CHARACTERIZATION OF CLOUD CHEMISTRY AND FREQUENCY OF CANOPY EXPOSURE TO CLOUDS IN THE SIERRA NEVADA

Final Report

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1800 15th. St. (15th. & R)
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Attn: Dr. John Holmes
Attn: Mr. Eric Fujita

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Professor Michael R. Hoffmann	Principal Investigator
Jeffrey L. Collett, Jr.	Graduate Research Assistant
Bruce C. Daube, Jr.	Research Engineer

Environmental Engineering Science
W. M. Keck Laboratories
California Institute of Technology
Pasadena, California 91125
(818) 356–4391

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CHAPTER 1

CLOUDWATER CHEMISTRY IN SEQUOIA NATIONAL PARK

Atmospheric Environment

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Abstract

Interception of cloudwater by forests in the Sierra Nevada may contribute significantly to acid deposition in the region. Cloudwater sampled in Sequoia National Park had pH values ranging from 4.4 to 5.7. The advance of cold fronts into the Park appears to lead to higher aerosol and gas phase concentrations than are seen under normal mountain/valley circulations, producing higher cloudwater concentrations than might otherwise be expected. Estimates of annual deposition rates of NO_3^- , SO_4^{2-}, NH_4^+, and H^+ due to cloudwater impaction are comparable to those measured in precipitation.

Executive Summary

Overview

Interception of acidic cloudwater has been implicated as a possible contributor to the decline of forest stands both in North America and Europe. Plant injury in forests has been observed to increase at higher elevations where immersion in cloudwater is more frequent and other stress factors become important. In order to estimate the potential impact of acidic cloudwater deposition on forest communities, several issues must be addressed. Aside from the difficult questions concerning dose–response relationships between ambient cloudwater and members of the plant community, these issues include the frequency of cloud interception in the area of interest, the rate of cloudwater deposition to the plant surfaces, and the chemical composition of the deposited cloudwater. Contributions by cloudwater to acidic deposition should also be compared to contributions by precipitation and dry deposition.

The Sierra Nevada of California have extensive stands of conifers which may be sensitive to acidic cloudwater deposition. Emissions from the San Joaquin Valley and clouds associated with incoming frontal systems frequently pass through the region. Interception of cloudwater by the forest canopy may contribute significantly to regional deposition budgets for water, nutrients, and pollutants, including acids. In addition to cloud interception associated with the passage of frontal systems, two other mechanisms are thought to lead to the interception of fog and clouds in the region: (1) local formation of fog due to the rapid cooling of moist air produced during snow melt on sunny days, and (2) the lifting of dense winter "Tule" fogs, previously trapped near the floor of the San Joaquin Valley, due to a reduction in atmospheric stability over the valley. These "Tule" fogs are often highly polluted, and their interception by Sierra vegetation may have important ecological consequences.

The initial chemical composition of cloudwater has been shown to be determined largely by the composition of the aerosol that serve as condensation nuclei and the ambient concentrations of soluble gases. The composition is altered as additional aerosol is scavenged and chemical reactions take place within the droplet. In order to understand what influences cloudwater chemistry at a particular location, therefore, it is necessary to understand the processes that control local concentrations of aerosol and gases, particularly during the period immediately preceding cloud formation. These processes include emission rates, atmospheric reactions, transport routes, and deposition.

Concentrations of most inorganic aerosol and gas phase species in the southern and central Sierra Nevada of California are controlled primarily by meteorological conditions affecting transport from distant sources. Both the San Joaquin Valley and the San Francisco Bay area are thought to be important pollutant source regions affecting air quality in the central and southern Sierra. Local Sierra sources of species such as SO_2, NO_x, and NH_3 are relatively unimportant by comparison.

Meteorology within the San Joaquin Valley is normally dominated by the presence of high mountains that border the valley on three sides. Net air flow into the valley is generally from the northwest, except during the winter. Air masses exit the valley predominantly by passing over the Tehachapi Mountains located at the southeastern border of the valley. Afternoon upslope flows on both sides of the valley, induced by preferential heating of the air along the mountain slopes, are thought to play a secondary role in transporting air out of the valley. The upslope flows form the primary mechanism for transport of air parcels from the valley floor up into the Sierra.

Temperature inversions in the air mass above the San Joaquin Valley floor are strongest in the winter, but occur frequently throughout the year. The presence of the mountains surrounding the valley combines with an inversion to trap pollutants within the valley. The passage of frontal systems through the valley can serve to alleviate this condition by eliminating the temperature inversion, thus permitting pollutants to mix up to elevations where they may exit over the Tehachapi Mountains. Increased wind speeds often associated with the fronts also aid in the removal of valley pollutants. Frontal systems may also change the predominant direction of air flow within the valley from northwesterly to southerly, thereby altering the importance of various regional emissions to Sierra air quality.

Pollutant concentrations in the Sierra are significantly affected by the passage of cold fronts, often increasing as a storm approaches. These increases may reflect an increase in the mixing height over the valley, a change in pollutant transport patterns, or some combination of these two factors. Increases in aerosol and gas concentrations with the advance of cold fronts may result in the production of cloudwater which is more polluted than might otherwise be expected, based on typical Sierra aerosol and gas concentrations. Interception of this polluted cloudwater by the forests on the slopes of the Sierra contributes to total pollutant deposition in the region.

The rate of cloudwater deposition to a forest canopy depends strongly on four factors: (1) the liquid water content (LWC) of the fog or cloud, (2) the droplet size distribution, (3) the structure of the forest canopy, and (4) the ambient wind speed. Cumulative deposition over a specified period of time also depends on the frequency and duration of fog or cloud interception in that interval. The quantity of cloudwater deposited to the forest on a mountain slope may vary significantly with elevation, due to variations in the parameters governing the deposition process. Cloudwater deposition may increase with elevation, due to increases in average wind speeds and higher liquid water contents. The most important factor determining the elevational dependence of cloudwater deposition, however, is the elevational pattern of cloud interception. Different meteorological conditions may tend to favor cloud interception at different elevations. Convective clouds associated with frontal systems often have base elevations exceeding 1500 m; thus, these clouds will be intercepted most frequently at elevations above 1500 m. The lifting of "Tule" fogs from the floor of the San Joaquin Valley, however, will more likely result in interception at lower elevations. Understanding elevational gradients in cloud interception is crucial to assessing the importance of cloudwater deposition for different regions in the Sierra Nevada.

Objectives

The principal objectives of this study are listed below.

1. Examine spatial and temporal variations in the chemical composition of intercepted cloudwater in the Sierra Nevada of central California, during the spring, summer, and fall. At the request of the California Air Resources Board (CARB), the project was expanded to include a study of winter cloudwater chemistry as well.

2. Investigate the relationship between Sierra cloudwater chemistry and the concentrations of precursor aerosol and gases. Examine the behavior of pollutant concentrations in the Sierra during the approach of frontal systems.

3. Characterize the frequency of cloud interception, as a function of elevation, in the Sierra. Determine those elevations subjected to the largest quantities of deposited cloudwater.

4. Design and construct five units of an automated fogwater sampling system for use by the CARB in a routine statewide monitoring network. Provide complete documentation on operation of the system and recommend monitoring sites.

Technical Plan

In order to achieve the objectives stated above, we operated a total of fourteen cloudwater monitoring sites in the Sierra Nevada of central California. Elevations of the sites ranged from 820 to 2360 m. Eight of the stations were located in Sequoia National Park, while the remaining six were located in Yosemite National Park. All of the sites were equipped with a system which monitored the frequency of cloudwater interception and the deposition rate of cloudwater to a standard collector. In addition, the system measured wind speeds and amount of precipitation.

Two of the sites were also equipped with a second system which was used to collect samples of cloudwater for chemical analysis. During the spring, summer, and fall, sub–event samples of cloudwater were collected and stored in a refrigerated environment. These samples were picked up at least once per week by a site operator. The system used to collect these samples included modified versions of the Caltech Active Strand Cloudwater Collector (CASCC), cloudwater sensor, and fractionating autosampler used by this group in previous studies for the CARB. During the winter, freezing temperatures necessitated the development of an entirely different collection system. This system incorporated a new cloudwater collector with internally heated collection surfaces and an optical cloudwater sensor to determine when the collector should be activated.

Measurements of aerosol and gas concentrations were made on an intensive basis at two sites in Sequoia National Park, and at one site on the floor of the San Joaquin Valley. Intensive measurements also were utilized to investigate concentrations of unstable species, including carbonyls, carboxylic acids, and peroxides, in Sierra cloudwater, and to examine elevational gradients in cloudwater chemistry and cloud liquid water content.

Major Accomplishments

The following accomplishments were achieved during this study.

1. The Caltech Active Strand Cloudwater Collector (CASCC), used in previous studies performed for the CARB, was modified to make it suitable for use in an automated cloudwater collection system. Automatically operated covers were added to the front and rear of the collector, to prevent accumulation of dry deposition between sampling periods. An automated rinse system was also added. All surfaces which come in contact with collected cloudwater are

rinsed by this system at the beginning and end of each cloud interception event.

2. The autosampler we have used previously for the collection of sub–event precipitation and cloudwater samples was modified to increase its sampling capacity, in order to allow the system to collect samples throughout extended, or multiple, events.

3. A passive cloudwater monitoring system was developed and constructed for use in monitoring the frequency of cloud interception, the amount of cloudwater deposited to a standard collection surface, the amount of precipitation, and the ambient wind speeds. The system includes a passive cloudwater collector, a rain gauge, an anemometer, and a data–logging system. Both the cloudwater collector and the data–logging system were designed and constructed specifically for this project.

4. The Caltech Heated Rod Cloudwater Collector (CHRCC), used for collection of cloudwater during freezing periods, was developed and constructed. The CHRCC utilizes internally heated stainless steel cylinders as a collection surface. The collector operates cyclically, sampling for 15 minutes followed by one minute of heating to melt off the rime which has formed on the rods, to minimize evaporation of collected cloudwater. Mass transfer calculations indicate that evaporation from the heated rods would be significant if the heating was conducted while the collector was in operation but should be small when performed on a cyclical basis. Collection characteristics of the CHRCC are very similar to those for the CASCC.

5. A backscattering–type cloudwater sensor was developed for use with the winter cloudwater sampling system. The sensor emits a modulated infrared beam and monitors the amount of light from the beam scattered back toward the sensor. When clouds are present, the backscattering increases dramatically. The sensor is insensitive to rainfall.

6. Cloudwater intercepting the slopes of the Sierra was automatically sampled at two locations between September of 1987 and November of 1988. One site was located at 1856 m in Sequoia National Park, while the second site was located at 1590 m in Yosemite National Park. Valid samples representing approximately 50% of the total interception time were collected at the Sequoia site and analyzed to determine the concentrations of major ions.

7. Intensive measurements of aerosol and gas concentrations were made at two sites in Sequoia National Park and at one site in the San Joaquin Valley during the period of April 26–29, 1988. Intensive measurements of cloudwater were made during this period on April 28, 1988 at the two Sequoia sites.

8. The spatial and temporal variations exhibited in patterns of precipitation and cloud interception were investigated at fourteen sites in the Sierra Nevada of California. The sites, located in Sequoia and Yosemite National Parks, were selected to represent an elevational gradient in each Park, ranging from approximately 800 to 2400 m in elevation. The study began in September, 1987 and continued through October, 1988.

9. A routine fogwater monitoring system was designed and five units were

constructed for use by the CARB in a statewide fog monitoring network. The system includes a backscattering–type fog detector, a new fogwater collector, and a new computer–controlled refrigerated autosampler for the fractionation and storage of collected fogwater. Both the autosampler and the collector were developed particularly for this system, which is designed to collect one sample per fog event.

Major Results

The major results of this study are presented below.

1. Clouds were observed to intercept the mountain slopes at the Sequoia site a total of 265 hours during the 12 month period between September 1987 and August 1988. Peak interception periods occurred in November and April, while the lowest activity was observed during the summer months.

2. The chemical composition of the sampled cloudwater in both Parks was dominated by NO_3^-, SO_4^{2-}, and NH_4^+. The balance between the cloudwater concentrations of NO_3^- and SO_4^{2-} vs. NH_4^+ was largely responsible for determining the cloudwater pH, although inputs of formic and acetic acid are also believed to be important in this regard, particularly for less polluted samples.

3. The pH of the cloudwater samples collected in Sequoia National Park ranged from 3.9 to 6.5; samples collected in Yosemite National Park had pH values between 3.8 and 5.2. During periods of simultaneous collection, and on average, Yosemite samples were more acidic than Sequoia samples. The pH

differential appears to be related to relatively small differences in the cloudwater concentrations of NO_3^-, SO_4^{2-}, and NH_4^+ at the two sites.

4. Large variations in the chemical composition of Sierra cloudwater were observed between cloud interception events and within the course of a single event.

5. The technique of principal factor analysis was applied to data representing the chemical composition of 45 cloudwater samples, collected in Sequoia National Park during the fall of 1987, in order to statistically reveal potential ion sources contributing to the sample composition. Four important sources were hypothesized based on this analysis: (1) a source dominated by NO_3^-, SO_4^{2-}, and NH_4^+, reflecting anthropogenic inputs; (2) a source representing sea salt inputs of Na^+, Cl^-, and Mg^{2+}; (3) a soil dust source comprised by Ca^{2+}, K^+, and Mg^{2+}; and (4) an H^+ source, probably associated with organic acids, which were not routinely analyzed.

6. Although the volume of water deposited to the canopy over the course of a year due to cloudwater interception is smaller than that due to precipitation, concentrations of NO_3^-, SO_4^{2-}, and NH_4^+ in the cloudwater at Lower Kaweah (elev. 1860 m) in Sequoia National Park are much higher than those typically observed in precipitation at the same site. Average concentrations of NH_4^+ and NO_3^- in cloudwater are more than ten times those observed in precipitation; cloudwater SO_4^{2-} concentrations are more than three times those observed in precipitation. Since the cloudwater concentrations are so much higher, even small inputs of cloudwater can contribute relatively large quantities of these species to the ecosystem.

7. Pollutant transport routes within the San Joaquin Valley and in the adjacent Sierra are altered considerably preceding periods of cloud interception when frontal systems are moving through central California. Concentrations of aerosol pollutants were observed to increase in Sequoia National Park immediately preceding the arrival of a cold front. This increase, which was consistent with similar observations made previously, appears to be related to both a breakdown in the vertical stability of the atmosphere above the San Joaquin Valley and an increase in southerly flow aloft. Increased aerosol concentration levels lead to the production of more polluted cloudwater in the Sierra than would be predicted based on average Sierra aerosol and gas concentrations.

8. Measurement of inorganic cloudwater ion concentrations indicates a frequent deficit of anions relative to cations. This deficit shows a positive correlation with sample pH (samples with higher pH tend to exhibit a greater anion deficit). In some samples, chloroform was added immediately after collection to prevent microbial degradation of low molecular weight organic acids. Concentrations of formate and acetate in these samples have been found to account for the measured inorganic anion deficit. In many samples these two organic acids, with smaller inputs from pyruvate, lactate, and propionate, are important contributors to total sample ionic strength and acidity, and may be important contributors to total acid deposition in the Sierra. Formic and acetic acid are believed to be largely responsible for determining the pH of Sierra cloudwater in the absence of strong anthropogenic inputs.

9. Intensive measurements of cloudwater chemistry revealed significant

quantities of aqueous phase H_2O_2 in Sequoia National Park. Significant concentrations of carbonyls were also observed in Sequoia cloudwater. Carbonyl concentrations were dominated by formaldehyde and glyoxal.

10. Rates of cloudwater deposition to the passive cloudwater collectors, which may be comparable to rates for exposed conifers, were observed to frequently exceed 1.0 mm hr^{-1} at several sites, and surpassed 20 mm hr^{-1} at one site in Yosemite National Park during passage of a strong Pacific cold front. Cloudwater deposition of NH_4^+, NO_3^-, SO_4^{2-}, and H^+ to exposed conifers near this site, during this single interception event, is believed to have contributed a significant portion of the total annual atmospheric flux of these species to nearby trees, and to the ground beneath them.

Major Conclusions

The following conclusions are based on the results obtained during this study.

1. The role of Sierra cloudwater acidity neutralization by inputs of ammonia was clearly observed. In the absence of large ammonia inputs, sample pH values in the Sierra may fall below 3.0.

2. Estimates of annual deposition rates of major ions via cloudwater interception to the forest canopy at the Sequoia site were calculated. The rates for NO_3^-, SO_4^{2-}, and NH_4^+ were calculated to be somewhat lower than previously were estimated for the same site, largely because wind speeds and cloud liquid water contents during interception turned out to be lower than

previously assumed. The current deposition estimates are still significant, however, with regard to measured contributions from precipitation and estimated contributions from dry deposition. Cloudwater interception may in fact be the dominant deposition mechanism for NO_3^- and NH_4^+, particularly for isolated trees or ridgetop canopies where wind speeds are higher and cloudy air parcels can impact directly on foliar surfaces.

3. Cloud interception was observed to contribute significantly to the total deposition budgets of water and pollutants in the Sierra. The contributions are particularly important for exposed conifers, which are subject to direct impaction of ambient clouds.

4. Most Sierra cloud interception events are believed to result from the interception of convective clouds, associated with frontal activity; however, there is some evidence to suggest that dense winter "Tule" fogs, formed near the floor of the San Joaquin Valley, may intercept lower elevation sites in Sequoia National Park, when the atmosphere over the valley is destabilized. Interception of convective clouds is observed most frequently at sites above 1500 m elevation. Ridge–top sites, which often experience the highest wind speeds, usually receive the greatest hydrological deposition fluxes from impacting cloudwater. Correlations of cloudwater deposition between sites in Sequoia National Park and similarly elevated sites in Yosemite National Park are often stronger than those between sites with differing elevations in a single Park.

Recommendations

The following recommendations are made with regard to the study of cloudwater deposition and chemistry in the Sierra Nevada of central California:

1. Continued monitoring of the chemical composition of cloudwater in Sequoia and Yosemite National Parks. Continuation of the monitoring network would help to document more completely annual variations in cloudwater interception and composition. It also would provide the basis for the eventual establishment of long–term monitoring capability in the harsh climate of the Sierra. When the cloudwater sampling program was initially planned, dry deposition monitoring stations were expected to be in operation in both Sequoia and Yosemite National Parks. With information on dry deposition and cloudwater deposition added to the existing deposition network for rain and snowfall, a relatively complete picture of atmospheric deposition could be completed for the two monitoring sites. Since installation and operation of the dry deposition stations was delayed until after most of the cloudwater data had already been collected, it is difficult to make estimates of total atmospheric deposition. This is particularly true since amounts of dry deposition may depend to a great extent on the frequency of both cloud interception and precipitation. Continuation of the cloud monitoring program is needed to significantly overlap the study of dry deposition.

2. Routine monitoring of the concentrations of organic acids in cloudwater in Sequoia and Yosemite National Parks. By modifying the sample delivery mechanism in the autosampler, it could be adapted to automatically preserve

separate aliquots of sample for later determination of organic acids. These preserved aliquots could also be used for measuring the sample pH, which can change rapidly in unpreserved samples with large concentrations of organic acids. The result will be a better characterization of the cloudwater acidity at the time it intercepts the forest canopy. Regular measurements of organic acid concentrations would help to determine their contribution to total acid deposition in the two Parks. These measurements would also enable seasonal variations in organic acid levels, which may be indicators of the strength of biogenic vs. anthropogenic sources, to be examined.

3. Continued testing and development of the Caltech Heated Rod Cloudwater Collector (CHRCC). Experimental documentation of the performance of the CHRCC is needed to verify the chemical integrity of the samples it collects. This should include a careful examination of evaporation from the rods during the heating cycle, as well as an investigation of the effect of changes in sample temperature upon sample chemistry. A comparison should also be made between simultaneously collected samples from the CHRCC and the Caltech Active Strand Cloudwater Collector (CASCC).

4. Evaluation of the performance of the backscattering cloud sensor in winter conditions. Evidence from the current study suggests that the backscattering sensor is not sensitive to the presence of rain drops, but may be sensitive to snowflakes crossing its field of view. This possibility needs to be thoroughly examined. Distinguishing between snow and cloud is crucial for the development of an automated winter cloudwater collection system since the sensor is responsible for identifying those periods when the collector should be operating, and snowflakes will be quite efficiently collected by the

collector.

5. Study the relationship between precipitation chemistry and the chemistry of cloudwater. Relationships between the chemical composition of cloudwater droplets and the chemical composition of snowflakes and rain drops are not well understood, other than to say cloudwater is typically much more concentrated in most major ionic species. An attempt should be made to define these relationships as they exist in the Sierra. Examination of ion ratios in cloudwater vs. precipitation would lend insight to whether lower concentrations in precipitation are due primarily to dilution associated with condensational growth of cloud droplets, or whether other mechanisms play an important role.

6. Continued monitoring of aerosol and gas concentrations at Yosemite, Sequoia, and selected sites in the San Joaquin Valley prior to and during cloud interception in the Sierra. Aerosol and gas concentrations are the primary determinants of the chemical composition of cloudwater formed in the same air mass. Intensive aerosol and gas monitoring efforts should be conducted for several events to determine the importance of the build–up of pollutants in the Sierra preceding arrival of a frontal system. Contrasts in concentrations between the monitoring sites, along with available meteorological data, would help to further identify important source regions and explain the differences observed in cloudwater chemistry at Sequoia and Yosemite.

7. Use of tracers to investigate the transport and dilution of pollutants, in the San Joaquin Valley and in the Sierra, preceding, and during, cloud

interception. This could include an investigation of the use of pesticides as tracers of regional San Joaquin Valley emissions impacts upon Sierra Nevada cloudwater. SF_6 could also be employed as a tracer for tracking emissions from areas such as the southern San Joaquin Valley oil fields which appear to contribute to sulfate and nitrate concentrations in Sierra cloudwater. The depth of the afternoon upslope flow in the Sierra is typically thought to increase with elevation. As the depth of the flow increases, the original air parcels brought up from near the valley floor are diluted by entrainment of air aloft. Use of SF_6 as a tracer of the initial air parcels in the upslope flow would provide valuable information on the degree of dilution that occurs. Understanding this dilution process, as it functions during periods of cloud interception, is crucial to developing an understanding of the importance of local vs. distant emissions sources in defining the chemical composition of the cloudwater.

9. Continued monitoring of the frequency of cloudwater interception as a function of elevation in Sequoia National Park. Understanding elevational gradients in cloudwater interception is important for understanding the role of cloudwater deposition in contributing to deposition of acids and other species at different elevations in the Sierra. Data collected during this study have illustrated the importance of cloudwater deposition, particularly at elevations above 1500 m. The data have also illustrated the potential importance of interception of highly polluted "Tule" fogs at lower elevations in the Park during the winter months. Continued monitoring of cloud interception frequency is needed to more accurately establish average deposition patterns over longer periods of time. This is particularly important in view of the abnormally dry year that occurred during this

study.

10. Monitoring of the chemical composition of cloudwater during the winter at a lower elevation (~ 800 m) site in Sequoia National Park, where highly polluted "Tule" fogs may be intercepted, as they rise above the floor of the San Joaquin Valley.

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Introduction

Interception of acidic cloudwater has been implicated as a possible contributor to the decline of forest stands both in North America and Europe (McLaughlin, 1985). Plant injury in forests has been observed to increase at higher elevations where immersion in cloudwater is more frequent and other stress factors become important (Johnson and Siccama, 1983). In order to estimate the potential impact of acidic cloudwater deposition on forest communities, several issues must be addressed. Aside from the difficult questions concerning dose–response relationships between ambient cloudwater and members of the plant community, these include the frequency of cloud impaction in the area of interest, the rate of cloudwater deposition to the plant surfaces, and the chemical composition of the deposited cloudwater. Contributions by cloudwater to acidic deposition should also be compared to contributions by precipitation and dry deposition.

Sequoia National Park (SNP), located in the southern Sierra Nevada of California, has extensive stands of conifers which may be sensitive to acidic cloudwater deposition. Emissions from the San Joaquin Valley and clouds associated with incoming frontal systems frequently pass through the Park (Smith et al., 1981). In order to assess the severity of the problem, we have initiated an extensive study of cloudwater chemistry in SNP. Early results of this investigation, the first of its kind in the Sierra Nevada, are discussed below.

Site Description and Measurement Techniques

Sampling Sites

Cloudwater samples were collected at two sites in SNP during the fall of 1985 and the spring of 1986. The main collection site is situated on a granite outcrop (elev. 1856 m) at the Lower Kaweah Research Site below Giant Forest (Figure 1). The surrounding forest is mixed conifer. Several factors were considered in selecting this site for use in the study. First, the site is located at an elevation frequently observed to be impacted by clouds during the passage of storm systems. Second, the site was already in use as an air quality monitoring site and as an NADP rain collection site (Stohlgren and Parsons, 1987). Third, it is one of very few locations in the Park which provides open exposure to impacting clouds, has electric power, and is readily accessible. It should be mentioned, however, that the complex topography of the site makes interpretation of the exact meteorological situation corresponding to the observed cloudwater compositions difficult. As at most locations on the western slopes of the Sierra, the lifting of moist air as it passes over the mountains may lead to the production of orographic clouds which augment clouds present due to convective activity (Wallace and Hobbs, 1977). Despite these factors, we feel that the Lower Kaweah research site is the best location presently available in the Park for conducting this type of study. The second site is located 3 km to the southwest at the Deer Ridge turnout on the General's Highway. The elevation of this site is approximately 1490 m. This site was selected as an alternate, to be used when temperatures at the Lower Kaweah site fell below freezing. Since no AC power is available at this site, the sampling equipment was operated using a 12 V battery.

Measurement Techniques

Cloudwater samples were collected with the Caltech Active Strand Cloudwater Collector (CASCC) depicted in Figure 2. The CASCC (Daube et al., 1987a) is an improved version of the collectors described in detail elsewhere (Jacob et al., 1985a; Daube et al., 1987b). In addition to being used in Caltech cloudwater studies, more than twenty–five CASCCs are currently in use by six other research groups. The CASCC employs a fan to draw air across six angled banks of 508 μm Teflon strands at a velocity of 8.5 $m \cdot s^{-1}$. Cloudwater droplets in the air parcel are collected on the strands by inertial impaction. The collected droplets run down the strands, aided by gravity and aerodynamic drag, through a Teflon sample trough into a collection bottle. The 50% collection efficiency size–cut predicted from impaction theory corresponds to a droplet diameter of $\simeq 3.5$ μm.

Data from a side–by–side comparison of the CASCC with the Caltech Rotating Arm Collector (RAC) indicate that the instruments collect samples of coastal stratus with statistically indistinguishable concentrations of NO_3^-, SO_4^{2-}, H^+, and NH_4^+ (Hoffmann et al., 1988). The RAC (Jacob et al., 1984) was earlier found to collect representative samples in an intercomparison with samplers of five differing designs (Hering and Blumenthal, 1985). Differences in the sample concentrations of ions associated with soil dust and sea salt (Ca^{2+}, Mg^{2+}, Na^+, and Cl^-), however, were observed among the samples collected by different instruments in both intercomparison studies. Hering and Blumenthal attributed some of the discrepancies to contamination of the samples by soil dust kicked up in the study area. In the CASCC–RAC study, higher concentrations of Ca^{2+}, Mg^{2+}, Na^+, and Cl^- measured in RAC samples have been attributed to the failure of this instrument to efficiently collect droplets smaller than about 15 μm. A separate study (Munger,

1989) has indicated that ions associated with large aerosol, such as sea salt and soil dust, are found predominantly in the larger portion of the cloud droplet size spectrum in coastal stratus. Based on these results, we believe that the CASCC provides a more representative sample of the chemical composition of the entire droplet spectrum than is provided by the RAC or other instruments with similarly low collection efficiencies for small droplets.

The major ions, Cl^-, SO_4^{2-}, and NO_3^-, were measured in our laboratory using a Dionex 2020i ion chromatograph with a Dionex AS–4 column and a bicarbonate–carbonate eluent. Na^+, Ca^{2+}, and Mg^{2+} concentrations were determined using a Varian Techtron AA6 atomic absorption spectrophotometer. NH_4^+ was measured by the phenol–hypochlorite method (Solorzano, 1967) using an Alpkem flow injection analyzer. Organic acids were preserved by adding chloroform (Keene et al., 1983) to an aliquot of the cloudwater sample immediately after collection and later analyzed by ion exclusion and normal ion chromatography run in parallel.

Aerosol and gas measurements were also made at the Lower Kaweah site using filter packs. Flow rates were controlled by critical orifices and verified with a calibrated flowmeter. Teflon filters (Gelman Zefluor, 1 μm pore size) were used to collect the aerosol for determination of major ions. An oxalic acid–impregnated glass fiber backup filter was used to collect $NH_3(g)$. A nylon backup filter was used to collect $HNO_3(g)$. The nylon filters were extracted in the bicarbonate–carbonate eluent; the rest of the filters were extracted in distilled, de–ionized water on a reciprocating shaker. The extracts were then analyzed by the same methods that were used on the cloudwater samples.

Results and Discussion

A total of twelve cloudwater samples were collected during five cloud impaction events. All of the sampled events were associated with cold fronts approaching from the north or northwest. As mentioned above, cloud liquid water contents at the collection sites may have been enhanced by an orographic effect due to passage of the air masses over the Sierra. The first eleven samples were collected at the Lower Kaweah site. The last sample was collected on May 6, 1986, at the Deer Ridge site because temperatures at Lower Kaweah were near 0 °C and the collected droplets froze on the strands of the CASCC.

Cloudwater Composition

Table 1 summarizes the chemical composition of the samples. In Figure 3 the cloudwater loadings of NH_4^+, NO_3^-, and SO_4^{2-} are presented. (The cloudwater loading of a species is defined as the amount of that species present in cloudwater per unit volume of air. It is equivalent to the cloudwater concentration multiplied by the liquid water content of the cloud). Also listed in Table 1 are the estimated values of cloud liquid water content (LWC). These values are derived from the quotient of the sample collection rate with the product of the flow rate through the CASCC (24.5 $m^3 \cdot min^{-1}$) and the theoretical collection efficiency of the CASCC. The collection efficiency of the CASCC is defined by the product of the overall strand collection efficiency (85% for a 10 μm droplet) and the percentage of air flowing through the collector that is sampled by the strands (86%).

Wide variations are seen in both the cloudwater concentrations and loadings of all the major species. The nitrate loading, for example, ranges from less than

1 neq·m^{-3} up to about 60 neq·m^{-3}. The ratio of NO_3^- to SO_4^{2-} varies from below 0.5 in the fall samples to more than 1.5 in some of the spring samples. The pH of the samples ranges from 4.4 to 5.7. The last sample, which is the most acidic, is not the sample with the highest ionic loading, indicating the importance of the ionic composition of the sample in determining its acidity.

The calculated inorganic ion balance for each sample (sum of measured inorganic anions/sum of measured cations) is shown in Table 1. For those samples with low ionic loadings, it is not surprising to see this ratio differ significantly from 1.0 since relative analytical error increases near the detection limits. With the exception of the May 6 sample, however, there seems to be a consistent anion deficit, even for those samples with higher loadings. Upon collection of samples 4/24c, 5/03b, 5/03c, and 5/03d, a 2 ml aliquot of each sample was set aside and preserved with 50 μl of chloroform. Each aliquot was analyzed for the presence of formic acid, acetic acid, lactic acid, pyruvic acid, and propanoic acid. Table 2 lists the concentrations of the organic anions expected to be in each sample based on the measured concentrations of each acid and the pH of the samples as measured in the field. Also listed here are the ion balances for all measured species in the samples, organic and inorganic. In sample 5/03b, the total of the concentrations of formate, acetate, lactate, and propionate is comparable to the nitrate concentration and is nearly twice the sulfate concentration. The concentrations in the other three samples are smaller, but still significant. Including these organic anions in the ion balances for the four samples changes the balances from 0.88, 0.62, 0.70, and 0.85, as listed in Table 1, to 0.95, 0.97, 0.97, and 1.10, respectively. These ratios are within the error of the analytical procedures.

Low molecular weight organic acids appear to be important contributors to the overall chemical composition of SNP cloudwater. This observation is consistent with our previous results for San Joaquin Valley fog. Lower molecular weight organic acids have been shown to be important components of fog and cloudwater in the San Joaquin Valley below SNP (Jacob et al., 1986b) and in rainwater collected at remote as well as urban sites (Galloway et al., 1984; Kawamura and Kaplan, 1984). The solubility of low molecular weight carboxylic acids in water is enhanced by their dissociation to their respective conjugate bases (eq. 2). Since most of the cloudwater samples had pH values above the pK_a values of the weak acids of interest, we expect that the organic acids will be effectively scavenged from the gas phase. When the pH of the cloudwater falls below the pK_a values of the organic acids, the solubility of these acids is correspondingly diminished.

$$(1) \qquad HA_{(g)} \overset{H_a}{\rightleftharpoons} HA_{(aq)}$$

$$(2) \qquad HA_{(aq)} \overset{K_a}{\rightleftharpoons} H^{+}_{(aq)} + A^{-}_{(aq)}$$

It is instructive to compare the cloudwater compositions observed in SNP with those measured at similar locations in other parts of the country. Average concentrations (and standard deviations) of NO_3^-, SO_4^{2-}, NH_4^+, and H^+ measured at two elevated sites in the northeastern U.S. (Whiteface Mountain, New York, and Mt. Moosilauke, New Hampshire) are listed in Table 3, along with the results of this study. Also listed here are results obtained at Laguna Peak, an elevated site located at the eastern end of California's Santa Barbara Channel. Average concentrations of H^+ measured in SNP cloudwater (11 μN were, on average, much lower than those observed at the other three sites (288 μN at Mt. Moosilauke, 280 μN at Whiteface Mountain, and 761 μN at Laguna Peak). These differences are correspondingly reflected by large differences in the typical cloudwater pH values measured at the sites. Cloudwater pH in SNP averaged about 5, while cloudwater at the two northeastern sites averaged about pH 3.5 and Laguna Peak averaged close to pH 3. Average concentrations of NO_3^- and SO_4^{2-} in SNP cloudwater (132 and 96 μN, respectively) were much lower than those observed in Laguna Peak cloudwater (571 and 462 μN, respectively), while concentrations of NH_4^+ were comparable (237 μN in SNP and 270 μN at Laguna Peak). The large excess of NO_3^- and SO_4^{2-} in the Laguna Peak cloudwater is balanced by the increased H^+, accounting for the difference in pH observed at the two sites.

Average concentrations of NO_3^- and SO_4^{2-} in cloudwater from Whiteface Mountain (110 and 140 μN, respectively) were comparable to those in SNP cloudwater. The large difference in average cloudwater pH observed at these two sites is largely accounted for by lower inputs of base at Whiteface Mountain, where cloudwater concentrations of NH_4^+ averaged only 89 μN, approximately one–third of the level observed in SNP cloudwater. The increased acidity observed at Mt. Moosilauke, relative to SNP, can be partially accounted for by the lower average cloudwater NH_4^+ concentration (108 μN) observed there, but must also be partially attributed to a higher acid input. Cloudwater SO_4^{2-} concentrations at Mt. Moosilauke averaged 342 μN. The average cloudwater NO_3^- concentration observed in Mt. Moosilauke cloudwater (195 μN), however, was only slightly higher than that observed in samples from SNP.

Aerosol and Gas Phase Measurements

During the period May 1 – 6, 1986, aerosol was continuously sampled at the Lower Kaweah site. The aerosol, collected generally in six hour samples, was analyzed for NO_3^- , SO_4^{2-} , Cl^-, NH_4^+ , Na^+, Ca^{2+}, and Mg^{2+}. In addition, simultaneous measurements of the gas phase concentrations of nitric acid and ammonia were made. Results obtained for the aerosol loadings of NO_3^- , SO_4^{2-}, NH_4^+, and Cl^- are shown in Figure 4. Under normal conditions, upslope winds, that are caused by the heating of the air along the mountain slopes, should transport pollutants from the San Joaquin Valley to the Lower Kaweah site. Drainage flows, that begin as the sun sets and the air in contact with the slopes cools, bring cleaner air to the site and transport the aerosol back down into the valley. This pattern seems to be reflected in the data for May 4.

The data for the periods May 2 – 3 and May 5 – 6 show a distinctly different trend. In both periods, aerosol loadings rose through the first day and continued to either rise or remain at elevated levels overnight and through some portion of the second day. A similar trend was observed in the gas phase concentrations. A cold front passed through the region during both periods. The arrows on Figure 4 show the approximate times at which clouds began to impact the cloud collection site at Lower Kaweah.

Figure 5 depicts the typical behavior of air masses during the passage of a cold front. The advancing denser cold air mass wedges its way under the warmer air mass. As the warm air mass is lifted and cooled, cloud formation and precipitation often result. Such a large scale lifting of a warm air mass previously in contact with the floor of the San Joaquin Valley could increase loadings of aerosol and gas phase species in the adjacent mountains. If the disturbance is large enough, the mountain/valley circulation may be overcome, resulting in a pattern of increased pollutant loadings at elevation until the front has passed. The data from May 2 – 3 and May 5 – 6 are consistent with this scenario.

It has been shown previously (Jacob et al., 1985, 1986a,b, 1987) that cloudwater composition is in large part determined by the composition of the precursor aerosol and soluble gases. The possible coupling of peak gas phase and aerosol concentrations with the arrival of a front, as mentioned above, suggests that cloudwater loadings in Sequoia National Park or similar locations might be expected to be higher than would be predicted based on average gas phase and aerosol concentrations at the same location.

Cloudwater Deposition

The volume–weighted average concentrations of the 12 cloudwater samples collected in SNP during this study provide the best available estimate of the average cloudwater composition there. These can be used, along with estimates of the average cloudwater deposition rate and the annual average number of hours of cloudwater impaction, to estimate the cloudwater contribution to acidic deposition in the vicinity of Lower Kaweah. Lovett (1984) estimated cloudwater deposition rates to a subalpine balsam fir forest that varied linearly from 0.2 to 1.2 $\mathrm{mm \cdot hr^{-1}}$ for canopy top wind speeds of 2 to 10 $\mathrm{m \cdot s^{-1}}$. The much taller forest in SNP should receive at least the same deposition rate under similar conditions. Selecting a moderate wind speed of 6 $\mathrm{m \cdot s^{-1}}$ yields a deposition rate of approximately 0.7 $\mathrm{mm \cdot hr^{-1}}$. Data from a current study we are conducting indicates that 100 hours per year of cloud impaction at 2000 m in the Park is a conservative estimate. Annual deposition rates of H^+, NH_4^+, NO_3^-, and SO_4^{2-} calculated using the above information are summarized in Figure 6. Also depicted in Figure 6 are the annual average deposition rates for the same ions at the Lower Kaweah site contributed by precipitation (Stohlgren and Parsons, 1987). The estimated cloudwater deposition rates of all four ions are comparable to the measured precipitation inputs. While the estimates of cloudwater contributions to deposition in the region are rough, an attempt has been made to keep them on the conservative side. The potential importance of this deposition mechanism therefore seems clear. Further investigation is needed to refine the estimates made above and to lead to an increased understanding of the relative contributions of the different pathways leading to acidic deposition in SNP.

Conclusions

Cloudwater was sampled during the fall of 1985 and the spring of 1986 in Sequoia National Park in the southern Sierra Nevada of California. Concentrations of major species in the cloudwater vary widely both within one cloudwater impaction event and from one event to another. The pH values of the samples range from 4.4 to 5.7. The most acidic sample was not the sample with the highest concentrations of NO_3^- and SO_4^{2-}; this result indicates the relative importance of the ionic composition of the sample as a primary determinant of acidity. Organic acids were found to be be important components of the chemical composition of the cloudwater in Sequoia National Park

A comparison of the chemical composition of the cloudwater in SNP with that collected at two elevated sites in the northeastern U.S. reveals that the SNP cloudwater is generally much less acidic. For one of the northeastern sites (Whiteface Mountain) this difference is largely due to smaller inputs of base, as evidenced by lower NH_4^+ cloudwater concentrations than were observed in SNP cloudwater. At the second northeastern site (Mt. Moosilauke) the levels of cloudwater NH_4^+ are similarly low, but at least part of the acidity is attributable to larger acid inputs. At an elevated site along the southern California coast (Laguna Peak), cloudwater NH_4^+ concentrations were comparable to those observed in SNP. Higher concentrations of NO_3^- and SO_4^{2-} in Laguna Peak cloudwater, however, account for sample pH values averaging almost 1.5 units less than were observed in SNP.

The advance of cold fronts seems to lead to higher aerosol and gas phase loadings in the Park than would be seen under normal mountain/valley circulations, particularly during the night and morning hours. The arrival of these increased loadings prior to and during cloud impaction on the mountain slopes leads to higher cloudwater concentrations than would otherwise be expected. Estimates of annual deposition rates of NO_3^-, SO_4^{2-}, NH_4^+, and H^+ due to cloudwater impaction are comparable to those measured in precipitation.

Acknowledgments

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Table 1. Chemical Composition of Sequoia Cloudwater

Date	Time	pH	Na^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	–/+	LWC
			←			μN			→		ml·m^{-3}
10/21/85											
a	0927–1000	5.0	8	29	12	4	4	11	28	0.62	0.15
b	1000–1100	4.8	2	16	9	1	1	6	18	0.57	0.21
c	1100–1200	5.1	1	8	4	1	3	3	13	0.84	0.21
d	1200–1410	5.4	1	*	2	1	*	*	*	**	0.09
4/24/86											
a	1142–1305	5.0	680	1526	308	266	491	1140	665	0.82	0.03
b	1305–1405	4.8	157	594	58	47	129	354	269	0.86	0.16
c	1405–1505	4.8	231	900	72	66	192	537	396	0.88	0.04
5/03/86											
a	1200–1300	5.4	35	448	41	20	44	205	121	0.68	0.24
b	1300–1335	5.7	27	493	34	16	29	206	120	0.62	0.10
c	2015–2115	5.6	11	149	24	8	17	62	58	0.70	0.22
d	2115–2215	5.6	10	93	22	8	18	44	54	0.85	0.06
5/06/86											
a	1200–1250	4.4	44	132	18	***	55	94	83	1.00	0.22

* below 1 μN, ** concentrations too low to make accurate calculation, *** not measured, ion balance calculated for measured species.

Table 2. Organic Anions in Sequoia Cloudwater

Sample	pH	Formate	Acetate	Pyruvate*	Lactate*	Propionate*	$(-/+)_{tot}$‡
		← μN →					
4/24/86							
c	4.8	68.5	13.8	10.4	0	5.2	0.95
5/03/86							
b	5.7	106.7	72.8	0	15.4	7.2	0.97
c	5.6	31.0	18.6	0	0	2.5	0.97
d	5.6	19.6	8.5	0	4.6	0	1.10

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* Identification of this species is tentative.

‡ This column denotes the total ion balance including all measured species, organic and inorganic.

Table 3. Comparison of Cloudwater Composition at Four Elevated Sites

Site	Elev.(m)	Date	Samples	NO_3^-	SO_4^{2-}	NH_4^+	H^+
				Average(Std. Dev.), μN			
Sequoia N. P., CA [1]	1860	1985–86	12	132(206)	96(127)	237(310)	11(11)
Mt. Moosilauke, NH [2]	1220	1980–81	10	195(175)	342(234)	108(89)	288(193)
Whiteface Mt., NY [3]	1500	1976	28	110(52)	140(150)	89(61)	280(220)
Laguna Peak, CA [4]	450	1986	20	571(203)	462(197)	270(111)	761(339)

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[1] This paper. Averages and standard deviations are weighted by the sample volumes.

[2] Lovett et al. (1982). Averages and standard deviations are not weighted by the sample volumes.

[3] Castillo et al. (1983). Data from non–precipitating stratiform. Averages and standard deviations are not weighted by the sample volumes.

[4] Munger (1989). Averages and standard deviations are weighted by the sample volumes.

Captions

Figure 1. Map of Sequoia National Park showing the two sites used for cloudwater sampling. The inset shows the location of the Park relative to the San Joaquin Valley and the rest of California.

Figure 2. The Caltech Active Strand Cloudwater Collector (CASCC). The length of the collector is 0.91 m (36 in.). Total sampled flow is 21.1 $m^3 \cdot min^{-1}$.

Figure 3. Cloudwater loadings of ammonium, nitrate, and sulfate in samples collected during the fall of 1985 and the spring of 1986 in Sequoia National Park.

Figure 4. Aerosol Loadings of sulfate, nitrate, ammonium, and chloride measured at the Lower Kaweah research site in Sequoia National Park during the period May 1 – 6, 1986. The arrows on the figures denote the times at which clouds were observed to begin impacting the hillside at the site.

Figure 5. Typical behavior of warm and cold air masses during the advance of a cold front. In the figure the cold air mass is moving toward the right, wedging itself under the less dense warm air mass.

Figure 6. Annual deposition of major ions to the Lower Kaweah research site in Sequoia National Park by rainwater (measured, Stohlgren and Parsons, 1987) and cloudwater (estimated). Rainwater includes unknown contributions from snowfall. Estimates of cloudwater deposition are based on a cloudwater deposition rate of 0.7 $mm \cdot hr^{-1}$ for 100 $hr \cdot yr^{-1}$ (see the text for details). The average chemical composition of the cloudwater was taken as the volume–weighted average composition of the cloudwater sampled in the Park during the fall of 1985 and the spring of 1986.

Table 1. Chemical composition of the cloudwater samples collected in Sequoia National Park during the fall of 1985 and the spring of 1986. Ion balances (–/+) were computed using the ions listed as well as H^+. These were computed prior to rounding the ion concentrations. Liquid water content (LWC) values are estimates based on the cloudwater collection rate and the theoretical collection efficiency of the Caltech Active Strand Cloudwater Collector (CASCC).

Table 2. Concentrations of carboxylate anions in cloudwater samples from Sequoia National Park collected during the spring of 1986. The ion balances $(-/+)_{tot}$ shown here include these carboxylate anions as well as the inorganic ions listed for these samples in Table 1.

Table 3. Comparison of cloudwater collected in Sequoia National Park with samples collected at other elevated sites in the U.S. Average cloudwater concentrations of major ions are presented for Mt. Moosilauke, NH, Whiteface Mt., NY, and Laguna Peak, CA.

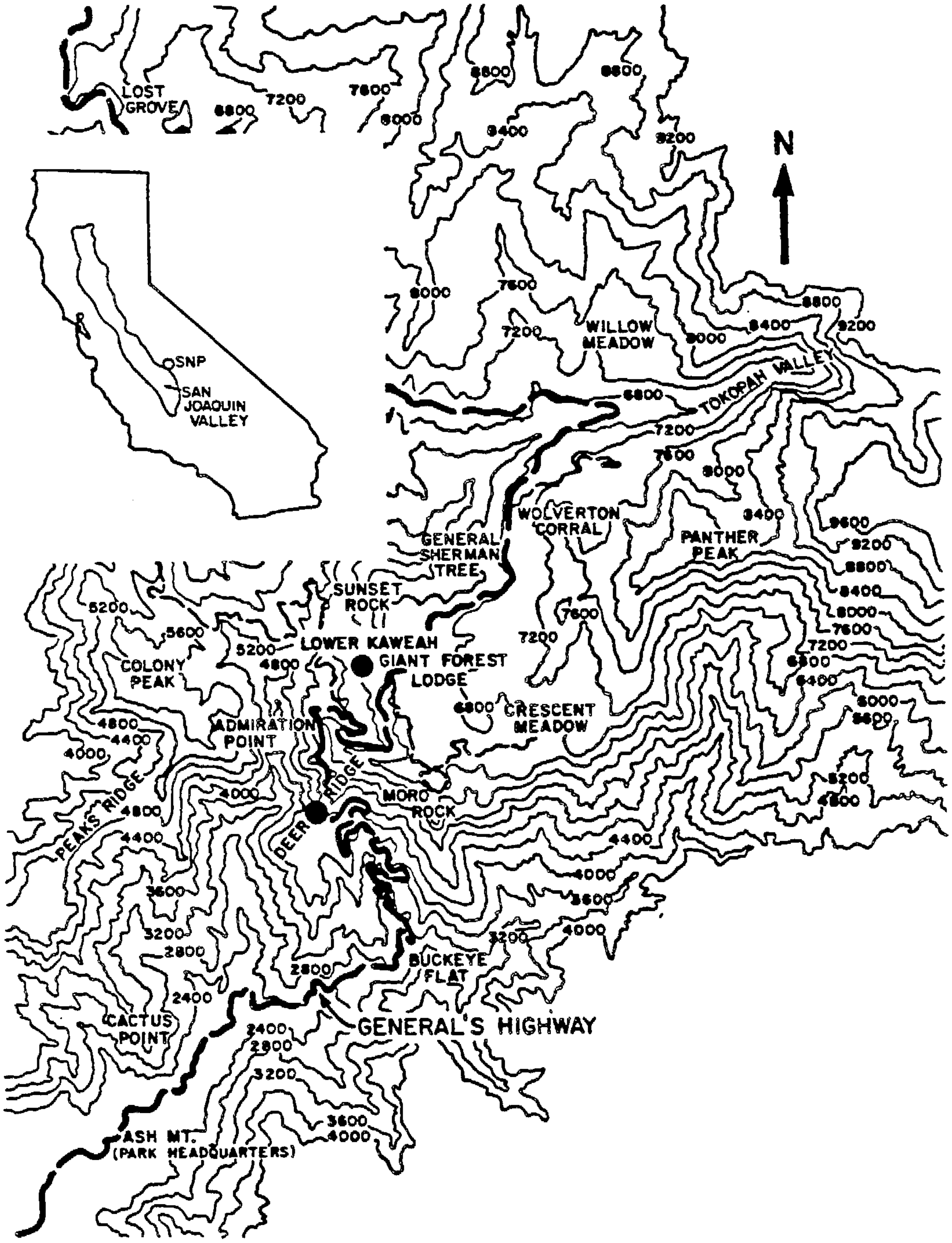

Figure 1. Map of Sequoia National Park showing the two sites used for cloudwater sampling. The inset shows the location of the Park relative to the San Joaquin Valley and the rest of California.

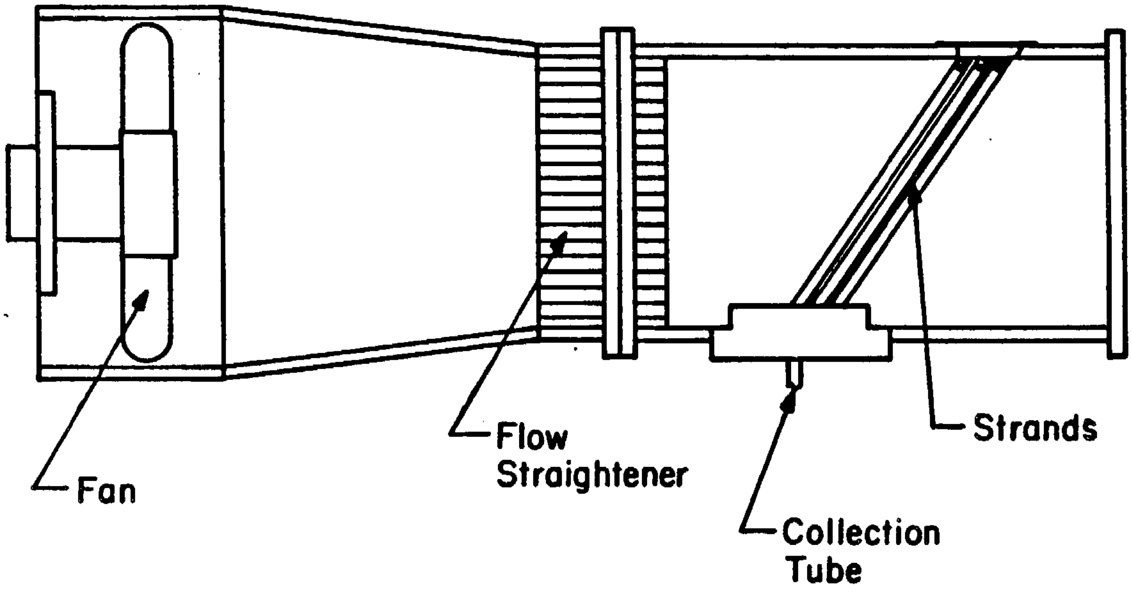

Figure 2. The Caltech Active Strand Cloudwater Collector (CASCC). The length of the collector is 0.91 m (36 in.). Total sampled flow is 21.1 $m^3 \cdot min^{-1}$.

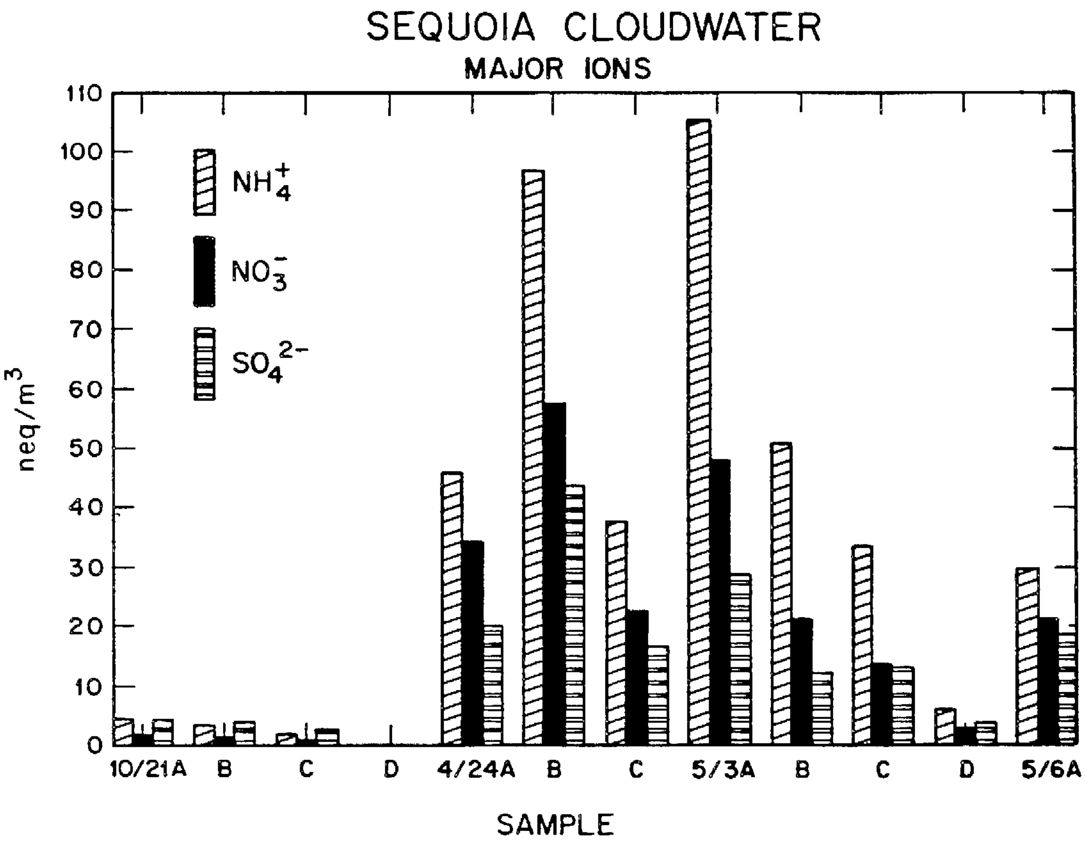

Figure 3. Cloudwater loadings of ammonium, nitrate, and sulfate in samples collected during the fall of 1985 and the spring of 1986 in Sequoia National Park.

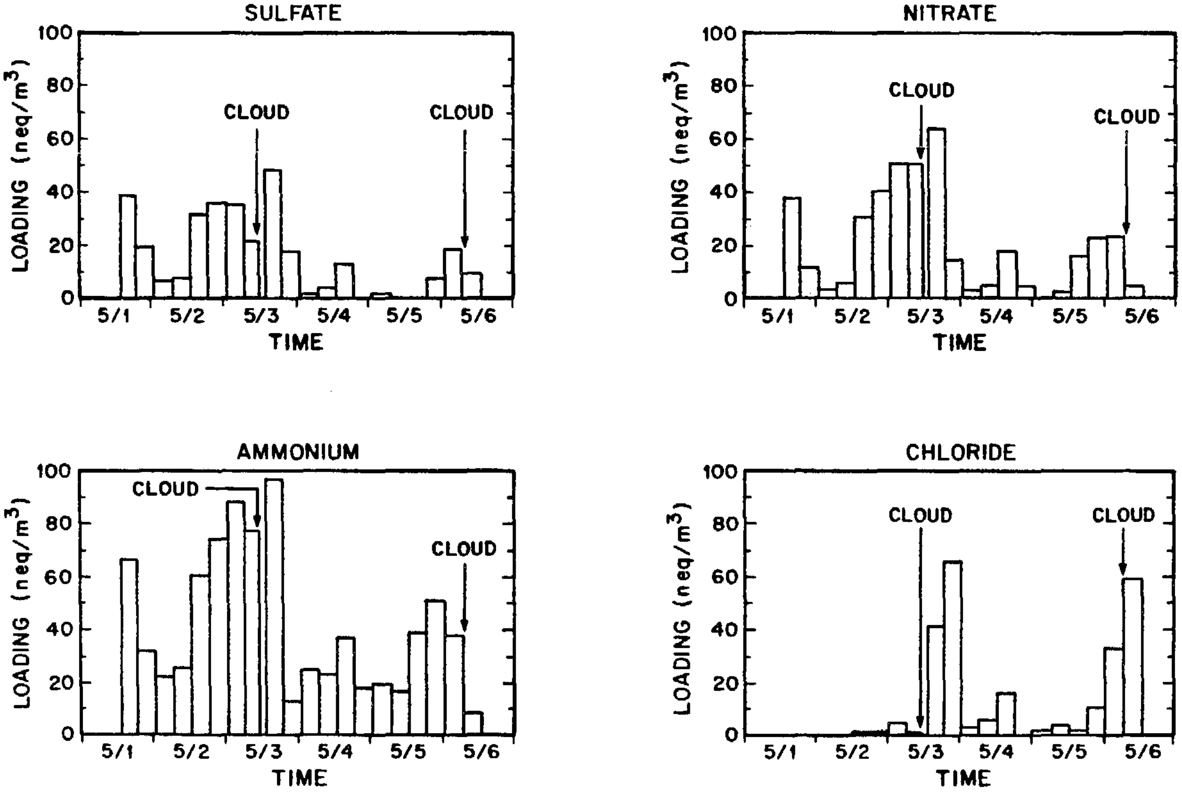

Figure 4. Aerosol Loadings of sulfate, nitrate, ammonium, and chloride measured at the Lower Kaweah research site in Sequoia National Park during the period May 1 – 6, 1986. The arrows on the figures denote the times at which clouds were observed to begin impacting the hillside at the site.

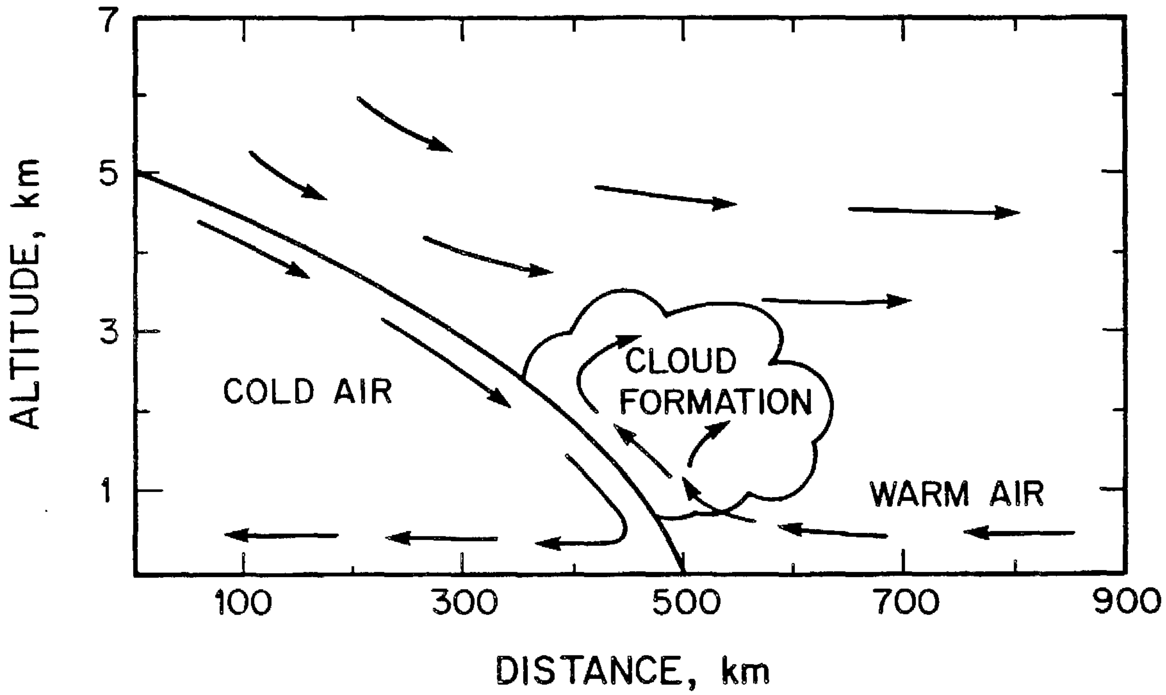

Figure 5. Typical behavior of warm and cold air masses during the advance of a cold front. In the figure the cold air mass is moving toward the right, wedging itself under the less dense warm air mass.

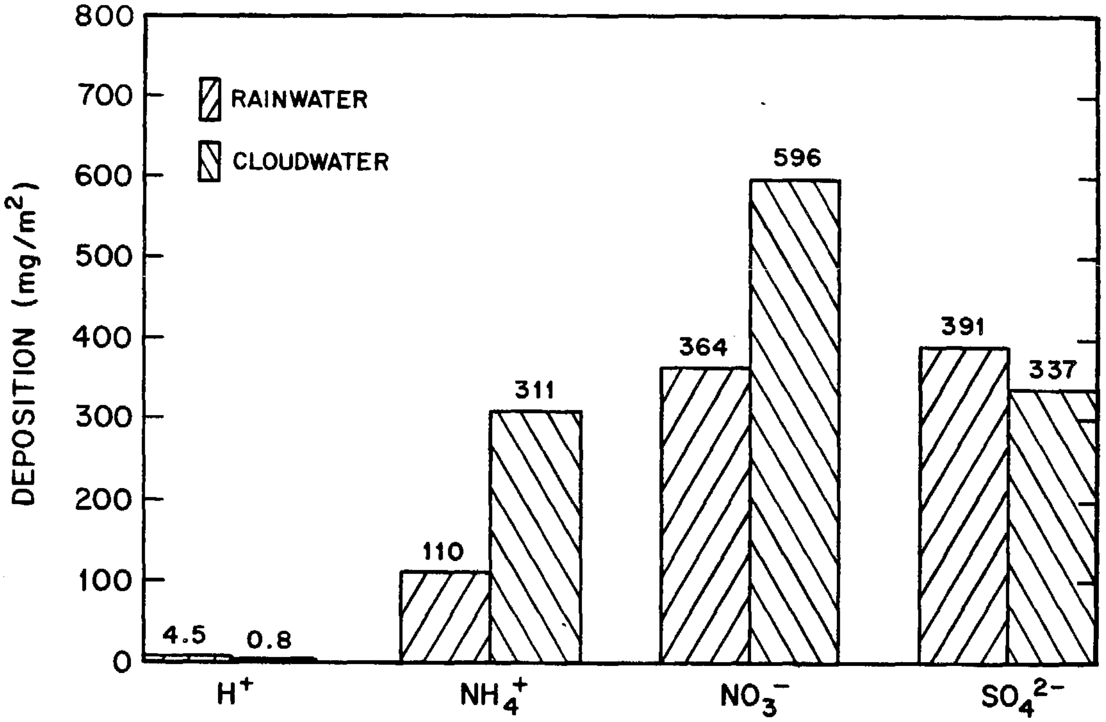

Figure 6. Annual deposition of major ions to the Lower Kaweah research site in Sequoia National Park by rainwater (measured, Stohlgren and Parsons, 1987) and cloudwater (estimated). Rainwater includes unknown contributions from snowfall. Estimates of cloudwater deposition are based on a cloudwater deposition rate of 0.7 mm·hr^{-1} for 100 hr·yr^{-1} (see the text for details). The average chemical composition of the cloudwater was taken as the volume–weighted average composition of the cloudwater sampled in the Park during the fall of 1985 and the spring of 1986.

CHAPTER 2

THE CHEMICAL COMPOSITION OF INTERCEPTED CLOUDWATER IN THE SIERRA NEVADA

Introduction

There is increasing recognition that deposition of cloudwater may significantly augment the deposition of acids and nutrients by precipitation and dry deposition, and of water by precipitation alone, particularly at elevated sites where immersion in clouds occurs frequently. This recognition stems largely from the recent issuance of several reports which address the frequency of cloud interception and/or the chemical composition of the intercepted cloudwater at a number of elevated locations, both in the U.S. (Lovett et al., 1982; Castillo et al., 1985; Waldman et al., 1985; Weathers et al., 1986, 1988; Mueller and Weatherford, 1988) and elsewhere (Dollard et al., 1983; Schemenauer, 1986; Schemenauer et al., 1987). In California, concern has been expressed about the damage acid deposition may inflict upon sensitive ecosystems in the Sierra Nevada. The deposition of acids by cloudwater interception in the Sierra has previously been estimated to be comparable to inputs from precipitation, based on preliminary measurements of cloudwater composition in Sequoia National Park (Chapter 1; Collett et al., 1989). Further study has since been undertaken to investigate more completely the frequency of cloud interception and the chemical composition of the impacting cloudwater in the Sierra. This chapter describes the results of this investigation.

Experimental Procedure

Two sites in the Sierra were chosen to serve as locations for monitoring the chemical composition of cloudwater. The first site, Lower Kaweah, is located at an elevation of 1856 m in Sequoia National Park. This site also was used for most of the preliminary measurements described in Chapter 1. Turtleback Dome (elev.

1590 m) in Yosemite National Park was selected as the second site. Both sites are located in open areas and are easily intercepted by approaching clouds. Both sites also are used for making a variety of other routine air quality measurements. There is very little traffic in the immediate vicinity of either site, although Highway 41 passes approximately 0.5 km from the Turtleback Dome site.

Beginning in September 1987, each site was equipped with an integrated cloudwater monitoring system. This system, described in detail in Chapter 5, included: (1) a Caltech Active Strand Cloudwater Collector (CASCC) to collect samples; (2) a cloudwater sensor to monitor the presence of clouds and to activate and deactivate the CASCC; and (3) an autosampler to fractionate the samples collected by the CASCC to reveal temporal changes in cloudwater chemistry. Use of this system enables automated collection of cloudwater samples on a sub–event basis. The CASCC is automatically rinsed with distilled de–ionized water (D^2H_2O) before and after each event to ensure the cleanliness of the collection surfaces.

As described in Chapter 5, the integrated cloudwater system is not functional when ambient temperatures fall below 0 °C, since the cloudwater droplets freeze on the collection surfaces in both the sensor and the CASCC. Operation of the autosampler during freezing conditions also poses considerable difficulty since collected sample may freeze in the autosampler distribution system. For these reasons, a separate winter cloudwater sampling system was developed and used at Lower Kaweah and Turtleback Dome from mid–January to mid–April of 1988. This system, described in Chapter 5, utilized a Caltech Heated Rod Cloudwater Collector (CHRCC). Stainless steel rods form the collection surfaces in this sampler, and are internally heated on a periodic basis when temperatures fall below 4.5 °C. When heated, accumulated frozen cloudwater (rime ice) on the rods melts and drains off of the rods to the sample bottle. A new optical cloudwater sensor was developed and used to monitor the presence of clouds during the winter sampling period. The output signal from the sensor was monitored by a Campbell CR10 programmable controller which was used to activate and deactivate the CHRCC, and to control the heating cycle.

The cloudwater monitoring sites were attended at least once per week by a site operator. The operator was responsible for picking up samples, replenishing the rinsewater reservoir, testing the operation of the equipment, and taking a blank to determine the cleanliness of the system. Samples were weighed by the operator and an aliquot was removed for determination of pH. pH was measured using a pH meter with a combination electrode calibrated with pH 4 and 7 buffers. Finally, the samples were frozen and packed in a refrigerated shipping container, along with ice packs, and shipped to Caltech.

Upon arrival at Caltech, samples were allowed to warm to room temperature and the pH was measured again. Samples were then refrigerated at 4 ^{o}C until further analysis could be completed. Concentrations of NO_3^-, SO_4^{2-}, and Cl^- were measured using a Dionex 2020i ion chromatograph equipped with an AS4 or AS4A column. A 2.8mM HCO_3^-/2.2 mM CO_3^{2-} solution was used as the eluent. Na^+, Ca^{2+}, Mg^{2+}, and K^+ concentrations were measured using a Varian Techtron AA6 atomic absorption spectrophotometer. An air/acetylene flame was used for Na^+ and K^+; N_2O/acetylene was used for Ca^{2+} and Mg^{2+} to minimize interferences. NH_4^+ was measured by the phenol–hypochlorite method (Solorzano, 1967) using an Alpkem flow injection analyzer.

Results and Discussion

Cloud Interception Frequency

Over 250 hours of cloudwater interception were observed at Lower Kaweah between September 1987 and August 1988. Figure 1 illustrates the number of hours of cloudwater interception observed during each of the twelve months of this period. The number of hours of interception is based primarily on data from the two cloudwater sensors. Data from early December were taken from a passive cloudwater collector located at the site (see Chapter 4). Periods when the integrated cloudwater monitoring system sensor data indicated interception durations less than 20 minutes were not included since the sensor reports a minimum of 15 minutes of interception each time it is activated.

The two peak months for cloudwater interception were November (74 hours) and April (63 hours). Approximately half of the interception in November was associated with a single storm system which immersed the site in clouds almost continuously for a day and a half. Most events were observed to be much shorter than this, typically on the order of a few hours. Smaller monthly interception amounts were observed in October (40 hours), January (25 hours), and May (32 hours). A few hours of interception were observed in each of the remaining months of the year, with the exception of September, during which no cloud interception was observed. Less precipitation fell in the Sierra during the period of the study than in most years. Since cloud interception at the site seems to be associated primarily with the passage of frontal systems, this suggests that cloud interception may have been somewhat below average for this period as well.

The number of hours that Lower Kaweah was immersed in cloud during the study year is much less than has been estimated for some elevated sites in the Eastern U.S. and Canada. Reiners and Lang (1979) estimated that the fir zone (1220 to 1450 m) on the western slopes of the Green Mountains in Vermont is covered by clouds between 30 and 50% of the time. This estimate was based on an interpolation between visual observations of cloud interception at similar elevations at other northeastern U.S. locations. Schemenauer (1986) estimated that the summit of Roundtop Mountain (970 m) was immersed in clouds 44% of the time in 1985, based on the fraction of observation times at which clouds were seen at the summit. Observations were made twice daily.

Reliance on periodic visual observations introduces a great deal of uncertainty into estimates of cloud interception frequency. The interpretation of what constitutes cloud presence varies from one observer to another. In some reports, fog is indicated anytime that visibility is reduced below a certain threshold; typically 1/8 or 1/4 mile. The thresholds for cloud observation by the two sensors in this study correspond to a visual range of less than 160 m (0.1 mile). This lower visibility threshold provides a better indication of when cloudwater deposition to the forest canopy is likely to be important. Observers may also tend to indicate clouds are present if they are observed anywhere in the vicinity of the observation post, rather than solely when a single point is immersed in clouds. Furthermore, it is very difficult to know what occurs between observation times. If observations are made on a fixed time schedule, as is usually the case, a bias may be introduced if actual cloud presence is correlated with time of day. Aside from the differences in observation methods, it is clear that the amount of cloud interception observed at Lower Kaweah during the study period is significantly lower than has been observed at some other locations.

Sampling Efficiency

Valid samples were obtained for approximately 50% of the 265 hours of cloudwater interception observed at Lower Kaweah. While we consider this sampling efficiency to be quite good for a study of this nature, it is possible to identify a number of reasons why the fraction of valid samples was not higher. Discussion of these reasons, which include the loss of sample at the beginning of each event during the collector rinse, exceedance of the finite sampling capacity of the autosampler, insufficient sample volume, problems associated with freezing temperatures, equipment malfunction, and human error, may aid the development of similar programs in the future.

While having an automated rinsing system was deemed necessary for obtaining valid samples of cloudwater using an automated sampling system, it does pose some limitations to sampling efficiency. Sample collected during the first 20 minutes of each event is discarded by the autosampler. This is done because the collection surfaces of the CASCC are rinsed with D^2H_2O at the beginning of each event; therefore, sample collected by the CASCC during the first few minutes of each event is diluted by rinsewater remaining on the collection strands. During short events, not collecting sample for the first 20 minutes can significantly reduce the fraction of interception time that is sampled.

The autosampler (Chapter 5), which contains 20 sample bottles, has a finite sampling capacity. While this capacity was designed to allow extended periods of cloudwater sampling by incorporating a sample distribution reservoir which saves only a portion of large samples, there were a few cases when the capacity was exceeded. An example of such an event is a 60 hour period between noon on October 31, 1987, and midnight on November 2, 1987, when over 40 hours of cloudwater interception were observed. The problem of exceeding the autosampler capacity is exacerbated by periods of intermittent cloud interception. The autosampler is designed to store samples from different events separately. An event is considered finished when there is a break of approximately 30 minutes in cloud interception. Therefore, several short periods of cloud interception, separated by breaks of at least 30 minutes, can use up several of the bottles in the autosampler carousel, significantly reducing the capacity of the autosampler to sample more extended events that may occur afterward. This limitation is particularly important since a number of periods of brief cloud interception often occur in association with the arrival of clouds on the leading edge of a frontal system, while the arrival of the main cloud mass may produce extended interception periods later.

Samples smaller than 10 ml in volume were not considered valid. The reason for this is that cloudwater collected by the CASCC, as well as by most other cloudwater collectors, may contact a considerable amount of surface area in transit to the sample bottle. The smaller the sample, the greater the possibility that the sample composition will be affected significantly by even small quantities of residual rinsewater or contamination. Small samples, which have a higher surface area to volume ratio, are also more prone to evaporation problems during collection and storage than are large samples. Finally, samples smaller than 10 ml are more difficult to analyze accurately in the laboratory, because of the need to increase the volume by dilution to provide a sufficient quantity for analysis.

While winters are not extremely cold at 2000 m in the Sierra, freezing temperatures may occur throughout most of the year. Often the freezing temperatures are associated with the passage of a cold front; the same condition which often produces cloudwater interception at Lower Kaweah. Deciding when to change from using the integrated cloudwater monitoring system to the winter collection system is difficult. Relatively warm temperatures during cloud interception in April of 1988 were followed by freezing temperatures during an event at the end of May. Use of the winter system reduces the amount of information that is obtained about the temporal variations in cloudwater composition, since only bulk cloudwater samples are obtained; use of the integrated cloudwater monitoring system permits freezing weather to halt operation, leaving gaps in the data base. We opted to use the winter system only during those months that we expected to be the coldest (January, February, and March), since the winter collector was previously untested and we were interested in obtaining data on temporal variations in cloudwater chemistry. As a consequence, there were several instances when freezing weather hampered operation, thereby reducing the total hours of valid cloudwater sample we obtained.

Overall, the performance of the collection systems was remarkably good, particularly considering that this was a pilot program employing a great deal of new and untested technology. There were relatively few cases of equipment failure or malfunction at Lower Kaweah, for either cloudwater monitoring system, throughout the course of the study. Those failures which did occur were often associated with pieces of equipment purchased from outside vendors and incorporated into the collection systems, and frequently were related to power loss and subsequent recovery. Equipment failure and malfunction led to very little down time at Sequoia.

More problems were encountered at Turtleback Dome in Yosemite. The most significant problem was a lightning strike which destroyed a National Park Service transformer at the site. The loss of the transformer left the site without power for approximately six weeks in the fall of 1987. Unfortunately, those six weeks comprised the most active autumn period of cloud interception. Several events were observed at Turtleback Dome during this period by the passive cloudwater monitoring system (see Chapter 4). As a consequence of the loss of power, no samples were collected for chemical analysis at Turtleback Dome during the fall of 1987. No samples were collected at Turtleback Dome during the winter either, due to malfunctions of the microprocessor in the controller which operated the winter collection system. These malfunctions, associated with poor electrical grounding through the AC power line, were remedied by wiring a direct line to the equipment; however, by the time the new line was installed, the limited number of interception events observed during the winter were over. Spring, summer, and fall sampling in 1988 were carried out at both Parks with relatively little equipment trouble.

Only a few samples failed to be collected or were compromised because of human error. The largest source of human error was associated with the high turnover rate of site operators in both Parks. This was particularly a problem in Sequoia National Park where six different people were responsible for operations at Lower Kaweah at different times during the 15 month study. The high turnover rate contributed to a lack of familiarity with equipment operation, which made it extremely difficult for the operators to deal with difficult or unusual situations that were not thoroughly documented in the procedure manual.

Cloudwater Composition

The pH of the cloudwater samples collected in Sequoia National Park ranged from 3.9 to 6.5 (see Figure 2). Samples collected in the fall tended to be somewhat more acidic than those collected in the winter or spring. Inorganic compositions of the Sequoia cloudwater samples are presented in Tables 1 and 2. Blank concentrations of the measured species were generally near the analytical detection limits, throughout the course of the study, indicating that the collector rinsing procedure was keeping the system clean. Two things are readily apparent from the cloudwater composition data. First, the inorganic composition of the cloudwater is dominated by NO_3^-, SO_4^{2-}, and NH_4^+. Second, the sample pH is not highly correlated with the total ionic strength of the sample. The presence of naturally occurring formic and acetic acid, along with CO_2, will render the cloudwater somewhat acidic as these species partition into the aqueous phase. Significant concentrations of weak organic acids previously have been observed in Sequoia cloudwater (Collett et al., 1989; Chapters 1, 3). The cleanest samples of cloudwater (those with the lowest concentrations of measured ions) collected in Sequoia National Park were found to have pH values near 5. This is consistent with pH values observed in samples collected in remote areas of the world (Keene et al., 1983). Deviations from this pH regime are largely determined by the balance of inorganic acids and bases introduced into the sample. As indicated above, the most important inorganic species are SO_4^{2-} and NO_3^-, which represent acidic inputs to the cloudwater, and NH_4^+ which represents the dominant basic input. Samples with large excesses of NH_4^+, relative to the sum of NO_3^- and SO_4^{2-}, exhibit pH values greater than 5, while those with excesses of NO_3^- and SO_4^{2-} tend to be more acidic.

The volume–weighted average composition of the cloudwater samples collected at Lower Kaweah during different periods of the year is presented in Figure 3. Samples collected in the fall and spring were obtained using the integrated cloudwater monitoring system; those collected in the winter were obtained with the winter collection system. Average cloudwater concentrations of the dominant species (NO_3^-, SO_4^{2-}, and NH_4^+) were highest during the winter, while fall and spring averages were more nearly equal. Since increased aerosol concentrations of these species at Lower Kaweah have been correlated with the breakdown of stable conditions in the atmosphere above the San Joaquin Valley (see Chapter 3), the higher concentrations observed in the winter may be associated with longer wintertime periods of stagnation in the valley, which allow a greater buildup of pollutants.

It is important to emphasize, however, that differences in the seasonal volume–weighted average concentrations of these species are no larger than many of the differences observed between events in a single season. There is also considerable variation observed within the course of a single event. An example of single–event variation is illustrated by the data from November 1 – 2, 1987. Concentrations of NO_3^-, SO_4^{2-}, NH_4^+, and H^+ observed in samples collected at Lower Kaweah during this event are depicted in Figure 4. Between approximately 1630 and 1830 PST on November 2, an increase of several hundred percent was observed in the concentrations of NO_3^-, SO_4^{2-}, and NH_4^+. The H^+ concentration in the cloudwater also was observed to increase by more than 100% during this period. The timing of the increases coincided with a cessation of rainfall observed at a nearby passive cloudwater monitoring station (Chapter 4).

Rain falling at lower elevations prior to 1630 may have scavenged a large fraction of the pollutants being transported up the slopes of the Sierra by the afternoon upslope breezes (Chapter 3) before they could be incorporated into the cloudwater at Lower Kaweah. When the rain stopped, the cloudwater loadings observed at Lower Kaweah began to increase. A dip in the cloudwater concentrations around 1930 PST corresponded to a brief period of additional rainfall. Rainfall had also been observed intermittently beginning around 1100 PST and may explain the drop in cloudwater concentrations between 1030 and 1630.

No rainfall was observed prior to 1100 on November 1. A comparison of cloudwater concentrations prior to 1100 with those observed during non–precipitating conditions later in the day illustrates an increase of more than 100% for NO_3^-, SO_4^{2-}, and NH_4^+ through the afternoon. The concentration increases of these three species, all of which are found at high concentrations in aerosol near the valley floor, may have been associated with increased vertical mixing over the valley due to the arrival of the frontal system, or simply with transport up from the valley floor by the afternoon upslope breezes.

The technique of principal factor analysis (Harman, 1967) was applied to the cloudwater composition data set collected in Sequoia National Park during the fall of 1987. Principal factor analysis involves determining a small number of vectors, composed of combinations of different ions, which explain a large portion of the variance in the data set. The combinations of ions in the vectors may suggest sources of the cloudwater ions. A similar approach has been found useful for identifying potentially important sources in other studies (Knudson et al., 1977; Cahill et al., 1986).

The analysis utilized IMSL STAT/LIBRARY FORTRAN subroutines (IMSL, 1987) which were incorporated into a FORTRAN program. The first step was to derive the correlation matrix depicted in Table 3. The upper half of the matrix illustrates the complete set of ion correlations; the lower half depicts only those correlations greater than 0.7. The data illustrate that there is a large degree of correlation between many of the measured ion concentrations. It is interesting to note that there are no negative correlations between any of the ions. The combination of these two factors indicates that most ion concentrations tend to rise and fall as a group in this data set. This trend is consistent with two major processes thought to control the cloudwater concentrations at Lower Kaweah. Increases in the mixing height over the San Joaquin Valley, as discussed in Chapter 3, are likely to lead to simultaneous increases in most, if not all, of the major inorganic species concentrations observed at Lower Kaweah. Alternatively, washout by rainfall will reduce ambient concentrations of the inorganic species.

The correlation matrix was diagonalized to yield nine eigenvectors and their respective eigenvalues. The four most important eigenvectors, explaining 99% of the total variance in the data, are listed in Table 4. The corresponding eigenvalues also are listed here. The percent of total variance in the original data set spanned by each of the eigenvectors is given by the quotient of the eigenvalue corresponding to that vector divided by the sum of the eigenvalues (Knudson et al., 1977). The variances explained by each of the four eigenvectors listed in Table 4 are 76%, 12%, 8%, and 3%, arranged in order of decreasing eigenvalue. The value of each factor loading in an eigenvector indicates the importance of that factor's contribution to the composition of the vector. The first eigenvector contains significant contributions from almost all of the measured ions and may be considered to represent the total dissolved ion concentration. A similar pattern was observed in the factor loadings for the principal eigenvector explaining spatial variations in the composition of Puget Sound rainfall (Knudson et al., 1977). The fact that such a vector explains the majority of the variance in the data set from this study might have been foreseen based on the high degree of inter–species correlation observed in the correlation matrix.

By rotating the vectors in space, it is possible to simplify the vector structures to aid interpretation of source contributions. One useful technique is the varimax rotation which maximizes the variance contained within each vector (Harman, 1967). The effect of this rotation is to force component contributions either toward one or zero. The rotated vectors obtained by transforming the four eigenvectors in Table 4 by the varimax rotation are listed in Table 5. The percent of variance explained by each vector is listed in the table as well. Like the eigenvectors, these four vectors together explain 99% of the total variance in the original data set; however, the contributions made by three of the four rotated vectors, unlike those of the eigenvectors, are comparable.

The first rotated vector contains large contributions from NH_4^+, NO_3^-, and SO_4^{2-}, with smaller contributions from the remaining ions. The composition of this vector suggests that aerosol containing NH_4^+, NO_3^-, and SO_4^{2-} contributes significantly to the composition of the cloudwater in Sequoia National Park. The vector may also include contributions from gas phase NH_3 and HNO_3, which readily equilibrate to NH_4^+ and NO_3^- upon dissolution in cloudwater. As discussed in Chapter 3, all of these species are found at high concentrations near the floor of the San Joaquin Valley and are transported by daytime upslope winds into the adjoining Sierra. The dominance of the NO_3^- loading over the SO_4^{2-} loading in the rotated vector indicates that this source component is probably dominated by NH_4^+ and NO_3^- with smaller inputs of SO_4^{2-}.

The second rotated vector is dominated by inputs from Na^+, Cl^-, and Mg^{2+}. This composition suggests that there is a strong contribution to variance in the cloudwater composition associated with inputs of sea salt which contains large concentrations of these ions. A third important source is suggested by the composition of the third vector, which includes large contributions from Ca^{2+}, K^+, and Mg^{2+}. These ions are representative of inputs of soil dust.

The combination of these three vectors accounts for 89% of the variance in the inorganic composition of the samples studied. The fourth vector accounts for most of the remaining variance. The only significant contribution to this vector comes from H^+. Small contributions from NO_3^- and SO_4^{2-} are also seen, suggesting that some of the H^+ may be associated with inputs of HNO_3 and H_2SO_4. Since the loadings of these species are so small (equivalent only to that from Mg^{2+}), however, a more reasonable hypothesis of the H^+ source might be weak carboxylic acids. Formic and acetic acid, as indicated above, often make important contributions to the acidity of the cloudwater at Lower Kaweah, particularly during periods with little anthropogenic input. Since these species undergo rapid biological degradation in unpreserved samples (see Chapter 1), they are not routinely analyzed and their cloudwater concentrations were not available to be included in this statistical analysis.

There is no strong evidence, based upon this principal factor analysis, indicating that different anthropogenic source regions were operative in contributing to variations of Sequoia cloudwater concentrations of NO_3^-, SO_4^{2-}, and NH_4^+ during different events in the fall of 1987. Rather, the analysis suggests that there was a single dominant source of these three species, represented by the first rotated vector. It is possible, however, that the hypothesized source represents a mixture of inputs from areas throughout the San Joaquin Valley and perhaps even the San Francisco Bay area. It is also possible that the regional signatures of NO_3^-, SO_4^{2-}, and NH_4^+ are not sufficiently different to allow them to be separated out by this analysis with only 45 samples. Since the variance in the high NH_4^+ concentrations observed in the cloudwater samples are explained so well by the first rotated vector, however, it seems that the hypothesized source is probably associated with the large emissions of NH_3 characteristic of the central and southern San Joaquin Valley.

The inorganic chemical composition of the cloudwater collected at Turtleback Dome in Yosemite National Park is listed in Table 6. Cloudwater samples collected at this site tended to be more acidic than those collected at Lower Kaweah during the spring of 1988. Figure 5 depicts the distribution of sample pH values observed at each site during this period. Sequoia samples had pH values between 4.4 and 6.5; samples at Yosemite had pH values between 3.8 and 5.2. Some of the difference in the distributions may be due to storms which produced interception events only at one Park or the other; however, samples collected on April 28 and 30 at Turtleback Dome were observed to be more acidic than those collected simultaneously at Lower Kaweah.

Volume–weighted average cloudwater concentrations of NO_3^- and NH_4^+ were observed to be quite similar in the two Parks during the spring. This is illustrated in Figure 6. The higher level of free acidity in the Yosemite cloudwater is also apparent from this figure. At least part of the increase appears, on an average basis, to come from higher inputs of SO_4^{2-} in Yosemite. Differences in inputs of formic and acetic acid may also contribute to increased acidity of the Yosemite cloudwater. An increase in sample pH was often observed between the time that samples were collected and measured in Yosemite and the time that the pH measurement was repeated a few days later in Pasadena. This increase was more prevalent among higher pH samples, suggesting that the rise may have resulted from microbial degradation of lower molecular weight organic acids, such as formic and acetic acid, in the samples. The rise in the pH of precipitation samples has previously been used to estimate sample concentrations of carboxylic acids (Keene and Galloway, 1984). While this evidence, along with the prevalence of formate and acetate in Sequoia cloudwater, suggests that organic acids are probably present at some level in Yosemite cloudwater, no direct determinations are available at this time to evaluate the importance of their contribution to cloudwater acidity at Turtleback Dome.

A comparison of the cloudwater concentrations observed at Turtleback Dome and Lower Kaweah on April 28, 1988, is presented in Figure 7. Once again the higher free acidity in the Yosemite cloudwater is evident, with the average pH slightly less than 4.0, compared to a pH of 4.5 at Sequoia. In this case, the higher H^+ concentration appears to be largely compensated for by a lower concentration of NH_4^+ and higher concentrations of NO_3^- and SO_4^{2-} at Yosemite. It is worth noting that relatively small percentage changes in the amounts of mineral acids and bases in the cloudwater, as observed in this example, can dramatically change the pH.

We previously have pointed out the role of ammonia in limiting the acidification of cloudwater in Sequoia National Park (Chapter 1; Collett et al., 1989). The neutralization of cloudwater acidity by ammonia is largely responsible for maintaining the pH of Sequoia cloudwater above levels commonly seen at elevated sites in the eastern U.S. In the absence of ammonia inputs to the cloudwater sampled on November 28, pH values would have dropped below 3.3 at Yosemite, provided other inputs remained constant. Sample pH values at Sequoia on February 16, 1988, could have fallen as low as pH 2.9 in the absence of neutralization by ammonia. Without the high degree of neutralization by ammonia, cloudwater in the Sierra might regularly have pH values well below 4.0.

The role of neutralization by ammonia has also been addressed with regard to the composition of fogwater sampled on the floor of the San Joaquin Valley (Jacob et al., 1986), where the balance of local emissions of NH_3 vs. NO_x and SO_2 often determines fogwater acidity. While considerably more mixing of valley emissions occurs before they are transported up the slopes of the Sierra, the comparison between Sequoia and Yosemite cloudwater illustrates that regional differences in cloudwater acidity, associated with relatively small differences in local balances of acids and bases, are important in the Sierra as well.

While the presence of ammonia serves to reduce the free acidity of Sierra cloudwater, and nitrogen in the form of NH_3 or NH_4^+ is an important plant nutrient, the atmospheric deposition of large quantities of NH_4^+ may have deleterious effects upon the Sierra ecosystem. Nitrification of NH_4^+ in the soil is known to produce nitric acid (van Breemen et al., 1982), leading to acidification of the soil column. The uptake of NH_4^+ by the roots of plants is usually accompanied by oxidation and release of hydrogen ions or organic acids (Nihlgard, 1985), which will also contribute to soil column acidification. Other problems associated with excess nitrogen deposition include increased susceptibility to frost, biological enemies, and other air pollutants; excess nitrogen deposition may also create a distorted mineral balance in the environment surrounding a plant, which may lead to deficiencies of magnesium, potassium, phosphorus, molybdenum, and boron, all of which are needed to assimilate nitrogen and synthesize proteins in plant cells (Nihlgard, 1985).

While concentrations of the inorganic species observed in the cloudwater appear to be insufficient to cause acute damage to vegetation, the concentrations of these species actually present at the vegetative surfaces, during and following periods of cloudwater interception, may be greater than those observed in the collected cloudwater samples. The chemical composition of cloudwater droplets collected along the California coast has been observed to vary with droplet size within a single cloud parcel (Hoffmann, 1988; Munger et al., 1989). Similar observations recently have been made indirectly by Noone et al. (1988) as well. Smaller cloud droplets in the coastal clouds were observed both to be more acidic than larger droplets and more concentrated in NO_3^-, SO_4^{2-}, and NH_4^+. Larger droplets were observed to be more concentrated in species associated with soil dust and sea salt: Na^+, Ca^{2+}, and Mg^{2+}. If such differences exist in the cloudwater in the Sierra, a more detailed picture of the chemical composition of individual droplets is needed to assess the potential for vegetative damage. Droplets deposited on vegetative surfaces also may interact with previously deposited material. Such material could include particles and gases deposited via dry deposition mechanisms, or residues of evaporated cloudwater droplets or rain drops. The interaction of the freshly deposited droplets with previously deposited materials could lead to the exposure of the plant surfaces to higher concentrations of acids and other species than are found in the cloudwater alone. Finally, evaporation of deposited cloudwater, either in subsaturated conditions during an interception event or following an event, will lead to increases in the aqueous concentrations present at the plant surface. The potential importance of this mechanism has been outlined by Unsworth (1984).

Clearly there is a strong possibility that the aqueous concentrations present at vegetative surfaces may, at times, significantly exceed those present in bulk samples of cloudwater. More work is needed to evaluate the importance of concentration enrichment to determine the potential for acute vegetative damage in the Sierra. Another issue of concern is the cumulative deposition of chemical species to the forest ecosystem. The role of cloudwater interception in contributing to this process is evaluated in the following section.

Cloudwater Deposition

Significant quantities of NO_3^-, SO_4^{2-}, H^+, and NH_4^+ are deposited at Lower Kaweah by precipitation (Stohlgren and Parsons, 1987). Dry deposition is also expected to contribute significantly to the total deposition of these species in the region, particularly during the long dry periods in the summer when pollutants are seldom scavenged by cloud processes or rainfall (Cahill et al., 1986; Bytnerowicz and Olszyk, 1988). We previously suggested that the deposition of NO_3^-, SO_4^{2-}, H^+, and NH_4^+ via cloudwater interception at Lower Kaweah may be comparable to amounts introduced by precipitation (Collett et al., 1989; Chapter 1). Although the volume of water deposited to the canopy over the course of a year due to cloudwater interception is smaller than that due to precipitation, concentrations of NO_3^-, SO_4^{2-}, and NH_4^+ in the cloudwater at Lower Kaweah are much higher than those typically observed in precipitation at the same site. Figure 8 illustrates this difference. Average concentrations of NH_4^+ and NO_3^- in cloudwater are more than ten times those observed in precipitation; cloudwater SO_4^{2-} concentrations are more than three times those observed in precipitation. Since the cloudwater concentrations are so much higher, even small inputs of cloudwater can contribute relatively large quantities of these species to the ecosystem. Our original estimates of cloudwater deposition values were based on a limited set of cloudwater composition data collected during the fall of 1985 and the spring of 1986. Given the considerable body of data that has been collected in the current study, it is now possible to refine the initial estimates, and to compare them with the precipitation deposition data and with dry deposition data recently collected in Sequoia National Park.

In order to determine the flux of a given species to a surface (or vegetation canopy) via cloudwater deposition, two parameters must be established. First, it is necessary to identify the gross flux of cloudwater to the surface. Second, the average cloudwater concentration of the species of interest must be known. The product of the gross cloudwater flux and the average cloudwater concentration of the species yields the flux of interest. The data gathered in this study enable us to identify the average cloudwater composition with reasonable confidence for the period studied. Estimating the total quantity of cloudwater deposited to the canopy is considerably more difficult.

The deposition rate of cloudwater to the canopy is largely controlled by the wind speed, the aerodynamic structure of the canopy, the droplet size distribution, and the cloud liquid water content (Lovett and Reiners, 1986). Several authors have utilized a variety of approaches to determine the deposition of cloudwater to a vegetation canopy. These approaches have included measurements of throughfall beneath the canopy during periods of cloudwater deposition (Yosida, 1953; Azevedo and Morgan, 1974; Olson et al., 1981; Dasch, 1988), micrometeorological methods (Dollard et al., 1983), and modeling (Lovett, 1984; Unsworth, 1984). Lovett's model design is analogous to Ohm's law for DC electrical circuits. The flux of droplets to the canopy is determined by the ratio of a potential gradient to a resistance. The gradient consists of the droplet concentration difference between the air above the canopy and the vegetation surface. The resistance is composed of two portions: the resistance to turbulent transfer of the droplets down through the canopy, and the resistance to droplet transport through the boundary layer to the plant surface. The model predicts cloudwater deposition rates, in a closed canopy of 10.5 m balsam fir, varying nearly linearly from 0.2 to 1.1 mm·hr^{-1} for canopy–top wind speeds of 2 to 10 m·s^{-1}, a liquid water content (LWC) of 0.4 g·m^{-3}, and a modal droplet diameter of 10 μm (Lovett, 1984). Local deposition fluxes along gaps in the forest canopy are expected to be higher due to increased penetration of droplet–laden air parcels from above the canopy into the gaps (Lovett and Reiners, 1986).

Some reports of cloudwater deposition, estimated from throughfall measurements, have indicated deposition rates comparable to those predicted by Lovett (1984). Yosida (1953) reported droplet deposition rates of approximately 0.5 mm·hr^{-1} in a coastal forest intercepted by dense fog. Azevedo and Morgan (1974) measured fog drip beneath a large redwood in northern California at rates as high as 4 cm·day^{-1} over a two day period (implying an average deposition rate greater than 1.6 mm·hr^{-1}) and rates up to 4.6 cm·day^{-1} (0.8 mm·hr^{-1}) under other trees located at a ridge–top. Dasch (1988) reported deposition rates averaging 0.3 mm·hr^{-1} to a single exposed tree on the summit of Clingmans Peak, North Carolina, but only 0.03 mm·hr^{-1} in a dense spruce–fir forest located just below the summit. The lower value was substantially below what Dasch predicted using Lovett's model, adapted for local conditions.

Given the discrepancy present in the literature over the validity of Lovett's (1984) model estimates, and the uncertainty associated with adapting the model to other forest canopies, it is difficult to assess what deposition rates should be assumed for the canopy at Lower Kaweah. The presence of large gaps in the canopy there suggests that, as was observed in the studies where the trees were more greatly exposed, Lovett's model estimates are probably not too high, and may underestimate actual local deposition rates. Since many of the trees in the vicinity of Lower Kaweah, including Giant Sequoia, are much taller than those modeled by Lovett (1984), we are further inclined to believe that the model deposition estimates, adjusted for local wind speeds and liquid water contents, will be conservative for Lower Kaweah.

Wind speeds measured at Lower Kaweah during periods of cloud interception typically were observed to be on the order of 3 $m \cdot s^{-1}$; values of cloud LWC typically were observed to be approximately 0.15 $g \cdot m^{-3}$. Lovett's (1984) model predicts a gross cloudwater deposition rate of approximately 0.3 $mm \cdot hr^{-1}$ for a 3 $m \cdot s^{-1}$ wind speed and a liquid water content of 0.4 $g \cdot m^{-3}$ for the balsam fir canopy he modeled. Scaling the model prediction for the lower values of LWC observed at Lower Kaweah yields an estimated deposition rate of approximately 0.12 $mm \cdot hr^{-1}$, implying that the 265 hours of cloud interception observed there should have deposited approximately 31 mm of cloudwater during the period from September 1987 to August 1988.

The annual cloudwater deposition of ions to the forest canopy at Lower Kaweah can be estimated by combining the amount of cloudwater deposited with the volume weighted average ion concentrations in the deposited cloudwater. Figure 9 illustrates the results of this calculation for NO_3^- (199 $mg \cdot m^{-2}$), SO_4^{2-} (52 $mg \cdot m^{-2}$), NH_4^+ (84 $mg \cdot m^{-2}$), and H^+ (0.4 $mg \cdot m^{-2}$). These estimates are substantially lower than were previously predicted (596, 337, 311 and 0.8 $mg \cdot m^{-2}$ for NO_3^-, SO_4^{2-}, NH_4^+ and H^+, respectively), based on preliminary observations of cloudwater composition from Sequoia National Park (Collett et al., 1989). The current estimates are lower largely because wind speeds during interception and values of cloud LWC were found to be smaller than expected. The revised cloudwater deposition estimates, however, are still significant compared to precipitation inputs. This is particularly true for NO_3^- and NH_4^+. For purposes of comparison, estimates of the annual deposition of the four species in precipitation also have been included in Figure 9. Precipitation deposition estimates were taken from Stohlgren and Parsons (1987) and are based on weekly samples collected at Lower Kaweah between 1981 and 1984. Annual deposition of NH_4^+ is slightly higher in precipitation (110 $mg \cdot m^{-2}$) than is predicted in cloudwater; NO_3^- deposition (364 $mg \cdot m^{-2}$) is 82% higher; SO_4^{2-} deposition (391 $mg \cdot m^{-2}$) and H^+ deposition (4.5 $mg \cdot m^{-2}$) are factors of seven and eleven higher, respectively, in precipitation. Since the cloudwater deposition estimates are calculated for a closed canopy, however, local cloudwater fluxes of these species to single trees, to trees near the edge of the canopy, or to trees on a ridge–top may be several times higher than predicted here, due to greater cloudwater hydrologic deposition rates observed in such regions (Lovett and Reiners, 1986; Dasch, 1988). Cloudwater hydrological deposition rates to a passive cloudwater collector located on a nearby ridge–top, in fact, were observed to exceed 4.0 $mm \cdot hr^{-1}$ (see Chapter 4), compared to the model estimate of 0.12 $mm \cdot hr^{-1}$ used here; rates of cloudwater deposition to a passive cloudwater collector located in Yosemite National Park have been observed to exceed 20 $mm \cdot hr^{-1}$, during periods of high wind (Chapter 4).

Dry deposition also is an important contributor to the deposition of pollutants in the Sierra. Bytnerowicz and Olszyk (1988) reported rates of dry deposition of NO_3^-, SO_4^{2-}, NH_4^+, and H^+ to natural and surrogate surfaces at Emerald Lake, a high elevation (2740 m) lake in Sequoia National Park, during three separate periods in the summer of 1987. Average deposition rates reported for Teflon–coated branches of lodgepole pine, western white pine, and Coulter pine correspond to approximately 282, 73, 56, and 0.5 $mg \cdot m^{-2} \cdot y^{-1}$ for NO_3^-, SO_4^{2-}, NH_4^+, and H^+, respectively, assuming similar deposition rates throughout the year. Since concentrations of these species generally average higher in the summer when rainfall is infrequent, these rates should be considered as upper limits to actual annual rates of dry deposition at Emerald Lake. These "upper limits" are quite comparable to the annual deposition rate estimates for the same species due to cloud interception at Lower Kaweah. Unfortunately, there is a lack of data representing actual dry deposition measurements at other sites on the western slopes of the Sierra (Bytnerowicz and Olszyk, 1988). Cahill et al. (1986) observed that summer concentrations of SO_4^{2-} at Lower Kaweah were approximately twice the levels observed at Emerald Lake, suggesting that summertime dry deposition of SO_4^{2-} at Lower Kaweah is probably higher than at Emerald Lake. Similar differences in concentrations and deposition rates are likely for the other species as well. Even if summertime rates of dry deposition at Lower Kaweah are twice those observed at Emerald Lake, however, annual deposition rates are not likely to greatly exceed the "upper limits" established for Emerald Lake, suggesting that dry deposition and cloud interception are both important contributors to total deposition in the region.

While considerable uncertainty remains in the estimates of ionic deposition due to cloudwater interception at Lower Kaweah, it seems clear that this deposition mechanism is important, and may even dominate the deposition of NO_3^- and NH_4^+ to exposed trees and ridge–top canopies. Stohlgren and Parsons (1987) observed annual variations in deposition of NO_3^-, SO_4^{2-}, and NH_4^+ in precipitation in excess of 100%. Similar variations are probable in cloudwater deposition. Longer term monitoring of the cloudwater composition in the region, as well as the frequency and duration of cloudwater interception, is needed to determine the importance of annual variations in cloudwater deposition. Field measurements of hydrologic deposition rates to the forest canopy during cloud interception also would aid the establishment of more accurate water and ion flux estimates. Finally, there is a need to measure rates of dry deposition to the forest canopy in the region of Lower Kaweah, so that the relative importance of the three deposition pathways (precipitation, cloud interception, and dry deposition) can be established. Since annual dry deposition fluxes are probably negatively correlated with the deposition fluxes associated with precipitation and cloud interception, it is desirable to measure contributions from all three deposition pathways concurrently.

Conclusions

Cloudwater intercepting the slopes of the Sierra was sampled at two locations between September of 1987 and November of 1988. One site was located at 1856 m in Sequoia National Park while the second site was located at 1590 m in Yosemite National Park. Automated cloudwater sampling systems were used to collect the samples. The time during which clouds were observed to intercept the mountain slopes at the Sequoia site totaled 265 hours for the 12 month period between September 1987 and August 1988. Peak interception periods occurred in November and April, while the lowest activity was observed during the summer months. Valid samples representing approximately 50% of the total interception time were collected at the Sequoia site and analyzed to determine the concentrations of major ions.

The chemical composition of the sampled cloudwater in both Parks was dominated by NO_3^-, SO_4^{2-}, and NH_4^+. The balance between the cloudwater concentrations of NO_3^- and SO_4^{2-} vs. NH_4^+ was largely responsible for determining the cloudwater pH, although inputs of formic and acetic acid are also believed to be important in this regard, particularly for less polluted samples. The pH of the cloudwater samples collected at the Sequoia site ranged from 3.9 to 6.5; samples collected in Yosemite had pH values between 3.8 and 5.2. During periods of simultaneous collection, and on average, Yosemite samples were more acidic than Sequoia samples. The pH differential appears to be related to relatively small differences in the cloudwater concentrations of NO_3^-, SO_4^{2-}, and NH_4^+ at the two sites. The role of cloudwater acidity neutralization by inputs of ammonia was clearly observed. In the absence of large ammonia inputs, sample pH values in the Sierra may fall below 3.0.

The technique of principal factor analysis was applied to data representing the chemical composition of 45 cloudwater samples, collected in Sequoia National Park during the fall of 1987, in order to statistically reveal potential ion sources contributing to the sample composition. Four important sources were hypothesized based on this analysis: (1) a source dominated by NO_3^-, SO_4^{2-}, and NH_4^+, reflecting anthropogenic inputs; (2) a source representing sea salt inputs of Na^+, Cl^-, and Mg^{2+}; (3) a soil dust source comprised by Ca^{2+}, K^+, and Mg^{2+}; and (4) an H^+ source, probably associated with organic acids which were not routinely analyzed.

Estimates of annual deposition rates of major ions via cloudwater interception to the forest canopy at the Sequoia site were calculated. The rates for NO_3^-, SO_4^{2-}, and NH_4^+ were calculated to be somewhat lower than previously were estimated for the same site, largely because wind speeds and cloud liquid water contents during interception turned out to be lower than previously assumed. The current deposition estimates are still significant, however, with regard to measured contributions from precipitation and estimated contributions from dry deposition. Cloudwater interception may in fact be the dominant deposition mechanism for NO_3^- and NH_4^+, particularly for isolated trees or ridge–top canopies where wind speeds are higher and cloudy air parcels can impact directly on foliar surfaces.

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Table 1. Chemical Composition of Sequoia Cloudwater CASCC Samples: 1987–88

Time	pH	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
		←			μN				→
10/22/87									
1253–1324	4.95	3	4	57	6	1	6	41	17
1324–1416	4.87	1	2	29	3	1	2	23	11
1416–1603	5.14	13	13	33	13	4	18	35	18
2234–0015	5.13	5	4	7	8	1	6	16	8
10/24/87									
1423–1553	5.09	1	2	137	4	1	4	78	21
10/27/87									
1647–1741	4.90	2	6	93	5	1	11	49	21
10/28/87									
0724–0805	3.93	8	26	592	33	8	21	549	180
2112–2141	4.65	2	7	180	9	3	6	148	41
2258–0012	5.65	2	9	457	6	1	11	274	67
10/29/87									
0012–0141	6.04	1	3	270	3	2	6	152	36
0141–0608	5.09	0	1	43	3	1	0	32	9
0914–1035	4.70	1	7	79	6	2	7	56	27
1357–1504	4.44	3	12	234	9	4	12	174	67
1637–1920	4.67	1	7	202	7	1	9	128	47
10/31/87									
1414–1705	4.60	1	6	369	8	3	8	273	56
1705–1759	4.94	0	3	214	3	1	6	151	25
1759–1910	5.01	0	1	132	2	1	2	104	15
11/01/87									
0537–0627	4.86	0	3	99	2	1	2	78	13
0725–0829	4.82	0	4	99	4	1	4	78	15
0943–1050	4.70	0	2	83	2	0	2	68	11

Table 1 (Cont'd). Sequoia Cloudwater CASCC Samples: 1987–88

Time	pH	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
		←				μN			→
11/01/87 (cont'd)									
1050–1218	4.75	0	1	62	1	0	2	55	7
1218–1339	5.35	0	0	44	1	0	1	33	4
1339–1457	4.72	0	1	47	2	0	2	43	6
1457–1628	4.96	0	1	32	1	0	0	25	5
1628–1831	4.57	0	3	225	2	1	7	163	33
1831–1950	4.94	0	2	145	1	1	5	98	21
1951–2109	4.62	0	3	284	2	1	11	196	40
11/02/87									
0135–0430	4.62	2	5	229	2	1	10	157	45
0430–0545	4.65	2	1	120	2	1	7	92	26
0545–0715	4.69	2	0	34	2	1	3	33	11
0715–0950	4.46	10	1	70	2	2	13	67	24
0950–1248	4.67	9	1	68	2	2	13	53	21
11/14/87									
1434–1523	4.36	15	8	441	7	6	37	365	93
1523–1558	4.80	5	2	180	2	2	20	137	37
1558–1639	4.93	3	1	122	2	2	12	93	25
1639–1720	4.98	3	0	106	1	1	11	81	21
1720–1812	4.96	2	1	112	2	1	10	85	22
1812–1906	4.94	1	0	97	2	1	9	74	18
1906–1959	4.98	0	0	75	1	1	6	59	15
1959–2126	4.70	1	1	114	2	1	14	92	24
11/17/87									
1110–1416	4.68	2	2	91	2	1	6	61	23
1416–1553	5.27	1	1	21	1	1	1	14	8
1553–1739	5.04	0	1	17	1	0	1	9	8
1739–1854	5.08	0	1	11	1	0	0	7	5
1854–2000	4.83	0	1	13	1	0	1	8	5
04/14/88									
0100–0156	5.07	19	4	613	20	7	18	265	136

Table 1 (Cont'd). Sequoia Cloudwater CASCC Samples: 1987-88

Time	pH	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
		←				μN			→
04/28/88									
1020–1238	4.56	27	4	418	20	10	20	224	184
1238–1423	4.47	13	2	398	10	6	13	193	164
04/30/88									
0607–0754	4.69	5	1	115	8	3	2	62	60
05/17/88									
1206–1600	4.87	3	3	25	4	2	7	25	16
1600–1745	4.83	8	2	69	4	3	13	52	32
1745–2009	4.67	17	3	158	6	6	24	114	65
2009–2321	5.03	54	6	462	17	15	55	322	157
2321–0050	5.39	22	3	244	9	8	27	161	81
05/28/88									
2210–0108	6.49	63	8	45	72	13	12	22	70
06/05/88									
0441–0733	5.38	106	14	377	67	38	70	287	135
0928–1055	5.04	25	3	135	20	10	24	84	65
06/06/88									
0936–1036	5.55	187	14	338	70	50	167	235	127
08/25/88									
1603–1645	4.98	6	6	35	20	9	18	47	24
09/20/88									
1258–1714	4.90	64	15	652	117	38	59	311	187
1914–1951	5.22	2	2	11	10	4	4	16	7
09/21/88									
0516–0826	4.33	321	56	1611	295	117	162	1290	528
11/06/88									
1649–1733	4.74	36	22	1724	79	26	0	1008	141

Table 2. Chemical Composition of Sequoia Cloudwater CHRCC Samples: 1988

Time	pH	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
		← μN →							
1/30/88									
1422–1640	4.92	6	2	253	3	2	10	140	44
1/30–1/31/88									
4 Intervals	4.95	5	2	221	3	1	11	141	40
2/02/88									
1903–2212‡	5.08	15	6	1095	20	6	32	693	191
2/16/88									
1521–1813	4.56	20	8	1334	29	8	39	950	268
2/28/88									
2 Intervals	5.22	14	7	194	5	3	14	115	44
3/05–3/06/88									
2 Intervals	5.8	6	2	330	3	2	6	187	59
3/06/88									
1720–2109	6	5	1	167	2	2	4	79	26

‡ Cloud interception was not continuous during this period.

Table 3. Sequoia Cloud Composition Correlation Matrix Fall 1987

	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	H^+
Na^+	1.00	0.48	0.29	0.45	0.74	0.82	0.37	0.44	0.41
K^+		1.00	0.67	0.95	0.84	0.53	0.73	0.84	0.74
NH_4^+			1.00	0.59	0.66	0.61	0.98	0.90	0.62
Ca^{2+}		0.95		1.00	0.84	0.44	0.70	0.82	0.79
Mg^{2+}	0.74	0.84		0.84	1.00	0.78	0.76	0.86	0.79
Cl^-	0.82				0.78	1.00	0.65	0.67	0.50
NO_3^-		0.73	0.98		0.76		1.00	0.95	0.76
SO_4^{2-}		0.84	0.90	0.82	0.86		0.95	1.00	0.85
H^+		0.74		0.79	0.79		0.76	0.85	1.00

Entries above the diagonal illustrate the entire correlation matrix. Only correlations greater than 0.7 are listed in the lower half of the matrix.

Table 4. Sequoia Cloud Composition Eigenvectors Fall 1987

Eigenvalue*	6.55	1.07	0.73	0.26
% Variance‡	76	12	8	3
Na^+ Loading	0.61	0.71	−0.03	−0.01
K^+ Loading	0.89	−0.10	−0.31	−0.23
NH_4^+ Loading	0.84	−0.30	0.44	−0.12
Ca^{2+} Loading	0.87	−0.15	−0.43	−0.12
Mg^{2+} Loading	0.94	0.23	−0.13	0.02
Cl^- Loading	0.76	0.51	0.30	0.01
NO_3^- Loading	0.91	−0.26	0.31	0.01
SO_4^{2-} Loading	0.97	−0.19	0.09	0.04
H^+ Loading	0.85	−0.16	−0.20	0.41

---

* Values of the remaining five eigenvalues are all less than 0.03

‡ The percent of the variance present in the original data set accounted for by each vector.

Table 5. Sequoia Cloud Composition Rotated Vectors Fall 1987

% Variance‡	34	25	30	10
Na^+ Loading	0.05	0.90	–0.26	0.09
K^+ Loading	0.40	0.26	–0.84	0.13
NH_4^+ Loading	0.94	0.18	–0.27	0.09
Ca^{2+} Loading	0.32	0.20	–0.88	–0.25
Mg^{2+} Loading	0.39	0.60	–0.59	0.30
Cl^- Loading	0.44	0.83	–0.13	0.11
NO_3^- Loading	0.87	0.23	–0.35	0.25
SO_4^{2-} Loading	0.73	0.28	–0.51	0.36
H^+ Loading	0.41	0.21	–0.51	0.69

---

‡ The percent of the variance present in the original data set accounted for by each vector.

Table 6. Chemical Composition of Yosemite Cloudwater CASCC Samples: 1988

Time	pH	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
		←——— μN ———→							
04/14/88									
1745–1921	4.66	5	2	10	8	3	5	16	13
1921–2031	4.90	2	1	5	3	2	0	6	4
2031–2115	5.05	7	2	4	6	2	5	8	6
04/15/88									
1054–2155	4.48	1	1	14	4	1	0	20	9
04/16/88									
1530–1908	4.41	4	14	83	6	2	14	62	31
04/23/88									
1435–1736	4.59	9	5	126	23	8	8	50	115
1736–1922	4.69	4	3	96	15	5	3	34	73
1922–2039	4.77	2	1	64	9	3	1	26	49
2039–2202	4.66	2	2	69	10	3	1	32	53
04/28/88									
1027–1130	4.00	16	4	447	20	9	9	245	197
1130–1221	3.96	12	2	325	11	6	9	227	173
1221–1323	3.96	8	2	330	7	4	8	205	170
1323–1417	3.88	9	2	379	8	4	10	236	204
04/30/88									
0126–0339	4.08	51	5	189	33	20	23	237	134
0409–0506	4.37	25	3	87	18	11	14	105	64
0506–0600	4.34	23	2	74	15	9	16	87	54
0600–0655	4.54	19	1	56	9	7	17	59	41
0655–0820	4.32	32	2	93	12	10	30	95	74
0956–1002	4.92	6	1	16	4	2	7	14	9
1353–1407	5.13	5	1	10	4	2	5	10	7
05/12/88									
2302–2354	4.52	12	3	115	14	8	5	67	54
2354–0031	4.43	8	2	91	11	5	6	81	68

Table 6 (Cont'd). Yosemite Cloudwater CASCC Samples: 1988

Time	pH	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
		←				μN			→
05/13/88									
0031–0148	4.25	6	1	104	8	3	4	92	76
0148–0236	3.89	19	5	252	22	12	16	230	186
05/17/88									
0243–0321	4.69	6	2	48	9	4	3	30	41
0421–0533	4.99	2	1	17	3	2	1	15	14
0616–0809	4.73	4	1	35	5	2	2	25	33
0809–0854	4.45	5	1	51	7	3	4	36	45
05/28/88									
1923–2003	4.95	1	2	62	5	2	11	33	23
2010–2150	5.08	0	1	20	5	0	4	15	9
2150–0007	5.08	1	0	13	1	1	5	10	9
05/29/88									
0125–0225	4.30	67	3	72	8	17	79	52	83
1041–1130	4.99	4	0	15	1	1	13	10	7
11/13/88									
0904–1109	4.68	13	9	32	35	13	19	58	27
1645–1802	5.04	4	1	20	4	2	4	10	8
1802–1945	5.15	1	1	8	2	2	0	5	1
1945–2036	5.26	0	0	3	0	0	9	3	1
11/14/88									
1326–1426	5.10	8	1	5	4	3	9	5	2
11/16/88									
1725–1930	4.61	1	2	9	4	2	1	6	10
1930–2054	4.75	1	1	7	2	1	0	5	7
2054–2240	4.75	4	1	13	2	2	4	13	7
2240–2358	4.28	30	3	56	6	7	33	65	35
11/23/88									
0621–0952	4.87	5	4	9	4	NA	4	10	4

NA denotes not available

Figure Captions

Figure 1. Number of hours of cloud interception observed at Lower Kaweah in Sequoia National Park for each month between September, 1987 and August, 1988.

Figure 2. Distribution of sample pH values observed for cloudwater samples collected at Lower Kaweah in Sequoia National Park between September, 1987 and November, 1988.

Figure 3. Seasonal comparison of volume–weighted average cloudwater compositions observed at Lower Kaweah in Sequoia National Park for the fall of 1987 and the winter and spring of 1988.

Figure 4. Cloudwater concentrations of major ions observed in samples collected at Lower Kaweah in Sequoia National Park on November 1 – 2, 1987. Breaks in the lines represent significant breaks in cloud interception at the site.

Figure 5. Comparison of pH values observed in samples collected at Lower Kaweah in Sequoia National Park and at Turtleback Dome in Yosemite National Park during the spring of 1988.

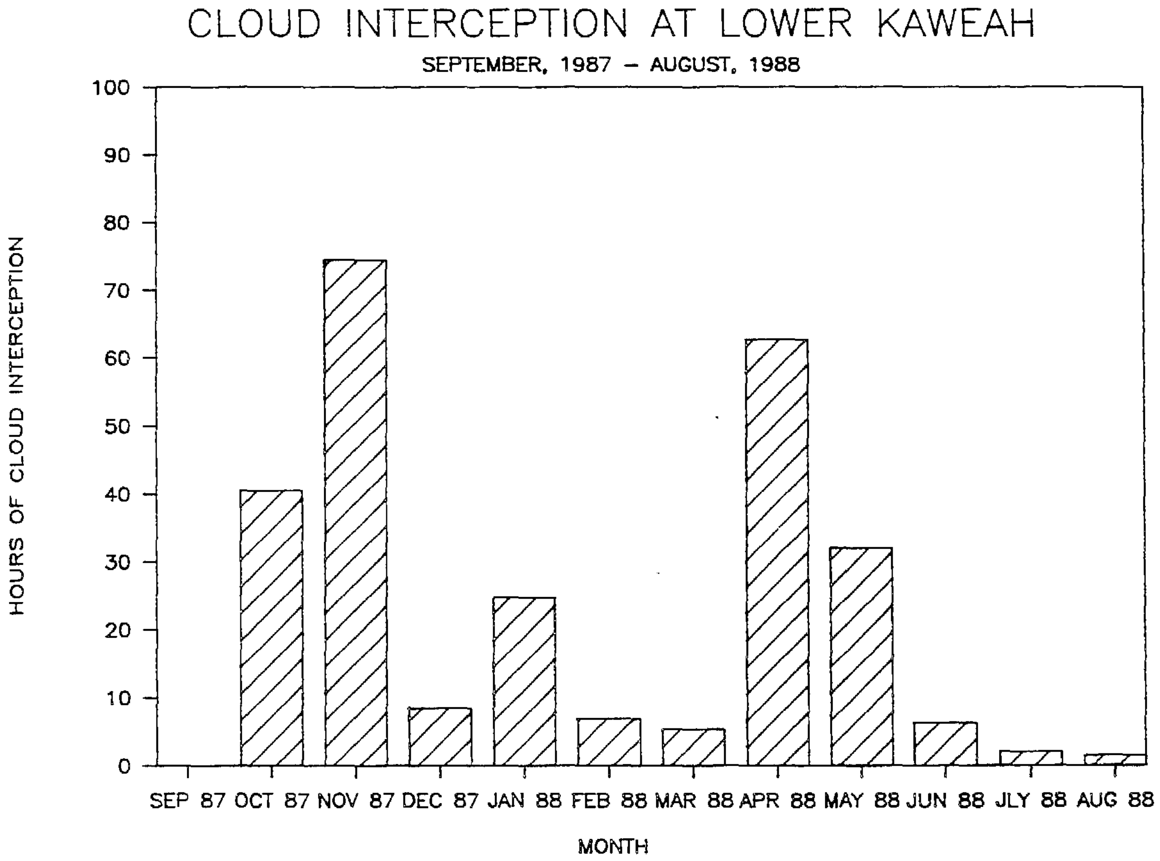
Figure 6. Volume–weighted average concentrations of major ions measured in samples collected at Lower Kaweah in Sequoia National Park and at Turtleback Dome in Yosemite National Park during the spring of 1988.

Figure 7. Volume–weighted average concentrations of major ions measured in samples collected simultaneously at Lower Kaweah in Sequoia National Park and at Turtleback Dome in Yosemite National Park on April 28, 1988.

Figure 8. Comparison of volume–weighted average cloudwater concentrations observed at Lower Kaweah in Sequoia National Park between September, 1987 and August, 1988 (this study) with volume–weighted

average concentrations observed in precipitation at the same site between 1981 and 1984 (Stohlgren and Parsons, 1987).

Figure 9. Annual deposition of major ions at Lower Kaweah in Sequoia National Park by precipitation (measured, Stohlgren and Parsons, 1987) and cloudwater interception (estimated). Estimates of ion deposition via cloudwater interception assume a hydrological deposition rate of $0.12\ \mathrm{mm} \cdot \mathrm{hr}^{-1}$. See the text for details.



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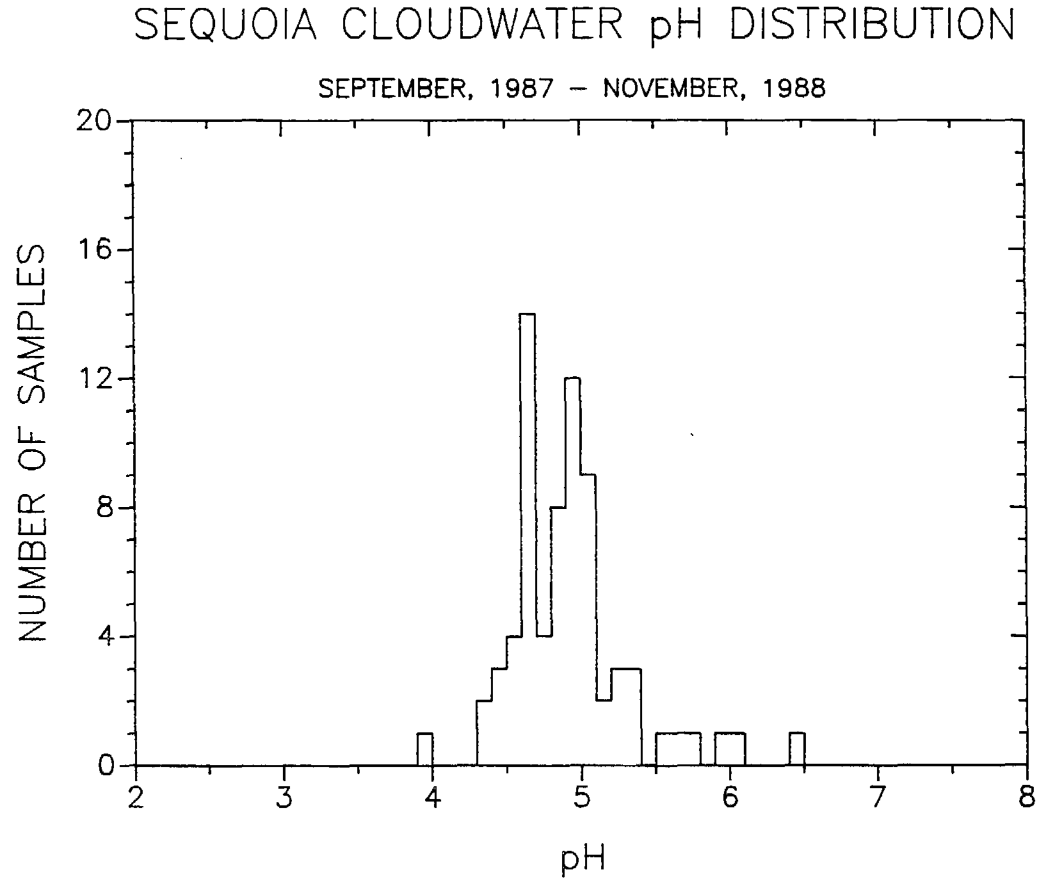
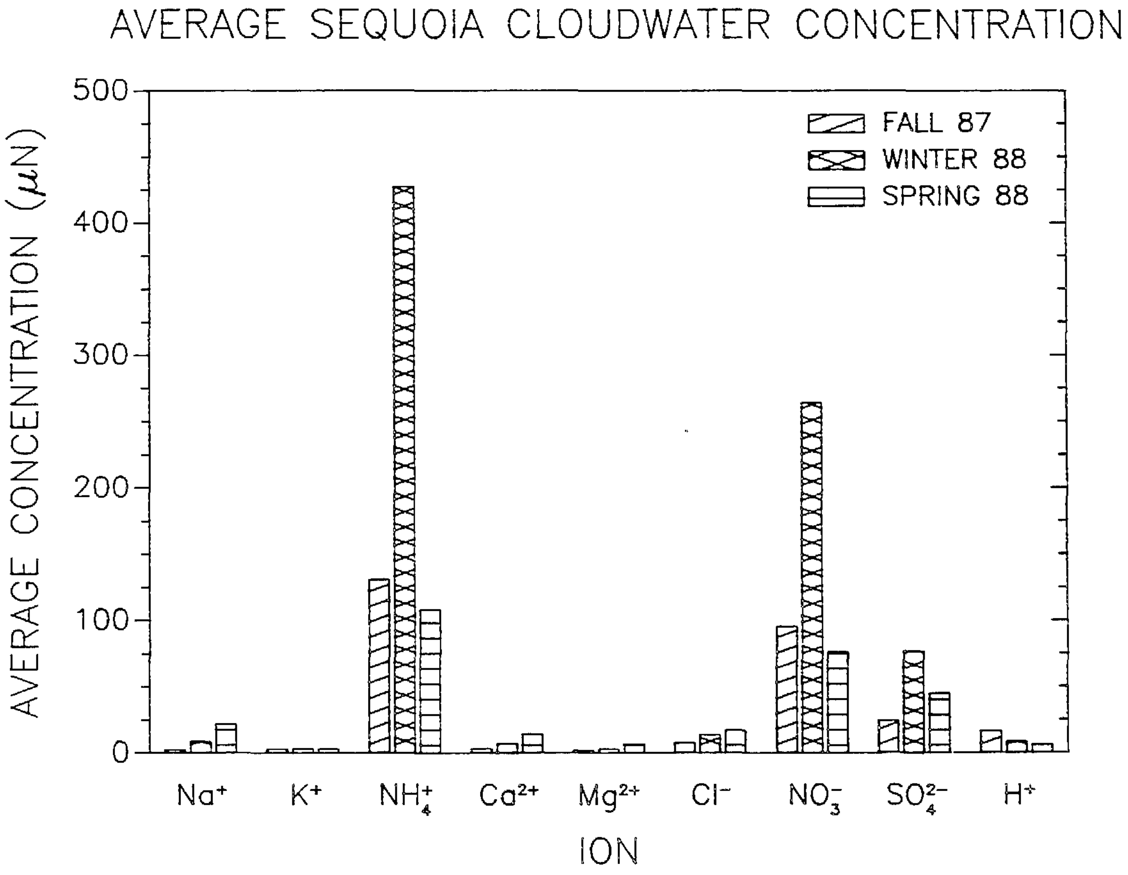


Figure 2. Distribution of sample pH values observed for cloudwater samples collected at Lower Kaweah in Sequoia National Park between September, 1987 and November, 1988.



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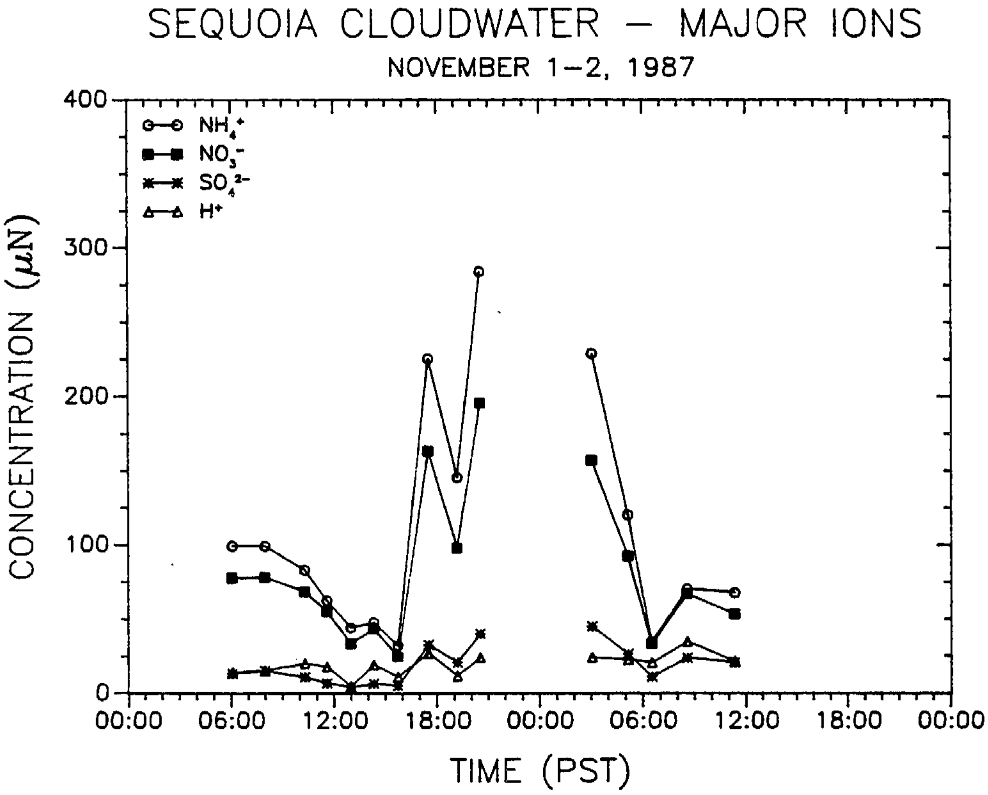

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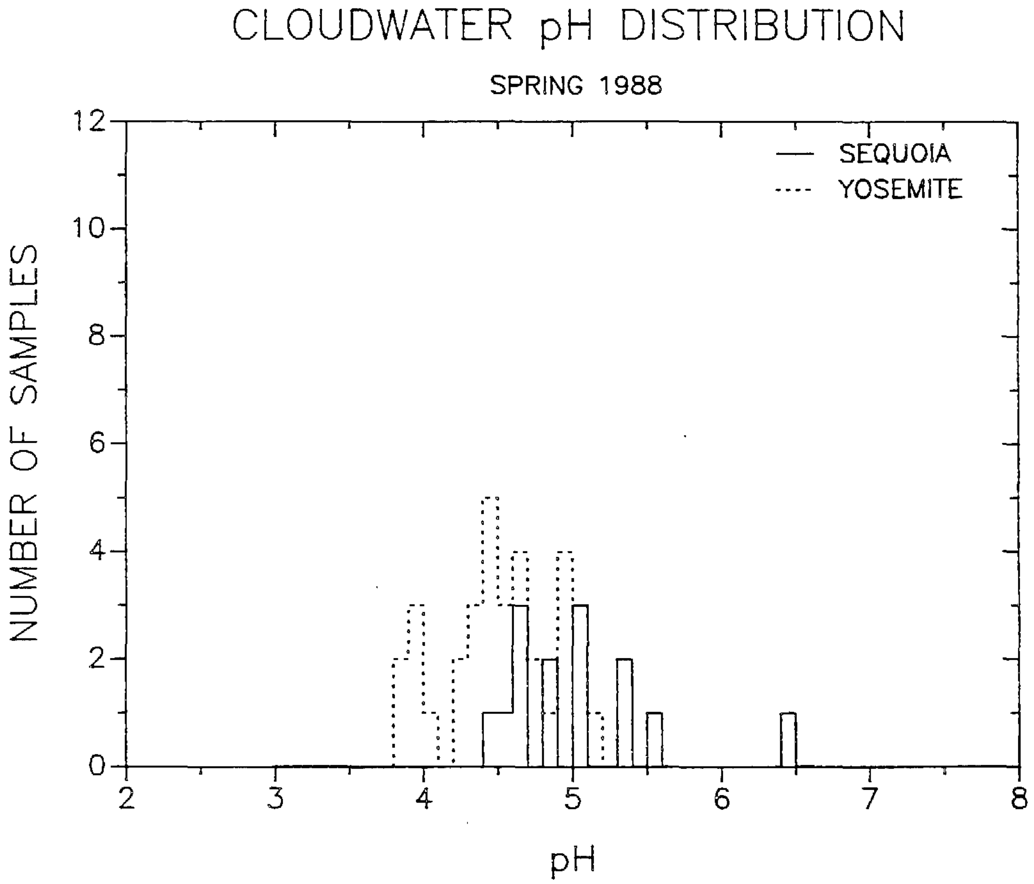


Figure 5. Comparison of pH values observed in samples collected at Lower Kaweah in Sequoia National Park and at Turtleback Dome in Yosemite National Park during the spring of 1988.

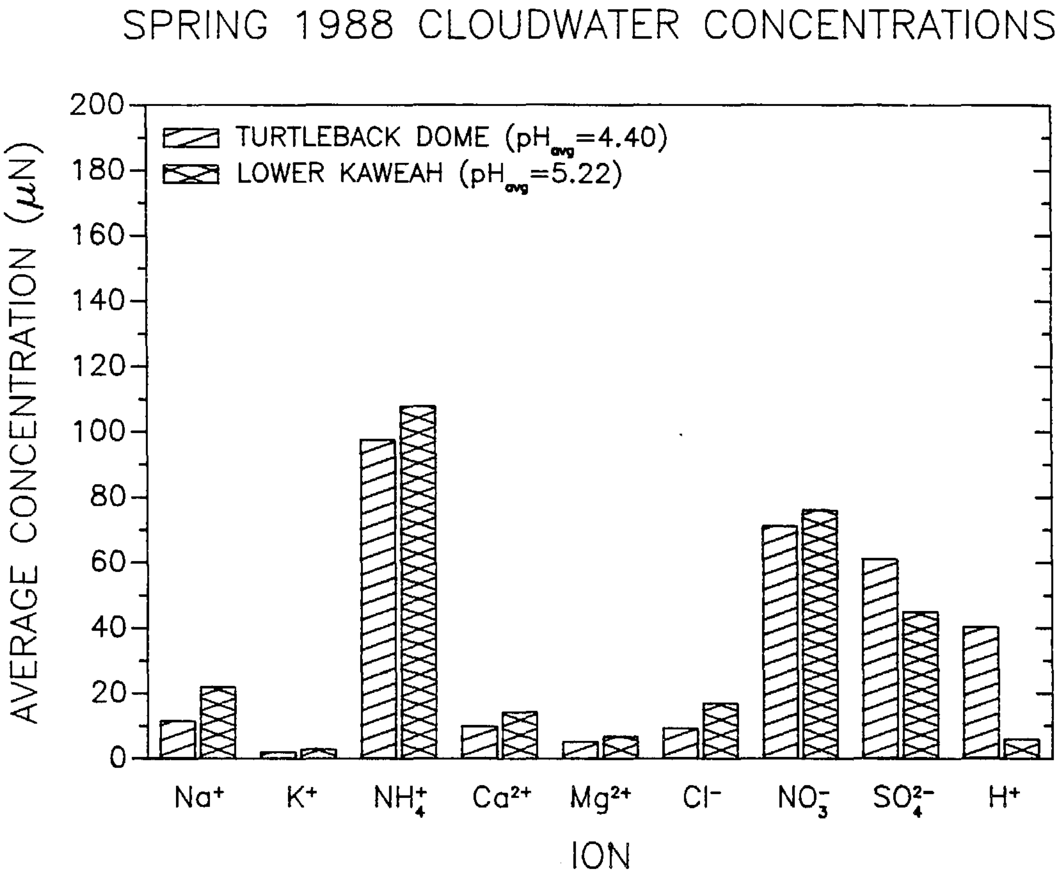


Figure 6. Volume–weighted average concentrations of major ions measured in samples collected at Lower Kaweah in Sequoia National Park and at Turtleback Dome in Yosemite National Park during the spring of 1988.

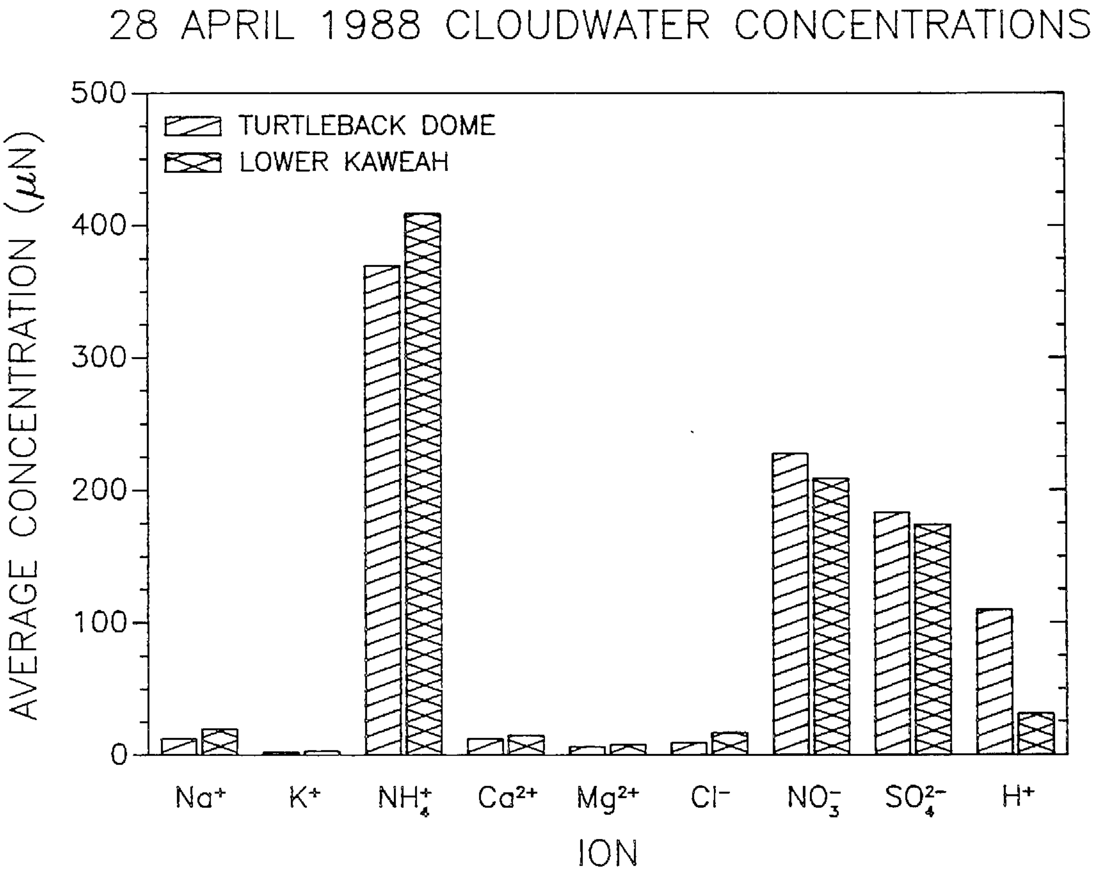
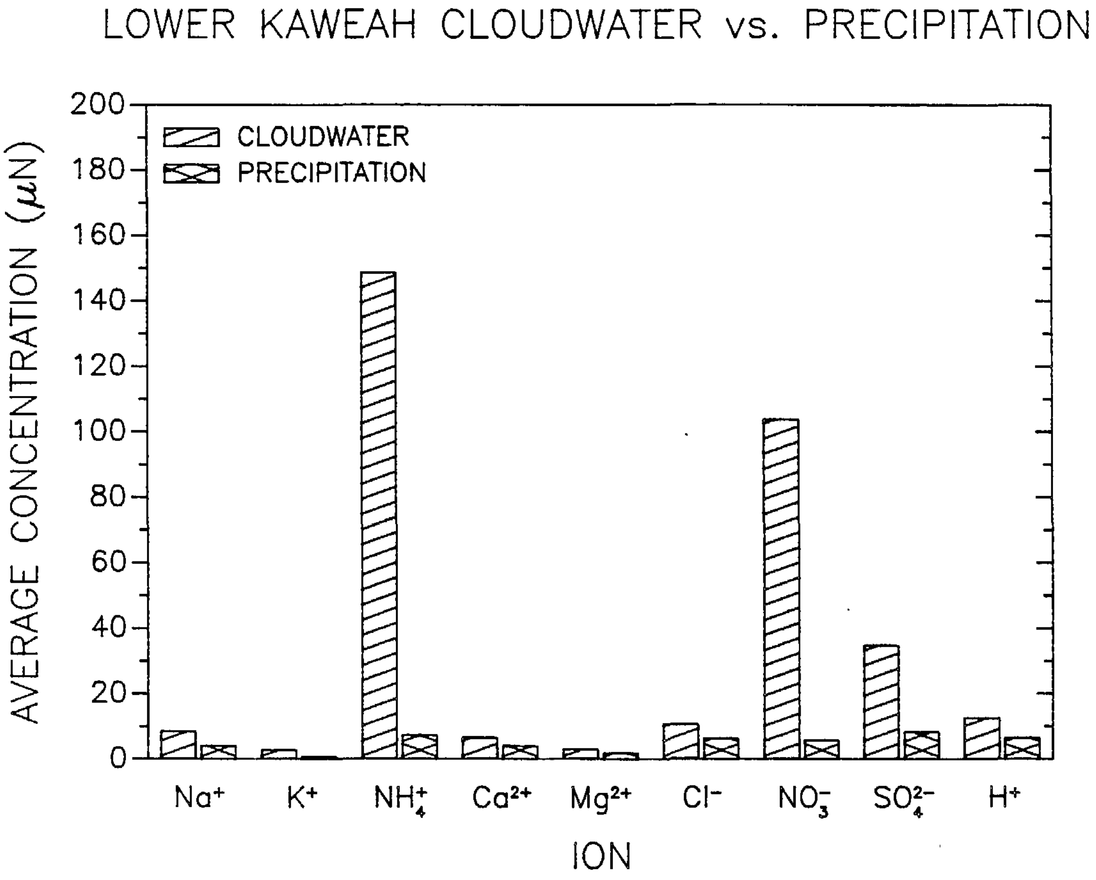


Figure 7. Volume–weighted average concentrations of major ions measured in samples collected simultaneously at Lower Kaweah in Sequoia National Park and at Turtleback Dome in Yosemite National Park on April 28, 1988.



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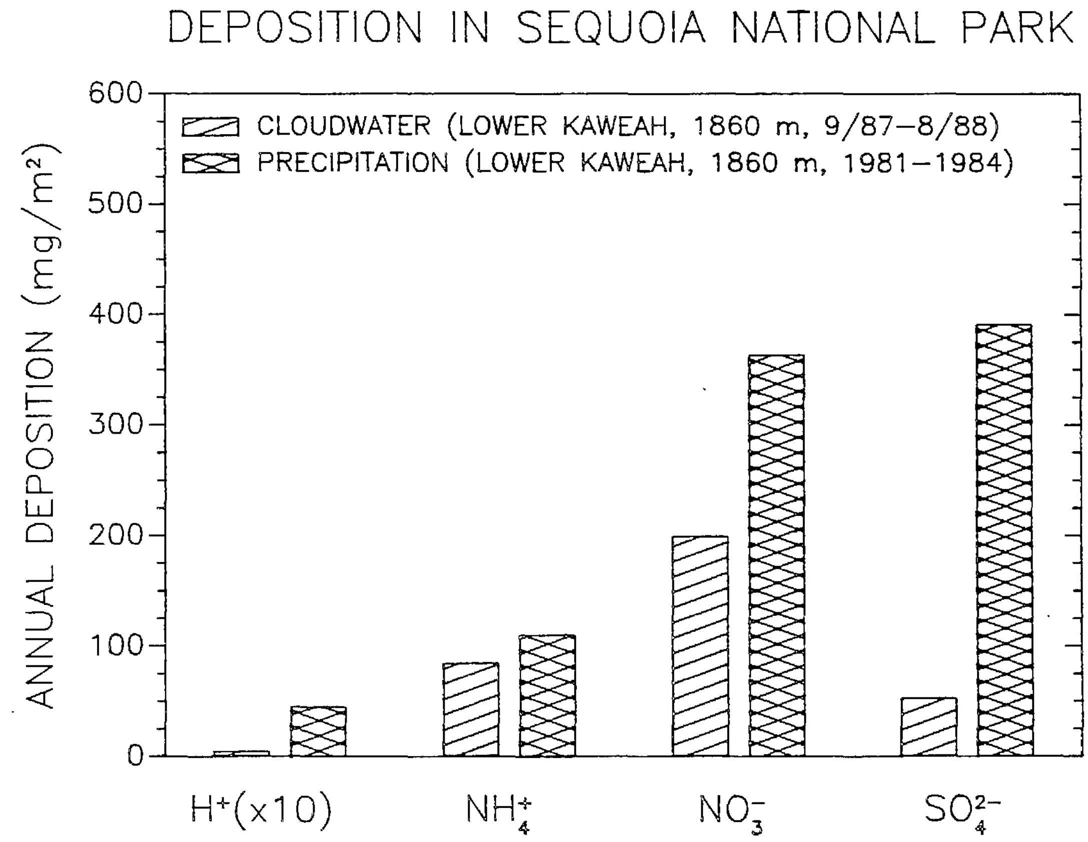

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