AA Technical Memorandum ERL ARL-133

THE CHEMISTRY OF PRECIPITATION FOR THE ISLAND OF HAWAII DURING THE HAMEC PROJECT

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**UNITED STATES
DEPARTMENT OF COMMERCE**

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**NATIONAL OCEANIC AND
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NOTICE

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ABSTRACT. During the Hawaii Mesoscale Energy and Climate Project (HAMEC), a program of precipitation chemistry measurements was conducted using daily and sequential collection techniques. Determination of pH and conductivity were made on site for the daily samples, and all samples were shipped to the Illinois State Water Survey for analysis of major ions. During the period of study, June 11-24, 1980, over 300 sequential rain samples were collected at the Hilo site. The acidity of these samples was very similar to the 5-year acidity distribution of Hilo with a median pH of 4.7. Enrichment calculations showed that the chloride and magnesium levels were consistent with seawater ratios; potassium and calcium levels were 20%-40% greater and sulfate was more than 100% in excess of levels expected from seawater ratios. The daily samples collected at nine sites from Hilo (60 m) to Mauna Loa Observatory (3400 m) showed a steady decrease in seasalt constituents with elevation. The acidity also decreased with elevation, a condition that did not follow the increase with elevation measured over the previous 5-year sampling program. It was also found that nitrate decreased less rapidly with elevation than did excess sulfate. Implications of these HAMEC results are interpreted in terms of long-range transport. Differences in field and laboratory pH measurements are explained as an indication of unmeasured inorganic acids. At the time of the field pH measurements (within 24 hours of the rainfall) the organic acids were calculated to contribute hydrogen ion concentrations that were from 35% to 282% of the levels from strong mineral acids.

1. INTRODUCTION

The Hawaiian islands, because of their unique location, have been used for a number of meteorological and atmospheric chemistry studies (Figures 1 and 2). The research has included both short-term expeditionary-type projects and long-term measurement programs (Eriksson, 1957; Seto et al., 1969; Davis, 1980; Miller and Yoshinaga, 1981; Bodhaine and Harris, 1982; and many others). During the summer of 1980, a special short-term project, the Hawaiian Mesoscale Energy and Climate Project (HAMEC), was conducted on the big island of Hawaii. The primary objective of the research was to measure the necessary parameters that would be used in the initialization and validation of the dependent variables that are incorporated in the Nickerson mesoscale warm-rain model. A secondary objective was to describe the atmospheric chemistry during the period using both surface and aircraft measurements. (For a more detailed description of the

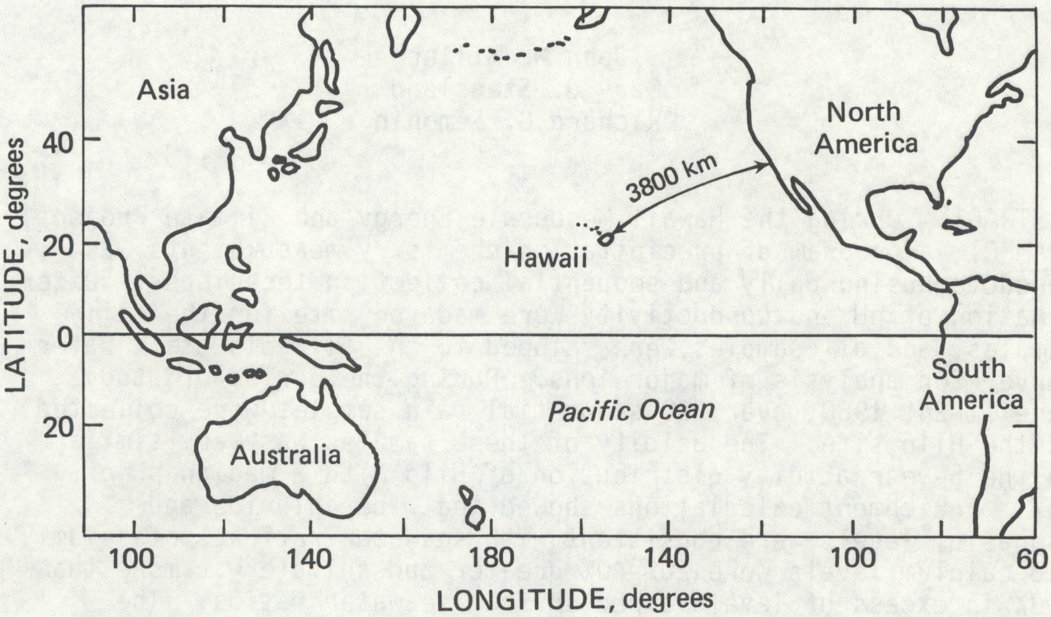

Figure 1. Location of the Hawaiian islands within the Pacific Ocean basin.

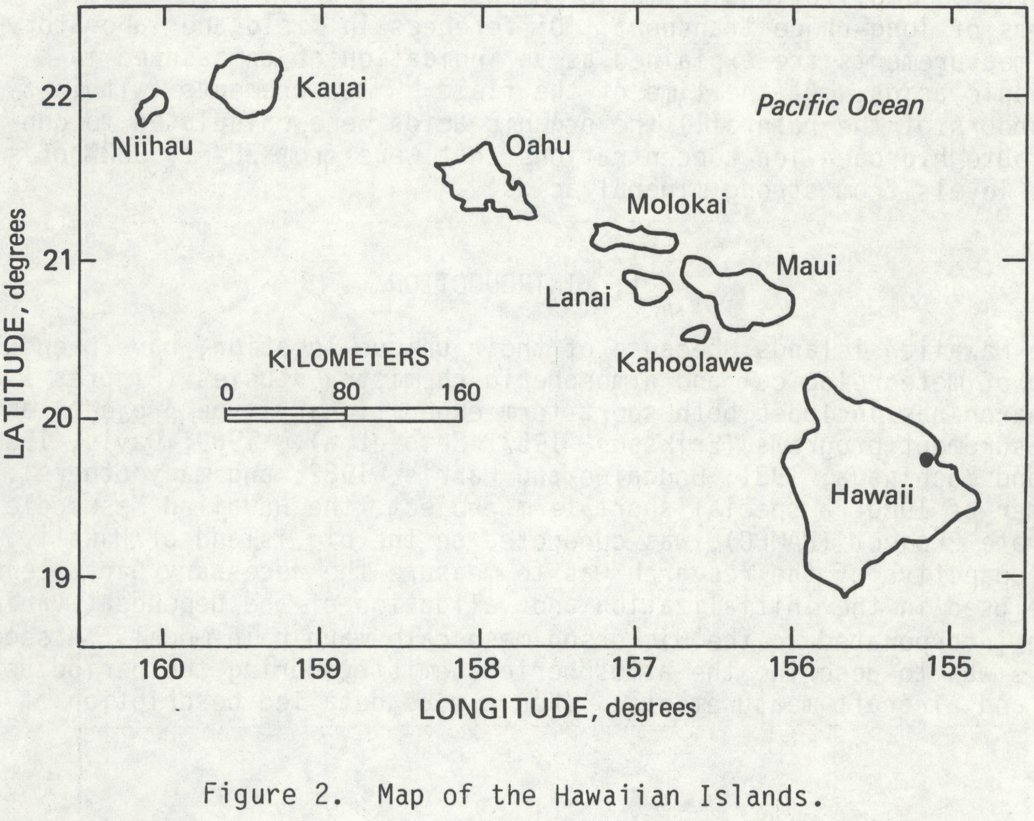

Figure 2. Map of the Hawaiian Islands.

overall project, see Nickerson et al., 1979; Nolt et al., 1980; Dias et al., 1981; Parungo et al., 1981; Parungo et al., 1982; Nickerson and Dias, 1981).

As part of this program, rain samples were collected on a daily basis at nine sites on the island of Hawaii. A central Hilo site had both a daily and sequential sampling protocol. This paper summarizes the chemistry of precipitation for over 400 samples collected during the HAMEC study period, June 11-24, 1980.

2. METHODOLOGY

2.1 Network Configurations

Members of the HAMEC project, in coordination with the Mauna Loa Observatory staff, established nine sites on the island of Hawaii. These sites are described and shown in Table 1 and Figures 3 and 4. Sites were either in low-density suburban areas (the four Hilo sites) or in uninhabited remote locations along the Saddle and Mauna Loa Roads. Four of the sites (1, 7, 8, and 9) are permanently maintained by the MLO staff.

2.2 Sample Collection and Analysis

Two types of sampling were performed during the period--sequential (site 3 only) and daily (at all sites). (See Table 2 for amounts of precipitation by site and date.) The daily samples were collected using an all-plastic bulk funnel and bottle arrangement patterned after the Hubbard Brook collector (Miller and Yoshinaga, 1981). Every morning starting on June 12, samples were collected. A clean funnel and bottle replaced the ones exposed during the previous 24 hours, even if there was no precipitation. On the same day, an aliquot was withdrawn from the sample for pH ("field pH") and conductivity measurements in the MLO laboratory. The remaining sample was then placed in a refrigerator and later shipped to the Illinois State Water Survey (ISWS) laboratory about 5 months later. Here pH ("laboratory pH") and conductivity were again measured and the samples filtered with an 0.45- m Millipore HA filter. The insoluble fraction retained on the filter was not analyzed for either the daily or the sequential samples.

The field measurements of the pH and conductivity of the daily samples at the MLO laboratory followed standard procedures used in the National Atmospheric Deposition Program (NADP) (Bigelow, 1982). A Corning model 130 and Beckman Type RB-5 were used for pH and conductivity. The chemical analysis procedures at the ISWS laboratory were the same as those used for NADP samples (Stensland et al., 1979).

The sequential sampler consisted of four components: a fraction collector, a two-speed event recorder, a tipping bucket raingage, and a wet/dry sampler (see Figure 5). The wet/dry sampler provided a platform for the 30.5 cm diameter polyethylene funnel and kept the funnel covered except during precipitation events. The wet/dry sampler malfunctioned before the experiment was started, so it simply served as a platform. The funnel was rinsed frequently to minimize the accumulation of dry deposition onto the funnel.

Table 1. Precipitation Chemistry Sites Used During the HAMEC Project

Identification Number	Location	Elevation (m)	Estimated Annual Rainfall (mm)	Equipment	Description
1	Halai Hill, Hilo	60	3300	Bulk collector, recording raingage	Isoloated cinder cone in low-density suburban location.
2	Hilo	180	3500	Bulk collector, recording raigage	Vacant lot in low-density suburban location.
3	Hilo	180	3500	Bulk collector, sequential sampler recording raingage	Low-density suburban location.
4	Hilo	180	3500	Bulk collector, recording raingage	Low-density suburban location.
5	10 mi marker, Saddle Rd.	700	6000	Bulk collector, plastic raingage	Some small trees; remote.
6	15 mi marker, Saddle Rd.	1300	5000	Bulk collector, plastic raingage	Scrub vegetation; remote.
7	22 mi marker, Saddle Rd.	1800	4000	Bulk collector, plastic raingage	Lava vegetation mix; remote.
8	Kulani Mauka	2500	825	Bulk collector, plastic raingage	Lava; remote.
9	Mauna Loa	3400	450	Bulk collector, plastic raingage	Lava; remote.

Figure 3. Map showing the nine precipitation chemistry sampling sites identified by number.

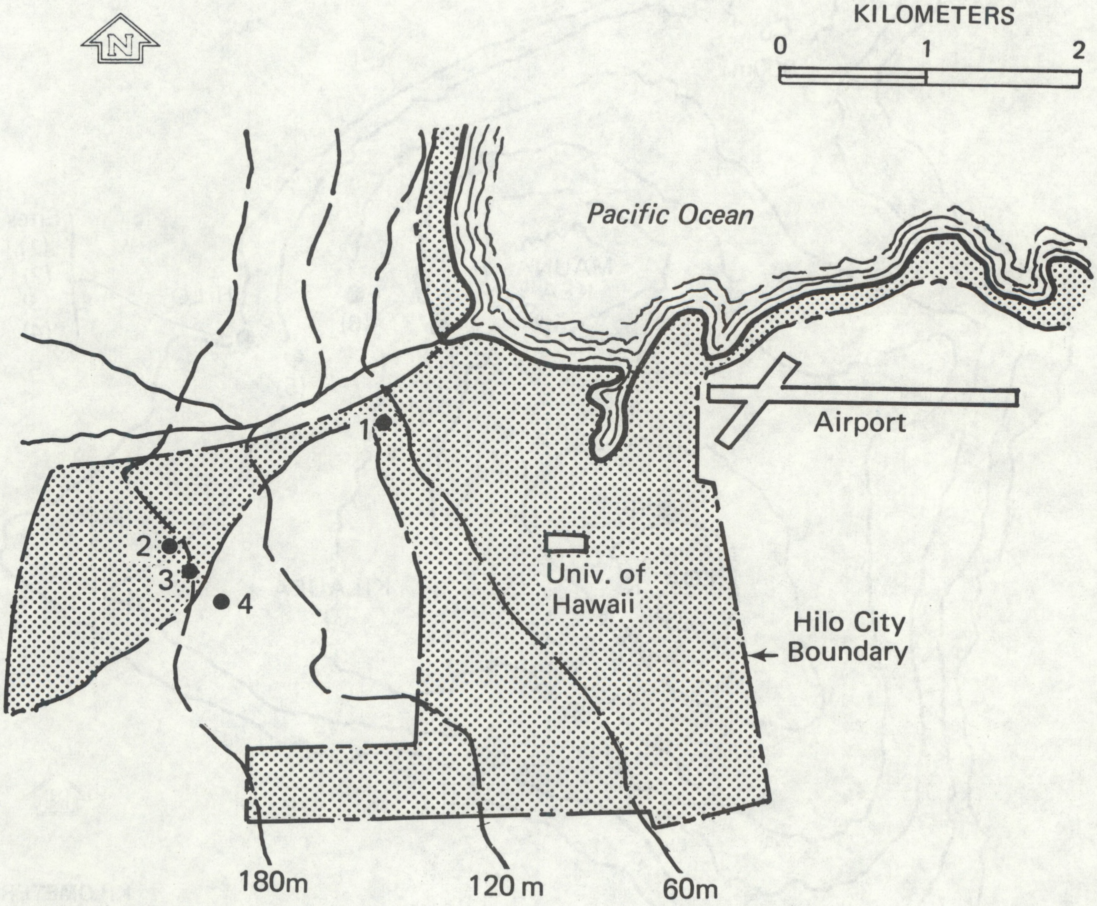

Figure 4. Map showing the four sampling sites in Hilo. Sequential sampling took place at site 3.

Table 2. Precipitation (mm) by site and date collected in 4 inch plastic raingages which were serviced each morning

	Sites								
Off Dates	1	2	3	4	5	6	7	8	9
12[a]	20.8	26.7	26.7	20.8	39.6	27.7	12.2	2.5	0
13[a]	30.0	36.1	27.7	23.6	42.7	36.3	16.5	5.6	0
14[a]	17.3	18.8	19.8	22.1	24.6	20.1	14.2	7.4	0
15[a]	9.9	10.2	10.2	10.9	8.9	9.1	5.6	5.8	3.6
16[a]	12.2	7.4	8.1	7.1	18.8	20.3	7.9	5.6	0
17	0	0	0	0	0	0	0	0	0
18	8.6	6.4	6.9	5.6	22.6	4.6	0	0	0
19	2.7	2.5	2.5	0	0	0	0	0	0
20	7.1	2.5	2.5	0	0	0	0	0	0
21	4.6	5.6	5.1	5.8	5.6	4.1	0	0	0
22	1.8	1.8	1.8	1.3	1.5	2.3	1.3	0	0
23[a]	2.5	1.0	1.0	1.5	10.2	5.8	1.5	0	0
Summary site for Off Dates 12, 13, 14, 15, 16, and 23									
n	6	6	6	6	6	6	6	5	
mean	15.4	16.7	15.6	14.3	24.1	19.9	9.6	5.4	
S.E.M.	3.9	5.3	4.4	3.7	5.9	4.6	2.3	1.7	

[a] Days emphasized for data summaries in this paper.

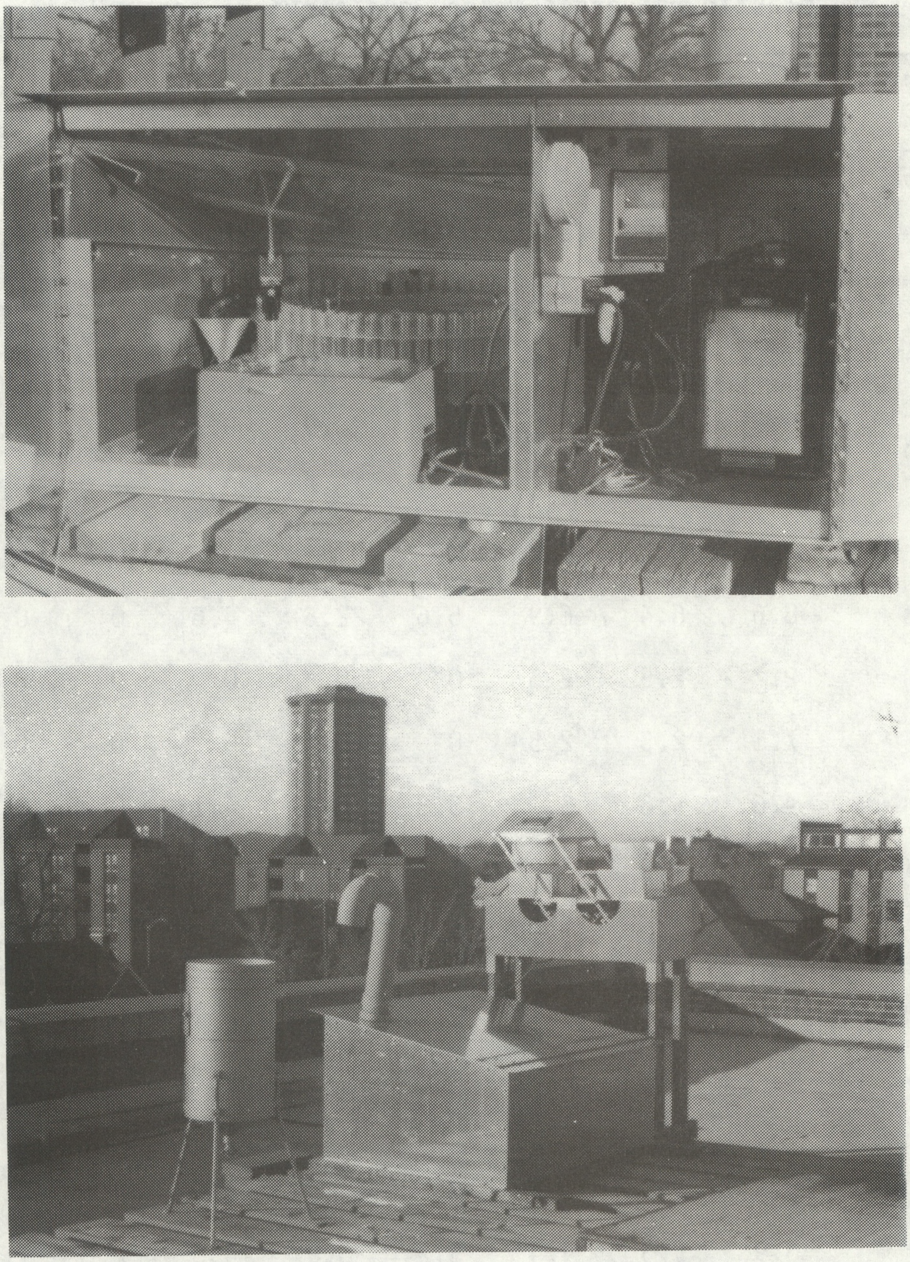

Figure 5. Sequential rainwater sampling system.

Rainwater intercepted by the funnel was directed into the 20 mL polystyrene test tubes in the rack of the fraction collector (the rack held 240 test tubes). The electrical signal from the tipping bucket raingage advanced the fraction collector so that each test tube captured the water for 0.01 inch of rainfall (about 17 mL). Electronic circuitry was built to switch the event recorder from slow to fast speed when rain was occurring. An event mark was recorded on the strip chart when each test tube advanced, for each time of switching the chart speed, and when the wet/dry sampler moved its cover from the wet side to the dry side or vice versa. After sampling a rain event the electronic timer circuit was designed to signal the wet/dry sampler to cover the funnel, and to switch the chart recorder to slow speed if there had not been a test tube advance within about a 10 minute interval. Test tubes containing rainwater were removed daily (or more frequently) from the sequential sampler. Some empty tubes were also removed daily to serve as system blanks for checks of chemical contamination. The test tubes had screw-on plastic covers, which allowed them to be shipped to the laboratory in Illinois without transferring the water to a different shipping container. All the sequential samples were filtered and measured for pH and conductivity at ISWS within 3 weeks of collection. Within 1 month after filtering, the set of major inorganic cations and anions were measured by the equipment and methods used for NADP samples (Stensland et al, 1979).

2.3 Meteorological Conditions

June was chosen for the HAMEC project because of the high persistence of the trade winds during that month. Strong trades were an important condition for the testing of the mesoscale model (Nickerson and Dias, 1981). During the HAMEC period, the configuration of the overall flow patterns remained constant with day-to-day differences in mesoscale disturbances. This can be seen from an examination of back trajectories from Hawaii calculated at 850 mb and 700 mb (Harris, 1982). The configurations remain essentially the same as shown in Figure 6. However, even though the flow pattern was relatively constant, the first week was highly disturbed with rain at all stations from sea level to 2500 m, possibly due to remnants of tropical storm Agatha that was in the area. A transition period took place on June 18 and 19, when the trajectories swung more to the north; on June 20, the typical trade wind regime was again established. In general it can be said that a strong southeasterly flow pattern dominated in the early part of the experiment. In the latter half of the period, the flow became more easterly and weakened. The local mixing ratios and temperature data from the Hilo rawinsonde observations are shown in Figure 7. It can be seen that the moisture levels (mixing ratio = 10 g/kg) are at a higher level during the first period, which reflects the increased precipitation amounts during this time. Reviewing all the data, it can be said that the meteorological conditions were more disturbed in the first week (June 12-17) and were more typical for the season during June 17-24.

3. RESULTS

3.1 Precipitation Chemistry Data from the Sequential Rainwater Sampling System Located in Hilo

The sequential sampler was operated continously from June 11 through June 24 at Hilo site 3. Rain occurred at this site on every day, and the heaviest rains were at the beginning of the time period (Table 2). The sequential

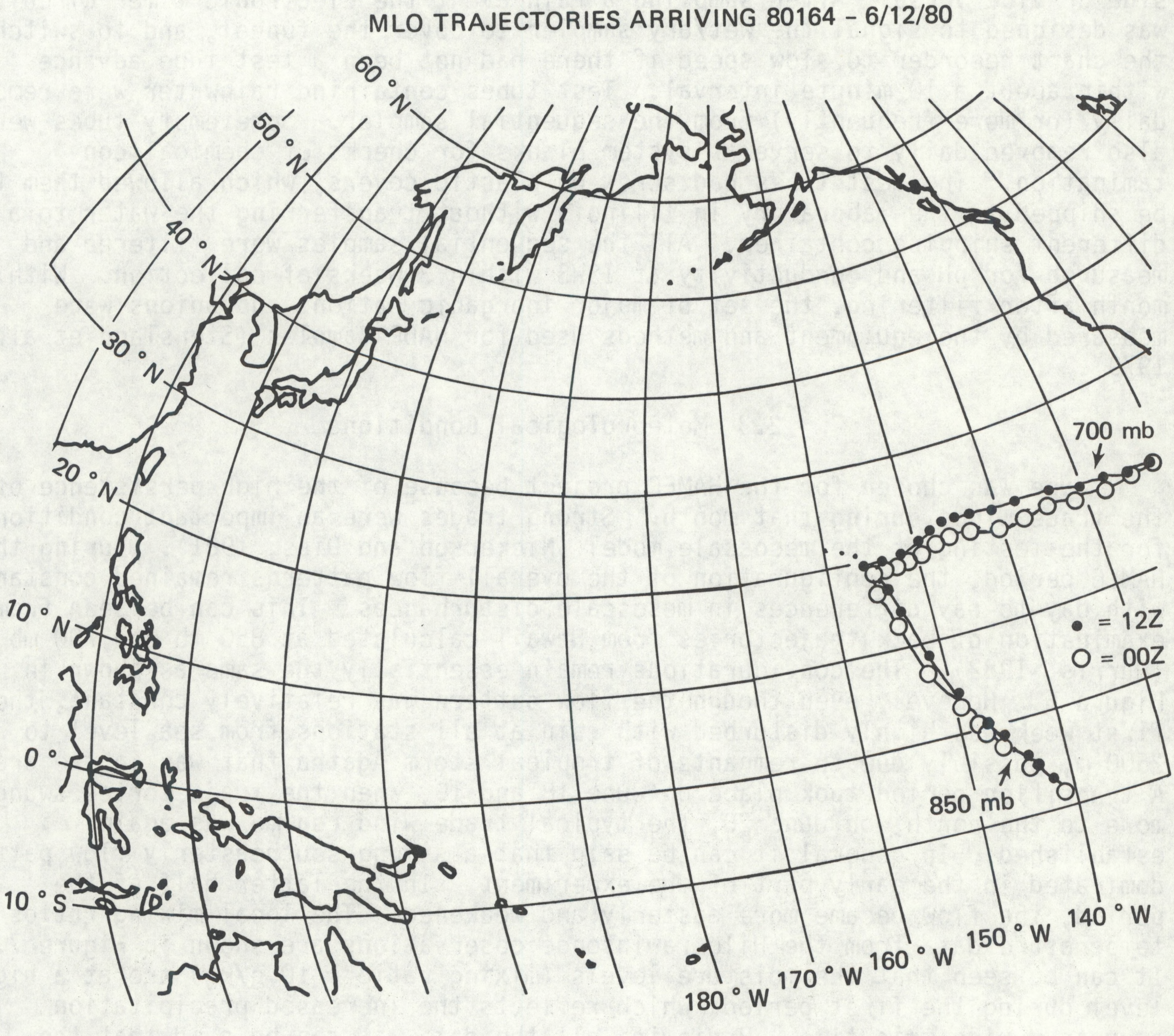

Figure 6. A back trajectory pattern typical for the HAMEC period of study. Example is on June 12, 1980.

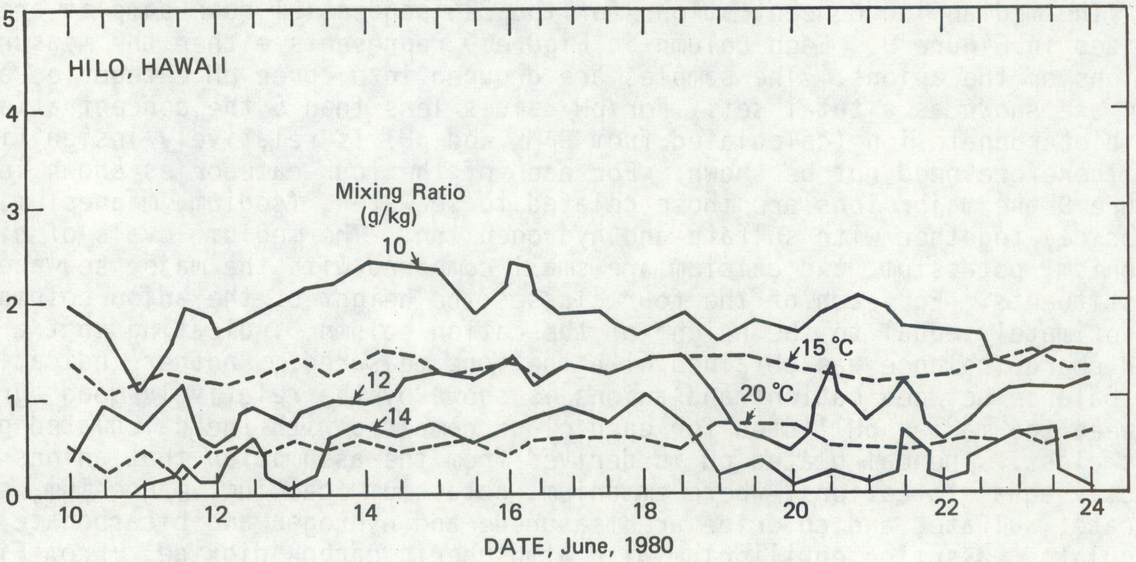

Figure 7. The relative humidity and temperature plotted against height for all soundings taken during HAMEC.

sampler collected one sample for chemical analysis for each 0.01 inch of rainfall. However, for some time periods the sampler malfunctioned and collected a sample for each 0.02 inch of rainfall. In these cases the test tubes overflowed, so the collected sample is some type of average. The pH for each of the sequential rain samples was measured at ISWS, from 5 to 20 days after the sample collection. These data are summarized in Figure 8. The histogram composed of dotted line segments is the pH distribution for the 324 sequential samples collected from June 11 to 24, 1980. The histogram composed of solid line segments is a summary of about 500 measurements on 1 day or 2 day bulk samples collected over a 5 year interval at the Hilo Halai Hill (Site 1) location (Miller and Yoshinaga, 1981). The two histograms are quite similar, with both having a median pH of 4.7. On the basis of this comparison, we will assume that the 324 sequential samples are fairly representative of the rain that would be sampled over a much longer time period.

The median ion concentrations for the 324 sequential rain samples are summarized in Figure 9. Each column in Figure 9 represents either the measured cations or the anions. The samples are grouped into three pH categories and then are shown as a total set. For pH values less than 5 the concentration of the biocarbonate ion (calculated from P_{CO_2} and pH) is relatively insignificant and therefore need not be shown. For each of the four categories shown in Figure 9 the major ions are those related to seawater, (sodium, magnesium, chloride) together with sulfate and hydrogen ion. The medium levels of nitrate, ammonium, potassium, and calcium are small compared with the major seawater constituents. For each of the four classes the height of the anion column was approximately equal to the height of the cation column, indicating that a rather good charge balance was obtained with the ions measured. Another indication of the balance between cations and anions is shown by the relatively good agreement between the median pH listed for each class compared with the calculated pH for that class. The calculated pH is derived from the assumption that anions are exactly equal to cations, where ammonium, potassium, calcium, magnesium, sodium, nitrate, sulfate, and chloride are measured, and hydrogen and bicarbonate are calculated, assuming equilibrium with atmospheric carbon dioxide. From Figure 9 we see that the total concentration of cations and anions increases as the pH for the class decreases.

The concentrations of sodium, chloride, magnesium, potassium, calcium, and sulfate can be adjusted (reduced) for seasalt. For our calculations we have assumed that the sodium is entirely from seasalt. The reduction in the other ions was made using the ratios shown in Table 3. In a small number of cases the seasalt-corrected concentration of calcium, magnesium, or potassium was negative; for these cases the negative value was replaced with a value of zero. The ion concentrations remaining after subtracting the seasalt contribution are referred to as excess concentrations. A summary of the sequential data, adjusted for seasalt, is shown in Figure 10 with the same four pH classes as in Figure 9. Notice that the ordinate has a different scale from that shown in Figure 9. Once again the cations are approximately equal to the anions for each of the four pH classes in Figure 10. With the removal the large contributions from seasalt it becomes very clear that the remaining ions are dominated by the hydrogen cation and the sulfate anion, and thus it is apparent that each of the four classes is dominated by sulfuric acid. The contribution of excess chloride is relatively small for each class shown in Figure 10. Nitrate concentrations are larger than excess chloride levels but much smaller than those for excess sulfate. The concentrations of nitrate and excess sulfate increase as the class pH decreases.

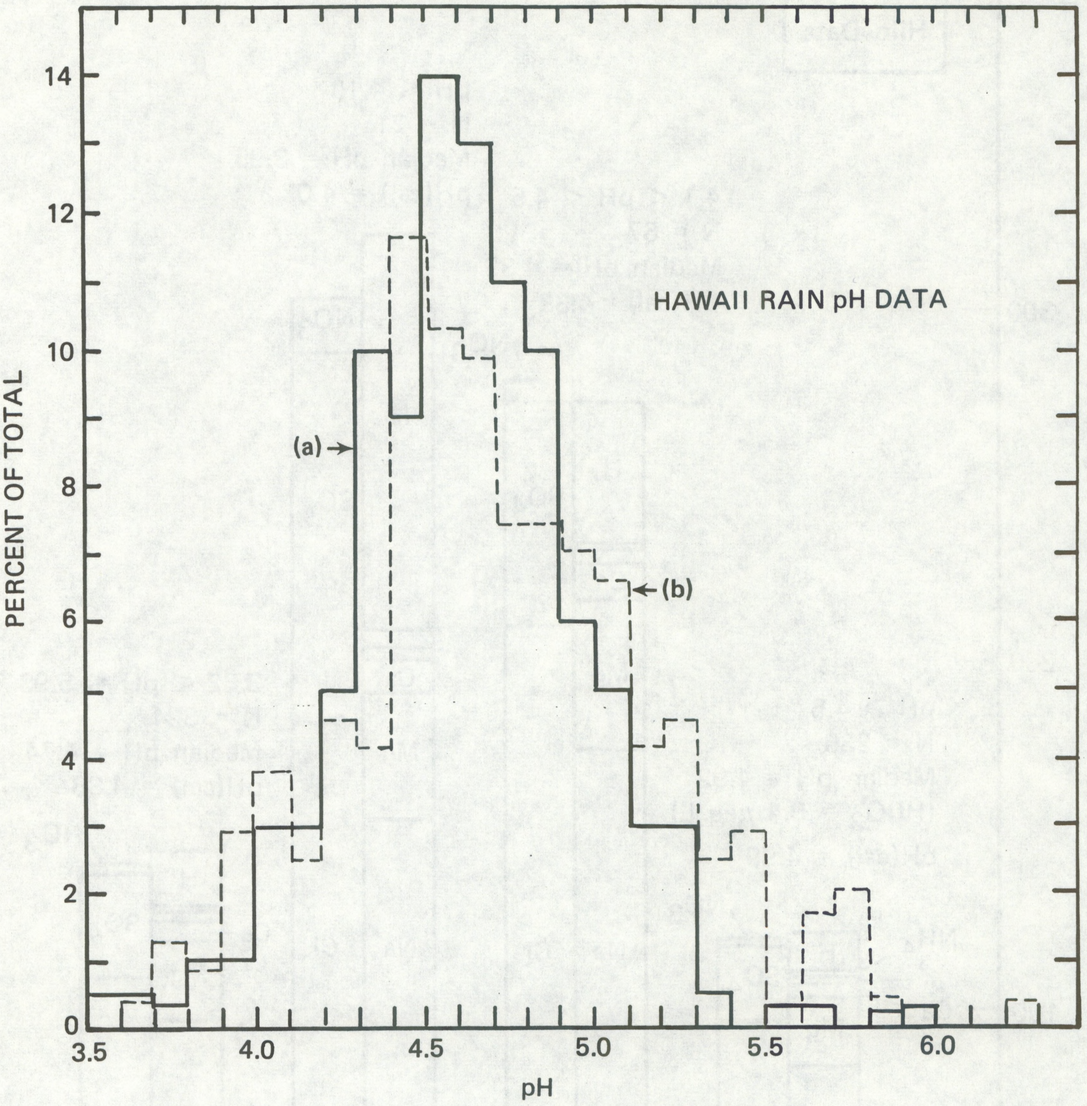

Figure 8. Histograms of pH for rain on the island of Hawaii for (a) 5 years of daily samples for Hilo and (b) sequential samples, June 1980.

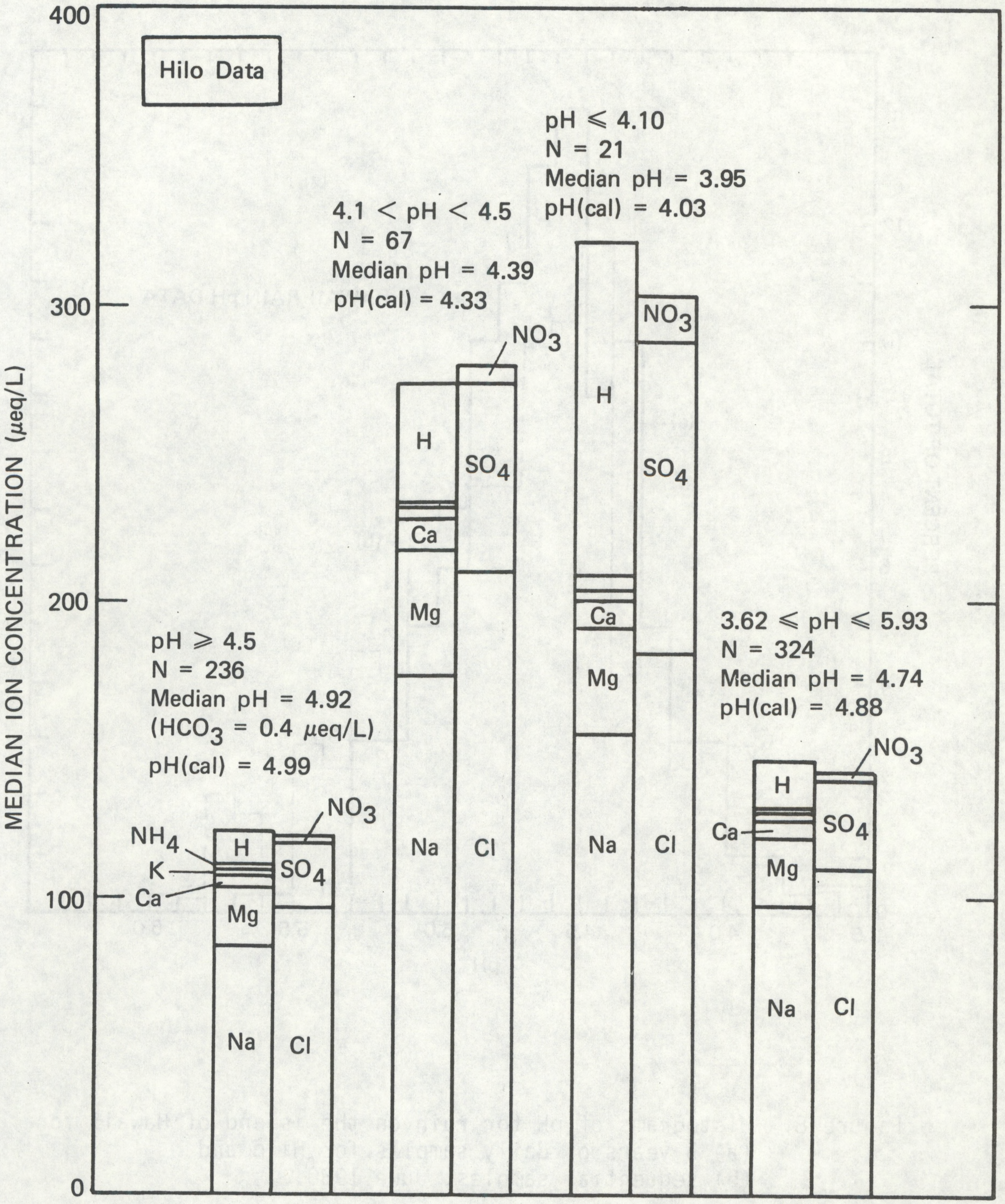

Figure 9. Median ion concentrations for 324 sequential rain samples for four pH classes.

Table 3. Ratios used for adjustment of ions for seasalt[a]

	Ratio Values	
	With Ions in Mass Units	With Ions in Equiv. Units
$(Na/Cl)_{s.w.}$	10.561/18.980 = 0.5564	0.8580
$(Na/Mg)_{s.w.}$	10.561/ 1.272 = 8.303	4.390
$(Na/K)_{s.w.}$	10.561/ 0.380 = 27.79	47.28
$(Na/Ca)_{s.w.}$	10.561/ 0.400 = 26.40	23.02
$(Na/SO_4)_{s.w.}$	10.561/ 2.65 = 3.985	8.3226

[a] Procedure used to calculate enrichments:

E_x = Enrichment for Element or Ion X

$$E_x = \frac{(Na/x)\text{ sea water}}{(Na/x)\text{ sample}} = \frac{(Na/x)\text{ s.w.}}{(Na/x)\text{ sample}}$$

Interpretations:

For $E_x = 1$, assume sea water is only source of x.

$E_x > 1$, there are sources of x in addition to sea water.

$Ex < 1$, there is Na from sources other than sea water, so Na is not a good choice for the reference element.

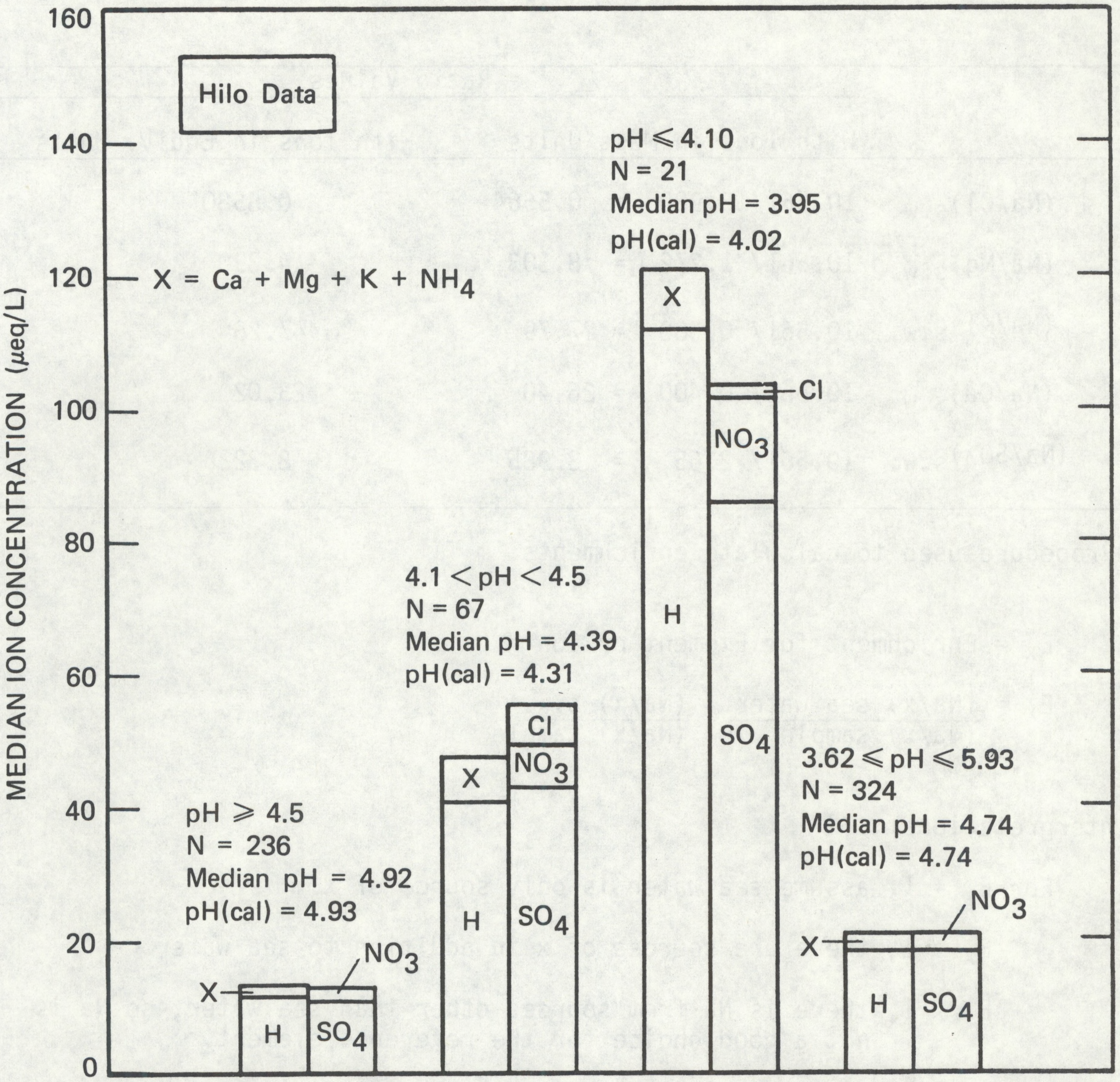

Figure 10. Median ion concentrations for 324 sequential rain samples for four pH classes, with the seasalt component subtracted out.

The individual sample enrichment values, with respect to seawater for chloride, magnesium, calcium, and sulfate are shown in Figure 11. The calculations were made as outlined in Table 3. To obtain more meaningful data, enrichment values are not shown in Figure 11 if either of the ions in the ratio were near the detection limit. Specifically, if Cl^-, Na^+, or Mg^{2+} were ≤ 12 times the detection limit or Ca^{2+} or SO_4^{2-} were ≤ 3 times the detection limit, then the enrichment value is not shown in Figure 11. This screening procedure eliminated the data for the samples for which the analytical uncertainty is indeed very great. The enrichment values for chloride, shown in Figure 11a, are typically very close to unity for the 324 sequential samples. Some of the sample peaks deviating from a value of approxiately 1 are probably due to imprecision related to the analytical measurements. The deviations from unity for samples located near #269 are probably not due to analytical imprecision because they appear also in Figures 11b-11d. These samples were all associated with one small rainshower occurring late in the evening of June 17.

The enrichment values for magnesium, shown in Figure 11b, are similar to those shown in Figure 11a for chloride. In Figure 11c, the enrichment values for calcium, show larger peak values than for chloride or magnesium; also, more samples were deleted by the screening criterion even though it was less stringent than the one for magnesium. This is due to calcium being generally at rather low concentrations in rain samples from Hilo, Hawaii. The enrichment values for sulfate in Figure 11d also contain more and larger peaks than are noted in Figures 11a and 11b. Note that the scales on the ordinates of Figures 11c and 11d are expanded.

The median concentration data for the three pH classes shown in Figure 9 can be used to produce enrichment values for these classes. The results of this calculation are shown in Table 4. The enrichment values for chloride and magnesium are very close to 1 for all three pH classes, as would be expected from the data in Figure 11. The enrichment values for potassium are all near a value of about 1.2, while the enrichment values for calcium are a little larger, with values from about 1.2 to 1.4. The enrichment value for sulfate is 2.15 for the class with samples having a pH greater than 4.5. The enrichment value of about 2 indicates that the sulfate measured in the rain samples was approximately one part associated with seasalt and one part associated with sources other than seasalt. The enrichment values for sulfate increase greatly as the class pH decreases.

The final summary for the sequential rain samples is shown in Table 5. In this case the elements of the factor matrix are listed, being calculated with a standard statistical program package (SPSS). The bottom line in Table 5 contains the matrix elements for rain rate, which was calculated by knowing rather precisely the volume in each sequential sample test tube and the time over which this sample was collected. A subjective judgement applied by some people is that factor-matrix elements with a value less than 0.50 are not too informative. With this criterion, the remaining elements in the first factor in Table 5 contains all the constituents associated with seasalt. It is interesting to note that sulfate has the lowest value of the major seasalt components in factor 1, which is reasonable since we know from the enrichment data that sulfate has major non-seasalt sources. Also the calcium and potassium factor values are less than those for chloride and magnesium, which again agrees with the enrichment results in Table 4. The larger valued matrix elements for factor 2 are for hydrogen, sulfate, and nitrate, which is an association that we had already

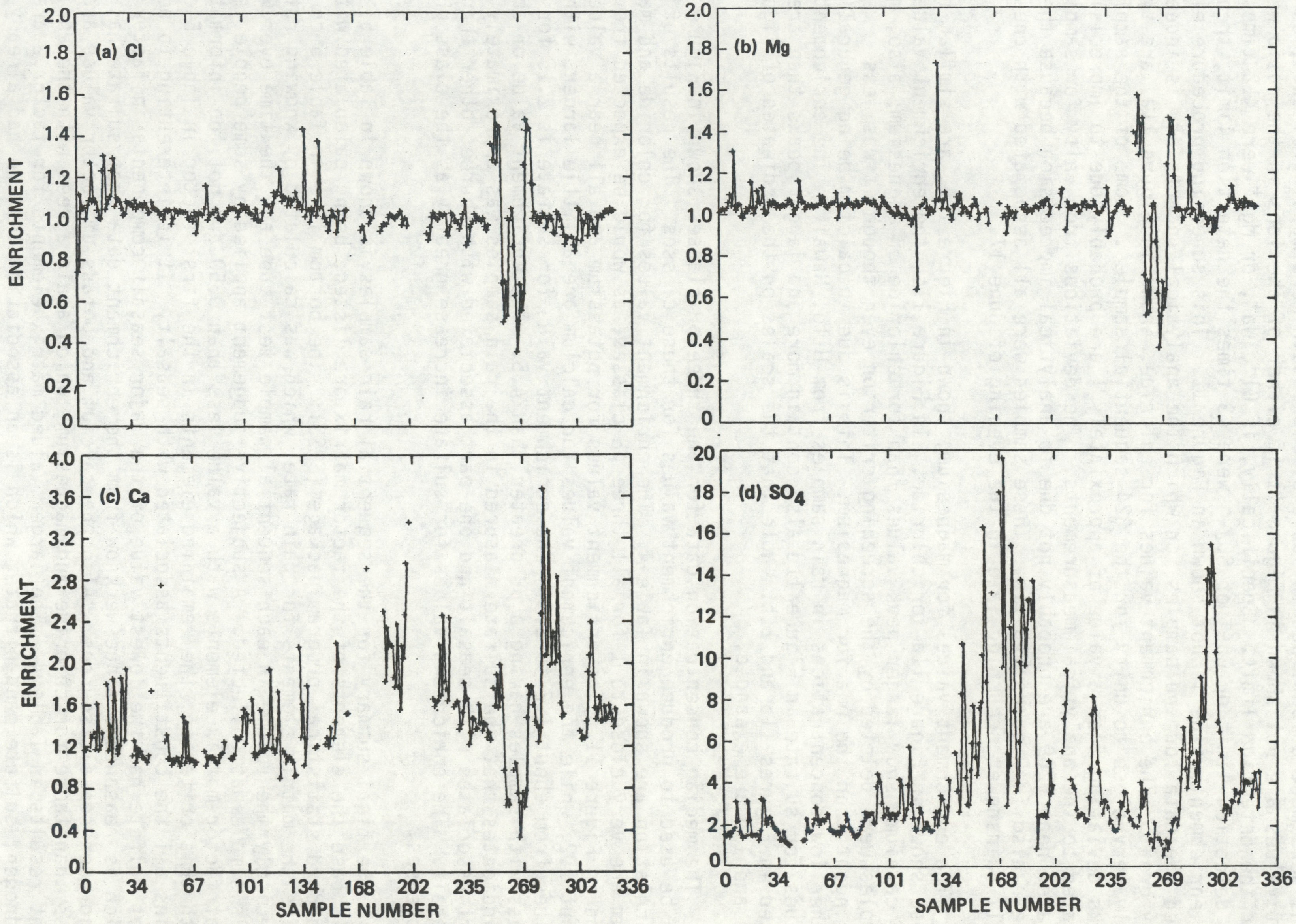

Figure 11. Enrichment for Hilo sequential rain samples for (a) chloride, (b) magnesium (c) calcium, and (d) sulfate.

Table 4. Sequential sample enrichment values for Hilo precipitation, calculated from median ion concentrations for three pH classes

	$pH \geq 4.5$	$4.1 < pH < 4.5$	$pH \leq 4.1$
N	238	67	21
E_{Cl}	0.99	1.03	1.01
E_{Mg}	1.02	1.05	1.00
E_K	1.17	1.25	1.21
E_{Ca}	1.23	1.44	1.40
E_{SO_4}	2.15	3.04	5.60

Table 5. Factor matrix[a] for 1980 Hilo data (321 sequential rain samples)

	Factor 1	Factor 2	Factor 3	Factor 4
H^+	0.19	0.96[b]	0.09	-0.07
SO_4	0.57[b]	0.76[b]	0.23	-0.07
NO_3	0.28	0.67[b]	0.53[b]	-0.17
NH_4	0.28	0.21	0.92[b]	-0.05
Cl	0.96[b]	0.18	0.12	-0.03
Ca	0.88[b]	0.31	0.26	-0.09
Mg	0.96[b]	0.20	0.14	-0.03
K	0.88[b]	0.28	0.25	-0.07
Na	0.95[b]	0.19	0.16	-0.02
Rain rate	-0.06	-0.11	-0.07	0.98[b]

[a] Factor matrix using principal factor, no iterations, and then varimax rotations with Kaiser normalization (SPSS program).

[b] Values $\geq$ 0.50.

recognized from Figure 10. Ammonium ion has the largest element in factor 3, but we need to note that these ion concentrations were quite low for the Hawaii rain samples, and in many cases were at or near the detection limit for the analytical technique. In factor 3, the second largest element is for nitrate, suggesting some association between it and ammonium ion. Finally, the rain rate is the only large matrix element for factor 4, indicating a clear lack of correlation between rain rate and the chemical constituents. In summary, the four factors can be described as the sea-salt, acid, nitrogen, and rain rate factors, respectively.

3.2 Precipitation Chemistry Data for Sites Located from Sea Level to 3400 m and Equipped with Bulk Funnel and Bottle Samplers

The funnel and bottle collection devices were placed at the field sites on June 11 and removed on June 24. The sites were serviced daily in this time interval except on June 17. The dry-deposition input to the bulk samplers was likely minimal because of the judicious placement of the samplers, the frequent rain, and the typical maximum exposure time of 24 hours. No significant amounts of biologic or mineral contamination was observed visually in the collected samples. Sites 1, 2, 3, and 4 were all within the city limits of Hilo, but they were in residential areas away from streets with heavy traffic, and in general were quite suitable for collecting wet-deposition-only samples, even with these bulk-sampling devices. The only abnormal ion concentrations were observed at site 2 where the sampler was located in a vacant lot in a residential area. Several of the samples from this site had high pH values (>6) and also high values of ammonium and potassium. These samples were obviously contaminated by bird droppings and easily recognized and deleted during the screening of the chemical concentration data. A 4 inch diameter plastic raingage at each bulk collection site, with a funnel and tube designed to minimize evaporation, was serviced whenever a bulk sample was collected for chemical analysis. These rainfall data are summarized in Table 2. From this table we observe that rainfall occurred at the highest elevation site (9), the Mauna Loa Observatory, during only one sampling interval. The rainfall during the period from June 11 through June 14 was essentially continuous throughout the day and produced the greatest daily rainfall amounts. After June 16 the rainfall amounts were much smaller and occurred during only a few hours of each day, generally between midnight and sunrise (at least for the sites in Hilo).

The major purpose of the bulk sampling was to determine the change in the chemistry of the precipitation with elevation. For the samples removed on June 12-16 and on June 23 there was a sufficient amount at each site for a complete chemical analysis. Only these 6 days are used for the data summaries in this section. By scanning the rows in Table 2, we see that the precipitation amounts increased with elevation and that a maximum often occurred at site 5, in agreement with the climatic data in Table 1. The mean, and standard error of the mean of the precipitation amount for the 6 study days are shown in Table 2. The mean is largest at site 5, at an elevation of 700 m, and decreased by about a factor of 5 from site 5 to site 8. The mean rainfall at the four Hilo sites, sites 1 through 4, was approximately the same.

The change in the rainwater ion concentration with elevation is shown in Figure 12. Again these data are derived from the 6 days when rain fell at all the sites. For the scale on the abscissa, sites 3 and 4 have been spaced rather closely together to indicate that they were both located in Hilo and separated

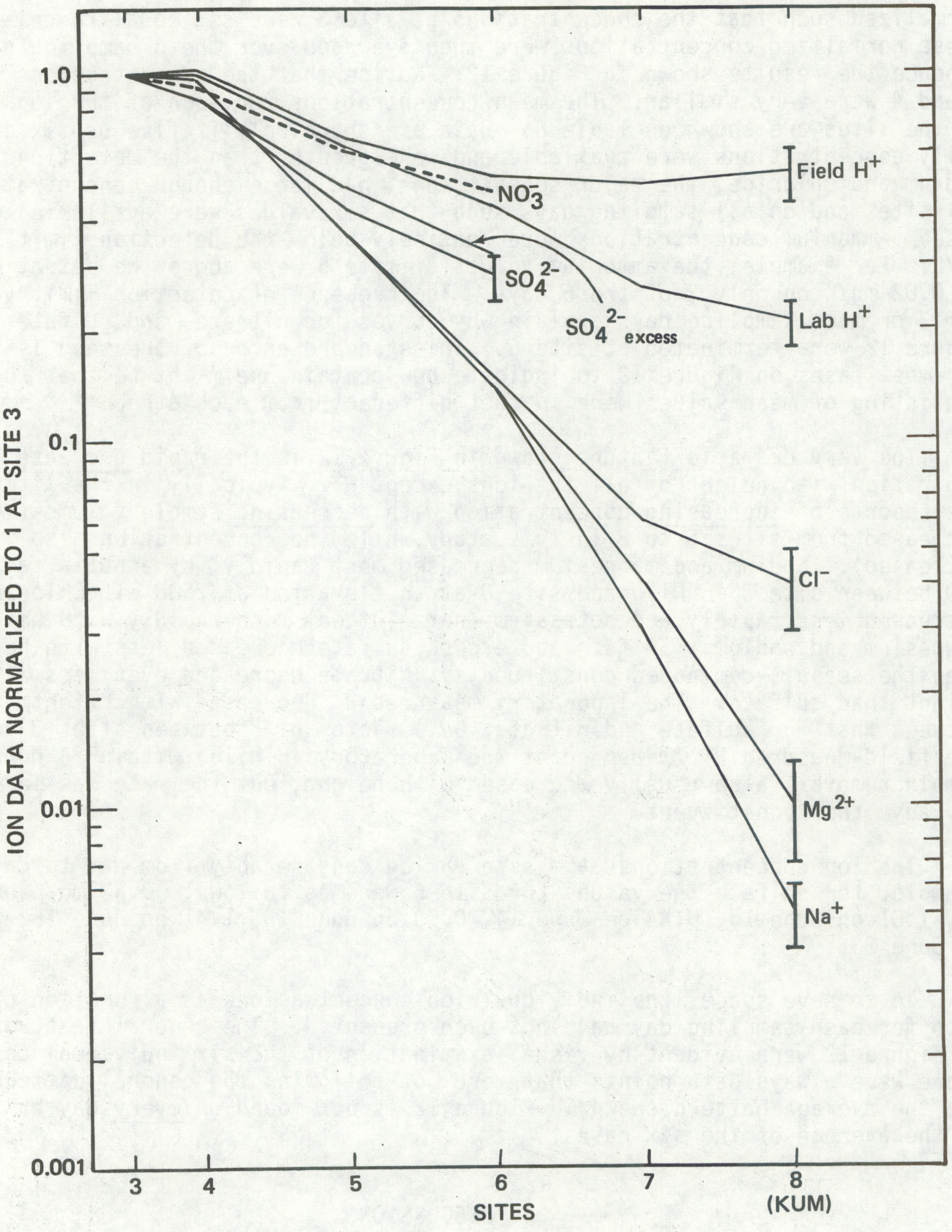

Figure 12. Rainwater ion concentrations normalized for each day to a value of 1.0 at site 3 and then averaged for June 12, 13, 14, 15, 16, and 23. Site elevation increases from about 180 m for sites 3 and 4 to 2500 m for site 8.

by only about 1 km. The chemical concentrations for each ion at each site were normalized such that the concentrations at site 3 were set equal to unity. These normalized concentrations were then averaged over the 6 sampling days to produce the results shown in Figure 12. Notice that the concentrations at sites 3 and 4 were very similar. The mean concentrations for each of the ions at each of the sites are shown on Table 6. Data are shown only if five or six of the daily concentrations were available and were greater than the detection limit. Sodium and chloride, the major seasalt ions, had large enough concentrations at all sites and on all sampling days such that six values were available in each case. Ammonium concentrations were routinely below the detection limit of 0.02 mg/L. For example, the ammonium values at site 5 were above the detection limit of 0.02 mg/L on only 2 of the 6 days. The presence of detection limit values for 2 or more sampling days explain why curves for nitrate, and sulfate, on Figure 12 were terminated at site 6. The standard error of the mean is shown for most cases on Figure 12 to indicate how certain one might be that the curves consisting of mean values were in fact different from each other.

The very dramatic feature shown in Figure 12 is the rapid decrease in concentration with height of all the ions except H^+. Typically in the literature are reports of increasing concentration with decreasing sample volume (volume decreased from sites 5 to 8 in this study while the concentration also decreased). Sodium and magnesium decreased most rapidly, by about a factor of 100 between site 3 in Hilo and site 8 at an elevation of 2500 m. Chloride decreased less rapidly and potassium (not plotted) more rapidly with height than magnesium and sodium. Sulfate and excess sulfate decreased less with height than the seasalt-dominated constituents. Nitrate decreased even less with height than sulfate. The laboratory measured H^+ decreased with height at a rate between that for sulfate and nitrate, by a factor of 5 between sites 3 and 8. The field-measured H^+ (measured at the laboratory in Hilo, within 24 hours of sample removal) also usually decreased with height, but the rate was less than for any other constituent.

The ion concentrations at a site varied considerably from day to day. For example, for sulfate the values for site 5 were as follows: 0.63 mg/L on June 12, 1.01 on June 13, 0.44 on June 14, 0.53 on June 15, 1.41 on June 16, and 2.50 on June 23.

To to save space, the individual ion concentrations as a function of elevation for each sampling day have not been presented. The general features noted in Figure 12 were evident by visual examination of the six individual cases, but there were always data points that were not following the general pattern. That is, the average pattern shown in Figure 12 is not found on every day but in fact is the average of the six cases.

4. DISCUSSION

There are always two potential problems when sampling with a bulk collection device. One problem is that the bulk collector is sampling both wet deposition and dry deposition. For our equipment, considering the terrain, vegetation, traffic flow, and the frequent rain or fog, we feel that the dry-deposition input between rain events would have been negligible. The second problem with bulk collectors is evaporation, which will increase the ion concentrations. The fact that there was a loop in the tubing between the funnel

Table 6. Arithmetic mean and standard error of the mean (S.E.M., in parentheses) of the rainwater ion concentrations for six sampling days (units are mg/L, except hydrogen ion is as µeq/L)

	Sites					
Ions	3	4	5	6	7	8
Cl	6.52(2.25)	5.82(1.56)	2.26(0.66)	0.71(0.13)	0.26(0.04)	0.14(0.01)
Na	3.66(1.26)	1.88(1.15)	1.28(0.39)	0.39(0.08)	0.08(0.02)	0.014(0.005)
Mg	0.446(0.153)	0.401(0.108)	0.158(0.047)	0.050(0.010)	0.013(0.004)	0.005(0.001)[a]
K	0.149(0.047)	0.129(0.035)	0.051(0.016)	0.012(0.004)[a]	--	--
Ca	0.184(0.072)	0.160(0.050)	0.062(0.022)	--	--	--
NO_3	0.49 (0.14)	0.0(0.0)	0.27(0.0)	0.1 (0.05)[a]	--	--
SO_4	2.81(1.11)	1.94(0.34)	1.08(0.32)	0.61(0.15)	--	--
Excess SO_4	1.90 (0.82)	1.19(0.16)	0.77(0.23)	0.51(0.14)	--	--
Field H	49 (20)	42 (12)	27 (7)	20 (4)	25 (11)	20 (4)
Lab H	39 (17)	23 (3)	15 (4)	11 (2)	6 (0.6)	5 (0.7)
Field pH[b]	4.31	4.38	4.57	4.70	4.60	4.70
Lab pH[b]	4.41	4.64	4.82	4.96	5.22	5.30

[a] Only 5 data points; concentrations were below the detection limit on the missing day. Detection limits in mg/L for HAMEC were: 0.05 for chloride, 0.002 for sodium, 0.002 for magnesium, 0.002 for potassium, 0.01 for calcium, 0.02 for nitrate, 0.10 for sulfate, and 0.02 for ammonium.

[b] Calculated from H^+ concentrations listed in this table.

and the collection bottle might suggest that evaporation would not be an important shortcoming for our experiment. The catch efficiency, defined as the catch by the bulk funnel/bottle divided by the catch by the 4 inch cyclindrical raingage, was calculated for all the samples listed in Table 2, and the results are shown in Figure 13. Surprisingly, the catch efficiency was relatively low on several days at several sites. The general pattern is that the lower catch efficiencies were associated with daily rainfall less than 10 mm. Our explanation for the relatively low catch efficiencies is that a certain amount of the rainfall was held up on the funnel surfaces for some period of time and was thus susceptible to evaporation. The magnitude of the evaporation effect will depend on many weather parameters, such as the amount of sunshine, wind speed, and relative humidity. Chemical residue remaining on the funnel after evaporation could be recaptured as subsequent rainwater washes down the funnel surface and reaches the collection bottle. The net result is that there are some concentrating effects in the bulk chemical data presented in this paper.

Summary statistics for catch efficiency are shown in Table 7 for the 6 sampling days used to produce the data in Figure 12. For the largest evaporation situation, at site 8, the evaporation could have produced a maximum increase of about a factor of 1.3 in the measured ion concentrations. Referring back to Figure 12 we note that constituents such as sodium and magnesium decreased by a factor of about 100 from the Hilo site to site 8, and therefore evaporation problems certainly do not explain this strong trend. Also in Figure 12 we notice that sodium and magnesium were lower by about a factor of 5 between sites 7 and 8, and again this is much greater than the possible evaporation factor of 1.3. Thus we conclude that the problem of evaporation is not the explanation for the major decrease with elevation observed in Figure 12. We think that the evaporation effect for bulk sampling would have been minimized if a different type of funnel, one with steeper sides, would have been used. Because of the lack of electricity, automatic wet/dry sampling devices could not have been used at sites 5-8.

The difference indicated in Figure 12 between the laboratory pH, measured approximately 6 months after sample collection of the daily samples, and the field pH is certainly a real phenomenon, not a statistical artifact of the data. Galloway et al. (1982) have reported large changes in hydrogen concentration during shipment of samples from remote sites to a laboratory in Virginia. They have explained the phenomenon as being due to the degradation of organic acids originally present in the rainfall. They determined that such biological changes could be stopped by adding chloroform to the sample at the time of collection. Studies with Illinois precipitation samples have shown that by filtering rainwater samples with a 0.45 m filter, the samples are generally stabilized against chemical change (Peden and Skowron, 1978). For the bulk samples collected in the HAMEC project, filtration was done only after arrival at ISWS, some 6 months after collection in the field. The samples had been stored in the refrigerator at approximately 4°C during the entire 6 mo interval, but it is clear that this did not inhibit the change in hydrogen ion concentrations in these samples. The relatively good balance between cations and anions for these bulk-collected samples after analysis at ISWS, as well as the rather good agreement between calculated and measured conductivity, suggests that the samples did not have a strong organic acid residual after the 6 mo period. Therefore we make the assumption that the difference between the field hydrogen ion concentration and the laboratory hydrogen ion concentration is an indication of the quantity of dissociated organic acids present in the samples at the time of collection.

These data are shown in the top portion of Table 8. We note that for samples removed on June 12 the organic derived hydrogen ion concentrations were rather uniform between sites 2 and 8, at a level of about 6 μeq/L. The data for June 23 indicate considerably higher levels of organic acid present in the samples at sites from 2 to 8, and a large variation from site to site.

The data in the bottom portion of Table 8 are a calculation of the hydrogen ion concentration from organic acids compared with that from mineral acids (assuming no organic acids remained at the time when low pH was measured). The average percentages are noted to increase with height, reaching a maximum of about 280% for the highest elevation site, at site 8. Therefore the problem of pH changes between the field laboratory and the central laboratory measurements has, for this experiment, provided a valuable piece of information concerning the relative importance of dissociated organic acids compared with the strong mineral acids. Referring back to Figure 12 we now interpret the trend in laboratory H^+ to be consistent with the trend observed for nitrate and sulfate, the anions associated with the strong mineral acids. The observation from Figure 12 that the field H^+ decreased much slower with height is now explained as being due to the relatively greater importance of the organic acids with elevation. In fact, for the higher elevation sites, such as the KUM site, the dominant source of acid for the samples was the dissociated organic acids.

The pH values of Illinois rain samples have been shown to sometimes increase more than 0.2 of a pH unit as a result of the relatively slow dissolution of soil mineral particles in the rainwater (Peden and Skowron, 1978). The possibility that this phenomenon could explain the observed pH increase for the Hawaii samples is considered with the data in Table 9. The approach is to compare H, the decrease in hydrogen ion concentration over time, with the levels of the ions that could possibly result from the soil dissolution process. The ions from soil dissolution are estimated by calculating the excess concentrations of calcium, magnesium, and potassium. The data in Table 9 show that the excess Ca varied from being approximately the same magnitude as the measured Ca (for site 7 on June 23) to less than one-tenth the measured Ca (for site 3 on June 13). The small negative values sometimes calculated for excess calcium, magnesium, or potassium were set equal to zero for the results in the last two columns in Table 9. The final column in the table lists the values for the ratio of the sum of the excess Ca + Mg + K to the hydrogen ion decrease. The individual values of the ratio range from 1% to 100%. The mean and S.E.M. for all 30 ratios was 16% ± 4%. The mean values of ratios by site were 39% for site 3, 20% for site 4, 10% for site 5, 6% for site 6, and 5% for site 7. The ratio value thus decreases with elevation, mainly because the numerator of the ratio decreases with increasing site elevation. The main point to be noted from the ratios in Table 9 is that the hydrogen ion change was probably not dominated by the slow soil particle dissolution phenomenon. Since any soil particles captured in the rain would have already been partially dissolved at the time of the field pH measurement, the soil effect on changing the hydrogen ion levels would on the average have been less than 16% ± 4%. Therefore the degradation of organic acids is probably the major phenomenon causing the hydrogen ion levels to change with time for the Hawaii rain samples.

The meteorology of the rain events for the island of Hawaii is rather complicated. The land-sea breeze daily cycle and the possible exchange of air across the inversion will perhaps be important factors in explaining the rain

Table 8. Comparison of field and laboratory-determined hydrogen ion concentrations as a function of site and date

Field H^+ - Lab H^+ (μeq/L)

Off Date	Sites 2	3	4	5	6	7	8
12	6.1	4.3	5.7	8.3	5.3	6.3	7.2
13	18.2	9.3	10.4	6.6	10.1	7.9	21.9
14	5.8	8.5	7.4	4.5	3.2	3.0	5.8
15	14.5	1.9[a]	6.8	15.0	11.1	14.5	13.9
16	27.3	10.8	14.2	12.4	11.1	9.3	10.0
23	30.7	26.3	72.8	25.0	15.3	72.1	34.0
Mean =		10.5	19.6	12.0	9.4	18.8	15.5
S.E.M. =		3.4	10.7	3.0	1.8	10.8	4.4

$$\text{Percent} = \frac{(\text{Field } H^+ - \text{Lab } H^+)}{(\text{Lab } H^+)} \times 100$$

Off Date	Sites 2	3	4	5	6	7	8
12	52	40	28	95	102	162	240
13	>1000	51	58	51	155	141	684
14	38	55	55	56	48	59	112
15	>1000	6.2[a]	26	158	58	184	214
16	>1000	35	48	70	119	135	161
23	19	22	247	74	86	>1000	>1000
Mean =		35	77	84	95	136[b]	282[b]
S.E.M. =		7.5	34	16	21	16	103

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[a] Used anions minus cations to estimate this lab H^+ value.

[b] Used only the five values <1000.

Table 9. Comparison of possible soil derived ions with the difference in field and laboratory-measured hydrogen ion concentrations (concentrations in µeq/L)

Off Date	Site	Field H^+ - Lab H^+	Meas. Ca	Excess Ca	Excess Ca+Mg+K	$\frac{(Ca + Mg + K)_{Excess} \times 100}{(Field\ H^+ - Lab\ H^+)}$ (%)
12	3	4.3	7.2	0.78	1.50	35
	4	5.7	8.5	0.69	2.00	35
	5	8.3	1.8	-0.24	0.43	5
	6	5.3	0.5	-0.34	0.18	3
	7	6.3	0.2[a]	0.02	0.06	1
13	3	9.3	5.7	0.34	1.20	13
	4	10.4	6.3	0.70	1.60	15
	5	6.6	2.5	0.20	0.91	14
	6	10.1	0.2[a]	-0.32	0.32	3
	7	7.9	0.2[a]	0.06	0.06	1
14	3	8.5	1.4	0.01	0.41	5
	4	7.4	1.1	-0.13	0.15	2
	5	4.5	0.4	-0.24	0.05	1
	6	3.2	0.2[a]	-0.08	0.02	1
	7	3.0	0.2[a]	-0.15	0.28	9
15	3	1.9	3.4	1.10	1.90	100
	4	6.8	3.1	0.98	1.60	24
	5	15.0	1.3	0.68	1.00	7
	6	11.1	0.9	0.46	0.74	7
	7	14.5	0.8	0.71	1.01	7
16	3	10.8	11.9	3.60	4.60	43
	4	14.2	11.9	3.60	4.80	34
	5	12.4	4.9	1.50	2.30	19
	6	11.1	2.1	0.92	1.40	13
	7	9.3	0.7	0.42	0.54	6
23	3	26.3	25.9	8.30	9.60	37
	4	72.8	17.7	5.60	6.50	9
	5	25.0	7.9	2.50	3.10	12
	6	15.3	1.8	0.67	1.00	6
	7	72.1	2.6	2.40	3.60	5

[a] Detection Limit

chemistry patterns. For rainfall during situations with upslope flow, the washout of particles and gases below the cloud might be an important factor in explaining a rapid decrease of the rainwater seasalt constituents with height, as has been documented in Figure 12. The less rapid decrease with height of sulfate and nitrate may be due to smaller scavenging coefficients for these species and the precursor species such as SO_2. For rainfall during downslope airflow, the concentrations of the ions in rain at all sites might be lower because the air has already possibly been cleansed during a previous upslope rainfall situation. In addition there is the possibility of the incorporation of some relatively clean air from above the inversion layer into the downslope air.

Previous work reported by Harding and Miller (1982) and further deliberations by the authors during this current experiment continue to support the idea that local volcanic sources and anthropogenic sources related to activities in the city of Hilo are not the major contributors of the sulfate and nitrate observed in the data presented in this paper. The question of whether the sulfate is therefore due to emission of sulfur compounds from oceanic areas and subsequent conversion to sulfuric acid in the atmosphere, or due to long-range transport from anthropogenic sources is an unresolved issue within the scientific community at this time. However the reported sulfur emissions from oceanic areas and the calculations concerning atmospheric transformations would suggest that the local oceanic source cannot be ignored when explaining the acidity at the Hawaii sites (Andreae and Raemdonck, 1983).

The trajectories shown at 850 mb and 700 mb in Figure 6, relevant for the chemistry data in Figure 12, are interesting in that the trajectories at 700 mb do originate from the east or northeast whereas the trajectories at 850 mb are from the southeast. Therefore one must consider whether nitrogen and sulfur emissions from the North American Continent could be transported at upper levels to Hawaii. The big island of Hawaii forms a barrier where a daily mixing, to some extent, of the air above the inversion with the maritime air below the inversion takes place. Therefore long-range-transported sulfur and nitrogen species could be injected on a daily basis into the marine layer and this could explain a portion of the sulfate and nitrate observed at the sampling sites below the marine layer. Furthermore if a significant source of these compounds is at the higher elevation, this would help to explain the rather sharp increases in concentration of nitrate at site 8 as compared with site 7 for several of the 6 sampling days (data not shown) and would help explain more generally why sulfate and nitrate decrease less rapidly with height than the seasalt constituents.

5. CONCLUSIONS

The 324 sequential rain samples collected at Hilo, Hawaii, between June 11 and June 24, 1980, are shown to be representative of the long-term chemistry at this site by making a comparison between the pH histograms for the sequential data versus the long-term daily data record. An analysis of these sequential data for Hilo established that the acidity of the rain can be, for the most part, explained by the strong mineral acids, sulfuric and nitric. Hydrochloric acid is of relatively minor importance. The enrichment values for the 324 sequential samples indicate that the soluble portions of sodium, chloride, and magnesium are due almost entirely to seasalt sources whereas potassium and calcium have somewhere between 20% and 40% contributions due to non-seasalt sources. For the sequential samples with a pH higher than 4.5, the sulfate contribution from non-seasalt sources was approximately equal to that from the seasalt sources. For the more acid samples the non-seasalt sulfate is more important than the seasalt component. The sequential samples were not filtered or otherwise preserved immediately after collection, so it would seem likely that organic acids might have been present at the time of collection. The median pH of the 324 sequential samples was 4.7.

The comparison of field pH and central laboratory pH for the bulk-collected rainwater samples indicated that organic acids probably contributed about one-third of the acidity at the Hilo sites. The percentage contribution of organic acids compared with mineral acids increased with elevation and was in fact about 4 times the mineral acid contribution for site 8 at 2500 m. Refrigeration at 4°C was apparently not sufficient to maintain the integrity of these organic acids in the rainwater samples.

Even after considering the evaporation effects, which were important for some bulk samples, there is still a strong decrease of the ion concentrations with increasing site elevation. The seasalt constituents decreased most rapidly with elevation, about a factor of 100 from the Hilo sites to site 8 at 2500 m. Sulfate and nitrate both decreased less rapidly with elevation than the major seasalt ions, and nitrate decreased less rapidly than sulfate. The hydrogen ion concentration present at the time of sample collection decreased with height and then increased slightly between sites at 1800 and 2500 m. This is explained as apparently due to the relatively greater importance of the organic acid contribution with increased elevation on the big island of Hawaii.

During the collection of the bulk samples on the 6 major study days the 700 mb trajectories were from the east. Therefore it is interesting to consider whether or not the sulfate and nitrate, which decreased less with height than the seasalt constituents, could have originated in part from long-range transport from the North American Continent. The 850 mb trajectories were from the southeast for the 6 major study days. The sulfate may also have an important source due to the emission of various gaseous compounds from the ocean with subsequent conversion to sulfate in the atmosphere. The important issues of sources and long-range transport cannot be resolved with the data collected in this experiment but only lead to the suggestion that they receive more attention in future studies.

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