

QC
807.5
.U6
A7
no.132

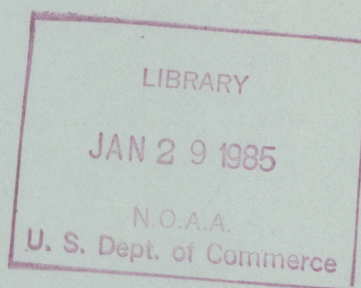
NOAA Technical Memorandum ERL ARL-132



THE ACIDITY OF SAMOAN RAIN -
TRENDS AND EVALUATION OF THE FIRST DECADE

U. Dayan
J. M. Miller
D. W. Nelson

Air Resources Laboratory
Silver Spring, Maryland
November 1984



noaa

NATIONAL OCEANIC AND
ATMOSPHERIC ADMINISTRATION

Environmental Research
Laboratories

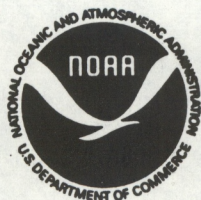
QC
807.5
.U6A7
no. 132

NOAA Technical Memorandum ERL ARL-132

THE ACIDITY OF SAMOAN RAIN -
TRENDS AND EVALUATION OF THE FIRST DECADE

U. Dayan
J. M. Miller
D. W. Nelson

Air Resources Laboratory
Silver Spring, Maryland
November 1984



UNITED STATES
DEPARTMENT OF COMMERCE

Malcolm Baldrige,
Secretary

NATIONAL OCEANIC AND
ATMOSPHERIC ADMINISTRATION

Environmental Research
Laboratories

Vernon E. Derr
Director

NOTICE

Mention of a commercial company or product does not constitute an endorsement by NOAA Environmental Research Laboratories. Use for publicity or advertising purposes of information from this publication concerning proprietary products or the tests of such products is not authorized.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	
1. INTRODUCTION	1
2. NETWORK MEASUREMENT PROBLEMS	4
3. METEOROLOGICAL EVALUATION OF THE DATA	10
4. SEA SALT INFLUENCE OF SAMOAN ACID PRECIPITATION	10
5. CHEMICAL CHARGE BALANCE CALCULATIONS FOR WESTERLY AND EASTERLY STORMS	17
6. SUMMARY AND CONCLUSIONS	21
7. ACKNOWLEDGMENTS	21
8. REFERENCES	21

THE ACIDITY OF SAMOAN RAIN - TRENDS AND EVALUATION OF THE FIRST DECADE

ABSTRACT. Samoan precipitation events are both plentiful and well distributed throughout the year. The chemistry of these rains shows from weekly sampling that the annual fluctuations of free acidity are almost negligible. The 10-year pH is 5.3 with no significant trend. However, on a seasonal basis, the correlation is significant between the amount of precipitation and the total anion content during the October-November period. During this period, characterized by very steady, strong, easterly trade winds, the ocean is probably the primary source of aerosol. In March and April, ion balances are consistently poorer, and anion deficits ($DF > 10 \mu\text{eq L}^{-1}$) are larger than observed during other periods. Decreases of acidity were also observed in samples measured first in the field and then in the laboratory for this season, suggesting the existence of another contributor of free protons in Samoan precipitation. The fall trajectories associated with precipitation events had almost 25% of their points of origin in the New Guinea area. It is speculated that during these flows, organic acids may be transported to Samoa.

1. INTRODUCTION

American Samoa, located in the Southwest Pacific ($14^{\circ}15'S$; $170^{\circ}34'W$), is one of the four background sites of the Geophysical Monitoring for Climatic Change (GMCC) Program and a baseline site in the World Meteorological Organization's Background Air Pollution Monitoring Network (WMO/BAPMoN). It is also one of the permanent sites in the Global Trends Network. Precipitation chemistry data collection at this site was initiated mainly for assessing the natural versus anthropogenic contribution to the precipitation chemistry in remote areas (Miller and Yoshinaga, 1981; Galloway et al., 1982; Miller and Dayan, 1983). Measurements of precipitation acidity were performed at the GMCC observatory at Cape Matatula on Tutuila Island (Fig. 1), which is situated at an elevation of 76 m above sea level and has an average annual precipitation of 320 cm. Because of its tropical marine climate, Samoa has abundant rain throughout the year. Ten years of data were compiled from several networks for this analysis (Table 1).

Collection of precipitation chemistry samples began in Tafuna during the early 1970's using a monthly wet-only collector. In mid-1976 the station was relocated to the NOAA/GMCC observatory roof on the easternmost part of Tutuila Island (Fig. 1). In 1976, a second monthly precipitation chemistry program was established at Cape Matatula, by the Environmental Measurements Laboratory (EML) of the Department of Energy (DOE) (Bogen et al., 1980, 1984). Because the results from the above networks showed that at times the acidity of precipitation in Samoa could be higher than expected in such a remote area in the Southern Hemisphere, a daily precipitation collection program was established at the Samoa GMCC observatory at the end of 1980. Also, the monthly WMO-NOAA network joined the National Atmospheric Deposition Program (NADP) in 1980 and switched to a weekly wet-only sampling protocol with much better quality control

AMERICAN SAMOA
TUTUILA ISLAND



Fig. 1. Cape Matatula and Tafuna on Tutuila Island, American Samoa.

Table 1. Inventory of Samoan precipitation chemistry networks (1973-1982)

Site	Period of operation	Operator	Collector	Sample protocol	Constituents
Tafuna	Aug. 1973-Jul. 1976	WMO, NOAA, EPA	Misco	Wet-only monthly samples	Conductivity & major ¹ ions
Cape Matatula	Apr. 1976-May 1980	DOE/EML	HASL	Wet/dry monthly samples	Conductivity & major ions +PO ₄ ⁻³ and Br ⁻
Cape Matatula	Jan. 1977-Jun. 1980	WMO, NOAA, EPA	Misco	Wet-only monthly samples	Conductivity & major ions
Cape Matatula	Jun. 1980-Present	NADP, WMO, NOAA	Aerochem Metrics	Wet-only weekly samples	Conductivity & major ions
Cape Matatula	Jan.-Feb. 1981 (22 samples) June-July 1981 (11 samples)	SEAREX Exchange Program	URI ² poly- ethylene funnel WHOI ³ and TAMU ⁴ stainless steel bowls	Wet-only event samples	pH, sodium, sulfate, nitrate
Cape Matatula	Sept. 1980-Present	NOAA/GMCC	Polyethylene funnel	Bulk daily samples	pH and conduc- tivity

¹ H⁺, Ca⁺², Mg⁺², K⁺, Na⁺, NH₄⁺, NO₃⁻, Cl⁻, SO₄⁻²

² University of Rhode Island

³ Woods Hole Oceanographic Institution

⁴ Texas A&M University

and quality assurance standards. In addition to the weekly NADP, monthly EML, and daily GMCC collection, the Sea/Air Exchange Program (SEAREX) operated its own precipitation collection and analysis program during approximately 4 months in 1981 (January, February and June, July) (Pszenny et al., 1982). Thus precipitation collection at the Samoa GMCC facility was conducted by a number of groups using different procedures and protocols for obtaining rain samples. Characteristics of samples collected by the various groups range from sequential sampling of a single shower event during periods of minimum local contamination, to daily bulk deposition (GMCC), to weekly wet deposition (NADP), to monthly bulk wet/dry deposition (DOE/EML).

2. NETWORK MEASUREMENT PROBLEMS

After completion of the 10-year data base review, an attempt was made to evaluate the measurements from the four networks operating in American Samoa since 1973. First, the monthly weighted averages of hydrogen ion concentration values were plotted for each of the sampling networks (Fig. 2). The total network results show an average pH value of 5.3, indicating a hydrogen ion concentration greater than that found in water in equilibrium with atmospheric CO₂ (pH ~ 5.6). The only network that displayed a tendency for increasing acidity was the EML network. To evaluate the quality of the EML precipitation data results, we calculated the mass ion balances and obtained a cation/anion ratio of 1.13 ± 0.17 . Ion balances only indicate that there may be a problem in analyzing all the important ions in the sample. Although we do not have an explanation for the trend from the EML monthly data, we do not attribute any significance to this phenomenon because the values measured were almost at the threshold of detection (within $\pm 1 \mu\text{eq L}^{-1}$). Annual weighted means and standard deviations for some of the major ions at American Samoa are shown in Figs. 3-5. Standard deviations were calculated using a formulation by Hawley (1984).

The wide variations in standard deviations may be indicative of large annual variations. However, because of the differences between pre-1980 and post-1980 collection methods, the variations are more likely due to long shipment and storage times, poor collection techniques, and other such problems (Tyree, 1981; Feeley and Liljestrand, 1983). No obvious trend can be seen in the Samoan data, though the weekly data were lowest in concentration and most consistent on an annual basis. Shorter periods of collection and immediate analysis following precipitation events using the GMCC daily bulk samples usually result in higher sample H⁺ concentrations, suggesting the existence of another contribution of free protons in Samoan precipitation (Fig. 6).

Another way of evaluating the data is by comparing the annual volume-weighted mean of hydrogen ion concentration versus the annual amount of precipitation. No correlation between these two variables can be detected in the monthly and weekly WMO networks. This can be contrasted with the strong decrease in acidity and sulfate with increased rain amounts in polluted areas. Although the rainfall is quite constant within an individual season, the total amount of rainfall may vary widely between individual years because of the position of the Samoan Archipelago in relation to the fluctuations of the Intertropical and Intratropical Convergence Zones (Bortniak, 1981). For this reason the GMCC daily data and the NADP weekly data were plotted as scattergrams of pH values versus total rainfall for 343 and 124 storms, respectively, for 1980-1982. The poor correlation coefficient found between these two parameters

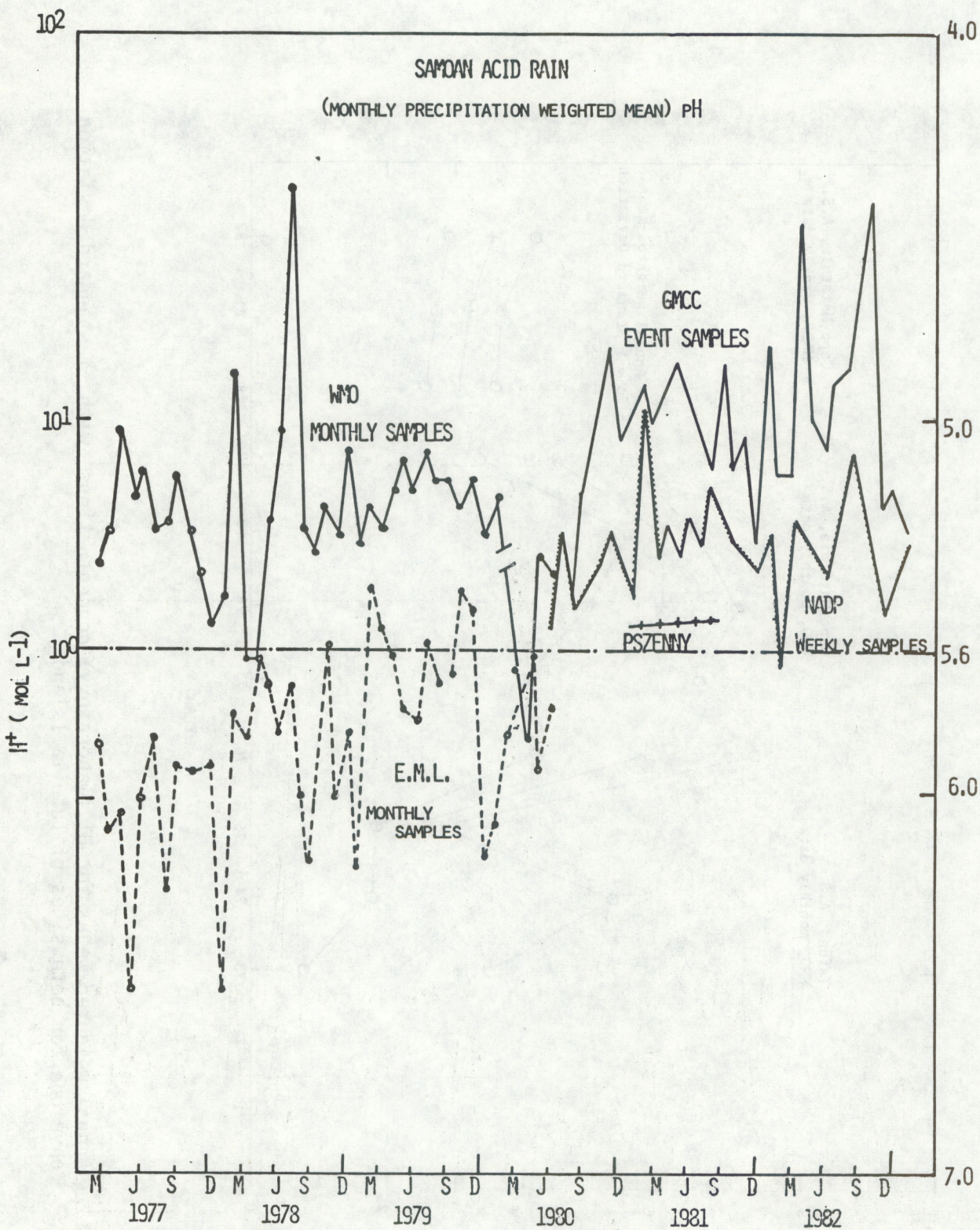


Fig. 2. Monthly precipitation weighted mean pH for the entire data record for all networks.

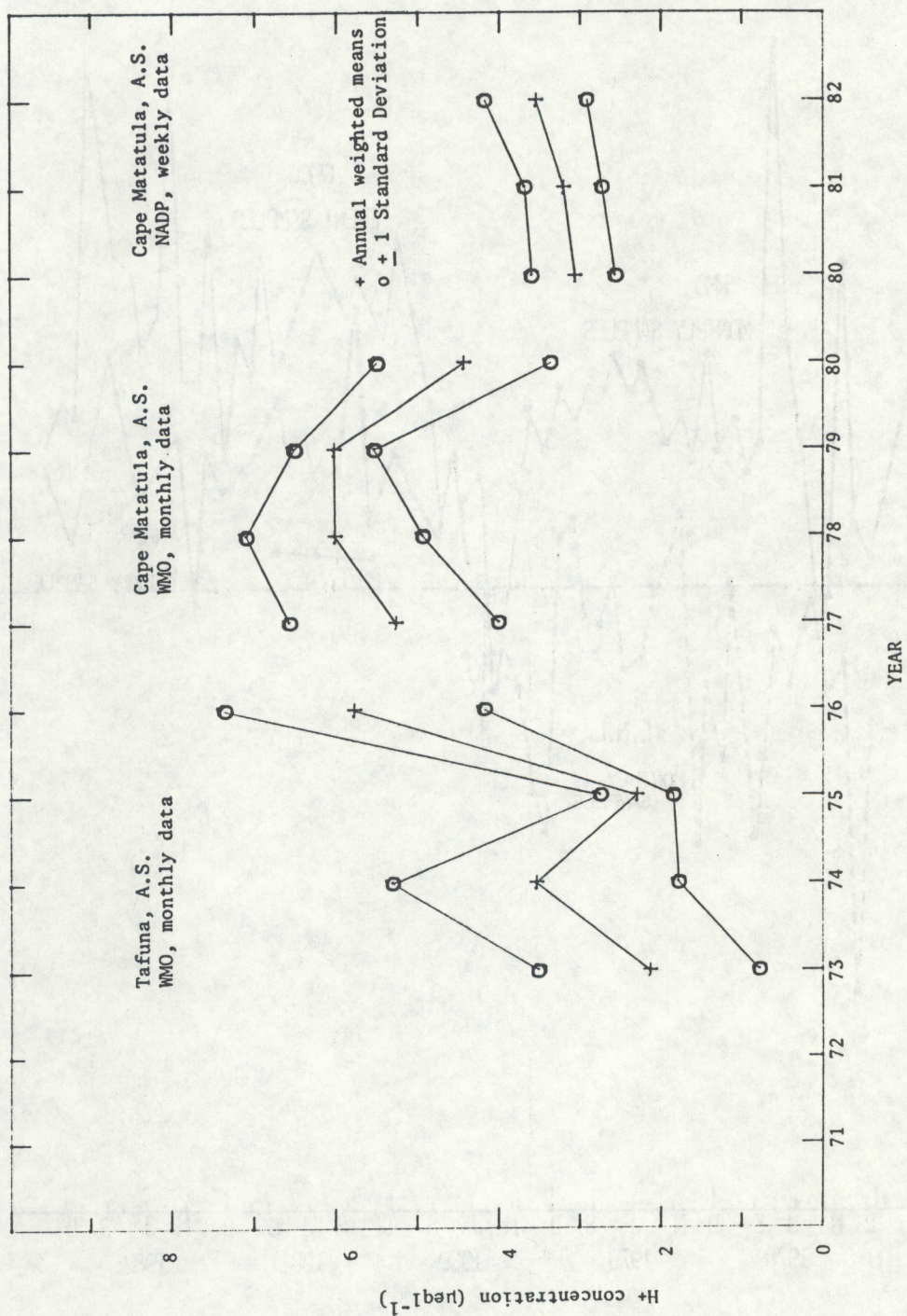


Fig. 3. Annual weighted means for H^+ (laboratory) concentrations, with ± 1 standard deviation envelope for both sites of Tutuila Island.

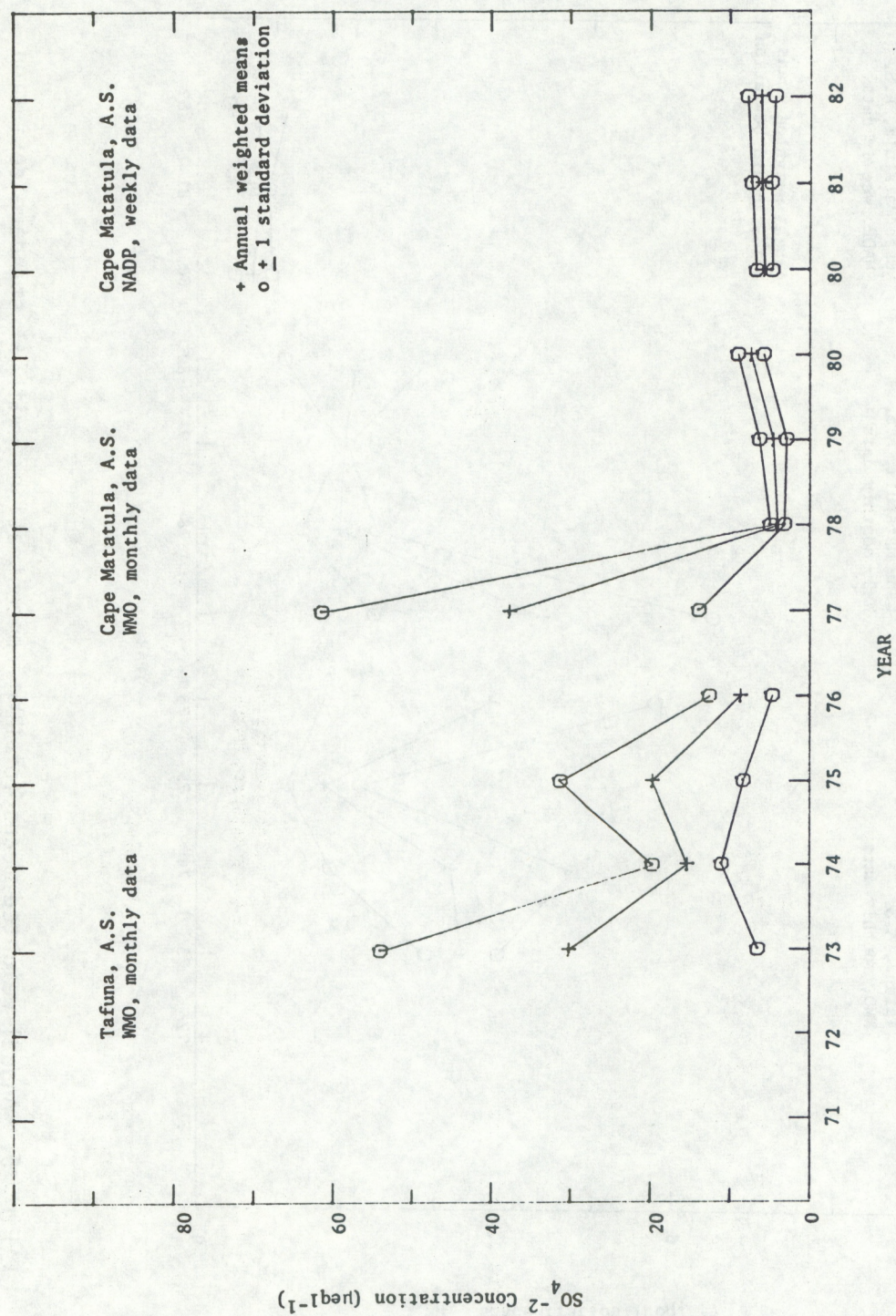


Fig. 4. Annual weighted means for excess SO_4^{2-} concentrations, with ± 1 standard deviation envelope for both sites of Tutuila Island.

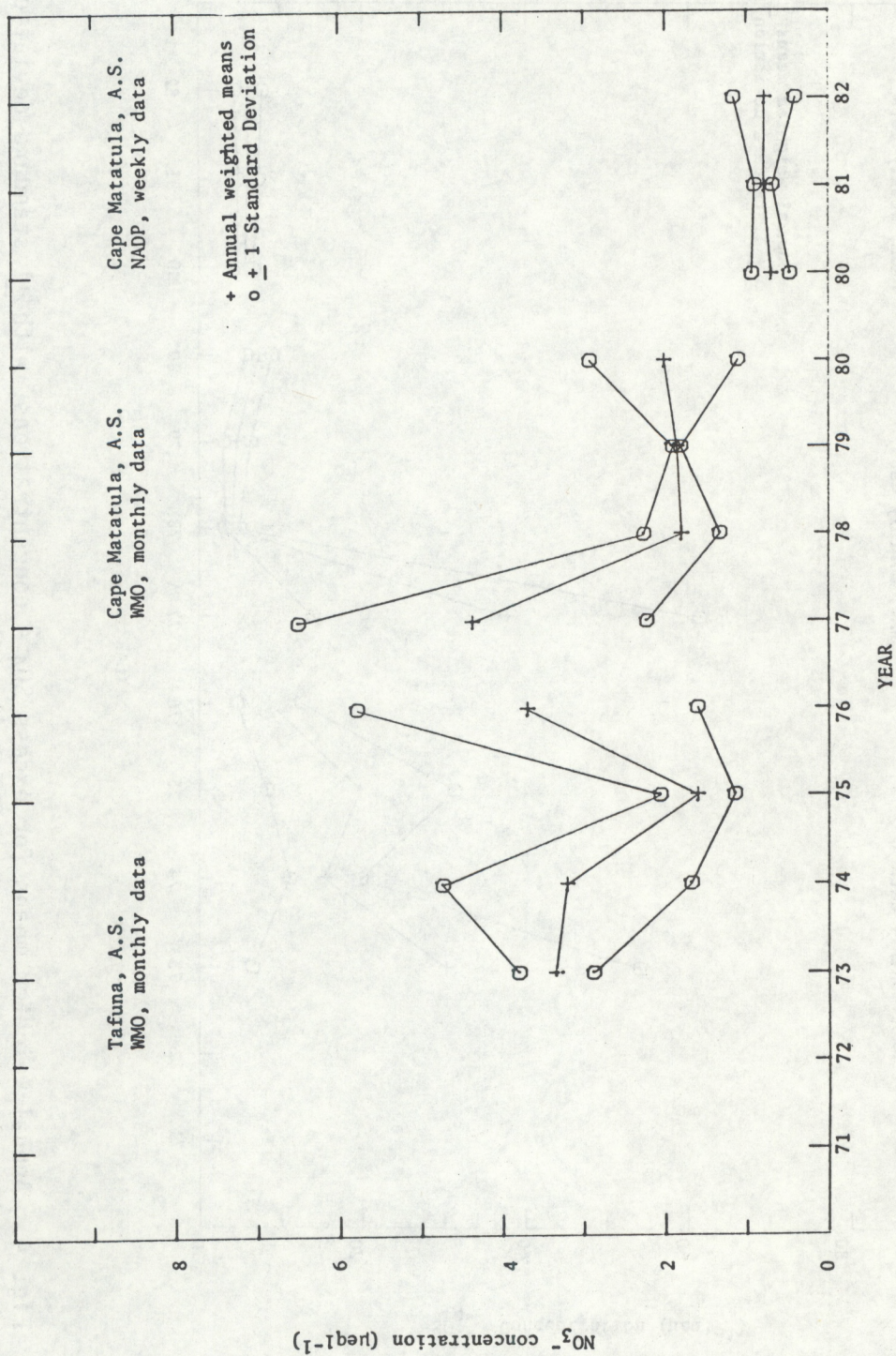


Fig. 5. Annual weighted means for NO_3^- concentrations, with ± 1 standard deviation envelope for both sites of Tutuila Island.

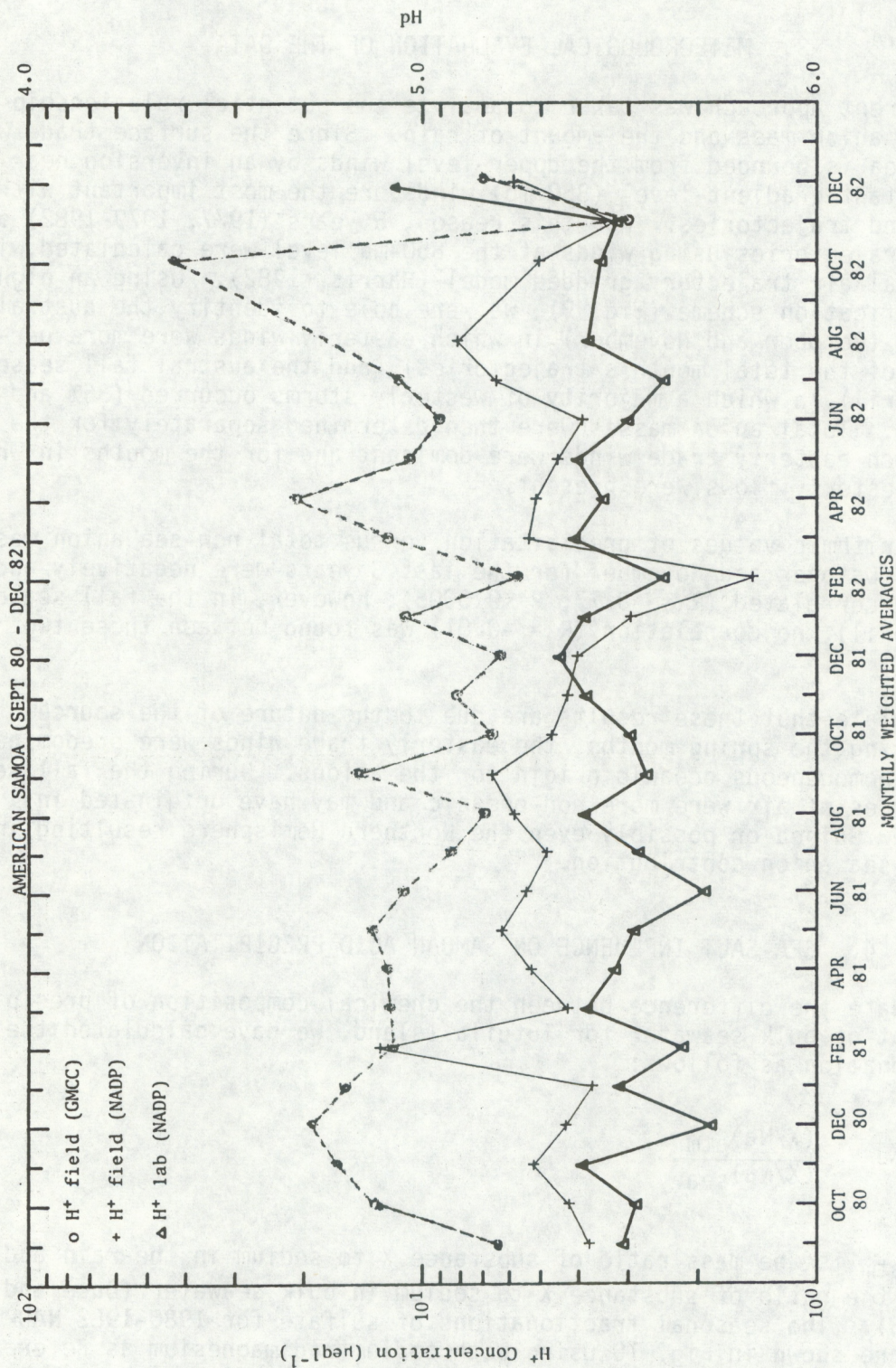


Fig. 6. Monthly distribution of H⁺ concentration for NADP weekly samples and GMCC daily bulk samples.

(Figs. 7, 8) may be explained by the very moist Samoan climate, which almost eliminates the evaporation of falling droplets, and by the predominant chemistry that takes place during the rainout process.

3. METEOROLOGICAL EVALUATION OF THE DATA

A different approach was taken to analyze the potential relationship between total anion mass and the amount of rain. Since the surface trade wind flow near Samoa is bounded from the upper-level winds by an inversion near 800 mb, the resultant gradient-level (850 mb) winds are the most important with respect to wind trajectories. For this reason, 5 years (1977, 1979-1982) of 10-day back-trajectories using winds at the 850-mb level were calculated with the operational air trajectory gridded model (Harris, 1982). Using an eight-sector classification scheme (Fig. 9), we were able to identify the austral spring season (October and November) in which easterly winds were more persistent (78% of the total month's trajectories), and the austral fall season (March and April) in which a majority of westerly storms occurred (36% and 27%) (Table 2, 2a). Total anion masses were then determined separately for the months in which easterly trade winds were dominant and for the months in which a majority of westerly flows were present.

The logarithmic values of precipitation versus total non-sea anion mass for the months of October and November for the last 3 years were negatively and significantly correlated ($R = -0.77$; $P < 0.0005$); however, in the fall season (March and April), no correlation ($R = -0.01$) was found between these two parameters.

We speculate that these results are due to the nature of the source regions. During the spring months, the easterly trade winds were predominant, suggesting a homogeneous oceanic origin for the anions. During the fall season, however, sources of air were more non-oceanic and may have originated in Australia, New Guinea or possibly even the Northern Hemisphere resulting in a measured non-sea anion contribution.

4. SEA-SALT INFLUENCE ON SAMOAN ACID PRECIPITATION

To evaluate the difference between the chemical composition of precipitation from that of bulk seawater for Tutuila Island, we have calculated the chemical fractionation as follows:

$$F(\text{Na}) [X] = \frac{(X/\text{Na})_{\text{atm}}}{(X/\text{Na})_{\text{sea}}}$$

where $(X/\text{Na})_{\text{atm}}$ is the mass ratio of substance X to sodium in the rain and $(X/\text{Na})_{\text{sea}}$ is the ratio of substance X to sodium in bulk seawater (Duce and Hoffman, 1976). The seasonal fractionations of sulfate for 1980-1982 NADP weekly data are shown in Fig. 10 using both sodium and magnesium as references to avoid suspected seawater sampling contamination. The figure shows the same temporal pattern, suggesting minimal values of excess sulfates for austral winter (July, August, September). Very similar patterns appeared for the years

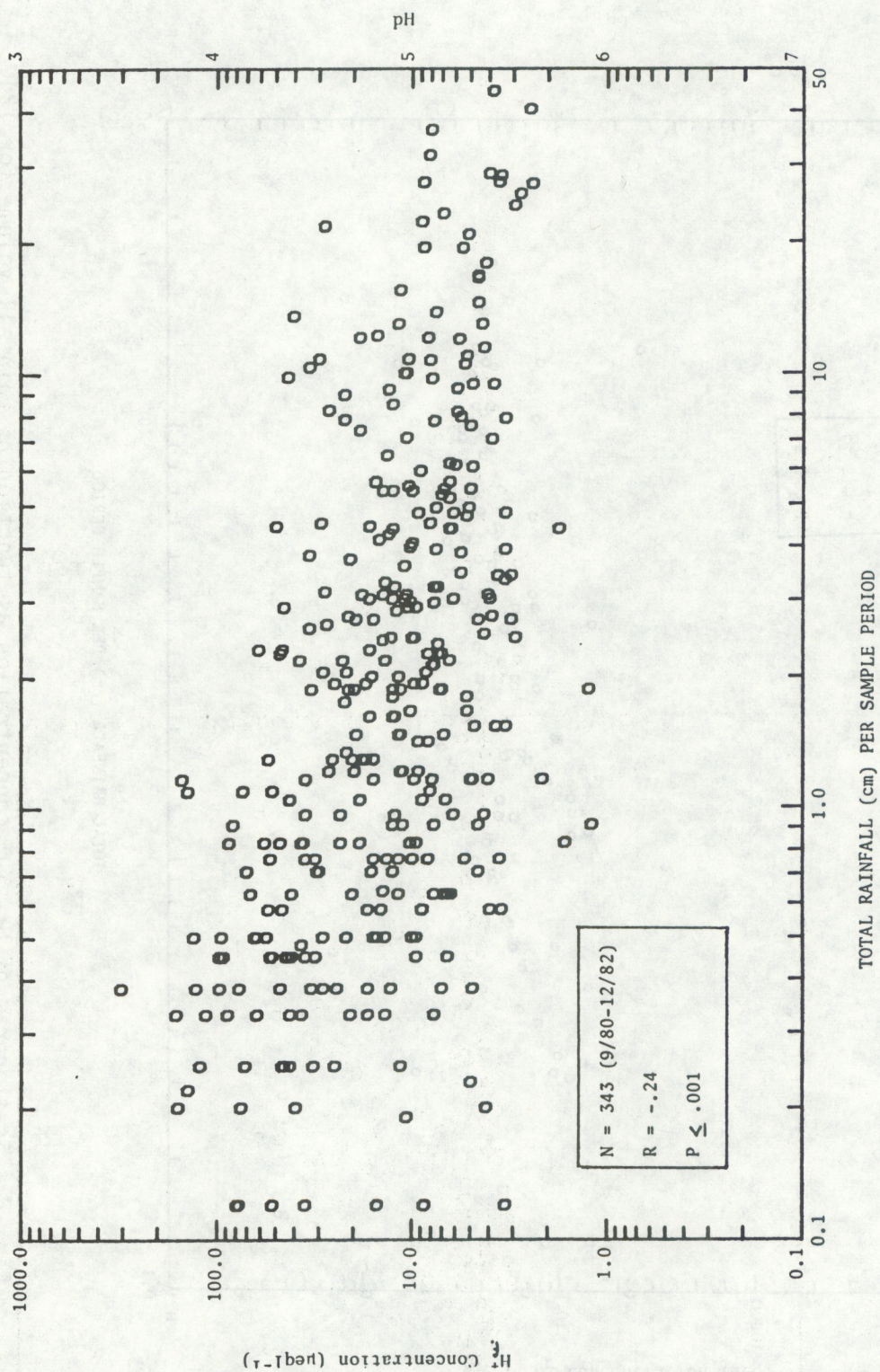


Fig. 7. Scattergram of H_f field⁺ concentration as function of rainfall volume for 343 GMCC daily bulk samples.

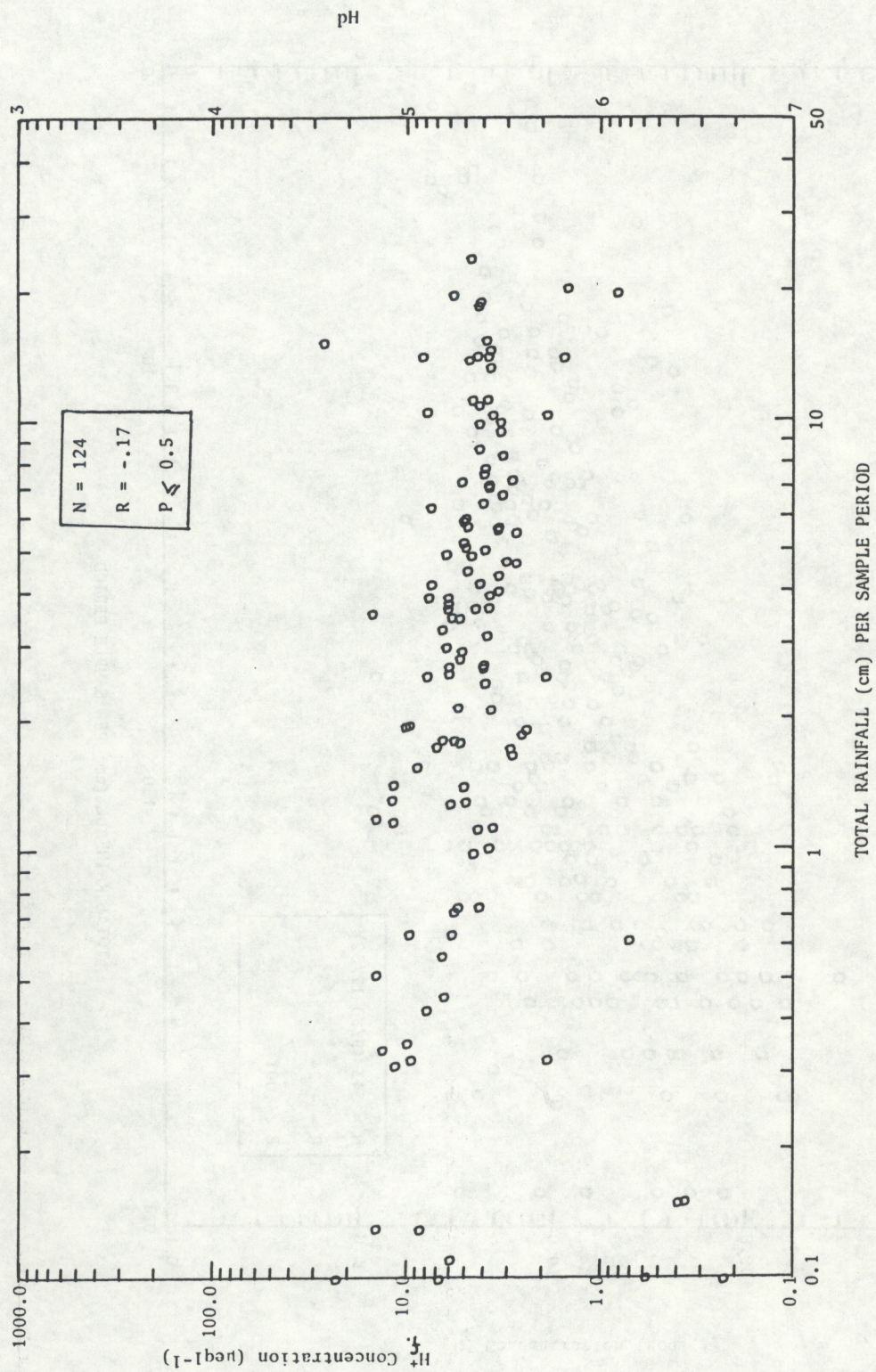


Fig. 8. Scattergram of H⁺ concentration as function of rainfall volume for 124 NADP weekly samples.

SMO TRAJECTORIES ARRIVING 80087 - 3/27/80

B: 0Z 850 MB D: 12Z 850 MB

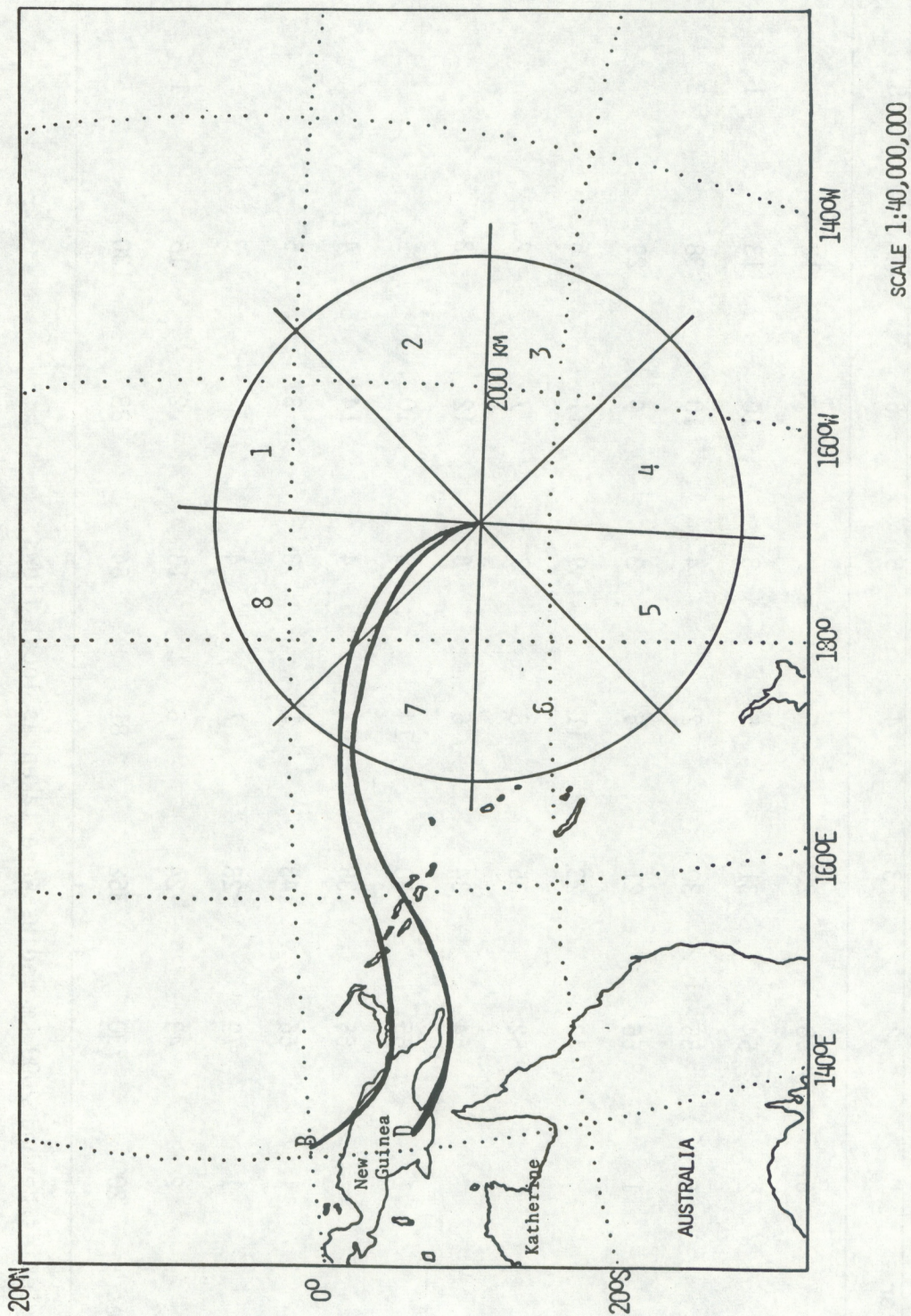


Fig. 9. Classification of American Samoa trajectories using an eight-sector classification. The example is from 27 March 1980.

Table 2. Frequency distribution of 850-mb 1200 GMT back trajectories reaching American Samoa for the years 1977, 1979, 1980, 1981, and 1982.

Month	Sector									beyond 2000 km*
	360°-045°	045°-090°	090°-135°	135°-180°	180°-225°	225°-270°	270°-315°	315°-360°		
	1	2	3	4	5	6	7	8		
JAN	6	58	28	5			12		37	
FEB	2	54	31	5	3	10	13	1	11	
MAR	6	55	30	2	4	10	38	3	9	
APR	1	66	21	5	3	9	29		17	
MAY		73	23	11	9	11	5		19	
JUN		52	35	8	7	7	2		25	
JUL		54	34	6	6	12	3		13	
AUG	1	65	30	14	8	10	1		11	
SEP		65	35	11	4	14	4		8	
OCT	1	66	43	1	3	3	5		21	
NOV	1	79	28	7	4		3		24	
DEC	2	43	24	6	13	2	15	1	24	
No. of cases per sector	20	730	362	81	64	88	130	5	219	

*All trajectories beyond 2000 km radius were taken as local flows

Table 2a. Frequency distribution (percents) for easterly and westerly storms.

General Sector of origin	East (Sectors 1-4)	West (Sectors 5-8)
Month		
JAN	66	8
FEB	71	21
MAR	59	36
APR	62	27
MAY	70	17
JUN	70	12
JUL	73	16
AUG	79	14
SEP	79	16
OCT	78	8
NOV	79	5
DEC	58	24

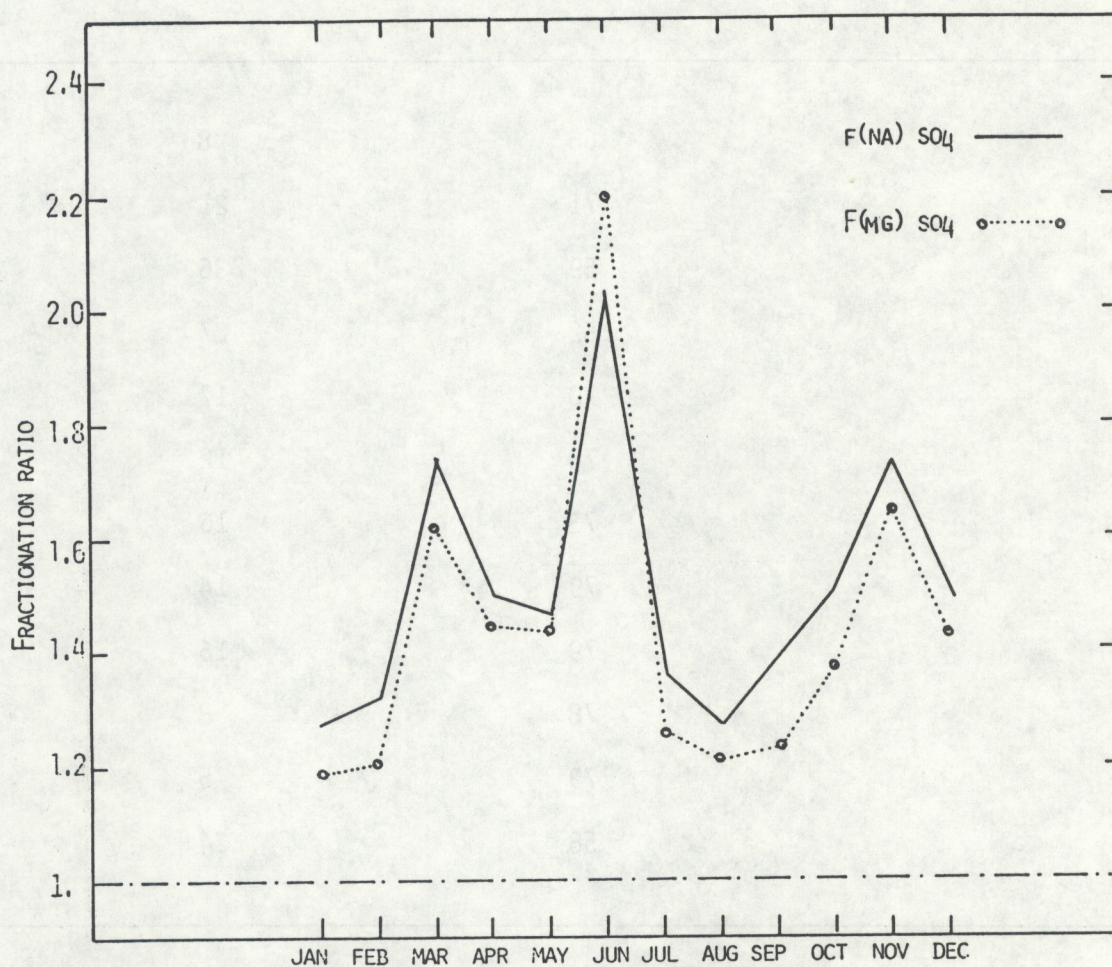


Fig. 10. Seasonal fractionation of sulfate with sea salt adjustment using sodium and magnesium for 1980-1982 weekly wet samples from American Samoa.

1979 and 1980 for both EML and WMO monthly samples (Fig. 11). Forty-four percent of the total number of trajectories during the austral winter seasons for these 5 years originated from the Southern Hemisphere (Table 2). In this season the fractionation values showed sulfate concentration in precipitation that was almost always present in a relative abundance similar to that of bulk seawater. These findings support Pszenny's (1982) conclusion that salinity might lower pH values of rain especially when climatic factors are favorable and rains are mostly of marine sources.

5. CHEMICAL CHARGE BALANCE CALCULATIONS FOR WESTERLY AND EASTERLY STORMS

To evaluate the net acidity of Samoan seasonal precipitation, volume-weighted mass ion balances were analyzed separately for spring easterly and fall westerly storms in conjunction with specific backward trajectories from American Samoa and NADP weekly precipitation chemistry data for 1980-1982. The means of the volume-weighted averages for this data set indicated that 27.5% of the H^+ measured in the field was consumed before it was remeasured at the central laboratory. Because of this nearly consistent shift to higher pH of laboratory samples from pH field values, the chemical charge balances were calculated using the pH field values (Table 3). All other ions were adjusted for sea salt contribution.

In air masses moving mainly over Australia and New Guinea (westerly trajectory) a significantly higher concentration of excess sulfate and free acidity could be detected (both showed significance at the 1% level, using the two-tailed t-test). These enriched air masses could have natural sources from biogenic emissions of reduced compounds such as dimethyl sulfide (Nguyen et al., 1974). Remaining cations (Ca^{++} , K^+ , Mg^{++}), adjusted for sea salt contribution and assumed to originate from terrestrial sources, were also significantly higher in their concentrations in westerly precipitation storm samples versus easterly storm samples.

The relatively large departure from a balance of cations and anions for constituents of westerly storms occurring during the fall season, shown in Fig. 12 and tabulated in Table 3, implies sources of protons other than strong acids. Note that hydrogen ion concentrations are field, not laboratory values. Formic and acetic acids contributing to free acidity and consumed by microorganisms could possibly explain this decrease in free acidity in Samoa. Weak organic acids were found to contribute over 60% of the free acidity in precipitation during the 1981-1982 wet season of Katherine, Australia (Keene et al., 1983). Weak organic acids might be from local sources, as suggested by Keene et al., 1984, in a study done on Amsterdam Island, or may be transported from a more distant source (Duce et al., 1980; Parrington et al., 1983). Australia and New Guinea, situated west of American Samoa at a distance of approximately 4000 km, may be a source of air masses enriched by weak organic acids. Such Australian air masses reaching Tutuila Island are frequent during the fall season (Fig. 9 and Table 2).

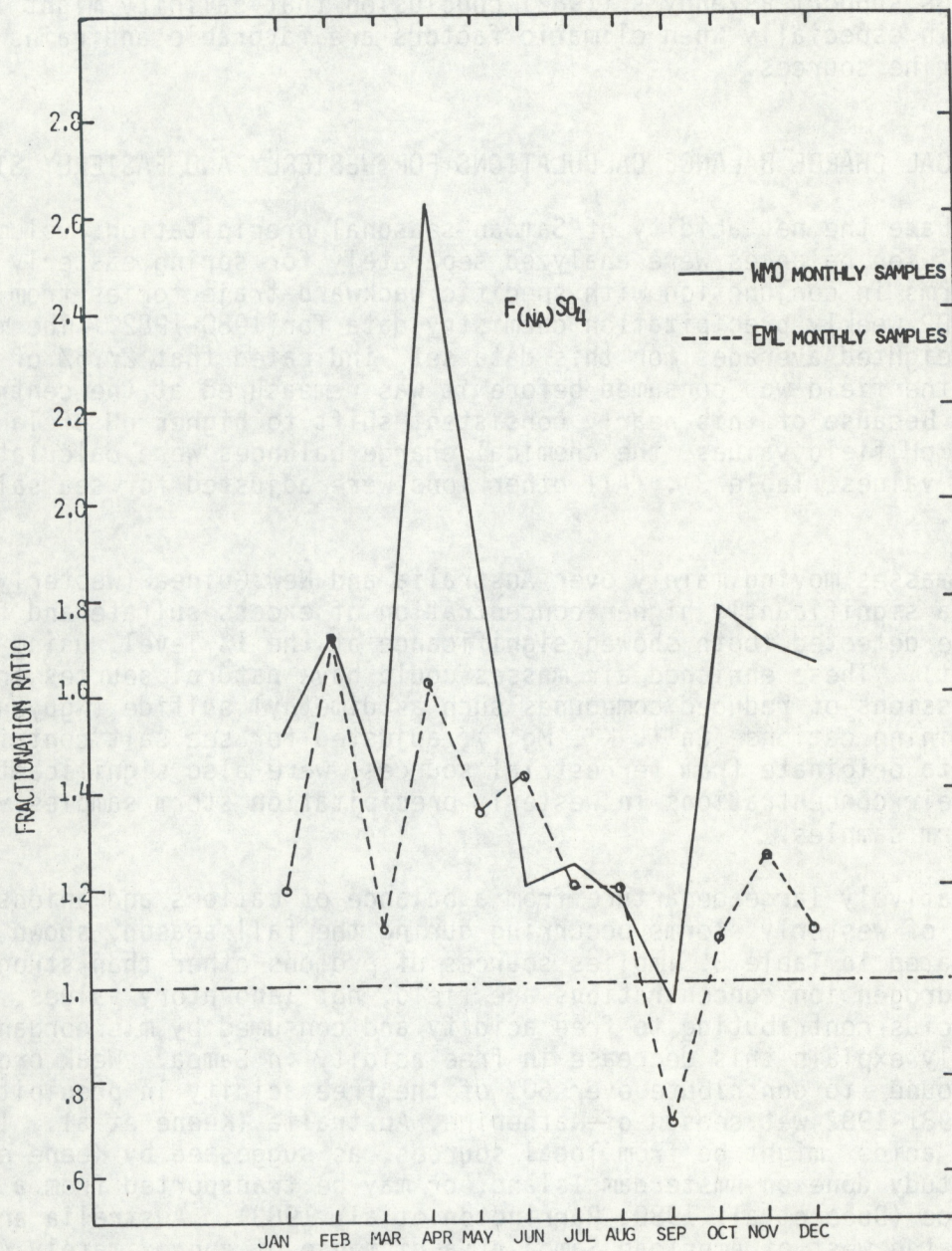


Fig. 11. Seasonal fractionation of sulfate with sea salt adjustment using sodium for EML and WMO monthly samples that were taken concurrently in 1979-1980.

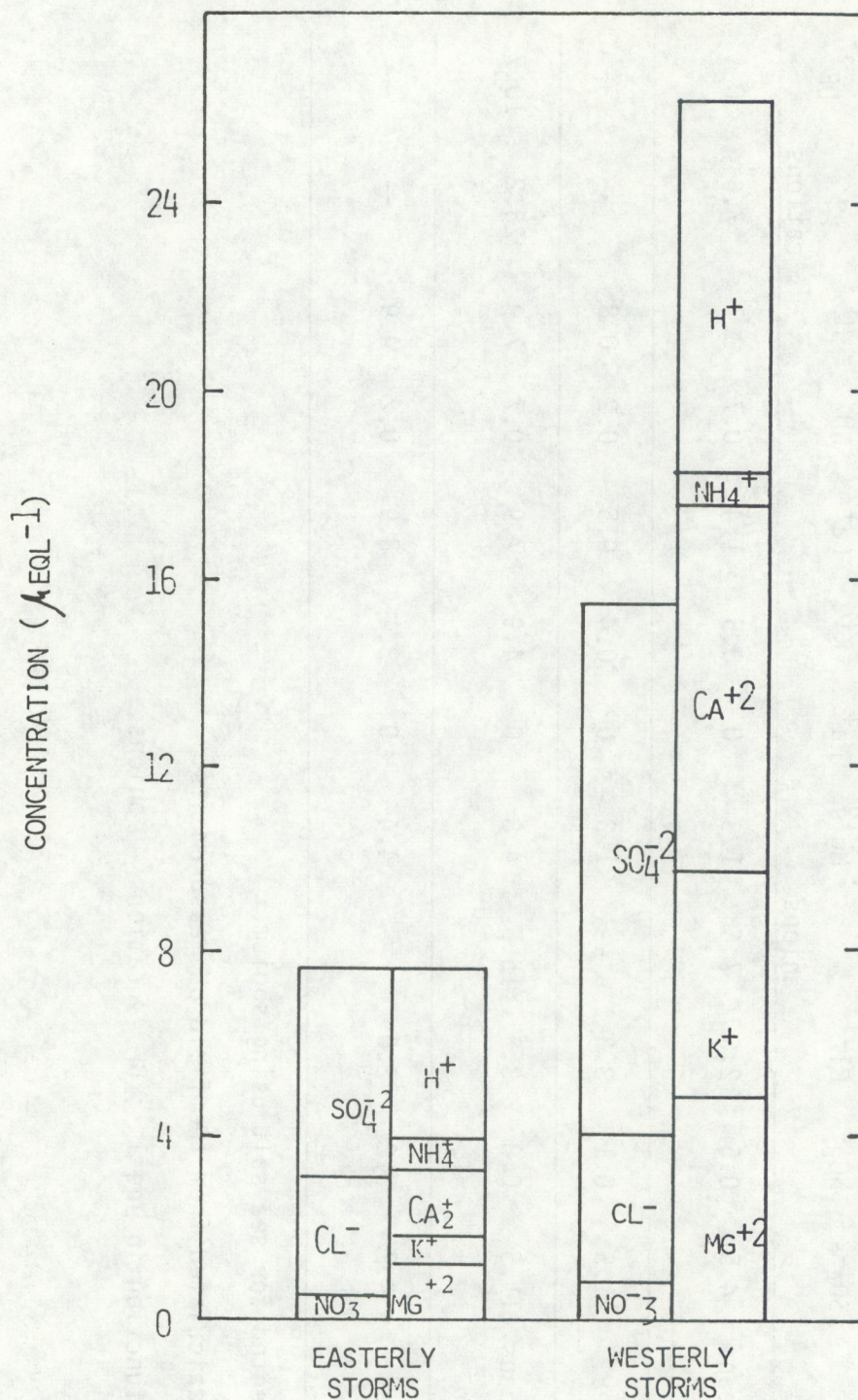


Fig. 12. Volume-weighted mass ion balance for selected easterly and westerly storms for 1980-1982 weekly wet samples from American Samoa. (The H^+ values were calculated from the field pH measurements.)

Table 3. Chemical mass ion balance for easterly and westerly storms for American Samoa during 1980-1982

Category	Values ¹	anions					cations					DF ³	
		SO ₄ ⁻²	NO ₃ ⁻	Cl ⁻	Σ	Mg ⁺²	Na ⁺	K ⁺	Ca ⁺²	NH ₄ ⁺	H ⁺ ²		Σ
Easterly storms	Weighted means (μeq l ⁻¹)	4.5	0.5	2.6	7.6	1.3	0	0.5	1.4	0.7	3.7	7.6	0
	Standard dev.	1.5	0.1	3.3	--	1.3	0	0.4	0.5	0.2	0.8	--	--
Westerly storms	Weighted means (μeq l ⁻¹)	11.5	0.8	3.2	15.5	4.8	0	4.9	7.9	0.7	7.9	26.2	10.7
	Standard dev.	4.7	0.2	2.0	--	4.4	0	3.1	3.9	0.2	4.9	--	--

¹The values are corrected for sea-salt using sodium.

²The H⁺ values were calculated from the field pH measurements.

³DF is a difference function in μeq l⁻¹; DF = Σ cations - Σ anions.

6. SUMMARY AND CONCLUSIONS

Results from the past decade indicate that Samoan rain is usually slightly more acidic than the pH level of 5.6, the level usually used to define acid rain. On the basis of NADP weekly samples measured at the Illinois State Water Survey, the annual mean pH of this remote region of the tropical South Pacific Ocean was 5.3 without any significant yearly trend fluctuations. On site, event pH measurements were lower. The 5-year trajectory climatology for American Samoa shows an easterly trade wind flow at the 850-mb level that is especially persistent during the southern spring. In this season, the variation of the chemistry of the rain was found to be minimal, and there were significant correlations between hydrogen ion concentration, total anion mass, and amount of rain. During austral winter, when trajectories frequently originated from the Southern Pacific Ocean; fractionation sulfate values for precipitation from these storms showed minimal values, (around 1) leading to the conclusion that almost all of the sulfate transported from this southerly direction and deposited in Samoa is of marine origin. During the Samoan fall months, the mass ion balances did not exhibit equality and revealed anion deficits and decreasing free acidity in samples. This suggests that organic acids may undergo long-range transport from the tropical forests of New Guinea and Australia and are contributing to free acidity that is quickly consumed by microorganisms during shipment and storage periods prior to reanalysis at the central laboratory. Besides the total anion deficits, sulfate values were also higher in the fall, which suggests a heterogeneous source for this constituent. One potential source of reduced sulfuric compounds could be a warm oceanic upwelling zone surrounding the Melanesian Islands. In contrast, storms originating in the east were more homogeneous in their precipitation constituents, appear to have purely maritime origins in the Southern Pacific Ocean, and do not exhibit the total anion deficits, and excess sulfate values found in westerly storm precipitation.

7. ACKNOWLEDGMENTS

We thank Donald C. Bogen, Environmental Measurements Laboratory, U.S. Department of Energy, for providing the chemical results for wet deposition samples collected at American Samoa and Joyce M. Harris, Geophysical Monitoring for Climatic Change, ARL, Boulder, CO, for help in providing American Samoa trajectories. We also thank Richard S. Artz for use of several computer programs that were of great help in data reduction. This work was partially funded under the National Acid Precipitation Assessment Program.

8. REFERENCES

- Bogen, D.C., S.J. Nagourney, and C. Torquato, 1980: A field evaluation of the HASL wet-dry deposition collector. Water Air Soil Pollut. 13: 453-458.
- Bogen, D.C., S.J. Nagourney, and C. Torquato, 1984: Major ion composition of atmospheric deposition and air particulates at American Samoa. Meteorological Aspects of Acid Rain, Ch. 10, C.M. Bhuralkar (Ed.), Ann Arbor Science, Boston, MA, 243 pp.
- Bortniak, J.C., 1981: The wind climatology of American Samoa. NOAA Tech. Memo. ERL ARL-98, Air Resources Laboratories, Silver Spring, MD, 67 pp.

- Duce, A.R., and E.J. Hoffman, 1976: Chemical fractionation at the air/sea interface. Ann. Rev. Earth Planet. Sci. 4: 187-228.
- Duce, R.A., C.K. Unni, B.J. Ray, J.M. Prospero, and J.T. Merrill, 1980: Long range atmospheric transport of soil dust from Asia to the tropical North Pacific: Temporal variability. Science 209: 1512-1514.
- Feeley, J.A., and H.M. Liljestrang, 1983: Source contributions to acid precipitation in Texas. Atmos. Environ. 17: 807-814.
- Galloway, J.N., G.E. Likens, W.C. Keene, and J.M. Miller, 1982: The composition of precipitation in remote areas of the world. J. Geophys. Res. 87: 8771-8786.
- Harris, J.M., 1982: The GMCC Atmospheric Trajectory Program. NOAA Tech. Memo. ERL ARL-116, Air Resources Laboratories, Silver Spring, MD, 30 pp.
- Hawley, M.E., 1984: Variance calculations for volume-weighted means. Atmos. Environ. (in press).
- Keene, W.C., J.N. Galloway, and J.D. Holden, Jr., 1983: Measurement of weak organic acidity in precipitation from remote areas of the world. J. Geophys. Res. 88: 5122-5130.
- Keene, W.C., J.N. Galloway, and J.D. Holden, Jr., 1984: Organic acidity in precipitation from remote areas of the world. Proceedings of Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources. Report #EPA-600/9-84-006. U.S. Environmental Protection Agency, Research Triangle Park, NC.
- Miller, J.M., U. Dayan, A.M. Yoshinaga, and D.W. Nelson, 1983: An evaluation of precipitation chemistry data at the U.S./WMO Baseline sites over the last ten years. Environmental Pollution Monitoring and Research Program No. 20, World Meteorological Organization, Geneva, 88 pp.
- Miller, J.M., and A.M. Yoshinaga, 1981: The pH of Hawaiian precipitation: A preliminary report. Geophys. Res. Lett. 8: 779-782.
- Nguyen, B.C., B. Bonsang, and G. Lambert, 1974: The atmospheric concentration of sulfur dioxide and sulfate aerosols over Antarctic, subantarctic areas and oceans. Tellus XXVI: 1-2.
- Parrington, J.R., W.H. Zoller, and N.K. Aras, 1983: Asian dust: Seasonal transport to the Hawaiian Islands. Science 220: 195-197.
- Pszenny, A.A.P., F. MacIntyre, and R.A. Duce, 1982: Sea-salt and the acidity of marine rain on the windward coast of Samoa. Geophys. Res. Lett. 9: 751-754.
- Tyree, S.Y., Jr., 1981: Rainwater acidity measurement problems. Atmos. Environ. 15: 57-60.