Final Report of the Research Project:

# "A SURVEY OF ACID PRECIPITATION IN NORTHERN CALIFORNIA."

Principal Investigator:

Dr. John G. McColl

Associate Professor
Department of Soils and Plant Nutrition,
University of California,
Berkeley, CA 94720.

Sponsored by:

California Air Resources Board
Contract A7-149-30

and

Agricultural Experiment Station
University of California, Berkeley
Project CA-B-SPN-3664-H

February 19, 1980

# CONTENTS

# ABSTRACT

The acidity of rain has been increasing in the N.E.-U.S.A. and elsewhere (e.g., Scandinavia) and is having adverse ecological effects. Relatively little is known about the chemical composition and acidity of atmospheric precipitation and subsequent effects in the western U.S.A., and thus this study was conducted to monitor the chemical characteristics of atmospheric precipitation in California. Wet and dry precipitation were monitored on an event basis at the following eight locations during the wet season, November 1978 through May 1979; Berkeley and San Jose (pollution source areas in the San Francisco Bay area), Davis and Parlier (in the central valley, agricultural areas), Hopland and Napa (coastal ranges, agricultural and rangelands), Challenge (lower Sierran forest), and Tahoe City (on the shore of Lake Tahoe). Acid rain ($pH < 5.6$) was common at all eight sites. Mean pH of storms varied from 4.42 at San Jose to 5.20 at Davis, and the lowest pH of any storm was 3.71 at San Jose. The primary cause of the acidity was probably the air pollutants $NO_x$ and $SO_x$, following their dissolution in wet precipitation. $NO_3^-$ was the anion most closely correlated with $H^+$, and nitrogen generally occurred in greater amounts than sulfur. Appreciable quantities of dry deposition were also measured, but more research is needed in procedures for quantifying dry atmospheric deposition. Although $NO_3^-$ concentration ($\mu g/l$) and acidity ($H^+$ concentration, $\mu g/l$) of wet precipitation were greatest in pollution source areas, total deposition (kg/ha) of $NO_3^-$ and $H^+$ were greatest in the non-urban receptor areas of Napa and Challenge; this was largely a function of the greater precipitation volumes at these two sites. Thus ecological effects may be expected in the coast ranges, Napa valley and Sierras within the general west-to-east "wash-out fan" of wet precipitation, as well as within pollution-

source areas. The concentrations of both $Cl^-$ or $Na^+$ in wet precipitation were found to be highly predictable functions of distance from the ocean, and provided useful tools to predict the contribution of oceanic salts at sites up to 280 km inland. Continued monitoring of atmospheric deposition in the western states should be made through interagency cooperation. Research efforts should also be encouraged to elucidate effects of "acid rain" on soil, water and plant resources, as the problem appears to be widespread and is likely to increase in severity.

## ACKNOWLEDGEMENTS

This study involved the coordination and cooperation of many people, many of whom donated their time and skills. I wish to thank Dr. Larry Monette (Post-doctoral Research Associate in my laboratory, U.C. Berkeley), who acted as Coordinator of the project. Very special thanks are due to the field operators (mentioned by name in Table 1, and Appendix 11.1), who diligently collected the field samples at the eight sites. Dr. Monette and my laboratory assistants also conducted the chemical analyses. Thanks are also due to Dr. Robert Leonard (of the Tahoe Research Group, U.C. Davis), who did some of the sulfur and all of the nitrogen analyses. Mr. Douglas Bush (a graduate student in my laboratory) helped in many ways, but particularly with statistical analyses and computations. Financial support was provided by the California Air Resources Board (A.R.B.), Contract # A7-149-30, and the Agricultural Experiment Station of the University of California, Berkeley. The work was performed at the University under Project # CA-B -SPN-3664-H.

# DISCLAIMER

# 1. OBJECTIVES

1. To determine whether California has an "acid rain" problem, by monitoring and characterizing both wet and dry atmospheric precipitation during the wet season of 1978-79, in air-pollution source areas and non-urban receptor areas where environmental effects may be most critical.
2. To determine which anion is most closely associated with the hydrogen ion, and thus indicate which air pollutant(s) are the most probable cause(s) of the acidity.
3. To determine correlations between chemical characteristics of atmospheric precipitation within and between sampling sites, and possible relationships with prevailing meteorological conditions, which may suggest the nature and geographical extent of the potential "acid rain" problems.

## 2. CONCLUSIONS

1. Acid precipitation commonly occurs and is widely distributed in northern California. Mean pH of storms in 1978-79 at the eight sampling sites varied from 4.42 at San Jose to 5.20 at Davis, and the lowest pH of any storm was 3.71 at San Jose. Thus rain was often about 10-100 times more acid than unpolluted rain, which has a theoretical pH of 5.6.
2. On a chemical-equivalent basis, more nitrate is present in wet precipitation than is sulfate. Nitrate is also the anion most closely correlated with the hydrogen ion at six of the eight sampling sites, thus air pollution by $NO_x$, forming nitric acid ($HNO_3$), is presumed to be the primary cause of the acidity of rain; $SO_2$, forming sulfuric acid ($H_2SO_4$), appears to be the secondary cause at the present time.

. Total dry depositions of chemical constituents between storms is less than, but of the same order as, total wet deposition during storms. Dry deposition during summer would greatly increase the dry deposition values recorded in this study which was conducted in the wet season.

4. Total deposition of ionic constituents of precipitation is a function of both ionic concentration, and total volume of rain or amount of dry material. Total wet depositions of both nitrate and hydrogen ions were greatest at the Challenge and Napa sites. As these sites are some distance from the San Francisco Bay area, it is concluded that acid rain is widely distributed from pollution source-areas to non-urban, receptor-areas. Thus ecological effects may be expected in the coast ranges and Sierras within the general west-to-east "wash-out fan" of wet precipitation as well as within the source area where total depositions are lower but concentrations are higher due to lower rainfall.

5. Coastal sites receive large amounts of oceanic salts. The highly significant correlations between concentrations of either sodium or chloride in wet precipitation with distance from the ocean, provide useful tools to predict the contribution of oceanic salts at sites up to 280 km inland.

## 3. RECOMMENDATIONS

1. Monitoring of both wet and dry atmospheric deposition should be continued in California with objectives similar to those of air-pollution monitoring schemes. A carefully designed network would give the most informative data, and monitoring on an event basis would permit the most legitimate predictions to be made of possible ecological effects. This continued monitoring task would be best undertaken by an agency or inter-agency organization. Integration with a national U.S. network of precipitation monitoring would also be advisable. An interagency symposium on the subject of "acid rain" is needed immediately, for educational and coordination purposes.
2. Close attention should be given to total deposition values (especially of $H^+$) as well as concentration values, to anticipate and/or interpret different types of ecological effects, e.g., plant or fish sensitivity to acidity may largely be determined by a "threshold pH", whereas accelerated soil leaching and rock weathering are more likely to be determined by increases in the total deposition of acidic material.
3. Although nitrate is the anion most closely correlated to acidity, sulfate in both wet and dry precipitation should also be given close attention from now on, particularly as sulfur pollution is the primary cause of major "acid rain" problems elsewhere (e.g. N.E.-U.S.A.), and because increased sulfur pollution is anticipated from recently proposed, coal-burning power plants to be built in California, and from tertiary oil-recovery activities.
4. More research is needed on the collection procedures and data interpretation of dry fallout, as this type of atmospheric deposition may be even more important in many areas of California than is wet deposition.

## 4. LIST OF TABLES

## 5. LIST OF FIGURES

## 6. KEY TO SYMBOLS AND ABBREVIATIONS

Study Sites:

| | |
|---|---|
| BE | Berkeley |
| TC | Tahoe City |
| KE | Kearney |
| CH | Challenge |
| SJ | San Jose |
| HO | Hopland |
| NA | Napa |
| DA | Davis |

Units of measurement:

| | |
|---|---|
| μeq | micro-equivalent |
| ml | milliliter |
| l | liter |
| cm | centimeter |
| m | meter |
| km | kilometer |
| g | gram |
| kg | kilogram |
| μmho | micromhos |

Chemical Symbols:

| | |
|---|---|
| H | hydrogen |
| C | carbon |
| O | oxygen |
| Na | sodium |
| K | potassium |
| Ca | calcium |
| Mg | magnesium |
| Fe | iron |
| Mn | manganese |
| Cu | copper |
| Zn | zinc |
| S | sulfur |

| | |
|---|---|
| N | nitrogen |
| Cl | chloride |
| $CO_2$ | carbon dioxide |
| $HCO_3$ | bicarbonate |
| $NH_4$ | ammonium |
| $NO_3$ | nitrate |
| $SO_4$ | sulfate |
| $HNO_3$ | nitric acid |
| $H_2SO_4$ | sulfuric acid |
| HCl | hydrochloric acid |
| $H_2CO_3$ | carbonic acid |

Superscripts (e.g. $Mg^{2+}$) indicate ion charge and valence.
Square brackets (e.g. $[Mg^{2+}]$) indicate ion concentration.
pH, a measure of acidity = $-\log [H^+]$.
$pH_{[LAB]}$, pH measured in the laboratory.
$pH_{[FIELD]}$, pH measured in the field.

Statistical symbols:

| | |
|---|---|
| n | sample number |
| r | simple correlation coefficient |
| $r^2$ | coefficient of determination |
| $\overline{X}$ | mean |
| S.E. | standard error of mean |
| $\alpha$ | alpha value, or probability level |
| * | 5% probability level |
| ** | 1% probability level |
| *** | 0.1% probability level |
| $\Sigma$ | sum |

## 7. INTRODUCTION

The purpose of this study was to monitor the main inorganic constituents of wet and dry atmospheric deposition in northern California, and to determine whether California has a potential "acid rain" problem. It is important, therefore, to understand what acid rain is, how it is formed, and what problems might arise if acid rain occurs. This introduction also documents the known reports and data that are relevant to California in particular, and outlines the general "acid rain" problem elsewhere.

Acidity of a solution can be described by its pH value. The pH scale ranges from 0 to 14, and pH 7 is usually considered to be neutral; above pH 7 a solution is alkaline (or basic), and below pH 7 a solution is acid. Because the pH scale is logarithmic, pH 4 is ten times more acid than pH 5, and one-hundred times more acid than pH 6, etc. However, rain is not pure water, but contains various dissolved salts and other substances. Rain in its normal, unpolluted state is slightly acid, with pH 5.6, this being due to carbonic acid ($H_2CO_3$) which is a product of the dissolution of atmospheric carbon dioxide ($CO_2$). Thus, "acid rain" is defined as rain with a pH less than 5.6.

The oxides of sulfur and nitrogen ($SO_x$ and $NO_x$) are oxidized in the atmosphere and form sulfuric and nitric acids ($H_2SO_4$ and $HNO_3$), which contribute to the acidity of rain. Chlorine emissions may also result in acidity (by hydrochloric acid, HCl), but usually only close to emission sources, whereas sulfur compounds (and maybe those of nitrogen too) can be transported several hundred kilometers per day in the atmosphere.

Sulfur oxides are primarily emitted from stationary sources such as utility and industrial coal-burning boilers. Nitrogen oxides are emitted from both stationary and mobile sources, especially automobiles. Recent data of the U.S. Environmental Protection Agency (E.P.A., 1979) show that about 56% of $NO_x$ emitted in 1977 was caused from the burning of fossil fuels by stationary sources, while 40% came from transportation-related sources. Emissions of $NO_x$ from stationary sources are likely to increase rapidly in the next 20 years, as combustion of fossil fuels is expected to rapidly increase in this period also (E.P.A., 1979).

The combustion of fossil fuels in the United States results in about 50 million metric tons of $SO_x$ and $NO_x$ being emitted to the atmosphere. In 1977, $SO_x$ accounted for 14% (27.4 million metric tons) of the total air pollution while $NO_x$ accounted for 12% (23 million metric tons) (E.P.A., 1979). These huge emissions of air pollutants result in acid-rain, which is now a common phenomena in the N.E.-U.S.A. (Likens, 1976), and also in Scandanavia where it was first identified in the early 1950's (e.g., Barrett and Brodin, 1955). According to Likens (1976) and others (Cogbill and Likens, 1974; Likens et al., 1979), the acidity of rain has been increasing in the N.E.-U.S.A. and is having adverse ecological effects such as degradation of water-quality, fish productivity, and possibly forest productivity, and may also cause accelerated soil-leaching. Similar effects have been widely documented by Scandanavian workers who have taken the pioneering role in studying acid rain effects as well as monitoring acid deposition.

The monitoring of acid rain at various locations in the world, and results of some studies on its effects, were documented at the First International Symposium on Acid Precipitation and the Forest Ecosystem (Dochinger and Seliga, 1976; McCormac, 1976, 1977). The following reports are also useful, general references on the subject, and essentially represent the present "state-of-the-art": Likens (1976), Likens et al. (1979), Glass et al. (1978), Galloway and Cowling (1978), E.P.A. (1979), U.S.D.I.-U.S.G.S. (1978), N.A.D.P. (1978), E.P.R.I. (1979), Niemann et al. (1979).

In contrast to Scandinavia or the N.E.-U.S.A., there has been much less concern (or knowledge) about atmospheric deposition in the western U.S.A. One of the main reasons for this apparent lack of concern, is that there are little data available for the western area that either document the chemical characteristics of precipitation, or that document environmental degradation caused by changes in precipitation chemistry. Another reason why data for the western U.S. is not very extensive, is that emissions of the air pollutants, $SO_x$ and $NO_x$, are not as great in the west as the eastern U.S., and thus ecological effects are thought to be less. For example, in the San Francisco Bay area, a 5-year average concentration of air borne $NO_3^-$ was 2.78 $\mu g/m^3$, exceeding the national urban average of 2.40 $\mu g/m^3$, and the 5-year average for $SO_4^{2-}$ was 2.68 $\mu g/m^3$, which is only slightly above the remote non-urban background level of 2.51 $\mu g/m^3$ (Sandberg et al., 1976).

As mentioned earlier, data on the chemistry of atmospheric precipitation in the western U.S. is fragmentary, and even less data exist on the acidity of precipitation in particular. For example, various inorganic ions measured in rain in the U.S. (including the western states) were reported by Junge and Werby (1958), but no pH measurements were made. Whitehead and Feth (1964) of the U.S. Geological Survey, monitored precipitation chemistry at Menlo Park on San Francisco Bay, California, in 1957-59. The U.S. Geological Survey has subsequently reported on rain at Menlo Park for a short period in 1971 (Kennedy et al. 1976), and for a three-month period in 1971-72, at both Menlo Park and Petrolia (Kennedy et al., 1979) which is located near the California coast about 500 km north of San Francisco. At Menlo Park, they found that the pH of rain averaged 5.9 in 1957-58, 5.3 in 1978-79, and ranged from about 4.5 to 6.0 in 1971. Liljestrand and Morgan (1978) monitored rain at Pasadena, California, where the mean pH was 4.06 in 1976-77, with nitric acid being 32% more important to the acidity than was sulfuric acid; these workers extended their study to 9 locations in S-California in 1978-79 (see footnote, p. 30). Acid precipitation has also been measured at Richmond and Livermore in California by the Department of Energy (DOE, 1979).

The author and associates have measured precipitation chemistry (including pH) at Berkeley on an event basis since 1974 except during the drought of 1975-77; the average pH in 1974-75 was 5.0 (McColl and Bush 1978), 4.8 in 1977-78 (Bush 1979), and 4.7 in 1978-79 (this report, 1979), and we conclude that "acid rain" is a common phenomena in the San Francisco Bay area, and that research must be now directed toward its possible effects, especially those on the water, plant and soil resources in California (McColl 1978).

Mr. Robert Reynolds recorded acid rain at Boonville and Sacramento, California, as documented in an Air Resources Board Internal Memorandum dated July 9, 1979; the lowest pH at Boonville was 3.6, and at Sacramento was 3.5 during the two rainy seasons of 1977-78 and 1978-79. Acid rain has also been measured at Lake Tahoe and Davis in 1971 (R. Leonard, pers. comm.). At Hopland, California (at the U.C. Hopland Field Station), sulfur and nitrogen depositions have been measured in rain since 1958, but not until this present study has pH been seriously measured there (Dr. Milton Jones, pers. comm.).

Similarly, acid rain has been measured during a short period in the Seattle-Tacoma area of Washington state, at distances from the major $SO_2$ sources at the Tacoma Smelter and nearby refineries (Larson et al., 1976). In other locations in the west, various inorganic constituents of rain have been monitored for different purposes, but these have not generally included measurement of pH (e.g., Hart et al., (1973) in Utah, and Schlesinger and Hasey (1979) in southern California).

Thus the time is overdue for the continuous monitoring of precipitation chemistry including pH measurement, and for the maintenance of air-quality to minimize the occurrence and effects of acid rain in the western states. This task will be especially difficult in California, in the light of increasing vehicular use, and the proposed building of a coal- fired power plant in the central valley.

Atmospheric precipitation is comprised of dry components (particulates) and wet components (rain, snow, fog). Sea-salts, natural air-borne dust, soil particles, air-pollutants, and the rate, frequency, and distribution of rainfall contribute to chemical characteristics of these components. The purpose of this research project was to collect both wet and dry components of such atmospheric precipitation in critical locations to determine the extent of "acid rain" in California and to anticipate its possible ecological effects.

## 8. METHODS

### 8.1 Sampling sites:

Eight sampling sites were located in northern California; at Berkeley, Tahoe City, Kearney (Parlier), Challenge, San Jose, Hopland, Davis, and Napa (Fig. 1). A summary description of these sites is given in Table 1, and more detailed descriptions in Appendix 11.1.

The sites were chosen as representative of different geographical and/or vegetation and land-uses. They also included pollution "source-areas" and potential "receptor areas" where ecological effects may be important. They also represent a network, each site being close enough to each other for interpretative purposes, e.g., to infer possible atmospheric transport between "source" sites (primarily Berkeley and San Jose) and "receptor sites" (all others).

### 8.2 Sampling equipment:

Collectors were of the wet/dry type, collecting samples of both wet precipitation and dry fallout. The instrument consists of a two-bucket system with a movable lid, designed to expose the wet bucket and cover the dry bucket during periods of wet precipitation, and vice versa (Fig. 2). Sensors, mounted on the lid, react electrically to the onset of precipitation causing the lid to move. Heaters mounted below the sensors, serve to melt both snow and ice, and to evaporate moisture from the sensing element. This instrument was purchased from "Aerochem Metrics" of Florida (Model 201), and is one of the few types recommended by Galloway and Likens (1976) and also by a subcommittee that established guidelines for precipitation measurements in the U.S. National Atmospheric Deposition Program (N.A.D.P.).

Field pH was measured at each site following each storm event using Corning pH meters, newly bought and calibrated for this particular study to

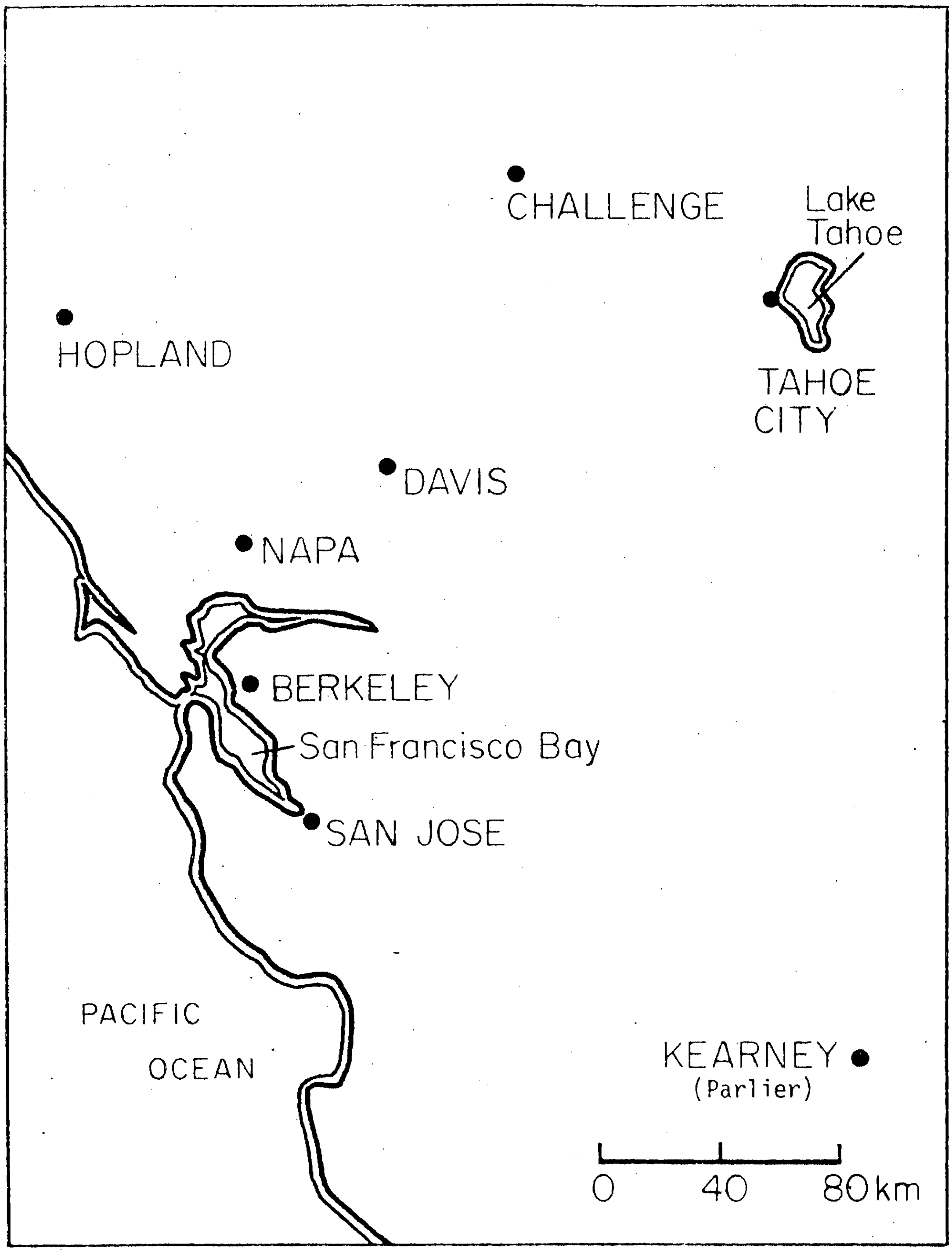


Fig. 1. Sites of sampling atmospheric precipitation in California, 1978-79.

Table 1. Description of study sites.

| Site Designation | Location & elevation | Description | Distance from ocean (km) | Field collector's name and institution |
|---|---|---|---|---|
| BE | Berkeley U.C. Space Sciences Lab., 37°53', 122° 15', 400 m. | Industrial and urban; pollution-source area; oceanic influence. | 20 | L. Monette and D. Bush, U.C. Berkeley. |
| TC | Tahoe City 39°08', 120°10', 2,076 m. | Sierra forest; watershed and recreation area. | 260 | R. Leonard, U.C. Davis, and Tahoe Research Group. |
| KE | Kearney Horticultural Field Station at Parlier. 36°46', 119°43', 100 m. | San Joaquin Valley; agriculture | 170 | R. Brewer, U.C. Davis, at Kearney Field Station, Parlier. |
| CH | Challenge Ranger Station, 39°39', 121°21', 790 m. | U.S. Forest Service Expt. Station; mixed conifer forest, lower Sierran foothills. | 215 | M. Heath, U.S.D.A. Forest Service. |
| SJ | San Jose State University, 37°21', 121°54', 22m. | Industrial and urban; pollution-source area; oceanic influence. | 30 | Jindra Goodman & Susan Fisher, San Jose State University. |
| HO | Hopland Field Station, 39°00', 123°03', 165 m. | U.C. Field Station Coast Range; grazing and watershed. | 40 | M. Jones, U.C. Davis, at Hopland Field Station. |
| DA | Davis U.C. Campus, 38°32', 121°46', 18 m. | U.C. Davis campus field plot; agricultural and urban. | 100 | G. Malyj, U.C. Davis and Tahoe Research Group. |
| NA | Napa, 38°17', 122°16', 280 m. | Woodland on ridge above Wooden Valley, Coast Range; Woodland and agricultural. | 55 | M. Linn, John Muir Institute. |

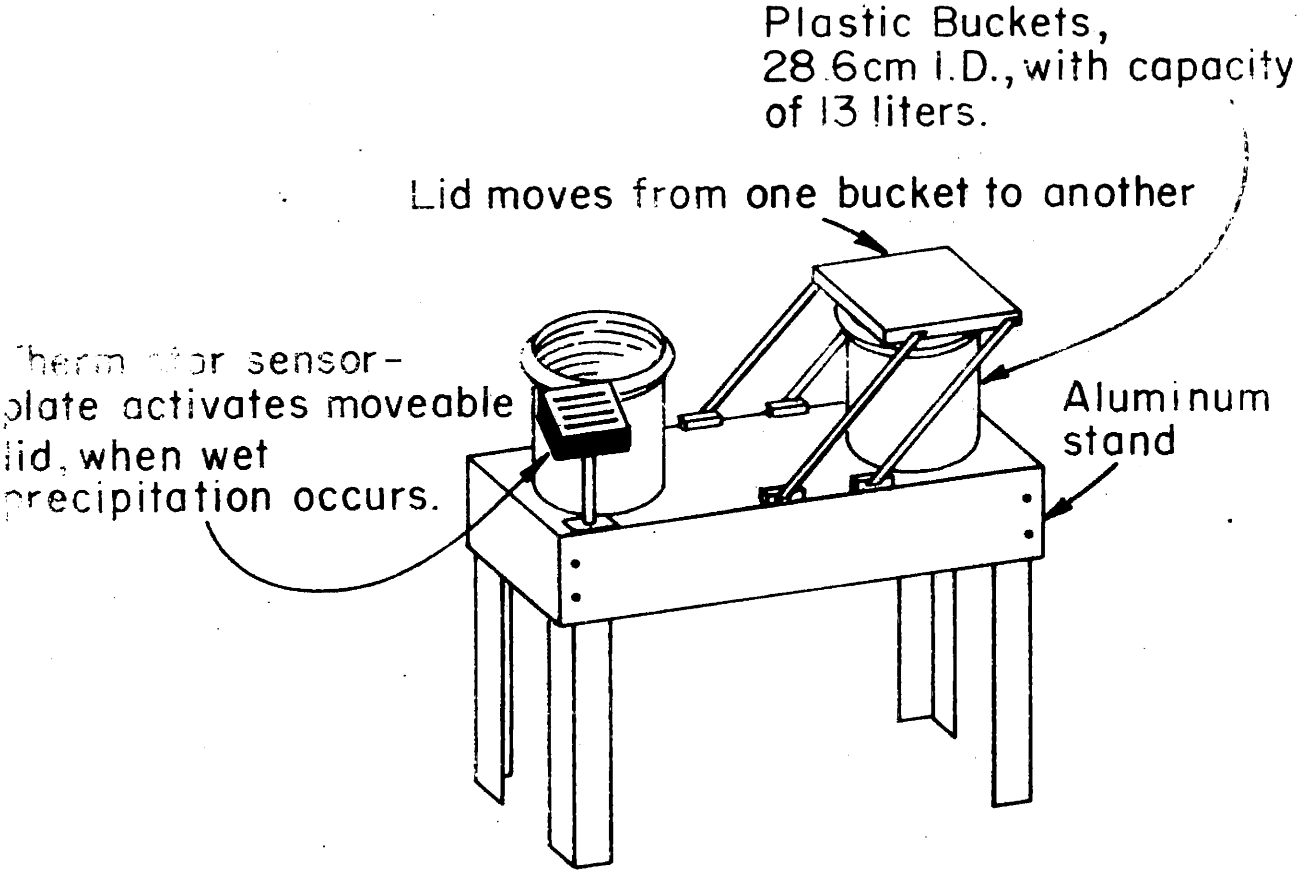


Fig. 2. "Aerochem Metrics Model 201", wet/dry precipitation collector for event monitoring.

ensure the best possible uniformity of measurement.

### 8.3 Sampling procedure:

Detailed instructions for event sampling, shipping and storage of both wet and dry precipitation that were used are given in Appendix 11.2; these were the procedures given to each field operator, together with the manufacturer's procedures for operating the pH meter. Detailed procedures were also demonstrated to each field operator.

### 8.4 Chemical analyses:

Concentrations of the following ions were determined: $H^+$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $Fe^{2+}$, $Mn^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $NH_4^+$, $NO_3^-$, $SO_4^{2-}$, $Cl^-$, and also electrical conductivity.

The pH of each sample was measured in the field, and was also measured in the laboratory using a Corning Digital 112 Research Meter, calibrated with buffers, pH 4 and pH 7, using the lower buffer first. 25 ml of solution was poured into a plastic beaker, and the meter allowed to equilibrate for 5 minutes before the pH reading was recorded. Electrical conductivity of solutions were also determined and results standardized at 25°C.

After filtration with a 0.45 millipore filter and chemical digestion with boiling nitric acid plus hydrogen peroxide, cations were determined by atomic absorption spectrophotometry using a Varian, Model AA6 (Isaac and Kerber 1971; and Appendix 11.3).

Chloride was determined using a spectrophotometric method (Florence and Farrar, 1971; and Appendix 11.4), sulfate using a barium chloroanilate spectrophotometric method (Bertolacini and Barney, 1958; and Appendix 11.5), nitrate by a hydrazine reduction method (Appendix 11.6), and ammonium by the indophenol method (Solorzano 1969).

## 8.5 Statistical analyses:

All data was punched on computer-cards and also recorded on permanent discs at the Computer Center, U.C. Berkeley. Summarization of data and subsequent statistical analyses, including computation of means, standard errors, various regressions, correlations, analyses of variance, etc., were made using the SPSS package programs i.e., "Statistical Programs for the Social Sciences" (Nie et al., 1975), which are on file at the U.C.B. Computer Center.

## 8.6 Quality assurance tests and comparisons:

Details of these tests and comparisons are given in Appendix 11.14 and Table 3. They include: (a) effects of storage temperature, filtration and storage time on hydrogen ion concentration of a wet sample, (b) correlation between acidity of wet precipitation measured in the field and laboratory (Table 3), (c) comparison of duplicate analyses of samples for $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $NO_3^-$-N, $NH_4^+$-N, $Cl^-$ and $SO_4^{2-}$, (d) comparison of wet depositions at Davis, California, from this study with that from a collector placed about 3 m away. The latter collector was one in the National Atmospheric Deposition Program (N.A.D.P.) network.

## 9. RESULTS AND DISCUSSION

Wet and dry atmospheric depositions were collected separately and analyzed at eight locations in California during the wet season, November 1978 through May 1979. The number of storms monitored at each site was as follows: Berkeley, 25; Tahoe City, 35; Kearney, 23; Challenge, 17; San Jose, 20; Hopland, 24; Davis, 26; and Napa, 17. Wet precipitation occurred as rain except for 13 events at Tahoe City and 8 events at Challenge that were snow.

Voluminous data for each site and storm-event were tabulated; one copy of these detailed, computerized results has been provided to the A.R.B. Statistical data, including standard errors for mean concentration data is also available for each site and storm. For purposes of this report, however, summarized data is sufficient to draw the necessary conclusions. Frequency distributions of volume, $[H^+]_{LAB}$, $[NO_3^-]$, $[SO_4^{2-}]$ and specific conductance for each site are given in Appendix 11.7.

### 9.1 Concentrations with emphasis on acidity:

Mean ionic concentrations of wet precipitation are given in Table 2. There were differences between sites for most ionic constituents. Overall trends are shown best by the sum of cations or anions and the electrical conductivity (which is a measure of total ionic strength).

The pH of precipitation was measured both at the field sites (immediately following precipitation events) and at the central laboratory on the U.C. Berkeley campus (about two days later). The correlations between the field and laboratory pH-measurements are given in Table 3. For all sites, with the exception of Tahoe City, there were statistically significant correlations between field and laboratory pH-measurements, but the measurements were not directly equivalent. Changes in solution pH during transportation to the laboratory and differences between field operators contributed to discrepancies. For uniformity of results, statistical

TABLE 2. MEAN IONIC CONCENTRATIONS OF WET PRECIPITATION DURING THE STUDY PERIOD IN 1978-9 (μeq/ℓ).

| | SITE | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Ion | BE | TC | KE | CH | SJ | HO | DA | NA |
| $H^+$ [Lab.] | 22.1 | 6.8 | 10.9 | 13.0 | 38.0 | 7.9 | 6.3 | 14.6 |
| $Na^+$ | 36.9 | 11.8 | 15.3 | 12.8 | 33.1 | 14.5 | 15.1 | 22.0 |
| $K^+$ | 1.5 | 0.6 | 1.4 | 2.1 | 1.5 | 1.1 | 1.1 | 1.4 |
| $Ca^{2+}$ | 6.0 | 4.3 | 8.0 | 10.9 | 12.6 | 3.3 | 5.6 | 4.6 |
| $Mg^{2+}$ | 9.6 | 1.7 | 3.6 | 7.0 | 9.7 | 3.8 | 5.7 | 5.3 |
| $Fe^{3+}$ | 0.3 | 0.0 | 0.6 | 0.4 | 0.8 | 0.2 | 0.4 | 0.4 |
| $Mn^{2+}$ | 0.1 | 0.0 | 0.1 | 0.6 | 0.1 | 0.1 | 0.1 | 0.1 |
| $Cu^{2+}$ | 0.1 | 0.1 | 0.1 | 0.2 | 0.3 | 0.1 | 0.2 | 0.7 |
| $Zn^{2+}$ | 0.3 | 0.1 | 0.2 | 0.2 | 0.6 | 0.1 | 0.1 | 0.2 |
| $NH_4^+$ | 8.0 | 4.1 | 40.0 | 11.9 | 19.1 | 9.7 | 35.5 | 12.1 |
| Σ Cations | 84.9 | 30.0 | 74.1 | 41.7 | 101.1 | 41.0 | 67.9 | 60.8 |
| | | | | | | | | |
| $NO_3^-$ | 13.7 | 6.7 | 43.4 | 19.9 | 16.4 | 11.1 | 22.6 | 16.4 |
| $Cl^-$ | 40.1 | 3.7 | 11.2 | 7.7 | 38.9 | 14.2 | 14.0 | 23.1 |
| $SO_4^{2-}$ | 10.2 | 13.3 | 13.8 | 8.6 | 10.0 | 6.2 | 19.0 | 11.7 |
| Σ Anions | 64.0 | 23.7 | 68.4 | 36.2 | 65.3 | 31.5 | 65.6 | 51.2 |
| | | | | | | | | |
| Conductivity (μmho/cm) | 13.9 | 3.9 | 17.4 | 10.6 | 16.2 | 6.4 | 9.6 | 10.7 |
| pH [Lab.] | 4.66 | 5.17 | 4.96 | 4.88 | 4.42 | 5.10 | 5.20 | 4.84 |
| Volume (cm) | 52.7 | 78.0 | 19.7 | 110.7 | 21.0 | 64.9 | 39.7 | 62.0 |

# TABLE 3. CORRELATION BETWEEN ACIDITY OF WET PRECIPITATION MEASURED IN THE FIELD AND LABORATORY

pH values converted to $[H^+]$, µeq/l

y = lab.   x = field.

| Site | Regression Equation | n | $r^2$ |
|---|---|---|---|
| BE | $y = -0.63 + 1.08x$ | 25 | $0.95^{***}$ |
| TC | $y = 6.84 - 0.00x$ | 35 | N.S. |
| KE | $y = 1.13 + 0.64x$ | 22 | $0.93^{***}$ |
| CH | $y = 9.06 + 0.67x$ | 16 | $0.20^{*}$ |
| SJ | $y = -31.66 + 1.08x$ | 16 | $0.80^{***}$ |
| HO | $y = 0.19 + 0.81x$ | 24 | $0.80^{***}$ |
| DA | $y = 0.84 + 0.78x$ | 24 | $0.55^{***}$ |
| NA | $y = 11.10 + 0.36x$ | 15 | $0.63^{***}$ |

$^{***}\alpha < 0.001$
$^{**}\alpha < 0.01$
$^{*}\alpha < 0.05$

TABLE 4. STATISTICS OF ACIDITY OF WET PRECIPITATION DURING THE STUDY PERIOD IN 1978-9.

| | SITE | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | BE | TC | KE | CH | SJ | HO | DA | NA |
| $[H^+]$ LAB. (μeq/l): | | | | | | | | |
| Mean | 22.1 | 6.7 | 10.9 | 13.0 | 38.0 | 7.9 | 6.3 | 14.6 |
| S.E. | 3.8 | 1.0 | 3.8 | 1.5 | 21.3 | 1.3 | 1.1 | 1.5 |
| Max. | 70.8 | 28.8 | 66.1 | 25.1 | 195.0 | 29.5 | 20.0 | 26.3 |
| Min. | 6.3 | 1.3 | 0.4 | 5.0 | 0.5 | 1.9 | 0.4 | 4.0 |
| n | 25 | 35 | 23 | 17 | 20 | 24 | 26 | 17 |
| Corresponding pH statistics: | | | | | | | | |
| Mean | 4.66 | 5.17 | 4.96 | 4.88 | 4.42 | 5.10 | 5.20 | 4.84 |
| Min. | 4.15 | 4.54 | 4.18 | 4.60 | 3.71 | 4.53 | 4.70 | 4.58 |
| Max. | 5.20 | 5.90 | 6.40 | 5.30 | 6.29 | 6.73 | 6.45 | 5.40 |

analyses related to pH differences between sites were made on the basis of the laboratory determinations. The non-significant correlation for Tahoe City (Table 3) may have been due to changes during the time of shipping. The buffering capacity of the Tahoe City samples was probably the least of all sites, as indicated by the very low mean conductivity of 3.9 μmho $cm^{-1}$ (Table 2).

Detailed statistics of the acidity of wet precipitation at all sites are given in Table 4. It is obvious that "acid rain" commonly occurred in California. San Jose was the site with the lowest mean pH of the storms sampled, with a mean of 4.42, and San Jose also recorded the storm having the lowest pH of any site with a value of 3.71. Davis was the site with the highest mean pH of 5.20 (Table 4). Thus all sites commonly received acid rain with pH values well below the "neutral" pH of 5.65, this being the pH of unpolluted rain in equilibrium with $CO_2$ in the atmosphere (as discussed in the introduction).

Relatively high maximum-pH values were recorded for storms at Kearney (pH 6.40), San Jose (pH 6.29), Hopland (pH 6.73) and Davis (pH 6.45). The high pH at San Jose was probably due to downwind emissions of alkaline particulates from a cement factory to the east (Dr. J. Goodman, San Jose State U., pers. comm.), and presumably due to dissolved soil-particles at the other sites which are representative of range and agricultural areas. The wide range of pH at San Jose (pH 3.71 to 6.29) illustrates the necessity for event monitoring (in contrast to weekly or monthly monitoring, for example), to provide data for interpretative purposes; quite possibly such pH ranges would not have been identified it collection times had been determined at regular intervals rather than being dictated by the time of occurrence of precipitation events.

On a chemical equivalent basis, the sum of cations (Σ cations) should equal the sum of anions (Σ anions) in solution. In all cases Σ cations > Σ anions (Table 2); the difference presumably being due to the bicarbonate ion ($HCO_3^-$) which was not measured directly, and/or to accumulative sampling and chemical-analysis errors.

The acidity of the precipitation was due to the anions, $SO_4^{2-}$ and $NO_3^-$. The chloride ion ($Cl^-$) is largely derived from neutral oceanic salts and would thus not usually contribute to the acidity of precipitation. Most of the $SO_4^{2-}$ and $NO_3^-$ ions, however, are products of the dissolution of $SO_2$ and $NO_x$ air-pollutants, and result in the formation of sulfuric and nitric acid, respectively. In N-California the $NO_3^-$ concentration was greater than the $SO_4^{2-}$ concentration. Similarly, Morgan and Liljestrand* found that the $NO_3^-/SO_4^{2-}$ ratio in rain exceeded 1.0 at 4 of their 9 sites in S-California. In the N.E.-U.S.A., however, the reverse is generally true (Likens, 1976). Presumably, emissions of $NO_x$ from automobile exhausts predominate in N-California, whereas $SO_2$ pollutants from coal-burning power plants predominate in the N.E.-U.S.A.

The ocean contributes large amounts of salts to both wet and dry precipitation and thus the concentrations of some ions (especially $Na^+$, $Cl^-$, $Mg^{2+}$) are largely functions of distance of the sampling sites from the ocean. This point is discussed in detail later.

Ionic forms of the elements, Fe, Mn, Cu and Zn (Table 2) may have originated as particulates rather than occurring in the free ionic state, but they are reported here as such because the sample solutions were analyzed following chemical digestion of the samples. In a previous study of precipitation at Berkeley in 1974-75 by the author (McColl and Bush, 1978), the only cations with any apparent correlation with $H^+$ were $Cu^{2+}$ and $Mn^{2+}$. Simple correlation coefficients for the relationship between $H^+$ concentration in precipitation and $Cu^{2+}$ and $Mn^{2+}$ concentrations were 0.36 ($\alpha<0.15$) and 0.45 ($\alpha<0.10$), respectively, and concentrations of $Cu^{2+}$ and $Mn^{2+}$, were themselves correlated ($r = 0.63$, $\alpha<0.05$). Multiple step-wise regression equations for this 1974-75 data, with $H^+$ concentrations as the dependent variable and concentrations of $NO_3^-$, $Cu^{2+}$ and $Mn^{2+}$ as three independent

---

*"Measurement and interpretation of acid rainfall in the Los Angeles Basin", draft report to Calif. Air Resources Board, October 15, 1979 (by permission).

variables, had multiple correlation coefficients of 0.54 ($\alpha = 0.04$) at step one ($NO_3^-$ only), 0.68 ($\alpha = 0.03$) at step two ($NO_3^-$ and $Mn^{2+}$), and 0.70 ($\alpha = 0.07$) at step three ($NO_3^-$, $Mn^{2+}$ and $Cu^{2+}$). The metallic ions may act as catalysts in photochemical oxidation of N and S oxides in the atmosphere (Cadle, 1972; Fennelly, 1976), and thus correlate with $H^+$. Alternatively, the correlations may simply be due to sources of the different ions being the same or geographically similar.

Concentrations of $NH_4^+$ in wet precipitation (Table 2) were highest at the Kearney and Davis sites, probably due to agricultural fertilizer salts in these central-valley locations.

### 9.2 Volume of wet precipitation:

Table 2 also lists the volume (cm) of wet precipitation collected at each site during the study period. Frequency distributions of storm volumes for each site are given in Appendix 11.7. It is important to note here that volumes differed widely (from 21.0 cm at San Jose to 110.7 cm at Challenge) and thus the total deposition of the ionic constituents of wet precipitation at a given site was affected both by the concentration of ions and the total amount of rainfall. Sodium deposition is given as an example in Appendix 11.8.

### 9.3 Total Depositions:

Total depositions of ions in wet precipitation are given in Table 5. Each value in kilograms per hectare is the sum of the product of ionic concentration and volume of storms. Corresponding amounts for dry deposition are given in Table 6. In both tables, total elemental nitrogen and sulfur depositions are listed, as well as deposition of these elements in their respective ionic forms ($NH_4^+$, $NO_3^-$ for nitrogen; $SO_4^{2-}$ for sulfur). Comparison of these two tables shows that dry deposition was appreciable, although not generally as great in magnitude as wet deposition. However, dry depositions

TABLE 5. WET IONIC DEPOSITION DURING THE STUDY PERIOD IN 1978-9 (kg/ha).

| ION | SITE | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | BE | TC | KE | CH | SJ | HO | DA | NA |
| $Na^{+}$ | 3.691 | 1.320 | 0.459 | 2.123 | 1.616 | 1.961 | 1.189 | 2.345 |
| $K^{+}$ | 0.273 | 0.127 | 0.074 | 0.501 | 0.090 | 0.261 | 0.114 | 0.252 |
| $Ca^{2+}$ | 0.519 | 0.486 | 0.263 | 0.982 | 0.380 | 0.280 | 0.335 | 0.362 |
| $Mg^{2+}$ | 0.490 | 0.189 | 0.056 | 0.407 | 0.264 | 0.339 | 0.178 | 0.261 |
| $Fe^{3+}$ | 0.023 | 0.034 | 0.014 | 0.132 | 0.015 | 0.019 | 0.022 | 0.038 |
| $Mn^{2+}$ | 0.008 | 0.007 | 0.005 | 0.059 | 0.004 | 0.013 | 0.010 | 0.009 |
| $Cu^{2+}$ | 0.022 | 0.024 | 0.003 | 0.141 | 0.015 | 0.019 | 0.019 | 0.009 |
| $Zn^{2+}$ | 0.036 | 0.019 | 0.010 | 0.050 | 0.031 | 0.013 | 0.016 | 0.030 |
| $NH_4^{+}$ | 0.589 | 0.373 | 1.205 | 1.481 | 0.672 | 0.590 | 2.454 | 1.375 |
| $NO_3^{-}$ | 3.447 | 2.224 | 4.142 | 7.912 | 1.466 | 3.043 | 4.957 | 5.724 |
| $Cl^{-}$ | 6.208 | 0.661 | 0.480 | 2.345 | 2.518 | 3.325 | 1.628 | 3.373 |
| $SO_4^{2-}$ | 1.969 | 2.341 | 1.367 | 3.067 | 1.226 | 1.381 | 2.634 | 3.840 |
| $H^{+}$ [LAB] | 0.083 | 0.052 | 0.016 | 0.121 | 0.027 | 0.046 | 0.021 | 0.082 |
| $H^{+}$ [FIELD] | 0.082 | 0.290 | 0.020 | 0.050 | 0.023 | 0.052 | 0.025 | 0.048 |
| $NH_4$-N | 0.458 | 0.291 | 0.940 | 1.155 | 0.524 | 0.460 | 1.914 | 1.073 |
| $NO_3$-N | 0.793 | 0.512 | 0.953 | 1.820 | 0.637 | 0.670 | 1.140 | 1.317 |
| Total N | 1.251 | 0.803 | 1.893 | 2.975 | 1.161 | 1.130 | 3.054 | 2.390 |
| $SO_4$-S | 0.653 | 0.780 | 0.456 | 1.022 | 0.409 | 0.460 | 0.878 | 1.280 |

TABLE 6. DRY IONIC DEPOSITION DURING THE STUDY PERIOD IN 1978-9 (kg/ha).

| ION | SITE | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | BE | TC | KE | CH | SJ | HO | DA | NA |
| $Na^+$ | 3.142 | 0.891 | 0.245 | 0.317 | 1.693 | 0.394 | 0.291 | 0.274 |
| $K^+$ | 0.397 | 0.056 | 0.063 | 0.154 | 0.290 | 0.151 | 0.115 | 0.065 |
| $Ca^{2+}$ | 0.926 | 0.226 | 0.239 | 0.402 | 1.646 | 0.151 | 0.373 | 0.107 |
| $Mg^{2+}$ | 0.513 | 0.053 | 0.037 | 0.088 | 0.369 | 0.083 | 0.128 | 0.093 |
| $Fe^{3+}$ | 0.022 | 0.017 | 0.007 | 0.014 | 0.023 | 0.018 | 0.007 | 0.006 |
| $Mn^{2+}$ | 0.017 | 0.005 | 0.003 | 0.060 | 0.016 | 0.008 | 0.009 | 0.002 |
| $Cu^{2+}$ | 0.010 | 0.006 | 0.011 | 0.004 | 0.097 | 0.016 | 0.009 | 0.002 |
| $Zn^{2+}$ | 0.070 | 0.015 | 0.017 | 0.018 | 0.090 | 0.034 | 0.080 | 0.005 |
| $NH_4^+$ | 0.470 | 0.070 | 0.552 | 0.097 | 0.328 | 0.364 | 0.453 | 0.157 |
| $NO_3^-$ | 2.826 | 0.470 | 1.803 | 4.284 | 2.937 | 1.170 | 1.449 | 0.877 |
| $Cl^-$ | 4.301 | 0.803 | 0.178 | 0.271 | 2.386 | 0.686 | 0.317 | 0.329 |
| $SO_4^{2-}$ | 1.248 | 0.972 | 0.579 | 0.658 | 1.134 | 0.720 | 2.058 | 0.145 |
| $H^+$[LAB] | 0.014 | 0.001 | 0.123 | 0.001 | 0.008 | 0.004 | 0.001 | 0.003 |
| $H^+$[FIELD] | 0.014 | 0.056 | 0.051 | 0.000 | 0.005 | 0.003 | 0.002 | 0.004 |
| $NH_4$-N | 0.367 | 0.055 | 0.431 | 0.076 | 0.256 | 0.294 | 0.353 | 0.122 |
| $NO_3$-N | 0.650 | 0.108 | 0.415 | 0.985 | 0.676 | 0.269 | 0.333 | 0.202 |
| Total N | 1.017 | 0.163 | 0.846 | 1.061 | 0.932 | 0.563 | 0.686 | 0.324 |
| $SO_4$-S | 0.416 | 0.321 | 0.174 | 0.197 | 0.340 | 0.216 | 0.264 | 0.044 |

listed are only for those dry periods between wet precipitation events; obviously dry deposition during California's long, dry, summer period (May-November) would considerably inflate the values given here. Effects of dry deposition during summer may be of serious ecological importance, as dry accumulations, when washed from surfaces by rains of early fall or combined with summer fogs, may cause the solubilization of dry acid deposits.

## 9.4 Site differences and Regional Trends:

Differences between sites for the various constituents of wet and dry precipitation were determined by statistical "analysis of variance" tests; mean values for each site were compared and least significant differences determined, then the sites were grouped into homogenous subsets as designated by sample means that were not significantly different. Results of these analyses for concentration of ions in wet precipitation, are summarized in Appendix 11.9. The results of such statistical analysis for the hydrogen ion are of most interest regarding "acid rain" and its occurence. For this reason the results for hydrogen are also diagrammed in Figs. 3 and 4, where the geographical location of the study sites can also be considered.

Firstly, Fig. 3 shows homogenous subsets of the mean hydrogen ion concentration ($[H^+]$) in wet precipitation, and indicates that the $[H^+]$ is significantly greatest at San Jose and Berkeley. The other sites fall into another subset with lower $[H^+]$, although the Berkeley site falls into both subsets, being intermediate in $[H^+]$. These results suggest that the origin of the acidity is in the industrial-urban Bay-area; typical storm "wash-out fans" confirm this conclusion (Appendix 11.10, provided by F. R. Smith of the A.R.B.).

But as mentioned earlier, volumes of precipitation vary with site

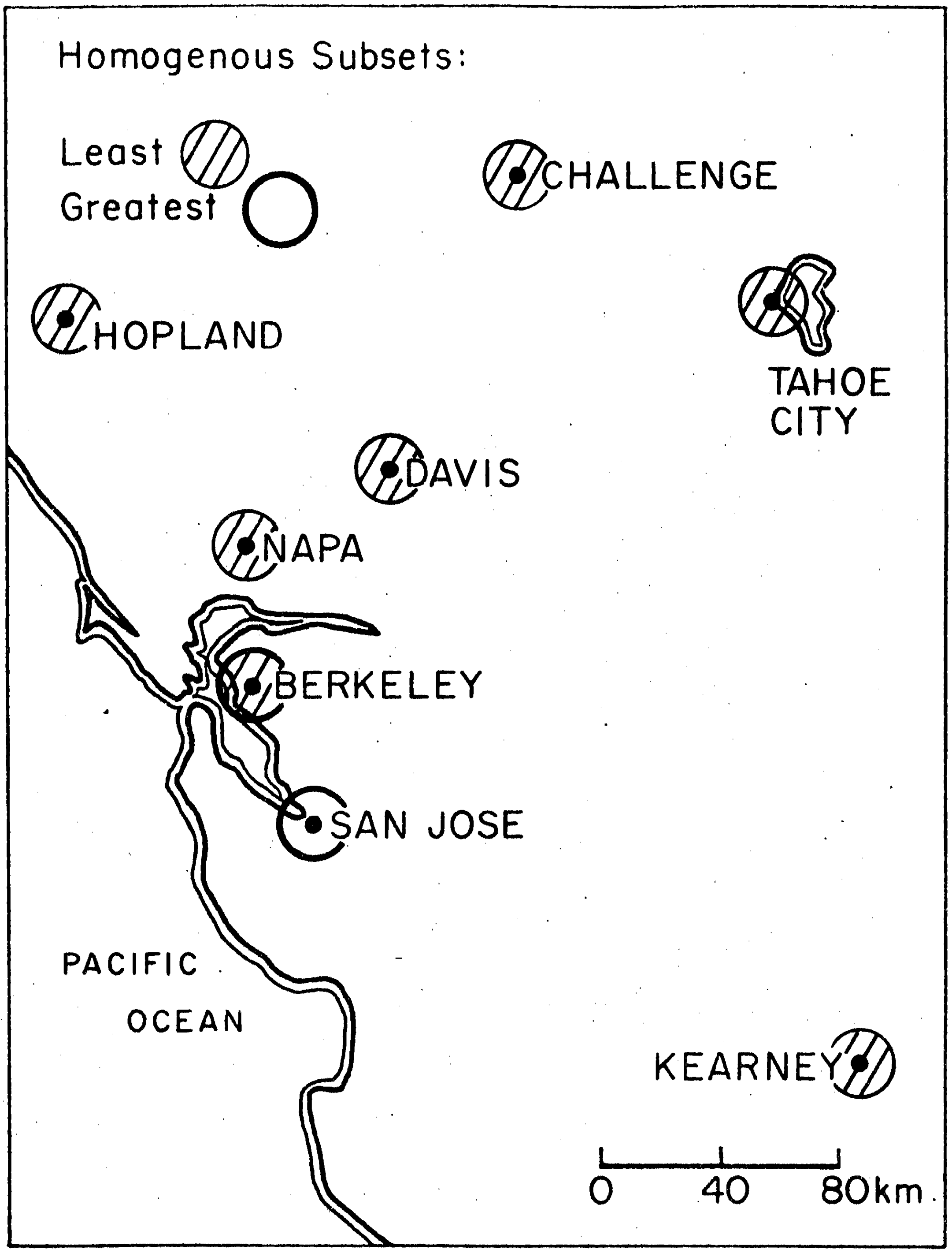


Fig. 3. Mean hydrogen ion concentrations of 1978-79 wet precipitation, designated by statistically significant homogenous subsets.

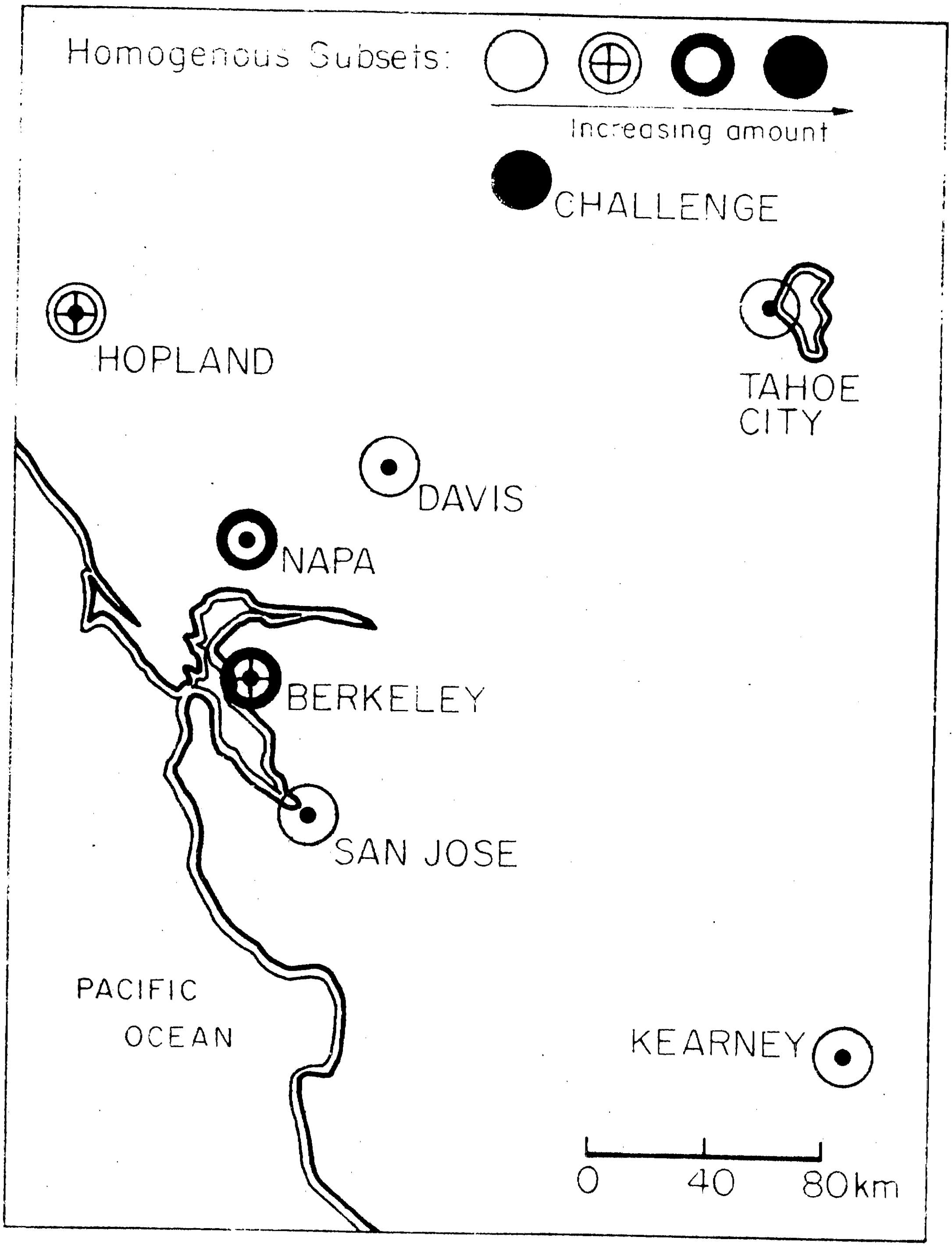


Fig. 4. Hydrogen ion deposition of 1978-79 wet precipitation, designated by statistically significant homogenous subsets.

(Table 2), and thus affect total deposition of ionic constituents of precipitation. Fig. 4 shows homogenous subsets of the total $H^+$ depositions. Here a different picture emerges from that just described for mean $[H^+]$. The statistical analysis for $H^+$ depositions distinguished four homogenous subsets (Fig. 4). The site with the significantly highest $H^+$ deposition was Challenge followed by Napa, Berkeley, and Hopland, with the remaining sites (Tahoe City, Davis, San Jose, and Kearney) being grouped in the subset with the least $H^+$ deposition. Fig. 4 suggests that the acidity originating in the Bay-area is carried inland with the predominate west-to-east movement of major rain storms (Appendix 11.10), and that total acid-deposition is significantly affected by total volume of precipitation as well as by the concentration of acidity.

The ecological implications of this result are complex, as the result raises the question of the relative effects of a "threshold acidity" versus those of the "total deposition of acidity" on ecosystems and their components. For example, the $[H^+]$ may be a more important parameter to determine "threshold-acidity" effects on aquatic life or plant growth, but the "total deposition of acidity" may be the main determinant of accelerated leaching of soil, and weathering of exposed rock surfaces and buildings. Obviously, future studies on effects of "acid rain" must address these questions in more detail.

## 9.5 Anion relationships with acidity:

Statistical correlation coefficients were calculated to determine which anions were most closely related to the $H^+$ in wet precipitation; these results are shown in Fig. 5, where geographical location of sites is also considered. Significant correlations of $[H^+]$ with $[NO_3^-]$ occurred at Berkeley,

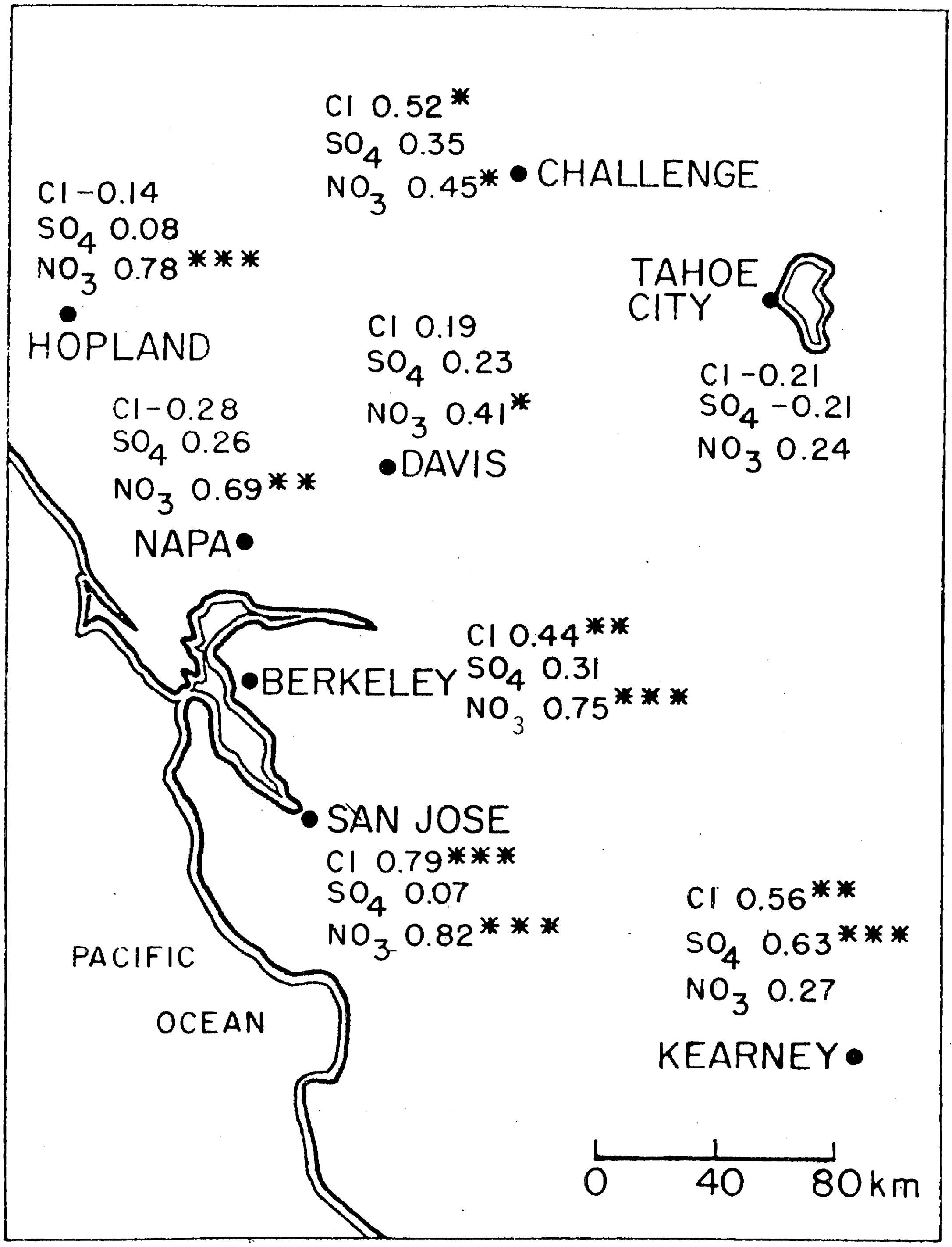


Fig. 5. Correlation of concentrations of hydrogen ion with anions of wet precipitation, 1978-79.

$***\alpha < 0.001$, $**\alpha < 0.01$, $*\alpha < 0.05$

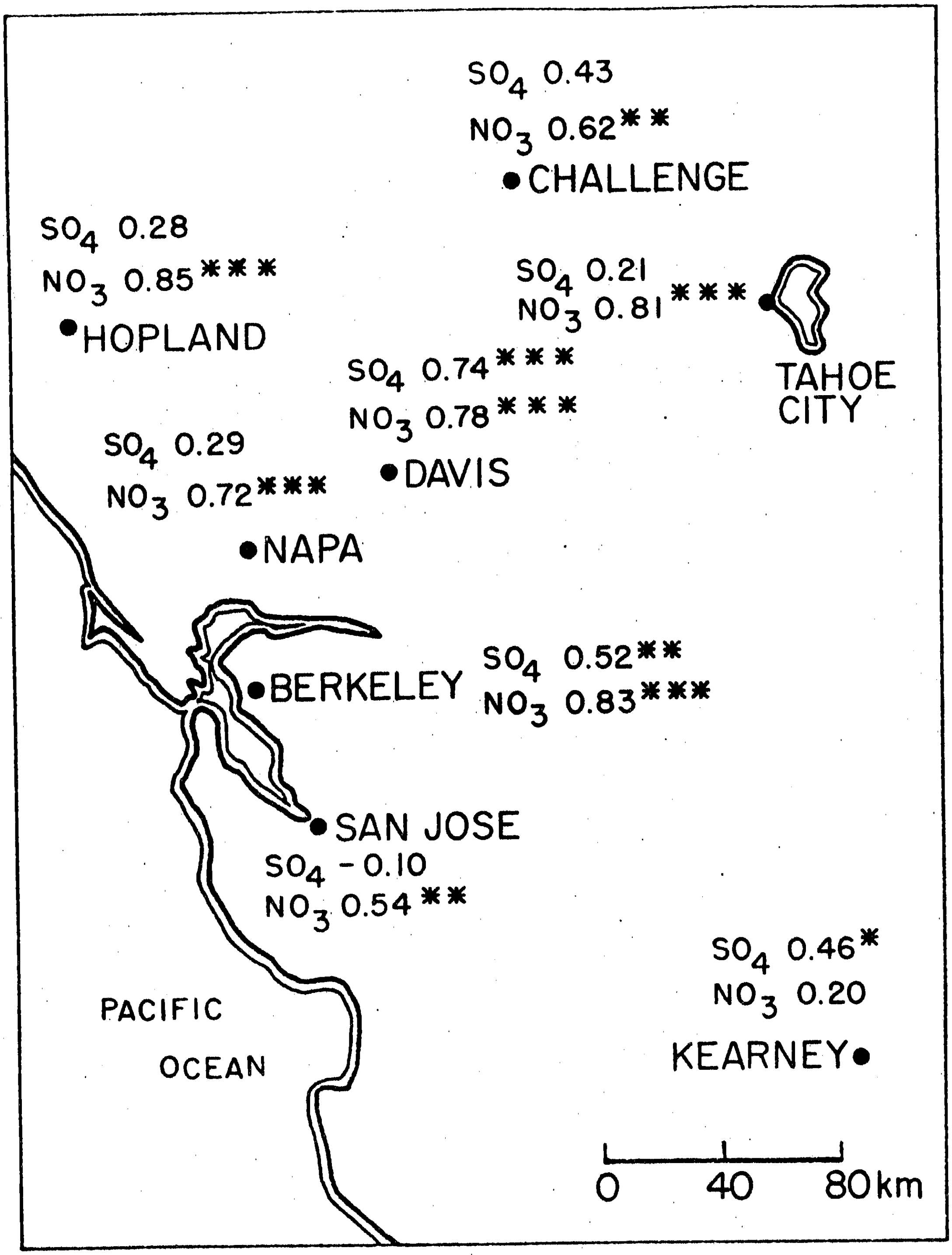


Fig. 6. Correlation of concentrations of ammonium ion with nitrate and sulfate ions of wet precipitation, 1978-79. $^{***}\alpha < 0.001$, $^{**}\alpha < 0.01$, $^{*}\alpha < 0.05$

San Jose, Napa, Davis, Hopland and Challenge, but not at Tahoe City or Kearney. Tahoe City was the only site with [$SO_4^{2-}$] > [$NO_3^-$], and with the lowest conductivity (Table 2). The precipitation at Tahoe City, although generally acid, was probably weakly buffered and thus a correlation with any one anion species did not exist.

The Kearney site was the only one with a significant correlation between [$SO_4^{2-}$] and [$H^+$], and the correlation of [$H^+$] with [$NO_3^-$] was not significant (Fig. 5). These results indicate that the source of acidity at Kearney was different from that of the other sites. It is likely that sulfuric acid in rain at Kearney originated from air-pollution from oil-fields upwind. Alternatively, local agricultural practices, such as addition of ammonium sulfate soil-fertilizer, could explain the high correlation between [$H^+$] and [$SO_4^{2-}$] at Kearney.

A strong correlation between [$H^+$] and [$NO_3^-$] during a large storm in March 1978 was documented in an earlier study (Bush 1979) at Berkeley (Appendix 11.11). In the present study the analysis of variance and subsequent designations of homogeneous subsets for nitrate deposition showed Challenge with the highest deposition (Appendix 11.9), as was also the case for hydrogen deposition discussed earlier. These facts strongly suggest that the acidity in the Bay-area, extending eastward to Challenge via Davis and northward to Hopland via Napa, is largely due to nitric acid. However, significant correlations between [$H^+$] and [$Cl^-$] indicate that hydrochloric acid may also contribute to the acidity of wet precipitation.

The nitrate ion is also correlated with the ammonium ion at all sites except Kearney, whereas sulfate is correlated with ammonium at only three sites; Berkeley, Davis and Kearney (Fig. 6).

## 9.6 Relationships with dry-period length:

The ionic concentration of precipitation is obviously determined by emissions of pollutants, but also by the amount and time-distribution of storms. In Table 7, correlation coefficients are given for correlation

TABLE 7. CORRELATION OF IONIC CONCENTRATIONS AND STORM VOLUME WITH LENGTH OF THE DRY PERIOD PRECEDING WET PRECIPITATION ($r$ VALUES AND SIGNIFICANCE).

| | SITE | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | DA | TC | KE | CH | SJ | HO | BE | NA |
| <u>WET PRECIPITATION</u>: | | | | | | | | |
| $[H^+]$ LAB. | 0.3 | -0.0 | $0.5^{*}$ | 0.4 | -0.2 | -0.2 | 0.2 | -0.1 |
| $\Sigma$ Cations | $0.7^{***}$ | -0.2 | $0.5^{*}$ | 0.1 | -0.2 | -0.1 | $0.6^{**}$ | 0.3 |
| $\Sigma$ Anions | $0.8^{***}$ | -0.1 | 0.3 | -0.1 | -0.2 | -0.2 | $0.7^{***}$ | 0.2 |
| Conductivity | $0.6^{***}$ | -0.1 | 0.2 | 0.1 | -0.2 | -0.2 | $0.7^{***}$ | 0.3 |
| Volume | -0.1 | 0.2 | $0.4^{*}$ | -0.2 | $0.7^{**}$ | -0.1 | -0.3 | -0.2 |
| <u>DRY PRECIPITATION (in 500 ml distilled water)</u>: | | | | | | | | |
| $[H^+]$ LAB. | -0.1 | 0.2 | 0.4 | -0.2 | 0.0 | -0.3 | 0.3 | 0.4 |
| $\Sigma$ Cations | 0.2 | $0.4^{*}$ | $0.9^{***}$ | $0.5^{*}$ | $0.7^{***}$ | $0.9^{***}$ | $0.6^{**}$ | -0.2 |
| $\Sigma$ Anions | 0.1 | $0.4^{*}$ | $0.9^{***}$ | 0.3 | $0.4^{*}$ | $0.8^{***}$ | $0.5^{*}$ | $-0.6^{*}$ |
| Conductivity | 0.2 | $0.5^{*}$ | 0.1 | $0.6^{**}$ | $0.8^{***}$ | 0.2 | $0.7^{**}$ | 0.1 |

$^{***}\alpha < 0.001$, $^{**}\alpha < 0.01$, $^{*}\alpha < 0.05$

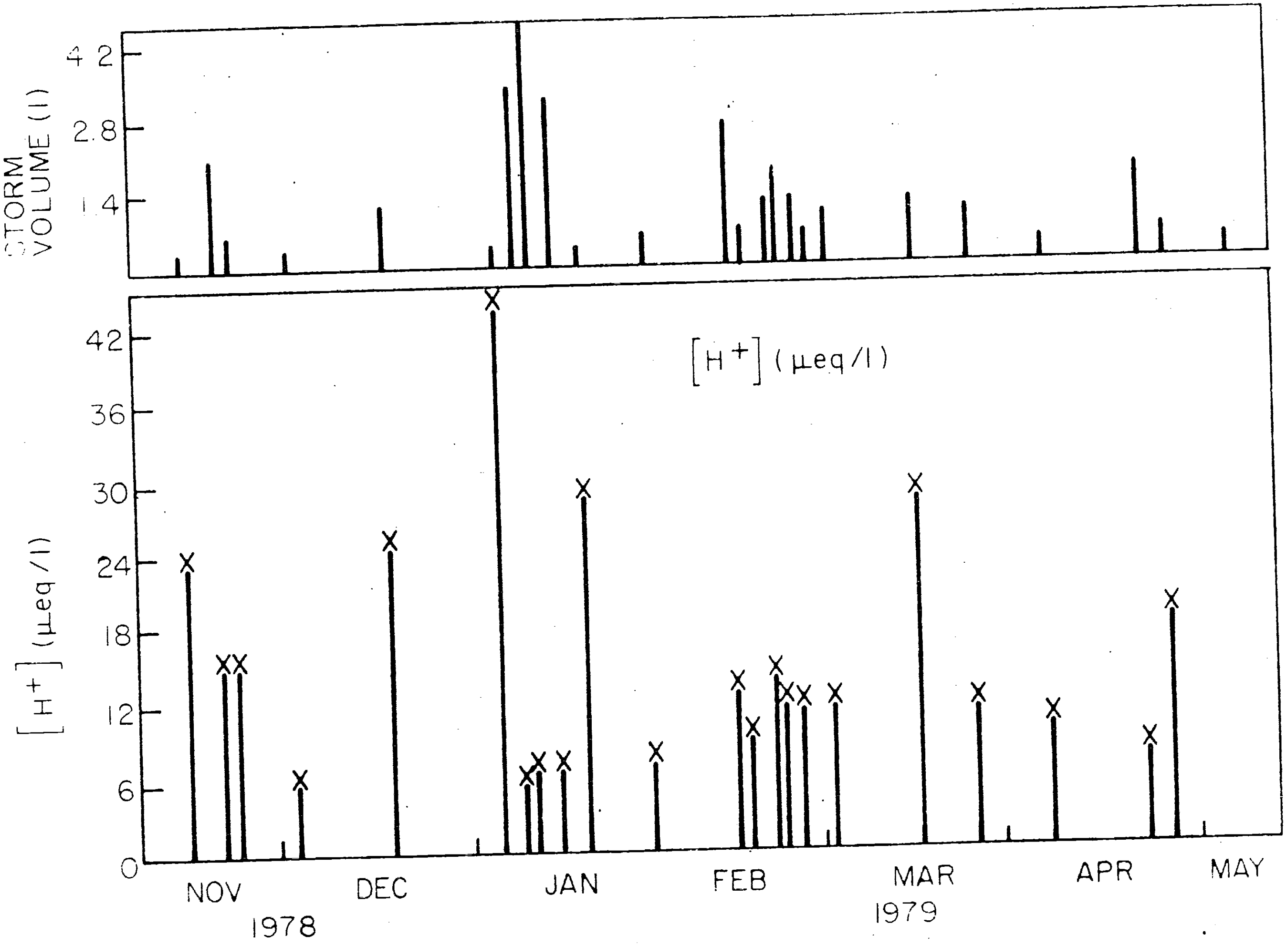


Fig. 7. Storm volume and hydrogen ion concentrations of wet precipitation at Berkeley, 1978-79.

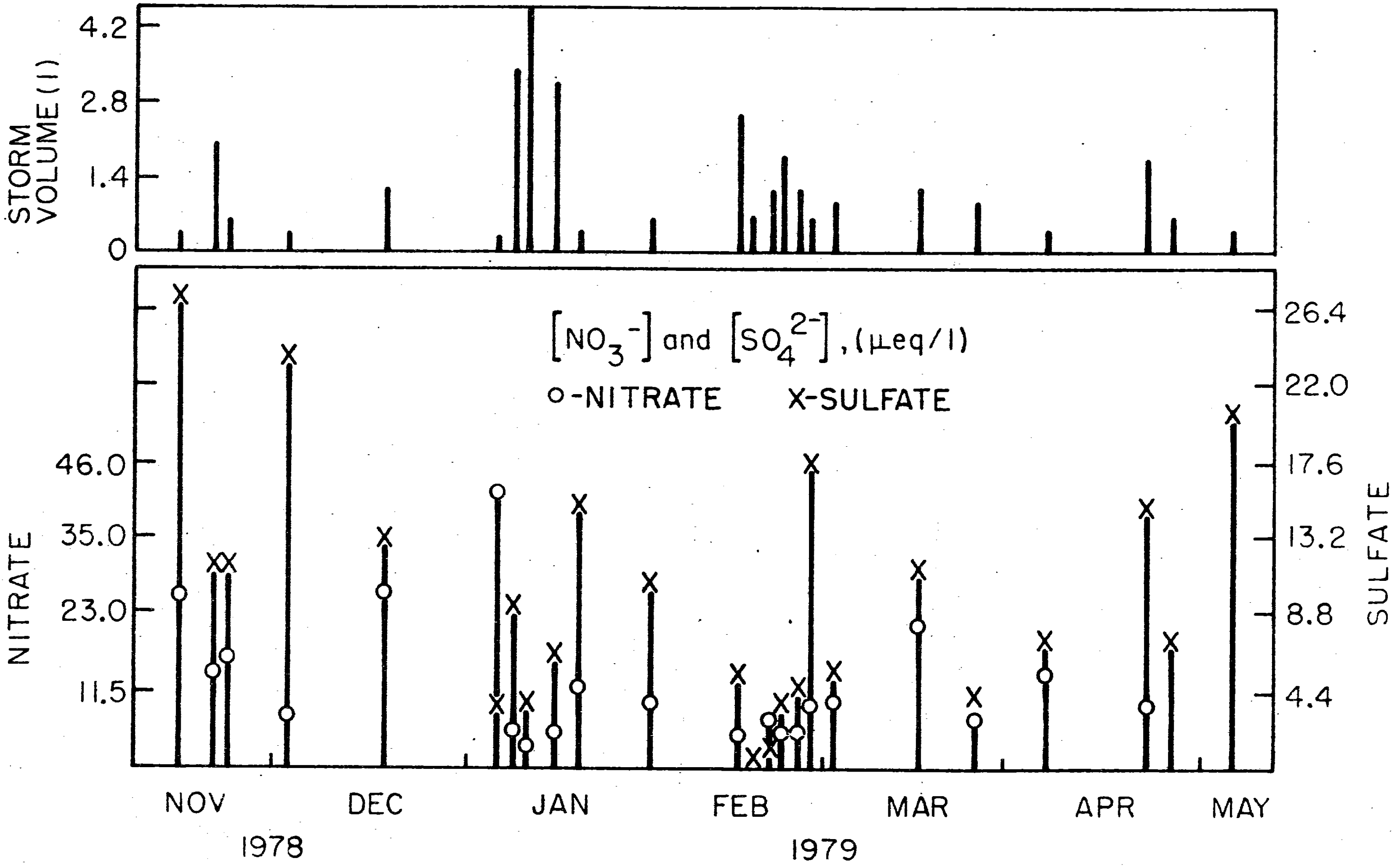


Fig. 8. Storm volume and nitrate and sulfate ion concentrations of wet precipitation at Berkeley, 1978-79.

between the length of the dry period preceding wet precipitation events, and both ion concentrations and storm-volume. Only Kearney and San Jose had statistically significant correlation coefficients for volume versus dry-period length, i.e., indicating a positive relationship between amount of wet precipitation and the length of the preceding dry-period. Significant positive correlations between ionic concentrations and dry-period length existed for the Davis and Berkeley sites (Table 7). At the other sites there was little or no evidence of correlations between dry-period length and ionic concentrations of wet precipitation.

For dry precipitation, however, there were many more significant correlation coefficients (Table 7), indicating that there was a fairly general relationship between the length of the dry-period and the total deposition of dry precipitation in that period at all sites, except Davis.

## 9.7 Concentration changes during study periods:

Ionic concentrations varied widely between storms at a given site. Concentrations of $H^+$, $SO_4^{2-}$, and $NO_3^-$ at the Berkeley site are presented in Figs. 7 and 8 as examples of the 8 sites monitored. In some cases, the $[H^+]$ decreased following rainfall, as shown for the series of storms in early January (Fig. 7). But this "dilution effect" was not general, as shown by the storms in mid-February (Fig. 7). The fluctuations in $[H^+]$ illustrate the fact that it is difficult to generalize or infer effects from mean data alone.

A similar set of graphs for $[NO_3^-]$ and $[SO_4^{2-}]$ at Berkeley are shown in Fig. 8. Concentrations of the two ions sometimes vary concomitantly, but not always. Thus it is also difficult to generalize about the relationship between storm frequency (or volume) and the corresponding ionic concentrations.

## 9.8 Historical changes of acidity:

As mentioned in the introduction, only fragmentary data of the chemical composition of precipitation for California exists but there is some evidence that the pH of rain in the San Francisco Bay area was higher 20 years ago. At Menlo Park, south of San Francisco, rain pH averaged 5.9 in 1957-58,, 5.3 in 1958-59 (Whitehead and Feth, 1964), and 5.2 in 1971 (Kennedy et al., 1976). At Berkeley, rain pH averaged 5.0 in 1974-75 (McColl and Bush, 1978), 4.8 in 1977-78 (Bush 1979), and 4.7 in 1978-79 (this study). As discussed in an earlier report of the author (McColl and Bush, 1978), the decrease in pH of rain seems to be related to [$NO_3^-$], as shown by the Menlo Park data previously cited: [$SO_4^{2-}$] dropped from 1.52 ± 0.38 ppm to 0.69 ± 0.18 ppm between 1957 and 1971. During the same period, [$NO_3^-$] remained almost the same (0.15 ± 0.03 ppm in 1957-58 and 0.16 ± 0.01 in 1971), even though total ionic concentration of rain water decreased from 22.9 ± 3.7 to 10.2 ± 1.5 µmho/cm, mean specific conductance. This result is consistent with those of this present study, which indicate that primarily nitric acid (and secondarily sulfuric acid) causes the acidity in rainfall at the study sites.

### 9.9 Contribution of oceanic salts:

As major storm-fronts move across California in an easterly direction (Appendix 11.10), oceanic salts are carried inland and deposited both as dry and wet precipitation. For example, Berkeley which is the site closest to the ocean, received relatively large amounts of both wet and dry depositions of $Na^+$ and $Cl^-$ (Table 2). The concomitant fluctuations in [$Na^+$] and [$Cl^-$] at Berkeley, in relation to storm frequency and volume over the study period are shown in Appendix 11.2. This oceanic contribution to the composition of rain must be distinguished if the contribution from anthropogenic air-pollution and/or terrestrial dust are to be quantified also. The fact that most $Na^+$ or $Cl^-$ in rain is of oceanic origin has been used by various workers as a basis for determining ionic contributions of other sea-salts to rain water (e.g. Cogbill and Likens, 1974; Granat, 1972; Junge and Werby, 1958; McColl and Bush, 1978).

The mean $[Na^+]$ and $[Cl^-]$ for the 8 study sites are plotted in Fig. 9, as a function of distance from the ocean. (These distances are simply the distance of the perpendicular drawn from each site to an average line describing the Californian coast). Clearly, there is a highly predictable and rather abrupt decrease in $[Na^+]$ and $[Cl^-]$, but beyond about 80 to 100 km inland, the concentrations level off (Fig. 9). Beyond about 80 km inland, chloride continues to decrease more than sodium, as soil particles can contribute to some sodium concentrations, whereas the source of chloride is almost entirely oceanic. Thus the ratio of $Cl^-:Na^+$ also decreases very predictably with distance from the ocean (Appendix 11.13).

These highly significant functions are useful tools to predict the contribution of other ionic constituents of rain derived from oceanic sources. For example, using $[Cl^-]$ as a basis, knowing that the $[Cl^-]:[Na^+]$ ratio (on a chemical equivalent basis) of seawater is 1.17 (Martin 1967) and assuming that all $[Cl^-]$ in rain is of oceanic origin, $[Na^+]$ can be calculated for all sites if their $[Cl^-]$ is known. Similarly the concentration of other ions ($Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, etc.) in rainwater due to oceanic origin can be predicted, as shown in Fig. 10. If the measured concentration of any of these ions in rain at each site (Table 2) exceeds that predicted in Fig. 10, the excess can be reasonably assumed to be due to a source other than the ocean. Data for nitrogen is not shown in Fig. 10, because amounts of nitrogen in seawater are negligible (McGill 1973); thus it can be reasonably assumed that all nitrogen in rainwater is of some other origin.

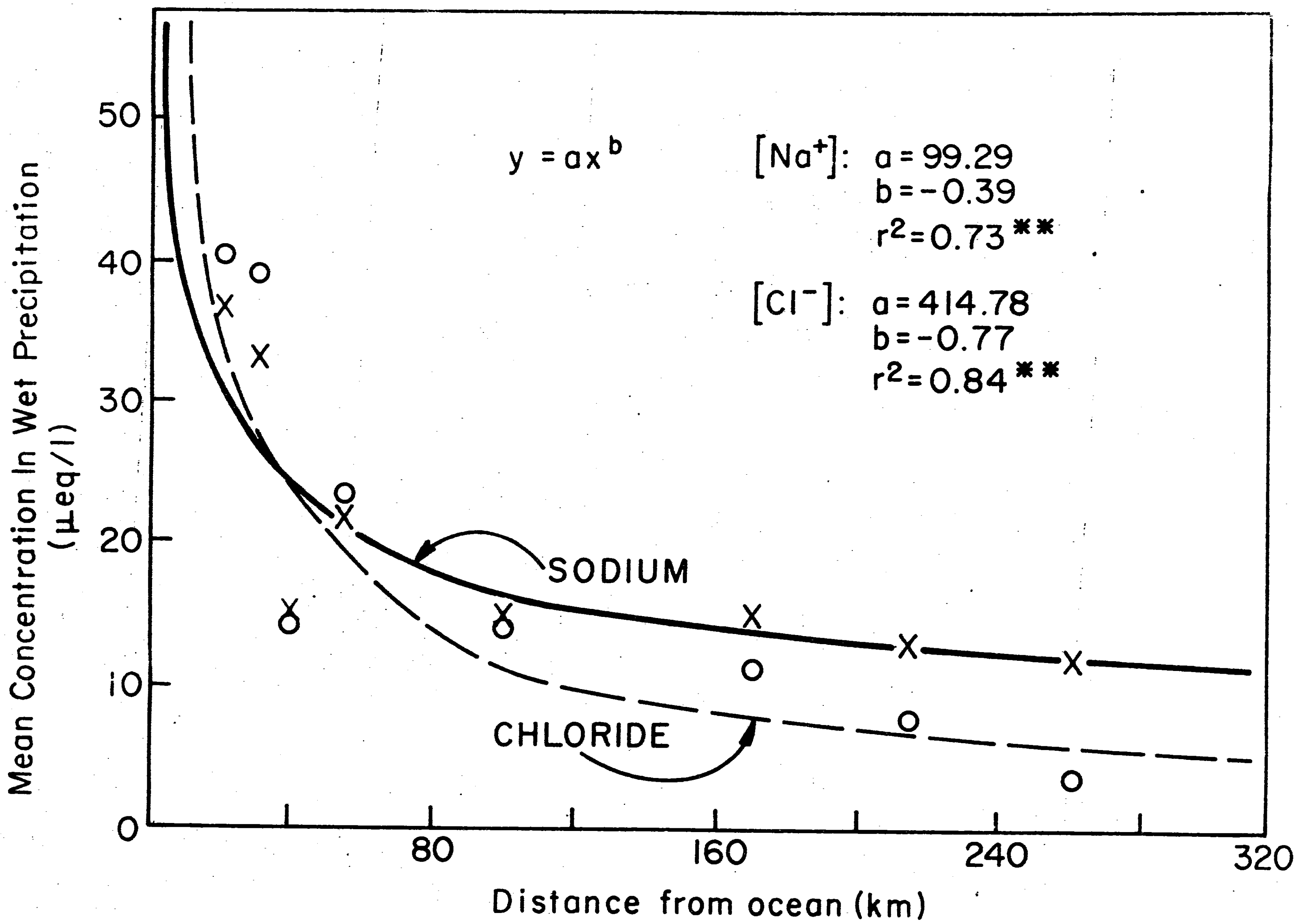


Fig. 9. Mean concentrations of sodium and chloride of wet precipitation as a function of distance from ocean, 1978-79. X = Sodium, O = Chloride. $**\alpha < 0.01$.

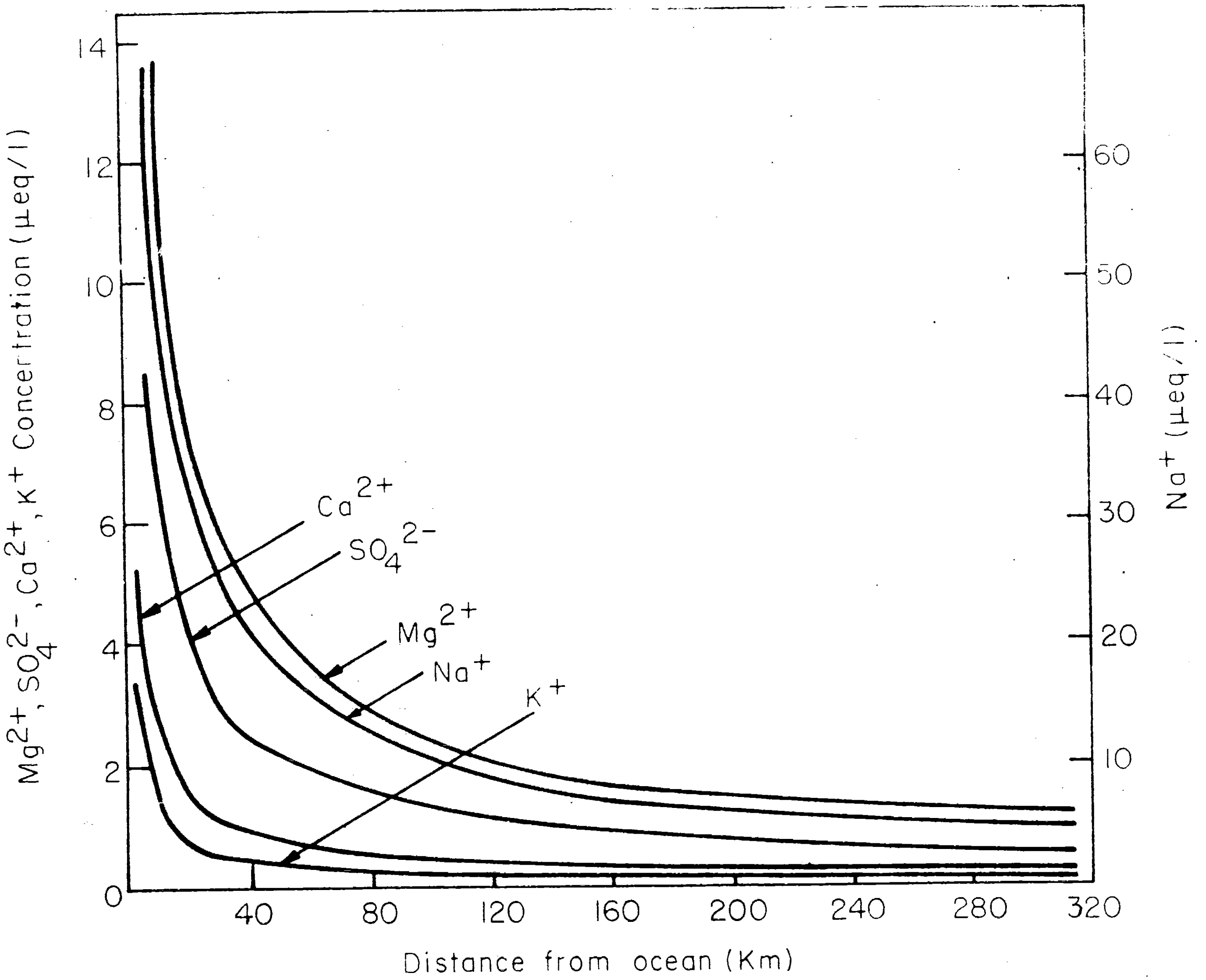


Fig. 10. Predicted contribution by sea-salts to ionic concentrations of wet precipitation as a function of distance from ocean (based on chloride ratio).

Similar calculations of ion ratios relative to specific elements uniquely derived from known sources, allows prediction of quantities of different elements from soil-dust or certain other air-pollution sources. For example, silica may be a good indicator for soil-derived, air-and rain-pollutants, whereas lead may indicate pollutants from automobile-exhaust emissions. Such indicator techniques have been used to some extent in air-pollution studies (John et al, 1973; Miller at al., 1971), but only to a very limited extent in rain-pollution studies.

### 9.10 Nitrogen:sulfur ratios:

Nitrogen:sulfur ratios were calculated for both wet and dry samples, using mean data from Tables 2, 5 and 6. For ionic concentrations data of wet samples, $[SO_4^{2-}]$ values were also "corrected" for sea-salt contributions; no corrections were made for $[NO_3^-]$, as the $[NO_3^-]$ in seawater is negligible. In most cases shown by the results of these calculations (Table 8), amounts of nitrogen exceeded those of sulfur at all sites with few exceptions, e.g., Tahoe City. Further interpretation of these ratios is beyond the scope of this report.

TABLE 8. NITROGEN:SULFUR RATIOS

| SITE | *RATIO 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| BE | 1.34 | 11.23 | 1.75 | 1.92 | 2.26 | 2.44 |
| TC | 0.50 | 1.44 | 1.05 | 1.03 | 0.48 | 0.50 |
| KE | 3.14 | 5.85 | 3.03 | 4.15 | 3.11 | 4.86 |
| CH | 2.31 | 2.93 | 2.58 | 2.91 | 6.51 | 5.39 |
| SJ | 1.64 | 4.32 | 1.20 | 2.84 | 2.59 | 2.74 |
| HO | 1.79 | $\alpha$ | 2.20 | 2.46 | 1.63 | 2.61 |
| DA | 1.19 | 2.05 | 1.88 | 3.48 | 0.70 | 2.60 |
| NA | 1.40 | 5.60 | 1.49 | 1.87 | 6.05 | 7.36 |

*1. Wet concentrations, $[NO_3^-]:[SO_4^{2-}]$, uncorrected for sea-salts.

2. Wet concentrations, $[NO_3^-]:[SO_4^{2-}]$, corrected for sea-salts.

3. Wet deposition, $NO_3^-:SO_4^{2-}$, uncorrected for sea-salts.

4. Wet deposition, Total-N:Total-S, uncorrected for sea-salts.

5. Dry deposition, $NO_3^-:SO_4^{2-}$, uncorrected for sea-salts.

6. Dry deposition, Total-N:Total-S, uncorrected for sea-salts.

## 10. REFERENCES

Barrett, E., and G. Brodin. 1955. The acidity of Scandinavian precipitation. Tellus 7:251-257.

Bertolacini, R. J., and J. E. Barney II. 1958. Ultraviolet spectrophotometric determination of sulfate, chloride and fluoride with chloranilic acid. Anal. Chem. 30:202-205.

Bush, D. S. 1979. Mechanisms controlling temporal variation in throughfall chemistry. M.S. Thesis, University of California, Berkeley.

Cadle, R. D. 1972. Formation and chemical reactions of atmospheric particles. J. Colloid Interface Sci. 39:25-31.

Cogbill, C. V., and G. E. Likens. 1974. Acid precipitation in the northeastern United States. Water Resour. Res. 10:1133-1137.

Dochinger, L. S., and T. A. Seliga (Ed.). 1976. Proc. of the 1st Int. Symp. on Acid Precipitation and the Forest Ecosystem. Northeast. For. Exp. Stn., Upper Darby, Pa. USDA For. Serv. Gen Tech. Rep. NE-23. 1074 p.

D.O.E. (Department of Energy). 1979. The chemical composition of precipitation and dry atmospheric deposition. Enviro. Measurements Laboratory, D.O.E., New York. IN Publ. EML-356. pp. I-251 to I-350.

E.P.A. (Environmental Protection Agency). 1979. Acid Rain Research Summary U.S.E.P.A., Office of Research and Development, EPA-600/8-79-028, Oct. 1979, 23 p.

E.P.R.I. (Electric Power Research Institute). 1979. Ecological effects of acid precipitation. Report on Workshops at Cally Hotel, Gatehouse-of-Fleet, Galloway, U.K., 4-7 Sept. 1978.

Fennelly, P. F. 1976. The origin and influence of airborne particulates. Am. Sci. 64:46-56.

Florence, T. M., and Y. J. Farrar. 1971. Spectrophotometric determination of chloride at the parts-per-billon level by the mercury (II) thiocyanate method. Anal. Chim. Acta 54:373-377.

Galloway, J. N., and E. B. Cowling. 1978. The effects of precipitation on aquatic and terrestrial ecosystems: a proposed precipitation chemistry network. Air Pollution Control Assoc. 28:229-235.

Galloway, J. N., and G. E. Likens. 1976. Calibration of collection procedures for the determination of precipitation chemistry. pp. 137-156. IN Proc. 1st Intern. Conf. on Acid Precipitation and the Forest Ecosystem. U.S.D.A. For. Serv. Gen Tech. Rep N.E.-23.

Glass, N. R., G. E. Likens, and L. S. Dochinger. 1978. The ecological effects of atmospheric deposition. EPA, ORD Decision Series, Energy/Environment III, EPA-600/9-78-022, Oct. 1978, p. 113-119.

Granat, L. 1972. On the relation between pH and the chemical composition in atmospheric precipitation. Tellus 24:550-560.

Hart, G. E., A. R. Southard, and J. S. Williams. 1973. Influence of vegetation and substrate on streamwater chemistry in northern Utah. Office Water Resour. Res. U.S.D.I., Project No. A-007-Utah. 53 p.

Isaac, R. A., and J. D. Kerber. 1971. Atomic absorption and flame photometry: techniques and uses in soil, plant and water analysis. p. 17-38. IN L. M. Walsh (Ed.), Instrumental methods for analysis of soils and plant tissues. Soil Sci. Soc. Am., Madison, Wis. 222 p.

John, W., R. Kaifer, K. Rahn, and J. J. Wesolowski. 1973. Trace element concentrations in aerosols from the San Francisco Bay area. Atmos. Environ. 7:107-117.

Junge, C. E., and W. T. Werby. 1958. The concentration of chloride, sodium, potassium, calcium and sulfate in rainwater over the U.S. J. Meteor. 15:417-425.

Kennedy, V., G. W. Zellweger, and R. J. Avanzino. 1976. Composition of selected rain samples collected at Menlo Park, California, in 1971. U.S. Geol. Surv. Open File Rep. 76-852. U.S. Geol., Surv., Menlo Park, Calif. 7 p.

Kennedy, V. C., G. W. Zellweger, and R. J. Avanzino. 1979. Variation of rain chemistry during storms at two sites in northern California. Water Resourc. Res. 15:687-702.

Larson, T. V., R. J. Charlson, E. J. Knudson, G. D. Christian, and H. Harrison. 1976. The influence of a sulfur dioxide point source on the rain chemistry of a single storm in the Puget Sound region. Water Air Soil Pollut. 4:319-328.

Likens, G. E. 1976. Acid precipitation. Chem. Eng. News 54:29-44.

Likens, G. E., R. F. Wright, J. N. Galloway, and T. J. Butler. 1979. Acid Rain. Sci. Am. 241:43-51.

Liljestrand, H. M., and J. J. Morgan. 1978. Chemical composition of acid precipitation in Pasadena, Calif. Enviro. Sci. & Tech. 12:1271-1273.

Martin, D. F. 1967. Coordination chemistry of the oceans. pp. 255-269. IN R. F. Gould (Ed.), Equilibrium concepts in natural water systems. Advances in Chemistry Series. Am. Chem. Soc. Publ. 344 p.

McColl, J. G. 1978. Atmospheric precipitation in northern California; its chemistry and some effects. IN Proc. Conf. at Univ. California, Davis, 10-9-78, on "Air pollution effects on vegetation in northern California", sponsored by the California Air Resources Board.

McColl, J. G., and D. S. Bush. 1978. Precipitation and throughfall chemistry in the San Francisco Bay Area. J. Enviro. Qual. 7:352-357.

McCormac, B. (Ed.). 1976, 1977. Proc. of 1st Int. Symp. on Acid Precipitation and the Forest Ecosystem. Water Air Soil Pollut. 6:135-514; 7:279-550; 8:31-129.

McGill, D. A. 1973. Light and nutrients in the Indian Ocean. pp. 53-102. IN B. Zeitzschel (Ed.). The Biology of the Indian Ocean. Springer-Verlag, Berlin. 549 p.

Miller, M. S., S. K. Friedlander, and G. M. Hidy. 1972. A chemical element balance for the Pasadena aerosol. J. Colloid & Interf. Sci. 39:165-176.

N.A.D.P. (National Atmospheric Deposition Program). 1978. A national program for assessing the problem of atmospheric deposition (acid rain). A report to the Council on Environmental Quality. N.A.D.P. Colorado State Univ., Fort Collins. 97 p.

Nie, H. N., C. H. Hall, J. G. Jenkins, K. Steinbrenner, and D. H. Bent. 1975. Statistical package for the social sciences. 2nd Ed. McGraw-Hill, NY. 675 p.

Niemann, B. L., J. Root, N. Van Z. Walenburg, and A. L. Mahan. 1979. An integrated monitoring network for acid deposition: a proposed strategy. Interim Reports, U.S. Enviro. Protection Agency. R-023-EPA-79. Teknekron Research Inc., Berkeley, CA 235 p.

Sandberg, J. S., D. A. Levaggi, R. E. DeMandel, and W. Siu. 1976. Sulfate and nitrate particulates as related to $SO_2$ and $NO_2$ gases and emissions. J. Air Pollut. Control Assoc. 26:559-564.

Schlesinger, W. H., and M. M. Hasey. 1979. The nutrient content of precipitation dry fallout and intercepted aerosols in the chaparral of southern California. Am. Midl. Nat. (in press).

Solorzano, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnol. Oceanogr. 14:799-801.

U.S.D.I.-U.S.G.S. (U.S. Dept. of Interior - U.S. Geological Survey). 1978. Research and monitoring of precipitation chemistry in the United States - present status and future needs. Interagency Advisory Committee on Water Data, U.S. Dept. of Interior, Geol. Survey, Office of Water Data Coordination, Reston, VA. 64 p.

Whitehead, H. C., and J. H. Feth. 1964. Chemical composition of rain, dry fallout and bulk precipitation at Menlo Park, CA., 1957-1959. J. Geophys. Res. 69:3319-3333.

## APPENDIX 11.1

## Detailed Descriptions of Study Sites

Berkeley:

The Berkeley site was on the roof of the Space Sciences Building, University campus (lat. 37°53', long. 22°15', elevation 400 m) on the east side of San Francisco Bay. The principal investigator (Dr. John G. McColl) was in charge of this station, assisted by Mr. Douglas Bush (graduate research assistant) and Dr. Larry Monette (post-doctoral research associate).

Precipitation is effected by proximity of Berkeley to the ocean, as well as being in a "pollution source" area. Berkeley is in the general "sulfate pollution" area, as defined by the Bay Area Air Pollution Control District (Sandberg et al., 1976), that extends from the Golden Gate through the heavy industry areas of Richmond and Pittsburg. Berkeley also has air pollution by $NO_x$ compounds, especially if winds bring such compounds from the "nitrogen pollution" area in the S.E. of the San Francisco Bay, extending from San Jose north to about Redwood City and N.E. through Fremont to Livermore.

Long-term meterological records exist for Berkeley, and air pollution is monitored in a number of nearby Bay Area locations. Mean annual rainfall is 56.80 cm (Jan. 11.70 cm; July 0.02 cm). Mean annual temperature is 13.9°C (Jan. 9.1°C; July 16.4°C). Summer fogs are frequent.

Davis:

The Davis site was on the University campus within the agricultural field-plots (lat. 38°32'N, long. 121°46'W, elevation 18 m). Dr. Robert L. Leonard, was in charge of this station although day-to-day operations of the station was conducted by George Malyj, a graduate biochemist at U.C. Davis.

The Davis campus is an excellent sampling site downwind of the San Francisco Bay Area. Prevailing winds during cyclonic storms often flow in SW-NE direction carrying air-borne substances directly from the Bay Area into the Sacramento Valley. Long-term meteorological records exist for Davis including precipitation and wind parameters. Average annual temperature is 60°F (Jan. 45.8°F; July 73.2°F), and average annual precipitation is 18.0" (Jan. 3.72"; July, none).

Tahoe City:

The Tahoe Research Group (Division of Environmental Science, U.C. Davis) maintains a laboratory on the northwest shore of Lake Tahoe (lat. 39°08'N, long. 120°10'W, elevation 2,076 m) at this precipitation sampling site. Precipitation is primarily snow in a normal year. The precipitation was sampled by Dr. Robert L. Leonard, Research Ecologist with the U.C. Davis, Tahoe Research Group.

The Lake Tahoe Basin is well-timbered; its scenic, recreational, watershed and timber characteristics are of world-wide fame. The west shore of Lake Tahoe is subject to strong air movements in any direction in any season. However, the major prevailing winds are from the southwest and carry air-borne substances from the Bay Area and Sacramento Valley into the Tahoe Basin during both dry periods and cyclonic storms. Infrequent continental storms with predominately north and northeast winds would be expected to have little influence from urban-industrial areas. Summer rains are often of tropical origin with SE winds. Mean annual precipitation is 33.13" (6.78" mean in Jan., 0.25" in July), and mean annual temperature is 43.2°F (28.2°F mean in Jan., 70.1°F in July).

Challenge:

This site is located in the U.S. Forest Service Experimental Forest on the roof of the Ranger Station at Challenge. This experimental forest is in one of the most productive forest areas in the state, and is located in the mixed-conifer zone on the western slope of the Sierra Nevada in Yuba County (lat. 121°21'N, long. 39°39'W, elevation 790 m). Annual precipitation is 173 cm with 90% falling between October and May. Mean annual temperature is 12°C (Jan. 5°C; July 24°C). Nearly all precipitation is rain.

Meteorological data are recorded at Challenge, and the principal investigator (Dr. J. G. McColl) has cooperative projects related to effects of forest-management practices with the U.S. Forest and Range Experiment Station at this location. Mr. Mike Heath (U.S. Forest Service) made the precipitation collections.

Napa:

This site was established 16 km NE of Napa, in the Wooden Valley and operated by Mr. Max Linn, owner of the property and an employee of the John Muir Institute in Napa. The site is just east of the eastern rim of the Napa Valley within 1 km of Rte. 121 (lat. 38°20', long. 122°12', elevation 280 m).

Wooden Valley is beyond direct influence of the Bay Area except under conditions of northerly air flow. Air quality is thought to be influenced primarily by oceanic air and agricultural lands in coastal areas and the Napa Valley to the west. Agriculture (including vineyards) and oak-woodland predominate. Mean annual rainfall is 24", with none in summer.

Kearney:

This site (lat. 36°11', long. 119°43', elevation 100 m) was located at the Kearney Agricultural Field Station of the University of California. The nearest city is Fresno. This site is representative of the San Joaquin Valley agricultural area. Collections were made by Dr. Robert F. Brewer of the University of California. Average temperatures are 36.7°F in January and 98.6°F in July. Average annual precipitation is 11.14", with none in July and 2.03" in January.

San Jose:

This location (lat. 37°21', long. 121°54', elevation 22 m) is in the "pollution source" area of the San Francisco Bay Area. Air pollution by $NO_x$ compounds is often high in this industrial/residential area.

Meteorological and air-pollution data is regularly collected at this site. Mean annual rainfall is 13.2", occurring in the period November - May, with none in summer and 2.7" in January. Temperatures average 40°F in June and 70°F in July, with an average annual temperature of 58°F.

The specific study site was located on a roof together with existing meteorological equipment on the campus of the San Jose State University. Collections were made by Susan Fisher and Dr. Jindra K. Goodman of the Dept. of Meteorology.

Hopland:

This site (lat. 39°00', long. 123°03', elevation 165 m), was located at the Hopland Field Station, an experimental station primarily concerned with range management, of the University of California. Dr. Milton Jones, of the U.C. Davis campus and the field station, made the precipitation collections.

The site is located well away from pollution-sources, in primarily oak-woodland that is very characteristic of the coast range at this latitude in California. Average annual rainfall is 35". The average summer and fall temperatures are in the 70's, and only traces of rain occur between June and September. Fog occurs frequently in the valley during late fall, winter, and early spring, and occassionally during the summer.

# APPENDIX 11.2

## Sample Collection Procedures

### Sample Identification

A. Each sample collected will be identified with a sample number which will consist of 3 parts:

1. Site Identification Code
2. Data Sample Collection
3. "Wet" or "Dry" Sample Designation

B. Site Identification Codes

| Collection Site | Code |
|---|---|
| Berkeley | BE |
| Challenge | CH |
| Davis | DA |
| Kearney | KE |
| Hopland | HO |
| Napa | NA |
| San Jose | SJ |
| Tahoe City | TC |

Example: "NA 110478W" would signify from Napa collected on Nov. 4, 1978, a wet sample.

C. If sequential sampling of a storm, or more than one sample collection on a given day, or separation of precipitation forms (snow, rain) is desired, then an additional digit will be added to the sample I.D. number.

Example: "CH 010678W-1" would signify from Challenge collected on

Jan. 6, 1978, a wet sample which is the first sample of a storm or a separation of precipitation forms etc.

"CH 010678W-2" would be the second sample in the series.

When the additional digit is added to the standard I.D. number, the reason for using the designation should be included on the "Field Sheet" under comments.

II. Sample Collection

Precipitation samples will be collected on a storm by storm basis. When precipitation (storm) ends, mix by swirling the contents of the wet pail and transfer via a polyethylene (PE) funnel to 500 ml PE sample bottles which should be properly labeled with the sample I.D. number. The volume of the wet sample can be determined by measuring the water level in the 500 ml sample bottle. One centimeter is equivalent to 36 ml of precipitation.

The dry precipitation sample can be taken the same time as the wet sample. Add 500 ml of distilled water to the dry pail. Secure the lid on the pail, shake the pail for approximately 1 minute, then transfer via a PE funnel to a 500 ml PE sample bottle properly labeled.

Precipitation samples and equipment should be handled carefully to prevent contamination. The concentration of ions in precipitation are very low and thus the slightest amount of contamination will result in grossly inaccurate chemical analysis. A fingerprint on the inside of a funnel or sample pail will add more sodium than that contained in the entire sample.

Rinse both wet and dry pails with distilled water, then replace on collection platform.

## III. pH Measurements

The pH of both the wet and dry samples are determined on a 20 ml aliquot of sample taken from the PE sample bottle. The pH meter should be standardized according to the instruction manual using a pH buffer of 4.00. After calibration the pH reading of a 7.00 buffer should be 7.0 ± 0.1. After the combination pH electrode is removed from the buffer, it should be thoroughly rinsed; using the squeeze bottle rinse with 250 ml distilled water. Dry the electrode with a Kimwipe, then measure the pH of the precipitation sample. Record the pH value of the Field Sheet.

Discard the 20 ml aliquot - do not pour back into the sample bottle.

## IV. Field Sheets

These sheets are to be completed in duplicate with the original copy sent along with the corresponding sample to Berkeley and the copy retained at the collection site. The time precipitation started and stopped should be reported (recording rain gauge if available). For dry precipitation samples it is not necessary to record times or durations as these can be determined from start/stop precipitation times.

## V. Shipment and Storage of Samples

Samples were shipped in 500 ml polyethyelene bottles filled to capacity, packed in styrofoam in card-board boxes, and shipped immediately by United Parcel Service (U.P.S.). The time between field sampling and receipt of sample in the laboratory was typically 2 to 3 days (see Appendix 11.14). The time between receipt of sample and subsequent chemical analysis varied with the particular analysis, but ranged between about 1-30 days. Samples were stored at $3^{0}$C in the dark during this storage time; no additives or preservatives were added to the samples at any time during shipping or storage. Interactions between sample solutions and storage bottles or ambient gases and potential losses of volatiles from the solutions were not studied specifically, but storage in new, completely-filled bottles, in the dark at $3^{O}C$ was the most reasonable way to minimize such effects.

## APPENDIX 11.3

## Chemical Digestion and Determination of Cations in Precipitation (Wet/Dry)

I. Equipment and Chemicals

(1) Aluminum Block heater with 25 mm diam.holes for Taylor tubes.

(2) Concentrated Nitric Acid ($HNO_3$) - Mercury (Hg) grade.

(3) Hydrogen Peroxide ($H_2O_2$) - 30% analytical reagent grade.

(4) Cesium (Cs)/Lanthanium (La) stock solution: Weigh 3.958 grams CsCl and 4.178 grams $LaCl_3 \cdot 7H_2O$ in a 500-ml volumetric flask and dilute to volume with distilled-deionized water.

(5) Taylor test tubes.

II Procedure

(1) Add 25.0 ml of sample to a Taylor tube, with paraffin on tops.

(2) Add 0.2 ml concentrated $HNO_3$.

(3) Add 0.2 ml $H_2O_2$ (30%).

(4) Place tubes in block heater and digest sample at 95-97°C until volume is less than 5 ml, for about 4 hours.

(5) Cool slightly than add 5 ml distilled-deionized water and 0.1 ml concentrated $HNO_3$.

(6) Heat for 5-10 minutes at 95-97°C, mix, and allow to cool to room temperature.

(7) Add 2.0 ml of Cs/La stock solution then dilute to 25 ml with distilled-deionized water.

(8) Mix thoroughly then transfer to plastic vials for analysis by Atomic Absoprtion.*

(9) Run one blank for every six (6) samples using distilled-deionized water. These blanks should be treated the same as samples.

III. Notes

(1) All glassware, plastic vials, etc., should be acid washed prior to use. Soak in 1 N $HNO_3$ overnight, rinse 3 times with distilled water then 3 times with distilled-deionized water. Dry in oven at 50°C.

* IV. General reference re Atomic Absorption Spectrophotometry:

Issac, R. A., and J. D. Kerber. 1971. Atomic absorption and flame photometry: techniques and uses in soil, plant, and water analysis. p. 17-38. In: L. M. Walsh (Ed.), Instrumental methods for analysis of soils and plant tissues. Soil Sci. Soc. Am., Madison, Wis. 222 p.

## APPENDIX 11.4

## Determination of Chloride in Precipitation

I. Reagents:

(a) Ferric Nitrate. Dissolve 15.1 grams of $Fe(NO_3)_3 \cdot 9H_2O$ in 45 ml of 70% Perchloric Acid and dilute to 100 ml with distilled-deionized water. The Ferric Nitrate/Perchloric Acid mixture will be cloudy but will clear with the addition of water.

(b) Mercury (II) Thiocyanate. Saturated solution in ethanol. This will be approximately 0.5 grams $Hg(SCN)_2$ in 100 ml of 95% Ethanol.

(c) Chloride Standard. Dissolve 824.1 mg Sodium Chloride (dried at 140°C) into 1 liter of distilled-deionized water. 1 ml = 500 μg Cl. Prepare 1-ppm Cl standard using appropriate dilutions.

II. Equipment:

(a) Spectrophotometer for absorbance measurement at 460 nm with 5-cm cell.

(b) Test tubes - pyrex, 25 mm x 150 mm.

III. Procedure:

(a) Pipette a 20-ml aliquot of sample, containing less than 50 μg of chloride, into a test tube. Add 2.00 ml Ferric Nitrate reagent and 2.00 ml mercurric thiocyanate reagent and then mix.

(b) Measure the absorbance against a reagent blank at 460 nm after 5 minutes using a 5-cm cell.

(c) Prepare a calibration curve by pipetting 0, 1, 2, 5, 10, and 20 ml of a 1-ppm Chloride standard into test tubes and develop color as described above. Use distilled-deionized water to bring the final volume to 24 ml.

IV. Notes:

(a) Use appropriate, safe techniques when using Perchloric Acid and Mercury.

(b) Do not excessively mix the sample with the reagents as this will result in high and erratic absorbance readings. Also do not mix when filling spectrometer cell.

(c) A sample run should be completed in 1-2 hours to avoid errors from unstable color.

(d) Use only low chloride (< 2.5 ppm) Ferric Nitrate to prepare the Ferric Nitrate reagent. Normal Analytical Reagent grade will have excessively high chloride contamination.

V. Reference:

Florence, T. M., and Yvonne J. Farrar. 1971. Spectrophotometric determination of chloride at the parts-per-billon level by the mercury (II) thiocyanate method. Anal. Chim. Acta. 54:373-377.

## APPENDIX 11.5

## Determination of Sulfate in Precipitation

I. Reagents:

(1) Buffer solution, pH = 4. Prepare a 0.05 M solution of reagent-grade potassium acid phthalate (KAPH). Dissolve 10.2 g KAPH in one liter distilled-deionized water.

(2) Barium chloranilate.

(3) Ethanol-95% by volume.

(4) Buffer solution plus sulfate spike. Prepare buffer as described only add 80 ml of 100 ppm sulfate prior to diluting to one liter.

II. Equipment:

(1) Spectrophotometer for absorbance measurement at 330 nm with one-cm cell.

(2) Dowex cation exchange column. Regenerate column after passing 100 samples through column. Pass 25 ml of 2 N HCl through column then rinse with 50 ml distilled water.

(3) Constant temperature bath.

III. Procedure:

(1) Pass 25 ml of sample through a cation exchange column. Discard this rinse. Next pass 50-60 ml of sample through the column collecting the effluent in a 100-ml plastic bottle.

(2) Pipet 40 ml of sample into a 125-m erlenmeyer flask.

(3) Add 10 ml of KAPH buffer and sulfete spike to each flask.

(4) Add 50 ml of Ethanol (95%) to each flask and swirl until thoroughly mixed.

(5) Weigh 0.20 ± 0.02 g of Barium chloranilate into each flask and again swirl until thoroughly mixed.

(6) Place the flasks in a constant temperature bath set at 37°C for two hours. Swirl the flasks several times during this period.

(7) Let the flasks stand undisturbed for approximately 1/2 hour to settle out suspended material.

(8) Slowly and carefully decant about 20 ml of clear solution into a 9 dram plastic vial.

(9) Measure the absorbance of the sample solutions in 1-cm cells at 330 nm against a blank treated in the same manner.

(10) The same procedure is used for preparation of a standard curve except the KAPH Buffer without sulfate is used. An appropriate standard curve should include 2.0, 2.5, and 3.0 ppm solutions.

IV. Notes:

(1) Sulfate standards and that used to prepare the Buffer solution spike should be prepared from ammonium sulfate (not sodium sulfate) and should also be passed through a cation exchange column to remove interfering cations.

(2) The color that is developed is stable for at least 4 days and probably longer.

(3) All glassware (and plastic) should be cleaned with 1:1 Nitric Acid then rinsed thoroughly with distilled water.

V. Reference:

Bertolacini, R. J. and J. E. Barney II. 1958. Ultraviolet spectrophotometric determination of sulfate, chloride, and fluoride with chloranilic acid. Analytical Chemistry 30:202-205.

# APPENDIX 11.6

## Nitrate Determination - Hydrazine Reduction

Introduction:

This method substitutes a hydrazine reduction of nitrate to nitrite for the Cd column reduction normally used ("Standard Procedures" D. K. Fujita, 1971). Since the hydrazine can be added as an aqueous reagent, several samples can be analyzed simultaneously thus avoiding the timing problems of the column method.

Reagents:

| | | |
|---|---|---|
| 1. Stock hydrazine sulfate | | |
| Hydrazine sulfate | 1.20 g | |
| QDW (quartz dist. water) | 250 ml | |
| 2. Copper solution | | |
| $CuSO_4 \cdot 5H_2O$ | 0.040 g | } Prepare fresh daily |
| QDW | 100 ml | |
| 3. Reducing solution | | |
| Stock hydrazine | 25 ml | } Prepare fresh daily |
| Copper solution | 5 ml | |
| QDW | to 50 ml | |
| 4. 1 N NaOH | | |
| NaOH | 40 g | |
| QDW | 1000 ml | |
| 5. Sulfanilamide | | |
| Sulfanilamide | 5 g | } Remains stable indefinitely |
| Conc. HCl (12 M) | 50 ml | |
| QDW | to 5000 ml | |
| 6. Napthlethylenediamine dehydrochloride (NED) | | |
| NED | 0.5 g | } Store in dark, refigerated |
| QDW | 500 ml | |
| 7. Phenate buffer | | |
| Phenol | 1.8 g | |
| 1 N NaOH | 16 ml | |
| QDW | to 100 ml | |

Method:

1. Measure and GF/C filter 50 ml of sample into an Erlynmeyer flask (125 M).
2. Place sample flasks and blanks and standards in a water bath controlled to ± 0.5°C, at a temp. of 37°C, and equilibrate for at least 45 minutes.
3. Without removing flasks from the bath, add 1 ml of reducing solution immediately followed by 2 ml phenate buffer. Swirl each flask.
4. Allow samples to react for exactly 30 min/flask taking into account the order and time of reagent addition.
5. The latter factor is best taken into account by removing the flasks from the bath to a cooling location in the same order and timing interval as in step 3. Cool to room temp. (at least 45 min. depending on ambient lab temp.)
6. Add 2 ml of a 1:1 mixture of sulfanilamide and NED to each flask.
7. Allow to develop color for 20 min. minimum but not longer than 2 hours.
8. Read absorbance at 543 nm.

Note: These reagent concentrations are appropriate for a concentration range of about 1 to 100 ppb (ug/l) $NO_3$-N. We recommend at least three standard concentrations (say 20, 50, 100 ppb) + blanks.

Nitrate Notes:

Prop of Std: (from Lake Tahoe Methods):

-100 ppm N as $KNO_3$

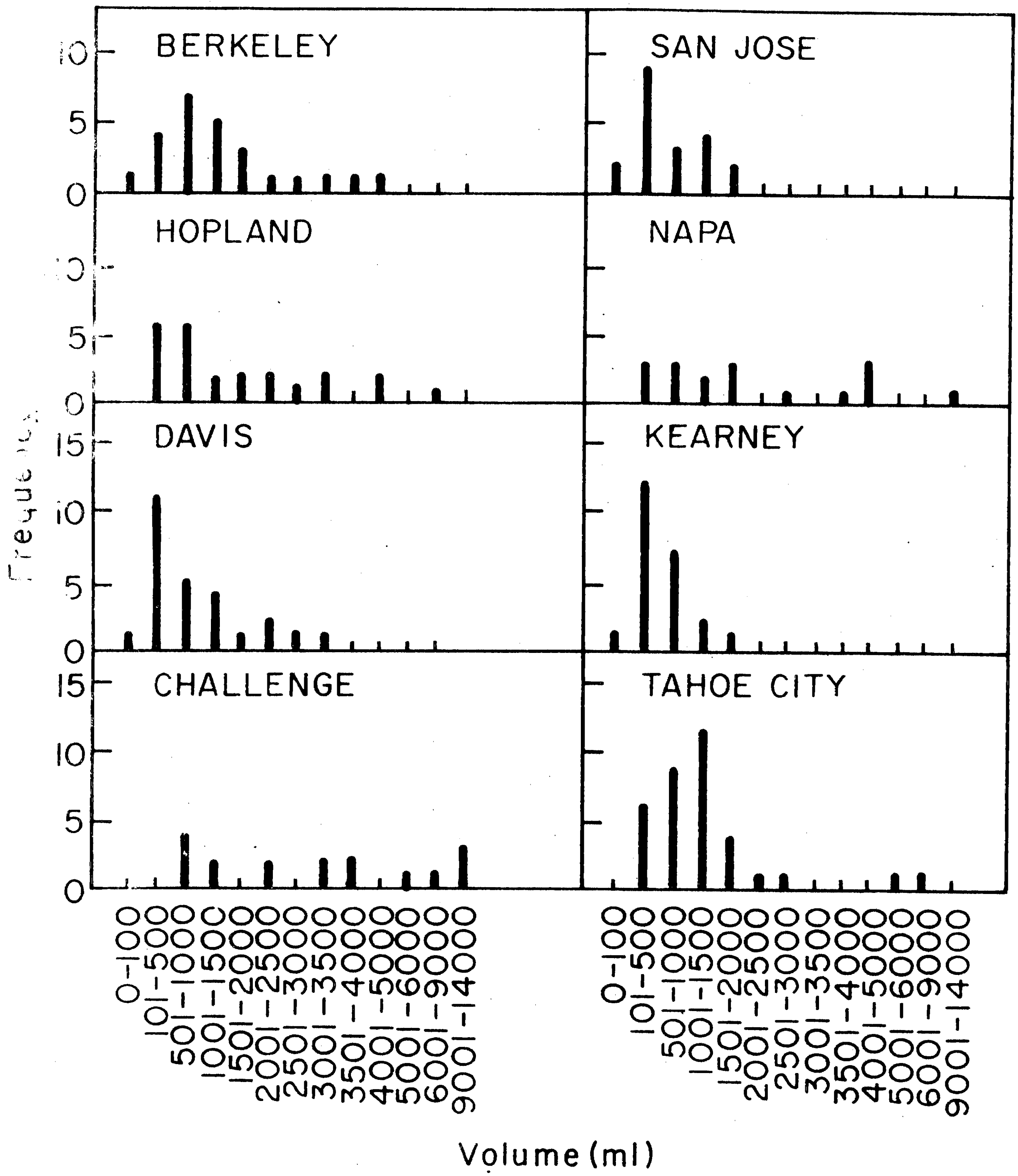
-oven dry AR grade $KNO_3$ C 110-120°C

-weigh out 0.7218 ± 0.00029 - dilute to 1 ℓ.

-store in glass

Discard monthly or more frequently if a yellow-brown coloration develops.

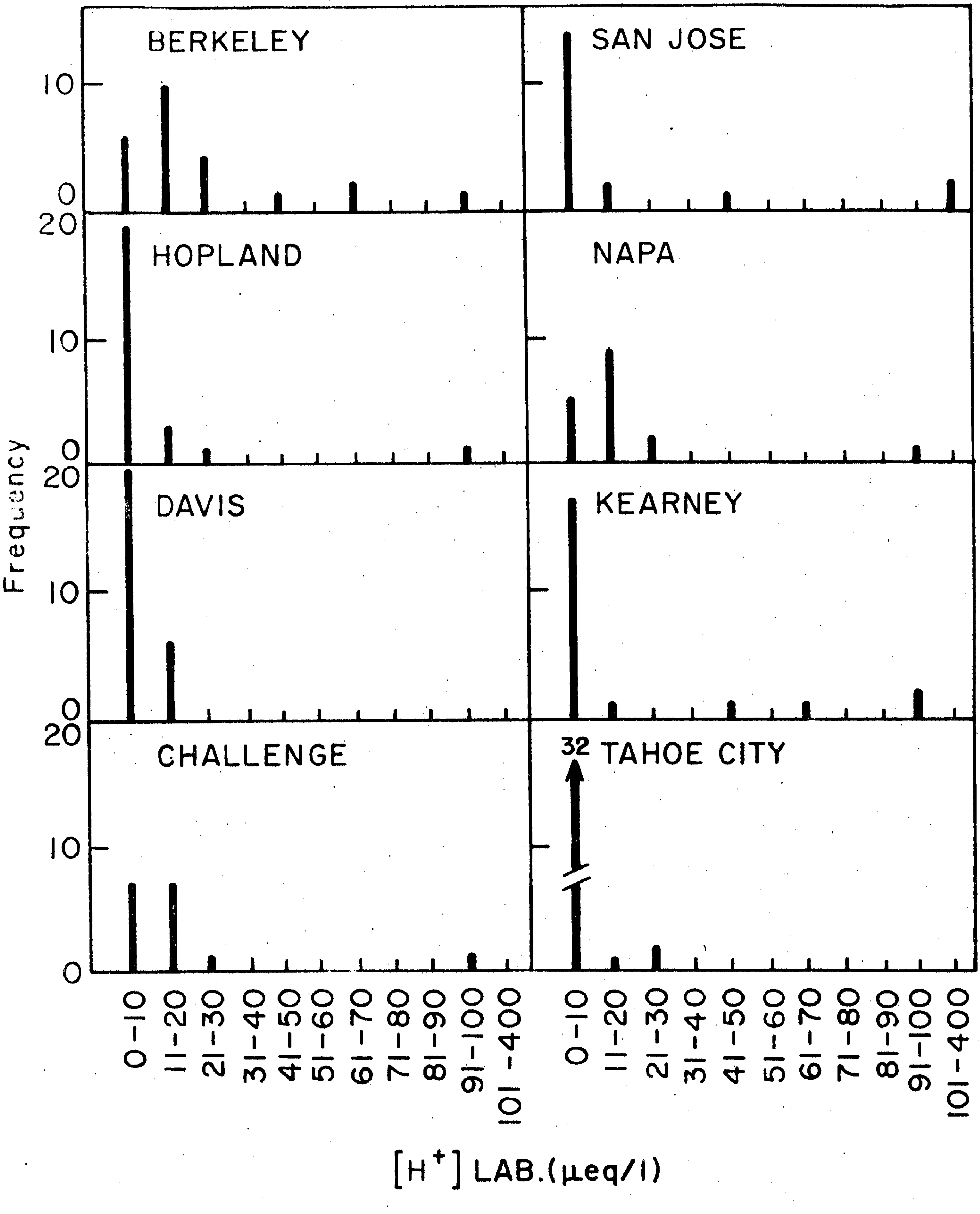
Sulfanilamide remains stable indefinitely in glass or P.E.



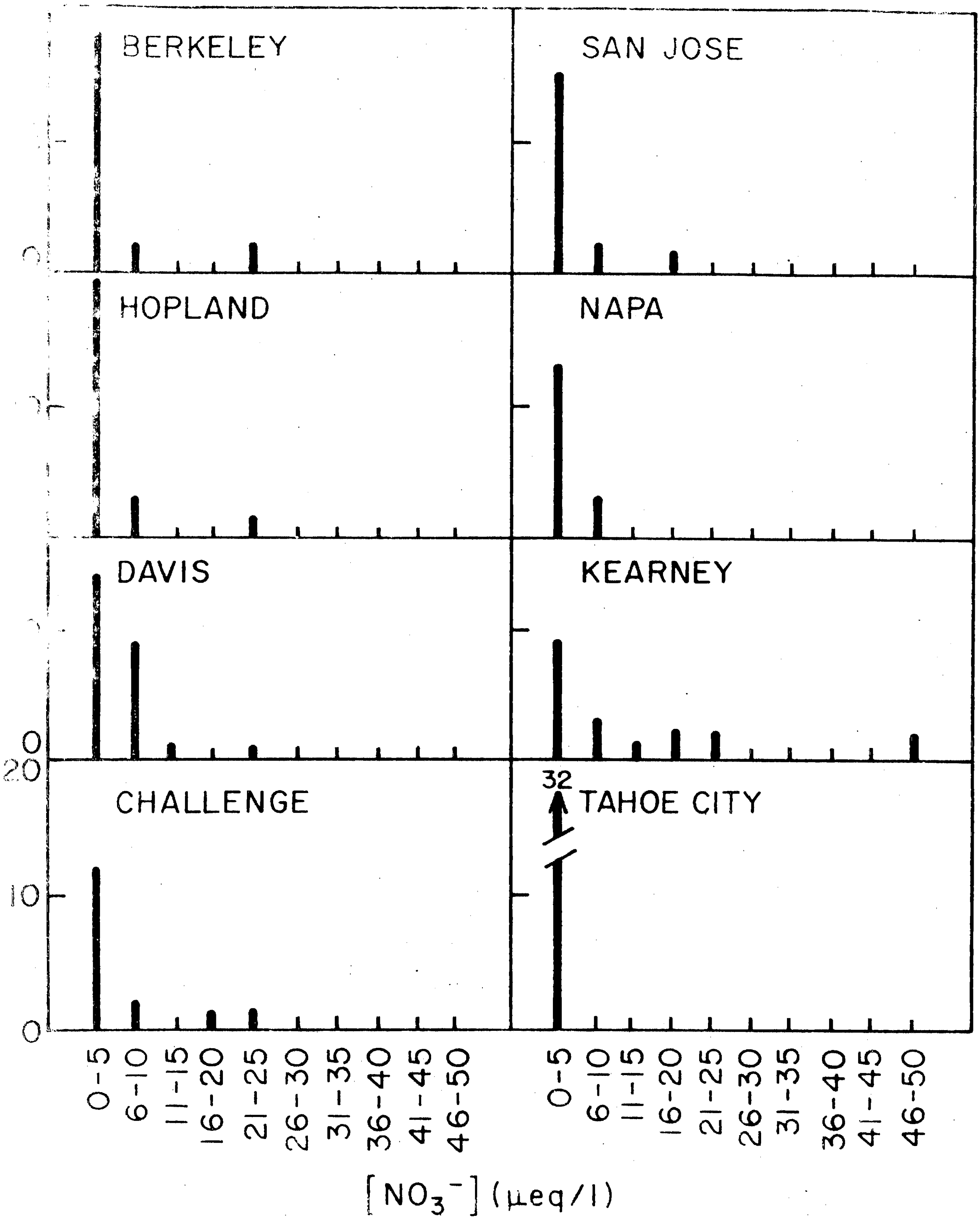
Appendix 11.7. Frequency distributions of storm volume,

$[H^+]_{LAB}$, $[NO_3^-]$, $[SO_4^{2-}]$,

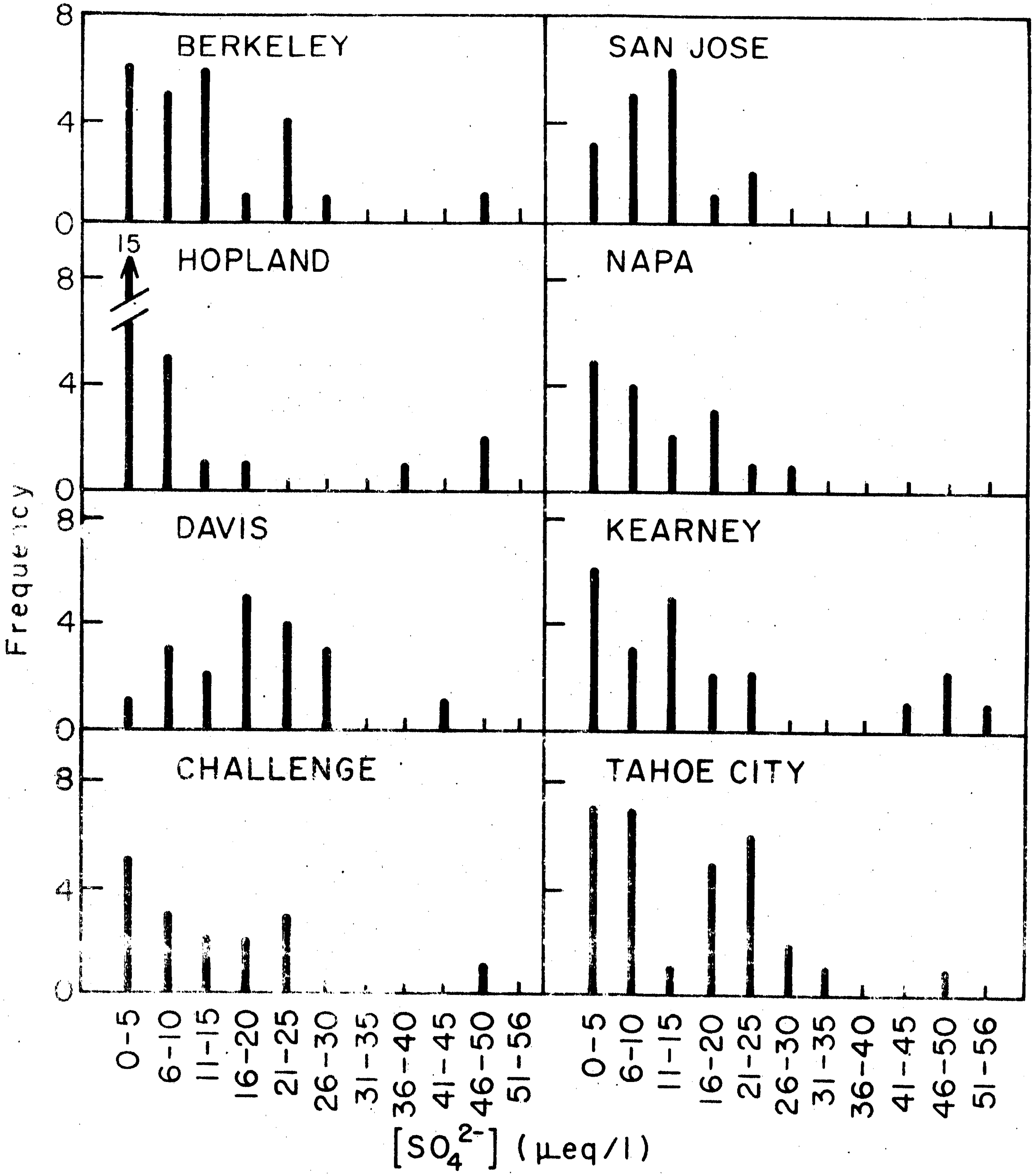
and specific conductance for each site.



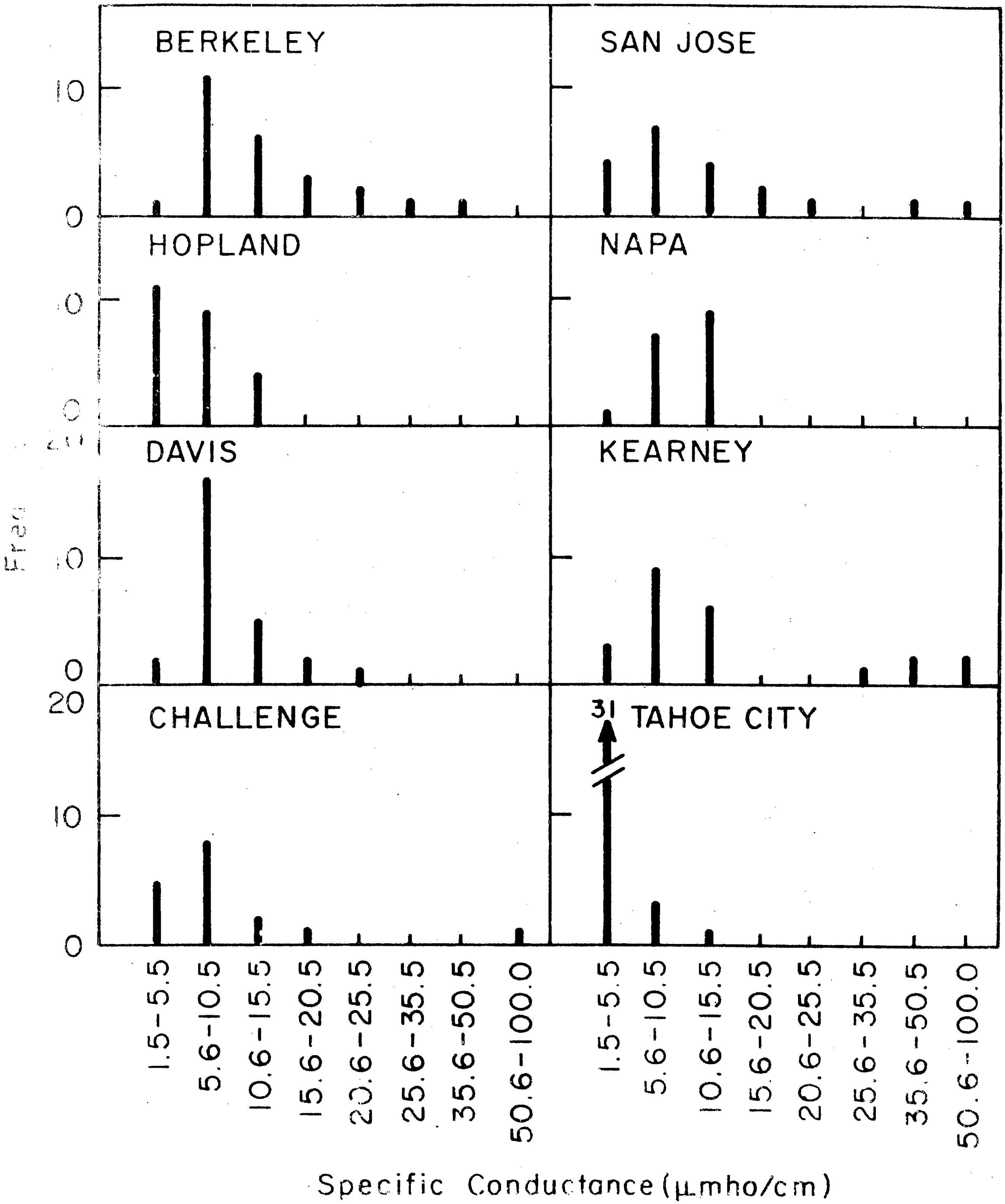
Appendix 11.7. Continued.



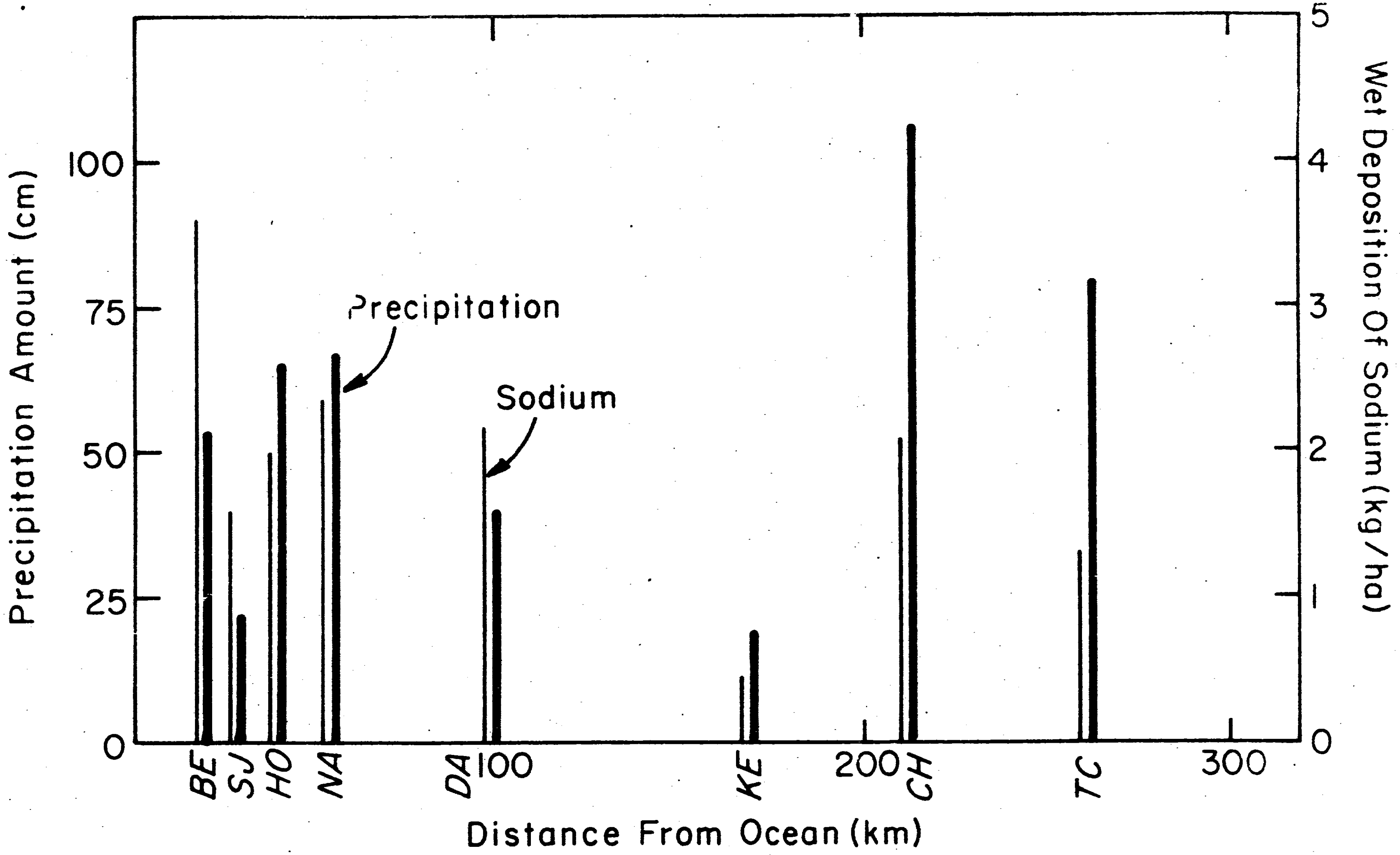
Appendix II. (continued).



Appendix 11.7. Continued.



Appendix II.A continued.



Appendix 11.8. Precipitation amount and wet deposition of sodium as a function of distance from ocean.

# APPENDIX 11.9

Sites grouped in homogenous subsets for ion concentrations and amounts of deposition.

Analyses-of-variance between mean values for sites were performed and F-ratios calculated. Where F-ratios were statistically significant, i.e., $\alpha < 0.05$, multiple-range tests were performed, and least-significant-differences between means determined; grouping of sites into homogenous subsets was then made on this basis. In the following tables, the lower the subset number, the lower the mean value of the subset. Sites are also listed within subsets in order of least to greatest magnitude of means.

## Appendix 11.9.1. Subsets for storm volume and mean ionic concentrations in wet precipitation

| Property | Subset Number | Sites within subset |
|---|---|---|
| Conductivity | 1 | TC HO |
| | 2 | HO DA CH NA |
| | 3 | DA CH NA BE |
| | 4 | CH NA BE SJ KE |
| Volume | 1 | KE SJ DA BE TC |
| | 2 | DA BE TC HO |
| | 3 | BE TC HO NA |
| | 4 | CH |
| $[Na^+]$ | 1 | TC CH HO DA KE NA |
| | 2 | NA SJ |
| | 3 | SJ BE |
| $[K^+]$ | $\alpha > 0.05$ for F-ratio | |
| $[Ca^{2+}]$ | $\alpha > 0.05$ for F-ratio | |
| $[Mg^{2+}]$ | 1 | TC KE HO NA |
| | 2 | KE HO NA DA CH |
| | 3 | NA DA CH BE SJ |
| $[NO_3^-]$ | 1 | TC HO BE SJ NA |
| | 2 | HO BE SJ NA CH DA |
| | 3 | KE |
| $[NH_4^+]$ | 1 | TC BE HO CH |
| | 2 | BE HO CH NA |
| | 3 | CH NA SJ |
| | 4 | DA KE |
| $[Cl^-]$ | 1 | TC CH KE |
| | 2 | CH KE DA HO |
| | 3 | KE DA HO NA |
| | 4 | SJ BE |

| Property | Subset Number | Sites within subset |
|---|---|---|
| $[SO_4^{2-}]$ | | |
| | 1 | HO CH SJ BE NA |
| | 2 | CH SJ BE NA TC KE |
| | 3 | KE DA |
| $[H^+]_{LAB}$ | | |
| | 1 | DA TC HO KE CH NA BE |
| | 2 | BE SJ |
| $[H^+]_{FIELD}$ | | |
| | 1 | CH DA HO KE NA SJ BE |
| | 2 | BE TC |
| $\Sigma$[Anions] | | |
| | 1 | TC CH HO |
| | 2 | CH HO DA KE TC |
| | 3 | BE SJ |
| $\Sigma$[Cations] | | |
| | 1 | TC HO CH |
| | 2 | HO CH NA DA |
| | 3 | NA DA KE BE |
| | 4 | BE SJ |
| $[Fe^{2+}]$ | | |
| | $\alpha > 0.05$ for F-ratio | |
| $[Mn^{2+}]$ | | |
| | $\alpha > 0.05$ for F-ratio | |
| $[Cu^{2+}]$ | | |
| | 1 | KE NA HO TC BE DA |
| | 2 | NA HO TC BE DA CH |
| | 3 | CH SJ |
| $[Zn^{2+}]$ | | |
| | 1 | TC DA HO NA CH KE |
| | 2 | DA HO NA CH KE BE |
| | 3 | SJ |

Appendix 11.9.2 Subsets for mean total-deposition in wet precipitation.

| Property | Subset Number | Sites within subset |
|---|---|---|
| $Na^+$ | | |
| | 1 | KE TC DA |
| | 2 | TC DA HO SJ |
| | 3 | HO SJ CH |
| | 4 | SJ CH NA |
| | 5 | CH NA BE |
| $K^+$ | | |
| | 1 | KE TC DA SJ HO BE |
| | 2 | SJ HO BE NA |
| | 3 | CH |
| $Ca^{2+}$ | | |
| | 1 | KE HO DA TC SJ NA BE |
| | 2 | CH |
| $Mg^{2+}$ | | |
| | 1 | KE TC DA |
| | 2 | DA SJ HO NA |
| | 3 | SJ HO NA BE CH |
| $NO_3^-$ | | |
| | 1 | TC SJ HO BE |
| | 2 | HO BE KE DA |
| | 3 | NA |
| | 4 | CH |
| $NH_4^+$ | | |
| | 1 | TC BE HO DA |
| | 2 | BE HO SJ KE |
| | 3 | KE NA |
| | 4 | NA CH DA |
| $Cl^-$ | | |
| | 1 | TC KE DA |
| | 2 | DA SJ HO CH |
| | 3 | SJ HO CH NA |
| | 4 | NA BE |

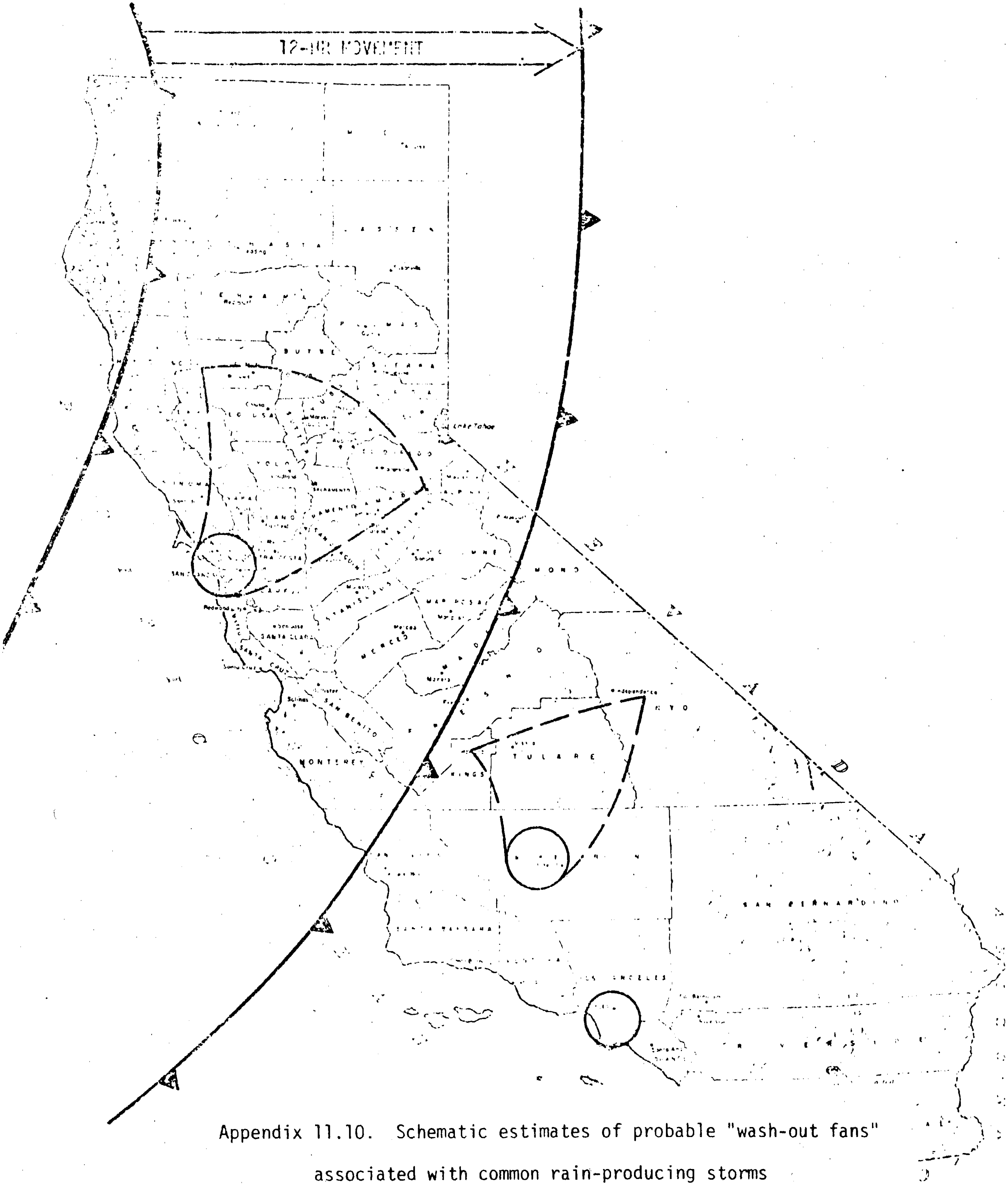
| Property | Subset Number | Sites within subset | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $SO_4^{2-}$ | | | | | | | | |
| | 1 | HO | KE | SJ | BE | TC | | |
| | 2 | TC | CH | DA | | | | |
| | 3 | CH | DA | NA | | | | |
| $H^+_{LAB.}$ | | | | | | | | |
| | 1 | KE | DA | SJ | TC | HO | | |
| | 2 | HO | BE | | | | | |
| | 3 | BE | NA | | | | | |
| | 4 | CH | | | | | | |
| $H^+_{FIELD}$ | | | | | | | | |
| | 1 | KE | DA | SJ | HO | CH | NA | BE |
| | 2 | NA | BE | TC | | | | |
| $Fe^{2+}$ | | | | | | | | |
| | 1 | KE | HO | SJ | DA | BE | TC | NA |
| | 2 | CH | | | | | | |
| $Mn^{2+}$ | | | | | | | | |
| | 1 | SJ | KE | TC | BE | DA | NA | HO |
| | 2 | CH | | | | | | |
| $Cu^{2+}$ | | | | | | | | |
| | 1 | KE | NA | DA | TC | HO | SJ | BE |
| | 2 | CH | | | | | | |
| $Zn^{2+}$ | | | | | | | | |
| | 1 | KE | TC | HO | DA | BE | | |
| | 2 | TC | HO | DA | BE | SJ | | |
| | 3 | HO | DA | BE | SJ | NA | | |
| | 4 | NA | CH | | | | | |

## Appendix 11.9.3. Subsets for mean total-depositions in dry precipitation.

| Property | Subset Number | Sites within subset |
|---|---|---|
| $Na^+$ | 1 | HO CH KE DA NA TC |
| | 2 | DA NA TC SJ |
| | 3 | BE |
| $K^+$ | $\alpha > 0.05$ for F-ratio | |
| $Ca^{2+}$ | 1 | HO TC NA KE CH DA |
| | 2 | NA KE CH DA BE |
| | 3 | SJ |
| $Mg^{2+}$ | 1 | TC HO KE CH NA DA |
| | 2 | NA DA SJ BE |
| $NO_3^-$ | 1 | TC HO CH NA |
| | 2 | HO CH NA BE DA |
| | 3 | NA SJ DA BE KE |
| $NH_4^+$ | 1 | TC CH HO SJ NA |
| | 2 | CH HO SJ NA BE |
| | 3 | NA BE DA |
| | 4 | DA KE |
| $Cl^-$ | 1 | CH KE DA HO TC NA |
| | 2 | NA SJ |
| | 3 | BE |
| $SO_4$ | $\alpha > 0.05$ for F-ratio | |
| $H^+_{LAB}$ | $\alpha > 0.05$ for F-ratio | |
| $H^+_{FIELD}$ | 1 | CH DA KE SJ HO NA BE |
| | 2 | TC |

| Property | Subset Number | Sites within subset |
|---|---|---|
| $Fe^{2+}$ | | |
| | $\alpha > 0.05$ for F-ratio | |
| $Mn^{2+}$ | | |
| | 1 | NA TC KE HO BE SJ DA |
| | 2 | CH |
| $Cu^{2+}$ | | |
| | $\alpha > 0.05$ for F-ratio | |
| $Zn^{2+}$ | | |
| | 1 | NA TC DA CH HO KE |
| | 2 | KE BE |
| | 3 | SJ |

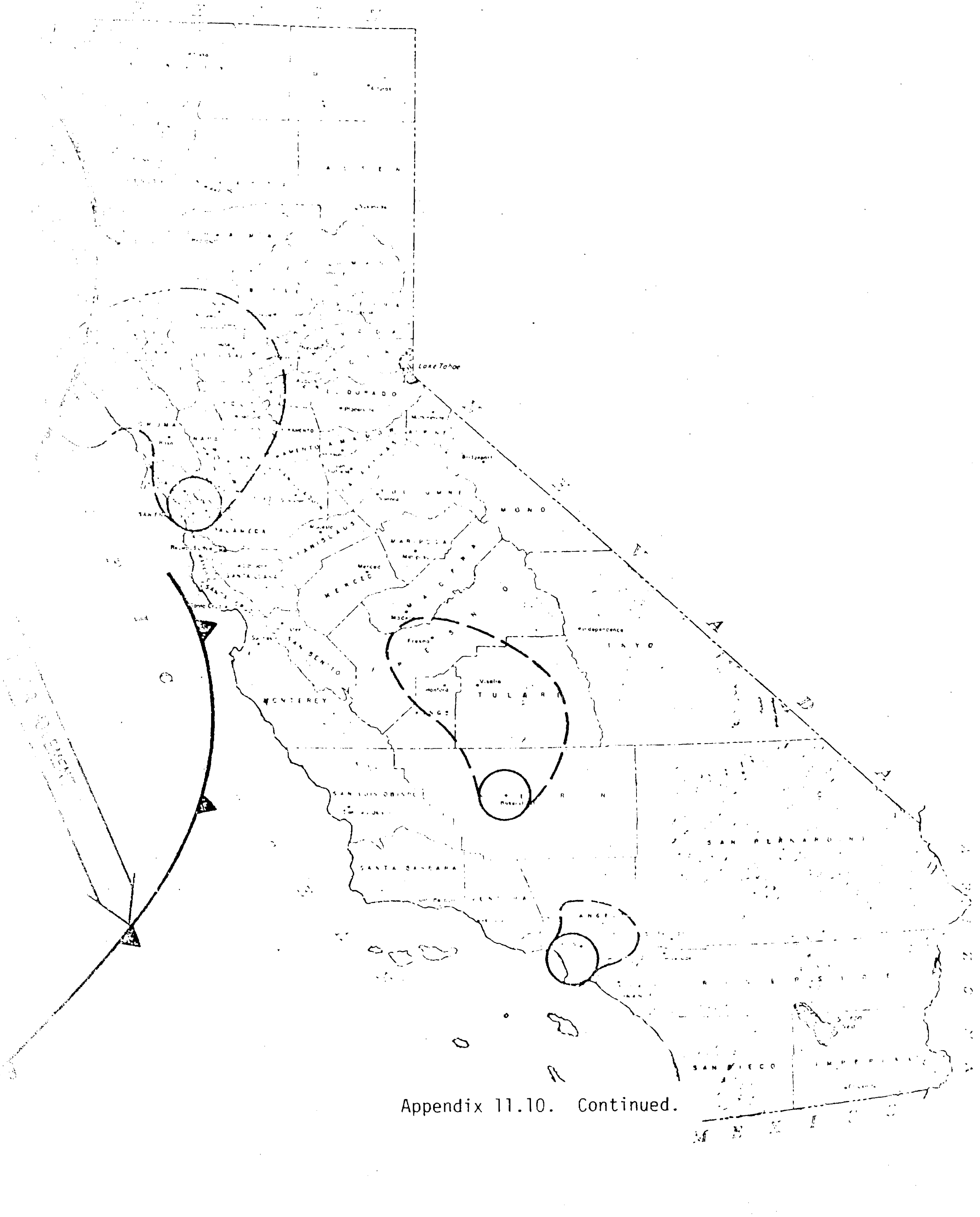
# EASTWARD MOVING STORM SYSTEM



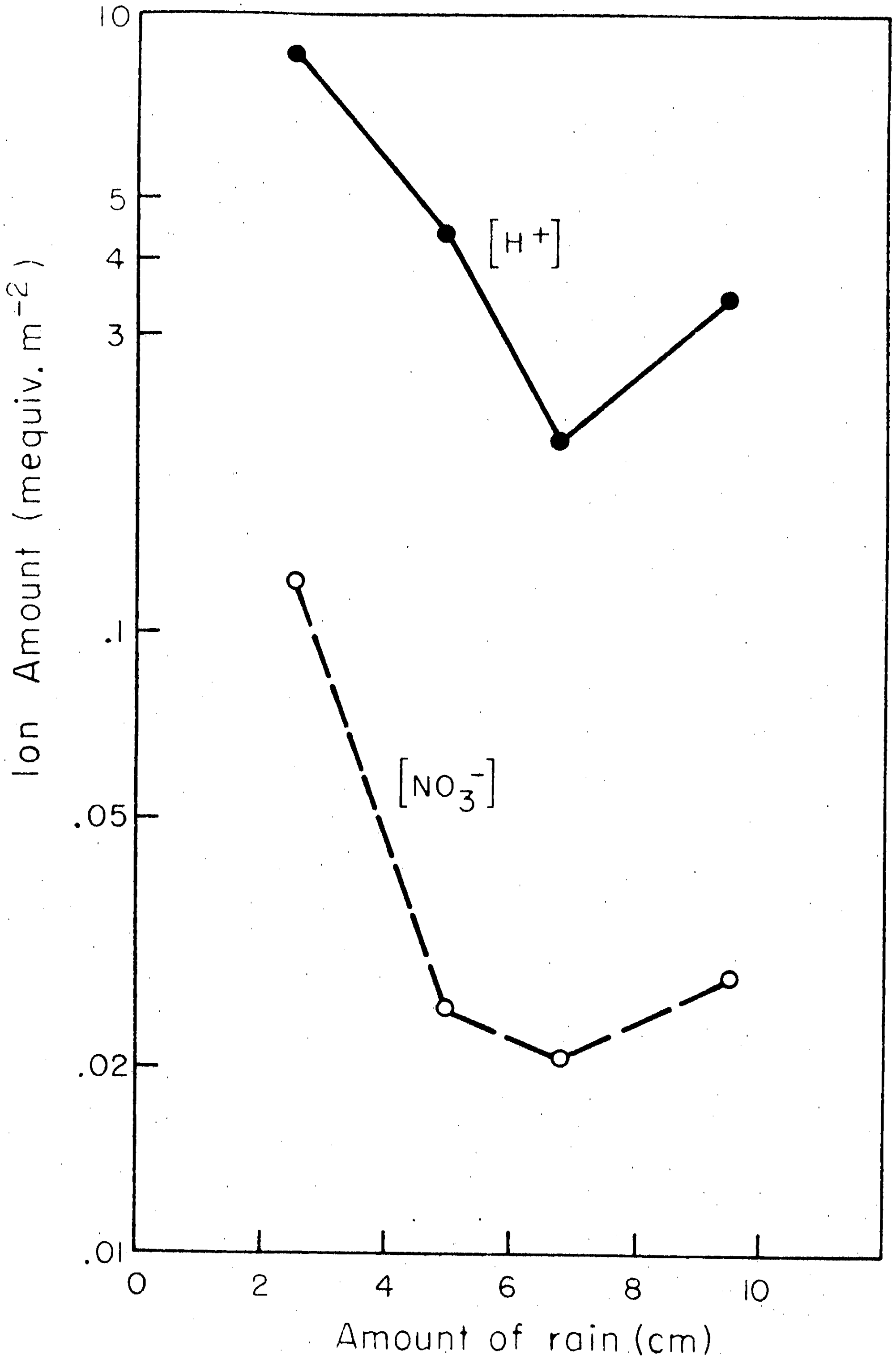
Appendix 11.10. Schematic estimates of probable "wash-out fans" associated with common rain-producing storms over California (from F. R. Smith of the A.R.B.).

F.R.S. MAY 11, 1977

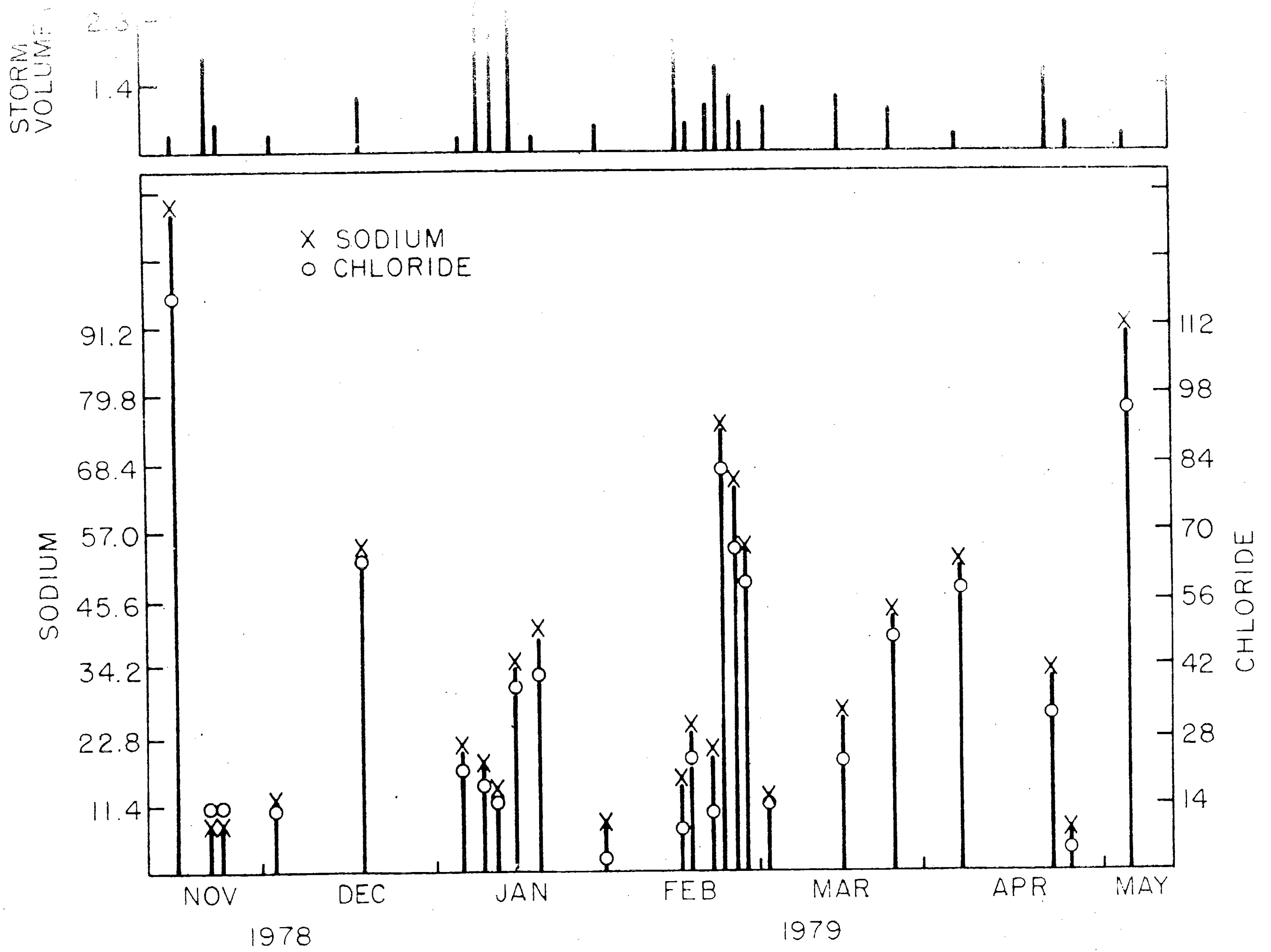
# SOUTHWARD MOVING STORM SYSTEM



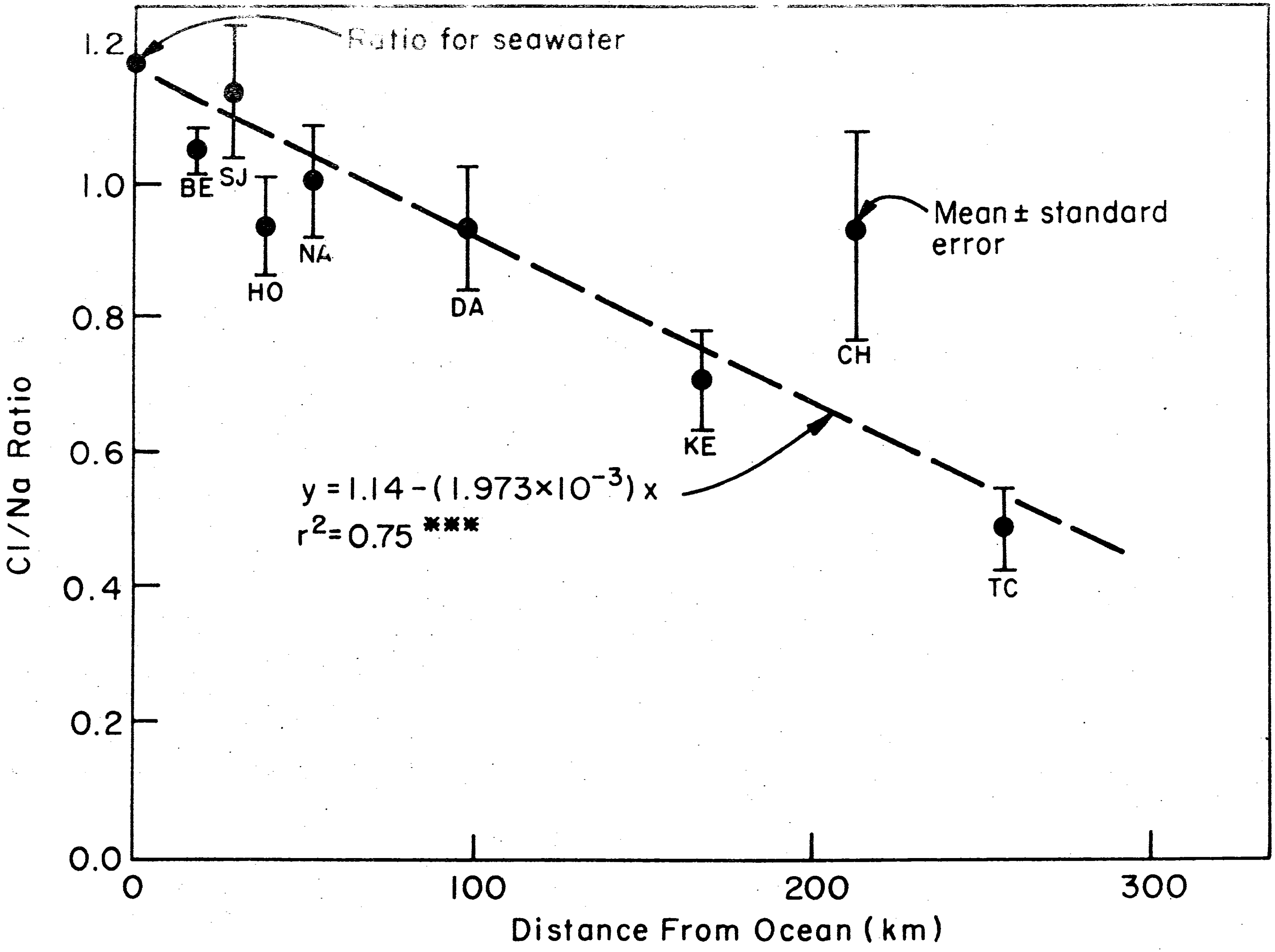
Appendix 11.10. Continued.



Appendix 11.11. Correlation of hydrogen and nitrate concentrations during a three-day rainstorm at Berkeley in March 1978.



Appendix 11.12. Storm volume and sodium and chloride ion concentrations of wet precipitation at Berkeley.



Appendix 11.13. Chloride:sodium ratio of wet precipitation as a function of distance from ocean. ***$\alpha < 0.001$.

## APPENDIX 11.14

## Quality Assurance Tests and Comparisons

A. Effects of storage temperature, filtration and storage time on [illegible] concentration of a wet sample (BE030179W), i.e., Berkeley rain event

Notes: Filtration was with a 0.45 millipore filter. Throughout the [illegible] was typically carried out within 2 days of receipt at the Berkeley [illegible], and the general procedure followed was that of filtration and [illegible]$^{\circ}$C. This procedure had minimal effect on changes in $[H^+]$ as shown [illegible] following test results where $[H^+]$ is expressed in μequiv./liter:

| Storage Time (Days) | Filtered | | Unfiltered | |
|---|---|---|---|---|
| | $4^{\circ}$C | $26^{\circ}$C | $4^{\circ}$C | $26^{\circ}$C |
| 0 | 13.18 | 13.18 | 13.18 | 13.18 |
| 4 | 13.18 | 15.14 | 13.18 | 22.39 |
| 5 | 12.02 | 14.45 | 13.18 | 15.14 |
| 7 | 12.59 | 11.22 | 10.96 | 13.18 |

B. Correlation between acidity of wet precipitation measured in [illegible] and laboratory: See Table 3 in Text.

C. Comparison of duplicate digestion-plus-chemical-analysis of [illegible] samples.

Notes: For any given sample, each of the duplicate analyses were [illegible] at a completely separate time. The samples were selected at random [illegible] sites and dates and include both "wet" and "dry" precipitation samples. [illegible] cases, duplication also included sample preparation (i.e. chemical digestion, etc.) as well as duplication of ionic analysis procedures.

At the foot of the columns in the following table, mean absolute values between duplicates ± the difference at the 95% Confidence Interval are shown. For a specific duplicate-pair this absolute value would tend towards the higher value within the Confidence Interval for high concentrations, and tend toward the lower value for low concentrations.

| 1st | 2nd | 1st | 2nd | 1st | 2nd | 1st | 2nd | 1st | 2nd | 1st | 2nd | 1st | 2nd | 1st | 2nd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.32 | 0.22 | 0.14 | 0.02 | 0.14 | 0.08 | 0.04 | 0.03 | 0.124 | 0.133 | 1.470 | 1.330 | 0.07 | 0.08 | 1.33 | 1.71 |
| 0.35 | 0.27 | 0.02 | 0.01 | 0.04 | 0.03 | 0.06 | 0.05 | 0.192 | 0.208 | 0.548 | 0.657 | 1.54 | 1.54 | 1.15 | 1.45 |
| 0.44 | 0.43 | 0.10 | 0.19 | 0.04 | 0.04 | 0.06 | 0.05 | 0.236 | 0.251 | 0.434 | 0.427 | 0.19 | 0.23 | 0.18 | 0.00 |
| 0.30 | 0.23 | 0.02 | 0.02 | 0.03 | 0.03 | 0.04 | 0.03 | 0.093 | 0.094 | 0.282 | 0.282 | 0.64 | 0.75 | 0.02 | 0.00 |
| 0.30 | 0.25 | 0.16 | 0.26 | 0.08 | 0.09 | 0.04 | 0.04 | 0.090 | 0.088 | 0.513 | 0.529 | 2.01 | 2.33 | 1.69 | 2.12 |
| 0.20 | 0.30 | 0.05 | 0.10 | 0.09 | 0.14 | 0.04 | 0.06 | 0.461 | 0.455 | 0.406 | 0.390 | 0.21 | 0.17 | 0.49 | 0.59 |
| 0.21 | 0.16 | 0.03 | 0.04 | 0.17 | 0.14 | 0.06 | 0.06 | 0.207 | 0.277 | 0.114 | 0.121 | 0.75 | 0.64 | 0.86 | 0.97 |
| 1.81 | 1.83 | 0.16 | 0.20 | 0.19 | 0.15 | 0.21 | 0.21 | 1.168 | 1.149 | 0.112 | 0.116 | 0.21 | 0.21 | 0.40 | 0.35 |
| 0.34 | 0.29 | 0.06 | 0.14 | 0.04 | 0.05 | 0.01 | 0.01 | 1.150 | 0.858 | 0.050 | 0.053 | 0.99 | 1.07 | 0.50 | 0.89 |
| 0.24 | 0.21 | 0.01 | 0.01 | 0.03 | 0.03 | 0.01 | 0.01 | 0.375 | 0.313 | 0.014 | 0.018 | | | 0.13 | 0.06 |
| 0.29 | 0.22 | 0.01 | 0.01 | 0.05 | 0.05 | 0.02 | 0.01 | 0.533 | 0.368 | 0.406 | 0.427 | | | 0.86 | 0.28 |
| 0.38 | 0.39 | 0.04 | 0.05 | 0.08 | 0.07 | 0.03 | 0.03 | 0.196 | 0.183 | | | | | 0.57 | 0.28 |
| 0.74 | 0.76 | 0.04 | 0.05 | 0.05 | 0.05 | 0.04 | 0.04 | 0.356 | 0.298 | | | | | 0.33 | 0.00 |
| 0.79 | 0.79 | 0.07 | 0.10 | 0.04 | 0.05 | 0.09 | 0.10 | 0.297 | 0.268 | | | | | 0.00 | 0.16 |
| 0.25 | 0.17 | 0.02 | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 | 0.427 | 0.353 | | | | | 0.50 | 0.47 |
| | | | | | | | | 0.052 | 0.054 | | | | | 0.33 | 0.33 |
| | | | | | | | | 0.109 | 0.109 | | | | | 0.88 | 0.81 |
| | | | | | | | | | | | | | | 1.07 | 0.84 |
| *0.05±0.02 | | 0.04±0.02 | | 0.02±0.01 | | 0.01±0.01 | | 0.050±0.40 | | 0.031±0.029 | | 0.08±0.08 | | 0.21±0.08 | |

*Absolute values of the difference ± 95% C.I.

D. Comparison of wet deposition at Davis, California, between the samples in this study and that of the N.A.D.P. network, sites about 3 m away.

Notes: The sampler-devices were both of the same design (Aerochem Metrics Model 201). However, the one in this study (designated as U.C.B. below) was sampled following each storm-event, and the chemical analysis were performed as detailed in this report. In contrast, the N.A.D.P. collector was sampled weekly, and the subsequent analyses were performed at the laboratory in Illinois where all N.A.D.P. network samples are sent. The comparison in the following table is in units of total wet deposition (mg/m$^2$). The N.A.D.P. results may be in error, because at the time of this writing, the computerized results of the N.A.D.P. contained some unresolved error, especially in the volume estimates. Nevertheless, deposition estimates from the two samples were reasonably comparable, considering all the differences in collection methods, analyses, etc.

## COMPARISON OF WET DEPOSITION IN MG/M$^2$

## DURING THE PERIOD 11-12-78 TO 3-27-79 AT DAVIS.

| Ion | N.A.D.P. (n=10) | U.C.B. (n=12) | Ratio N.A.D.P./U.C.B. |
|---|---|---|---|
| $Ca^{2+}$ | 28.32 | 30.70 | 0.92 |
| $Mg^{2+}$ | 13.29 | 15.3 | 0.87 |
| $K^+$ | 8.45 | 10.2 | 0.83 |
| $Na^+$ | 141.38 | 110.9 | 1.27 |
| $NH_4^+$ | 192.92 | 225.9 | 0.85 |
| $NO_3^-$ | 457.69 | 466.9 | 0.98 |
| $Cl^-$ | 149.59 | 149.9 | 1.00 |
| $SO_4^{2-}$ | 378.15 | 420.7 | 0.90 |
| $H^+_{[LAB]}$ | 1.69 | 2.0 | 0.85 |
| Volume(1) | 25.17 | 23.60 | 1.08 |