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Origin and composition of Samoan acid precipitation

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ABSTRACT

Samoan precipitation events are both plentiful and well distributed throughout the year. The chemistry of this rain, determined from weekly samples from 1980 to 1983, shows that the annual fluctuations of free acidity are almost negligible. The 3-year pH is 5.3, with no significant yearly trend. Classification using trajectory analyses of storm events that originated from westerly sources and occurred mainly during the March–April austral fall period, have revealed consistently poorer equivalent ion balance, e.g., anion deficits of 10 μeq L^{-1} larger than observed from other sources. The austral spring period (October–November) is characterized by very steady, strong, easterly trade winds and the ocean is probably the primary source of aerosol. Decreases of acidity are also observed in samples measured first in the field and then in the laboratory, suggesting the existence of another contributor of free protons in Samoan precipitation in addition to the long-range transport of sulfate aerosols. Air masses arriving from westerly sources and 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°15′ S, 170°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 under the National Acid Deposition Program (NADP). 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 et al., 1983). Measurements of precipitation acidity were performed at the GMCC Observatory at Cape Matatula on Tutuila Island, Samoa (Fig. 1), which is situated at an elevation of 76 m above sea level and has an average annual precipitation of 320 cm.

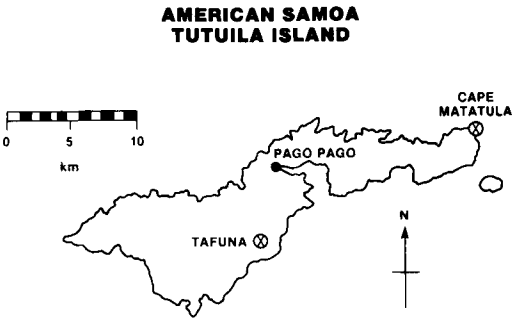

Fig. 1. Tutuila Island, American Samoa.

2. Precipitation chemistry data, sampling and analytical techniques

The data used in this report for characterizing the precipitation chemistry of this remote island

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in the southern hemisphere were derived from samples collected at the Samoa GMCC Observatory from the end of 1980 until 1983. The sampling was done daily in open collectors, as well as weekly using a wet-only protocol. The daily collectors were positioned on the GMCC Observatory roof adjacent to the NADP weekly collectors. A simple bulk-type polyethylene collector is used on the GMCC daily samples. The pH and conductivity are determined immediately after a sample is collected at a field laboratory with a Corning Model 125 meter with semimicro combination electrode and conductivity with a Beckman Model RD-16C meter. Samples are sent within 24 h to the Hilo MLO laboratory for a second measurement of pH and conductivity. Further details concerning analytical procedure are given by Dayan et al. (1984, 1985). The NADP wet-only weekly samples are sent weekly to the Atmospheric Chemistry Laboratory at the Illinois State Water Survey. Basic measurement techniques employed by this laboratory include glass electrode used for pH and conductivity measurements, atomic absorption for metal determinations, automated wet chemistry for $SO_4^{=}$, NO_3^-, and Cl^- using a Technicon Auto Analyzer system. More detailed descriptions of this subject may be found in the 1979 NADP Quality Assurance Report (Stensland et al., 1980).

3. Results and discussion

Although rainfall events are frequent within an individual season in Samoa, the total amount of rainfall may vary widely from year to year because of the position of the Samoan islands in relation to the fluctuations of the intertropical and intratropical convergence zones (Gruber, 1972).

A scattergram of hydrogen ion concentrations versus rainfall amounts for 343 GMCC samples is shown in Fig. 2 suggesting a rather small negative correlation between the two variables. The same results were obtained for the 124 NADP weekly samples. These findings can be contrasted with the strong negative correlation between rainfall amounts and sample acidity in polluted areas (Likens et al., 1984). The slight negative correlations illustrated by the GMCC and NADP sample plots may simply be a consequence of whatever local "pollution" may be present as a result of GMCC and NADP collector locations. These subcloud scavenging processes and their effects on Samoan rain would be minimal, since there is little material for potential dilution to be washed out. The maritime air around Samoa is extremely "clean", exhibiting some of the lowest dust-loading levels measured (Prospero, 1985). In addition, evaporation effects on raindrops would also be minimal because of the extremely moist maritime air associated with Samoa's tropical location. This suggests, then, that the dominant chemistry of Samoan rain is a result of an in-cloud scavenging process.

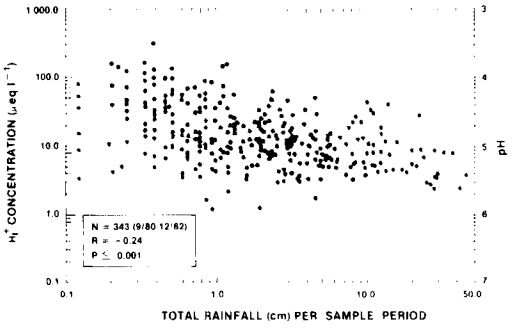

Fig. 2. Scattergram of H^+ field concentration as a function of rainfall volume for 343 GMCC daily bulk samples (September 1980–December 1982).

GMCC and NADP monthly weighted averages of hydrogen ion concentration (Fig. 3) show an average pH value of 5.3. Pszenny et al. (1982), performing an independent precipitation collection based on a much smaller sample set under

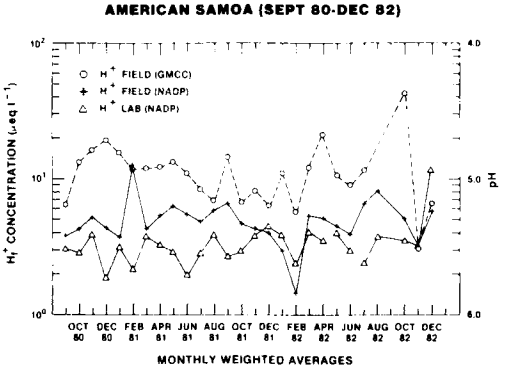

Fig. 3. Monthly distribution of H^+ concentration for NADP weekly samples and GMCC daily bulk samples.

the Sea/Air Exchange Program (SEAREX), found a mean pH value of 5.5.

No obvious temporal trend can be seen in the hydrogen ion concentration in Samoan precipitation, although the weekly data were lowest in H^+ 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 (Fig. 3), suggesting the existence of another labile contributor of free protons in Samoan precipitation. We describe below a method used to attempt an explanation for the free acidity of the Samoan rain samples, based upon the potential relationship between total anion mass, rainfall amount, and wind trajectories.

Since the surface trade wind flow near Samoa is separated 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). The procedure for classifying the Samoan trajectory duration is shown in Fig. 4. Trajectory direction was divided into 8 equal sectors. A 9th category was added to differentiate between trajectory speeds, in which all trajectories within a 2000 km radius of Samoa were taken as local, weak, and meandering flow. Using this classification scheme, 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%) (Tables 1, 2).

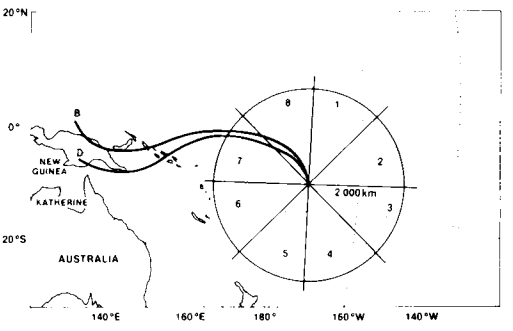

Fig. 4. Classification of American Samoa trajectories using 8 sectors. The example is from 27 March 1980. (B: 850 mb, 00Z; D: 850 mb, 12Z.)

The volume-weighted concentration of major inorganic chemical constituents were determined separately for the group in which easterly trade

Table 1. *Frequency distribution, by sector, of 850 mb 12.00 GMT back trajectories reaching American Samoa for the years 1977, 1979, 1980, 1981, and 1982*

Month	1 (360°–045°)	2 (045°–090°)	3 (090°–135°)	4 (135°–180°)	5 (180°–225°)	6 (225°–270°)	7 (270°–315°)	8 (315°–360°)	Beyond 2000 km*
Jan.	6	58	28	5	0	0	12	0	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	0	17
May	0	73	23	11	9	11	5	0	19
Jun.	0	52	35	8	7	7	2	0	25
Jul.	0	54	34	6	6	12	3	0	13
Aug.	1	65	30	14	8	10	1	0	11
Sep.	0	65	35	11	4	14	4	0	8
Oct.	1	66	43	1	3	3	5	0	21
Nov.	1	79	28	7	4	0	3	0	24
Dec.	2	43	24	6	13	2	15	1	24
total	20	730	362	81	64	88	130	5	219

For 125 days out of a total of 1824 days, back trajectories were not available due to the missing input winds from the National Meteorological Center's Northern Hemisphere gridded fields for standard pressure levels.

* All trajectories within 2000 km radius were taken as local flows.

Table 2. *Frequency distribution (percent) for easterly and westerly storms*

Month	East (sectors 1–4)	West (sectors 5–8)	East/west	Local
Jan.	66	8	8.25	26
Feb.	71	21	3.4	8
Mar.	59	36	1.6	5
Apr.	62	27	2.3	11
May	70	17	4.1	13
Jun.	70	12	5.8	18
Jul.	73	16	4.6	11
Aug.	79	14	5.6	7
Sep.	79	16	4.9	5
Oct.	78	8	9.75	14
Nov.	79	5	15.8	16
Dec.	58	24	2.4	18

winds was the air mass origin and for the group in which westerly flows were present. In order to detect a possible additional acid, a difference function was evaluated by analyzing separately the volume-weighted concentration ion balances in μeq L^{-1} ($DF = \sum[\text{cations}] - \sum[\text{anions}]$) for easterly and westerly storms in conjunction with specific backward trajectories from American Samoa and with NADP weekly precipitation chemistry data for 1980–1982. Unfortunately, NADP collection periods are weekly in duration making individual event chemistry and trajectory assessments very difficult. In order to assign appropriate air trajectories, only weekly measurements covering single events were considered, as determined from official NMC reports, reducing the total number of the 124-week record to 26 individual events (Table 4). In the westerly sector storms, ion balance was found to be characterized by an anion deficit of about 10 μeq L^{-1}.

The means of the volume-weighted averages for all the weekly samples indicated that 27.5% of the H^+ measured in the field was consumed before it was remeasured at the central laboratory at the Illinois State Water Survey. Because of this nearly consistent shift toward higher pH values for laboratory samples than for field samples, the chemical charge balances for each sector were calculated using the field pH values (Table 3). All other ions were adjusted for sea-salt contribution using sodium measurements and the mean composition of ocean water, $SO_4^{=}:Na^+ = 0.25$ (Church, 1984, personal communication).

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

	Easterly storms*		Westerly storms*	
Ions, I	weighted means (μeq L^{-1})	std. dev.	weighted means (μeq L^{-1})	std. dev.
SO_4^{-2}	4.5	1.5	11.5	4.7
NO_3^-	0.5	0.1	0.8	0.2
Cl^-	2.6	3.3	3.2	2.0
$\sum I^-$	7.6	—	15.5	—
Mg^{+2}	1.3	1.3	4.8	4.4
Na^+	0	0	0	0
K^+	0.5	0.4	4.9	3.1
Ca^{+2}	1.4	0.5	7.9	3.9
NH_4^+	0.7	0.2	0.7	0.2
H^{+**}	3.7	0.8	7.9	4.9
$\sum I^+$	7.6	—	26.2	—
DF	0	—	10.7	—

* The values are corrected for sea salt using sodium.

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

DF is a difference function in μeq L^{-1}, $DF = \sum I^+ - \sum I^-$.

The relatively large departure from a balance of cations and anions for constituents of westerly storms shown in Fig. 5 and tabulated in Table 3, and occurring mainly during the austral fall season (March, April) (Table 2), implies sources of protons other than strong acids. The two-sided alternative (two-tailed) *t*-tests were used to evaluate the significance of differences between the two difference functions (DF) of the volume-weighted averages for precipitation from each source region (Table 4). The standard deviations of volume-weighted averages ($S.D._{WA}$) for the two category storm's origin were calculated from:

$$S.D._{WA} = \left[\frac{N \sum_{i=1}^{N} P_i^2 [x]_i^2 - \left(\sum_{i=1}^{N} P_i [x]_i \right)^2}{\left(\sum_{i=1}^{N} P_i \right)^2 (N-1)} \right]^{\frac{1}{2}},$$

where P_i is the precipitation amount corresponding to the ith sample, x_i is the chemical constituent of interest and N is the number of samples (Galloway et al., 1985). When using this test, we made the reasonable assumptions that the sampling distribution of the differences between volume-weighted averages was normally distrib-

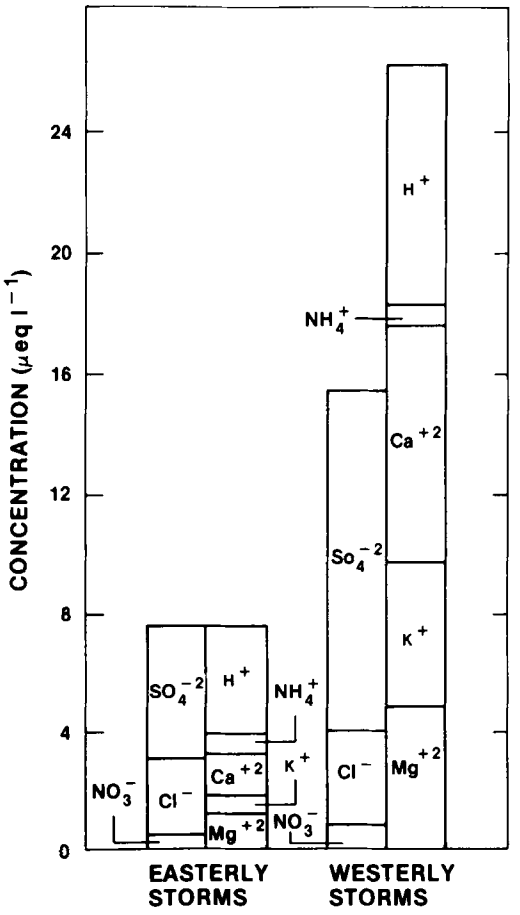

Fig. 5. Volume-weighted mass ion balance for easterly and westerly storms for 1980–1982 weekly wet samples from American Samoa. (The H^+ values were calculated from the field pH measurements.)

Table 4. *Statistical parameters characterizing storms of easterly and westerly origins*

Statistical parameter \ Origin	Easterly storms	Westerly storms
$\overline{D.F.}$	0	10.7
S.D.	4.48	13.73
N	14	12

uted. Studies have shown that this *t*-test is fairly robust to deviations from normality even for smaller samples drawn from populations that might not be normally distributed as might be the case for our data set (Hays, 1981). These tests showed significance at the 1% level rejecting our null hypothesis, assuming $DF_1 - DF_2 = 0$. This anion deficiency may be due to analytical error or an unmeasured anion. Both are probable since an accurate determination of anions at the low $\mu eq\ L^{-1}$ range is difficult. Sequeira (1981), concluded that weak acids controlled the pH of rain at American Samoa during the first 10 months of 1977. 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). These acids might be from local sources, or may be transported as aerosols from a more distant source. 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. 4, Table 2).

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.) Remaining cations (Ca^{+2}, K^+, Mg^{+2}), adjusted for sea-salt contribution and assumed to originate from terrestrial sources, also had significantly higher concentrations in westerly precipitation storm samples than in easterly storm samples suggesting continental sources for excess sulfate. We are initiating a program to collect and analyze precipitation samples on the western tip of Tutuila Island in order to assess the possibility of island contamination during westerly storms, accounting for the presence of the excess Ca, K, and Mg as well as the proposed labile weak acids.

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