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CHEMISTRY AND ACIDITY OF CLOUD WATER AT MOUNT WASHINGTON, NH

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**CHEMISTRY AND ACIDITY
OF CLOUD WATER
AT
MOUNT WASHINGTON, NH**

**Byard W. Mosher
Complex Systems Research Center**

Technical Completion Report #55

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Water Resource Research Center
University of New Hampshire
Durham, New Hampshire

June 1992

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.....	1
LIST OF FIGURES.....	2
LIST OF TABLES.....	3
ABSTRACT.....	4
INTRODUCTION.....	6
RESEARCH OBJECTIVES.....	7
RESEARCH METHODOLOGY.....	8
Sampling Location.....	8
Cloud Water Sampling Methodology.....	9
Cloud Water Deposition Sampling Methodology.....	10
Cloud Water Sample Analysis.....	10
RESULTS AND DISCUSSION.....	12
CONCLUSIONS.....	31
REFERENCES.....	32

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LIST OF FIGURES

	Page
Figure 1. Cloud Chemistry - June 23, 1988.....	17
Figure 2. Frequency Distribution for pH.....	18
Figure 3. Cloud Chemistry - August 5-6, 1988.....	20
Figure 4. Cloud Chemistry - August 12, 1988.....	21
Figure 5. Cloud Chemistry - June 28-29, 1989.....	23
Figure 6. Cloud Chemistry - September 30, 1987.....	25
Figure 7. Sulfate + Nitrate vs Ammonium.....	26
Figure 8. Frequency Distribution for SO ₄ /NO ₃	28

LIST OF TABLES

	Page
Table 1. Summary of cloud water sampling and chemical analysis.....	13
Table 2. Summary of Mount Washington cloud chemistry.....	14
Table 3. Summary of Mount Washington cloud + rain chemistry.....	15
Table 4. Cloud Chemistry Correlation Matrix.....	29

ABSTRACT

Cloud water and mixed wet deposition samples were collected at the summit of Mount Washington (1914 meters elevation) during the summer months of 1987, 1988, and 1989. Cloud water deposition measurements were also conducted in a balsam fir krummholz community at 1525 meters elevation on the west slope of Mt. Washington from July to September, 1988. Acidity, major ion chemistry and organic acid analyses were conducted on cloud water and precipitation samples collected at the summit.

Cloud water pH levels as low as 2.7 were recorded. It was found that vegetation at this high elevation site may be exposed to very acidic cloud water (pH 2.7 - 3.5) deposition for continuous periods as long as 14 hours. The acidity and ionic content of cloud water was typically observed to be substantially greater than that of attendant rain. The pH of cloud water samples varied from 2.7 - 6.4. The high pH, low acidity samples were typically collected under conditions where orographic clouds formed close to the summit as air swept up the mountain and cooled, resulting in condensation and cloud formation. The low cloud water acidity observed under these conditions is undoubtedly due to the fact that these clouds had formed minutes to seconds prior to being sampled. Thus the only appreciable source of acidity was the solubilization of condensation nuclei or aerosols upon which the cloud droplets coalesced. There was very little time for the incorporation of gas phase species such as SO₂ and HNO₃ into these cloud droplets. Very acidic cloud water samples were typically collected under very different conditions. Stagnant meteorological circulation conditions were observed to contribute to the build-up of high gaseous and particulate pollutant concentrations in the northern New Hampshire atmosphere. Clear air visibility was at times reduced to less than 5 miles at the summit when a strong inversion and stagnant regional circulation patterns led to high pollutant levels in the lower atmosphere. Formation of clouds under these circumstances resulted in the extremely high (pH ≤ 3) cloud water acidity levels which we have observed.

We have found that the SO_4/NO_3 ratio of cloud water changes drastically over time periods as short as 2-3 hours. This ratio has been observed to drop rapidly from the range of 5 to approximately 1 during the passage of a cold front. The frequency distribution of SO_4/NO_3 concentrations found in clouds at Mount Washington exhibits a distinct bimodal distribution. Peaks are observed at ratio values of 1.5 and 3.0.

Net cloud water deposition represented about 43% of total wet deposition to the krummholz study area during the observation period in 1988, and gross cloud-water deposition rates averaged 0.90 mm/hour during cloud immersion periods.

INTRODUCTION

It has been realized for some time that the horizontal deposition of cloud and fog water can contribute significantly to the hydrological and chemical balance in elevated forested regions. Factors such as increased cloud cover at the surface, relatively high wind speeds, and the fragile nature of alpine ecosystems combine to enhance net deposition and possible ecological effects of acid deposition and nutrient input at higher elevations. While a clear cause and effect relationship relating acid deposition with forest decline and dieback has not been demonstrated, cloud water deposition has been identified as a potentially important input which may adversely affect the ecological and chemical balances in mountainous areas. Mortality and damage to conifers has been observed over a wide variety of soils and geographical range and the severity of this damage in general increases with elevation (Johnson and Siccama, 1983). In addition, there is ample evidence of definitive damage to plants exposed, under laboratory conditions, to acid mists of $\text{pH} \leq 3$. Increased foliar leaching of K, Mg, and Ca as well as leaf and needle damage in species such as spruce, birch, pine, soybean and bush beans has been observed at these acidity levels (Wedding et al., 1979; Hindawi et al., 1980; Scherbatskoy and Klein, 1983; Skeffington and Roberts, 1985).

Studies in the Green Mountains of Vt and the White Mountains of NH (Reiners and Lang, 1980) indicate that $\geq 30\%$ of annual wet deposition may result from horizontal deposition of cloud droplets. Similarly, in the northern Appalachian mountains Lovett et al (1982) found that about 45% of annual wet deposition was the result of direct cloud water capture in the forest canopy while 60-80% of the input of chemical species such as H^+ , SO_4^{2-} , and NO_3^- were deposited in this manner.

It is evident that data concerning the chemical composition of cloud water are essential if the potential ecological impact of man's activities at high elevation sites is to be realistically assessed.

RESEARCH OBJECTIVES

The objectives of this research project are the following:

- 1) Examine the chemical composition and acidity of cloud water deposited at a high elevation site in the White Mountains of NH.
- 2) Evaluate the importance of cloud water deposition to the chemical and hydrological balance of the study area.
- 3) Study temporal changes in cloud water chemistry and examine possible mechanisms responsible for these changes.

RESEARCH METHODOLOGY

Sampling Location

The summit of Mount Washington is enveloped in clouds approximately 60% of the time. The Mount Washington Observatory is manned continuously and thus provides an excellent site at which to conduct cloud water sampling for extended periods of time. Laboratory space at the Observatory as well as food and lodging available at the summit facilitate work under the difficult meteorological conditions often encountered there. Basic meteorological data such as wind speed, direction, temperature, dew point, and visibility are available at the site. The auto road to the summit provides ready access during the months May-October.

The cloud water collector was secured on the Observatory meteorological tower approximately one meter below the anemometers. The location of this tower provided an unobstructed sampling sector in the prevailing westerly wind direction. Summit building and diesel generator exhaust vents were located well downwind of the cloud water sampler during all collection periods. There are two additional local sources of contamination which also must be considered when sampling at this location: the Mount Washington Cog Railway line and automobile traffic along the road to the summit. Cloud water sampling was stopped and the collector covered during the short periods when cog trains were upwind of the sampling site. These coal-fired trains emit profuse amounts of particulate material and the potential for sample contamination was very real. Traffic on the auto road was not considered to be a problem and thus no effort was made to stop sampling during periods when cars were traversing the auto road. It was observed that the auto road was seldom directly upwind of the sampling site. It was also felt that automotive emissions, predominantly in the form of primary gaseous species such as CO, CO₂ and NO_x (NO₂ + NO), would not contaminate cloud water samples.

The cloud water deposition study was conducted at a site in Ammonoosuc Ravine immediately below the Lake of the Clouds on the

west face of Mount Washington. The krummholz study patch was roughly elliptical in shape with an approximate area of 300 m². The patch consisted almost entirely of balsam fir (*Abies balsamea*) ranging in height from 0.20 to 1.75 meters. This location is immersed in cloud roughly 42% of the time (K. Kimball, AMC, personal communication). A totalizing anemometer at the site recorded wind run during study periods. A Weathermeasure 280 mm capacity rain gauge was located in an open area adjacent to the study plot. The aperture of the rain gauge was set at ground level in order to sample rainfall in as representative a manner as possible (Helvey and Patric, 1983). Wind direction and average temperature during the collected periods were also recorded.

Cloud Water Sampling Methodology

The design and collection characteristics of various cloud water collectors have been reviewed by Jacob et al. (1984). Passive collectors such as screen and grid surfaces exhibit limited and variable sampling rates due to their dependence upon the ambient wind for sample collection. The very strong wind regime at the summit of Mount Washington where typical winds speeds may be in the range of 20-40 ms⁻¹ makes the use of a passive type collector very difficult as cloud water may be stripped off the collector surface as rapidly as it is collected. For this reason it was decided that an active cloud water collector would be better suited to the rigorous conditions often encountered at the Mount Washington Summit. A mesh impaction fog sampler (MIFS) described by Brewer et al. (1983) was used for all cloud water collection. This collector was robust enough to function in the 25 ms⁻¹ wind speeds typical at the summit of Mount Washington, and withstood winds speeds in excess of 35 ms⁻¹. Suspended cloud droplets are collected on a polypropylene mesh at a flow rate of 1.6 m³ /min. The coalesced moisture subsequently runs down a teflon lined intake arm which is mounted at a 45 degree angle, into a polyethylene collection bottle. Sample bottles had been rinsed in deionized water (DI) and were kept soaking in DI until use. Prior to each collection period the collector was cleaned with DI water and the polyethylene screening was continuously soaked in DI water prior to use. In wind tunnel evaluations this device has been shown to exhibit a collection efficiency of $\geq 95\%$ for

droplets of cloud water size and the 50% cut-off in sampling efficiency is approximately $5.0 \mu\text{m}$ droplet diameter (Huang et al., 1985). The MIFS collector has been evaluated in field tests and was found to compare favorably with other cloud water collector designs currently in use (Hering et al., 1987). At the high wind speeds typically encountered at the Mount Washington summit it was not possible to selectively collect cloud water during periods when it was also raining. At 25 ms^{-1} both a $50 \mu\text{m}$ cloud droplet and a $500 \mu\text{m}$ rain droplet are essentially moving horizontally. It was possible to collect several discrete rain samples during cloud deposition events by placing a clean rain funnel and polyethylene bottle in a location which was sheltered from horizontal cloud water deposition but open enough to allow collection of rain droplets. Sampling times for cloud water varied from five minutes to approximately one hour depending on the liquid water content of the clouds. Sample volumes varied from several milliliters to 120 ml. Typically when the collector was first set out on the sampling platform the initial aliquot of cloud water was discarded. This was done to flush the collector thoroughly and remove any residual DI from the screen and collector surface.

Cloud Water Deposition Sampling Methodology

Throughfall in the krummholz study patch was collected in cylindrical plastic containers placed on an approximate $1.2 \text{ m} \times 1.2 \text{ m}$ grid pattern beneath the krummholz. Forty one of these 8.2 cm diameter collectors were set out on this predetermined grid prior to each deposition event. Collections were made during eighteen cloud water deposition events. Sampling times ranged from 2 - 16 hours with a mean of 9.9 hours. The containers were retrieved at the end of the collection period and throughfall volumes determined using a graduated cylinder.

Cloud Water Sample Analysis

Sample acidity determinations were made immediately after sample collection using a calibrated Ross combination pH electrode and Corning Ion Analyzer (Model 250). The electrode tip was immersed in a small aliquot of the sample placed in a rinsed 4ml poly vial. The sample was allowed to equilibrate to room temperature and the pH was recorded when

the reading had stabilized. The remaining sample aliquot was immediately frozen in DI water soaked low-density polyethylene bottles, transported back to the laboratory frozen and kept in a -30°C freezer until subsequent analyses were performed.

Samples were analyzed for a number of ionic species by ion-chromatography (IC). Sulfate, nitrate, chloride and oxalate were first determined with a carbonate/bicarbonate eluent using a Dionex HPIC-AS4A column.

Determination of the major cations sodium, calcium, potassium, and magnesium was accomplished by flame atomic absorption spectroscopy on a Perkin Elmer 2280 AA Spectrophotometer with an air/acetylene flame. Ammonium concentrations were determined using the colorimetric method of Solorzano (1969).

A second IC analysis was conducted if the remaining sample volume was sufficient. Carboxylic acids - formic, acetic, glycolic, and lactic acid - and fluoride were analyzed using a weak borate eluent with a Dionex HPIC AS-4 analytical column. We must consider the values reported for lactic acid to be semi-quantitative as it was not possible to effect complete separation of lactic acid using this technique.

RESULTS AND DISCUSSION

A total of 369 cloud water and mixed precipitation samples were collected during the summers of 1987, 88 and 89. A summary of the sampling periods, number of samples by type, and specific chemical analysis conducted is found in Table 1 for each of the sampling seasons. One snow and six rain samples were also collected at the Observatory during the summer of 1987. As was mentioned above, at the high wind speeds typically encountered at the summit both rain and cloud droplets are collected by the MIFS during periods when rain and clouds are present. Samples collected under these conditions were classified as "cloud + rain".

The mean acidity and chemical composition of the 266 cloud water samples collected during three summers of work on Mount Washington is summarized in Table 2. A similar summary of the 96 mixed cloud water + rain samples is found in Table 3. Chemical concentrations in cloud water collected during the summer of 1988 appear to be substantially greater than those observed in either 1987 or 1989. However for the cloud + rain samples concentrations in 1989 are greater than those of the preceding two summers. A rigorous comparison of mean concentrations observed during the three sampling seasons should not be attempted as sampling was conducted during different periods of the year and it was not possible to sample every cloud water event during these three summer periods.

A comparison of the chemistry of cloud water and cloud + rain samples can be made however and this shows without exception that all chemical species and acidity are much higher in cloud water than in cloud water + rain. Species concentrations measured in cloud water samples were on average 4-5 times those observed in cloud + rain samples collected from the same clouds. This phenomena wherein cloud water is found to be much more acidic and exhibit higher ionic concentrations than that of rain falling from the same clouds has been reported by other researchers as well (Falconer and Falconer, 1980). The reduced acidity and ionic content of cloud + rain versus cloud water is believed to be the result of dilution processes within the cloud as cloud water droplets grow and

Table 1. Summary of cloud water/precipitation sampling and chemical analysis.

Year	Sampling Period	Cloud	Cloud + rain	pH	Anions	OA	Cations
1987	8/17-10/8	108	19	X	X	X	X
1988	6/21-8/25	79	56	X	X	X	X
1989	5/31-6/29	79	21	X	X		

OA= organic acids - formic, acetic, lactic, glycolic, and oxalic acid.

Anions= sulfate, nitrate, chloride, fluoride.

Cations= ammonium, sodium, potassium, calcium, magnesium.

Table 2. Summary of Mount Washington Cloud Chemistry.

Species	1987	1988	1989	All samples
pH	4.41±0.50	3.99±0.68	4.51±0.83	4.31±0.69
SO ₄	6.74±10.8	20.0±22.2	6.18±3.74	10.5±15.3
NO ₃	4.45±7.48	13.7±14.6	3.37±1.74	6.84±10.3
NH ₄	0.95±1.32	3.32±2.47	-	1.85±2.17
Cl	0.87±1.64	1.64±1.91	0.24±0.30	0.91±1.57
F	0.052±0.10	0.076±0.12	-	0.063±0.11
Fo	1.03±1.17	3.13±1.80	-	1.91±1.79
Ac	0.50±0.48	1.83±1.07	-	1.07±1.03
La	0.12±0.23	2.39±3.04	-	1.10±2.29
Gl	0.21±0.31	1.40±1.27	-	0.76±1.07
Ox	-	0.68±0.59	0.25±0.13	0.47±0.48
Na	0.68±1.02	0.93±1.14	-	0.77±1.07
K	0.58±1.09	0.95±1.67	-	0.72±1.34
Ca	0.78±1.15	2.00±1.80	-	1.24±1.54
Mg	0.096±0.15	0.20±0.19	-	0.14±0.17

Concentration units are parts per million (ppm), with the exception of pH

Values are arithmetic mean and standard deviation

Fo= formic acid, Ac= acetic acid, Gl= glycolic acid, Ox= oxalic acid,

La= lactic acid (values should be considered semi-quantitative)

Table 3. Summary of Mount Washington Cloud + Rain Chemistry

Species	1987	1988	1989	All samples
pH	4.84±0.32	4.65±0.63	4.13±0.47	4.58±0.59
SO ₄	0.92±1.20	2.86±4.85	5.76±4.33	3.11±4.51
NO ₃	0.65±0.78	1.43±2.75	2.05±1.53	1.41±2.28
NH ₄	0.13±0.19	0.32±0.46	-	0.27±0.42
Cl	0.12±0.20	0.21±0.46	0.16±0.08	0.18±0.36
F	0.010±0.017	0.019±0.033	-	0.016±0.029
Fo	0.33±0.20	1.26±0.85	-	0.89±0.81
Ac	0.17±0.094	0.68±0.45	-	0.48±0.44
La	0.018±0.035	0.62±1.19	-	0.38±0.96
Gl	0.046±0.021	0.34±0.43	-	0.23±0.37
Ox	-	0.19±0.20	0.22±0.16	0.20±0.18
Na	0.080±0.14	0.24±0.79	-	0.20±0.69
K	0.086±0.15	0.11±0.30	-	0.10±0.26
Ca	0.052±0.15	0.10±0.23	-	0.091±0.21
Mg	0.012±0.017	0.026±0.052	-	0.022±0.046

Concentration units are parts per million, with the exception of pH.

Values are arithmetic mean and standard deviation.

Fo= formic acid, Ac= acetic acid, Gl= glycolic acid, Ox= oxalic acid,

La= lactic acid (values should be considered semi-quantitative)

subsequently fall as rain. One would reasonably expect that the acidity and ionic content of rain only samples would be lower still than the cloud + rain samples. This was indeed the case for five rain samples collected in September, 1987 during a period when cloud and cloud + rain samples were also collected. An example of this phenomena is presented in Figure 1. It should be noted that in this and all subsequent figures the time plotted is the mid-point of the sampling interval. Cloud water pH, sulfate, nitrate, and SO_4/NO_3 ratio are plotted versus time for an eight hour period on June 23, 1988. Shortly after sampling was initiated rain began to fall and continued for two hours and thus during this period the MIFS collector sampled cloud and rain. While it was raining, sample acidity decreased by a factor of six while sulfate and nitrate levels dropped by a factor of eleven. Conversely, the sample collected at the time rain ceased exhibits increased acidity, sulfate and nitrate levels and concentrations continued to increase subsequently. Thus it is evident that the input of chemical species at high elevation sites due to cloud water deposition is substantially enhanced in relation to the hydrological input.

It is also interesting to note the the SO_4/NO_3 ratio did not change substantially until late in the rain period, when it decreased from 3.5-4.5 to less than one. This may reflect a change in air mass and source region for the acidic cloud water species. In fact there were indications of a frontal passage during this period. Between nine and noon the temperature at the summit dropped 9°F . The passage of this cold front signalled a change in air mass. Sulfate was the major acidic species in clouds preceding the front while nitrate was dominant after frontal passage.

The frequency distribution of cloud water pH measured at Mount Washington during the three summers of sampling is shown in Figure 2. The distribution is essentially Gaussian with a mean cloud water pH of 4.3. Cloud water pHs varied over a wide range from very acidic levels of 2.74 to near neutral pH values of 6.36.

The sample exhibiting the highest acidity, a pH of 2.74, was collected August 5, 1988 from 2030 to 2134 LST. At the time it was extremely hazy at the summit and horizontal visibility was reduced to approximately 4 miles. Winds were from the WSW at about 25 ms^{-1} , RH was 98.7%, the temperature was 56.5°F and convective cumulus clouds were observed in all directions about the summit. Cloud water sampling

Cloud Chemistry

June 23, 1988

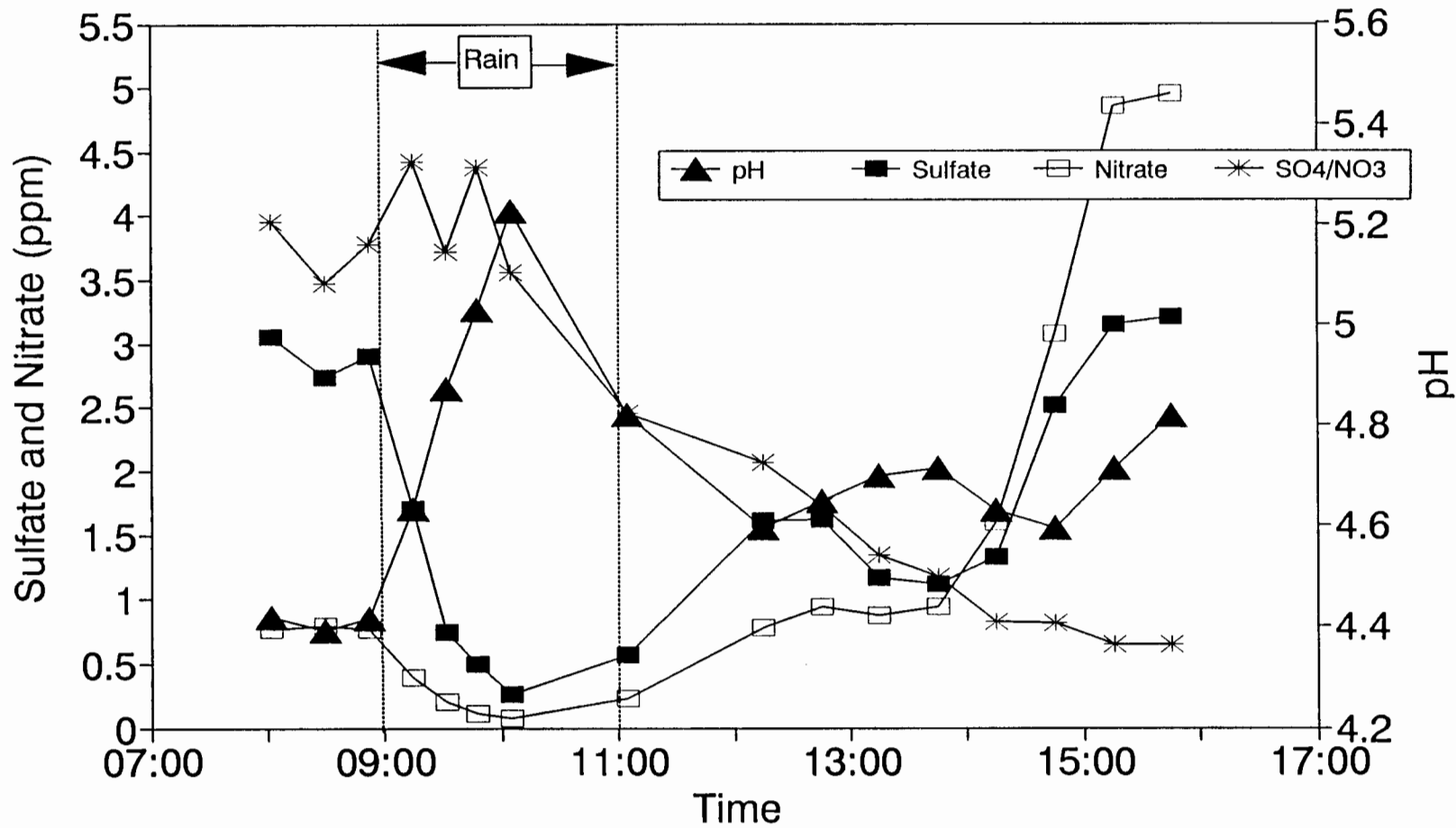
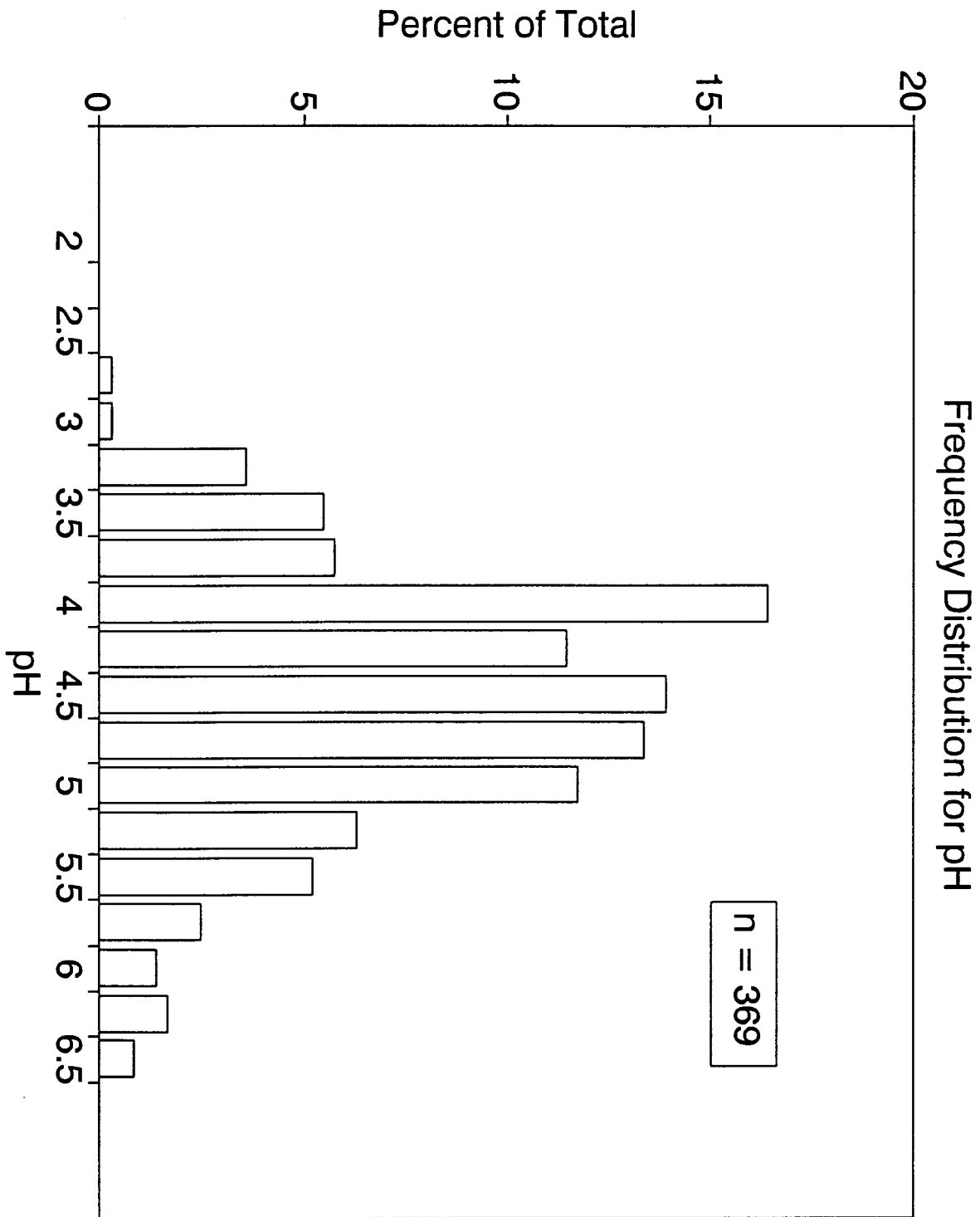


Figure 1.

Figure 2



continued at an hourly interval throughout the night until 1030 the next morning when clouds lifted from the summit. The sulfate and nitrate concentrations and pH observed in these 14 samples are shown in Figure 3. Cloud water acidity which was extremely high at the onset of cloud decreased substantially with time but pH levels remained in the range of 3 to 3.5 over the entire thirteen hour sampling period. As the acidity decreased over the period the sulfate/nitrate ratio also decreased substantially falling from an initial value >2.5 to a point where sulfate and nitrate concentrations were roughly equal. In this particular instance cloud water acidity decreased markedly with time and by the time the cloud lifted from the summit the pH of cloud water being deposited was in the range of 3.4-3.5.

We have also observed cases where the reverse was true. An example is presented in Figure 4. Here cloud chemistry data are plotted for a six hour period on August 12, 1988, several days after the preceding event. In this case cloud water acidity and sulfate and nitrate concentrations are initially relatively low but increase substantially during the cloud event. This increase in acidity and ionic content which we observed appears to be the result of a decrease in the liquid water content (LWC - gm H₂O per m³ of air) or a drying out of the cloud with time. The sampling duration for each of these thirteen samples was thirty minutes. During the first two sampling intervals 100 and 55 ml respectively were collected while by the third thirty minute sampling period only 40 ml was collected. The remaining sample volumes were in the range of 20-35 ml while during the last sampling interval only 15 ml was collected before cloud at the summit dissipated completely. Thus it appears that the cloud was becoming progressively drier, that is the LWC was decreasing, and ionic species in the cloud were being concentrated. In this instance the sulfate to nitrate ratio did not change substantially (0.95 - 1.7) over the six hour period. The two instances cited above illustrate that changes in cloud water acidity and ionic content can be driven by a number of different mechanisms.

It should be noted that the acidity and ionic concentration of cloud water deposited at the time when a cloud deposition event ends may be of significance in assessing the potential impact of this deposition on vegetation. In the case of the August 12, 1988 event the vegetation was

Cloud Chemistry August 5-6, 1988

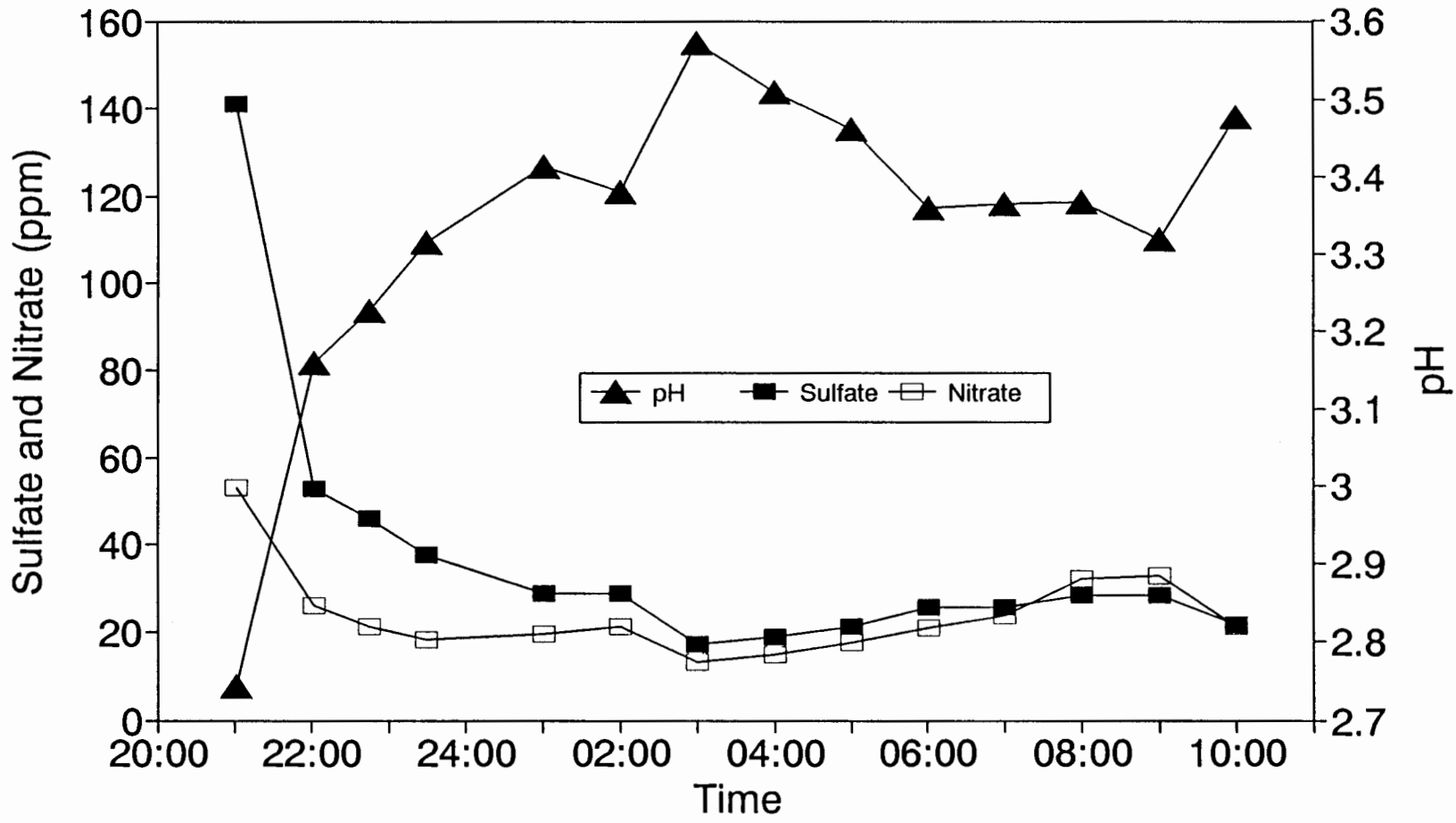


Figure 3

Cloud Chemistry

August 12, 1988

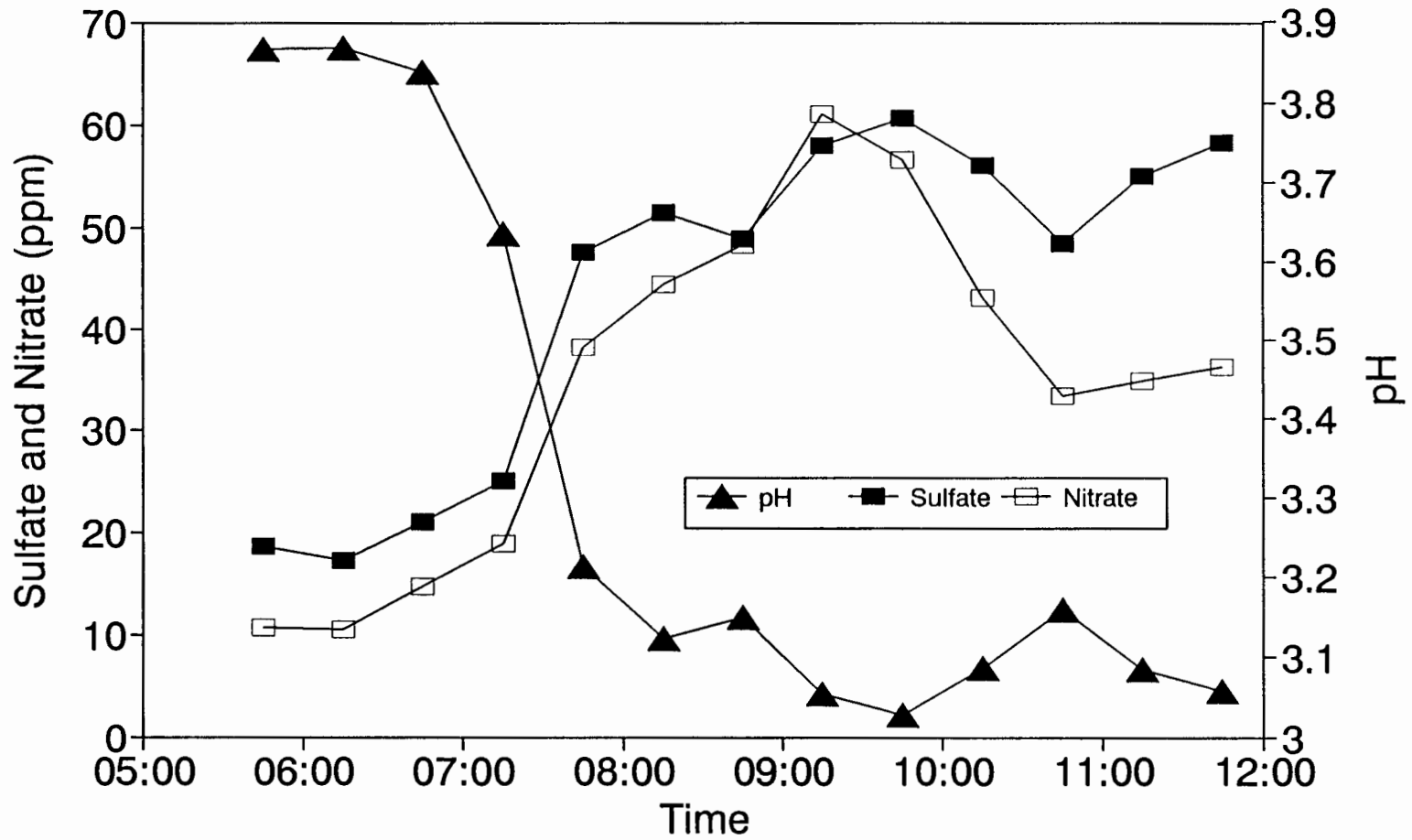


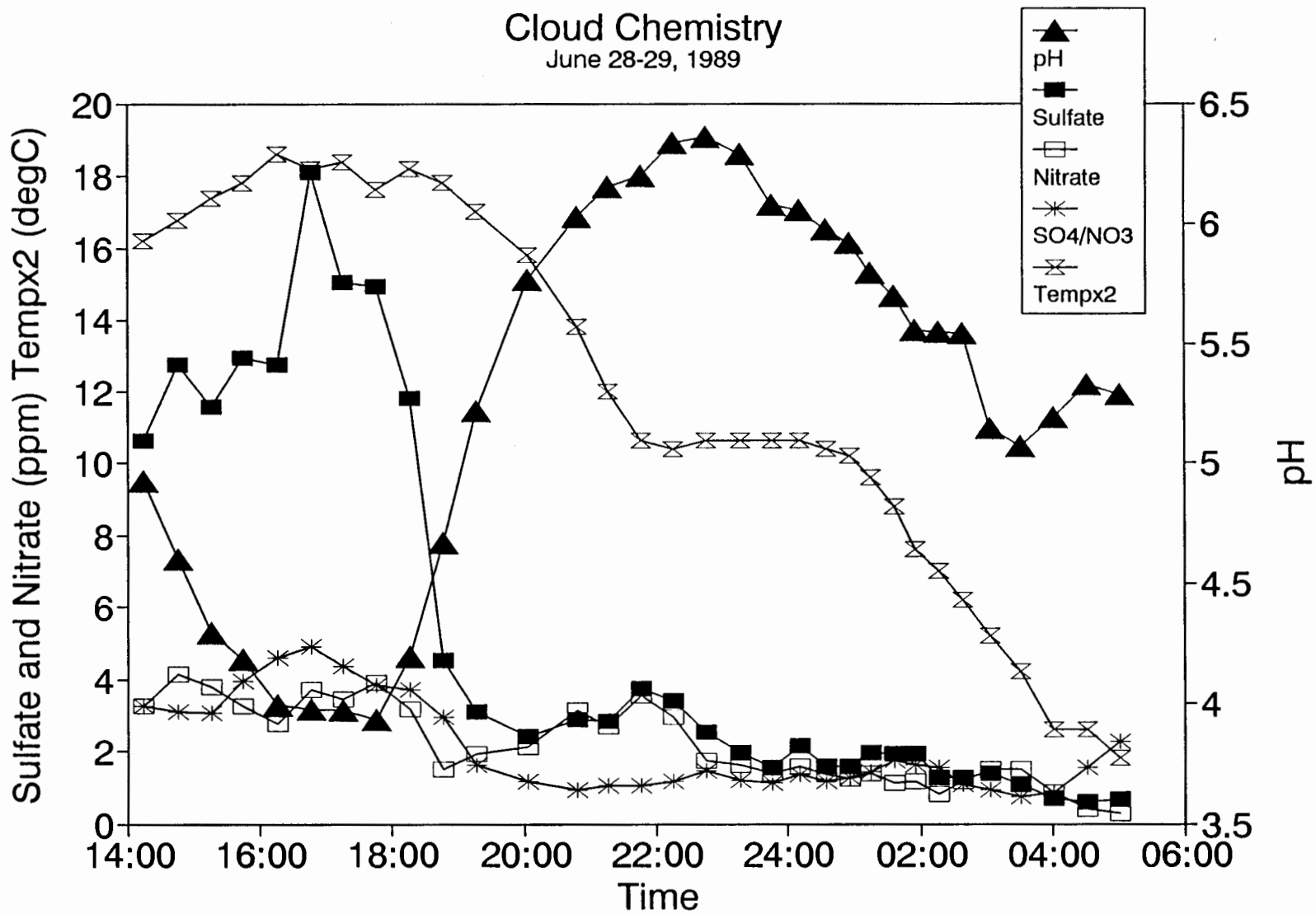
Figure 4

exposed in the final stages to wet deposition with a pH of 3.06 whereas the final pH for the August 5-6, 1998 event was 3.48. This difference in pH represents a factor of 2.6 change in the acidity of the deposited liquid.

As is evident from the pH frequency distribution plot in Figure 2, cloud water pHs below three were observed very infrequently. In fact samples exhibiting this level of acidity were collected only once in 1987 and once during the summer of 1988. Obviously, not all cloud water events during the three summers were sampled but we believe that these rather rare extremely acidic cloud water deposition events do not represent a substantial chemical or hydrological input to the region. However, the importance of these sporadic events to the health of the vegetation in this region is still an important consideration which this study did not address.

In a number of instances cloud water acidity levels were observed to be extremely low. In fact pH levels as high as 6.36 were measured. Typically high pH, low acidity cloud water samples were collected during periods when orographic clouds were present at the summit. Orographic clouds form when air sweeps up the mountain slope and in the process cools sufficiently to result in condensation and cloud formation. Thus the resultant clouds reach the summit and are sampled seconds to tens of seconds after formation. In this case the only appreciable source of ionic species and acidity will be constituents which rapidly solubilize from the condensation nuclei upon which the cloud droplets form. Incorporation of gaseous acidic species such as sulfur dioxide (SO_2) and NO_x will not take place to an appreciable degree in such a short time period. In circumstances such as this soluble alkaline species such as Ca^{+2} may actually raise cloud water pH levels above the value of 5.2 one would expect for pure water in equilibrium with typical atmospheric CO_2 levels. In Figure 5 cloud chemistry data from a fifteen hour period on June 28-29, 1989 illustrate a case of very low acidity cloud deposition. In this instance we believe that there were two primary mechanisms driving changes in cloud chemistry - the passage of a cold front and a change in the type of clouds sampled. For approximately the first four hours of sampling acidity continuously increased along with sulfate levels as the nitrate concentration and temperature remained relatively constant. There was a short ten minute period of rain at 1900 hours while at approximately the same time sulfate concentrations dropped precipitously and temperature also began to

Figure 5



decrease. We believe that this marked the passage of a cold front. This is supported by a report received at 2000 hours from the base of the mountain indicating that while the summit was continuously in cloud, the cloud ceiling surrounding the summit was broken and the humidity had decreased markedly. By 2130 hours the temperature at the summit had stabilized at roughly 5.3°C and cloud water pH had increased to 6.1 - 6.4. It is probable that the clouds sampled during this time period were orographic in nature and formed as relatively clean, cool and unstable air behind the cold front swept up the mountain face.

Cloud water sampling intervals were typically thirty minutes in duration whenever a sample volume sufficient for chemical analysis (≥ 25 ml) could be collected in this time period. In an effort to evaluate the magnitude of changes in chemistry which take place on shorter time scales we decreased the sampling interval to five minutes during a one hour period on September 30, 1987. These data are presented in Figure 6. The collector was deployed one half hour before sample collection began and approximately one hundred and twenty milliliters of liquid passed through the collector prior to actual sample collection. This should have ensured that the collector and screen were thoroughly flushed. It should also be noted that it was raining during this one hour sampling period. Typical collection rates under cloud only conditions would not have allowed us to collect sufficient volume at such short time intervals. Five minute sample volumes during this time period were approximately 30 ml. It is evident that wet deposition chemistry can change substantially over short time periods. Acidity, sulfate and nitrate concentrations were seen to increase by 37-46% in the five minute period from 1110 to 1115.

The major acidic species in all cloud water and cloud + rain samples were sulfate and nitrate. The organic acids - lactic, acetic, formic, glycolic and oxalic, typically contributed from 10 to 30% of the acidity in cloud and cloud + rain samples. Ammonium is the major base in these cloud water systems and a plot of sulfate plus nitrate versus ammonium concentration (Figure 8.) exhibits a strong correlation between the two major acidic species and ammonium ion concentrations.

As we have seen above, cloud water sulfate to nitrate ratios changed markedly over relatively short time periods. This may be the result of changes in air mass origins associated with frontal passage at the sampling

Cloud Chemistry

September 30, 1987

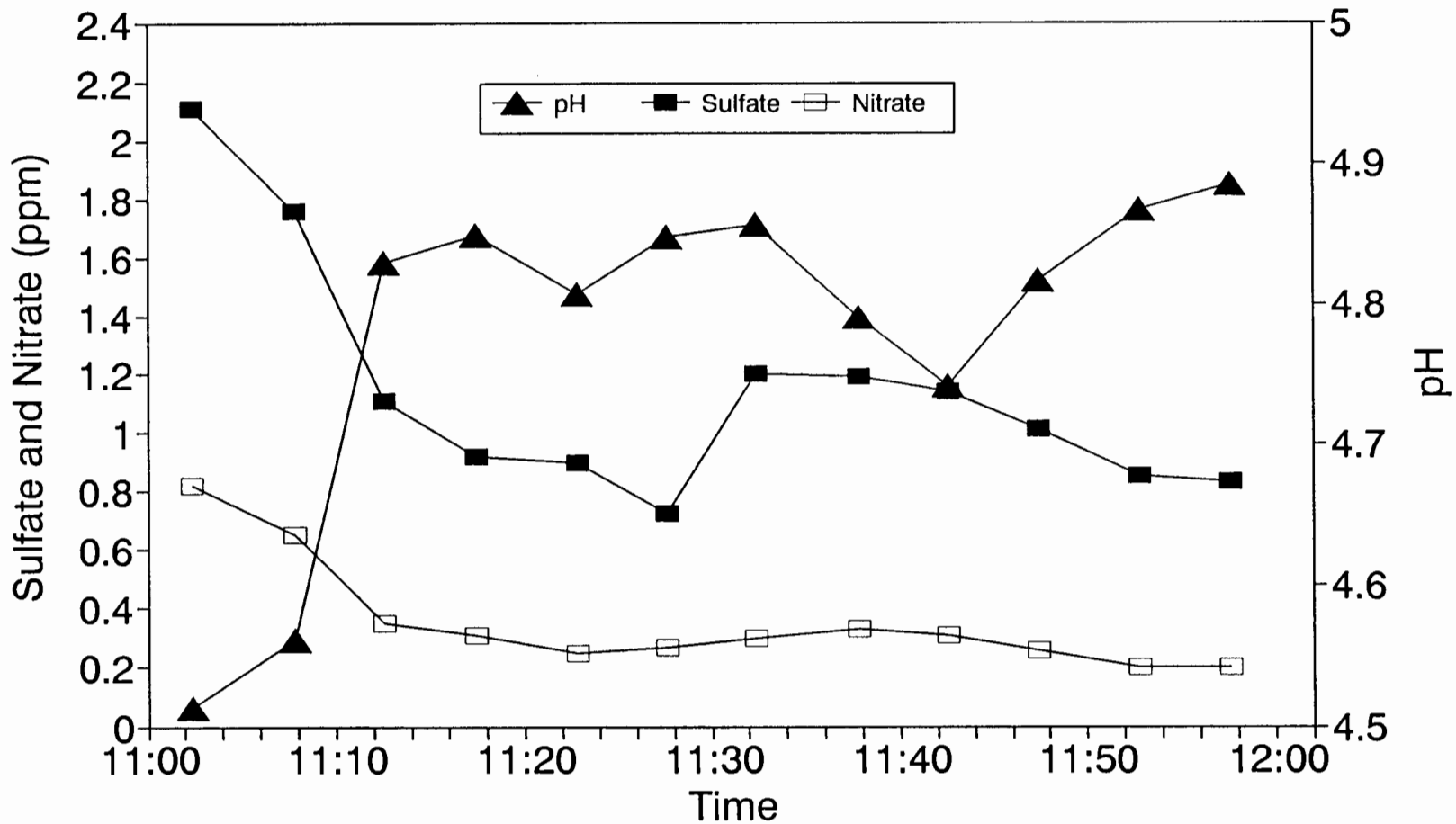
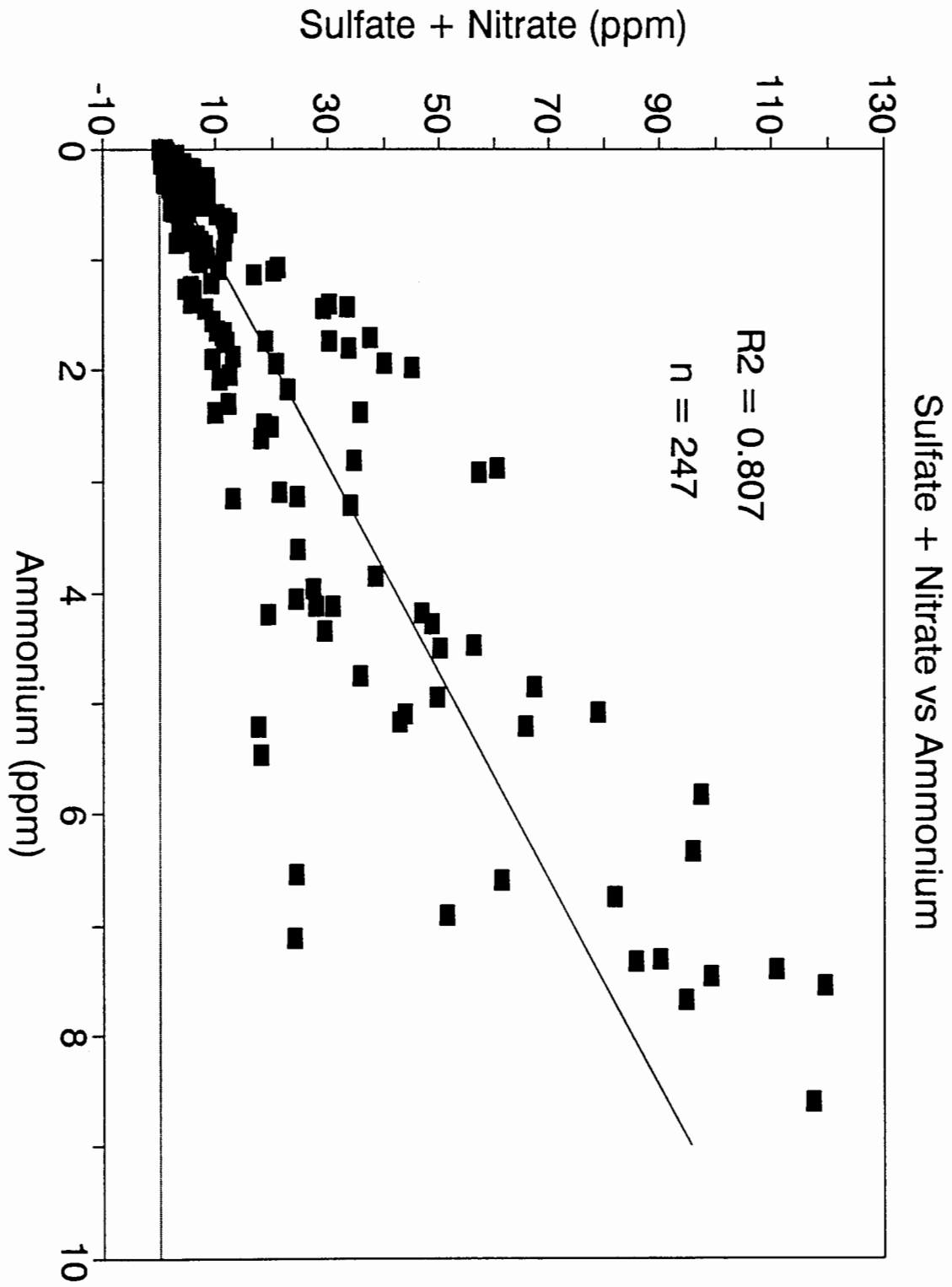


Figure 6

Figure 7



site. The SO_4/NO_3 frequency distribution is shown in Figure 8. The distribution is bimodal with peaks at ratios of 1.5 and 3.0. It is interesting to speculate on the origin of air masses which produce clouds of such different SO_4/NO_3 ratios. One might expect that cloud formed in an air mass originating in the mid-west and Ohio River valley region of the U.S. would exhibit a relatively high SO_4/NO_3 as this is a region where coal (a source of SO_2 and subsequently SO_4^{2-}) is burned. Conversely clouds having a lower SO_4/NO_3 may form in air masses originating along the northeast corridor (Washington to Boston). In this areas there is substantially more automobile traffic (a NO_x and thus NO_3^- source) where oil (with substantially lower SO_2 emissions than coal) is the major fuel utilized for power generation. It is also interesting to note that the low SO_4/NO_3 occurs more frequently than the higher ratio. While the data we have collected during these three summers are certainly not sufficient to definitively answer questions as to the origin of cloud water acidity on Mount Washington, they do suggest that cloud water chemistry combined with meteorological information such as air mass trajectories may provide answers to questions such as this.

In Table 4 a correlation matrix for chemical species found in cloud water and cloud water + rain samples at Mount Washington during the three summers of sampling is presented. Once again it is evident that the acidity of these samples is determined in large measure by sulfate, nitrate, and ammonium concentrations. Chloride ion shows a strong correlation with sodium. This is somewhat surprising as almost all sampling was conducted under westerly wind flow. While the Mt Washington site is approximately 90 miles west of the Gulf of Maine, the prevailing wind pattern would seem to limit the influence of oceanic aerosols on cloud condensation nuclei. The average Na/Cl ratios for the summers of 1987 and 1988 were 0.78 and 0.57 respectively, while the seawater ratio is 0.85. Of course air masses moving up along the Atlantic seaboard into the study area would be influenced by marine aerosols to a greater degree.

The strong correlation observed for fluoride with lactic acid may be an artifact of the analytical procedure as it was not possible to affect complete separation of these two species under any chromatographic conditions which were employed. In general the organic acids were well correlated amongst themselves. They also correlated to varying degrees

Figure 8

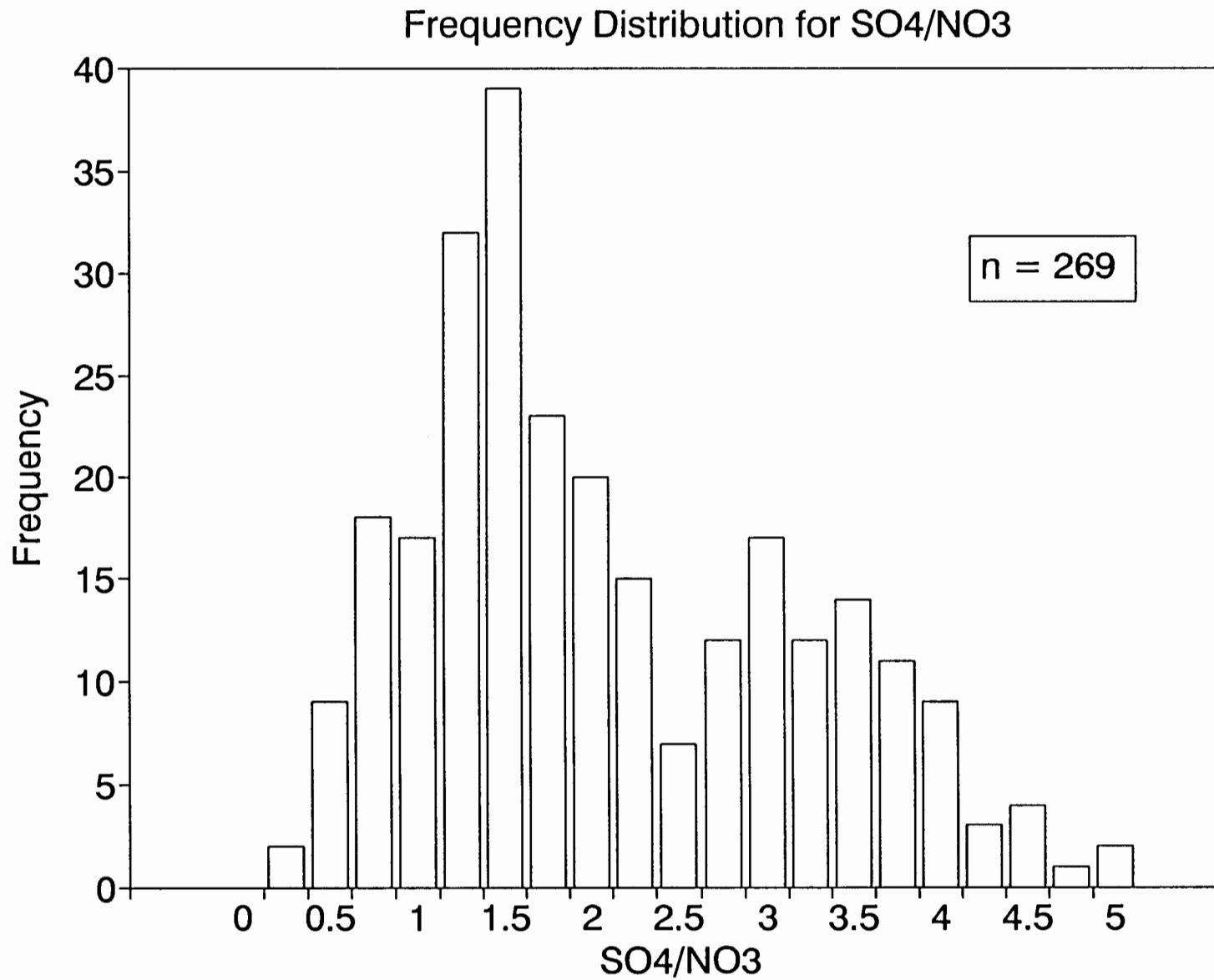


Table 4. Cloud Chemistry Correlation Matrix

	pH	SO4	NO3	NH4	Cl	F	Fo	Ac	La	Gl	Ox	Na	K	Ca	Mg
pH	1														
SO4	.98	1													
NO3	.94	.95	1												
NH4	.79	.88	.88	1											
Cl	.39	.51	.48	.72	1										
F	.10	.26	.23	.54	.89	1									
Fo	.61	.67	.61	.79	.68	.45	1								
Ac	.56	.65	.60	.84	.83	.63	.96	1							
La	.01	.17	.13	.48	.87	.98	.41	.61	1						
Gl	.63	.66	.58	.70	.61	.32	.96	.90	.29	1					
Ox	.75	.79	.67	.75	.62	.37	.90	.85	.31	.92	1				
Na	.22	.34	.24	.53	.90	.81	.73	.82	.80	.71	.69	1			
K	-.07	.09	.07	.41	.87	.94	.35	.56	.96	.24	.25	.78	1		
Ca	.71	.80	.87	.90	.61	.50	.60	.66	.43	.49	.58	.39	.35	1	
Mg	.43	.54	.47	.69	.81	.65	.86	.89	.61	.83	.83	.89	.58	.58	1

with sample acidity. Acetic and formic acids are known to have both natural (vegetative) and pollution derived sources (Keene, W.C. and J.N. Galloway, 1986). The cations sodium, calcium, potassium and magnesium exhibit strong to moderate correlations with chloride and fluoride and calcium and ammonium are highly correlated.

The cloud water deposition study conducted in a krummholz community on the west slope of Mount Washington (Farrell, 1989) revealed that interception loss for wet deposition at this site was roughly 45%. That is only about 55% of the deposited cloud water and/or rain incident on the canopy actually reached the ground. The remainder being either re-evaporated or absorbed directly by the vegetation. Net cloud water input was found to be 43% of total wet deposition during the study period. Thus it is easy to see that net chemical input as a result of cloud water deposition may be as important a source of nutrients and acidity as rain.

CONCLUSIONS

The mean pH of cloud water samples collected during three summers at the summit of Mount Washington, NH was 4.31. The acidity level in samples of cloud + rain was roughly a factor of two lower. In virtually all cases ionic content and acidity was substantially lower in cloud water samples containing rain samples. Cloud water pH levels ranged from 2.76 to 6.36. Very acidic cloud water was observed under stagnant meteorological conditions when high levels of gaseous and particulate pollutants were present. Under these conditions deposition of very acidic cloud water (pH 3 - 3.5) was observed at this high elevation site for periods as long as twelve hours. Conversely, orographic cloud formation resulted in clouds of very low acidity and ionic content. Changes in cloud water acidity are driven by a number of different mechanisms such as frontal passages and associated changes in air mass and variations in cloud liquid water content. These changes can be significant over time scales as short as five minutes.

Net cloud water deposition during the summer of 1988 was found to represent 43% of total wet deposition along the west face of Mount Washington. Cloud water deposition thus obviously represents a very significant if not dominant source of chemical input to this high elevation regime.

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