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Monitoring of Wet Deposition in Alpine Areas in the Sierra Nevada

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Monitoring of Wet Deposition in Alpine Areas in the Sierra Nevada

Final Report

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precipitation averaged 22.3 μEq L^{-1} (STD, 22.7).. Spring storms had the lowest nitrate levels, averaging 17.3 μEq L^{-1} (STD, 16.9).

Summer rains had sulfate levels that averaged 26.8 μEq L^{-1} (STD, 19.9) during the years of study. Sulfate was significantly lower in spring and autumn precipitation means, 16.4 and 14.0 μEq L^{-1}, respectively (STDs, 12.3 and 14.3).

Mean concentrations of acetate and formate in summer rains were ca. 12 to 14 μEq L^{-1} and mean values measured in spring and autumn precipitation were on the order of 3 to 5 μEq L^{-1}, respectively. High levels of organic anions occurred in small (less than 5 mm) summer storms and exceeded 60 μEq L^{-1} on numerous occasions.

Mean annual hydrogen ion deposition at the study sites ranged from 24.1 Eq ha^{-1} to 60.9 Eq ha^{-1}. At the majority of stations and during most years, deposition of hydrogen was greater in winter than in non-winter seasons.

For ammonium, average annual loading varied from 21.6 Eq ha^{-1} to 58.4 Eq ha^{-1}. Mean nitrate deposition ranged from 22.4 Eq ha^{-1} to 53.7 Eq ha^{-1}. For sulfate, average annual deposition ranged from 16.9 Eq ha^{-1} to 44.5 Eq ha^{-1}.

Average annual deposition of calcium varied from 14.6 Eq ha^{-1} to 38.6 Eq ha^{-1}. Sodium deposition ranged from 4.8 Eq ha^{-1} to 27.8 Eq ha^{-1}. Deposition of magnesium and potassium on an annual basis ranged from 2.9 to 11.0 Eq ha^{-1}. The amount of acetate and formate deposition at most sites was similar and ranged from 2.2 Eq ha^{-1} and 19.1 Eq ha^{-1}, respectively.

Abstract

The quantity and chemical composition of precipitation in the Sierra Nevada was monitored at high elevation stations during the period of 1990 through 1995. From 1990 through 1993, eleven sites were included in the network. For 1994 the number was seven and during the spring of 1995, the snowpack was sampled at six stations. During the course of the study a total of 1546 snow samples were collected from 225 snowpits and an additional 514 non-winter precipitation events were sampled. All major solutes in wet deposition were measured and a rigorous quality assurance-quality control protocol was followed.

The amount of winter precipitation during the study was variable (range ca. 250 to 3000 mm). Winter precipitation accounted for the majority of the input of water to high elevations of the Sierra Nevada. Non-winter precipitation events ranged in size from trace amounts to over 100 mm. The annual amount of non-winter precipitation in the Sierra Nevada varied widely (range ca. 10 to 200 mm).

Snow chemistry was similar among the six years of study and among the sampling stations. Samples from the spring snowpack had pH levels typically between 5.3 and 5.6 (hydrogen concentration, 2 to 4 μEq L^{-1}). After hydrogen ion the most abundant solutes were ammonium and nitrate with concentrations usually 1.5 to 4.5 μEq L^{-1}. Sulfate concentrations ranged from ca. 1.0 to 3.0 μEq L^{-1}. Organic anions (acetate and formate) were usually found in low concentrations (i.e. < 0.5 μEq L^{-1}). The specific conductance of snow in the Sierra Nevada was usually between 2 and 4 μS cm^{-1}.

The mean pH of summer rain in the Sierra Nevada measured during the study period was 4.65. The lowest pH measured during this period was 3.86. The range of pH in spring and autumn storms was 4.4 to 6.0 with mean values of 5.05 for spring storms and 5.00 for autumn storms.

Spring storms had a mean ammonium concentration of 18.9 μEq L^{-1} (standard deviation (STD), 14.2; N = 67)) and range of 1.1 to 80 μEq L^{-1}. The mean ammonium concentration in summer storms was 36.5 μEq L^{-1} (STD, 27.1; N = 365) and ranged up to ca. 160 μEq L^{-1}. Mean ammonium concentration in autumn storms was 28.1 μEq L^{-1} (STD, 33.8; N = 82) and ranged from ca. 1.0 to 160 μEq L^{-1}.

Mean nitrate concentration in summer rain was 36.4 μEq L^{-1} (STD, 26.3) and samples with levels over 40 μEq L^{-1} were common. Nitrate concentrations in autumn

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nitrate and ammonium levels and higher than chloride. Of the remaining solutes, only calcium and sodium were found to have concentrations much above the detection limit. Organic anions (acetate and formate) were difficult to measure in the Sierran snowpack and were usually found in low concentrations (i.e. < 0.5 µEq $L^{-1)}$. Snow chemistry from stations in the southern Sierra had slightly higher solute concentrations than stations in the northern Sierra.

The amount of winter precipitation during the study was variable. The winters of 1989-90 and 1991-92 were relatively dry (snow-water equivalence range, ca. 250 to 1000 mm). The winter of 1990-91 had nearly normal precipitation (snow-water equivalence range, ca. 500 to 1500 mm) and the winters of 1992-93 and 1994-95 were wetter than normal (snow-water equivalence range, ca. 1000 to 3000 mm). Stations in the northern and western Sierra Nevada received more winter precipitation than stations in the southeastern portion of the range. Winter precipitation accounted for the majority of the input of water to high elevations of the Sierra Nevada.

Non-winter Precipitation

Non-winter precipitation chemistry was variable, with solute concentrations ranging from near detection limits to levels in the tens of microequivalents per liter. Most of the variability is associated with the timing of the precipitation; spring and autumn storms being most dilute and summer rains being enriched with solutes. The annual volume-weighted mean concentration of non-winter precipitation depended on the mix of samples (i.e. spring, summer or autumn) obtained. Spring and autumn precipitation derived from large-scale Pacific weather systems and from localized thunderstorms. Summer rains were derived exclusively from local air masses during afternoon convective storms.

Non-winter precipitation events ranged in size from trace amounts to over 100 mm. Summer storms tended to be small (mean, 7.1 mm) and lasted only a few hours. Spring storms, being a combination of snow and rain, were typically larger (mean, 10.2 mm). Autumn storms ranged in size from a trace to as much as 130 mm and were on average twice as large as summer storms (mean, 14.9 mm). The annual amount of non-winter precipitation in the Sierra Nevada varied widely. Ranking the years of study, 1992 was the wettest (precipitation ca. 90 to 200 mm) and 1993 the driest (precipitation ca. 13 to 100 mm). Almost no precipitation was measured in the Sierra Nevada during the spring and summer of 1993.

Summary and Conclusions

The quantity and chemical composition of precipitation in the Sierra Nevada was monitored at high elevation stations during the period of 1990 through 1995. Eleven stations were monitored from 1990 to 1993, seven in 1994 and winter snowfall was sampled at six sites in the spring of 1995. The main purpose of the study was to measure the loading of solutes that may acidify the surface waters of these mountains. Wet atmospheric deposition of solutes was measured by event collections of spring, summer and autumn precipitation and by sampling the aggregate of winter precipitation in the snowpack in early spring (i.e. maximum accumulation). All major solutes in wet deposition were measured and a rigorous quality assurance-quality control protocol was followed.

The monitoring network consisted of the following stations from 1990 through 1993: Alpine Meadows, Angora Lake, Sonora Pass, Tioga Pass, Mammoth Mountain, Eastern Brook Lake, Kaiser Pass, South Lake, Onion Valley, Emerald Lake and Mineral King. During 1994 the number of stations was reduced to seven for rain and seven for snow and included Emerald Lake, Kaiser Pass, Mineral King, Tioga Pass, Mammoth Mountain, Eastern Brook Lake, Angora Lake (rain only) and Alpine Meadows (snow only). During the spring of 1995, snow surveys were conducted at Emerald Lake, Kaiser Pass, Tioga Pass, Mammoth Mountain, Eastern Brook Lake. Because of road damage we were unable to travel to the Mineral King Valley in the spring of 1995. Due to a freezer malfunction the samples from Eastern Brook were lost. Snow surveys from Ruby Lake were substituted for the lost data from Eastern Brook. For 1995, snow survey data from Topaz Lake included to make up for missing data from Mineral King..

The elevation of the study sites ranged from ca. 2000 to over 3000 meters ASL. The network spanned nearly the entire north-south extent of the Sierra Nevada and stations were located on both the western and eastern flanks of the range.

Winter Snow

Snow chemistry was similar among the four years of study and among the sampling stations. Samples from the spring snowpack had pH levels typically between 5.3 and 5.6. After hydrogen ion the most abundant solutes were compounds of nitrogen (ammonium and nitrate) with concentrations usually between 1.5 to 4.5 $\mu Eq\ L^{-1}$. Sulfate concentrations (ca. 1.0 to 3.0 $\mu Eq\ L^{-1}$) in Sierran snow tended to be slightly less than

Sulfate levels in non-winter precipitation were slightly lower than nitrate. Summer rains had the highest sulfate values and averaged 26.8 μEq L^{-1} (STD, 19.9) during the five years of study. However, in contrast to nitrate and ammonium, sulfate was lower in autumn precipitation (mean, 14.0 μEq L^{-1}; STD, 14.3) than in spring storms (mean, 16.4 μEq L^{-1}; STD, 12.3).

Seasonal changes in base cation levels (calcium + magnesium + sodium + potassium) of non-winter precipitation were similar to those for other solutes. Summer rains had the highest levels, with base cations ranging from 20 to over 200 μEq L^{-1} and a mean concentration of 33.8 μEq L^{-1} (STD, 43.0). Base cation concentrations in spring and autumn storms were similar and less than those in summer rain, averaging 19.7 and 22.1 μEq L^{-1} respectively (STD's, 23.4 and 32.6 respectively). During the course of the study, several storms had high levels of base cations i.e. greater than 200 μEq L^{-1}. These events were small storms generally less than 5 mm in size with the majority of them occurring at Tioga Pass and Mammoth Mountain.

Seasonal variability of acetate and formate was large. Mean summer concentrations (sum of acetate plus formate) were three times as large (26.3 μEq L^{-1}; STD, 26.0) as values measured in spring and autumn precipitation (8.6 and 8.7 μEq L^{-1}, respectively; STD's 8.9 and 12.9). Overall formate exceeded acetate in non-winter precipitation in the Sierra Nevada. High levels of organic anions usually occurred in small (less than 5 mm) summer storms and exceeded 60 μEq L^{-1} on numerous occasions.

Solute Loading

For the period of 1990-94, the average annual hydrogen deposition at the study sites ranged from 24.1 Eq ha^{-1} to 60.9 Eq ha^{-1}. The stations with the least hydrogen deposition were located in the southern and south-eastern Sierra and those with the most loading of hydrogen were in the northern and central Sierra. The dose of hydrogen received at a station was strongly affected by the amount of snowfall received in the winter and, at the majority of stations and during most years, deposition of hydrogen was greater in winter than in non-winter seasons.

Along with hydrogen, most deposition of chloride, sodium and potassium occurred during the winter at most stations. For the five years of study, non-winter loading of chloride comprised less than 37% of annual deposition. For sodium and potassium, non-winter precipitation contributed less than 50%.

Chemistry of non-winter precipitation was different among the three seasons (i.e. spring, summer and autumn) and much of the differences are related to storm size. Small storms more commonly had high solute concentrations and large storms had relatively dilute chemistry.

Summer rain had the lowest pH of any non-winter precipitation; pH ranged from less than 4.0 to near 6.0. The mean pH of summer rain in the Sierra Nevada measured during the study period was 4.65. The lowest pHs measured during the study period were a pH of 3.86 from an 8.4 mm storm at Eastern Brook Lake on August 16, 1992 and a pH of 4.01 from a small storm (1.4 mm) at South Lake on August 2, 1993. The range and mean pH of spring and autumn storms was similar. Values ranged from 4.4 to 6.0 with mean values of 5.05 for spring storms and 5.00 in autumn storms.

Large differences in ammonium levels were found among the three types of storms. Spring storms had a mean ammonium concentration of 18.9 μEq L^{-1} (STD, 14.2) and a range of 1.1 to 80 μEq L^{-1}. The mean concentration in summer storms was 36.5 μEq L^{-1} (STD, 27.1) and ranged up to ca. 160 μEq L^{-1}. Samples with concentrations above 60 μEq L^{-1} constituted about 30% of all summer rain samples collected. Moderate levels of ammonium were typically found in autumn storms. While the mean concentration was 28.1 μEq L^{-1} (STD, 33.8), very few samples had values greater than 40 μEq L^{-1}. The range of ammonium concentration in autumn storms was 1.0 to 160 μEq L^{-1}.

The seasonal differences in chloride concentrations were similar to those for ammonium. Summer storms had the highest levels of chloride (mean, 6.0 μEq L^{-1}; STD, 5.7) followed by spring and autumn storms (means, 3.2 and 3.3 μEq L^{-1} respectively). Concentrations in summer rains were as high as 50 μEq L^{-1}. Typical spring and autumn storms had chloride levels less than 5 μEq L^{-1}.

Nitrate was one of the major constituents of non-winter precipitation. Mean concentration in summer rain was 36.4 μEq L^{-1} (STD, 26.3), and samples with levels over 40 μEq L^{-1} were common. Nitrate concentrations were significantly lower in autumn precipitation with a mean value of 22.3 μEq L^{-1} (STD, 22.7) and relatively few samples with values over 40 μEq L^{-1}. Spring storms had the lowest nitrate levels, averaging 17.3 μEq L^{-1} (STD, 16.9). Only a handful of spring storms had nitrate greater than 40 μEq L^{-1}.

Recommendations

1. We recommend that monitoring of wet deposition be continued in the Sierra Nevada. This includes monitoring of the winter snowpack at maximum accumulation. Because of seasonal and interannual variability in non-winter precipitation chemistry and quantity, many years of data will be necessary to detect changes in non-winter precipitation chemistry brought about by anthropogenic activities (i.e. acid deposition, climate change etc..). Trends in snow chemistry should be easier to detect given the less variable nature of this type of precipitation in the Sierra Nevada.

2. Dry deposition should be monitored in high elevations of the Sierra Nevada. Dry deposition is likely a significant component of the annual flux of compounds to the Sierra Nevada.

Ions such as the organic anions, ammonium, nitrate and sulfate typically had higher rates of deposition during non-winter periods. For most years, non-winter loading comprised from ca. 50% to 60% of the annual loading of nitrogen and sulfate and from about 60% to 80% of the annual deposition of acetate and formate.

For ammonium the range of average loadings varied from 21.6 Eq ha^{-1} to 58.4 Eq ha^{-1}. Mean nitrate deposition was lower than ammonium loading at 7 out of 11 sites and ranged from 22.4 Eq ha^{-1} to 53.7 Eq ha^{-1}. For sulfate, average annual deposition ranged from 16.9 Eq ha^{-1} to 44.5 Eq ha^{-1}. Average annual sulfate deposition was lower than nitrate loading overall, but was equal to or higher than nitrate deposition at 9 of the 11 stations during 1993.

Average annual deposition of calcium varied from 14.6 Eq ha^{-1} to 38.6 Eq ha^{-1}. Sodium deposition was lower, ranging from 4.8 Eq ha^{-1} to 27.8 Eq ha^{-1}. Deposition of magnesium and potassium on an annual basis ranged from 2.9 to 11.0 Eq ha^{-1}. For the organic anions, the amount of acetate and formate deposition at most sites was similar and averaged 2.2 Eq ha^{-1} and 19.1 Eq ha^{-1}, respectively.

The northern Sierra Nevada generally received more loading of solutes than the southern Sierra. This is a result of higher rates of both winter and non-winter precipitation in the north. However, loading of solutes per unit of precipitation is greater in the southern Sierra because of higher solute concentrations in winter and non-winter precipitation.

2. Quantified the year-to-year variability in concentrations and loading of solutes in wet deposition during this period.

3. Estimated the regional differences of wet deposition using data from our monitoring program and related data collected by others.

4. Provided atmospheric inputs to models of acidification in Sierran lakes and streams (e.g. Wolford and Bales 1996).

In addition to the above accomplishments, we developed a rigorous set of quality control and assurance results that guaranteed the credibility of our data. These QA/QC results are needed to properly interpret the deposition data from the monitoring network.

Description of Sampling Network

All stations in the network were located in the Sierra Nevada of California (Table 1). The stations spanned nearly the entire north-south extent of the range from southern Sequoia National Park to the north shore of Lake Tahoe, and stations were located on both western and eastern slopes of the Sierra. All study sites were located in National Forests or National Parks.

Sites were accessed in the winter by a combination of snowmobile and skiing. During other times of year, access was accomplished by car and short hikes on established trails. All stations were located near or at timberline. Samples were collected at elevations ranging from just over 2000 meters near Lake Tahoe to over 3000 meters in the east-central Sierra Nevada.

The Alpine Meadows station was located in the Tahoe National Forest and within the Alpine Meadows ski area. Rain was collected on the roof of the terminal building of the Alpine Bowl chairlift. The chairlift was not used during the operational period of the rain collector. The collector was five meters off the ground and 10 meters from a dirt road that receives very light traffic. The vegetation was sparse, mixed subalpine forest. The exposure was east-northeast. Snow was sampled approximately 3 km south, out-of-bounds of the ski area in an area know locally as SP Bowl. The snow was sampled on a small knob that has generally east-southeast exposure. The knob was open but the hillsides have mixed subalpine forest. The elevation of the rain collection station was 2,164 meters.

Chapter I

Introduction

As evidence for acidic deposition in California and its potential consequences has increased (California Air Resources Board 1988), the chemical and biological conditions in the lakes and streams of the Sierra Nevada have become special concerns. Most of the precipitation to the Sierra Nevada falls as dilute snow. When combined with the more acidic summer rain, annual volume-weighted mean pH values are between 5.2 and 5.5 (Dozier et al. 1989, Melack and Stoddard 1993). Experimental acidification of stream channels and enclosures in Emerald Lake indicate major biological changes at pH values of 5.5 (Cooper et al. 1988, Melack et al. 1989, Melack et al. 1993). Under current atmospheric deposition, pH values in the streams and lakes in the High Sierra fall to between 5.8 and 5.6 during snowmelt (Melack et al. 1996).

Regional patterns of atmospheric deposition in the Sierra Nevada are not well understood because of the inadequate number of monitoring sites and their location at moderate elevations, the strong influence of topographic relief on the amount of precipitation and importance of dry deposition during the summer. At high elevations (greater than 2500 m) snowfall accounts for the majority of the input of water (Melack et al. 1996) and the snowpack accumulates through the winter without much melt until March or April. Hence, regional surveys of snow depth and density in late winter or early spring permit reliable estimation of the contribution of snow to the annual deposition of water (e.g. California Cooperative Snow Survey).

Before deposition standards can be set to protect watersheds and lakes of the Sierra Nevada from changes caused by acidic deposition, long-term monitoring of atmospheric deposition and ecosystem responses are needed throughout the Sierra. The major component of these requirements is the monitoring of wet deposition of solutes to high-elevations. Thus, the primary objective of our study was to determine the wet deposition of solutes to high-elevations in the Sierra Nevada. To determine this component we conducted a monitoring program that:

1. Accurately measured the dose or loading of solutes that may acidify or help ameliorate acidification in the dilute waters of the Sierra Nevada during the years 1990, 1991, 1992, 1993, 1994 and during the winter of 1995.

northwestern exposure. In the summer, maintenance vehicles use dirt roads within 100 m of the site on a daily basis. A fuel pumping station is located adjacent to the Mid-Chalet building. During the winter, high levels of traffic access the ski area approximately 1 km and 1500 m below the site. The town of Mammoth Lakes lies 4 km east of the station.

Rain was collected at Eastern Brook Lake in a small clearing just upslope and west of the outlet of upper Eastern Brook Lake. The elevation of the site was 3,170 m. Eastern Brook Lake lies in the Rock Creek Canyon of the Inyo National Forest near the edge of the John Muir Wilderness. The collector was mounted on a platform, approximately 7 meters above the ground. The vegetation was mixed conifer forest and even allowing for the elevated height of the collector, the clearing size was slightly smaller than NADP guidelines suggest. The site was generally level with an eastern exposure and was over a ridge approximately 1 km from the trailhead parking lot. Snow was sampled in the inlet meadow of upper Eastern Brook Lake. The vegetation here was meadow grasses and sedges with some willow. The winter road closure varies from 8-12 km away.

Kaiser Pass is near Huntington Lake on the western slope of the Sierra Nevada. The rain collector was located east of and slightly downslope from a point known as White Bark Vista Point. An undeveloped dirt road branches from the Kaiser Pass road and leads to within 200 m of the rain collector. The site was sparsely forested with Western White Pine, Lodgepole Pine and Juniper and on a west facing slope. Snow was sampled near the ridgetop, 200 m upslope from the rain collector. The station was located in the Sierra National Forest at an elevation of 2,941 m.

South Lake is located 25 km southwest of Bishop California on the eastern slope of the Sierra Nevada within the Inyo National Forest. Rain was collected on a small knob, above and approximately 50 meters north of the trailhead parking and at an elevation of 3,100 meters. The site was rocky with low pine and shrub vegetation. The collector was located on a knob which was east facing. Snow was sampled on relicted lake bottom along the eastern shore of South Lake. The nearby vegetation was mixed conifer forest. The site was generally level, with a slight west exposure. The road was closed in the winter approximately 8 km away.

Onion Valley is located directly east of Independence, California, on the way to Kearsarge Pass within the Inyo National Forest. Rain was collected approximately 50 meters past the end of the Onion Valley Road, adjacent to the Cooperative Snow Survey hut at an elevation of 2,800 meters. It was an open site, with mixed meadow and montane

The rain collector at Angora Lake was located adjacent to the Angora Lakes resort at an elevation of 2,286 meters. Snow samples were collected at Lost Lake which was 3 kilometers east and 189 meters higher than Angora Lake. The rain collector was located in a small clearing about 100 meters east of the outlet to Upper Angora Lake. The terrain around the collector was predominantly east facing and was sparsely forested. The Lost Lake watershed, located in the Desolation Wilderness of Eldorado National Forest, was a small north-facing cirque, sparsely forested with Hemlock, Lodgepole Pine and Western White Pine. During the summer, the ten or so cabins around Angora Lake are occupied by tourists and the lake is a popular spot for swimming and picnics. The dirt road leading up to the lake is closed to the public and visitors must walk about 1 km from an unpaved parking lot to reach the resort. The resort is operated from late May until mid-September and is located in the Eldorado National Forest.

At the Sonora Pass station, rain was collected on top of a small ridge approximately 2 km northeast of Sonora Pass, at an elevation of 2,937 meters in the Toiyabe National Forest. A lightly traveled dirt road was 30 meters below the site. The site was near treeline with sparse grass and low shrub vegetation. The site was level with an eastern exposure. Snow was sampled in an adjacent meadow where vegetation was grass, sedge and willow. The site sloped gently with an eastern exposure. Winter road closure was approximately 6 km away and considerably downslope.

The Tioga Pass station consisted of a rain collector located at the Carnegie Research Station in the Hall Research Natural Area. This region is administered by the Inyo National Forest. The site was at the bottom of a valley near Lee Vining Creek, and the station was surrounded by a large meadow. The terrain was almost flat with a southeastern exposure. The rain collector was at an elevation of 2,993 meters. Snow samples were collected in the Spuller Lake watershed situated 1.5 km south-southwest from the Carnegie Station. The watershed is a modest-sized cirque ranging in elevation from 3,131 m to 3,668 m with a predominantly southeastern aspect. The watershed is completely devoid of trees, and vegetation is confined to a small meadow at the inlet to the lake.

At the Mammoth Mountain station, rain and snow were collected at the same site, a small knoll approximately 200 m east of the Mid-Chalet building at Mammoth Mountain Ski Area. The station was situated at an elevation of 2,940 m within the Inyo National Forest. The rain collector was mounted on a platform 7.5 m above the ground. The site was rocky, near treeline, with scattered Western White Pine. The site was level with a

Chapter II

Methods for Chemical and Physical Measurements of Precipitation

Snowpack Sampling and Analyses

Samples of snow were collected from pits which were dug to the ground, by hand, using plastic, aluminum or steel shovels. During the six years of the study snowpits ranged in depth from less than 1 meter to over 6 meters in depth. Once the pit was dug, a vertical wall was created on a portion of the pit (using a plastic shovel) which was not exposed to direct sunlight. All snowpack measurements and samples were taken from this wall. Snowpack sampling coincided with the period of maximum snow accumulation which was usually in early April.

At each study site two pits located side by side were sampled. The locations for these pits were chosen after extensive depth-probing at each site, and the pits were located at points where the snow depth was representative of the larger probed area. Pits were located away from vegetation and exposed rocks. For the majority of the study sites the snowpits were dug in nearly the same location all six years. A total of 225 snowpits were sampled during the course of the study.

In order to estimate snow-water equivalence (SWE) for each study site, snow density and snow depth were determined. Snow density was measured in vertical 10 cm intervals in each pit using a wedge shaped, stainless steel cutter and portable electronic balance. All cutters sampled 1000 cubic cm of snow and were calibrated to have less than 1% error in volume. To collect a sample for weighing, the cutter was pushed into the wall of the pit until it was filled with snow. A flat metal blade was used to cut a wedge of snow from the pack. The weight of the snow was then measured on the balance (tared for the cutter weight). Since the volume of the cutter was 1 liter, the density (gm L^{-1}) of the snow sample was its weight in grams.

Great care was taken not to push the cutter in beyond the point of fullness since this would compact the snow and cause an overestimation of density. Conversely, we also made sure the cutter was completely filled since pockets of air would result in underestimating snow density. Measurements were made through the entire depth of the snowpack. In almost all of the pits two density profiles were measured.

chaparral vegetation. The elevation was 2,800 meters. Mixed conifer forest starts approximately 100 meters upslope. The slope was very slight, southeast facing. The collector was located on the ground. Snow was sampled adjacent to Heart Lake which was several kilometers up the Kearsarge Pass trail. The site was at least 8 km from the typical winter road end and was near timberline with scattered Western White Pine and willow vegetation. The site was gently sloping and generally north facing with an elevation of approximately 3,150 meters.

Emerald Lake is located in the western portion of Sequoia National Park in what is known as the Tokopah Valley. The rain collector was situated 50 m east and upslope from the lake. Emerald Lake is located in a modest size, west-facing cirque. The basin is granitic, with sparse vegetation which includes scattered Lodgepole and Western White pine, willows and sedges. The nearest road to Emerald Lake is Highway 198 located 6 km away. Snow was collected nearby the rain collector and at various stations throughout the Emerald Lake basin. The elevation of the watershed ranges from 2,800 m to 3,416 m; the altitude of the collector was approximately 2,824 meters.

The most southern station, Mineral King, is named for the Mineral King Valley of Sequoia National Park. The valley lies in the extreme southern portion of the Park. Rain and snow were collected at a spot known as Groundhog Meadow. It was situated in the bottom of a narrow valley adjacent to Monarch Creek. Vegetation surrounding the collector was predominantly high-elevation chaparral including sagebrush and manzanita. The collector sat on a small, flat hill in an otherwise west-facing canyon. Within the Mineral King Valley are several privately owned cabins and Park Service campgrounds. The unpaved road leading into the valley was about 4 km distant from the rain collector and closed between November and May during most years.

separation column, a weak borate eluent, conductivity detection and a micro-membrane suppressor. Calcium, magnesium, sodium and potassium were measured by flame atomic-absorption spectroscopy. In 1990 and 1991 a Varian model AA6 spectrophotometer was used. In later years a Varian SpectrAA model 400 equipped with an auto sampler was used for cation analyses.

Non-Winter Precipitation Sampling and Analyses

During the period of late May or early June until October or November, precipitation was collected in Aerochemetrics collectors. Concurrently, precipitation quantity was measured at or near each collector using a tipping-bucket rain gauge (Qualimetrics model 6011-B) connected to a solid-state datalogger. At some stations a small plastic raingauge was also deployed. Alter-type shields were used on the tipping bucket gauges at all stations to enhance collection efficiency.

Samples were collected on an event basis and a concerted effort was made to retrieve the samples within 24 hours of the end of the rain event. The mean amount of time elapsed from the cessation of rain until samples were collected for all sites during the study period was slightly more than one day (Figure 1). In addition the average time a bucket was installed prior to collecting a sample was 4.7 days (Figure 1). The volume of water in the bucket was measured with a graduated cylinder and a new bucket installed. Samples were filtered within a few hours of collection, most often in the laboratory; at Emerald Lake, Angora Lake, Kaiser Pass and Mineral King, filtering took place in the field. Samples awaiting analysis were stored at 5°C in a refrigerator or coldroom. A total of 514 individual precipitation events were sampled during the non-winter periods of 1990 through 1994.

Within 72 hours of collection, pH was determined on unfiltered sample using an Orion model 920 meter and Ross (Orion) combination electrode. All pH measurements were made under ambient air. Specific conductance of unfiltered precipitation was measured with a YSI Model 34 conductivity bridge and electrode (cell constant = 0.1) and readings corrected to 25°C. All samples for major solutes and nutrients were filtered through Nuclepore polycarbonate filters (1.0 micron pore size). A separate filtered subsample was made for organic anions and preserved with chloroform and kept frozen until just before they were analyzed. Ammonium was determined on filtered samples generally within a few days by the indophenol blue method (Strickland and Parsons 1972). Chloride, nitrate and sulfate were measured by ion chromatography on a DIONEX model

2010i ion chromatograph, employing an AS4A separation column, carbonate-bicarbonate eluent, conductivity detection and a micro-membrane suppressor. Acetate and formate were measured by ion chromatography on a DIONEX model 2010i ion chromatograph, employing an AS4A separation column, a weak borate eluent, conductivity detection and a micro-membrane suppressor. Calcium, magnesium, sodium and potassium were measured by flame atomic-absorption spectroscopy. In 1990 and 1991 a Varian model AA6 spectrophotometer was used. During 1992 through 1994 a Varian SpectrAA model 400 equipped with an auto sampler was used for cation analyses.

Between the time of the snow survey and the deployment of the Aerochemetrics collectors, snow storms were sampled using snowboards or by digging shallow pits. Snowboards were deployed at Emerald Lake, Spuller Lake, Lost Lake and Mammoth Mountain. Samples were collected from the boards after any significant snowfall using the PVC snowtube used in snowpit sampling. When significant snowfall occurred and no snowboard was deployed, the fresh snow was sampled by digging a shallow snowpit. In appearance, the fresh snow was readily discernible from the older more compacted snowpack. Snow density was measured and samples collected using the same techniques and equipment as used in normal snowpit sampling.

No Precipitation Bucket Rinses

If at the end of the 7 to 14 day installation period no rain had occurred, the bucket was rinsed with 250 ml of deionized water. The water was added to the bucket and slowly swirled to contact all internal surfaces of the bucket. The rinse water was then subsampled into a 125-ml bottle for subsequent determination of ammonium, chloride, nitrate, sulfate, calcium, magnesium, sodium and potassium. In addition, a 30-ml subsample was collected, preserved with chloroform and stored in the freezer for later analyses of organic anions (acetate and formate). Deionized water samples were analyzed concurrently with the no-precipitation bucket-rinse (NPBR) samples to rule out background contamination in the DI water.

Solute Loading

Ionic loading was calculated for both snow surveys and for non-winter precipitation. We assumed that the spring snowpack in the Sierra Nevada integrated all solute loading (precipitation and dry deposition) for the period of November through March. Loading was calculated from average snow chemistry and snow-water equivalence at each study site. Non-winter solute loading was calculated by multiplying the volume-weighted mean chemistry for each site by the total precipitation. This loading included all measured precipitation for the period of May through October. Dry deposition was not included. Annual solute loading is the sum of winter and non-winter loading.

At most of the study sites, rain and snow samples were collected at nearly the same location. However, at Angora Lake and Tioga Pass, snow samples were collected some distance away from the rain collector site. Snow data for Tioga Pass were from surveys conducted in the Spuller Lake watershed (3 kilometers distance, 134 meters higher than rain collector). Snow chemistry and SWE for Angora Lake were collected at Lost Lake (3 kilometers distance, 189 meters higher than rain collector).

Snow samples from Eastern Brook Lake were lost during 1995 (freezer malfunction). Data from Ruby Lake were substituted for the lost samples from Eastern Brook. During 1995, no snow survey was conducted at Mineral King because the road was impassable (washouts and debris) and instead data from Topaz Lake was substituted. Ruby Lake is located 5 km southwest and 220 meters above the Eastern Brook station. Topaz Lake is located in Sequoia National Park at an elevation of 3,218 meters and nearby Emerald Lake.

Quality Assurance and Control

A long-term effort investigating regional differences in precipitation chemistry requires a strong quality assurance (QA) plan for sampling and analysis. The QA plan comprises rigorous field and laboratory quality control (QC) procedures which are prerequisite to the production of credible data. UCSB has implemented a QA program to ensure the integrity of precipitation samples collected in the field and to produce reliable analytical data for samples analyzed in the laboratory.

In an assessment of methods for monitoring snowfall, Berg et al (1989) employed UCSB's quality assurance protocols for precipitation and documented guidelines for sampling interval, collection, storage, transport and processing of snow. These protocols have been used by UCSB in monitoring the chemistry of Sierra Nevada lakes and were followed during the course of the present study.

Our QC procedures included the following components: Identical instruments were used and adherence to standardized data collection procedures and field analysis protocols was emphasized with the field staff at all sites; the sampling procedures are described in the methods section of this report. Procedural variability in the field was assessed by duplicate cores. In the laboratory, blanks included deionized water processed through plastic bottles, filters and buckets which assess contamination from buckets employed to melt snow, from the membranes used to filter melted snow, and from bottles used to contain precipitation water.

Our analytical procedures incorporated a variety of internal and external checks to generate precision and accuracy statistics. The following is a summary of the internal checks used for each analysis.

pH: After a two-point calibration with NBS-traceable buffers, the accuracy of the electrode was checked using dilute solutions of HCl (10^{-4} and 10^{-5} N).

Specific Conductance: A 10^{-4} M KCl conductivity standard, which has a theoretical specific conductance of 14.7 $\mu S \cdot cm^{-1}$ at 25°C was measured frequently. In 1990 two audits (high and low, 118 and 6.5 $\mu S \cdot cm^{-1}$ at 25°C, respectively) were prepared from Orion low ionic strength buffers and measured throughout a six month period.

Cations and Anions: Duplicate samples are run at a 5% frequency in each assay session for estimation of within-run precision. Known additions are made to samples and standards in duplicate at a 5% frequency in each assay session for estimation of within-run accuracy.

We employed three different, independent (external) checks on the accuracy of our chemical analyses. Routine analysis of standard reference materials from the National Bureau of Standards was performed. This material is synthetic rainwater with certified concentrations for major cations and anions. The second independent check on our chemical data involves participation in the U.S. Geological Survey's Analytical Evaluation Program (AEP). Twice yearly the USGS distributed a water sample to participants at laboratories and universities nationwide for major cation and anion analysis. Participants returned their results to the USGS. The USGS assigns a score to each laboratory based on how close their results come to the mean value obtained from all participants. The third independent check we employed was our participation, since 1992, in the LTRAP program of the Canadian Environmental Protection Agency. This program is very similar to the USGS AEP.

In addition to the above procedures, the internal consistency of our chemical data was validated by adherence to two criteria (Drouse et. al. 1985). Tests for consistency of data included departure from electroneutrality and comparison of calculated and measured specific conductance. Charge balance was evaluated as an ion balance ratio and as the absolute value of the sum of positive ions minus the sum of negative ions. Theoretical specific conductance was calculated from measured ion concentrations and compared with measured specific conductance as the conductance balance (theoretical conductance divided by measured conductance). If measured ionic concentrations are accurate and all the major constituents measured, the sum of cations should equal the sum of anions. If measured conductance was the same as theoretical conductance, then our analytical protocol determines all the important ionic species and our measurements are not biased.

Chapter III

Quality Assurance and Quality Control

In this chapter we present the results and a discussion of the results from the QA/QC program for chemistry. In many of the tables and figures study sites are referred to by code letters which are described in Table 2.

Specific Conductance

The accuracy of the YSI 3402 ($K = 0.1$ cm^{-1}) cell was checked with 10^{-4} N KCl throughout the measurement period. Two different QA solutions prepared from diluted Orion low ionic strength buffers and stored in individual 60 ml polyethylene bottles at 4°C were measured monthly during 1990. The specific conductance of the KCl standard was always within ± 12% of the theoretical value of 14.9 μS cm^{-1} at 25°C. Overall precisions in 1990 were 4.9, 5.0 and 4.5 percent relative standard deviation (%RSD) for the KCl, high QA and low QA solutions, respectively. For 1991 through 1995, an overall precision of 5.1 %RSD was realized for the KCl standard solution.

pH Measurement

The Orion EA 920 meter equipped with a Ross 8104 electrode was first calibrated with NBS traceable pH 7.00 and pH 4.00 buffers. A further calibration with various concentrations of HCl prepared from certified 10^{-2}N HCl (Fisher -SA62-1) solution was then performed. For additional QA, the pH of high and low buffers of low ionic strength were determined throughout the measurement period during 1990. Overall precisions computed from these data are 1.6 %RSD for HCl solutions and 1.7 and 3.6 %RSD for high and low QA buffers, respectively. Precisions of 0.6 %RSD for pH measurements on a single day were computed using replicate measurements of snowmelt samples and of a USGS simulated snowmelt sample. Overall precisions for 1991 through 1995 were ≤ 2.3 %RSD for 10^{-4} and for 10^{-5} N HCl solutions.

Acetate and Formate

Accuracy of analysis of acetate and formate was assessed by recovery after known additions to duplicates of actual samples since certified controls with these solutes do not exist (Figure 2, all samples). For snow from 1990, recovery of acetate varied from 80 to 130% over a range of 0.8 to 3.8 microequivalents per liter. Recovery of formate was problematic due to degradation of the formate spike over the time period of an automated run; spiked samples may have waited up to 10 hours at 30°C before injection. For 1991 through 1993, recoveries of acetate and formate varied from 40-180 percent (Figure 2). Recovery of know additions was not done during 1994 and 1995.

Precision was computed from duplicates of actual and augmented samples for the years of 1990 through 1993 (Figure 3, all samples). Precision was not determined for 1994 and 1995 but is probably similar to levels measured for earlier years given that identical laboratory equipment, practices and personnel were used. For snow samples occasional poor duplicates yielded 40-60 %RSD; the majority of samples had %RSD $\leq$ 16%. The high variability of the accuracy and precision determinations is attributed to unstable baselines in the step gradient elution technique that we employed. This technique works best with a gradient pump to change eluants dynamically; at UCSB we use the controller to change eluants discretely. An overall mean of 107% recovery was computed for acetate and for formate. The overall precision for acetate and formate was 5.8 and 3.5 %RSD, respectively.

Overall precision for acetate and formate, for rain samples, at levels of 2-20 μeq L^{-1} was 1.2 and 1.0 %RSD, respectively. Average recovery of known additions of 1 or 3 μeq L^{-1} of acetate and formate were 120 and 98 percent, respectively .

Given the labile nature of the organic anions, holding times were computed for these solutes. These data indicate the necessity to analyze melted snow samples for acetate and formate within 24 hours. Losses of 0.1 to 2.2 microequivalents per liter of organic anions occurred in chloroform preserved samples stored at 4°C for up to 2 months. Commencing in 1991 snow samples were melted in smaller batches so that organic anions in a chloroform-preserved subsample could be analyzed within 24 hours of phase change. Rain samples were preserved with chloroform and stored frozen at -20°C. Installment of an air conditioner in proximity to the ion chromatograph decreased the ambient temperature. Smaller automated runs with sample cassettes held at 4°C minimized the time a sample was at room temperature. Typically organic anion samples were exposed to room temperature less than two hours during processing and analysis.

Major Anions

Accuracy was assessed by comparing measured values with the certified values for NBS 2694-II simulated rainwater during all years and also by recovery after known addition to duplicates of actual samples during 1990 through 1993 (Tables 3 and 4; Figure 4, all samples). Precision was computed from measured values of replicates of laboratory duplicates during 1990 through 1993 only (Figure 5, all samples). For snow samples, recoveries for NO_3 and SO_4 were usually within ± 10% of 100%; recovery of Cl ranged 67-117%. Within run precisions for NO_3 and SO_4 were generally <10%; the imprecision in Cl was greater. The poorer accuracy and precision in measuring Cl are attributed to partial inclusion of the Cl peak within the water dip thereby affecting the area quantified by the integrator. The overall precisions (%RSD) for 1990, computed as the mean of all within-run precisions, were 11.2, 2.4 and 3.2 for Cl, NO_3, and SO_4, respectively; in 1991 they were 3.7, 1.2 and 1.5, respectively. For 1992 through 1993 overall precisions for Cl, NO_3 and SO_4 were 4.1, 1.5 and 2.0 %RSD, respectively.

For rain, recoveries of known additions of 3 $\mu eq \cdot L^{-1}$ each in Cl, NO_3 and SO_4 were within ±10% of 100 percent. Similarly, agreement with NBS-simulated rainwater controls was within ±10% of the certified values for these anions. Overall precision for chloride at levels of 0.2 to 22 $\mu eq \cdot L^{-1}$ was 1.0 %RSD, and for NO_3 and SO_4 at levels of 4 to 46 $\mu eq \cdot L^{-1}$ an overall precision of 1.0 %RSD was realized.

Major Cations

Accuracy for cations was assessed by comparing measured values with the certified values for NBS 2694-II or NBS 2694-I simulated rainwater during all years and also by recovery after known addition to duplicates of actual samples during 1990 through 1993 (Figures 2 and 6, all samples). Precision was computed from measured values of replicates of laboratory duplicates during 1990 through 1993 only (Figures 3 and 7, all samples). Agreement with certified values of NBS simulated-rainwater (SRM) controls for 1990 through 1995 were within ± 10%; the certified value of calcium (18.2 $\mu eq \cdot L^{-1}$) in reference materials is outside the dynamic range of our calibration standards and is therefore excluded from the accuracy statement (Table 3). Recovery of known additions of cations varied from 80-130 percent. Overall precision for 1990 through 1993 was $\leq$ 5.0 %RSD for snow and $\leq$ 1.0 %RSD in rain samples.

Field Blanks

Prior to installation, the buckets on the Aerochemetrics collectors were rinsed three times with deionized water ($\leq$ 1 $\mu S\ cm^{-1}$, 25°C). A final fourth rinse with ca. 250 ml was collected for chemical analysis. Ionic chemistry for a subset of field blanks was determined. With the exception of Alpine Meadows in 1990, and Mineral King and Kaiser Pass in 1993, contamination with major ions was negligible. At these stations DI water was stored in carboys for several weeks before use and contamination probably occurred during storage. These sites had no ready source of fresh DI water so water had to be periodically shipped to them and stored on site.

Bucket rinses with 250 ml of deionized water collected when no precipitation occurred during the biweekly interval were analyzed for chemical constituents. The chemistry of the rinse water gives an indication of possible bucket contamination from sources other than wet deposition. We also analyzed the deionized water at each site that was used for these operations to assure that any measured contamination was from the bucket itself. These data show measurable levels of ions and also suggest that a site specific component is operating (Table 5).

It is more meaningful to examine no precipitation data on a loading basis. In addition, small moisture events may trigger the Aerochemetrics sensor and allow small amounts of water to enter the bucket; subsequently this water may evaporate yielding a false no precipitation sample. These kinds of samples may be eliminated by examining rain gauge data for trace precipitation. The no precipitation data are dealt with in more detail in Chapter VII of this report.

Laboratory Blanks

Plasticware blanks included ziplock bags, 125 ml and 30 ml high density polyethylene bottles, and filter blanks sampled at ca. 10% frequency. Plasticware was soaked in deionized water ≥ 3 days and then rinsed 5 times with deionized water. Filter blanks were obtained from the buckets used to melt snow by filtering (1.0 micron polycarbonate membrane) a ca. 100 ml portion of the 250 ml of deionized water kept in contact at 4°C with the bucket for 24 hours. No significant contamination was detected in any of these blanks. The inorganic chemistry of these blanks was typically less than 0.2 microequivalents per liter.

Interlaboratory Comparisons

Fifteen samples were interchanged between the ARB laboratory in El Monte and UCSB for analysis of pH, chloride, nitrate, sulfate, sodium, potassium, magnesium and calcium. UCSB samples included snow, lake, and rainwater (Table 6). With the exception of calcium, ionic chemistry is in good agreement for lakewater and rainwater.

For four separate snowmelt samples, calcium measured at UCSB was 5 to 9 $\mu eq \cdot L^{-1}$ lower than calcium measured at El Monte; sulfate measured at UCSB was also a few $\mu eq \cdot L^{-1}$ lower than that measured at El Monte. Calcium measured at UCSB in four of the five rain samples was lower than Ca measured at El Monte in those rain samples.

The measured value of pH differed between UCSB and El Monte for all three types of samples but was least discrepant for lakewater (0 - 0.6 pH unit differences). Measurements of pH on rainwater at UCSB were 0.2 to 0.8 pH units lower than pH values determined at El Monte.

UCSB has been a continuing participant in the U.S. Geological Survey's (USGS) interlaboratory analytical evaluation program for the USGS low ionic strength standard reference sample since 1988. Natural-matrix reference materials are used in this program; the low ionic strength sample is melted snow. Analytical data received semiannually by the USGS are evaluated with respect to: overall laboratory performance and relative laboratory performance for each analyte. Laboratory performance is rated on a scale 4 to 0, based on the absolute Z-value (4: 0.00-0.50, 3: 0.51-1.00, 2: 1.01-1.50); the Z-value is the number of deviations the reported value is from the median value. Ratings greater than 2.4 are considered satisfactory. UCSB received the following average ratings for 1990-1993: 3.2, 3.3, 3.8 and 3.0

UCSB is also a participant in the LRTAP Interlaboratory Comparability Study of the Canada Centre for Inland Waters. Measured values for major ions, pH, specific conductance and alkalinity on 10 different types of samples are submitted for evaluation. The types of samples include lakewater, rainwater, streamwater, river outflow and river inflow. At UCSB, these samples require high dilutions when analyzed along with snow and rain samples from the central Sierra Nevada. Hence the potential exists for additional variability and error with the LRTAP samples. Table 7 presents comparative data among participating laboratories for a set of results submitted in May 1994 (UCSB's laboratory code is L122); Figure 8 depicts measured values of individual analytes with respect to the interlaboratory median values of those analytes.

Holding Time Tests

A holding time test for anions was performed using eight separate melted snow samples (Table 8). After melting, the snow samples were filtered into high density polyethylene bottles and maintained at 4°C. Major anions were analyzed at 2, 6 and 33 days and at 4 months. A general pattern of increased Cl, NO_3, and SO_4 was observed; the increases ranged 5-20 percent.

Another time test over an 8-month period on six replicates of a synthetic sample of 2.0 microequivalents each on Cl, NO_3, and SO_4 showed a similar but more muted pattern (Table 9).

Discussion of Charge and Conductance Balances

The internal consistency of the chemical data is validated by the application of two criteria to the data set: charge balance and conductivity balance. In the former, lack of departure from zero for electroneutrality indexed as the absolute value of the sum of positive ions minus the sum of negative ions affirms that measured ionic concentrations are accurate and that all major constituents are measured. Figures 9 and 10 depict the frequency distribution, as a percent of total charges, of the difference between cations and anions for snow and rain samples for the study as a whole. The absolute difference between cations and anions in snow samples for the same period is shown in Figure 11.

For snow, excess of cations was found during all years (Figure 9). The amount of excess was similar among the years and ranged from 23.3 to 24.7 percent ion difference (%IOD). While this difference is large on a percent basis, in absolute terms the differences are small. The difference between cations and anions in snow showed an excess of 3.9 μEq L^{-1} of cations overall for the study. There was little difference among the years in the difference between cations and anion or in %IOD. An excess of cations in this analysis could be the result of underestimating anion concentrations.

Charge balances were better for non-winter precipitation samples owing to overall higher concentrations of ions in these storms compared to winter snow (Figure 10). Percent ion difference varied slightly from year to year. For most years there was a slight negative bias in the charge balance. The overall %IOD was only 0.1, with the majority of samples falling within ± 5% of electroneutrality. Samples with large positive charge imbalance tended to be snow events from the spring and autumn period that had low solute concentrations. Charge balances in the range of -10% to -30% were summer rains with high concentrations of nitrate, sulfate and organic anions.

The second criterion applied to the data set is the computation of a conductance balance i.e. theoretical conductance divided by measured conductance. Measured conductance is simply the specific conductance of samples measured with the conductivity meter. Theoretical conductance is the calculated conductance of the sample based on the concentrations of all ions in solution. It is based on the equivalent conductance for each ion which is a measure of the conductance of an ion per unit of concentration. If the conductance balance is unity, then all important ionic species have been determined and measured without bias. Ratios less than one indicate that theoretical conductance is too small meaning some important ionic species was underestimated. Balances with ratios greater than one indicate that theoretical conductance is too large and thus some ion's (or ions') concentration was over estimated.

The mean conductance balance (theoretical divided by measured conductance) for snow samples ranged from 0.66 to 1.02, and was less than one in most years. The overall mean conductance balance for snow during the period of 1990 through 1995 was 0.83 (Figure 9). During 1990 the balance was 1.02 which may be a result of overestimating formate concentrations. That the mean balance was less than one indicates that a deficit exists in the ions measured. This fact coupled with the finding that %IOD was biased toward positive charge suggests that an anion was underestimated (Figure 12).

Unmeasured bicarbonate is a possible contributor to the charge and conductance imbalances in snow samples. Because our detection limit for the Gran titration is 2 $\mu eq \cdot L^{-1}$, we have not detected HCO_3^- when snow has been analyzed for acid neutralizing capacity. An overestimation of H^+ may contribute to the observed biases during 1990 and 1991 when samples were measured under ambient air, however this possibility is unlikely. Results from 1992 on 350 measurements of pH on melted snow under argon and after four hours exposure to ambient CO_2 levels in the laboratory do demonstrate up to 3 $\mu eq \cdot L^{-1}$ (mean = 1.5 $\mu eq\ H^+ \cdot L^{-1}$) more H^+ in the latter samples (Figure 13). However, %IOD and the conductance balance did not improve during later years despite the switch to argon. Other causes for an anion deficit could include a systematic underestimate of measured anions (see discussion of accuracy, below) or the unlikely possibility that there is some other undiscovered anion in the samples.

The mean conductance balance for rain during the study was 1.01 and ranged from 0.96 to 1.03 (Figures 10). No significant or consistent bias was seen in either the charge or conductance balances in non-winter precipitation as a whole. These results indicate that, for non-winter precipitation samples as a whole, we have demonstrated that the internal consistency of the chemical data are valid and no significant bias exists in these analyses (Figure 12).

Discussion of Accuracy

Reviewing the accuracy measurements obtained during the study suggests that bias exists in our estimates of organic anions, sulfate, magnesium, potassium and sodium (Table 4). For acetate and formate a small positive bias of 107% was found. This bias translates into an average overestimate of organic anions of 0.14 μEq L^{-1} or 2.0% of average total anions in solution. Similarly, overall average sulfate recovery was 106% or 0.12 μEq L^{-1}. This small overestimate represents 1.7% of total anions in solution. For cations, the overall means for accuracy of magnesium, sodium and potassium were 104%, 110% and 105%, respectively. Together this bias would equal an overestimate of 0.17 μEq L^{-1} or 1.6% of all cations in solution. Given that the charge balance in snow samples already shows an excess of positive charges (i.e. %IOD > 0), the net effect of correcting for the above biases would be to *increase* the imbalance by 2.1 % (i.e. 23.8% + 2.1% = 25.9%).

Errors in preparing standards, in pipetting solutions or contamination of samples may have caused the calculated biases. However, primary standards are obtained commercially and are traceable to NBS, pipettes are routinely calibrated and various types of blanks are included in analyses to verify that no contamination is occurring. Chemical interferences may contribute to the biases. However, none of these problems are likely causes for the consistent, positive biases we experienced in our analyses. The analytical protocols followed during the study are internally consistent. All working standards used in an analytical run were prepared fresh using the same stock solutions and the same pipettes. In addition, standards were run simultaneously with samples and handled in exactly the same manner as samples. Furthermore, the chemical matrix of the samples is relatively simple and not much different from that in the standards. Interferences among ions, if any, should be the same in both the sample and standard solutions. Thus, neither matrix affects, pipetting errors, inaccuracies in standards nor handling techniques can explain the consistent over-recovery of solutes we experienced.

Accuracy was also determined by repeated analyses of certified control samples. These results indicate there is no overall bias in any of the assays (Table 3). Furthermore, if solute concentrations are really being overestimated, then theoretical conductance should exceed measured conductance. The opposite is true. Theoretical conductance was usually less than actual measured conductance in snow samples. This would indicate that we are underestimating solute concentrations and may help to explain the biases in our analyses.

Snow chemistry is very dilute and solute concentrations are typically less than 1 or 2 μEq L^{-1}. Despite our use of state of the art methods and instruments, these chemical concentrations are difficult to detect and measure accurately (Table 10). What may be happening is that the error lies not in the determination of concentration in the spiked sample (KALD) but rather in the measurement of the original sample's concentration. If the original sample concentrations (LD) were *under*estimated, it would appear there was an over-recovery in the spiked (KALD) samples. The appearance of over-recovery becomes more likely when the sample concentration is near the method detection limit (MDL) and the amount of spiked solutes (and the final concentration) are small.

At concentrations near the MDL it is difficult to get reliable results from standards. Moreover, the signal-to-concentration relationship will usually become non-linear at this point (Figure 13), exhibiting a tailing off toward an X-intercept at the MDL. When sample concentrations near the MDL are calculated using standards in the linear portion of the signal-to-concentration relationship, the true concentration can be underestimated. In the example in Figure 13, the sample signal is 0.003 units. Using standards in the linear portion of the curve (extrapolated standard curve) yields a concentration of 0.6 units, however the true concentration is 1.0 units. If we were to raise the concentration by 2 units the ending concentration would be measured to be 3.0 not 2.6 because at this level the signal-to-concentration relationship is linear. This would appear as a recovery of 120%. The more the true and extrapolated calibration curves diverge the worse the underestimate of sample concentration becomes.

If the above explanation is correct than recoveries should improve if initial sample concentrations increase. Examining recoveries of cations and anions in Sierran lake and stream samples, yields the following measures of accuracy: chloride, 92%; nitrate, 99%; sulfate, 104%; calcium 97%; magnesium, 102%; sodium, 104%; potassium, 101% (Melack et al. 1993). In all cases recoveries in these samples (which were analyzed during 1990 and 1991) were lower than in the snow samples. Furthermore, in all cases except chloride, recoveries were closer to 100% in lake samples than in snow samples. In addition charge and conductance are good in these samples, indicating all ions were accurately measured. Initial solute concentrations in the lake samples were from two to more than 10 times higher than in snow.

To eliminate the positive biases in the future would require us to change our analytical protocols. One solution for cations would be to employ the graphite furnace technique for atomic absorption (AA) spectrophotometry. Detection limits for this method are much lower than for typical flame AA. For anions, the ion chromatograph (IC) could be operated at a lower signal-attenuation setting or samples could be concentrated prior to analysis. Lastly, for all solutes, more standards at low concentrations would help to more accurately define the calibration curves near the detection limits. All of the above solutions would increase the labor and time involved in analyzing snow samples. In addition, since one of the goals of CARB research in the Sierra Nevada is to collect long-term data sets for detecting changes in water quality, changing analytical protocols may be ill-advised.

Chapter IV

Snow Chemistry

Variability of Snow Chemistry

Volume-weighted-mean (VWM) snow chemistry was calculated for study sites for the winters of 1990 through 1995. These data are presented in Tables 11 through 21 along with the date of the snow surveys. Snow samples were also collected prior to and after the normal surveys at Emerald Lake, Mammoth Mountain and Onion Valley. These samples had chemistry similar to the spring surveys (Table 22).

At Emerald Lake VWM pH ranged from 5.29 to 5.55, and hydrogen ion was the dominant cation in four of the six years (Table 11). The pH of 5.55 was from 1992 and was the second highest VWM pH measured at any site during the study period. Ammonium concentration exceeded hydrogen ion during 1992 and 1994 and ranged from 1.8 to 4.6 μEq L^{-1}. Of the remaining cations, concentrations were near the detection limits for magnesium and potassium and from 0.7 to 2.5 μEq L^{-1} for calcium and sodium. Inorganic anion concentrations were low, ranging from 1.0 to 2.1 μEq L^{-1} for chloride, from 1.7 to 3.0 μEq L^{-1} for nitrate and from 1.2 to 2.9 μEq L^{-1} for sulfate. Concentrations of organic ions were less than 1.0 μEq L^{-1} for both acetate and formate. In general, the order of ions based on concentration was: $H^+ > NH_4^+ > NO_3^- \cdot SO_4^{2-} \cdot Cl^- > Ca^{2+} \cdot Na^+ > HCO_2^- \cdot Mg^{2+} \cdot CH_2CO_2^- \cdot K^+$.

Snow chemistry at Onion Valley was very similar to Emerald Lake (Table 12). VWM pH ranged from a low of 5.15 during 1990 to a high of 5.55 during 1992. These pH levels were the lowest and second highest measured at any site during the study period. Hydrogen ion was generally the dominant ion in solution. Ammonium concentrations were slightly lower than hydrogen ion and ranged from 2.2 to 3.8 μEq L^{-1}. Calcium was next in concentration (0.9 to 4.8 μEq L^{-1}) followed by sodium (0.8 to 1.5 μE L^{-1}), magnesium (0.5 to 1.0 μEq L^{-1}) and potassium (0.1 to 2.0 μEq L^{-1}). The large calcium value was from 1990 and was the highest concentration measured at any site during the study. During 1990, calcium and potassium concentration were relatively high when compared to the other three years of study. Nitrate was the dominant anion in three of the four years and ranged from 1.8 to 4.0 μEq L^{-1}. VWM sulfate concentration were generally lower than nitrate (1.9 to 2.4 μEq L^{-1}) but exceeded nitrate in 1993. Chloride concentrations ranged from 1.3 to 2.8 μEq L^{-1}. Acetate and formate concentrations were low, ranging from 0.2 to 1.4 μEq L^{-1}. Overall the order of ions based on concentration was: $H^+ > NH_4^+ > NO_3^- \cdot Ca^{2+} > SO_4^{2-} \cdot Cl^- > Na^+ > K^+ \cdot Mg^{2+} \cdot CH_2CO_2^- \cdot HCO_2^-$. Comparing the four years of study, snow at Onion Valley in 1990 was enriched with base cations (calcium, magnesium, sodium and potassium) and had a lower pH.

pH varied little during the four years of study at South Lake, ranging from 5.39 to 5.45 (Table 13). Hydrogen ion was the dominant ion in solution. In contrast to Emerald Lake and Onion Valley, nitrate concentration were greater than ammonium all four years (nitrate, 1.4 to 3.9 μEq L^{-1}; ammonium, 1.1 to 2.5 μEq L^{-1}). Sulfate concentrations were slightly lower and ranged from 1.6 to 1.9 μEq L^{-1}. Chloride concentrations were lower and more variable, ranging from 0.6 to 1.7 μEq L^{-1}. Of the base cations, only calcium exceed 1.0 μEq L^{-1}, the others were at or near the detection limit all four years. Acetate and formate concentrations were also low and ranged from 0.2 to 0.7 μEq L^{-1}. The order of ions based on concentration at South Lake was: $H^+ > NO_3^- > NH_4^+ \cdot SO_4^{2-} \cdot Ca^{2+} \cdot Cl^- > Na^+ \cdot CH_2CO_2^- \cdot HCO_2^- \cdot Mg^{2+} \cdot K^+$. With the exception of nitrate, solute chemistry was remarkably similar among the four years.

Dilute snow chemistry was also found at Eastern Brook Lake (Table 14). Hydrogen ion was once again the dominant ion, and pH ranged from 5.30 to a high of 5.62 during 1994 (this was the highest VWM pH for snow measured during the six years of record). Nitrate concentration (1.5 to 3.8 μEq L^{-1}) was usually slightly greater than ammonium (1.0 to 3.6 μEq L^{-1}). Sulfate, chloride and calcium were the next most abundant ions and their concentrations ranged from 0.6 to 2.5 μEq L^{-1}. The remaining base cations had concentrations typically less than 1.0 μEq L^{-1} except for magnesium in 1992 (2.4 μEq L^{-1}) and sodium during 1994 (1.2 μEq L^{-1}). Organic anions were at the detection limits all four years. The order of ions based on concentration was: $H^+ > NO_3^- > NH_4^+ \cdot Ca^{2+} \cdot SO_4^{2-} > Cl^- \cdot Mg^{2+} > Na^+ \cdot K^+ > CH_2CO_2^- > HCO_2^-$.

Snow chemistry at Mammoth Mountain was typical of the Sierra Nevada (Table 15). pH ranged from 5.20 to 5.44, and hydrogen ion was the dominant ion during all years except 1994 when it was exceed by ammonium. Nitrate and ammonium concentrations were similar and ranged from 1.9 to 5.8 μEq L^{-1} both were lowest during 1993. Calcium and chloride were the next most common ions with concentrations ranging from 1.0 to 2.2 μEq L^{-1}. Sodium concentrations were slightly lower: from 1.1 to 2.3 μEq L^{-1}. Potassium and magnesium levels were near the detection limit (typically less than 0.5 μEq L^{-1}). Acetate and formate concentrations were slightly higher and ranged from 0.2 to 1.6

μEq L^{-1}. The order of ions based on their concentrations was: $H^{+} > NH_4^{+} > NO_3^{-} > SO_4^{2-} > Ca^{2+} \cdot Cl^{-} > Na^{+} \cdot CH_2CO_2^{-} \cdot HCO_2^{-} > K^{+} \cdot Mg^{2+}$.

At Tioga Pass (Spuller Lake) pH in snow ranged from 5.25 in 1990 to 5.50 in 1993 (Table 16). As is typical in Sierran snow, VWM nitrate and ammonium concentrations were similar and ranged from 1.4 to 3.0 μEq L^{-1}. Sulfate concentrations ranged from 1.3 to 2.2 μEq L^{-1}, chloride from 1.0 to 1.3 μEq L^{-1} and calcium from 0.9 to 2.0. Sodium, potassium and magnesium were less than or equal to 1.0 μEq L^{-1} for all years. Acetate and formate levels were similar and ranged from below detection to 0.8 μEq L^{-1}. The general order of ions was: $H^{+} > NH_4^{+} \cdot NO_3^{-} > SO_4^{2-} \cdot Ca^{2+} \cdot Cl^{-} > Na^{+} \cdot K^{+} \cdot HCO_2^{-} \cdot CH_2CO_2^{-} \cdot Mg^{2+}$.

During the four years of study at Sonora Pass, pH ranged from a low of 5.19 in 1990 to a high of 5.53 in 1992 (Table 17). Hydrogen ion was the dominant ion in three out of four years, however, in 1991 it was equaled or surpassed by sulfate (1.0 to 3.7 μEq L^{-1}) and calcium (1.3 to 3.3 μEq L^{-1}). The VWM sulfate concentration at Sonora Pass during 1991 was the highest measured at any site during the four years of study. VWM nitrate in snow at Sonora Pass ranged from 1.5 to 2.1 μEq L^{-1}, and chloride levels were from 0.7 to 1.8 μEq L^{-1}. The remaining cations concentrations were generally low (less than 2.0 μEq L^{-1}) except for sodium during 1991 with a concentration of 3.1 μEq L^{-1}, the highest chloride concentration measured during the study. In comparison to other years, snow during 1991 was enriched with sulfate, calcium and sodium. Acetate and formate ranged from the detection limit to 1.0 μEq L^{-1}. Excluding data from 1991, the order of ions based on concentration was: $H^{+} > NO_3^{-} \cdot Ca^{2+} \cdot NH_4^{+} \cdot SO_4^{2-} > Cl^{-} > Na^{+} \cdot K^{+} \cdot Mg^{2+} \cdot CH_2CO_2^{-} \cdot HCO_2^{-}$. In 1991 the order was very different: $SO_4^{2-} > H^{+} \cdot Ca^{2} > Na^{+} > NH_4^{+} > NO_3^{-} > Cl^{-} > Mg^{2+} > K^{+} \cdot CH_2CO_2^{-} > HCO_2$.

Snow chemistry at Alpine Meadows was typically dilute (Table 18). pH ranged from 5.24 in 1990 to 5.56 during 1993 which was the second highest pH measured at any site during the four years of study. After hydrogen ion, ammonium was the most common ion in solution closely followed by nitrate, sulfate and chloride. These anions ranged from 1.0 to 2.9 μEq L^{-1} during the study period. Base cations concentrations were very low, ranging from 1.4 μEq L^{-1} to the detection limit. In contrast to most other sites, sodium concentrations equaled or exceeded calcium concentrations during four or five years. Organic anion levels were less than 1.0 μEq L^{-1} during the study period. The general order of ions based on concentration at Alpine Meadows was: $H^{+} > NH_4^{+} \cdot NO_3^{-} > SO_4^{2-} \cdot Cl^{-} > Na^{+} \cdot Ca^{2+} > Mg^{2+} \cdot K^{+} \cdot HCO_2^{-} \cdot CH_2CO_2^{-}$.

Snow chemistry and deposition at Angora Lake was from snow surveys conducted 3 kilometers away at Lost Lake (Table 19). pH varied only slightly during the study period ranging from 5.37 to 5.53. Snow at Angora Lake was largely a solution of hydrogen ion, ammonium, nitrate, sulfate and chloride. These five ions comprise 70% of the ions in solution. The range of VWM concentrations of these solutes was: hydrogen ion, 2.9 to 4.3 μEq L^{-1}; ammonium, 1.7 to 3.3 μEq L^{-1}; nitrate, 1.6 to 2.9 μEq L^{-1}; sulfate, 1.3 to 2.3 μEq L^{-1} and chloride, 1.2 to 2.1 μEq L^{-1}. Base cation levels at Angora Lake were similar to those at Alpine Meadows with sodium concentrations equal to calcium concentration. Magnesium and potassium concentrations were at or near the detection limit during the study period. Acetate and formate concentrations at Angora Lake ranged from 0.1 to 1.0 μEq L^{-1}. The order of ions based on concentration was: $H^+ > NH_4^+ \cdot NO_3^- > SO_4^{2-} \cdot Cl^- > Na^+ \cdot Ca^{2+} \cdot HCO_2^- \cdot CH_2CO_2^- > Mg^{2+} \cdot K^+$.

In contrast to the other study sites, snow chemistry at Mineral King was enriched with several ions (Table 20). pH levels were fairly typical but ammonium and nitrate concentrations were high. Volume-weighted mean ammonium concentration during 1991 and 1992 exceeded 7 μEq L^{-1}. Nitrate was also elevated during the same two years: 5.5 μEq L^{-1} in 1991 and 4.8 μEq L^{-1} in 1992. These values were the highest levels measured at any site during the study. Also unusual was that calcium concentrations were generally greater than sulfate in the snowpack. In addition, VWM snow chemistry during 1990 had the highest specific conductance, acetate and potassium levels of any site during the study period. Formate during 1991 was 1.5 μEq L^{-1}; the second highest level measured at all sites during the study. Overall the order of ions based on concentration at Mineral King was: $NH_4^+ \cdot H^+ \cdot NO_3^- > Ca^{2+} \cdot SO_4^{2-} > Cl^- > Na^+ \cdot K^+ \cdot HCO_2^- \cdot Mg^{2+} \cdot CH_2CO_2^-$.

At Kaiser Pass no snow survey was conducted during 1990. During the period of 1991 through 1995, pH of snow at Kaiser Pass ranged from 5.36 to 5.51 (Table 21). Ammonium concentrations were relatively high, ranging from 0.8 μEq L^{-1} during 1995 to 4.8 μEq L^{-1} during 1991. Major anions ranged in concentration from 1.0 to 2.9 μEq L^{-1} during 1991 through 1994 but snow chemistry was more dilute during the large winter of 1995. Calcium was generally highest in concentration of the base cations and ranged from 1.2 to 3.4 μEq L^{-1}. However, potassium was the dominant base cation during 1994 (2.9 μEq L^{-1}). The remaining base cations were less than 1.2 μEq L^{-1} during the study period. Acetate levels in snow at Kaiser Pass were similar to other sites being at or near the detection limit during all years. Formate concentration varied widely however. VWM formate was 1.7 μEq L^{-1} in 1991 and 2.5 μEq L^{-1} during 1994, the highest levels measured at any site during the study. In contrast, concentrations during 1992 and 1993 were less than or equal to 0.1 µEq L^{-1}. The order of ions based on concentration at Kaiser Pass was fairly typical: $H^{+} \cdot NH_4^{+} > NO_3^{-} > Ca^{2+} \cdot SO_4^{2-} \cdot Cl^{-} \cdot Na^{+} \cdot CH_2CO_2^{-} \cdot K^{+} \cdot Mg^{2+} \cdot HCO_2^{-}$.

Snow surveys were conducted at Kirkwood Meadows only during 1990. Snow chemistry at this site was similar to other sites with the exception of relatively low pH of 5.19 (Table 23). Hydrogen ion dominated the solution chemistry followed by nitrate, sulfate and chloride. Base cation and organic anion concentrations were less than or equal to 1.0 µEq L^{-1}. The order of ions based on concentration at Kirkwood Meadows was: $H^{+} > NH_4^{+} > NO_3^{-} > SO_4^{2-} \cdot Cl^{-} > Ca^{2+} > Na^{+} > K^{+} \cdot HCO_2^{-} > Mg^{2+} > CH_2CO_2^{-}$.

One objective of our study was to describe the site to site and year to year differences in snow chemistry in the Sierra Nevada. To do so we conducted statistical analyses on the volume-weighted mean snow chemistry described above. With only eleven study sites and only four years of study it was necessary to lump the data together to obtain meaningful results from the analyses. For example instead of testing for site to site differences for each year we chose to lump all four years of chemistry together. Similarly, instead of testing for year to year differences in snow chemistry at each study site we decided to combine data from all sites for these tests.

Examination of the snow chemistry data indicated that the data did not have normal distributions. Attempts were made to normalize the data using typical transformations (e.g. log, square) with no success. Instead, nonparametric statistics were performed to test for differences among sites and years. We chose to use the Kruskal-Wallis one way analysis of variance (ANOVA). This procedure tests for differences for a single variable (i.e. solute) across two or more independent groups (study site or years) using ranked data. The Kruskal-Wallis test transforms the values of a variable to ranks and uses these ranks to test that there is no shift in the center of the groups. This test is the nonparametric analog of a one-way ANOVA. When significant differences were found at the 95% confidence level ($P < 0.05$), a Dunn's multiple-comparison test was used to isolate the group or groups that differ from the others.

Statistical analyses were performed on all measured chemical parameters except for pH; pH values were converted to hydrogen ion concentrations for the tests. The single year of data from Kirkwood Meadows was not included. The number of pits used in the analyses (N) was sixteen except at Emerald and Spuller Lakes with 24 pits and Kaiser Pass with only 12 pits. Given the large number of possible comparisons (i.e. 11 study sites times 12 chemical parameters equals 132 comparisons), many significant differences in chemistry among the sites were detected. These differences are summarized in Table 24. Some of the differences are probably meaningless and simply an artifact of the large number of comparisons or analytical error. An example of this is the finding that potassium in the snow at Emerald Lake is significantly lower than is snow at Onion Valley, Sonora Pass or Mineral King. However, some of the differences are real and important. When a solute at one site was found the be significantly different from several other sites this difference was considered to be genuine. This is especially true since the tests were made with four years of data.

Sulfate was found to be significantly higher at Mammoth Mountain than at seven of the ten other sites (Table 24). No other significant differences were noted for sulfate. The difference in concentration at Mammoth was not large; mean VWM differences were less than 1.0 μEq L^{-1}. Higher sulfate at Mammoth Mountain may be due to the relatively close proximity of this site to an urban area (Mammoth Lakes) and ski resort.

Sodium concentrations in snow at South Lake were significantly lower than at eight of the ten other sites. As with sulfate the absolute differences were small. While no explanation for this difference was obvious, it may be that a source of sodium found at most study sites (i.e.. dust, vegetation litter or other dry deposition) was absent or smaller at South Lake.

No other strong differences were observed for other chemical parameters. However, from looking at the occurrences of differences among the sites some patterns appear. Table 24 also contains a summary of the instances, for each study site, where a significant difference was observed. For example, there were 15 instances where snow at Onion Valley had significantly higher conductivity or solute concentration. Conversely, there were 18 cases when snow at South Lake had significantly lower solute levels. By subtracting the number of less than cases from the greater than cases for each site three classes of sites become evident. One class of sites is 'enriched' with solutes compared to other locations and includes Onion Valley and Mineral King. A second class of sites is 'depleted' of solutes compared to other sites and includes South Lake, Sonora Pass and Eastern Brook Lake. The remaining sites, with the exception of Mammoth Mountain, are not enriched nor depleted of solutes.

Explanations for the distribution of the study sites among these classes could include proximity of urban areas, differences in surrounding vegetation, local geology and soils, snowfall quantity and timing or the occurrence of snowmelt prior to our surveys.

Annual Variability of Snow Chemistry

Taken as a whole, the snow chemistry at the eleven study sites demonstrates the dilute nature of snow chemistry in the Sierra Nevada. In the previous section we described the volume-weighted mean chemistry at each site during the study period. This approach is useful as a means of comparing typical snow chemistry among the sites and in tracking year to year variations of snow chemistry at an individual site. To describe and contrast the aggregate snow chemistry for each year, a different approach was needed. In this analysis volume-weighted snow chemistry from individual pits was used. Chemical data from all pits dug during an annual survey were combined and frequency histograms were made for each chemical constituent. Figures 14 through 17 are frequency histograms for pH, ammonium, chloride, nitrate, sulfate, base cations, organic anions and density for the study period.

Snow profiles from 1990 had a relatively large range of VWM pH values compared to other years. They varied from 5.0 to 5.7 units with a mean value of 5.27. During 1991 and 1992 the range of pH was smaller, varying from 5.3 to 5.7. Mean pH from these years was 5.42 and 5.44 respectively. pH in 1993 ranged from 5.2 to 5.8 with a mean value of 5.45. VWM pH in 1994 and 1995 were generally in the range of 5.4 to 5.5. The overall mean volume-weighted mean pH for snow samples collected during 1990 through 1995 was 5.39 (Figure 14).

Ammonium concentration in snow was similar during 1990-92 and 1994. Values ranged from 1.0 to 10.0 μEq L^{-1} and the mean values for these years ranged from 2.4 to 3.2 μEq L^{-1}. Mean ammonium concentration were lower in 1993 and 1995 and measured values were less than 5.0 μEq L^{-1} in virtually all profiles. Sierran snow during the six years of study had a mean ammonium concentration of 2.7 μEq L^{-1} (Figure 14).

Snow samples from all six years had similar levels of chloride. Samples ranged from 0.1 to 3.0 μEq L^{-1} with a few profiles from 1993 with levels from 4.0 to 6.0 μEq L^{-1}. The mean chloride concentrations ranged from 1.1 to 1.6 μEq L^{-1} during the study period with an overall average of 1.4 μEq L^{-1} (Figure 15).

As was the case with ammonium, nitrate levels during 1990-92 and 1994 were similar. Overall the range of concentration was from 1.0 to 7.0 μEq L^{-1} with samples from 1991 exhibiting the largest variability. Mean values for these years ranged from 1.9 to 4.4 μEq L^{-1}. Lower nitrate concentrations were observed in 1993 and 1995 (range 1.0 to 4.0 μEq L^{-1}), similar in magnitude to the decline of ammonium. This resulted in an average nitrate concentration of 2.5 μEq L^{-1} for the study (Figure 15).

Sulfate concentrations were relatively consistent during the study. Mean levels ranged from 1.8 to 2.1 μEq L^{-1} with slightly lower concentrations during the wet winter of 1995. There was more variability in sulfate levels during 1991 with a few pits having VWM concentrations above 5.0 μEq L^{-1} (Figure 16). Sulfate concentrations averaged 1.9 μEq L^{-1} during the study.

The variability of the sum of base cations (calcium + magnesium + sodium + potassium) in Sierran snow was relatively large compared to other solutes. While the vast majority of snow profiles concentrations were below 5.0 μEq L^{-1}, there were several pits with levels above 11 μEq L^{-1} in (Figure 16). The range of observed concentrations was greatest during 1990 and smallest during 1992. Mean values for the study period were: 1990, 4.0 μEq L^{-1}; 1991, 4.1 μEq L^{-1}; 1992, 4.6 μEq L^{-1}; 1993, 3.5 μEq L^{-1}; 1994, 5.1 μEq L^{-1}; 1995, 2.8 μEq L^{-1}; and overall, 4.1 μEq L^{-1} (Figure 16).

Organic anion (acetate plus formate) concentrations were uniformly low during all four years. Because of analytical problems (see QA/QC section), values were higher and more variable during 1990. Mean values ranged from a high of 1.5 μEq L^{-1} in 1990 to around 1.0 μEq L^{-1} during the remaining years. Including 1990, the overall range of concentrations of acetate plus formate were from near zero to over 6.0 μEq L^{-1} with the mean level being 1.0 μEq L^{-1} (Figure 17).

Specific conductance of snow samples was very low with most samples falling between 2 to 3 μS cm^{-1} (Figure 17). Specific conductance tended to be lower during wet winters such as 1993 and 1995. The overall mean conductance for the period of 1990 through 1995 was 2.8 μS cm^{-1}.

Mean snow water equivalence (SWE) in snowpits varied by more than 10 fold during the six years of study (Figure 18). Values ranged from ca. 300 to over 3000 mm. SWE was greatest during 1995 and 1993 and lowest during 1990, 1992 and 1994;

snowfall for 1991 was intermediate overall. The mean SWE measured at all sites during the study was 870 mm.

Density of snow samples was measured concurrently with chemical sampling primarily to estimate snow-water equivalence. Density from 10 cm intervals of the snowpack ranged from less than 100 kg m^{-3} to nearly 600 kg m^{-3} (Figure 18). Samples with density less than 200 kg m^{-3} were fresh snow. High densities (> 450 kg m^{-3}) were always found in isothermal snowpacks (temperature ~ 0 °C) in the spring and in deep snowpacks at low temperature (temperature < -3 °C).

The winters of 1990, 1992 and 1994 were relatively dry and had mean densities of between 384 and 365 kg m^{-3} (Figure 19). Snowfall during the winter of 1991 was greater than in 1990, 1992 or 1994, and the snowpack had a higher density during the spring surveys (mean, 400 kg m^{-3}). Depending on the station, precipitation during the winters of 1992-93 and 1994-95 was 2 to 3 fold greater than in other years. In addition, much of the snow that fell was deposited in December and January which allowed the snowpack a relatively long period of time to settle. The distribution of snow density from these years indicates that the snowpack was very dense, with most samples having density in the range of 450 to 550 kg m^{-3}. The mean density of snow in 1993 was 428 kg m^{-3} and 464 kg m^{-3} in 1995.

Statistical analyses were used to detect significant differences in solute concentrations among years. The procedures used were identical to those used in comparing chemistry among sites and included the Kruskal-Wallis one-way ANOVA and Dunn's post-hoc test. Profile data used in the analyses numbered 44 in 1990, 48 in 1991 and 1992 and 46 in 1993. Since the number of stations and their locations changed in 1994 and 1995, statistical test were only run on the complete data sets from 1990 through 1993.

The significant differences found with the tests are summarized in Table 25. Many strong differences were detected. Specific conductance of snow samples during 1992, which had the lowest snow deposition, were significantly greater than in all other years. Ammonium, calcium and magnesium concentrations were also significantly higher in 1992 compared to other years. In contrast ammonium and nitrate levels in 1993, with the wettest snow season, were significantly lower than those in 1990, 1991 and 1992. In addition, potassium and sodium concentrations were also significantly lower in 1993 compared to 1992. These results suggest that solute concentrations tend to be highest in snow from dry winters and lowest during years with large snowpacks.

Changes in analytical methods may explain most of the significant differences found in snow chemistry in 1990. Formate, chloride and hydrogen ion concentrations were all higher in 1990 compared to other years. Problems with formate analyses in 1990 are the likely cause for greater formate concentrations in 1990. Explanations for differences in pH among the years are more complicated.

pH measurements were made under argon atmospheres in 1992 and 1993 and under air in 1990 and 1991. During 1992 pH in snow was also measured under air atmosphere in many samples. In the vast majority of these samples, pH was higher in samples measured under argon than under air (Figure 12). This suggests that pH was higher in 1992 and 1993 compared to 1990 because we changed from air to argon for pH measurements. However, mean pH in 1991 was only slightly lower than in 1992 and 1993, and the difference was not significant at the 95% confidence level. In addition, pH in 1991 was significantly greater than in 1990. These results are contradictory and suggest that changes in the pH analysis do not completely explain the observed pH differences among the years.

The fact that snow from 1990 had significantly lower pH and higher chloride than all other years is troubling. Bags used for sampling snow in 1990 were rinsed with HCl and then soaked in deionized water for several days. After 1990 the HCl rinse was eliminated in the washing procedure. It may be that acid contamination is partly responsible for increased levels of chloride and hydrogen ion in snow samples from 1990. However, HCl contamination was mild and can account for only a portion of the observed differences. Mean chloride concentration in 1990 was 0.3 to 0.4 μEq L^{-1} higher than in 1992 and 1993, but the hydrogen ion concentration in 1990 was more than 1.7 μEq L^{-1} greater than in 1992 and 1993. Assuming a 1:1 relationship between hydrogen ion and chloride with HCl contamination, less than 25% of the difference in pH among these years is due to acid contamination. Changes in analytical procedure and annual variability in snow chemistry must account for the majority of the differences.

In summary, snow samples collected in the Sierra Nevada during 1990 through 1995 had pH levels typically between 5.3 and 5.6; which is slightly less than expected if carbonic acid was the only acid present. After hydrogen ion, the next most abundant ions in solution were compounds of nitrogen (ammonium and nitrate). Sulfate concentrations in Sierran snow tend to be slightly less than nitrate and ammonium levels and higher than chloride. Of the remaining cations, only calcium and sodium levels were found to be much above the detection limit. Organic anions (acetate and formate) were difficult to measure in the Sierra snowpack and were usually found in low concentrations (i.e. $< 0.5\ \mu Eq\ L^{-1}$).

Chapter V

Non-winter Precipitation

Variability of Non-winter precipitation

As previously stated, non-winter precipitation is all rain and snow which was sampled from the date of the spring snow-surveys (early April) until the snowpack began to accumulate again in October or November. Most of the samples were collected with an Aerochemetrics rain collector except for a few samples collected from snowboards or shallow snowpits during the spring and autumn.

In contrast to snowpack samples, non-winter precipitation chemistry was quite variable, with solute concentrations ranging from near detection limits to levels in the tens of microequivalents per liter. Most of this variability was due to the timing of the storm; spring and autumn storms being most dilute and summer rains being enriched with solutes. Therefore, the annual volume-weighted mean concentration at any station depended on the period of time samples were collected and the 'mix' of samples obtained. Due to logistical constraints, spring and autumn precipitation was often missed at remote sites such as Sonora Pass and South Lake. In contrast, stations such as Emerald Lake and Mammoth Mountain have nearly complete records because of their accessibility.

Tables 11 through 21 contain the VWM chemistry for non-winter precipitation at the eleven study sites. The sampling periods for each station are also shown for comparison.

pH in non-winter (NW) precipitation at Emerald Lake was relatively high (range, 5.12 to 5.44) compared to other sites (Table 11). Ammonium, nitrate and sulfate were the dominant ions in solution and, in contrast to snow, exceeded hydrogen ion concentrations. During 1991, levels of these solutes were quite high: ammonium, 41.1 μEq L^{-1}; nitrate, 22.5 μEq L^{-1}; sulfate, 15.2 μEq L^{-1}. While lower in concentration, the organic anions were still an important component in non-winter precipitation. The order of ions based on their concentration at Emerald Lake was variable. In general nitrate equaled ammonium and exceeded sulfate. For the base cations, calcium was most abundant followed by sodium.

Because of its remote location, relatively few late-autumn storms were sampled at Onion Valley. Consequently, VWM chemistry at this station was less dilute than at

Emerald Lake (Table 12). pH was similar among the four years of study, ranging from 4.72 to 4.89. Ammonium was the dominant ion in solution with VWM concentrations in three out of four years greater than 30 μEq L^{-1}. Nitrate levels were usually a little lower than ammonium (range, 20.1 to 32.6 μEq L^{-1}) and slightly higher than sulfate (range, 15.9 to 28.9 μEq L^{-1}). Calcium was the major base cation in these samples. Formate concentrations were higher than acetate and ranged from 3.4 to 15.3 μEq L^{-1}.

Chemistry of non-winter precipitation at South Lake was similar during the four years of study (Table 13). Since the rain collector was installed relatively late in the spring and removed relatively early in the autumn, summer rains had a large impact on VWM chemistry. pH was low in NW precipitation at South Lake and ranged from 4.60 to 4.72. Hydrogen ion levels equaled ammonium levels during most years. Nitrate concentrations ranged from 18.5 to 30.6 μEq L^{-1} and slightly exceeded sulfate. As at other stations, calcium was the major base cation in solution. Substantial amounts of organic anions were present in NW precipitation at South Lake with nearly equal amounts of acetate and formate measured.

Eastern Brook Lake was another station with few late season storms sampled. This resulted in relatively high VWM solute concentrations during 1990, 1991 and 1992 (Table 14). However, due to a paucity of summer rains during 1993 and 1994, spring and autumn storms had a large effect on VWM chemistry during these years. NW precipitation during 1993 had chemistry that was quite dilute and which closely resembled snow chemistry. pH during the period of 1990 through 1992 ranged from 4.66 to 4.73. These samples had relatively high levels of ammonium (range, 22.5 to 34.5 μEq L^{-1}), nitrate (range, 23.7 to 28.2 μEq L^{-1}) and sulfate (range 15.3 to 22.6 μEq L^{-1}). Organic anions during the same period ranged from 4.5 to 13.7 μEq L^{-1} with formate exceeding acetate during all years. During 1993, VWM solute concentrations were below 10 μEq L^{-1} and near the detection limit for some of the base cations.

A similar pattern was found in non-winter precipitation chemistry at Mammoth Mountain. Chemistry during the first three years of study had high solute levels while 1993 and 1994 (due to few summer rains and abundant spring/autumn precipitation) had chemistry that was quite dilute (Table 15). Indeed, except for ammonium, nitrate and sulfate, NW precipitation during 1993 and 1994 was almost indistinguishable from winter snow. pH for the years of 1990 to 1992 ranged from 4.65 to 4.87. Ammonium and nitrate levels were high during these years and ranged from 18.7 to 30.6 μEq L^{-1}. Sulfate concentrations were slightly less than nitrate (range, 13.8 to 21.8 μEq L^{-1}) and higher than calcium (6.0 to 16.2 µEq L^{-1}). Appreciable amounts of organic anions were measured during this period with concentrations ranging from 6.9 to 15.0 µEq L^{-1}; formate levels exceeded acetate during all years.

At Tioga Pass, pH in non-winter precipitation ranged from 4.59 in 1991 to 5.05 in 1994 (Table 16). Ammonium and hydrogen ion were the major cations in solution with levels from 9.0 to 32.8 µEq L^{-1}. Nitrate concentrations usually equaled ammonium in precipitation at Tioga Pass, ranging from 11.8 µEq L^{-1} (1994) to 31.2 µEq L^{-1} (1990). As was the case at other stations, sulfate concentrations were slightly less than nitrate and ranged from 8.0 to 21.9 µEq L^{-1}. Of the base cations, calcium was the most abundant followed by sodium, magnesium and potassium. Substantial amounts of organic anions were measured in NW precipitation at Tioga Pass. Concentrations ranged from 8.9 to 20.0 µEq L^{-1} during the first three years of study; levels were lower during 1993 and 1994.

Concentrations of solutes in non-winter precipitation at Sonora Pass fell within the range of values measured at the other study sites during most years. pH was unusually low during 1991 which coincided with high concentrations of nitrate, acetate and formate (Table 17). Formate and acetate concentrations were 24.4 and 31.1 µEq L^{-1} respectively, the highest VWM levels measured at any study site during the study period. Three fairly large rain events were sampled during July and August which had high levels of organic anions (range, 20 to 40 µEq L^{-1}). Since the no-precipitation bucket rinses that bracket this period had little organic anion contamination, it is likely that high levels of acetate and formate in these samples are not due to contamination. Chemistry in 1990, 1992 and 1993 was typical with pH ranging from 4.69 to 4.87, ammonium from 19.9 to 28.9 µEq L^{-1}, nitrate from 19.2 to 23.3 µEq L^{-1}, sulfate from 15.5 to 16.0 and organic anions from 3.5 to 16.5 µEq L^{-1}.

Lack of summer rains during 1993 had a large effect on VWM chemistry at Alpine Meadows. Chemistry of NW precipitation in 1993 was similar to winter snow chemistry except for nitrate and ammonium which were a few microequivalents higher (Table 18). Excluding 1993, pH at Alpine Meadows ranged from 4.77 to 4.83. Nitrate concentrations were slightly greater than ammonium and ranged from 14.5 to 34.5 µEq L^{-1}. Sulfate levels were lower than nitrate during all four years, ranging from 7.6 (1993) to 24.5 µEq L^{-1} in 1992. Organic anions were below the detection limit in 1993 and ranged from 2.4 to 16.0 µEq L^{-1} during the other years.

At Angora Lake only 0.1 mm of precipitation fell during the period between June 20, 1993 and October 4, 1993. This was the longest rainless period at any of the stations during our study period. As a result, VWM chemistry for this year was calculated exclusively from a single storm in the autumn. For pH, chloride and organic anions, concentrations were very similar to those found in snow (Table 19). Other solute levels in 1993 were more similar to typical NW precipitation. Ammonium ranged from 10.4 to 23.7 µEq L^{-1}, nitrate from 17.9 to 28.8 and sulfate from 13.2 to 19.5 µEq L^{-1}. For these ions levels were highest in 1993. Calcium was the most abundant base cation followed by sodium. Organic anion concentrations were typical of NW precipitation in the Sierra, however, acetate exceeded formate in 1990 and 1991.

Non-winter precipitation chemistry at Mineral King varied widely during the study period (Table 20). Levels of ammonium, nitrate and sulfate during 1990 were the highest measured at any of the study sites. During the study the following range of concentrations were measured: ammonium, 16.8 to 60.9 µEq L^{-1}; nitrate, 15.3 to 43.7 µEq L^{-1} and sulfate, 11.2 to 34.9 µEq L^{-1}. Base cation levels were typical and ranged from 0.8 to 17.7 µEq L^{-1}. Except for 1991 when levels were below detection, organic anions concentrations were moderate at Mineral King ranging from 2.0 to 16.2 µEq L^{-1}. Formate usually exceeded acetate.

During most of the summer of 1994, wildfires were burning in the vicinity of rain collector in Mineral King. In August, fire swept through the rain collector site, damaging or destroying all of our equipment. New gear was deployed soon thereafter, but, it was impossible to keep ash out of the collection buckets. All samples in August, September and October were contaminated with ash to some extent. This ash contributed measurable ANC and high levels of calcium to rain samples (Table 20). However, concentrations of other solutes were similar to those measured in previous years so it is difficult to ascertain if ash contamination affected these constituents in the samples.

Precipitation was not monitored at Kaiser Pass during 1990. Volume-weighted mean pH ranged from 4.93 to 5.27 and was relatively high in 1992, 1993 and 1994 because spring and autumn storms were relatively abundant compared to summer rains (Table 21). Ammonium values ranged from 6.3 to 27.2 µEq L^{-1} and were highest during the relatively wet summer of 1992. Nitrate concentrations usually equaled or exceeded sulfate and ranged from 11.0 to 22.9 µEq L^{-1}. Base cation and organic anion levels were in the range of values measured at other station except for calcium in 1993 with a concentration of 25.8 µEq L^{-1}. This high VWM concentration was caused by a single high calcium event on October 15, 1993. This storm had a calcium concentration of over 50 μEq L^{-1}. Since other solute levels in this sample were fairly typical it may be that much of this calcium was from contamination. Other NW precipitation during 1993 at Kaiser Pass had calcium concentrations near 10 μEq L^{-1}.

Annual Variability of Non-winter Precipitation Chemistry

Most of the variability in NW precipitation chemistry among study sites is caused by differences in the installation period of the rain collectors. For example, the rain collector at Mammoth Mountain was typically set up by early May but, the collector at Sonora or Mineral King might not be operational until mid June during the same year. Therefore, comparisons of solute chemistry among sites and among years are problematic. At some stations a single large storm in the spring may deposit ten times as much water as all summer storms combined. Thus the annual VWM chemistry for these stations may appear quite different from stations where spring storms were not sampled.

Precipitation in the Sierra Nevada comes from two types of storms: large-scale Pacific weather systems and localized thunderstorms. Thunderstorms mainly occur from late spring through early autumn, develop from local air masses and deposit rain. In contrast, large-scale low pressure systems form in the Gulf of Alaska, reach California most frequently from late autumn until early spring and can deposit snow as well as rain. At the two extremes, the winter snowpack is formed from Pacific weather systems and summer rains in the Sierra derive mainly from infrequent summer thunderstorms. Precipitation in the spring and autumn is a mixture of both types of storms. Therefore, four categories of precipitation arise: winter snow, summer rains, spring rain/snow and autumn rain/snow. Since winter snow has been discussed in Chapter III we will, in the following section, compare and contrast the three types of non-winter precipitation.

The criterion used to classify precipitation into the three categories was the date on which the precipitation began. Precipitation which fell after the snow surveys through the first few days of June was classified as spring storms and were a mix of rain and snow. Summer storms were precipitation that fell between mid June and the end of September. These storms were virtually all rain events. The combination of rain and snow storms in October and November were classified as autumn storms.

The Kruskal-Wallis ANOVA (nonparametric) was used to determine significant differences in chemistry among the three class of non-winter precipitation. When the

ANOVA indicated significant differences ($p<0.01$), a Dunn's multiple-comparison test was used to isolate the group or groups that differ from the others. In the figures, each class of precipitation is assigned a letter. Classes with different letters are significantly different from one another. In addition, classes with letters lower in the alphabet are significantly greater than those with letters higher in the alphabet (i.e. a > b > c).

Precipitation Quantity and Storm Size

Non-winter storms ranged in size from trace amounts to over 100 mm (Figure 20). Summer rain storms tended to be small (mean, 7.1 mm) and last a few hours. Spring storms, being a combination of snow and rain, were a little larger in size (mean, 10.2 mm). Autumn storms ranged in size from a trace to more than 100 mm and were on average twice as large as summer storms (mean, 14.9 mm). During October 1992, a large storm struck Emerald Lake and deposited rain and snow which totaled 133 mm of water equivalence. During the course of the study several large autumn storms occurred in the Sierra Nevada. Because of their large size, these storms represent the majority of non-winter precipitation and solute loading during most years.

The amount of NW precipitation in the Sierra Nevada varies widely from year to year. Ranking the years of study, 1992 was by far the wettest and 1993 and 1994 the driest. Many modest summer storms and large autumn storms occurred during 1992 throughout the Sierra range. Spring precipitation was fairly abundant during 1994. In contrast, virtually no precipitation was measured during the late spring and summer of 1993 and the few autumn storms were relatively small. It is interesting to note that the wet winter of 1992-93 was preceded by the relatively wet summer and autumn of 1992.

Chemistry of NW precipitation was different among the three seasons, and many of the differences are related to storm size. Figures 21 through 24 are plots of solute concentration versus storm size. For all solutes the relationship between these parameters is an inverse function with the X and Y axes as asymptotes. Thus, small storms more commonly have high solute concentrations and large storms have relatively dilute chemistry.

Not unexpectedly, summer rain had significantly lower pH than the other classes of non-winter precipitation (Figure 25). In these samples, pH ranged from less than 4.0 to near 6.0. The mean pH of summer rain in the Sierra Nevada measured during the study period was 4.65. The lowest pHs measured during the study period were a pH of 3.86

from an 8.4 mm storm at Eastern Brook Lake on August 16, 1992 and a pH of 4.01 from a small storm (1.4 mm) at South Lake on August 2, 1993. The range and mean pH of spring and autumn storms was similar. Values ranged from 4.4 to 6.0 with mean values of 5.05 for spring storms and 5.00 in autumn storms.

Large differences in ammonium levels exist among the three types of storms (Figure 26). Spring storms had a mean ammonium concentration of 18.9 μEq L^{-1} and a range of 1.1 to 80 μEq L^{-1}. Summer rains had significantly higher ammonium levels. The mean concentration in summer storms was 36.5 μEq L^{-1} and ranged up to 160 μEq L^{-1}. Samples with concentrations above 60 μEq L^{-1} constituted about 30% of all summer rain samples collected. Moderate levels of ammonium were typically found in autumn storms. While the mean concentration was 28.1 μEq L^{-1}, very few samples had values greater than 40 μEq L^{-1}. The range of ammonium concentration in autumn storms was 1.0 to 160 μEq L^{-1}.

The seasonal differences in chloride concentrations were similar to those for ammonium (Figure 27). Summer storms had the highest levels of chloride (mean, 6.0 μEq L^{-1}) followed by spring and autumn storms (means, 3.2 and 3.3 μEq L^{-1} respectively). Concentrations in summer rains were as high as 30 μEq L^{-1}. Typical spring and autumn storms had chloride levels less than 5 μEq L^{-1}.

Nitrate was one of the major constituents of non-winter precipitation. Mean concentration in summer rain was 36.4 μEq L^{-1}, and samples with levels over 40 μEq L^{-1} were common (Figure 28). Nitrate concentrations were significantly lower in autumn precipitation which had a mean value of 22.3 μEq L^{-1} and relatively few samples with values over 40 μEq L^{-1}. Spring storms had the lowest nitrate levels, averaging 17.3 μEq L^{-1}. Only a handful of spring storms had nitrate greater than 40 μEq L^{-1}.

Sulfate levels in non-winter precipitation were only slightly lower than nitrate (Figure 29). As was the case with nitrate, summer rains had significantly higher sulfate values than spring or autumn precipitation and averaged 26.8 μEq L^{-1} during the five years of study. However, in contrast to nitrate and ammonium, VWM sulfate was lower in autumn precipitation (mean, 14.0 μEq L^{-1}) than in spring storms (mean, 16.4 μEq L^{-1}).

In addition to seasonal differences in the absolute concentrations of ammonium, nitrate and sulfate, there were differences in the relative proportions of these solutes. In spring storms the concentrations of these solutes were nearly equal, i.e. ammonium: nitrate

~ 1:1; ammonium to sulfate ~ 1:1. In summer rains, the ratio of ammonium to nitrate was still 1:1 but the ratio of ammonium to sulfate changed to ~ 1:0.7. In autumn storms, both nitrate and sulfate became less abundant relative to ammonium with ratios of ~ 1:0.8 and 1:0.5 respectively.

Seasonal changes in base cation levels (calcium, magnesium, sodium and potassium) of non-winter precipitation were similar to those for other solutes (Figure 30). Summer rains had the highest levels, with base cations ranging from 20 to over 200 μEq L^{-1} and a mean concentration of 33.8 μEq L^{-1}. Base cation concentrations in spring and autumn storms were similar and less than those in summer rain, averaging 19.7 and 22.1 μEq L^{-1} respectively. During the course of the study, several storms had extremely high levels of base cations i.e. greater than 200 μEq L^{-1}. These events were small storms generally less than 5 mm in size with the majority of them occurring at Tioga Pass and Mammoth Mountain.

Seasonal variability of acetate and formate was large. Mean summer concentrations were three times as large (26.3 μEq L^{-1}) as values measured in spring and autumn precipitation (8.6 and 8.9 μEq L^{-1}, respectively; Figure 31). Overall formate exceeded acetate in non-winter precipitation in the Sierra. High levels of organic anions usually occurred in small (less than 5 mm) summer storms and exceeded 60 μEq L^{-1} on numerous occasions.

The chemistry of non-winter precipitation in the Sierra Nevada is likely to be affected by the air masses that produce the storms. Large-scale weather systems in the spring and autumn tend to drop more precipitation than summer thunderstorms and this precipitation has lower solute concentrations. Summer storms derive from local, relatively dirtier air masses and are enriched with ammonium, nitrate, sulfate and organic anions relative to other types of precipitation. The pH of non-winter precipitation in the Sierra is generally less than 5.0 with chemistry dominated by compounds of nitrogen and sulfate. The major cations in this precipitation are ammonium and calcium with the former being two to three times more abundant.

Solute Relationships

In non-winter precipitation in the Sierra Nevada, concentrations of many solutes were strongly correlated. Figures 32 through 35 show scatterplots of some relationships among ions.

One important question to ask with respect to acid deposition in the Sierra Nevada is, what compounds are contributing acidity to the precipitation? We have demonstrated that small storms in the summer tend to be acidic with high concentrations of ammonium, nitrate and sulfate ions. A linear regression between hydrogen ion concentration and specific conductance illustrates this point. The coefficient of variation (R^2) indicates that 50% of the variability in acidity of non-winter precipitation is explained by specific conductance (Figure 32). Solutes such as ammonium, nitrate and sulfate show a significant ($P < 0.05$) positive correlation with hydrogen ion, however, R^2 values are relatively low (Figure 33).

Chloride was strongly correlated with nitrate (R^2, 0.60), sulfate (R^2, 0.62) and sodium (R^2, 0.53) (Figure 34). In addition, the correlation between nitrate and ammonium was strong (R^2,0.66) as was the relationship between nitrate and sulfate (R^2, 0.86) (Figure 35). There was also a strong correlation between acetate and format; $R^2 =0.77$ (Figure 35).

Chapter VI

Solute Loading

Solute loading in the Sierra Nevada is the sum of mass contributed by wet and dry atmospheric deposition. For wet deposition, loading is a function of the volume of precipitation deposited and the concentrations of solutes present in the precipitation. Dry deposition varies with the concentration of solids and aerosols in the air and the quality and quantity of depositional surfaces in a specific area. In the present study we have focused our efforts on quantifying wet atmospheric deposition of solutes since determining the amount of dry deposition in the Sierra Nevada is problematic at best.

The spring snowpack is a good integrator of both wet and dry deposition during the period of December through March and yields an accurate measure of solute loading during the winter. However, by collecting only wet deposition during the remainder of the year, we are underestimating non-winter mass loading. Dry deposition of ions in the Sierra Nevada has been measured by other researchers (Bytneriwicz et al. 1991, Brown and Lund 1994) and is likely a source of deposition our study sites.

Solute loading was calculated for both the spring snowpack and non-winter precipitation. In addition, these quantities were summed to estimate annual mass deposition and to compare the relative proportion each contributed. Tables 26 through 36 list solute loading for each type of precipitation for each station by year.

Seasonal Variability of Solute Deposition

At Emerald Lake, hydrogen ion loading by non-winter precipitation ranged from 4.7 to 10.7 Eq ha^{-1} (Table 26). Hydrogen ion loading during the winter was greater during all years and ranged from 18.2 to 113 Eq ha^{-1}. Ammonium loading in NW periods was quite variable, ranging from 11.2 to 58.4 Eq ha^{-1}. During winter, ammonium loading ranged from 20.3 to 48.0 Eq ha^{-1} at Emerald Lake. For nitrate and sulfate, loading was usually greater during non-winter periods with the exception of wet winters such as 1993 and 1995. Non-winter loading of these solutes ranged from 7.8 to 31.9 Eq ha^{-1} for nitrate and from 7.2 to 23.4 Eq ha^{-1} for sulfate. Nitrate loading from winter storms ranged from 14.2 to 57.8 Eq ha^{-1} while sulfate deposition varied from 11.5 to 54.6. It was unusual that sulfate deposition during winter 1993 was greater than loading of nitrate and ammonium. Base cation loading was fairly similar between winter and non-winter precipitation. For organic anions, more loading typically occurred during non-winter periods and ranged from 1.9 to 24.5 Eq ha^{-1} for acetate and from 4.9 to 17.6 Eq ha^{-1} for formate. For winter precipitation acetate and formate loading ranged from 0 to 13.8 Eq ha^{-1} and 0 to 5.4 Eq ha^{-1} respectively; organic acid concentrations during the winter of 1995 were below the detection limit.

Loading at Onion Valley tended to be lower than at most other sites owing to lesser amounts of precipitation. Hydrogen ion loading ranged from 5.2 to 15.8 Eq ha^{-1} during non-winter periods and from 15.9 to 38.3 Eq ha^{-1} during the winter (Table 27). Winter loading of hydrogen ion exceed non-winter loading all years, but was only slightly greater in 1990. Ammonium loading was variable from year to year for both winter and non-winter precipitation. During NW periods, ammonium loading ranged from 5.5 to 27.4 Eq ha^{-1}. Loading from winter snow varied from 5.9 to 23.3 Eq ha^{-1}. Nitrate loading was usually greater from winter precipitation, ranging from 5.3 to 24.7 Eq ha^{-1}. Non-winter storms deposited from 7.5 to 18.9 Eq ha^{-1} of nitrate. Sulfate deposition was similar in both types of precipitation, ranging from 6.0 to 16.7 Eq ha^{-1} for NW precipitation and from 4.6 to 20.7 Eq ha^{-1} during the winter. For most base cations loading from winter storms exceeded that from non-winter precipitation. Acetate loading ranged from 0.8 to 6.5 Eq ha^{-1} from NW precipitation and from 0.9 to 4.8 Eq ha^{-1} during the winter. Formate loading was generally higher than acetate loading at Onion Valley, ranging from 1.3 to 11.3 during non-winter seasons and from 0.7 to 8.9 during the winter.

Hydrogen ion loading at South Lake varied more than one-order of magnitude between the winter and non-winter periods of 1993 (Table 28). Winter loading during 1993 was 36.5 Eq ha^{-1} compared to only 3.3 Eq ha^{-1} during the very dry NW period. In the remaining years, hydrogen ion loading ranged from 11.0 to 21.0 Eq ha^{-1} during NW periods and from 12.2 to 19.1 Eq ha^{-1} during the winter. Except for 1993, ammonium loading was greater during non-winter periods, ranging from 2.2 to 28.0 Eq ha^{-1}. Winter loading of ammonium ranged from 6.7 to 18.8 Eq ha^{-1}. The majority of nitrate loading occurred during non-winter periods at South Lake except in 1993. The range of values measured during these periods ranged from 2.8 to 27.7 Eq ha^{-1} and from 6.7 to 18.8 Eq ha^{-1} during winter. Sulfate loading was lower than nitrate loading in all cases except 1993. Loading ranged from 1.8 to 21.8 Eq ha^{-1} during non-winter period and from 5.4 to 19.8 Eq ha^{-1} during the winter seasons. Base cation loading was similar between the two types of precipitation. Except for the dry non-winter period of 1993, organic anion loading was greater in NW seasons than in the winter with depositions ranging from 3.2 to 8.4 Eq ha^{-1} for acetate and from 3.6 to 11.8 Eq ha^{-1} for formate.

Loading of these solutes in NW 1993 was less than 1.0 Eq ha^{-1}. Loading of acetate and formate in winter ranged from about 1 to 7 Eq ha^{-1}.

The range of solute loading at Eastern Brook Lake was lower than at most sites because of less winter precipitation. Loading of hydrogen ion was similar during winter and non-winter periods, ranging from about 10 to 20 Eq ha^{-1} (Table 29). Exceptions were the dry, non-winter period of 1993 and the winter of 1995 (2.3 and 117 Eq ha^{-1}, respectively). Ammonium and nitrate loading tended to be greater in NW periods and ranged from 2.7 to 23.9 Eq ha^{-1} and 3.0 to 24.8 Eq ha^{-1} respectively. Winter loading was similar among first five years of study varying only from 5.1 to 10.0 Eq ha^{-1} for ammonium and from 5.0 to 12.1 Eq ha^{-1} for nitrate. Loading of ammonium and nitrate was high during the winter of 1995 with rates of 31.6 and 46.2 Eq ha^{-1}, respectively. Sulfate loading was less than nitrate loading in all instances but the winter of 1993. Values ranged from 2.6 to 21.0 Eq ha^{-1} for non-winter periods and from 3.0 (1990) to 31.5 (1995) Eq ha^{-1} during the winter. With the exception of 1995, there was no large difference in base cation loading between winter and non-winter periods. As was the case at most stations, the majority of organic anion loading at Eastern Brook Lake took place during non-winter seasons. Values for acetate and formate ranged from 0.8 to 7.8 Eq ha^{-1} and 1.3 to 9.3 Eq ha^{-1} respectively, during NW periods. Winter loading of these solutes ranged from less than 0.1 Eq ha^{-1} to a little less than 4.0 Eq ha^{-1}.

Owing to relatively high snowfall, deposition of hydrogen ion was greater at Mammoth Mountain compared to other stations (Table 30). Values during the winter ranged from 33.0 (1992) to 180 (1995) Eq ha^{-1}. For non-winter periods deposition was much lower, ranging only from 8.1 to 16.4 Eq ha^{-1}. Deposition of ammonium, nitrate and sulfate were also relatively large during the winter. Winter loading of ammonium was, 27.5 to 95.0 Eq ha^{-1}; nitrate 24.7 to 87.8 Eq ha^{-1}; sulfate 17.9 to 75.4 Eq ha^{-1}. Nitrate loading exceeded sulfate loading in all years except 1993. Non-winter deposition of ammonium and nitrate was similar, ranging from about 10 to 30 Eq ha^{-1}. Sulfate loading was usually lower during these periods and ranged from 9.5 to 16.9 Eq ha^{-1}. Most base cation deposition occurred during winter, and the amounts measured were higher than at most stations. Deposition of organic anions was split fairly evenly between winter and non-winter precipitation. Loading of acetate ranged from about 1 to 8 Eq ha^{-1} and deposition of formate varied from about 3 to 10 Eq ha^{-1}.

The station at Tioga Pass had hydrogen ion loadings that varied from 3.5 to 44.2 Eq ha^{-1} during non-winter periods and from 24.5 (1992) to 155 (1995) Eq ha^{-1} during winter (Table 31). Loading was especially high in the NW period of 1992 and during the winters of 1993 and 1995 primarily because of large amounts of precipitation. Ammonium and nitrate deposition was generally higher during NW seasons, the exceptions of 1993 and 1995. Loading of these compounds ranged from 7.1 to 38.9 Eq ha^{-1} and from 5.3 to 38.1 Eq ha^{-1}, respectively, during non-winter seasons. Winter deposition of ammonium and nitrate was similar and varied from about 10 to 63.7 Eq ha^{-1}. As was the case at most stations, sulfate loading was less than nitrate loading with the notable exception of 1993. Values ranged from 3.7 to 32.3 Eq ha^{-1} during non-winter periods and from 8.7 to 41.2 during the winter. Calcium loading at Tioga Pass was relatively large during both periods of the year. This was especially true during the winter of 1993 when calcium loading exceeded loading by ammonium, nitrate and sulfate. For organic anions most loading took place during non-winter periods with the exception of the winters of 1993 and 1995. Deposition for the winter of 1993 was odd. Acetate loading was quite high (15.3 Eq ha^{-1}) while deposition of formate was low (1.9 Eq ha^{-1}). Relatively large differences in acetate and formate loading were also observed at several other stations during 1993. In contrast, formate loading was 3 times larger than acetate loading during the winter of 1995 (Figure 31).

At Sonora Pass, hydrogen ion loading by non-winter precipitation ranged from 3.1 to 28.8 Eq ha^{-1} (Table 32). Hydrogen ion loading during the winter ranged from 13.4 to 31.9 Eq ha^{-1}. Ammonium loading in NW periods was variable, ranging from 4.5 to 30.1 Eq ha^{-1}. During the winter, deposition of ammonium was relatively low and ranged from 6.1 to 13.7 Eq ha^{-1}. For nitrate and sulfate, loading at Sonora Pass was usually greater during non-winter periods. Non-winter loading of these solutes ranged from 5.1 to 34.2 Eq ha^{-1} for nitrate and from 3.5 to 23.6 Eq ha^{-1} for sulfate. Nitrate loading from winter storms ranged from 7.3 to 15.8 Eq ha^{-1} with sulfate loading varying from 4.8 to 19.1 Eq ha^{-1} during the same period. Sulfate loading exceeded nitrate and ammonium deposition during the winters of 1991 and 1993. Base cation loading was similar between winter and non-winter precipitation and was quite high for calcium compared to most stations. For organic anions, more loading typically occurred during non-winter periods and ranged from 1.0 to 20.2 Eq ha^{-1} for acetate and from 0.8 to 25.8 Eq ha^{-1} for formate. For winter precipitation acetate and formate loading ranged from 1.6 to 3.0 Eq ha^{-1} and 0.4 to 5.4 Eq ha^{-1}, respectively.

Loading of hydrogen ion at Alpine Meadows was relatively high during winter periods (Table 33). Amounts deposited ranged from 30.6 to 52.0 Eq ha^{-1}. Except for the relatively wet, non-winter period of 1992, hydrogen ion deposition was much higher during the winter. Non-winter loading of hydrogen ion at Alpine Meadows ranged from 2.6 to 35.1 Eq ha^{-1}. The range of ammonium loading measured during winter and non-winter periods was similar, ranging from about 10 to 30 Eq ha^{-1}. Nitrate loading was also consistent between these periods (~ 10 to 30 Eq ha^{-1}) except for the non-winter period of 1991 when nitrate loading reached 45.7 Eq ha^{-1}. Sulfate loading was a little lower than nitrate deposition in all periods except 1993. Sulfate loading in non-winter precipitation at Alpine Meadows ranged from 6.5 to 24.2 Eq ha^{-1} while winter deposition during the same period varied from 9.9 to 26.3 Eq ha^{-1}. As was the case at most stations, base cation loading was similar between winter and non-winter precipitation. Excluding 1993, deposition of organic anions was greater from non-winter precipitation. Values ranged from 0.6 to 13.8 Eq ha^{-1} for acetate and from 0.6 to 15.7

Winter precipitation at Angora Lake was estimated from snow surveys conducted at the Lost Lake watershed. Because of the watershed's orientation and topography, much of the snow that enters the basin blows in from adjacent terrain. While this phenomenon does not affect snow chemistry, it does skew our estimates of solute loading. During the winter of 1993, snow-water equivalence at Lost Lake averaged over 3 meters. Snow depths and densities measured during the surveys define the upper limits for a Sierra snowpack. Results from our surveys strongly suggest that a large amount of snow blows into the basin and forms a dense, wind-packed snowpack. Hilltop areas along the border of the watershed were nearly snow-free, indicating these zones are the source of much of the blowing snow.

Winter loading of hydrogen ion at Lost Lake was very high and ranged from 31.9 to 88.5 Eq ha^{-1} (Table 34). Non-winter loading nearby at Angora Lake ranged from 2.1 to 21.5 Eq ha^{-1} during the same period. During 1990, 1991 and 1992 loading of ammonium and nitrate was similar during winter and non-winter periods with deposition ranging from about 15 to 30 Eq ha^{-1}. In 1993 loading of these compounds was 5 to 10 times higher during the winter. Loading of ammonium and nitrate from winter storms was 99.8 Eq ha^{-1} and 68.3 Eq ha^{-1} respectively. During the non-winter period of 1993 loading of these forms of nitrogen combined was less than 20 Eq ha^{-1}. combined. Sulfate loading was equal to or slightly less than nitrate loading at Angora/Lost Lake. Measured depositions ranged from 6.5 to 23.5 Eq ha^{-1} during the non-winter seasons and from 11.2 to 68.6 Eq ha^{-1} during the winter. Compared to most stations calcium and sodium loading was high at Lost Lake during the winter. Deposition of these solutes ranged from about

10 to over 60 Eq ha^{-1} during the winter season. Despite the large amount of winter precipitation at Lost Lake, deposition of organic anions at Angora Lake during non-winter periods was usually greater. However, owing to a paucity of rain, there was very little deposition of acetate and formate during the non-winter periods of 1993 or 1994. For winter periods acetate loading varied form 4.1 to 22.4 Eq ha^{-1} and from 1.1 to 14.0 Eq ha^{-1} for formate. Non-winter loading of these solutes ranged from less than 0.1 Eq ha^{-1} to about 15 Eq ha^{-1}.

Deposition of hydrogen ion at Mineral King was generally greater during the winter; the exception being the wet, non-winter period of 1992 (Table 35). Loading ranged from 2.2 to 15.2 during non-winter seasons and from 13.5 (1992) to 55.7 (1995) Eq ha^{-1} during the winter. Ammonium concentrations in rain and snow at Mineral King was relatively high and as a result loading of ammonium was large. Values measure in NW periods ranged from 5.2 to 51.2 Eq ha^{-1} and from 13.9 to 42.5 Eq ha^{-1} during the winter. Loading of nitrate varied from 5.8 to 36.7 Eq ha^{-1} in NW seasons and from 12.0 to 32.7 Eq ha^{-1} during the winter. Surprisingly, winter nitrogen loading was lower during the wet winter of 1993 and than in 1991. This difference is a result of high nitrogen levels in snow from 1991 and relatively low concentrations in 1993. Sulfate loading was greater than nitrate during the wet winters of 1993 and 1995 (overall range, 9.8 to 21.1 Eq ha^{-1}) and the majority of sulfate deposition was generally measured during non-winter periods (range, 2.8 to 29.3 Eq ha^{-1}). The dry, non-winter period of 1993 was an exception however. Loading of base cations was similar between the two periods at Mineral King. Ignoring the summer of 1992, loading of organic anions was greater in winter than in non-winter seasons. Deposition of acetate and formate was less than 5 Eq ha^{-1} during the non-winter periods of 1990, 1991 and 1993; loading during the NW period of 1992 was greater than 25 Eq ha^{-1} for both ions. Winter loading of organic anions varied from about 1 to 12 Eq ha^{-1}.

At Kaiser Pass, loading was not measured during 1990. Hydrogen ion loading was much greater in winter periods compared to non-winter seasons at the Kaiser Pass station (Table 36). Loading during non-winter periods ranged from 1.9 to 12.8 Eq ha^{-1} and from 26.9 to 46.2 Eq ha^{-1} during the winter. The relative contribution of non-winter precipitation to annual ammonium loading was variable. During 1991, 1992 and 1994 non-winter deposition of ammonium was a large component of the annual flux while in 1993 it represented less than 20%. Values ranged from 4.3 to 27.5 Eq ha^{-1} in non-winter periods and from 19.8 to 36.6 Eq ha^{-1} during the winter. Despite a deep snowpack, ammonium loading during 1995 was relatively low compared to other years. Nitrate and sulfate loading during non-winter periods was very similar and ranged from about 10 to 40 Eq ha^{-1}. In four out of five winters nitrate loading was greater than sulfate loading, the exception being 1993. Kaiser Pass was one of several stations where sulfate deposition exceeded nitrate loading in the winter of 1993. Base cation deposition was generally greater during the winter. This was especially true for calcium during the winter of 1993. The combination of high calcium concentrations in snow at Kaiser Pass and the large snowpack resulted in a loading of 48.3 Eq ha^{-1}. Acetate deposition was not greatly different between the two seasons. Levels varied from 1.4 to 4.6 Eq ha^{-1} during the non-winter periods and from 0 to 15.0 Eq ha^{-1} during the winter. In contrast, winter loading of formate varied from 0 Eq ha^{-1} during 1995 to 15.0 Eq ha^{-1} during 1991. During the same period, non-winter deposition of formate ranged from 1.4 to 7.7 Eq ha^{-1}.

Variability of Annual Solute Loading

Annual loading of solutes was calculated for each station by combining the deposition from winter and non-winter periods of each calendar year. These data, along with the average deposition of solutes for the study period, are presented in Table 37. The amount of annual deposition of mass in the Sierra Nevada was dependent on the amount of precipitation that fell and the concentration of ions in the precipitation. Much annual variability was seen in both precipitation and quantity and quality.

Average annual precipitation during the five years of complete data (i.e. winter and non-winter precipitation records) ranged from 402 mm at Eastern Brook Lake to 1541 mm at Angora Lake (Table 37). On an annual basis, average precipitation at Alpine Meadows, Emerald Lake, Mammoth Mountain and Tioga Pass were very similar, ranging from about 1100 to 1300 mm. The driest stations tended to be located in the southern or south-eastern portion of the Sierra while the wettest stations were found near Lake Tahoe and in the central Sierra. Exceptions to this rule were Emerald Lake and Sonora Pass. Winter snowfall constituted the majority of precipitation at all stations.

For the five years of study, the average annual hydrogen ion deposition at the 11 study sites ranged from 24.1 Eq ha^{-1} (Eastern Brook Lake) to 60.9 Eq ha^{-1} (Angora Lake). The stations with the least hydrogen ion deposition were located in the southern and south-eastern Sierra and those with the most loading of hydrogen ion were in the northern and central Sierra. The dose of hydrogen ion received at a station was strongly affected by the amount of snowfall received in the winter and, at the majority of stations, winter deposition of hydrogen ion was greater than in non-winter seasons. Stations such as Eastern Brook Lake, South Lake, Onion Valley and South Lake had relatively low snowfall during the winter and were stations where a larger proportion of annual hydrogen ion deposition occurred in the spring, summer and autumn seasons. In contrast, Mammoth Mountain, Emerald Lake, Tioga Pass and Alpine meadows had more winter snow and proportionately more annual hydrogen ion deposition.

The influence of winter deposition is clearly seen when contrasting solute loading among the five years of study. This is especially true for hydrogen ion loading. Table 38 contains information on the percentage of annual solute loading contributed by non-winter precipitation. Even during the drought years of 1990, 1992 and 1994, winter deposition still contributed the majority of annual hydrogen ion loading. In a large snow years such as 1993 and 1995, winter deposition of hydrogen ion can comprise more than 90% of the annual total.

For other solutes there is a group which were deposited primarily during the winter and another group where the majority of the flux occurred during non-winter periods. Along with hydrogen ion, most deposition of chloride, sodium and potassium occurred during the winter at most stations. For the five years of study, non-winter loading of chloride was less than 37%, and for sodium and potassium non-winter precipitation contributed less than 50%.

Ions such as the organic anions, ammonium, nitrate and sulfate typically had higher rates of deposition during non-winter periods, the exception being 1993. During 1990 through 1992 and 1994, non-winter loading comprised from ca. 45% to 60% of the annual loading of nitrogen and sulfate and from about 60% to 80% of the annual deposition of acetate and formate. It is noteworthy that during 1993, despite an unusually dry non-winter season and an very wet winter, non-winter loading of ammonium and nitrate was still greater than 20% and was nearly 40% for formate.

Site to Site Variability of Solute Deposition

Average annual deposition of ammonium and nitrate were similar among stations. For ammonium the range of average loadings varied from 21.6 Eq ha^{-1} at Eastern Brook Lake to nearly 60 Eq ha^{-1} at Angora Lake (Table 37). Mean nitrate deposition for the study was lower than ammonium loading at 7 out of 11 sites and ranged from 22.4 Eq ha^{-1} at Eastern Brook Lake to 53.7 Eq ha^{-1} at Angora Lake. Excluding Angora Lake, nitrate loading was highest at Mammoth Mountain (five-year mean, 47.8 Eq ha^{-1}). The same pattern was found for sulfate loading, average annual sulfate deposition was highest at Angora Lake and Mammoth Mountain (means, 44.5 Eq ha^{-1} and 40.4 Eq ha^{-1}, respectively) and lowest at Eastern Brook Lake (mean, 16.9 Eq ha^{-1}). Average annual sulfate deposition was lower than nitrate loading overall, but was equal to or higher than nitrate deposition at 9 of the 11 stations during 1993.

On an annual basis, the base cation with the highest amount of deposition was calcium. Average annual deposition varied from 13.7 Eq ha^{-1} at South Lake to 38.6 Eq ha^{-1} at Mineral King. Sodium deposition was lower, ranging from 4.8 Eq ha^{-1} at Eastern Brook Lake to 27.8 Eq ha^{-1} at Angora Lake. Deposition of magnesium and potassium on an annual basis was similar. Amounts overall ranged from 4.5 to 9.2 Eq ha^{-1} for magnesium and from 3.5 to 11.0 Eq ha^{-1} for potassium. For the organic anions, the amount of acetate and formate deposition at most sites was similar. Lowest annual deposition was measured at Eastern Brook Lake (five-year means for acetate and formate, 4.8 Eq ha^{-1} and 6.6 Eq ha^{-1}, respectively). Deposition of acetate was greatest at Angora Lake and Tioga Pass (means, 19.1 Eq ha^{-1} and 15.1 Eq ha^{-1}). Sonora Pass had the largest amount of formate deposition during the study: 16.7 Eq ha^{-1}.

Regional Solute Deposition

The next logical step in examining acid deposition in the Sierra Nevada is to investigate regional differences in the loading of solutes. The monitoring network we operated through the period of 1990 through 1993 overlapped the majority of the Sierran range. This allows us to not only calculate mass deposition at our stations but to extrapolate our precipitation chemistry to large areas of the Sierra Nevada. This was accomplished through the use of precipitation quantities measured by other investigators in the higher elevations of the range. Note, these analyses were not done for 1994 and 1995 due to the reduced number of stations.

The only large-scale synoptic measurements of precipitation quantity made in the High Sierra Nevada (other than the present study) are snow surveys conducted by the California Department of Water Resources (DWR). These surveys, known as the California Cooperative Snow Survey (CCSS), are conducted on a periodic basis through the winter and spring at more than 400 stations in the Sierra Nevada. There is usually survey data on or near April 1 of each year which coincides well with our own efforts.

In this analysis the Sierra Nevada was divided into subunits based on latitude and altitude. Selection criteria for the CCSS snow courses were based on minimum elevations and latitude intervals, and SWE are shown in Tables 39 through 42. The latitude interval for each subunit was constrained by the availability of chemistry data from the UCSB monitoring network. Since the number of stations in our network were small we were forced to divide the Sierra Nevada into large subunits.

Snow course numbers, their names, elevations, latitudes and longitudes are also shown in tabular form, divided by latitude zone, for reference in Tables 43 through 48. Only those courses satisfying the selection criteria are listed. The data source was the on-line historical record maintained by DWR in Sacramento. The record consists of all snow course mean values collected for some 400 plus sites throughout the Sierra Nevada, from the beginning of the survey effort in the first half of the century through water year 1993.

The values for peak accumulation found in the summary tables are based on the spring surveys for the specified years. However, due to weather and labor constraints, the actual date of the snow course surveys vary. The selection criteria used for peak survey dates was any measurement recorded for a given snow course between the dates of 16 March and 15 April for each year. In reality, 90 percent of all the measurements fall with ±5 days of 1 April and the statistics should be little affected by the changes in dates. If there is an effect, it would probably be a slight underestimate of the April 1 true value. No attempt was made to adjust the values for the 1 April forecast date.

The mean of the snow courses found in each latitude range and above the elevation constraint are listed, as well as the standard deviation of the measurements and the sample size (number of snow courses used). The combination of these three statistics makes possible the calculation of confidence intervals for the means for a particular zone and desired confidence level. Where $n < 20$, the means and standard deviations of the sample populations should be used with caution.

Several of the CCSS snow courses located in the northern latitude zones are not located in the Sierra Nevada proper, and were excluded from the analysis. A few of the snow courses registered zero SWE values for the surveys in the 1990 water year. The data analysis was carried out both including and excluding the zero values and both are listed in the 1990 water year summary table. In addition, the number of snow courses in the lowest latitude region were so small (3) that the analysis was also done combining the region with the adjacent region (36° - 37°). Both the separate and combined results are presented in the summary tables.

Snow water equivalence from the CCSS surveys were combined with snow chemistry from our monitoring network to calculate solute deposition in each region. Snow chemistry from Pear Lake, Topaz Lake, Ruby Lake and Crystal Lake were also used in these calculations (Melack et al. 1996). Mass deposition for each subunit of the Sierra are presented in tabular form in Tables 49 through 52 . The data cover the period of 1990 through 1993.

Mass deposition within each region varied slightly among the three elevation classes. Loading in most cases was greatest in the >2500m category. The range of mass depositions in each subunit agreed well with loadings at stations in our monitoring network. Among the first four years of study, 1993 had by far the most deposition of solutes; 1990 had the least.

Loading of most solutes tended to be highest in the northern subunits and least in the southern regions of the Sierra Nevada. To better illustrate this trend, graphs were drawn showing the amount of solute loading versus latitude (Figures 36 through 39). Only stations above 2500 m were plotted in these figures.

As a general rule, precipitation quantity increased with latitude (Figure 36). Minor variation in this rule occurred between the two northern subunits but the overall trend was strong. The latitudinal difference in SWE was greatest during 1993. The difference in SWE between 1993 and the drier years was greatest in regions of the northern Sierra and relatively small in the southern Sierra.

Latitudinal trends in solute loading loosely followed the same patterns as precipitation quantity. During 1991, 1992 and 1993 hydrogen ion deposition in the Sierra Nevada decreased from north to south (Figure 36). During 1990 this trend was less strong because of differences in pH among the subunits.

For ammonium, deposition was highest in the 39° to 38°30' region during 1993 and 1991, the two wettest winters (Figure 37). During the relatively dry years of 1990 and 1992, deposition was greatest in the far north subunits. During all years there appears to be a loading minima at the mid-latitude subunit which was followed by a slight increase in ammonium deposition as one goes south. This indicates that precipitation quantity is not the sole factor regulating deposition rates.

Regional loading of nitrate had patterns fairly similar to ammonium. During wet years highest deposition occurred in the northernmost regions (Figure 37). During dry years deposition varied little from north to south but did increase slightly southward in 1992. It is important to note that while SWE was higher in all regions of the Sierra during 1993, winter loading of ammonium and nitrate was the same or higher during 1991 in the southern Sierra. Fairly similar patterns were observed in chloride deposition in the Sierra Nevada (Figure 38).

Sulfate and base cation loading showed interesting trends during 1991 and 1992 (Figures 38 and 39). There was a peak in loading of both in the central Sierra with lessening amounts going northward and southward. During 1993, sulfate and base cation deposition was greatest in the 39° to 38°30' subunit and decreased going south. Sulfate deposition in the two driest years, 1990 and 1992, and base cations loading in 1990 varied little among the regions but tended to be highest in the northern and southern regions.

During 1991, 1992 and 1993, highest levels of organic anion deposition were measured in the 39° to 38°30' subunit (Figure 39). Loading was lower in the other regions but there was very little variability among these subunits. During 1990 loading of acetate and formate was greatest in the northern and southern Sierra and lowest in the central Sierra Nevada. Despite greater precipitation during 1993, loading of organic anions in the southern Sierra did not vary much among the years of study.

As shown previously, solute loading can vary considerably from site to site and among regions in the Sierra Nevada. The differences observed are explained by two factors: variability in precipitation quantity and variability in precipitation chemistry. The regional deposition data indicate that the southern Sierra Nevada receives more loading of ions per unit of precipitation compared to the northern Sierra. This suggests that solute concentrations have a strong influence on the amount of loading an area receives. Determining the relative influence of precipitation chemistry and precipitation quantity on deposition variability may help us explain differences in sources of solutes to the Sierra Nevada.

In winter snowfall the relative importance of these two factors can be seen when comparing solute loading to snow-water equivalence. In Figures 40 through 43 plots were drawn showing the relationship of winter solute deposition versus SWE. Data from 11 of our study sites plus Pear Lake, Topaz Lake, Ruby Lake and Crystal Lake were used in this analysis.

For certain ions there is a strong linear relationship between winter loading and SWE. For instance, 83% of the variability in sulfate loading in the Sierra Nevada is explained by SWE (Figure 40). For hydrogen ion the relationship is almost as strong with 81% of hydrogen ion loading explained by precipitation quantity. The correlation coefficient for sodium and chloride indicate that differences in SWE account for 70-75% of the variability in winter loading of these ions (Figures 40 and 41). In contrast, less than 50% of the variability in organic anions and potassium was explained by SWE (Figures 42 and 43). For nitrate, ammonium and the other base cations, SWE explained approximately 50% of the variability in loading. These data indicate a common source for most of the sulfate, hydrogen ion, sodium and chloride deposited in the Sierra Nevada during the winter. This source in all likelihood would be oceanic. Data for the other ions suggests that local sources of solutes exist and vary from region to region.

Chapter VII

No-Precipitation Bucket Rinses

To accurately estimate solute deposition to the Sierra Nevada it is necessary to account for contamination of precipitation samples. During snow surveys great care was taken to avoid contamination of samples in the field and laboratory. Examination of QA/QC data for these samples indicates that we were successful and that our estimates of winter loading are not complicated by sample contamination. Non-winter precipitation was collected in buckets installed in automated samplers and the possibility existed that the buckets could be contaminated while installed. Recognizing this possibility, a large effort was made to detect and accurately quantify the amount of contamination in non-winter samples during 1990 through 1993. Bucket rinses were not done during 1994.

The largest potential source of contamination to non-winter precipitation samples are dusts, debris and insects that could enter the samples while still in the rain collector. Efforts were made to ensure a tight fit between the sample bucket and the protective roof pad but contamination to some extent was unavoidable. Many samples, especially during windy conditions, had visible dust, insects and vegetation in them. In the following section we will examine the impact of this contamination on our estimates of non-winter solute deposition.

In order to determine the nature and extent of contamination to samples in the collectors, bucket rinses were collected. Bucket rinses were done at the weekly or biweekly bucket change when no precipitation was seen in the bucket. These QA/QC samples are hereafter referred to as No-Precipitation-Bucket-Rinses or NPBR. A NPBR was collected by adding 250 ml of deionized water to the bucket and slowly swirling so that the water contacted all internal surfaces. The rinse water was then subsampled into a 125-ml bottle for subsequent determination of major cations, major anions and organic anions. Deionized water samples were collected and analyzed concurrently with the NPBR samples to rule out any background contamination in the DI water. Analytical methods for these samples are presented in Chapter II of this report.

Average chemistry of NPBR from each station for most years of study was calculated. These data are presented in tabular form in Table 53 along with the overall mean chemistry at each site. Also shown is the average number of days buckets spent installed in the collectors prior to being rinsed. Data were not used from NPBR samples when rain-gauge records indicated precipitation had occurred during the installation period of the bucket. No NPBR samples were collected during 1990 at Emerald Lake, Kaiser Pass and Mineral King.

Site to Site Variability in NPBR Chemistry

Overall the mean concentrations of ions in the NPBR samples were low. For ammonium, overall mean concentrations ranged from 0.5 µEq L^{-1} at Angora Lake to 3.2 µEq L^{-1} at Mammoth Mountain. For nitrate, levels varied from 0.4 µEq L^{-1} at Angora Lake to 6.4 µEq L^{-1} at Mammoth Mountain. During 1990, solute concentrations were high in NPBR samples from Mammoth Mountain due to a poor fit between the bucket and roof-seal. This situation was corrected in later years. Sulfate concentrations in the NPBR samples tended to be lower than nitrate, ranging from 0.2 µEq L^{-1} at Angora to 3.4 µEq L^{-1} at Mammoth Mountain. Chloride levels in rinses were very low and varied little among the sites (range, 0.2 to 1.7 µEq L^{-1}).

Except at the Mammoth Mountain and Onion Valley stations, mean base cations concentrations in NPBR were low, ranging from about 0.1 to 2.0 µEq L^{-1}. The same was true for the organic anions with the exception of Emerald Lake during 1991. Levels of organic anions in these samples were extremely high because of contaminated chloroform used to preserve the samples.

Statistical tests were used to determine whether differences in NPBR chemistry among stations were significant. These procedures were identical to those used to analyze snow chemistry in Chapter IV (i.e. Kruskal-Wallis ANOVA, Dunn's MCT). Results from tests on the NPBR data are summarized in Table 54. Data from all years was lumped together for these tests in order to increase the power of the tests.

Many statistically significant differences in NPBR were expected because of the large number of comparisons possible. However, few significant differences were found in NPBR chemistry among the eleven study sites. Solute levels in Angora Lake NPBR samples were significantly lower than at a few other stations. Likewise, some ion concentrations in NPBR from Onion Valley were greater than at a few other stations. Taken as a whole the tests indicate there is little to distinguish NPBR chemistry among the 11 study sites.

It seemed likely that stations with shorter bucket duration (i.e.. Angora Lake, Kaiser Pass and Mineral King) would have more dilute NPBR chemistry than other stations. This was not the case however. Bucket duration had no significant effect on contamination of buckets.

Annual Variability of NPBR Chemistry

Statistical tests identical to those above were used to determine if there were significant differences in NPBR chemistry among years. Data from all stations were lumped together for these analysis.

In contrast to differences among sites, NPBR chemistry was significantly different among years (Table 55). Overall, chemistry from NPBR's done in 1993 was significantly lower in sulfate, formate, nitrate, sodium, ammonium, magnesium, calcium and chloride than one or more other years. No significant differences among years were found for acetate, potassium and bucket duration.

Contamination Loading

The next step in the analysis of NPBR data was to express the contamination in units that relate to solute deposition. Using the mean chemistry for each year and the mean bucket duration, the rate of bucket contamination was estimated. This rate is expressed as milliequivalents per hectare per day (mEq ha^{-1} da^{-1}) and are presented in Table 56.

Average contamination rates during the 1990 through 1993 ranged from less than 1 to nearly 10 mEq ha^{-1} da^{-1} for most ions during most years. Conspicuous exceptions were 1990 at Mammoth Mountain (most solutes), calcium at Kaiser Pass and Onion Valley during most years and organic anions at Emerald Lake during 1991 (contaminated chloroform).

These rates were use to estimate the amount of non-winter loading of solutes that was caused by contamination loading. Contamination loadings by site for the period of 1990 through 1993 are presented in Table 57. This quantity was calculated by multiplying the contamination rate for an ion by the installation interval and converting to units of Eq ha^{-1} by dividing by 1000. The installation interval was the number of days buckets were installed when there was a rain event sampled. Only when a rain event was sampled could contamination loading have an effect on non-winter solute deposition since NPBR chemistry was not used as an estimate of dry depositional loading.

Average contamination loading for most ions at most sites was small. To facilitate comparisons, the data are also expressed as a percent of non-winter solute loading in Table 58. Loading from contamination was typically below 1 Eq ha^{-1} in absolute terms and usually from 1% to 10% of total non-winter loading.

For ammonium the contribution of contamination loading to non-winter deposition averaged 2.9% during the study. The percentage of nitrate in non-winter loading from contamination was similar to that for ammonium and averaged 2.8% overall. Similar results were found for sulfate (mean, 2.6%). For chloride percentages ranged from 5.2% to 8.2% with an average overall of 6.8% of non-winter loading attributed to contamination.

The contribution of contamination loading of base cations was higher. For calcium, magnesium, sodium and potassium contamination represents 10.7%, 10.5%, 8.1% and 16.2%, respectively, of non-winter loading of these constituents. For organic anions contamination loading contributed from about 2% to 7% of non-winter loading of acetate and formate.

On a percentage basis and in absolute terms, contamination loading was larger during 1992 compared to other years (Table 58). For example, contamination represented more than 20% of non-winter deposition of calcium, magnesium and potassium. Two factors account for this finding. First, the cumulative installation intervals used to calculate contamination loadings during 1992 were large owing to the large number of precipitation events that occurred during 1992. Second, the concentrations of solutes in NPBR from 1992 were relatively high compared to other years. The combination of these factors resulted in relatively high levels of contamination loading during 1992.

Taken together, the results from the NPBR analyses indicate that we have overestimated non-winter wet-deposition of solutes by a few percent. During some years the overestimates exceeded 20% of non-winter loading. These effects are reduced when contamination loading is compared to annual loading. For example, while contamination loading of calcium during 1992 averaged 20.7% of non-winter deposition, it contributed less than 9% of annual loading of calcium for 1992. Likewise, 6.0% of non-winter nitrate loading is attributed to contamination, but this represents less than 4% of all nitrate loading for 1992.

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Table 1. Geographic location of study sites. Elevations are meters. Sites are listed by decreasing latitude.

Site	Location	Elevation	Latitude	Longitude
Alpine Meadows	Tahoe N.F.	2,164	39°08'33"	120°13'40"
Angora Lake	Eldorado N.F.	2,286	38°51'45"	120°03'50"
Sonora Pass	Toiyabe N.F.	2,937	38°19'55"	119°36'11"
Tioga Pass	Inyo N.F.	2,993	37°57'37"	119°16'47"
Mammoth Mountain	Inyo N.F.	2,940	37°38'36"	119°01'41"
Eastern Brook Lake	Inyo N.F.	3,170	37°25'59"	118°44'35"
Ruby Lake	Inyo N.F.	3,390	37°24'50"	118°46'15"
Kaiser Pass	Sierra N.F.	2,941	37°17'23"	119°05'08"
South Lake	Inyo N.F.	3,010	37°10'17"	118°33'50"
Onion Valley	Inyo N.F.	2,800	36°46'29"	118°20'13"
Topaz Lake	Sequoia N.P.	3,218	36°37'30"	118°38'11"
Emerald Lake	Sequoia N.P.	2,824	36°35'49"	118°40'29"
Mineral King	Sequoia N.P	2,694	36°27'21"	118°35'05"