CHAPTER 10

Cloudwater Chemistry in Sequoia National Park

by

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Abstract

Cloudwater was sampled during the fall of 1985 and the spring of 1986 in Sequoia National Park in the southern Sierra Nevada Mountains 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. Organic acids are seen to be important contributors to the chemical composition of the cloudwater at this site.

The advance of cold fronts seems to lead to higher aerosol and gas phase concentrations in the Park than would be seen under normal mountain—valley circulations, particularly during the night and morning hours. The arrival of these increased concentrations 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 from rainfall.

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 rainfall and dry deposition.

Sequoia National Park (SNP), located in the southern Sierra Nevada Mountains 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 began a preliminary study of cloudwater chemistry in SNP. The results of that study, the first of its kind in the Sierra Nevada Mountains, 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 (see Fig. 1). The surrounding forest community is mixed conifer. The same site is used for NADP rainfall collection (Stohlgren and Parsons, 1987). The second site is located 3 km to the southwest at the

Deer Ridge turnout on the General's Highway. The elevation here is approximately 1490 m.

· Measurement Techniques

Cloudwater samples were collected with the Caltech Active Strand Collector (CASC) depicted in Figure 2. The CASC (Daube et al., 1987a) is an improved version of the collectors described in detail elsewhere (Jacob et al., 1985a, Daube et al., 1987b). The CASC employs a fan to draw air across six angled banks of 510 μm teflon strands at a velocity of 9 m 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 forces, through a teflon sample trough into a collection bottle.

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 and the rest of the filters in distilled, deionized 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. 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 CASC.

· 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 here are the estimated values of cloud liquid water content (LWC), derived from the sample collection rate and the theoretical collection efficiency of the CASC.

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 next to the last column of Table 1 presents the calculated inorganic ion balance for each sample (sum of measured inorganic anions/sum of measured cations). 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. In sample 5/03b the total of the concentrations of formate, acetate, lactate, and propionate is comparable to the sulfate concentration and is nearly twice the nitrate concentration. The concentrations in the other two samples are smaller, but still significant. Including these organic anions in the ion balances for the three samples changes them from 0.88, 0.62, 0.70, and 0.85 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 are seen to be important contributors to the overall chemical composition of SNP cloudwater. This is not surprising since lower molecular weight organic acids have been shown to be important components of fog and cloudwater in the San Joaquin Valley below (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 is enhanced by their dissociation (see eqn. 2). Because the cloudwater samples had pH values above the pK_a values of these acids they effectively scavenged the organic acids 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 diminished.

$$HA_{(g)} \xrightleftharpoons[]{H_a} HA_{(aq)} \tag{1}$$

$$HA_{(aq)} \xrightleftharpoons[]{K_a} H^+_{(aq)} + A^-_{(aq)} \tag{2}$$
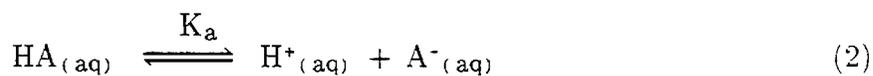
· Aerosol and Gas Phase Measurements

During the period May 1 to May 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+}. Simultaneous measurements were made of the gas phase concentrations of nitric acid and ammonia. Figure 4 presents the results obtained for the aerosol loadings of NO_3^-, SO_4^{2-}, NH_4^+, and Cl^-. Normally, upslope winds, caused by the heating of the air along the mountain slopes, should transport pollutants from the San Joaquin Valley to Lower Kaweah. 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 – May 3 and May 5 – May 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 mm hr^{-1} for canopy top wind speeds of 2 to 10 m s^{-1}. The much taller forest in SNP should be expected to receive at least the same deposition rate under similar conditions. Selecting a moderate wind speed of 6 m s^{-1} yields a deposition rate of approximately 0.7 mm 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 here are the annual average deposition rates for the same ions at the Lower Kaweah site contributed by rainfall (Stohlgren and Parsons, 1987). The estimated cloudwater deposition rates of all four ions are comparable to the measured rainfall inputs. While the estimates of cloudwater contributions to deposition in the region are crude, 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 Mountains 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-}, indicating the importance of the ionic composition of the sample in determining its acidity. Organic acids are seen to be important contributors to the chemical composition of the cloudwater here.

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 from rainfall.

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$_4^{2-}$	$-/+$	L
						μN					ml/m
10/21a	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
4/24a	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
5/03a	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
5/06a	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[*]	−/+
		←			μN		→
4/24c	4.8	68.5	13.8	11.5	0	5.2	0.95
5/03b	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

* Identification of this species is tentative.

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 Collector (CASC). The length of the collector is 0.91 m (36 in.). Total sampled flow is 21.1 m³/min.

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 (−/+) are given for the ions listed. Liquid water content values are estimates based on the cloudwater collection rate and the theoretical collection efficiency of the Caltech Active Strand Collector (CASC).

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.

Table 2.   Concentrations of carboxylate anions in cloudwater samples from Sequoia National Park collected during the spring of 1986. The ion balance (−/+) shown here includes these carboxylate anions as well as the inorganic ions listed for these samples in Table 1.

Figure 4.   Aerosol Loadings of sulfate, nitrate, ammonium, and chloride measured at the Lower Kaweah research site in Sequoia National Park during the period 5/1–5/6/87. 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). Estimates of cloudwater deposition are based on a cloudwater deposition rate of 0.7 mm/hr for 100 hr/yr (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.
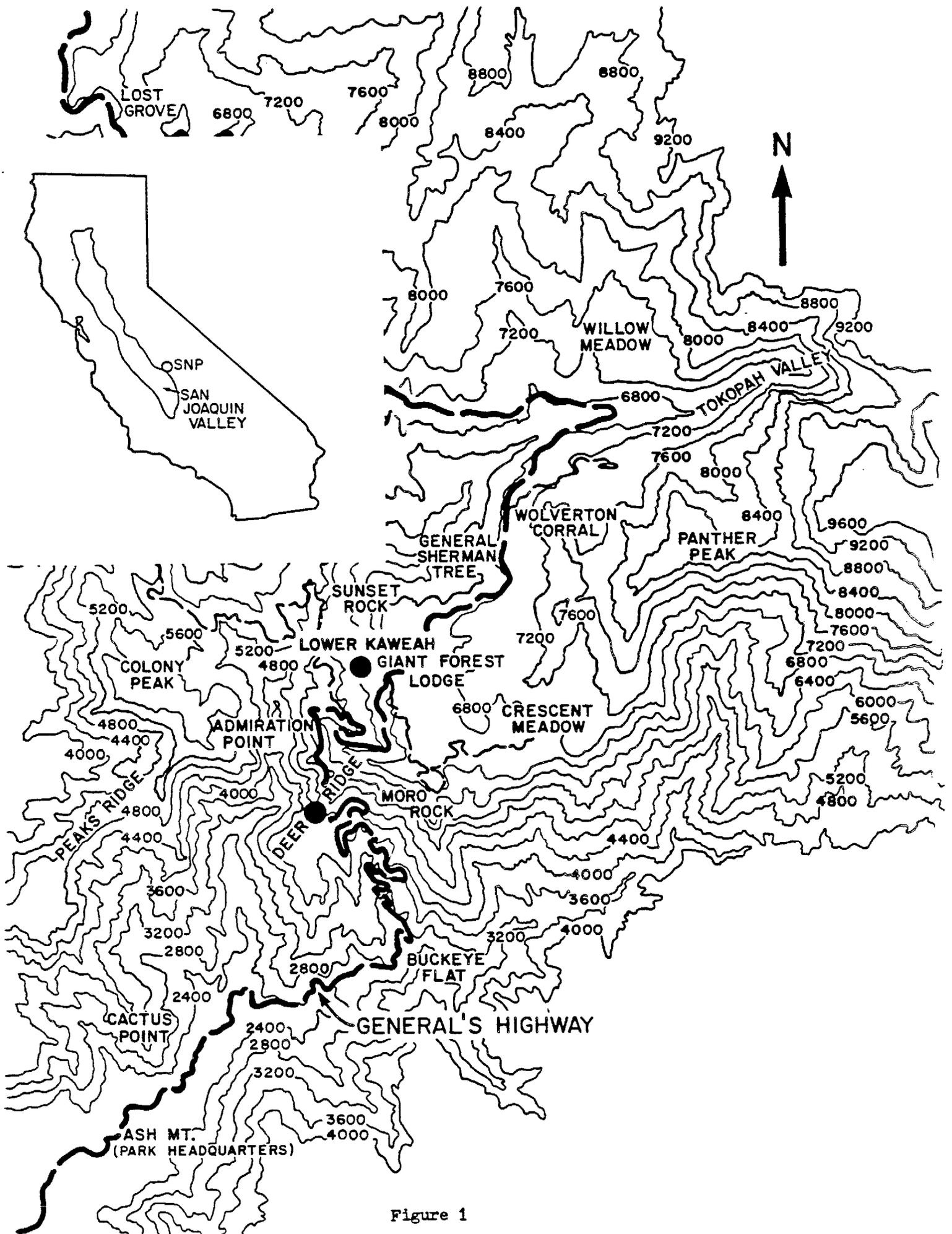
Figure 1
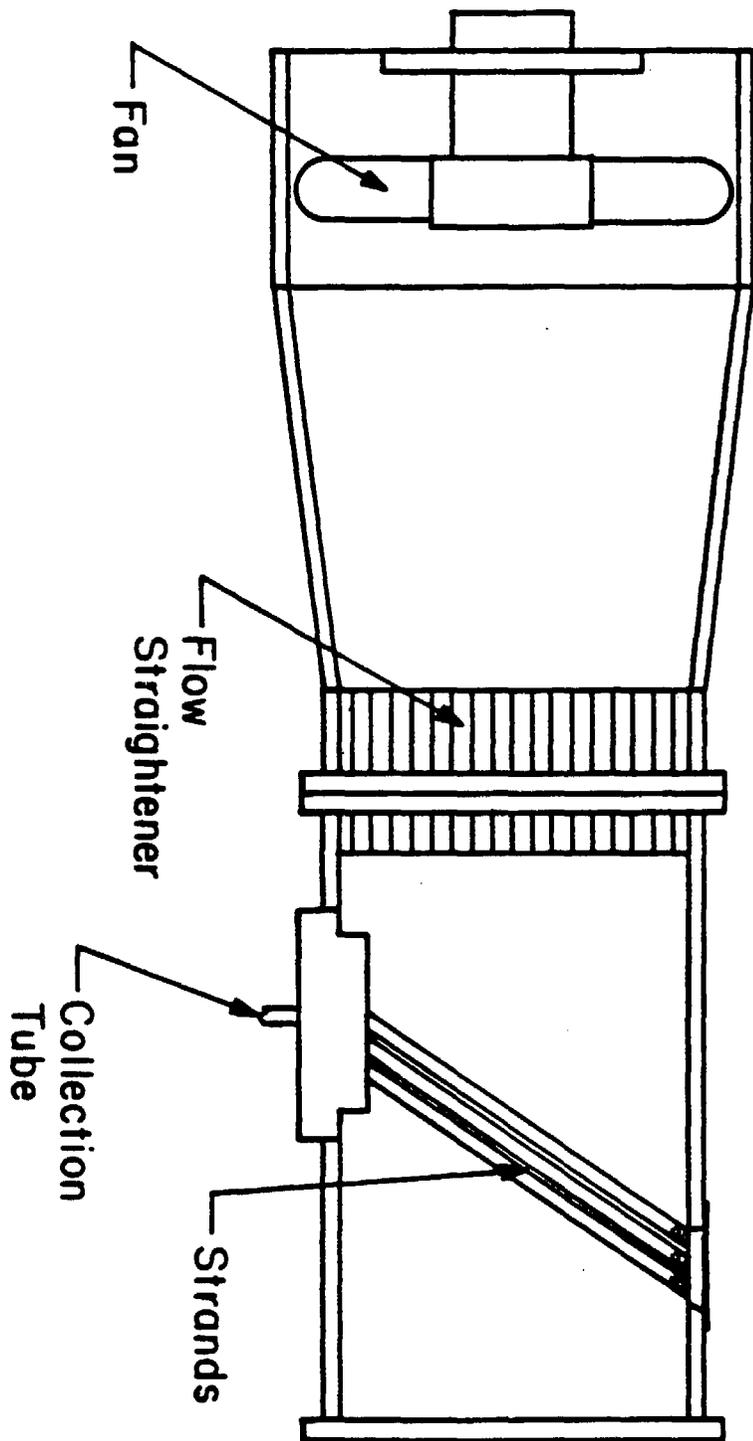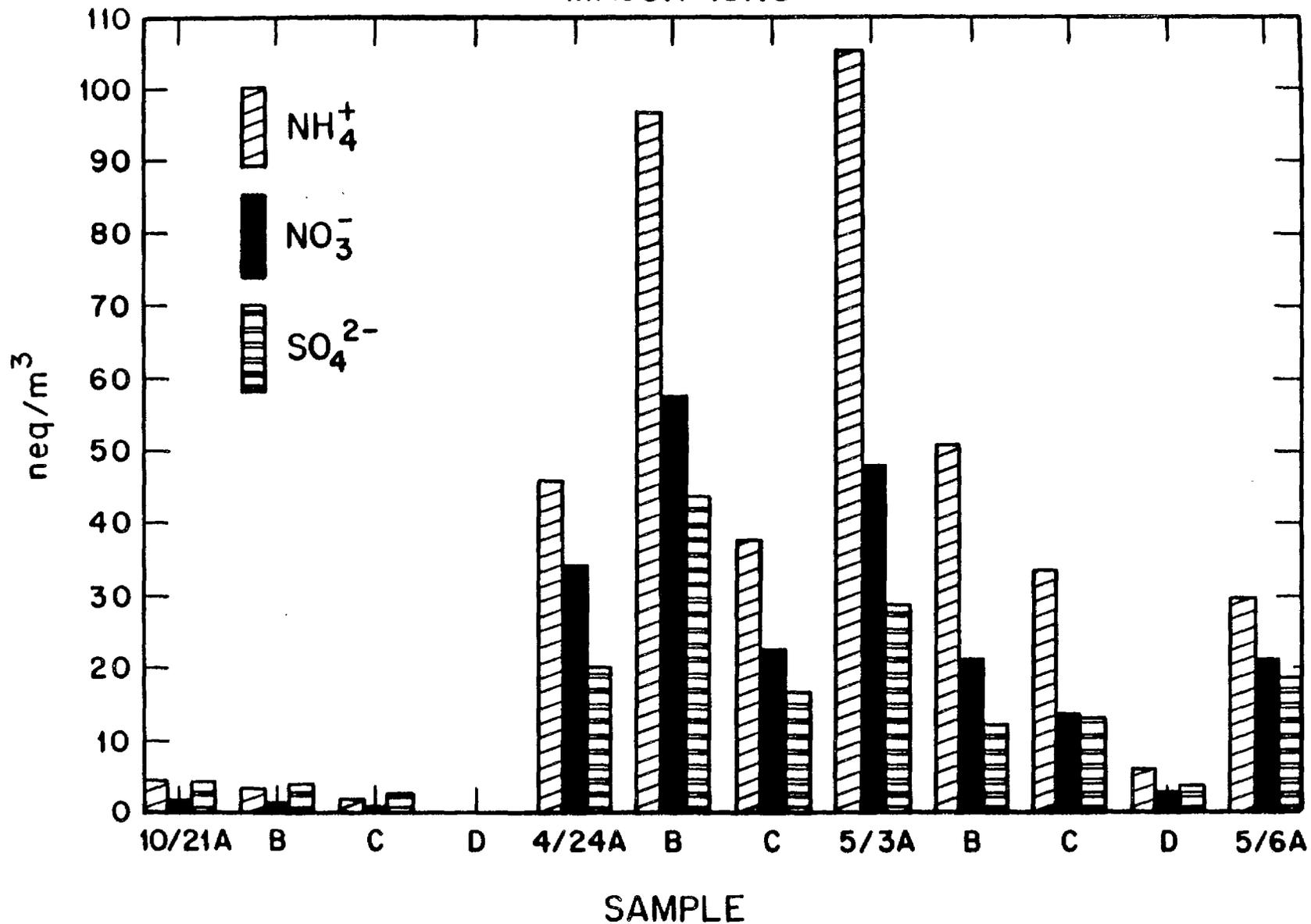
Active Strand Fogwater Collector

Fan

Flow Straightener

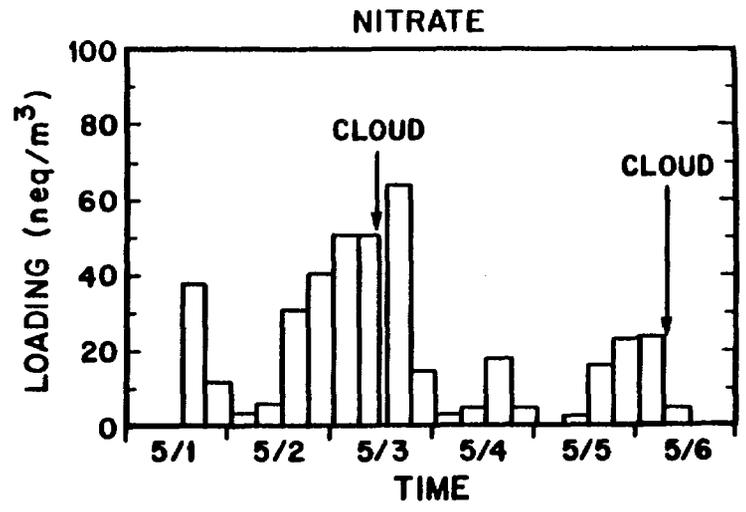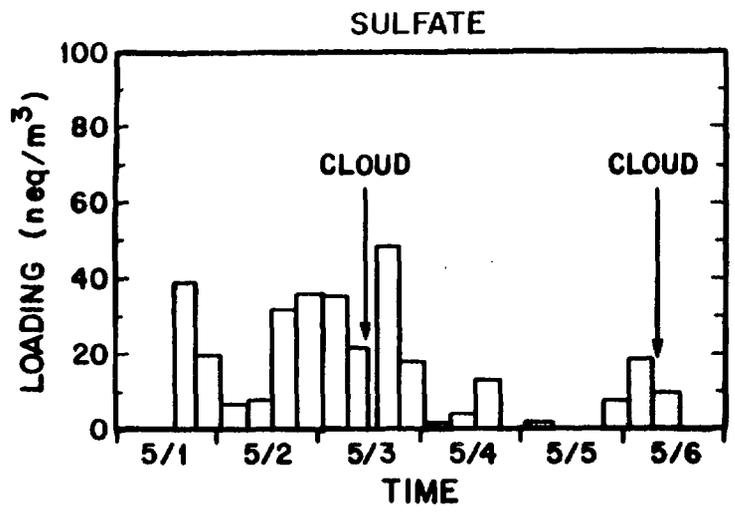Collection Tube

Strands

Figure 2

SEQUOIA CLOUDWATER
MAJOR IONS

Figure 3
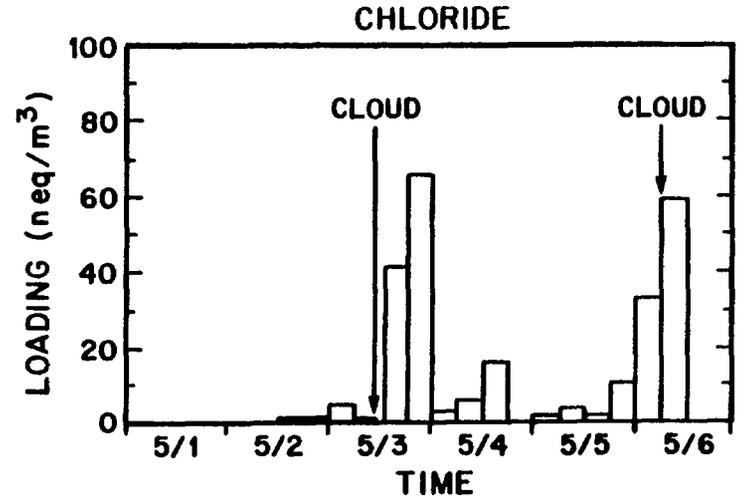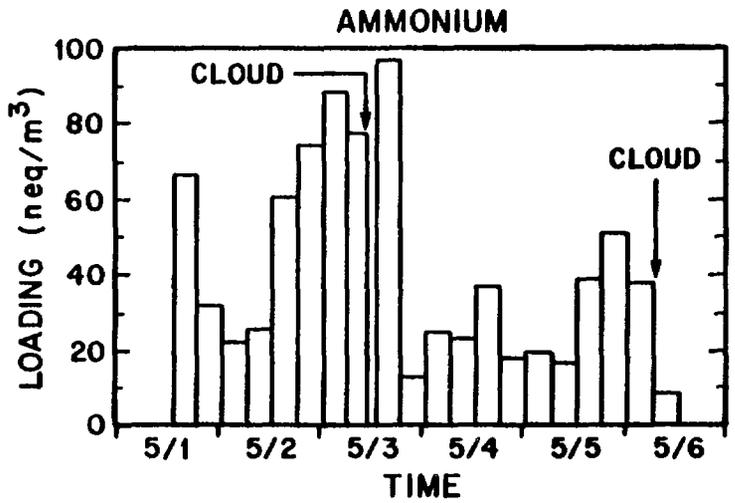
Figure 4

Figure 5

Figure 6