4) Elevation
(5) Maximum surface infiltration rate
(6) Stream subunit (if there are more than one) that provides water for riparian recharge
(7) Method for adjusting the subunit's rainfall and snowfall relative to that observed at a base station (for example using subunit elevation relative to that of the base station).
(8) Initial values of snowpack water equivalence (SWE) and snowpack free water content
(9) Constants for maximum interception volume for rainfall on canopy, snowfall on canopy, and rainfall on litter, grass, or rock surface (and initial values)
(10) Amounts of chemical species in each subunit horizon
(11) Date upon which accelerated elution rates begin for chemical species in the melting snowpack
(12) Lake surface area and discharge as function of stage (for lake subunits)

Parameters applying to soil layers within a subunit

(1) Soil depth, bulk density and specific surface area for each soil horizon (in order to calculate total surface area of soil for weathering and other kinetic reactions)
(2) Saturated hydraulic conductivity
(3) Soil water content (a) at saturation, (b) when hydraulic conductivity approaches zero, and (c) at the vegetative wilting point (the latter for calculation of ET from soils).
(4) Initial chemical storage by species
(5) Mineral weathering reactions for each soil horizon

Wet and Dry Deposition. For some chosen base elevation, the user must provide data on the precipitation amount (rain or snow) and concentration of chemical species for each precipitation event. If subunits (talus vs rock vs lake, for example) receive different amounts of precipitation, this can be accounted for in the model by providing 1) a relative elevation for the subunit and (2) a parameter derived from snow surveys and estimates of snow-water equivalence (SWE) in the various subunits. Dry deposition for each chemical species is handled as a source term for each subunit.

Snowpack and Snowmelt. The model requires the input of daily estimates of both SCA and snowmelt rates. If these values are not available, one can provide the model with estimates of SCA and snowfall amounts for each subunit, and then the model will calculate snowmelt using the observed watershed outflow and the precipitation record. Chemical species are eluted out of the snowpack at the same rate. The rate used by the model is calculated using a two-part exponential function related to the fraction of snowpack melting. The parameters for this function have to be provided by the user, and can be estimated from field data or a separate solute transport model (described by Bales 1991).

The model requires a daily value for potential evapotranspiration (PET) and sublimation rates for each subunit, and lake evaporation rates. ET from soil subunits is calculated by the model in a different fashion depending on the water content of the soil: ET = PET when soils are water saturated; ET = 20% of PET when hydraulic conductivity approaches zero; and ET = zero when water content reaches or is below the vegetative wilting point.

Soil Properties. Soil subunits can be assigned one to several horizons. Water can only drain vertically from one horizon to the next, until it reaches the bottommost horizon, through which it drains horizontally. Surface runoff is produced by the model when water enters the soil subunit in excess of the soil's infiltration capacity. CO_2 concentrations may be adjusted as often as daily in individual soil horizons. At the user's discretion, some fraction of the soil water in the surface horizon may be allowed to mix with surface runoff. The model requires as input the total initial moles of each chemical species present in the soil solution compartments (horizons), and the total moles of exchange sites present in the soil horizon.

Riparian zones. The water content of soil in riparian zones is maintained at the average of the saturated water content and the water content when the hydraulic conductivity reaches zero.

Weathering reactions. Five weathering reactions were utilized by the model to transform snowpack concentrations into lake inflow stream concentrations. These were the weathering of (1) biotite, with vermiculite as a weathering product, (2) vermiculite, with kaolinite as a weathering product, (3) plagioclase, with kaolinite as a weathering product, (4) anorthite, with kaolinite as a weathering product, and (5) kaolinite, with gibbsite as a weathering product. The method employed to use weathering reactions to produce observed solute concentrations, and to account for resulting ANC generation, was essentially that of Garrels & MacKenzie (1967). Details of the stepwise computations applied to chemical input data are provided in Sorooshian et al. (1992).

Other kinetic reactions. Non-weathering kinetic reactions include nitrogen reactions and bacterial degradation of organic acid anions. These two groups of reactions are handled by the AHM in separate subroutines that are simplifications of the real biogeochemical processes. Simply put, a user-defined fraction of NH_4^+ and NO_3^- becomes organic-N, to similate biological uptake. A user-defined fraction of NH_4^+ is nitrified to NO_3^-. Denitrification is appararently unaccounted for by the AHM.

In addition to the data requirements described above, a record of outflow volume from the watershed can be utilized to optimize snowmelt rates, and make adjustments to hydrologic parameters, as described more fully by Wolford et al. (1996). In fact, in the case of Emerald Lake Watershed, detailed records of outflow discharge and stream and lake chemistry were used in a variety of manners to set values for snowpack and soil hydrologic factors, to adjust routing between subunits, to compute weathering rates for chemical species, and finally to compare model predicted and field measured values for lake, stream and soil solution chemistry as a test of the model. Of course, it cannot be expected that in every application of the AHM, such extensive field data will be available. Indeed, a requirement for the amounts and quality of data obtained from intensive study of the Emerald Lake Watershed would defeat in part the purpose of such a model.

5.6.4. Assumptions about watershed processes inherent in the AHM

Depending on the field data available in any particular study, the user of AHM may have to employ any number of assumptions about hydrologic or biogeochemical processes in a particular watershed in order to assign input values and estimate the 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. A non-exhaustive list follows:

1. Chemical species in rain or snow intercepted by canopy or litter remain well mixed in the water intercepted and move proportionately with the water out of the canopy or litter. Therefore, preferential uptake or adsorption, or leaching, of individual chemical species by litter or foliage is not accounted for by the AHM.
2. The rates at which all chemical species are released from the snowpack are be described by a single two-part exponential function. Apparently, preferential elution is not accounted for in the AHM. The ionic pulse is accounted for by an accelerated elution rate, which "kicks in" on an assigned date, however, the rates of individual chemical species do not differ from each other either before or after this date.
3. Denitrification is unaccounted for in the modeled nitrogen dynamics.
4. Inflows to and outflows from lake subunits are allowed from the epilimnion only.

5.6.5. Application of the AHM model to the Emerald Lake Watershed

Data from field studies of the Emerald Lake Watershed from 1985 to 1987 were used to test the AHM (Wolford et al. 1996). As described above, the AHM requires that the user specify and/or estimate a wide range of hydrological and chemical parameters. Parameter estimation for the ELW was done in two stages: (1) as many parameters as possible were estimated from process level field studies and measurements *other than those carried out in the stream or the lake*, and (2) remaining parameters were estimated from field data of lake and stream chemistry and discharge from water year 1987. The purpose of this procedure was to avoid using data from WY 86 to both estimate parameters *and* test the model. The intent of Wolford et al. (1996) was to test the suitability of the AHM by comparing model predictions of stream and lake chemistry (using required user input for water year 1986) with the field measurements of stream and lake chemistry obtained in WY 86. What follows is a non-exhaustive account of the steps undertaken to prepare the AHM for application to the Emerald Lake Watershed.

Straightforward estimates based on field measurements. Many user specified parameters were estimated in a straightforward fashion from field data obtained in the Emerald Lake Watershed study. These parameters included (1) amounts of exhangeable base cations, cation exchange capacity, exchangeable sulfate, (2) soil pH, (3) lake bathymetry, (4) starting values for amounts (moles) of chemical species in Emerald Lake, (5) seasonal hypolimnion depths (from lake temperature profiles), (6) in-lake ANC generation rates. In addition, annual moles of cations, silica and alkalinity produced by weathering were obtained by subtracting loadings (from wet and dry deposition) of chemical species from fluxes measured in streamflow.

Linear extrapolations of field data. In several cases, the AHM requires daily values for variables which can only reasonably be measured periodically in the field. In these cases, values for dates between actual field measurements were estimated by linear extrapolation. Examples include snow covered area, ice thickness on Emerald Lake

Simplifications. (1) Watershed subunits--for the case studies of ELW, the watershed was divided into five subunits: soil, talus, rock, stream and lake. This involved lumping a large number of noncontiguous parcels of each subunits type. Soils are generally < 1 m deep, and water drains rapidly through the layer (order of minutes). Soil and talus subunits were assigned 2 horizons-which differed not in chemical characteristics, but in rates of evapotranspiration. (2) The routing of water from the rock subunit was set so that soil and talus subunits each received one half of the rock runoff. No water passed directly into the stream except as surface runoff from the soil or talus subunits. (3) Although the AHM is capable of varying CO_2 in soils as frequently as daily, constant values for P_{CO2} were assigned to the soil and talus subunits for the whole year. This was done because field studies in the ELW revealed that spatial variation in measured P_{CO2} exceeded whole watershed temporal trends. (4) Water drainage to the stream from the soil and talus subunits were was allowed in the model run only after passage to the bottom horizon, however, field data suggested that late season rainfall in the ELW did not reach the bottom soil and talus horizons.

Parameters obtained from the literature. Despite the intensive nature of study of the ELW, many parameters and measurements required as input by the AHM were unavailable from research at Emerald Lake. In some cases, estimates for parameters were obtained from the literature or on the basis of similar studies. Examples are (1) constants for rainfall litter interception, canopy snowfall interception, and canopy rainfall interception, (2) constant for snowpack-free water (0.2 cm per cm of SWE), and the fraction thereof that drains from the snowpack each day (0.6), (3) percent of chemical species leaving the snowpack in the first 20% of meltwater (set to 70-80%), (4) particle surface area of soil (for weathering rate determinations)

Parameter estimation based on hydrologic data. Empirical procedures were used to estimate some parameters on the basis of stream chemical and discharge data. Snowmelt was optimized based on data for precipitation and snow covered area. In the application of AHM described by Wolford et al. (1996), only a few hydrologic parameters were adjusted. These included the maximum fraction of PET that occurs as ET, saturated hydraulic conductivity for the bottom soil horizon, the soil water content below which unsaturated flow ceases, between subunit flow routing, intial water contents of soil and talus. In addition, the fraction of NH_4^+ converted to organic nitrogen was estimated from the difference between input loadings and streamflow concentrations.

Special difficulties. Avalanches redistributed snow to a large degree during the wet winter of 1986. Because the avalanches caused snow to move from rock outcroppings to lower elevations (some areas of which belonged to the talus subunit), and because snow remained later in the season on talus than rock, an arbitrary decision was made by Wolford et al. (1996) to reduce snowfall by 20% on the rock subunit, and increase snowfall 48% on the talus subunit (note this change did not disturb water balance).

5.6.6. Results of applying AHM to ELW

Wolford et al. (1996) present the results of model runs as plots of predicted values for discharge, ANC, pH, Ca^{2+}, NO_3^-, Cl^-, SO_4^{2-} and Si over time versus the observed values from field studies. The model was successful in predicting discharge except that many small snowmelt events had to be similuated during the winter to maintain sufficient discharge to match field observations. The model overpredicted Cl^- and SO_4^{2-} in streamwater during September. This was believed to be caused by inadequate modeled water retention in soils or talus during late summer. The model also overpredicted ANC during late summer. Field data suggested that late season rainfall was not reaching lower soil or talus horizons. If true, soil solution ANC would be higher in lower soil horizons than higher soil horizons during late summer. The fact that AHM requires drainage from soil subunits to occur from lower soil horizons may have been a cause of excess modeled ANC in streamflow during the late season.

AHM predictions of lake epilimnion chemistry were reasonably successful. Modeled nitrate in lake water chemistry was too high for 1986, for which in-lake nitrate assimilation was set to zero. This problem was solved in the 1987 simulation by setting in-lake nitrate assimilation to 5.3% of excess nitrate (excess nitrate being nitrate over baseline stream concentrations). Underpredictions of epilimnetic pH were assumed to be caused by inadequate description of lake mixing during snowmelt.

Attempts to correct discrepancies between model predicted and observed patterns for chemical species are difficult because of the interdependencies of the processes controlling the behavior of individual species. Wolford et al. (1996) provide many examples of these difficulties. For example, the AHM underpredicted the amount of NO_3^- in streamflow. When the users tried to raise NO_3^- in streamflow by increasing the rate of chemical elution from the early season snowpack, they caused excess Cl^- to appear in the modeled streamflow. Alternatively, when they attempted to correct the nitrate concetrations by increasing the amount of NH_4^+ nitrified to NO_3^-, they generated acidity, which was already overpredicted in streamflow by the model.

Some discrepancies between predicted and observed behavior of chemical species is believed to be due to oversimplification of water routing between watershed subunits. The ways in which water was routed from rock surfaces into the stream had major consequences on predicted streamflow concentrations. For example, when even a samll faction of rock surface runoff was routed directly to the stream, runoff events predicted one-day spikes in streamflow concentrations that exaggerated actual watershed responses. Wolford et al. (1996) suggested two explanations for this difficulty. First, that dry deposition onto rock surfaces is insufficiently described, and secondly, that much of the runoff from rock surfaces probably mixes with soil solution, due to the highly interspersed nature of the parcels of rock and soil and talus in the actual watershed. Ultimately, the model was run with one half of the rock subunit runoff routed to the talus subunit, and the other half of the rock subunit runoff routed to the soil subunit.

When a model simulates as many biogeochemical and hydrological processes as does the AHM, a multitude of options exist to manipulate model parameters to match predicted values to observed values. Some of the choices made by Wolford et al. (1996) to fit model outcomes to field observations seem questionable. If the model underpredicts annual yield for a chemical species, then it seems most appropriate to alter a source term, or propose an unaccounted for source term. However, if modeled and observed annual yields are close, it may be appropriate to adjust the rates and parameters embedded in the model already that affect concentration of that chemical species. For example, Wolford et al. (1996) state that they suspected NO_3^- and K^+ released by decay over the winter was a missing *source term* contributing to the consistent underprediction of nitrate in streamflow. However, instead of adding in a new source term, they tried to compensate for this potential flaw by adjusting biologically unrelated rates and parameters (such as nitrification rates, and snowpack elution rates) without real-world justification for doing so.

5.6.7. Simulation of increased acid deposition using the AHM

Subsequent to model development and testing, the AHM was used to predict the effects of increased acid deposition and climate warming on the Emerald Lake Watershed (Wolford & Bales 1996). In this work, the model output used to describe current or "base" conditions was the output generated by the AHM using the data from the 1986 water year for Emerald Lake Watershed. The base case was then compared to the model output when the input data and parameters were altered to simulate (1) snowmelt rates at 130% of base case rates (2) a doubling of concentrations of all chemical species in rain and snow, (3) absence of an ionic pulse during snowmelt, (4) a change in the date at which accelerated elution from the snowpack begins, (5) cessation of ammonium and nitrate assimilation, (6) the direct routing of 20% of rock surface runoff into stream water. Only the first two of these perturbations were designed to simulate possible anthropogenic effects. The doubling of chemical species in wet precipitation was used to investigate model predictions under a scenario of increased loading of atmospheric pollutants. The 30% increase in snowmelt rates was used to investigate model predictions under a scenario of climate warming. The other perturbations were designed to test the sensitivity of the AHM to selected hydrologic and biogeochemical parameters. Results for simulated climate warming, and for changes in the timing and chemical elution rates of snowmelt are not discussed here, but may be found in Wolford & Bales (1996). The model outcomes for other pertubations are described briefly below.

Doubling the chemical loading in snow resulted in a more pronounced ionic pulse during early snowmelt. The ANC and pH of streamflow were reduced year round compared to the base case. The model predicted streamflow ANC very close to zero for several days during early snowmelt in 1986. Additionally, the summer rains of 1987 dropped streamflow ANC to near zero values with the scenario of doubled chemical loading rates.

Eliminating N assimilation resulted in predicted nitrate concentrations greatly above those of the base case in stream flow (base flow) during winter before snowmelt. However, the model prediction of nitrate concentrations in stream water for this scenario during peak discharge did not diverge noticeably from the normal case. When nitrate assimilation was eliminated, but ammonium assimilation allowed, the large summer rains of 1987 led to more severe drops in ANC and pH than in the base case. This is explained by Wolford & Bales (1996) as a result of the continuation of a H^+-producing process (NH_4^+ assimilation) in the absence of a counterbalancing H^+-consuming process (NO_3^- uptake).

As discussed above, the AHM had been parameterized such that one half of the rock subunit's runoff was routed to the talus subunit, and the other half of the rock subunit runoff was routed to the soil subunit. Wolford & Bales (1996) perturbed the initial settings of the AHM to allow 20% of surface runoff from the rock surface directly to the stream. The model predicted in this case sharp decreases in ANC, pH and Ca^{2+} with each rainfall or snowmelt event, and in NO_3^- except after high concentration fall rains . These severe downward spikes predicted by the model associated with days of high snowmelt runoff or rain were not observed in situ in the Emerald Lake Watershed.

5.6.8. Applicability of AHM to other catchments

AHM was designed with the intention of application to both watersheds with geologic, geographic, soil and hydrologic features similar to the Emerald Lake Watershed and watersheds with quite different hydrologic features. The difference in application lies in appropriate subdivision of the watershed into subunits, and the assignment of appropriate parameters. In order to apply the AHM to other high elevation watersheds in the Sierra Nevada (which will have more or less similar geologic, soil, and hydrologic features) the minimum data required, according to Wolford et al. (1995) are (1) values of the state variables used for calibration and evaluation, (2) a general soil survey, (3) 3-5 SCA 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) estimate of dry deposition, (7) base saturation of the soil, (8) values for sublimation and PET. If a complete record of winter precipitation (#5 above) is unavailable, Wolford et al. (1996) suggest that snow amount and composition at peak accumulation can substitute for the winter record (i.e. a spatial survey of snow depth, with snowpit data for SWE and chemical species).

Note that the routines for optimization of snowmelt in the AHM required field measurements of lake (catchment) outflow (in the case of ELW, daily) and SCA on at least several dates. Year-round gauging of discharge in outflow streams is not a trivial exercise. An optional modeling approach is under development, which would require as inputs (1) the spatial distribution of snow water equivalence at peak snow accumulation (requiring early spring snow survey), (2) time series measurements of solar radiation, temperature, wind velocity, and relative humidity (such as from a meteorological station), and (3) a digital elevation model.

5.7. SUMMARY AND CONCLUSIONS

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'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 with 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 Melack et al. (1996) in only 3 cases did sulfate behave even close to conservatively ("close to conservatively" indicating that net watershed flux of sulfate was within 10% of total loading).

The second objective was not met by Nishida and Schnoor's application of the 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 seriously 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 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. Values obtained by Melack et al. (1996) for overall average watershed retention rate and average nitrate loading produce a removal fraction for nitrate 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. Their simple mixing model, dubbed the EEM, 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. Specifically, 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. This assumption seriously damages the usefulness of the model.

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 lakes 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. The small differences in the chemistry of a late or early thaw may be less consequential to the biota of high altitude Sierran lakes 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 Forcaster (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). Although a crude simplification of chemical weathering was built into the model, cation exchange processes in soils were not included. A extremely simplified nitrogen cycle was described, specifying proportions of NH_4^+ and NO_3^- taken up by biota. The hydrological component of the ALF was, on the other hand, 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 detailed 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 extremely complex and densely parameterized. A myriad of hydrologic and biogeochemical processes were modeled, requiring a wide array of field data for callibration. Application of the AHM to the Emerald Lake Watershed proved to be extremely labor intensive and problematic, despite the availability of data from several years of intensive hydrochemical research. In fact, the ELW is the only Sierra Nevada watershed that has been, or is likely to be, studied in sufficient detail for application of the AHM. As stated above, 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 scenes or maps of snow convered area 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) estimate of dry deposition, (7) base saturation of the soil, (8) values for sublimation and PET.

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.

5.7. REFERENCES

Chen C., S. Gherini, R. Hudson and J. Dean (1983) The integrated lake-watershed acidification study. Volume 1. Model principles and application procedures, Report EA-3221, Research Project 1109-5, Tetra Tech Inc., Lafayette, California.

Garrels R. and F. MacKenzie (1967) Origin of the chemical compositions of some springs and lakes, in Equilibrium Concepts in Natural Water Systems, Vol. 67, Adv. Chem. Ser., 222-242.

Hooper R. and N. Peters (1992) Sensitivity Analysis of the Alpine Lake Forecaster (ALF), A Hydrochemical Simulation Model, and its Application to Four Alpine Watersheds in the Sierra Nevada, California. Final Report to the C.AR.B., Contract No. A932-076.

Hooper R., C. West and N. Peters (1990) Assessing the Response of Emerald Lake, an Alpine Watershed in Sequoia National Park, California, to Acidification During Snowmelt Using a Simple Hydrochemical Model. Final Report to the C.A.R.B., Contract No. A732-034.

Landers D., J. Eilers, D. Brakke, W. Overton, P. Kellar, M. Silverstein, R. Schonbrod, R. Crowe, R. Linthurst, J. Omernik, S. Teague and E. Meier (1987) Characteristics of lakes in the Western United States. Volume I. Population descriptions and physico-chemical relationships. EPA/600/3-86/054a. U.S. Environmental Protection Agency, Washington, D.C.

McCleneghan K., J Nelson, J. King and S. Baumgartner (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.

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 acidificiation. Final Report to the C.A.R.B., Contract No. A932-060.

Melack J., J. Stoddard and C. Ochs (1985) Major ion chemistry and sensitivity to acid precipitation of Sierra Nevada lakes. Water Resour. Res. 21: 27-32.

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 C.A.R.B., Contract No. A032-188.

Nikolaidis N., J. Schnoor and V. Nikolaidis (1989) Assessment of episodic acidification in the Sierra Nevada of California. Final Report to the C.AR.B., Contract No. A732-036B

Nishida A. and J. Schnoor (1989) Steady state model to determine lake resources at risk to acid deposition in the Sierra Nevada, California. Final Report to the C.AR.B., Contract No. A732-036A

Ohte N. and R. Bales (1994) Multi-parametric sensitivity analysis and optimization of the Alpine Hydrochemical Model, Tech. Rep. 94-020, Dep. Hydrol. and Water Resourc., Univ. of Ariz., Tucson.

Sorooshian S., R. Bales , V. Gupta, P. Noppe and R. Wolford (1992) Development of Watershed Models for Emerald Lake Watershed in Sequoia National Park and for Other Lakes of the Sierra Nevada. Final Report to the C.AR.B., Contract No. A732-035.

Wolford R., R. Bales and S. Sorooshian (1996) Development of a hydrochemical model for seasonally snow-covered alpine watersheds: Application to Emerald Lake watershed, Sierra Nevada, California. Water Res. Research 32: 1061-1074.

Wolford R. and R. Bales (1996) Hydrochemical modeling of Emerald Lake Watershed, Sierra Nevada, California: Sensitivity of stream chemistry to changes in fluxes and model parameters. Limnol. Oceanogr. 41: 947-954.

Wright R. and A. Henriksen (1983) Restoration of Norwegian lakes by reduction in sulphur deposition. Nature 305: 422-424.

PART 6

ANALYSIS OF THE POTENTIAL USE OF BIO-INDICATORS IN THE SIERRA NEVADA

PART 6

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6.1. INTRODUCTION

Considerable information regarding the vulnerability of Sierran aquatic biota to acid deposition resulted from research carried out under a number of CARB projects supervised by John Melack, Scott Cooper, Tom Jenkins and Dave Bradford (Contracts A3-096-32, A5-139-32, A6-184-32, A932-139, A932-138, A932-060). Data were generated by a combination of in situ lake and stream experiments, laboratory exposure-response studies, and survey and monitoring data. These data will be coalesced and summarized in order to answer the following questions: (1) which vertebrate and invertebrate species are potential indicators of acidification, based either on their vulnerability *or* resistance to low pH, (2) what are the pH thresholds of sensitive species, (3) are there any lakes whose biota appear to have been influenced by acidity, (4) how does the timing of episodic acidification in Sierra Nevada lakes affect the use of vertebrates and invertebrates as bio-indicators.

6.2. FINAL REPORTS TO THE C.A.R.B. CONTRIBUTING INFORMATION ABOUT SIERRA NEVADA BIOTA

Bradford D. and Gordon M. (1992) Aquatic Amphibians in the Sierra Nevada: Current Status and Potential Effects of Acid Deposition on Populations. **Final Report No. A932-139.**

Bradford D., Cooper S., Brown A., Jenkins T., Kratz K. and Sarnelle O. (1994) Distribution of Aquatic Animals Relative to Naturally Acidic Waters in the Sierra Nevada. **Final Report No. A132-173.**

Cooper S., Kratz K., Holmes R. and Melack J. (1988) An Investigation of the Biota in the Emerald Lake System and Stream Channel Experiments. **Final Report No. A5-139-32.**

Jenkins T., Knapp R., Kratz K. and Cooper S. (1993) Aquatic Biota in the Sierra Nevada: Current Status and Potential Effects of Acid Deposition on Populations. **Final Report No. A932-138.**

Melack J., Cooper S., Holmes R., Sickman J., Kratz K., Hopkins P., Hardenbergh H., Thieme M. and Meeker L. (1987) Chemical and Biological Survey of Lakes and Streams Located in the Emerald Lake Watershed, Sequoia National Park. **Final Report No. A3-096-32.**

Melack J., Cooper S., Jenkins T., Barmuta L., Hamilton S., Kratz K., Sickman J. and Soiseth C. (1989) Biological and Chemical Characteristics of Emerald Lake and Streams and Their Responses to Acidic Deposition. **Final Report No. A6-184-32.**

Melack J., Sickman J., Setaro F., and Engle D. (1993) Long-term Studies of Lakes and Watersheds in the Sierra Nevada, Patterns and Processes of Surface-Water Acidification. **Final Report No. A932-060**.

6.3. JOURNAL PUBLICATIONS RELEVANT TO THE USE OF BIO-INDICATORS IN THE SIERRA NEVADA

Barmuta L.A., Cooper S.D., Hamilton S.K., Kratz K.W. and Melack J.M. (1990) Responses of zooplankton and zoobenthos to experimental acidification in a high-elevation lake (Sierra Nevada, California, U.S.A.) Freshw. Biol. 23: 571-586.

Bradford D.F. (1983) Winterkill, oxygen relations, and energy metabolism of a submerged dormant amphibian, *Rana muscosa*. Ecology 64: 1171-1183.

Bradford D.F. (1988) Allotopic distribution of native frogs and introduced fishes in high Sierra Nevada lakes of California: Implication of the negative effect of fish introductions. Copeia 3: 775-778.

Bradford D.F., Gordon M.S., Johnson D.F., Andrews R.D., and Jennings W.B. (1994) Acidic deposition as an unlikely cause for amphibian population declines in the Sierra Nevada, California. Biol. Conserv. 69: 155-161.

Bradford D.F., Swanson C. and Gordon M.S. (1991) Acidic deposition in the Sierra Nevada - Effects of low pH and inorganic aluminum on two declining species of amphibians. Am. Zool. 31: 114A.

Bradford D.F., Swanson C. and Gordon M.S. (1992) Effects of low pH and aluminum on two declining species of amphibians in the Sierra Nevada, California. J. Herpet. 26: 369-377.

Engle D. and Melack J.M. (1995) Zooplankton of high elevation lakes of the Sierra Nevada, California; potential effects of chronic and episodic acidification. Archiv Hydrob. 133: 1-21.

Erman D, E. Andrews and M. Yoder-Williams (1988) Effects of winter floods on fishes in the Sierra Nevada. Can. J. Fish. Res. Man. 45: 2195-2200.

Hopkins P.S., K. Kratz and S. Cooper (1989) Effects of an experimental acid pulse on invertebrates in a high altitude Sierra Nevada stream. Hydrobiol. 171: 45-58.

Jennings W., D. Bradford and D. Johnson (1992) Dependence of the garter snake *Thamnophis elegans* on amphibians in the Sierra Nevada of California J. Herpet. 26: 503-505.

Kondolf G., G. Cada, M. Sale and T. Felando (1991) Distribution and stability of potential salmonid spawning gravels in steep boulder-bed streams of the eastern Sierra Nevada. Trans. Am. Fish. Soc. 120: 177-186.

Kratz K., S. Cooper and J. Melack (1994) Effects of single and repeated experimental acid pulses on invertebrates in a high altitude Sierra Nevada stream. Freshw. Biol. 32: 161-183.

Soiseth C.R. (1992) The pH and acid neutralizing capacity of ponds containing *Pseudacris regilla* larvae in an alpine basin of the Sierra Nevada. Calif. Fish. Game 78: 11-19.

6.4. INFORMATION PRODUCED UNDER C.A.R.B. CONTRACTS ADDRESSING THE POTENTIAL USE OF BIOINDICATORS IN THE SIERRA NEVADA

6.4.1. Types of biological studies carried out with CARB support.

1. 1985 stream channel experiments in the Emerald Lake Watershed (Contract A3-096-32).
2. 1986 stream channel experiments in the Emerald Lake Watershed (Contract A5-139-32).
3. 1985 bag experiments in Emerald Lake (Contract A3-096-32).
4. 1987 bag experiments in Emerald Lake (Contract A6-184-32).
5. Long-term monitoring of the zooplankton of seven Sierran lakes (Contract A932-060).
6. Survey of amphibian habitats in 235 15-km^2 areas above 2440 m, conducted in the summers of 1990 and 1991 (Contract A132-173).
7. Dose response tests with acid and aluminum for *Rana muscosa*, *Bufo canoris*, *Pseudacris regilla*, *Ambystoma macrodactylum* (Contract A932-139).
8. Survey of the biota of naturally acidic lakes in the Bench Lake-Mt. Pinchot area (Contract A132-173).
9. Behavioral trout study in the Emerald Lake region (Contract A4-122-32).
10. Survey of 30 randomly chosen lakes for fish inventory and acid-dose response experiment with golden trout eggs in artificial stream channels (Contract A932-138).

6.4.2. Experimental Studies

1985 Experimental Stream Channels in Sequoia National Park (Contract A3-096-32)

In August, 1985, a pilot test of experimental stream channels was conducted on the Marble Fork of the Kaweah River near Emerald Lake in Sequoia National Park. A six hour acid addition was carried out on August 7 between 11:30 to 17:30 bringing pH down to ca. 5.0 in treatment channels. The timing of the treatment was chosen to simulate an afternoon rain event, which is the major form of precipitation in summer months. Stream benthos inside the experimental channels was sampled 1 day before and 2 days after treatment. In this experiment, incoming drift from upstream was not blocked at the entrance of the stream channels. This design feature was assumed responsible for the failure to detect changes in benthic density after acidification. Much of the drift measured in the stream channels originated from insects coming into the channels during the treatment that proceeded to drift through, either live or dead. The results of this experiment were confounded somewhat by the rapid drying of the Kaweah River during the experiment, which dropped discharge over the course of the experiment. The drift rates of some taxa (e.g. simuliids) increased in the afternoon of the third day, when stream discharge fell to very low levels. This may represent drift induced by the stress of rapidly decreasing discharge.

The results of this study are located in the following publications:

Melack J., Cooper S., Holmes R., Sickman J., Kratz K., Hopkins P., Hardenbergh H., Thieme M. and Meeker L. (1987) Chemical and Biological Survey of Lakes and Streams Located in the Emerald Lake Watershed, Sequoia National Park. Final Report to the C.A.R.B., Contract No. A3-096-32.

Hopkins P.S., Kratz K.W. and Cooper S.D. (1989) Effects of an experimental acid pulse on invertebrates in a high altitude Sierra Nevada stream. Hydrobiologia 171, 45-58.

1986 Experimental Stream Channels in Sequoia National Park (Contract A5-139-32)

In the summer of 1986, four experiments were conducted using a set of 12 artificial stream channels fed with water from the Marble Fork of the Kaweah River. In every case, the experiment consisted of a single 8 h acid addition between 10:00 and 18:00, done in order to simulate afternoon rain. Treatment levels were control (pH 6.5 - 6.7), intermediate (pH 5.1-5.2), and low (pH 4.4-4.6), with 4 channels assigned to each treatment. Experiments 1-4 took place on 4-8 Aug., 19-22 Aug., 3-6 Sept., and 16-19 Sept., respectively. A period of pre-colonization by invertebrates from the Marble Fork was allowed in the stream channels preceding experiments 1-3. During the experiments, immigration from upstream was prevented by blocking drift at the head of the experimental channels. Benthos in the channels were sampled 24 h before, and 40 h and 2 weeks after the treatments. Drift nets at the bottom of the channels were sampled four times pre-treatment, two times during treatment, and six times after treatment. For 3 taxa (*Baetis, Epeorus* and chironomids), live vs. dead drift were differentiated. High discharge due to rain caused difficulties in maintaining target pHs during experiment 2, so the results are not reported. In the stream channel experiments, the common taxa were chironomids, *Baetis, Paraleptophlebia, Epeorus, Isoperla, Rhyacophila, Hydroporus*, mites and oligochaetes.

The results of this study are located in the following publications:

Cooper S., Kratz K., Holmes R. and Melack J. (1988) An Investigation of the Biota in the Emerald Lake System and Stream Channel Experiments. Final Report to the C.A.R.B., Contract No. A5-139-32.

Kratz K.W., Cooper S.D. and Melack J.M. (1994) Effects of single and repeated experimental acid pulses on invertebrates in a high altitude Sierra Nevada stream. Freshw. Biol. 32, 161-183.

1985 Bag Experiments in Emerald Lake (Contract A3-096-32)

Field experiments were conducted during the summer of 1985 in large bags suspended in the middle of Emerald Lake. Bags were constructed of 4 mil polyethylene, with a 1 m diameter, and were suspended from a floating wooden platform. Bags were tied off at the bottom in Experiments 1-3. In Experiment 4, half of the bags were inserted into the sediment. Responses by phytoplankton, zooplankton and zoobenthos were monitored by intermittent sampling inside the bags. Design features of the experiments were as follows:

Exp. 1: Dates: June 30-July 17 Length: 17 days

Treatments: (a) sulfuric + nitric acid, pH 4.2
(b) sulfuric + nitric acid, pH 4.8
(c) controls

Sample times: immed. after, 8 d, and 17 d

Exp. 2: Dates: July 18-26 Length: 8 days

Treatments: (a) sulfuric + nitric acid, pH 5.2
(b) sulfuric + nitric acid, pH 4.2
(c) controls

Sample times: before, and 8 d.

Exp. 3: Dates: July 28-Sept 2 Length: 35 days

Treatments: (a) sulfuric + nitric, pH 5.3
(b) HCl, pH 5.2
(c) HCl, pH 5.8
(d) K-phosphate
(e) K-nitrate + Na-sulfate
(f) sulfuric + nitric acid + K-phosphate, pH 5.6
(g) controls

Sample times: before, 1, 9, 23, and 35 d

Exp. 4: Dates: Sept. 9 - Oct. 3 Length: 24 days

Treatments: (a) pH 5.6, no sediment
(b) control, no sediment
(c) pH 5.7, with sediment
(d) control, with sediment

Sample times: before, 11, and 24 d

The zooplankton of Emerald Lake were dominated by *Diaptomus signicauda, Daphnia rosea, Holopedium gibberum, Bosmina longirostris, Keratella cochlearis, Polyarthra vulgaris, Conochilus unicornis*. In Experiment 1, *Keratella, Conochilus*, and

Diaptomus were less abundant in acidified bags than in controls. The response of *Diaptomus* was immediate. The response of the other species occurred after 1 week. In Experiment 2, *Conochilus, Daphnia*, and *Diaptomus* were very sensitive to pH 5.2, *Holopedium* and *Bosmina* were reduced at pH < 5, and *Keratella* and *Polyarthra* were more abundant in the pH ≈ 5 treatment, than either in controls or in the pH 4 treatment. In Experiment 3, *Daphnia*, *Conochilus*, and *Diaptomus* were more abundant when pH > 5.5. *Keratella* was less abundant when pH > 5.5.

Overall conclusions from the 1985 bag experiments were as follows: *Diaptomus*, *Daphnia*, *Conochilus* are are sensitive to acid addition. *Diaptomus* and *Daphnia* declined precipitously at pH 5.5 and below. *Bosmina* and *Keratella* were favored when pH was between 5.1 and 5.5, but were lower in abundance both in controls and below pH 5.0. *Holopedium* was sporadically favored at intermediate acid additions (pH > 5.1), but at pH < 5.0 was reduced to less than 25% of its abundance in the controls. *Polyarthra* also responded variably, but was more acid tolerant and remained abundant even at the lowest pHs (4.0).

Further results of this study are located in the following publication:

Melack J., Cooper S., Holmes R., Sickman J., Kratz K., Hopkins P., Hardenbergh H., Thieme M. and Meeker L. (1987) Chemical and Biological Survey of Lakes and Streams Located in the Emerald Lake Watershed, Sequoia National Park. Final Report to the C.A.R.B., Contract No. A3-096-32.

1987 Emerald Lake Bag Experiments (Contract A6-184-32)

This experiment took place between 5-Aug and 9-Sept-1987, lasting 35 days. Enclosures were bags constructed in the same way, and suspended in the lake in the same manner described above. As in the 1985 bag experiments, responses by phytoplankton, zooplankton and zoobenthos were monitored by intermittent sampling inside the bags. Treatments were as follows: Control, pH 5.8, pH 5.4, pH 5.3, pH 5.0, pH 4.7.

The results of this study are located in the following publications:

Melack J., Cooper S., Jenkins T., Barmuta L., Hamilton S., Kratz K., Sickman J. and Soiseth C. (1989) Biological and Chemical Characteristics of Emerald Lake and Streams and Their Responses to Acidic Deposition. Final Report to the C.A.R.B., Contract No. A6-184-32.

Barmuta L.A., Cooper S.D., Hamilton S.K., Kratz K.W. and Melack J.M. (1990) Responses of zooplankton and zoobenthos to experimental acidification in a high-elevation lake (Sierra Nevada, California, U.S.A.) Freshw. Biol. 23, 571-586.

Acid and aluminum dose response experiments with *Rana muscosa* and *Bufo canorus* (Contract A932-139)

Embryos and hatchlings of *Rana muscosa* and *Bufo canorus* were kept for 7 days in reconstituted soft water (RSW) at pH levels 4.0, 4.25, 4.5, 4.75, 5.5 and 6.0, and subsequently for a post-treatment period of 4 to 14 days in RSW at pH 6.0. Aluminum was added to treatments of pH 5.0, 5.5, and 6.0. Aluminum added was in the form of inorganic monomeric aluminum, and treatment levels of aluminum were 39, 70, and 80 $\mu g\ L^{-1}$ in the pH 5.0, 5.5, and 6.0 treatments, respectively. Survival endpoints were determined as (1) Treatment Survival = percent survival during 7 d exposure to experimental conditions, (2) Survival to Hatching = percent of embryos that hatched, and (3) Post-Treatment Survival = percent survival to end of the post-treatment period. Embryos and larvae did not show decreasing survival until pH was below 5.0. LC_{50}'s were in the low to mid pH 4s. Mortality of embryos and tadpoles at LC_{50} and below occurred mostly during the first day of treatment.

The results of this study are located in the following publications:

Bradford D. and Gordon M. (1992) Aquatic Amphibians in the Sierra Nevada: Current Status and Potential Effects of Acid Deposition on Populations. Final Report to the C.A.R.B., Contract No. A932-139.

Bradford D.F., Swanson C. and Gordon M.S. (1991) Acidic deposition in the Sierra Nevada - Effects of low pH and inorganic aluminum on two declining species of amphibians. Am. Zool. 31, 114A.

Bradford D.F., Swanson C. and Gordon M.S. (1992) Effects of low pH and aluminum on two declining species of amphibians in the Sierra Nevada, California. J. Herpet. 26, 369-377.

Bradford D, Swanson C. and Gordon M. (1994) Effects of low pH and aluminum on amphibians at high elevation in the Sierra Nevada, California. Can. J. Zool. 72, 1272-1279.

Acid dose-response experiment with eggs of golden trout (Contract A932-138)

A dose-response experiment was conducted during snowmelt in artificial stream channels located next to the outlet stream of Spuller Lake. Buried eggs of golden trout (*Oncorhynchus mykiss aguabonita*) were exposed to a gradient of six pH levels ranging from 4.8 - 6.6 for 40 hours, and the survivorship of eggs determined 9-10 days later. A geochemical model was constructed that predicted aluminum concentrations in water flowing through a typical high elevation basin in the Sierra Nevada as a function of pH. In this way, acid/aluminum treatments were chosen that would mimic aluminum concentrations expected under different pH levels in the Sierra Nevada. According to the model, toxic levels of aluminum would be expected only if pH < 5.0.

Experimental pH levels were 6.6 (ambient), 5.7, 5.4, 5.2, 5.0, and 4.8. Newly fertilized golden trout eggs were placed in the channels on 2-July. Acid was delivered to the channels for 40 hours. Water samples were taken before, during, and after the experiment for determinations of pH, ANC, specific conductance, Al, and major ions. Eggs were excavated July 26-27. There were no significant differences in egg survival among the six pH treatments, despite treatment pH as low as 4.8. Thus, golden trout eggs do not appear very sensitive to acid pulses.

The results of this study are located in the following publication:

Jenkins T., Knapp R., Kratz K. and Cooper S. (1993) Aquatic Biota in the Sierra Nevada: Current Status and Potential Effects of Acid Deposition on Populations. Final Report to the C.A.R.B., Contract No. A932-138.

6.4.3. Descriptive Studies

Observation of trout and amphibian populations near Emerald Lake (Contract A4-122-32)

This study was intended to provide baseline data on the population and behavioral characteristics of fish and amphibians in the Emerald Lake Basin. Brook trout are the only fish in the system. Although the fish were originally stocked, they are now maintained by natural reproduction. Among the goals of the research were to (1) census fish populations and estimate fish growth rates in lake and stream habitat in the vicinity of Emerald Lake, (2) study egg production, hatching success, and recruitment of the fish, (3) determine survivorship for early life history stages, (4) investigate seasonal diets and movements of the fish.

The results of this study are located in the following publications:

Jenkins T., Knapp R., Kratz K. and Cooper S. (1993) Aquatic Biota in the Sierra Nevada: Current Status and Potential Effects of Acid Deposition on Populations. Final Report to the C.A.R.B., Contract No. A932-138.

Soiseth C.R. (1992) The pH and acid neutralizing capacity of ponds containing *Pseudacris regilla* larvae in an alpine basin of the Sierra Nevada. Calif. Fish. Game 78, 11-19.

Survey of potential breeding sites of amphibians at high altitude in the Sierra Nevada (Contract A932-139)

A survey of 235 potential breeding sites in 30 randomly selected 15-km^2 areas was conducted in the summer of 1990 and 1991. Minimum elevation for the survey sites was 2440 m. All of the survey areas were in the known geographic ranges of *P. regilla* and *R. muscosa*, and 23 of the areas were within the known range and *B. canorus*. The survey areas were searched during the day from 31-May to 23-July-1990, and 12-June to 2-August-1991, which is when amphibian larvae were most abundant and visible in shallow water near shore. Each area was searched in a non-random fashion until five separate sites containing larvae or eggs of each species were found, and until five separate sites were found which were judged to be potential breeding habitat, but which lacked the species. Water chemistry samples were taken at each site, and presumed to have the low annual minimum values for ANC, pH, and EC, because sampling took place during or within a few weeks of peak watershed discharge due to snowmelt.

The results of this study are located in the following publications:

Bradford D. and Gordon M. (1992) Aquatic Amphibians in the Sierra Nevada: Current Status and Potential Effects of Acid Deposition on Populations. Final Report to the C.A.R.B., Contract No. A932-139.

Bradford D.F., Gordon M.S., Johnson D.F., Andrews R.D., and Jennings W.B. (1994) Acidic deposition as an unlikely cause for amphibian population declines in the Sierra Nevada, California. Biol. Conserv. 69, 155-161.

Survey of 30 randomly selected lakes for fish and macroinvertebrates using EPA's EMAP area-based sampling technique for lake selection (Contract A932-138)

The objectives of this study were to (1) estimate the number and status of populations of sensitive invertebrate and fish species in lakes and associated streams above 2440 m in the Sierra Nevada, and (2) relate the distributions of these organisms to water chemistry. Thirty lakes above 2440 m were randomly selected with EPA's EMAP area-based sampling technique. Populations of fish and macroinvertebrates were qualitatively sampled. Surface water near lake outlets was sampled for chemical analysis.

The results of this study are located in the following publication:

Jenkins T., Knapp R., Kratz K. and Cooper S. (1993) Aquatic Biota in the Sierra Nevada: Current Status and Potential Effects of Acid Deposition on Populations. Final Report to the C.A.R.B., Contract No. A932-138.

Survey of biota of naturally acidic lakes in Bench Lake-Mt. Pinchot area (Contract A132-173)

Chemical conditions (pH and EC) and the presence/absence of vertebrate populations were surveyed in 104 lakes in the Bench Lake-Mt. Pinchot area of Kings Canyon National Park in the early summer of 1992. The lakes ranged in pH from 5.0 to 9.3, and included 10 naturally acidic lakes with pH < 6.0. Subsequently, 33 lakes were chosen for detailed analyses of their chemical and biological characteristics, including 8 acidic lakes. In the second study, samples of water chemistry (pH, ANC, EC, major ions, Al), fish, amphibians, zooplankton, and macroinvertebrates were collected from these lakes in August and early September, 1992.

The results of this study are located in the following publication:

Bradford D., Cooper S., Brown A., Jenkins T., Kratz K. and Sarnelle O. (1994) Distribution of Aquatic Animals Relative to Naturally Acidic Waters in the Sierra Nevada. Final Report to the C.A.R.B., Contract No. A132-173.

Multi-year sampling of zooplankton in seven high altitude Sierra Nevada lakes (Contract A932-060)

The zooplankton of seven high altitude lakes in the Sierra Nevada were sampled for three to six years. Emerald, Pear and Topaz Lakes occur in granitic watersheds in Sequoia National Park on the western slopes of the Sierra Nevada. Crystal, Ruby, Spuller and Lost Lakes occur on the eastern slopes. The lakes were sampled every other month in 1990 to 1992. Four of the lakes (Crystal, Ruby, Topaz, and Pear) were additionally sampled twice in 1989. Zooplankton were sampled by vertical tows in the deepest part of the lake. The zooplankton assemblages were considered in relation to physical and biological factors and in terms of the sensitivities of the zooplankton species to acidification. The seasonal patterns of acid-sensitive species were evaluated in light of the likely timing of episodic acidification.

The results of this study are located in the following publications:

Melack J., Sickman J., Setaro F., and Engle D. (1993) Long-term Studies of Lakes and Watersheds in the Sierra Nevada, Patterns and Processes of Surface-Water Acidification. Final Report to the C.A.R.B., Contract No. A932-060.

Engle D. & Melack J.M. (1995) Zooplankton of high elevation lakes of the Sierra Nevada, California; potential effects of chronic and episodic acidification. Archiv Hydrob. Arch. Hydrobiol. 133, 1-21.

6.5. FISH

6.5.1. Potential effects of acidification

There are at least three potential ways in which acidification of lakes and streams could affect the survival and distribution of fish in the Sierra Nevada. First, chronically low pH can lead to adult mortality. Second, intermediate pH levels can be fatal to eggs or fry, and can disrupt spawning activity by adults. Finally, many of the macro-invertebrates known to be important elements of trout diet in the Sierra can also be reduced or eliminated by low pH.

Depending on the exact timing of snowmelt and the species involved, fish at high elevation in the Sierra Nevada could be spawning adults, ripening gametes, hatching eggs, or larvae emerging from the gravel and beginning to feed, when pH depressions occur in lakes and streams. The majority of laboratory studies testing the effects of pH and Al on fish have involved trout (*Salmo* sp., *Oncorhynchus* sp.) and char (*Salvelinus* sp.). Trout belonging to the genus *Onchorhyncus* (golden, rainbow, and cutthroat trout) are more susceptible to acid inputs than trout belonging to the genera *Salvelinus* (brook trout) or *Salmo* (brown trout) (Baker et al. 1990).

Elevated concentrations of inorganic monomeric Al are often associated with acidic surface waters, and in some cases toxicity associated with Al may be as or more detrimental to biota than concentrations of H^+. The harmful effects of aluminum include disruption of body salt balance, leading to ionoregulatory failure, and respiratory impairment. Aluminum toxicity varies widely among species and among developmental stages of single species. Several investigators have shown that that the pH sensitivity of early life stages of trout (fertilized eggs through feeding fry) decreased with age, while yolk-sac and swim-up fry were more sensitive to Al than eggs (Baker & Shofield 1982, Holze 1984, Ingersoll 1986). In addition, at pH < 5.0, mortality of eggs of golden trout and brook trout may actually be reduced by high aluminum concentrations (Ingersoll et al. 1990). Examples of studies showing harmful effects of Al on trout species are shown in Table 1.

In general, fish can tolerate lower pH levels and higher Al concentrations in waters with higher Ca concentrations. Experiments with brown trout (Leivestad et al. 1980, Brown 1982, Howells et al. 1983) suggest that the positive effects of increased Ca occur principally at low Ca levels (< 100-150 μeq L^{-1}). In the lake survey of Jenkins et al. (1993), the median Ca concentration was 55 μeq L^{-1} and Ca ranged from 13 - 384 μeq L^{-1}. Thus, interactions between calcium concentrations and aluminum and proton toxicity cannot be ruled out in high altitude lakes of the Sierra Nevada.

Laboratory experiments have used eggs and fry because these stages are more sensitive to pH depressions than adults. It appears that acid pulses associated with snowmelt will not affect the eggs of spring spawning species until pH is reduced to < 4.5. A variety of laboratory experiments using fertilized eggs of golden trout, brook, cutthroat, lake, and brown trout show significant mortality occurring only at pH 4.5 in the absence of aluminum (Baker et al. 1990).

The swim-up fry stage of trout is especially sensitive to high aluminum concentrations. pH depressions to ca. 5.0-5.5, when coupled with high Al concentrations and coincident with fry emergence from spawning gravels, could result in declines in trout populations. For spring spawning trout (such as golden, rainbow and cutthroat trout), swim-up fry could be affected by the low pH of summer rain storms. For fall spawning populations (such as brook and brown trout), swim-up fry could be exposed to low pH during ionic pulses produced by snowmelt.

Trout diet. Examination of brook trout stomachs from Emerald Lake revealed that consumption rates of prey peak in September or August (Cooper et al. 1988a). In summer and autumn, trout diets were dominated by chironomid larvae and pupae, cladocerans and terrrestrial insects (including winged ants and spiders). Dominant cladocerans taken were *Daphnia rosea* and *Eurycercus lamellatus*. Fingernail clams (*Pisidium*) and chironomid larvae were important diet items in winter and spring when the lake was ice covered. Cladocera were the most important prey for younger fish (10-20 cm), whereas terrestrial arthropods became increasingly important prey for fish larger than 20 cm.

Brook trout from the outlet stream of Emerald Lake fed principally on terrestrial arthropods, chironomids, simuliids, trichopterans, ephemeropterans and plecopterans. Winter diets were dominated by simuliid larvae and terrestrial arthropods. Terrestrial arthropods and chironomid larvae were important summer food for trout in the outlet stream. Lake young-of-the-year (YOY) ate primarily chironomids and cladocerans, while stream YOY ate chironomids.

6.5.2. Status of fish at high elevation in the Sierra Nevada

Fish in Sierra Nevada waters that are sensitive to acidification are nearly all introduced and non-native. Six species of fish have been successfully introduced to high elevation lakes and streams in the Sierra. These are brown, brook, rainbow, golden, and cutthroat trout, and Owens tui chub. In the Bradford et al. (1994a) study of the Bench Lake-Mt. Pinchot area, four species of trout were found; rainbow trout (*Oncorhynchus mykiss*), golden trout (*Onchorhynchus aguabonita*), brook trout (*Salvelinus fontinalis*), and brown trout (*Salmo trutta*). The distribution of the trout is apparently related to stocking history, rather than water chemistry. Trout were found in 18 of the 104 lakes surveyed in the synoptic survey carried out by Bradford et al. 1994. Trout were absent from all 10 naturally acidic lakes in the region with pH < 6, but were also absent from 76 of the 94 lakes with pH ≥ 6. Conductivity was similar in lakes with and without trout, but lakes with trout tended to be deeper than those lacking trout. Trout were not found above 3515 m in elevation. In the companion detailed survey of 33 lakes, trout were present in seven lakes. The pH range for these lakes was narrow (pH 6.9 to 7.5). The lakes with trout were larger and deeper than the fishless lakes (Bradford et al. 1994).

In the lake survey of Jenkins et al. (1993) only brook, golden and rainbow trout were common in the sample lakes. Twelve of the 30 sampled lakes contained one species, 11 lakes contained two species, and 7 lakes contained no fish. Using EMAP protocols to extrapolate these results to the entire population of lakes above 2400 m in the High Sierra, they estimated that golden trout are the most widely dispersed fish in the High Sierra, occurring in 36% of the lakes above 2400 m. Rainbow trout were estimated to occur in 33% of the lakes, brook trout in 16%, brown trout in 8%, and cutthroat trout in only 0.5% of the target population. Aluminum concentrations ranged from 0.14 to 2.32 μM, except for one lake (Lake 45) in which Al was 29.33 μM. Golden trout were only weakly associated with conditions found at high elevation, such as lower pH and ANC. Although golden trout abundance was negatively associated with aluminum concentrations (Table 2), the majority of aluminum values encountered in the survey lakes were below those firmly established as toxic to trout.

6.5.3. Responses of individual trout species to acidification

Brown trout (*Salmo trutta*). Brown trout spawn in the fall from September to late November, and only in streams (Figure 1a). Their eggs hatch from January to March. Young fish emerge from the gravel and begin feeding in the spring. Only late alevins and swim-up fry would be subjected to snowmelt pulses of low pH. Brown trout are considered more tolerant of low pH and high aluminum than rainbow trout (Baker et al. 1990), with embryos dying at ca. pH 4.5 - 5.0. In the Sierra Nevada, brown trout were planted in waters of generally lower elevation than the other species, and as a consequence, the waters containing brown trout are more highly buffered. Brown trout are likely to be one of the last species to show effects of acid deposition.

Brook trout (*Salvelinus fontinalis*). Members of the genus *Salvelinus* are among the fish species most affected by acidification on the European and Atlantic seaboards. As a result of numerous studies it is possible to generalize about the effects of various levels of acidity on the reproductive cycle of salvelinids (Baker et al. 1990). Below pH 4.0 egg survival decreases; between pH 6.5 - 5.1 the growth and survival of sac fry and alevins may decline; at ca. pH 5.6 ovulation and spawning time is delayed; at ca. pH 5.2 growth of reproductive adults and egg production decline; and at pH < 4.1 adult fish are killed within hours. As a result of these general responses, the reduced abundance or disappearance of brook trout from acid stressed systems is usually related to recruitment failure rather than mortality of juveniles and adults.

Brook trout are one of the most common fish found in lakes of the Sierra Nevada. Brook trout are fall spawners, and are capable of spawning in lakes as well as streams (Figure 1b). Life history attributes of brook trout were intensively studied in the Emerald Lake Basin, Sequoia National Park (Cooper et al. 1988a). Spawning occurs in October and November, and hatching takes place between January to April. As a consequence, brook trout would be exposed to acidic snowmelt pulses as sac fry or swim-up fry. Only 3-5 % of brook trout eggs deposited in the Emerald Lake system survived to the end of the spawning period because there was insufficient gravel in spawning sites, and the eggs of early spawners were destroyed by the reworking of gravel by later spawners. If eggs were undisturbed, survival to hatching was very high - approaching 90%. The number of eggs present at the end of the spawning season remains relatively constant from year to year. However, abundance of YOY shows high interannual variation, due to egg or sac fry destruction from natural disturbances such as floods (avalanche induced), droughts (drying up of gravel beds), and interstitial ice formation in gravel. Consequently, less than 1% of brook trout eggs survive to become YOY the following autumn.

Jenkins et al. (1993) contend that brook trout populations would probably be the last trout populations to disappear due to episodic deposition, and that it is likely that responses to short-term episodic pulses of acid might not be observed until pH is lowered to 4.5. Young-of-year brook trout emerge from gravel in late June to early July (in a low snowpack year) or late July-early Aug (in a high snowpack year). Length characteristics of aging trout show that adult brook trout were allocating most of their energy to reproduction and maintenance rather than growth after they reach maturity. Lake populations were found by Jenkins et al. (1993) to be dominated by fish 3-6 years old.

There is some evidence that episodic acidification may affect recruitment of brook trout in the Emerald Lake System. During snowmelt of 1986, pH values dipped to 5.5 during snow melt in late May to early June. This acid pulse, which as stated above, was sufficiently low to decrease survival of sac fry and alevins, would have coincided with emergence of brook trout fry. However, recruitment failure due to delayed maturity, decreased fecundity and fertility are not likely to take place in the Emerald Lake system at this time, because current periodic pH depressions are not severe enough to influence these life history characteristics.

Golden trout (*Oncorhynchus mykiss aguabonita*) Golden trout are one of the Sierra trout species that spawn in the spring. Those living above 2500 m in the Sierra Nevada typically spawn from mid-June to mid-July, when much of the Sierra Nevada is still snow covered (Figure 2). The spawning begins as soon as ice on lakes and streams begins breaking up. The survivorship of newly fertilized eggs is first affected at pH 4.5. Alevin mortality starts at pH 5.0, and swim-up fry experience mortality starting at 5.5. Golden trout populations might be reduced after repeated acid pulses of pH 4.5 coinciding with these early developmental stages. However, because swim-up larvae are not present in streams until at least August, they are not likely to be exposed to periodic lows in pH due to snowmelt. The relative insensitivity of golden trout eggs to pH levels between 6.6 and 4.8 suggests that egg survival would not be affected by foreseeable increases in acid deposition in the Sierra Nevada.

Cutthroat trout (*Oncorhynchus clarki*) Cutthroat trout are spring spawners. At the high elevations typical of trout habitat in the Sierra Nevada, spawning may take place as late as June, July, or August (Figure 2). Young emerge and begin feeding in mid-summer. Cutthroat trout are apparently the trout most sensitive to low pH and high aluminum (Woodward et al. 1989). Freshly fertilized eggs die after 7 days of exposure to pH 4.5. Alevin and swim-up larvae are severely reduced at pH 5.5, especially if combined with aluminum levels up to ca. 4 mM. Cutthroat trout probably spawn during or after peak runoff, so the egg stage would be the most susceptible to pH depressions during snowmelt. Summer convective storms could affect later stages, such as alevins or swim-up fry, if pH dropped below 5.0.

Rainbow trout (*Oncorhynchus mykiss*) Acid sensitivity of rainbow trout is believed to be similar to those of golden and cutthroat trout (Figure 2). Thus several consecutive years of either (1) acid pulses as low as pH 4.5 early in the summer, or during snowmelt, when eggs and embryos are vulnerable, or (2) acidic summer rain with pH $\leq$ 5.5, when alevins or swim-up fry are vulnerable, could reduce populations of these rainbow trout, as well as its congeners, golden and cutthroat trout.

6.6. AMPHIBIANS

6.6.1. Potential impacts of acidification on amphibians.

Breeding sites of amphibians include temporary ponds, permanent ponds, lakes and rivers, bogs, small streams and soil. These habitats are differentially affected by acidic precipitation. It has been estimated that 30% of all salamander and newt species (Caudata) and 50% of all frog and toad species (Anura) in North America use temporary ponds for breeding (Baker et al. 1990). These ephemeral and shallow water bodies are highly influenced by the chemistry of precipitation, especially in the spring when they are flushed by snowmelt and when amphibian eggs are typically deposited. Hatchling tadpoles are generally the most sensitive life stage to aluminum exposure. In larger, permanent bodies of water, adults (e.g. ranid frogs) tend to establish territories and breed throughout the summer. Therefore, their eggs and tadpoles are less likely to coincide with acid-metal pulses. Mountain headwater streams in the eastern United States are habitat for the adults and larvae of plethodontid salamanders. These amphibians are thus susceptible to acid pulses during snowmelt season. Some salamanders undergo their entire life cycle in soil, and the adults of some aquatic breeding salamanders (e.g. *Ambystoma*) live underground for much of the year. There is accumulating evidence that decreases in soil pH reduce the densities of fully terrestrial salamanders (Baker et al. 1990).

Although there is variation in the acid sensitivity of amphibian species, field surveys and in situ toxicity tests conducted in North America allow estimation of approximate pH and Al levels required to reduce the survival of amphibians. Between pH 4.5 and 5.0, the growth and recruitment of the tadpoles and salamander larvae of sensitive species decline. Below pH 4.5, complete mortality of embryos of the most sensitive species can be expected. Adult amphibians tend to be much more tolerant of low pH, surviving at pHs down to 3.5. The LC_{50} for total dissolved aluminum for embryos and tadpoles of other species is generally much higher than 80 $\mu g\ L^{-1}$. The highest extractable aluminum concentration measured in the field is 36 $\mu g\ L^{-1}$ (Baker et al. 1990). An estimate of the minimum pH likely to be experienced by amphibians in the Sierra Nevada can be obtained from data for snowpack meltwater. To date, the lowest pH measured in such water is 5.0 (Williams & Melack 1991). Although it is possible that the lowest pH in the field could occur as a result of summer rains rather than snowmelt, the older life stages that occur at this time are expected to be much more tolerant of low pH than embryos or hatchling tadpoles.

6.6.2. Summaries for individual amphibian species

Pacific Tree Frog (*Pseudacris regilla*)

Despite declines of many amphibian populations in the Sierra Nevada over the last two to three decades, populations of *Pseudacris regilla* have remained stable or declined to a lesser extent at high elevation. In Bradford & Gordon's (1992) survey of amphibian habitat in the Sierra Nevada, *P. regilla* was found in 25 of 30 15-km^2 survey sites. The survey took place in July 1990 and June 1991 - a time of year when larvae are most abundant and visible in shallow water near shore of water bodies. In addition to the fact that one-time measurements of pH and ANC were unassociated with the frog's distribution, conductivity was statistically higher in sites lacking the frog. However, in the Bradford et al. (1994a) survey of the Bench Lake-Mt. Pinchot area, *P. regilla* was found in only a few of the 104 lakes of the synoptic survey, and in none of the 33 lakes of the detailed survey. In the biological survey of ponds of the Marble Fork in the Emerald Lake region in the summers of 1985-1987 (Cooper et al. 1988a), *Pseudacris regilla* was present in 12 of 15 ponds. The frogs laid their eggs in ponds near the Marble Fork shortly after snowmelt. Approximately 1-2 weeks elapsed between egg fertilization and hatching. Larvae metamorphosed by September, except in 1986 when late snowmelt and lower temperatures delayed egg laying and development.

Evidence from the Sierra Nevada as to whether or not the distribution of *P. regilla* is related to ambient pH is equivocal. In the Cooper et al. (1988a) study, pH varied from 4.06 to 6.88 in ponds with tadpoles, and from 5.50 to 7.15 in ponds without tadpoles. Ponds that lacked tadpoles were heavily shaded by mountains or vegetation. Catastrophic events, such as pond drying or early freezing, decimated tadpole populations in some ponds. In the Bradford et al. (1994a) synoptic survey of the Bench Lake-Mt. Pinchot area, *P. regilla* tadpoles were collected from 6 fishless lakes with pH > 6 and from one naturally acidic lake (pH = 5.96).

<u>Mountain Yellow-legged frog (*Rana muscosa*)</u>

Rana muscosa is one of the amphibian species that has dramatically declined over the past two decades at high elevation in the Sierra Nevada, and has completely disappeared from many pristine environments, including areas within Sequoia, Kings Canyon and Yosemite National Parks. In Bradford & Gordon's (1992) survey of 30 randomly selected 15-km^2 survey sites, *R. muscosa* was only found in six sites. However, in their study, patterns of presence/absence were unexplained by pH, ANC or EC (electrical conductivity).

In the synoptic survey of the Bench Lake-Mt. Pinchot area (Bradford et al. 1994a), *R. muscosa* was found in 36 of 104 lakes, making it relatively abundant in this area compared to other areas in the Sierra Nevada, where its distribution is much more sparse and where many populations have disappeared. Tadpoles of this species were found in 22 lakes, all with pH > 6, in some cases together with adults. Of these 22 lakes, only one had trout. Conductance and elevation did not affect the distribution of adults or tadpoles. Tadpoles were absent in deep lakes (> 10 m), which is probably due to the presence of trout in most of the deeper lakes. Adults were found in 29 lakes, four of which contained trout. The absence of tadpoles is not necessarily indicative of mortality of tadpoles due to acidity - it could also be indicative of a failure of eggs to hatch or embryos to develop.

In the detailed survey of 33 lakes conducted by Bradford et al. (1994a), tadpoles of *R. muscosa* occurred in 12 lakes. Eleven of these were fishless lakes and one of these contained golden trout; all of the 12 lakes had pH > 6.0. *R. muscosa* adults occurred, alone or together with tadpoles, in 18 lakes. Three of the lakes containing adults had fish.

Five of the lakes in which adult *R. muscosa* were observed were acidic. In naturally acidic lakes in the Bench Lake-Mt. Pinchot area, *R. muscosa* tadpoles were one of the few organisms that were lacking. Adult *Rana*, however, were often found in lakes with pH as low as 5. Thus the distribution of tadpoles is restricted by acidic conditions to a different extent than are the adults.

In the dose-response tests of Bradford et al. (1992), survival of *R. muscosa* embryos and tadpoles declined dramatically as a function of pH in the mid to low 4s. Tadpoles were more tolerant of low pH than embryos. LC_{50} for post-treatment survival was 4.4 and < 4.0 for embryos and tadpoles, respectively. Hatching time was not affected by pH in *R. muscosa* and *R. muscosa* was tolerant of the Al levels used in the experiments. Some sub-lethal effects of pH were observed; *R. muscosa* embryos were smaller at pH 5.25.

There was an apparent conflict between the results of Bradford et al.'s (1992) lab experiments and the survey of naturally acidic lakes (Bradford et al. 1994a) with respect to *R. muscosa* tadpoles. In the field, *Rana* tadpoles were not found in lakes with pH < 6.0, but in the dose-response experiments, survivorship of embryos and tadpoles exposed for 7-day intervals, was not significantly affected by pH as low as 4.75. Thus it must be considered that factors related to pH in the field, which were not factors in the dose-response experiments, may affect tadpole survival in nature. The naturally acidic lakes contained higher levels of sulfate and aluminum than the experimental treatments (for Al: in the field - median 69 $\mu eq\ L^{-1}$, in experiments - 9 $\mu eq\ L^{-1}$; for sulfate: in the field - median 410 $\mu eq\ L^{-1}$, in experiments 100 $\mu eq\ L^{-1}$). In addition, the one-time sampling for pH in the field survey may have failed to coincide with even lower pH that may occur periodically or briefly in these lakes.

Yosemite toad (*Bufo canorus*)

Bufo canorus is another of the amphibian species that has dramatically declined over the past two decades at high elevation in the Sierra Nevada. In Bradford et al.'s (1994a) synoptic survey of lakes in Kings Canyon National Park, *Bufo canorus* was not found. In the dose-response experiments of Bradford et al. (1992), tadpole and embryo survival declined dramatically with pH in the mid to low 4s. Tadpoles were more tolerant of low pH than embryos. The LC_{50} for post-treatment survival was 4.7 and 4.3 for embryos and tadpoles, respectively. Sub-lethal effects of pH were observed; embryos hatched at an earlier time at pH < 5.0. Aluminum both caused a significant reduction in length of *B. canorus* tadpoles at pH 5.3 and 5.8, and a reduction in hatching time at all pHs.

Long Toed Salamander (*Ambystoma macrodactylum*)

Ambystoma macrodactylum is an amphibian species that is not apparently declining at high elevation in the Sierra Nevada. However, in Bradford et al.'s (1994a) synoptic survey of lakes in Kings Canyon National Park, *Ambystoma macrodactylum* was not found.

6.7. ZOOPLANKTON

High altitude Sierra Nevada lakes contain many species of zooplankton classified as acid intolerant or tolerant based on survey data and experimental data from studies at a variety of sites in the United States and Canada (Table 3). Several of these species are known to decrease at low pH, and are thus considered to be acid-sensitive: *Diaptomus signicauda*, *Tropocyclops prasinus*, *Daphnia rosea*, *Conochilus unicornis*, and *Keratella cochlearis*. Other zooplankton species occurring in the same lakes are known to increase in dominance at low pH, and thus may be considered as acid resistant: *Bosmina longirostris*, *Holopedium gibberum*, *Keratella taurocephala*. These principal species are listed below, along with the evidence originating from CARB-sponsored studies as to whether they are acid sensitive or resistant.

Daphnia spp. In general, *Daphnia* are much reduced or absent in acidic lakes. Evidence that *Daphnia* in high Sierran lakes are at risk from lake acidification comes both from experimentation and surveys. *Daphnia* were absent from naturally acidic lakes (pH < 6.3) in the survey of 104 lakes by Bradford et al. (1994a). *Daphnia rosea* decreased in abundance below pH 5.5-5.8 and virtually disappeared below pH 5.0 in the 1987 Emerald Lake bag experiments (Barmuta et al. 1990).

Diaptomus spp. (*D. eiseni*, *D. shoshone*, *D. signicauda*). *Diaptomus signicauda* is the only widespread small calanoid copepod in the Sierra Nevada range. There is evidence that *D. signicauda*, together with its congeners *D. shoshone* and *D. eiseni*, are at risk from chronic acidification. *Diaptomus* (all three species) were rarely collected (12-25% of lakes sampled) in naturally acidic (pH < 6.0), fishless lakes in Bradford et al.'s (1994a) survey. *Diaptomus signicauda* decreased in abundance below pH 5.5-5.8 and virtually disappeared below pH 5.0 in the 1987 Emerald Lake bag experiments (Barmuta et al. 1990).

Conochilus . Emerald Lake field experiments indicate that *Conochilus* is one of the most acid sensitive zooplankton genera. They were reduced by pH < 5.2 following only one week of treatment (Barmuta et al. 1990)..

Bosmina . In general, *Bosmina* became more abundant with decreasing pH in the Emerald Lake bag experiments, although it became rare in the lowest pH treatment (pH 4.7) in the experiments of 1987. The ability of *Bosmina* to increase numerically under conditions of increasing acidity was attributed by Barmuta et al. (1990) as a numerical response to decreased competition with *Daphnia* at low pH.

Chydorus. *Chydorus sphaericus* was collected in similar frequencies in naturally acidic and non-acidic lakes of the Sierra Nevada in Bradford et al.'s (1994a) detailed survey. Although *Chydorus* increased over time in even some of the acidified enclosures at Emerald Lake, its increases were attributed by the investigators to the increase in substrate area afforded by the sides of the enclosures, rather than an advantage due to pH per se (Barmuta et al. 1990). However, the fact that *Chydorus* did not decrease after experimental exposure to acidic conditions for 35 days in the bag experiments at Emerald Lake is consistent with the results of the larger survey (Bradford et al. 1994a).

Keratella . *Keratella taurocephala* became more abundant with decreasing pH in the 1987 Emerald Lake enclosure experiments, which is consistent with its known acid resistivity. *Keratella* spp. were collected in similar frequencies in naturally acidic and non-acidic Sierra Nevada lakes in Bradford et al.'s (1994a) detailed lake survey.

Polyarthra. *Polyarthra vulgaris* did not show a significant response to lowered pH in the Emerald Lake enclosures, and remained present in the lowest pH treatments. This experimental evidence is somewhat at odds with available survey results. *Polyarthra* sp. were collected less frequently in acidic lakes than non-acidic lakes in Bradford et al.'s

(1994a) lake survey (species found in 25% of acidic fishless lakes, and 70% of non-acidic fishless lakes).

Based on the results of experimental acidification, the principal zooplankton genera occuring in high altitude Sierra Nevada lakes can be ordered according to their relative acid sensitivities (Figure 3). *Daphnia* and *Diaptomus* are the most sensitive, disappearing from lake enclosures below pH 5.5. *Conochilus* is also very acid-sensitive, declining below ca. pH 5.3. *Bosmina* and *Holopedium* were more resistant to pH, dropping out of the zooplankton assemblage once pH declines to ca. 4.7. The most acid-resistant of the common zooplankton were *Polyarthra* and *Keratella taurocephala*, which remained in even the lowest pH treatments (pH 4.0).

If the threshold pH values for these zooplankton species are compared to the current chemical condition of surface waters in the Sierran watersheds studied, it becomes evident that lake pH is not sufficiently low on a chronic basis to threaten zooplankton populations. The lowest pH observed in lake outflows (which occurs during early snowmelt, when ionic pulses are most likely) was 5.5 in 1991 in Lost Lake and Pear Lake (Table 3). The lowest volume-weighted mean lake pH in this data set (5.5) was observed in Lost Lake in 1991. This value is at the threshold pH value for the most sensitive of the major zooplankton species - *Daphnia rosea* and *Diaptomus signicauda*, and approaches the threshold value of *Conochilus,* which is threatened by sustained pH below 5.3. However, these lower-end pH values were observed in lakes before ice out, when the lakes may still be inversely stratified. Low pH water entering the lakes from snowmelt at this time is likely to skim across the lake just below the ice, and may not greatly influence the pH throughout the water column.

6.8. MACROINVERTEBRATES

6.8.1. Macroinvertebrate taxa sensitive to acidification.

Synoptic surveys of benthic macroinvertebrates have been carried out in streams and lakes in North America, Scandinavia, United Kingdom, New Zealand and Germany. Such surveys always reveal an absence of some macroinvertebrate species in lower pH habitats. Among these apparently sensitive species are several mayflies (e.g. *Baetis* spp.), amphipods (e.g. *Hyalella aztea*, *Gammarus lacustris*), crayfish (e.g. *Orconectes* spp.), and snails and clams (Baker et al. 1990). Among apparently unaffected taxa are sambarid crayfish, true bugs (*Hemiptera*), dragonflies, some species of caddisflies, stoneflies (*Leuctra* and *Isoperla* spp.) and some species of mayflies (e.g. *Leptophlebia* spp.). In North American stream surveys, the mayflies of the genera *Baetis*, *Heptagenia*, and *Ephemerella* are consistently absent in low pH streams. It has been hypothesized that mayfly nymphs which are epibenthic and active, such as *Baetis*, may be more susceptible to acid pulses in streams than taxa such as chironomid larvae, which may escape deleterious conditions by burrowing into the substrate (Baker et al. 1990).

6.8.2. Descriptive surveys of macroinvertebrates in the Sierra Nevada.

In high altitude Sierra lakes, many macroinvertebrates are rare or absent in lakes owing to the presence of fish, even if pH is within a tolerable range. Among these taxa are baetid and siphonolurid mayflies, hemipterans (notonectids and corixids), limnephilid caddisfly larvae, and dytiscid beetle larvae. In studies outside of the Sierra Nevada, corixids and dytiscids have been shown to be reduced by fish, but if the fish are eliminated by acidification, the species can persist, showing their potential to be acid tolerant.

In the 1987 Emerald Lake Bag Experiments, two sediment cores were taken for enumeration of zoobenthos. The benthic taxa most often cited as being good indicator species in lakes (*Orconectes virilis*, *Lepidurus arcticus* Pallas, *Asellus aquaticus*) are absent from Emerald Lake, or found only occasionally (*Hyalella azteca*). In Bradford et al.'s (1994a) detailed survey of 33 lakes, limnephilid caddis larvae (esp. *Hesperophylax*) were the only commonly collected macroinvertebrates that were significantly less abundant in the benthos of acidic than non-acidic lakes. Limnephilid caddis larvae were found in only 37% of acidic lakes of this survey, but in 81% of non-acidic lakes. One genus in particular, *Hesperophylax*, was absent from acid lakes in the survey. Baetid and heptogenid mayflies, amphipods, sphaerid clams, *Notonecta* and *Sialis latreille* were absent from acid lakes, but also not frequently enough collected in non-acid lakes to make a valid statistical comparison. In this study, the occurrence of many common macroinvertebrate taxa was related to the presence or absence of fish, rather than lake pH. Among these taxa were limnephilid caddis larvae, mayfly nymphs, dytiscid beetles, and corixids. In Jenkins et al.

(1993), *Callibaetis*, chironomids, *Pisidium* were not found in fishless lakes with pH < 6. In outlet streams, *Baetis*, *Pisidium* and *Rhyacophila* tended to be absent at pH ≤ 6. In Bradford et al.'s (1994a) survey of naturally acidic lakes in the Mt. Pinchot area of Kings Canyon National Park, baetids were not found in naturally acidic lakes, but were also rare overall.

6.8.3. Experimental studies of macroinvertebrates in the Sierra Nevada.

The relevance of short-term experimental acidification of streams is increased by the fact that taxa that drift following short-term acid additions in streams closely correspond to the species lost from streams following long-term acidification (Hall et al. 1987). What follows is a summary of the responses of stream macroinvertebrates which showed negative responses to experimental acidification in the CARB sponsored artificial channel experiments conducted in the Marble Fork of the Kaweah River near Emerald Lake. The macroinvertebrate taxa common in the Marble Fork at the time of the acidification experiments in the summers of 1985 and 1986 were *Baetis*, *Paraleptophlebia*, *Epeorus*, *Isoperla*, *Rhyacophila*, *Hydroporus*, *Simulium*, mites, oligochaetes, Chironomidae.

Chironomid larvae. All increased drift of chironomids in acidified channels that took place in the1986 experiments during the treatment period was due to the drift of dead individuals (Kratz et al. 1994).

Epeorus mayfly nymphs. *Epeorus* had significantly higher drift rates during acidification, and up to 90% of the increased drift was due to dead individuals. In the 1986 experiments, increased drift by *Epeorus* was largely restricted to the more extreme treatment (pH 4.6).

Baetis mayfly nymphs. In the 1985 stream channel experiment, the number of *Baetis* drifting from acidified channels during the acid addition was approximately three times the number drifting from the control channels. 54% of this enhanced drift was due to toxicity (drift of dead insects), the remainder being live *Baetis* that drifted. Changes in benthic density were not detected in this experiment because drift from upstream was not blocked.

In the1986 stream channels, very high percentages of increased *Baetis* drift were due to killed drift (76-100% in pH 4.6, 31-73% at pH 5.2). The majority of this toxic drift took place within the first 4 hours of acid addition. Benthic densities in acidified channels declined to 10-16% of the density in control channels 2 days after acidification.

Paraleptophlebia mayfly nymphs. In the 1986 experiments, drift of *Paraleptophlebia* increased when pH was lowered to 4.6, and acidified channels showed statistically significant decreases in benthic densities of nymphs at the end of the experiment.

6.9. STREAM PERIPHYTON

In the 1986 stream channel experiment, ceramic tiles were used to examine responses of benthic algae to acid addition (Cooper et al. 1988b). The only non-diatom alga found on the colonized tiles was *Zygnema* sp. Seven days after acid addition, diatom densities were significantly lower than in pH 4.6. Taxa which showed decreases in density with acid addition were *Achnanthes minutosima*, *Gomphonema subclavatum* and *Fragilaria* vaucheri. *Eunotia* species (e.g. *Eunotia tenella*) tended to be more abundant after moderate acid addition (pH 5.2) then in control treatments. In other stream studies examined the effects of chronic and continuous acid additions, and in these cases, increases in filamentous taxa like *Mougeotia* were reported (Hall et al. 1980).

6.10. SUMMARY AND CONCLUSIONS

Amphibians. Generally, the embryos and larvae of amphibians are more susceptible to low pH than adults. Usually, between pH 4.5 - 5.0, the growth and recruitment of tadpoles and salamander larvae decline. Below pH 4.5, complete mortality of embryos can occur. Amphibians that occupy temporary ponds are more vulnerable to acidification of surface waters than permanent pond species because they rely on explosive spring breeding tactics and thus are especially vulnerable to snowmelt chemistry. Adults of permanent pond species establish territories and breed throughout the summer, thus sensitive embryonic stages of these species do not coincide with snowmelt.

There are five species of breeding, aquatic amphibians that occur at high elevation in the Sierra Nevada: *Bufo canorus* (Yosemite toad); *Bufo boreas* (western toad), *Pseudacris regilla* (Pacific tree frog), *Rana muscosa* (mountain yellow-legged frog); and *Ambystoma macrodactylum* (long-toed salamander). Evidence of acid sensitivity is available for *Rana muscosa* and *Bufo canorus* and consists of the following experimental and survey data:

Rana muscosa:

LC_{50} of embryos is pH 4.4

LC_{50} of tadpoles is pH 4.0

Rana tadpoles are not found in lakes with pH < 6.0. High concentrations of other solutes may be involved in the field distribution of this species (e.g. Al and sulfate). Also, in eleven of twelve lakes where *Rana* tadpoles were found in Bradford et al.'s (1994a) synoptic survey, trout were absent, implying that presence/absence of trout may be at least as important in establishing the range of Rana muscosa as is surface water chemistry.

Bufo canorus:

LC_{50} of embryos is pH 4.7

LC_{50} of tadpoles is pH 4.4

Bufo canorus was not found in the CARB sponsored biological survey work (Bradford & Gordon 1992).

In light of the current condition of surface waters in high elevation Sierra Nevada watersheds, **we make the following conclusion: 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.**

Trout. 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. Of the three *spring-spawning* trout species, experimental data on acid sensitivity is most complete for golden trout and cutthroat trout. Briefly, the experimental data can be summarized as follows:

Golden Trout:	eggs die < pH 4.5
	alevins decline < pH 5.0
	swim-up fry decline < pH 5.5
Cutthroat Trout	eggs die < pH 4.5
	swim-up fry decline < pH 5.5

Of the two *fall-spawning* species of trout in the Sierra Nevada, more is known about the acid-sensitivity of brook trout than is known about brown trout. Briefly, the experimental data available are as follows:

Brown trout:	Embryos die < pH 4.5 - 5.0
Brook trout:	Eggs die < pH 4.0
	Fry and alevins decline between pH 6.5 - 5.1
	Egg production by adults declines < pH 5.6
	Adult growth declines < pH 5.6
	Adults die < pH 4.1

In light of the current condition of surface waters in high elevation Sierra Nevada watersheds, **several conclusions are possible:**

1) The fertilized eggs of spring spawning 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.

2) The swim-up fry of spring-spawning trout could be damaged by episodic acidification due to runoff from summer storms.

3) 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.

Stream Invertebrates. 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:

1. *Baetis* mayfly nymphs
2. *Paraleptophlebia* mayfly nymphs
3. *Epeorus* mayfly nymphs
4. chironomid 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.**

Zooplankton. Based on the available descriptive and experimental information, certain changes in zooplankton community structure we predict the following consequences *if Sierra Nevada lakes become subjected to chronic acid stress in the future*.

(1) *Daphnia rosea*, *Daphnia middendorffiana* and *Diaptomus signicauda* are likely to be removed if pH levels reach as low as 5.0. The apparent acid intolerance of *Diaptomus signicauda*, and its widespread distribution in the Sierra Nevada, imply that acidification in this region would eliminate the calanoid copepod component in the plankton of many high altitude lakes.

(2) 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.

(3) Where they occur, *Conochilus unicornis* and the genera *Asplanchna*, *Filinia*, *Ascomorpha*, and *Ploesoma* may be expected to decline, and *Kellicottia* and *Keratella cochlearis* may be expected to increase with acidification, but predictions for these taxa remain speculative.

(4) 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 (Yan & Geiling 1985, Yan et al. 1982, Brett 1989).

In some Sierra Nevada lakes, a cyclopoid species (*Macrocyclops albidus* or *Cyclops vernalis*) is currently a frequent dominant. Information is lacking about the acid sensitivity of *Macrocyclops albidus*, and considerable variation in the tolerance level of *Cyclops vernalis* is apparent from the literature (Yan & Strus 1980, Carter et al. 1986). Thus, we are unable to predict whether these species will be removed along with known sensitive species, or whether they stand to increase at some point in an acidification process due to competitive release from more sensitive calanoid and cladoceran competitors. The potential responses to low pH by the large-bodied zooplankters of fishless Sierra Nevada lakes, *Daphnia middendorffiana*, *Diaptomus eiseni* and *Diaptomus shoshone*, have not been experimentally determined in a Sierra Nevada lake to date, although evidence from other studies implies strongly that *D. middendorffiana*, will be negatively impacted by low pH, as are essentially all of its congeners (Havas & Hutchinson 1983, Brett 1989).

If bio-monitoring of zooplankton is to be used to detect chronic acidification, we recommend that attention be focused on the most acid-sensitive species and that sampling be concentrated in times of the year in which they are characteristically abundant. In the case of *Daphnia rosea*, *Daphnia middendorffiana* and *Diaptomus signicauda*, sampling from June through November would be sufficient in all of the CARB survey lakes to detect major changes in abundance. Upward shifts in abundance of more acid-tolerant species due to competitive release may be hard to detect in a time series, because many of the tolerant species are already numerically dominant in survey lakes during much of the year.

More frequent sampling (at least once/month) is advisable in order to ensure the detection of annual population peaks for important species, and to avoid incorrectly designating species as absent at certain times of the year.

The utility of using zooplankton to detect episodic acidification of lakes in the Sierra Nevada depends on the acid tolerance of zooplankton species which occur in the lakes when acid pulses take place. The only crustacean species which occur frequently in samples obtained during snow melt periods in the Sierra Nevada lakes studied to date are *Diaptomus signicauda*, *Macrocyclops albidus*, *Tropocyclops prasinus*, and *Bosmina longirostris*. *Daphnia rosea* has been sampled very rarely during snow melt, making it a particularly unsuitable species for detecting early response to acidic snowmelt. The frequency of *Bosmina longirostris* in snow melt samples is of little use for early detection of acidification because of its known acid tolerance. Learning more about the tolerance range of *Macrocyclops albidus* would be useful due to its widespread occurence and its frequent appearance in samples during snow melt. *Keratella taurocephala*, *Keratella quadrata* and *Polyarthra vulgaris* were the most often encountered rotifers during snow melt periods. However, *Keratella taurocephala*, like *Bosmina longirostris*, is not likely to yield information about early acidification due to its known acid tolerance. Further defining the acid tolerance ranges of *K. quadrata* and *Polyarthra vulgaris* may be important if they are focussed upon as potential indicators of processes during snow melt periods. Although the timing of snow melt varies annually and spatially, the entire phenomenon could be safely bracketed in a group of lakes by regular sampling between the months of March and June. We cannot recommend a monitoring program to detect the effect of acidic summertime precipitation on zooplankton due to the unpredictability of storms and the small and ephemeral nature of the pH depressions they cause.

6.11. REFERENCES

Almer B., W. Dickson, C. Ekstrom, E. Hornstrom and U. Miller (1974) Effects of acidification on Swedish lakes. Ambio 3:30-36.

Baker J. and C. Scholfield (1982) Aluminum toxicity to fish in acidic waters. Water Air Soil Pollut. 18:289-309.

Baker J., D. Bernard, S. Christensen, M. Sale, J. Freda, K. Heltcher, D. Marmorek, L. Rowe, P. Scanlon, G. Suter, W. Warren-Hicks and P. Welbourn (1990) Biological effects of changes in surface water acid-base chemistry. NAPAP Report 13. *in* National Acid Preciptiation Assessment Program, Acidic Depostiion: State of Science and Technology. Volume II, 1990.

Barmuta L., Cooper S., Hamilton S., Kratz K. and Melack J. (1990) Responses of zooplankton and zoobenthos to experimental acidification in a high-elevation lake (Sierra Nevada, California, U.S.A.) Freshw. Biol. 23, 571-586.

Bradford D. and Gordon M. (1992) Aquatic Amphibians in the Sierra Nevada: Current Status and Potential Effects of Acid Deposition on Populations. Final Report to the C.A.R.B. Contract No. A932-139.

Bradford D., Cooper S., Brown A., Jenkins T., Kratz K. and Sarnelle O. (1994a) Distribution of Aquatic Animals Relative to Naturally Acidic Waters in the Sierra Nevada. Final Report to the C.A.R.B. Contract No. A132-173.

Bradford D.F., Gordon M.S., Johnson D.F., Andrews R.D., and Jennings W.B. (1994b) Acidic deposition as an unlikely cause for amphibian population declines in the Sierra Nevada, California. Biol. Conserv. 69, 155-161.

Bradford D.F., Swanson C. and Gordon M.S. (1991) Acidic deposition in the Sierra Nevada - Effects of low pH and inorganic aluminum on two declining species of amphibians. Am. Zool. 31, 114A.

Bradford D, Swanson C. and Gordon M. (1992) Effects of low pH and aluminum on two declining species of amphibians in the Sierra Nevada, California. J. Herpet. 26, 369-377.

Bradford D, Swanson C. and Gordon M. (1994) Effects of low pH and aluminum on amphibians at high elevation in the Sierra Nevada, California. Can. J. Zool. 72, 1272-1279.

Brett M. (1989) Zooplankton communities and acidification processes (a review). Water Air Soil Pollut. 44, 387-414.

Brown D.J. (1982) The effect of pH and calcium on fish and fisheries. Water Air Soil Pollut. 18:343-351.

Brown D.J. (1983) Effect of calcium and aluminum concentration on the survival of brown trout (*Salmo trutta*) at low pH. Bull. Environ. Contam. Toxicol. 30:582-587.

Bruns D.A. and G.B. Wiersma (1988) Laboratory acidification of a crustacean zooplankton assemblage from a Rocky Mountain subalpine lake (U.S.A.) Environ. Toxicol. Chem. 6:807-814.

Carter J.C., W.D. Taylor, R. Chengalath, and D.A. Scruton (1986) Limnetic zooplankton assemblages in Atlantic Canada with special reference to acidification. Can. J. Fish. Aquat. Sci. 43:444-456.

Cooper S., Jenkins T. and Soiseth C. (1988) Integrated Watershed Study: An Investigation of Fish and Amphibian Populations in the Vicinity of Emerald Lake Basin, Sequoia National Park. Final Report to the C.A.R.B. Contract No. A4-122-32.

Cooper S., Kratz K., Holmes R. and Melack J. (1988) An Investigation of the Biota in the Emerald Lake System and Stream Channel Experiments. Final Report to the C.A.R.B., Contract No. A5-139-32.

Engle D. and J. Melack. (1995) Zooplankton of high elevation lakes of the Sierra Nevada, California: potential effects of chronic and episodic acidification. Arch. Hydrobiol. 133: 1-21.

Frost T.M. and P.K. Montz (1988) Early zooplankton responses to experimental acidification in Little Rock Lake, Wisconsin, USA. Verh. Int. Verein. Limnol. 23:2279-2285.

Hall R., G. Likens, S. Fiance and G. Hendrey (1980) Experimental acidification of a stream in Hubbard Brook Experimental Forest, New Hampshire. Ecology 61, 976-989.

Hall R., C. Driscoll and G. Likens (1987) Importance of hydrogen ions and aluminum in regulating the structure and function of stream ecosystems: An experimental test. Freshw. Biol. 18, 17-44.

Havas M. and T. Hutchinson (1983) Effect of low pH on the chemical composition of aquatic invertebrates from tundra ponds at the Smoking Hills, NWT. Canada. Can. J. Zool. 61, 241-249.

Havens K. and J. DeCosta (1985) The effect of acidification in enclosures on the biomass and population size structure of *Bosmina longirostris.* Hydrobiologia 122:153-158.

Havens K. and J. DeCosta (1987) The role of aluminum contamination in determining phytoplankton and zooplankton responses to acidification. Water Air Soil Pollut. 33:277-293.

Havens K. and J. DeCosta (1987b) Freshwater plankton community succession during experimental acidification. Arch. Hydrobiol. 111:37-65.

Havens K. and J. DeCosta (1988) An experimental analysis of the acid sensitivity of the common planktonic rotifer *Keratella cochlearis.* Int. Revue. ges. Hydrobiol. 73:407-416.

Hobaek A. and G. Raddum (1980) Zooplankton communities in acidified lakes in South Norway. SNSF Report IR 75/80. 132 pp.

Holze K.E. (1984) Effects of pH and ionic strength on aluminum toxicity to early developmental stages of rainbox trout (*Salmo gairdneri* Richardson). Ontario Ministry of the Environment, Quality Protection Section, Water Resources Branch, Rexdale, Ontario. 39 pp.

Hopkins P.S., Kratz K.W. and Cooper S.D. (1989) Effects of an experimental acid pulse on invertebrates in a high altitude Sierra Nevada stream. Hydrobiol. 171, 45-58.

Howells G.D., D.J. Brown and Sadler K. (1983) Effects of acidity, calcium, and aluminum on fish survival and productivity: A review. J. Sci. Food Agric. 34:559-570.

Ingersoll C. (1986) The effects of pH, aluminum and calcium on survival and growth of brook trout (*Salvelinus fontinalis*) early life stages. Ph.D. Thesis, Department of Zoology and Physiology, University of Wyoming, Laramie, WY. 122 pp.

Ingersoll C., D. Mount, D. Gulley, T. LaPoint and H. Bergman (1990) Effects of pH, aluminum, and calcium on survival and growth of eggs and fry of brook trout (*Salvelinus fontinalis*). Can J. Fish. Aquat. Sci. 47, 1580-1592.

Jenkins T., Knapp R., Kratz K. and Cooper S. (1993) Aquatic Biota in the Sierra Nevada: Current Status and Potential Effects of Acid Deposition on Populations. Final Report to the C.A.R.B., Contract No. A932-138.

Keller W. and J. Pitblado (1984) Crustacean plankton in northeastern Ontario lakes subjected to acidic deposition. Water Air Soil Pollut. 23:271-291.

Kratz K., Cooper S.D. and Melack J.M. (1994) Effects of single and repeated experimental acid pulses on invertebrates in a high altitude Sierra Nevada stream. Freshw. Biol. 32:161-183.

Leivestad H., I. Muniz and B. Rosseland (1980) Acid stress in trout from a dilute mountain stream, pp. 318-319. In: D. Drablos and A. Tollan, eds. Proceedings of the International Conference on the Ecological Impact of Acid Precipitation. SNSF Project, Oslo, Norway.

MacIsaac H., T. Hutchinson and W. Keller (1987) Analysis of planktonic rotifer assemblages from Sudbury, Ontario, area lakes of varying chemical composition. Can. J. Fish. Aquat. Sci. 44:1692-1701.

Malley D., D. Findlay and P. Chang (1982) Ecological effects of acid precipitation on zooplankton, pp. 297-327. In: F.M. D'Itri, ed. Acid Precipitation: Effects on Ecological Systems. Ann Arbor Science, Ann Arbor, MI.

Marmorek D.R. (1983) Effects of lake acidification on zooplankton community structure and phytoplankton-zooplankton interactions: An experimental approach. M.S. Thesis, Department of Zoology, University of British Columbia, Vancouver. 397 pp.

Marmorek D.R. (1984) Changes in the temporal behavior and size structure of plankton systems in acid lakes, pp. 23-41. In: G.R. Hendrey, ed. Early Biotic Respones to Advancing Lake Acidification. Butterworth, Boston.

Melack J., Cooper S., Holmes R., Sickman J., Kratz K., Hopkins P., Hardenbergh H., Thieme M. and Meeker L. (1987) Chemical and Biological Survey of Lakes and Streams Located in the Emerald Lake Watershed, Sequoia National Park. Final Report to the C.A.R.B., Contract No. A3-096-32.

Melack J., Cooper S., Jenkins T., Barmuta L., Hamilton S., Kratz K., Sickman J. and Soiseth C. (1989) Biological and Chemical Characteristics of Emerald Lake and Streams and Their Responses to Acidic Deposition. Final Report to the C.A.R.B., Contract No. A6-184-32.

Melack J., Sickman J., Setaro F., 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 C.A.R.B., Contract No. A932-060.

Roff J.C., and R. Kwiatkowski (1977) Zooplankton and zoobenthos communities of selected northern Ontario lakes of different acidities. Can. J. Zool. 55:899-911.

Sadler K., and S. Lynam (1987) Some effects on the growth of brown trout from exposure to aluminum at different pH levels. J. Fish. Biol. 31:209-219.

Scholfield C. and J. Trojinar (1980) Aluminum toxicity to brook trout (*Salvelinus fontinalis*) in acidified waters, pp. 341-366. In: T.Y. Toribara, M.W. Miller and P.E. Morrow, eds. Polluted Rain. Plenum Press, New York.

Siegfried C., J. Bloomfield and J. Sutherland (1989) Planktonic rotifer community structure in Adirondack, New York, USA. lakes in relation to acidity, trophic status and related water quality characteristics. Hydrobiologia 175:33-48.

Siegfried C., J. Sutherland, S. Quinn and J. Bloomfield (1984) Lake acidification and the biology of Adirondack lakes: I. Rotifer communites. Verh. Int. Ver. Limnol. 22:549-558.

Soiseth C.R. (1992) The pH and acid neutralizing capacity of ponds containing *Pseudacris regilla* larvae in an alpine basin of the Sierra Nevada. Calif. Fish. Game 78, 11-19.

Sprules W.G. (1975a) Factors affecting the structure of limnetic crustacean zooplankton communities in central Ontario lakes. Verh. Int. Ver. Limnol. 19:635-643.

Sprules W.G. (1975b) Midsummer crustacean zooplankton communities in acid-stressed lakes. J. Fish. Res. Board Can. 32:389-395.

Tessier A. and R. Horwitz (1988a) Analysis and interpretation of zooplankton samples collected during Phase II of the National Lakes Survey. Report 88-18, Academy of Natural Sciences of Philadelphia. 313 pp.

Tessier A. and R. Horwitz (1988b) Zooplankton community patterns and relationships to environmental paramenters in high elevation lakes of Maine. Report 88-25, Academy of Natural Sciences of Philadephia. 102 pp.

Turnpenny A., K. Sadler, R. Aston, A. Milner and S. Lynam (1987) The fish populations of some streams in Wales and northern England in relation to acidity and associated factors. J. Fish Biol. 31:415-434.

Williams M. and J. Melack (1991b) Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada. Water Resour. Res. 27:1575-1588.

Woodward D., A. Farag, M. Mueller, E. Little, and F. Vertucci (1989) Sensitivity of endemic Snake River cutthroat trout to acidity and elevated aluminum. Trans. Am. Fish Soc. 118:630-643.

Yan N.D. and R. Strus (1980) Crustacean zooplankton communities of acidic metal contaminated lakes near Sudbury, Ontario. Can. J. Fish. Aquat. Sci. 37:2282-2293.

Yan N.D. and W. Geiling (1985) Elevated planktonic rotifer biomass in acidified metal-contaminated lakes near Sudbury, Ontario. Hydrobiologia 120:199-205.

Yan N., C. Lafrance and G. Hitchin (1982) Planktonic fluctuations in a fertilized acidic lake: The role of invertebrate predators, pp. 132-154. In: R. Johnson (ed.) Acid Precipitation and Fisheries: Impacts in Northeastern North America. American Fisheries Society, Bethesda, Maryland.

Table 1. Studies showing harmful effects of Al on trout species.[a]

Reference	Type of study	Taxa	pH	Al (μM)	Result
Sadler & Lynam (1987)	Lab bioassay	brown trout	5.2	1.11	Significant reduction in fish growth
Turnpenny et al. (1987)	Field Survey	brown trout	---	1.48	Fish absent or rare in such streams in Wales and England
Holze (1984)	Lab Bioassay	rainbow trout	4.5	3.70	> 50% fry mortality
Brown (1983)	Lab Bioassay	brown trout	4.5-5.4	9.25	> 50% fry mortality
Scholfield & Trojnar (1980)	Field Study	brook trout	4.9	10.59	Stocking failure

[a]Adapted from Jenkins et al. (1993).

Table 2. Mean Al (μM) in lakes where trout are absent or present.

	Absent	Reproducing	Stocked
Golden*	1.016 (0.126)	0.489 (0.066)	0.995 (0.345)
Rainbow	0.871 (0.13)	0.758 (0.144)	1.198 (0.259)
Brook	0.915 (0.14)	0.792 (0.146)	1.115 (0.225)

*Differences between categories were significant based on one-way Kruskal-Wallis ANOVA (p = 0.023).

Table 3. Zooplankton species occurring in the Sierra Nevada that are known to be acid sensitive or acid resistant.[a]

Species	Response to low pH	Reference
Diaptomus signicauda	Decrease (pH 5.0)[b]	Melack et al. (1989)
Tropocyclops prasinus	Decrease (pH 4.7)	Havens & DeCosta (1985) Havens & DeCosta (1987b) Keller & Pitblado (1984) Malley et al. (1982) Roff & Kwiatkowski (1977) Sprules (1975 a,b) Tessier & Horwitz (1988a,b)
Daphnia rosea	Decrease (pH 5.0-5.3)	Marmorek (1983, 1984) Melack et al. (1989) Bruns & Wiersma (1988)
Conochilus unicornis	Decrease (pH 4.6)	Almer et al. (1974) Havens & DeCosta (1987a,b) Hobaek & Raddum (1980) Roff & Kwiatkowski (1977)
Keratella cochlearis	Decrease	Havens & DeCosta (1988) MacIsaac et al. (1987) Roff & Kwiatkowski (1977) Siegfried et al. (1984, 1989) Frost & Montz (1988)
Bosmina longirostris	Increase	Melack et al. (1989) Havens & DeCosta (1987a) Malley et al. (1982) Marmorek (1983, 1984) Keller & Pitblado (1984) Yan & Strus (1980)
Holopedium gibberum	Increase	Malley et al. (1982) Marmorek (1983, 1984) Keller & Pitblado (1984)
Keratella taurocephala	Increase	MacIsaac et al. (1987) Melack et al. (1989) Carter et al. (1986) Marmorek (1983, 1984) Roff & Kwiatkowski (1977) Siegfried et al. (1984, 1989) Yan & Geiling (1985)

[a]Adapted from Baker et al. (1991).
[b]Approximate pH threshold reported from experimental studies, referring either to a 48-h LC_{50} from single species toxicity experiments, or the approximate pH at which the species was eliminated during an acidification experiment.

Table 4. Information on lake pH obtained from seven high altitude lakes in the Sierra Nevada.[a]

Lake	Year	Months of greatest snowmelt discharge	Lowest pH observed in lake outflow	Lowest volume weighted mean lake pH	End of ice cover
Crystal Lake	1990	May-June-July	6.0 (repeated)	6.3 (June)	mid-May
	1991	May-June-July	5.6 (May)	5.9 (Apr)	end-May
Emerald Lake	1985	May-June	6.1 (May)	--------	---------
	1986	May-June-July	5.7 (June)	--------	---------
	1987	Apr-May-June	5.7 (May)	--------	---------
	1990	Apr-May-June	5.9 (May)	6.2 (June)	end-May
	1991	Apr-May-June	5.6 (May)	5.7 (Apr)	end-May
Lost Lake	1990	Apr-May-June	5.7 (Apr)	5.8 (June)	end-May
	1991	May-June	5.5 (June)	5.5 (Apr)	mid-June
Pear Lake	1990	Apr-May-Jun-July	5.8 (May)	6.2 (June)	mid-May
	1991	May-June-July	5.5 (May)	5.6 (Apr)	end-June
Ruby Lake	1990	June-July-Aug	6.2 (June)	6.1 (June)	end-May
	1991	June-July-Aug	5.8 (June)	5.8 (Apr)	end-June
Spuller Lake	1990	June-July	6.1 (June)	6.1 (June)	end-May
	1991	June-July	5.7 (June)	5.8 (July)	end-June
Topaz Lake	1990	Apr-May-June	6.1 (June)	5.9 (June)	mid-May
	1991	May-June	5.6 (July)	5.6 (Apr)	end-June

[a]Data obtained from Melack et al. (1993).

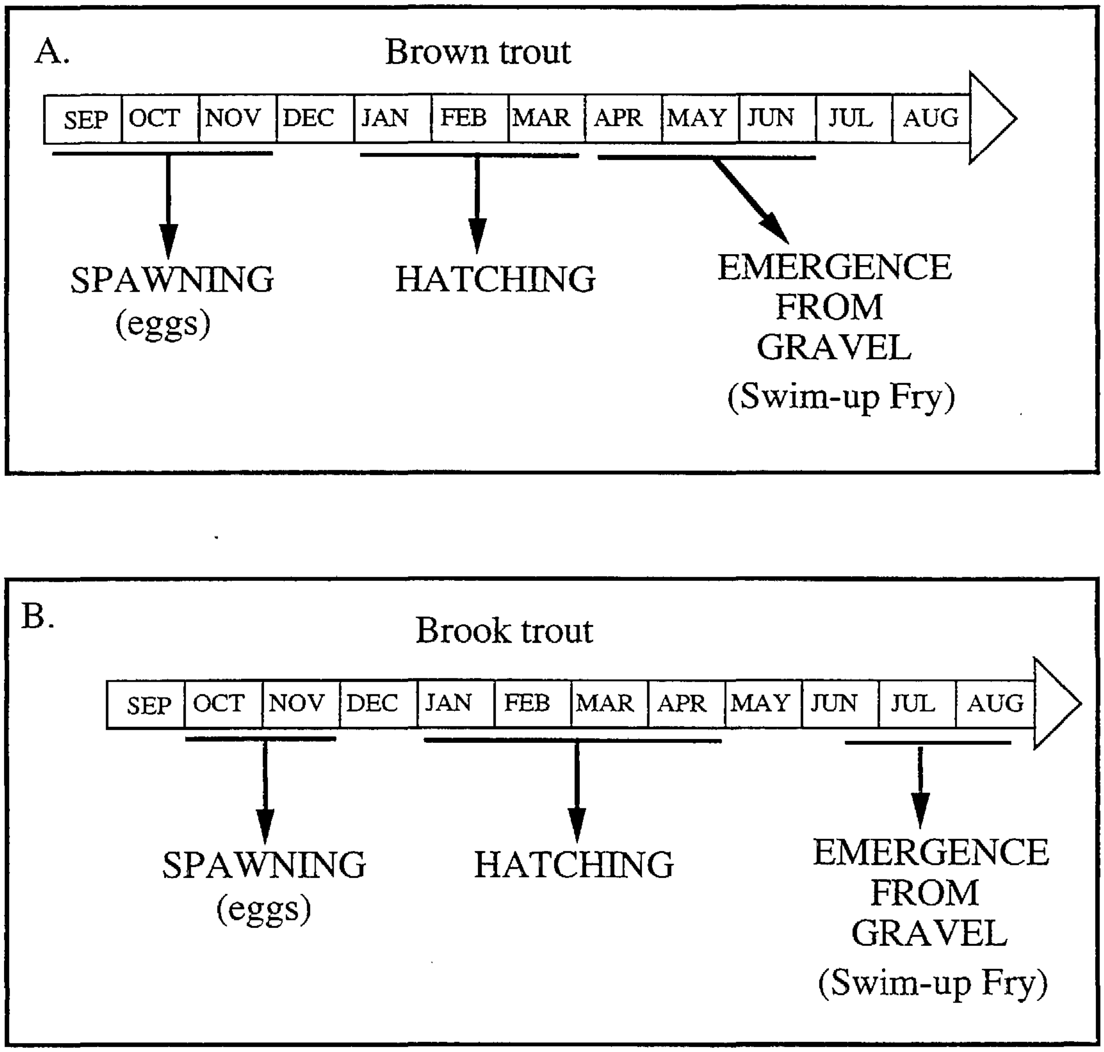

Figure 1. Timing of the occurrence of early life stages of fall-spawning trout of the Sierra Nevada. A. Brown trout (*Salmo trutta*). B. Brook trout (*Salvelinus fontinalus*).

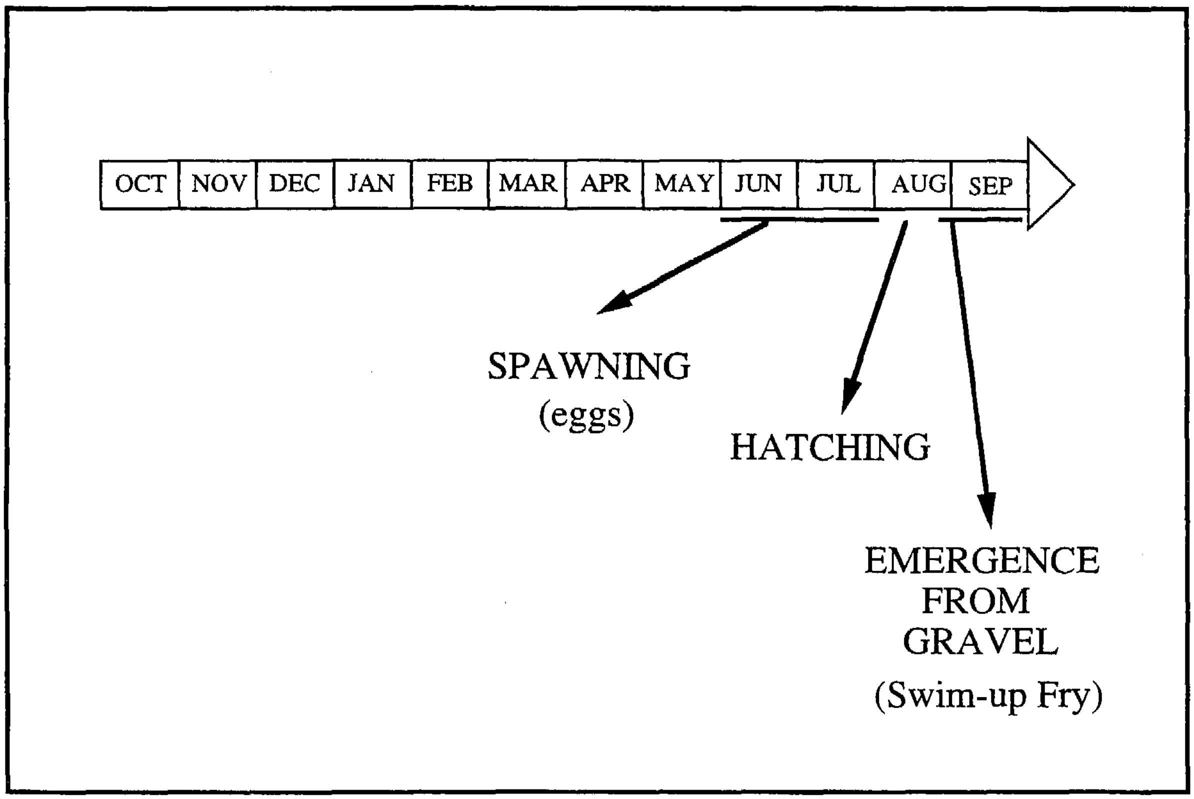

Figure 2. Timing of the occurrence of early life stages of spring-spawing trout of the Sierra Nevada. Spring-spawning trout of the Sierra Nevada include *Oncorhynchus aguabonita* (golden trout), *O. mykiss* (rainbow trout), and *O. clarki* (cutthroat trout).

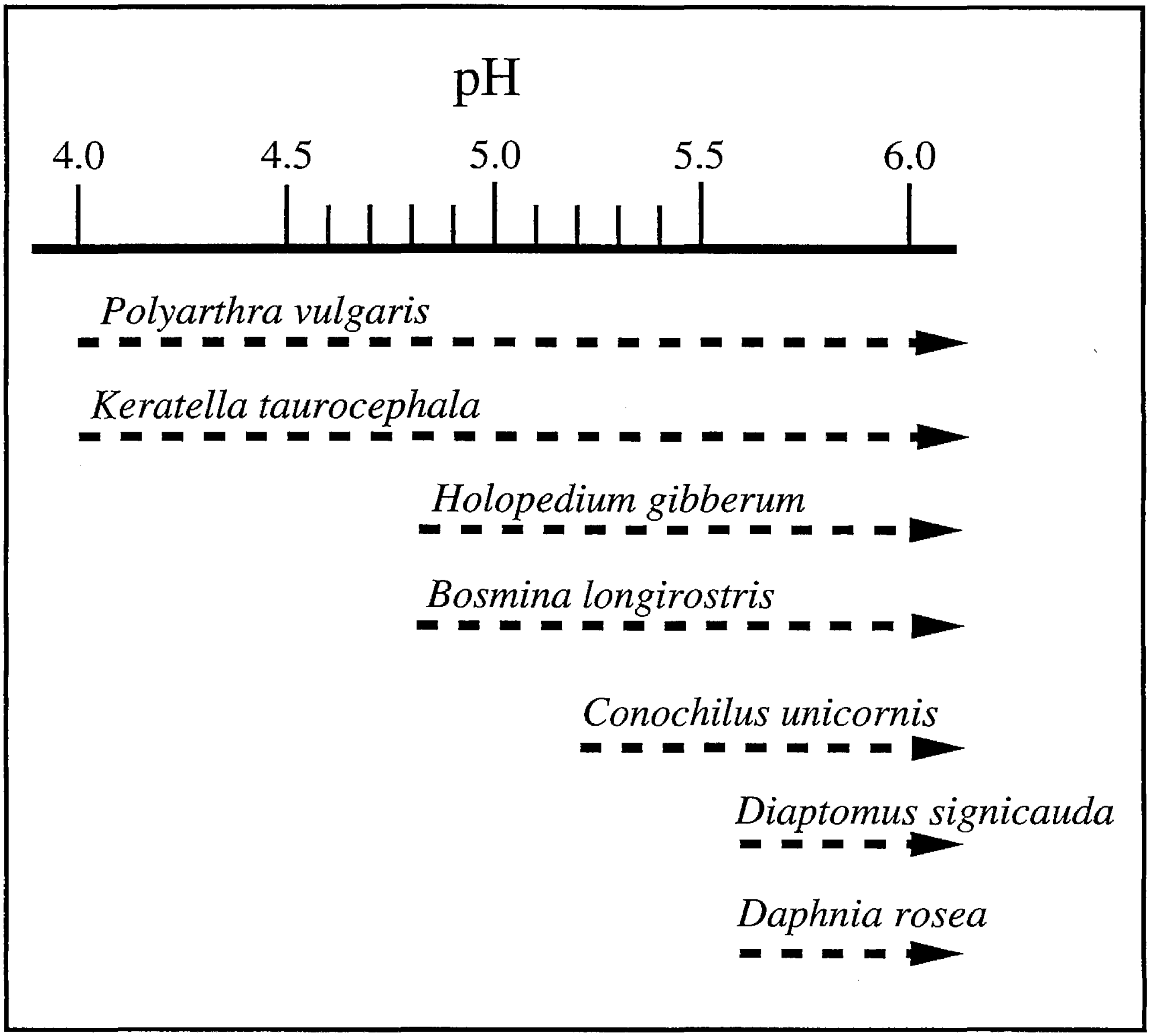

Figure 3. Ranges of pH tolerance for important Sierra Nevada zooplankton species.

PART 7

RECOMMENDATIONS FOR FUTURE MONITORING

Recommendations for future monitoring

We recommend a limited program of continued monitoring of the hydrochemistry and biology of high elevation Sierra Nevada watersheds. The intent of continued monitoring would include the detection of future changes in levels of precipitation-borne acidity, or in the ANC of surface waters, at well-studied sites. However, it may occur that atmosphere-related changes in the hydrochemistry and biology of Sierra Nevada watersheds will be more related to future delivery rates of nutrient elements (such as nitrate and ammonium), than to future delivery rates of acidity per se. Such changes may affect rates of biogeochemical processes in both the terrestrial and aquatic portions of watersheds, and may indirectly alter the trophic status and species composition of surface waters. Thus a program limited to the measurement of ANC and pH of precipitation and surface water would be too narrowly designed. Although CARB-sponsored lake and precipitation sampling has not revealed inter-annual trends in biological or chemical parameters in the Sierra Nevada to date, the detection of subtle changes in the chemical and/or biological functioning of watersheds has in the past occurred after sampling across more than two decades, rather than several years (e.g. Hubbard Brook and Lake Tahoe).

High elevation precipitation. We recommend that snow and rain continue to be monitored at at least five high elevation stations between Lake Tahoe and Mineral King. Both precipitation quantity and chemistry (pH, alkalinity, conductivity, base cations, nitrate, sulfate, chloride and silicate) should be measured.

High elevation watersheds. We recommend that hydrology and solute export (pH, alkalinity, conductivity, base cations, nitrate, sulfate, chloride and silicate) continue to be monitored year-round at two high elevation sites in the Sierra Nevada, each of which should consist of guaged streams at the outlet of lakes for which a record of hydrology and hydrochemistry already exist. One of the sites should be located on the east slope of the central Sierra Nevada (i.e. Spuller Lake). The other site should be located on the western slope of the southern Sierra Nevada (i.e. Emerald Lake).

Lake surveys. We recommend that annual surveys of autumn surface chemistry be carried out for a group of at least ten of the high elevation lakes than have been sampled since the early 1980s. These lakes should include any of the following lakes (see Appendix 2.2 in this report for lake locations and sampling history): Spuller Lake, Gaylor Lake, Granite Lake, Crystal Lake, Ruby Lake, Upper Treasure Lake, Gem Lake, Monarch Lake, Aster Lake, Topaz Lake, Pear Lake, Emerald Lake, Heather Lake, and Upper Mosquito Lake. These lakes have the most consistent records of autumn synoptic sampling, and many were first sampled in 1983. Care should be taken that the lakes are visited after the cessation of snowmelt and when the lakes are experiencing fall overturn. Homothermy should be confirmed at the time of sampling by depth profiles of dissolved oxygen and temperature. Duplicate vertical tows for zooplankton should be carried out, however the samples should be used to generate presence/absence data rather than abundance data.