THE CONTRIBUTION OF SULFATE TO RAINFALL pH AROUND KILAUEA VOLCANO, HAWAII

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Abstract. Between December 1986 and June 1987, the mean pH of rainfall downwind of the Kilauea main vent was found to be 4.5 (range 4.0 to 5.6), 1.2 units higher than the year before (1985–86), although 84% of the 12 sequential samples fell below pH 5.0. The SO_4 content, however, was 34% higher, averaging 18.5 mg L^{-1}. Upwind, in open forest the mean pH 4.7 was little changed from that measured before. Mean SO_4, however, has fallen to a low of 2.5 mg L^{-1}, but, more significantly, in 9 out of 12 sequential samples SO_4 was not detectable at all (i.e. <0.5 mg L^{-1}). The calculated pH, assuming 100% H_2SO_4 would be 5.3 yet 58% of these samples fell below pH 5.0, the lowest being 4.0. Disparities between pH measured and calculated on the basis of SO_4 content indicated that other acid species were present in the precipitation. Oxidation of rain samples with H_2O_2 greatly increased SO_4 content and lowered pH downwind, but failed in most samples to alter either parameter in the upwind collections. These observations, together with the elimination of HCl and NO_3 by others, suggested that SO_2 contributes significantly to acidity downwind, but that in most upwind samples a source of H^+ other than mineral acids, presumably organic compounds, must be of major importance.

1. Introduction

The assumption that SO_2 is one of the major sources of rainfall acidity and the responsible agent for the injurious biological effects of acid rain, has been frequently questioned (Abrahamsen *et al.*, 1976, 1977; Kerr, 1981; Abelson, 1983, 1987; Katzenstein, 1985; Reich and Amundson, 1985; Gaffney *et al.*, 1987), even though it is widely accepted and often verifiable.

As a follow-up to previous studies in this laboratory (Siegel *et al.*, 1987; Nachbar-Hapai *et al.*, 1989) we have confirmed the existence of acid precipitation not only over the barren lava fields of the Southwest Rift Zone, downwind of the Kilauea main vent, but also upwind around Hawaii Volcanoes National Park Headquarters, where both native forest and ornamental plantings show no signs of acid damage.

In spite of the nearly 100 kt, of SO_2 produced annually at the Kilauea main vent, rainfall acidities down to pH 4.0 in samples without detectable sulfate or

of an oxidizable sulfate precursor (i.e. SO_2) have been observed.

2. Materials and Methods

The present study sites have been detailed, including map locations (Nachbar-Hapai *et al.*, 1989) and correspond to stations 85–3 and 85–6 in the previous study (Figure 1). Station 85–4 lies near the Hawaii Volcanoes National Park Visitor Center and
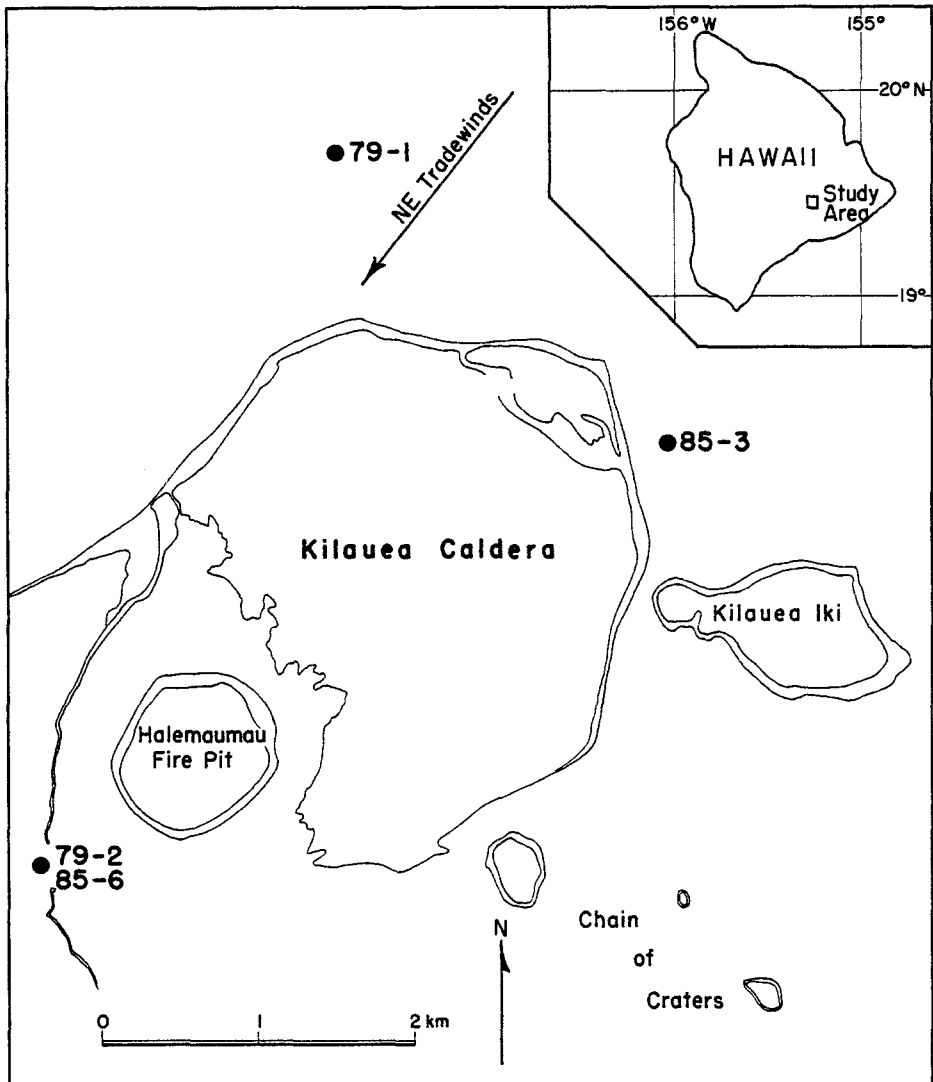

Fig. 1. Locations of rainfall stations around Kilauea Caldera and its main vent, Halemaumau. For purposes of this study, stations 79–1 and 85–3 are considered equivalent upwind; station 79–1 also coincides with Harding and Miller's 1982 and Nachbar-Hapai's 1985 sites. 79–2 and 85–6 are identical in both references cited.

Headquarters 4.5 km ENE of the Kilauea main vent, Halemaumau. It is only 3 km distant from our site 79–1, which is identical with Harding and Miller's (1982) Volcano Golf Course location. These two areas are closely similar in temperature, precipitation and wind patterns (see Table I).

Our previous station, 85–6 (79–2), is located on the nearby barren Ka'u desert at the intersection of the Chain-of-Craters Road and the S.W. Rift. It lies *ca* 0.5 km SW of the Halemaumau fire pit, i.e. downwind. It is identical with Harding and Miller's SW Rift Station.

In the 1979 preliminary study, weekly sample collections were pooled to give monthly rain volume and mean pH values. In the 1985 series, collections were made at 2-week intervals. Rain volume, pH, and soluble sulfate were determined.

Forestry Suppliers, Inc., U.S. Weather Bureau-specification rain gauges were used in duplicate sets at each station. These instruments are rated at a capacity of 27.9 cm $\times$ 2 mm.

During this program, H^+ levels in rain samples have been determined, using four different instruments: the LaMotte pH-mV Digital meter; the Orion Analog pH meter, the Coleman Metrion IV, and the Beckman Expandomatic Digital pH meter. Beckman buffers at pH 4.01 $\pm$ 0.02 (25 °C) and 7.00 $\pm$ 0.02 (25 °C) were

TABLE I

A six month sequential analysis of rain samples at two stations in Hawaii Volcanoes National Park

Sample period[a]	Upwind-visitor center			Downwind-SW rift		
	Rain[b] mm	pH[b]	Sulfate[c] ppm	Rain mm	pH	Sulfate ppm
1	30.9±0.9	4.3	<0.5	5.7±1.7	4.1	22
2	48.1±1.1	4.0	<0.5	8.2±2.1	4.1	32
3	108.7±1.0	5.3	<0.5	39.5±4.4	4.8	10
4	24.9±0.8	4.7	<0.5	20.5±1.8	4.7	10
5	32.6±0.9	4.7	8	11.3±1.5	5.0	16
6	9.5±1.1	4.0	<0.5	3.6±0.5	4.3	28
7	19.8±4.3	4.3	10	12.6±1.5	4.3	28
8	76.3±1.2	4.5	<0.5	35.8±1.6	4.3	18
9	82.3±1.2	5.0	<0.5	22.5±4.2	4.4	19
10	81.9±1.3	5.1	<0.5	50.6±4.0	4.3	10
11	146.9±1.1	5.6	<0.5	78.1±3.6	4.5	10
12	70.9±0.6	5.3	12	432.0±2.0	5.0	19
Total	733	–	–	331	–	–
Mean/Period	61.1	4.7	2.50	27.6	4.5	18.5
Range	9.5–146.9	4.0–5.6	<0.5–12	3.6–78.1	4.1–5.6	10–32
% Below pH 5.0	–	58	–	–	84	–

[a] Sequential 2 wk samples beginning December 22, 1986.
[b] Rain volumes based on quadruplicate samples; all others based on duplicate collecters differing at most by 6% (pH) or 13% (sulfate).
[c] Assuming that 0.5 ppm SO_4 is 100% H_2SO_4, the lowest calculable pH would be 5.3.

used as standards. The instruments all agreed within ± 5%, although duplicate pH determinations fell within ± 2%.

Additional duplicate rain gauges containing H_2O_2 peroxide were deployed at each station to retain deposited SO_2 by its oxidation to H_2SO_4. Each unit contained 2 mmol of H_2O_2, an amount sufficient to convert 128 mg of SO_2 to nearly 200 mg of H_2SO_4, a yield over 10-fold greater than the highest absolute quantity found in the present samples over any 2–wk collection period.

The physical chemistry of natural waters is complex. And nowhere is this more evident than in concepts and computations relating to pH (Bates, 1959; King, 1965). On the other hand, properly standardized pH electrometry has provided data of sufficient accuracy to meet our present needs, namely to obtain a year-round record of pH patterns as they relate to sulfate deposition and the location of SO_2 sources. Sulfate analysis was made by the Hach EPA approved turbidimetric procedure with the DR/1A colorimeter (range 0 to 80 mg L^{-1}. Duplicate rain gauges, on the average, agreed to within ± 11% in sulfate content.

3. Results

From December 1986 to June 1987, two-week rain volumes varied from less than 10 mm to a high value of 147 mm at the Hawaii Volcanoes National Park Visitor Center, totalling 733 mm (Table I). The drier Kilauea SW Rift station low value of less than 4 mm coincided with the Visitor Center station in minimum value in Period 6, as did the maxima at Period 11. The pH of 4.7 at the Visitor Center was only slightly higher than that at the SW Rift station, 4.5, and their ranges were similar. Nevertheless, 58% of the sequential Visitor Center samples fell below pH 5.0, as compared with 84% at the SW Rift. Interestingly, the sulfate content differed greatly between the two stations: in 9 out of 12 samples collected at the Visitor Center station, no SO_4 was detected (limit 0.5 ppm) and the mean was 2.5 ppm; whereas the mean for SW Rift collections was 18.5 ppm and during all collection periods at least 10 and as much as 32 ppm sulfate were found. The possible significance of these disparities between pH and sulfate at the two stations will be considered further.

The peroxidation of rain samples at the Visitor Center also reflects upon a different rain composition relative to the SW Rift collection (Table II). The acidity upwind remains essentially unchanged, overall, whereas peroxide treatment lowers the pH of SW Rift rain by 0.7 units, approximately a 5-fold increase in [H^+].

A closer examination of individual 2-week samples shows that upwind 6 samples did not change at all, 4 changed minimally and only 2 were found to be substantially more acidic. In contrast, downwind Rift samples underwent a sizeable increase in acidity in 10 out of 12 cases.

Sulfate increases of any degree occurred in only 3 of 12 sample periods resulting in a small mean increase – ca 1 ppm, whereas SW Rift sulfate contents were doubled, rising from 16 to 38 ppm.

TABLE II

pH and sulfate content in oxidized rain samples collected in 0.1 M hydrogen peroxide[a]

| Sample period | Upwind-visitor center | | | | Downwind-SW rift | | | |
	pH[c]	Δ[b]	Sulfate ppm[d]	Δ	pH	Δ	Sulfate ppm	Δ
1	4.3	0	<0.5	0	3.2	−0.9	53	+31.0
2	4.0	0	<0.5	0	3.25	−0.85	32	+49.0
3	5.3	0	<0.5	0	4.6	−0.2	15.5	+ 5.5
4	4.7	0	<0.5	0	4.7	0	15.5	+ 6.0
5	4.6	0	8.5	+0.5	4.35	−0.65	54	+38.0
6	3.6	−0.4	<0.5	0	3.5	−0.8	33.5	+ 5.5
7	3.75	−0.55	20	+10	3.5	−0.8	44.5	+16.5
8	4.6	+0.1	<0.5	0	3.8	−0.5	49	+31.0
9	5.1	+0.1	<0.5	0	3.5	−0.9	61	+45.5
10	4.9	−0.2	<0.5	0	3.5	−0.9	30.5	+19.5
11	5.4	−0.2	<0.5	0	3.9	−0.6	27	+18.5
12	5.3	0	13.5	+2.0	4.0	−1.0	34.5	+15.5
Mean	4.6	−0.1	<3.9	+1.0	3.8	−0.7	38.0	+22.5

[a] See Table I for the record of unoxidized samples.
[b] All Δ values are unoxidized – oxidized, both for pH and SO_4.
[c] All values based on duplicates differing by at most 10% (pH) or 11% (SO_4).
[d] For SO_4 0.5 ppm is the limit for the $BaCl_2$ turbidimetric method used.

Of the 9 Visitor Center 2-wk samples in which no sulfate was found initially (i.e. < 0.5 ppm) none yielded analytical quantities of sulfate after peroxidation. Only in the three initially positive for SO_4 did the analytical value change after oxidation.

4. Discussion

Assuming that our 1979–87 collections and those of Harding and Miller in 1978–79 are comparable, there appears to have been a marked increase in rainfall acidity after early 1979 and through mid-1980's (Table III). Whatever changes may have occurred over the next 5 yrs went unrecorded but from mid-1985 to mid-1986 the mean pH values recorded fell even lower. From 1978 to 1986, the downwind pH values were consistently 0.5 to 0.7 units lower than those upwind, as expected.

In our most recent measurements, which reflect a major decrease in acidity, these upwind-downwind differences have all but disappeared.

Harding and Miller reported, on the basis of their 1978–79 data, that a direct relationship existed between rain volume and pH which we did not observe in our subsequent month-to-month studies of 1979–80 and 1985–86.

We have again failed to find this relation comparing the three 6-mo SW Rift collections 1979–87 (Table IV). Here, the smallest volume coincides with the highest pH.

TABLE III

Weighted mean pH values in precipitation in the Hawaii Volcanoes National Park Area, 1978–1987

Date	Site					Reference
	Upwind – visitor center		Downwind – SW rift			
	x	Range	x	Range		
5/78–2/79[a]	4.5	3.8–4.7	3.8	3.3–4.0		Harding and Miller (1982)
7/79–5/80	4.2	3.4–4.4	3.5	3.0–4.1		Siegel *et al.* (1987)
7/85–7/86	3.9	2.9–4.2	3.3	2.6–3.6		Nachbar–Hapai *et al.* (1989)
12/86–6/87	4.9	4.0–5.6	4.7	4.1–5.6		This Study

[a] Harding and Miller's location corresponds to Siegel *et al.* (1987) station site 79-1, 3 km NW of our more recent station 85-4. Both of these upwind stations have similar, unobstructed airways and are at similar distances from Kilauea main vent.

TABLE IV

December to June rainfall and weighted mean pH values at the Kilauea SW rift station , 1979–1987

Period	6 Month volume mm	Mean pH	N
1979–80	436	3.5±0.5	48
1985–86	574	4.2±0.8	24
1986–87	331	4.9±0.8	24

TABLE V

December to June weighted mean rain sulfate and pH data comparing the periods 1985–1986 and 1986–1987

Period	Location		Ratio
	Upwind visitor center	Downwind SW rift	
1985–1986			
Sulfate (ppm)			
Mean	4.3± 1.3	13.4± 7.3	3.1
Range	1.5– 7.5	2.0–32.6	
pH			
Mean	4.3± 1.3	3.2± 0.4	0.73
Range	3.0– 5.7	3.0– 4.6	
1986–1987			
Sulfate (ppm)			
Mean	2.6± 3.5	19.2± 6.4	7.4
Range	<0.5–12.0	10.0–32.0	
pH			
Mean	4.9± 0.8	4.7± 0.6	0.96
Range	4.0– 5.6	4.1– 5.6	

On the basis of our 1985–86 data, SO_4 was 3-fold higher and pH 27% lower at the SW Rift station than at the upwind Visitor Center (Table V). This virtually self-evident observation based on year-long mean values was, however, clouded by many individual samples in which SO_4 could not account for measured pH even if it was assumed to be 100% H_2SO_4. Eliminating volcanic HCl as an acid source (Miller et al., 1984), and NO_x at our remote stations, we suggested, as have others (Abelson, 1983; Kerr, 1985) a significant organic acid contribution. In our current sample sets, where the mean pH values at upwind and downwind stations are within 4% of one another, there is still a more than 7-fold greater SO_4 level at the SW Rift site.

The altered downwind/upwind ratio observed between the 1985–86 and 86–87 sample years originates from a 45% reduction in rainfall SO_4 content upwind and a 34% increase downwind. This change in mean SO_4 values might reflect fewer variations in wind direction from the dominant NE to SW vector in the more recent period. If, however anti-trades were less frequent, the increase in pH upwind (0.2) should have been beyond experimental error, which was not the case. The NE trades characteristically dominate wind direction at the elevation of the Kilauea plateau (1000–1300 m) 70–80% of the year (S. Price, Regional Climatologist, pers. comm.). Further, the pH of SW Rift precipitation rose between the two sample years, although SO_4 increased at the same time. Obscured here by a discussion based on averages, is the time-to-time variation of SO_4 during the 12 periods. Whereas the deposition of SO_4 in rainfall in 1985–86 lay between 4 and 8 mg L^{-1} in 75% of the serial rain collections over a 1 yr program (Nachbar-Hapai et al., 1989), no SO_4 was detected at or above analytical limit (0.5 mg L^{-1}) during 1986–87 in 75% of the sequential collections.

The absence of SO_4 in 9 of the 2 week samples was associated with pH values ranging from 4.0 to 5.3. Therefore SO_4 cannot account for acidity here.

Upwind, there is obviously no difference between pH levels in the two sample years whereas downwind, the 1.2 unit increase was highly significant (t = 2.80, p < 0.01).

Downwind at the SW Rift station, when measured pH values of individual samples were compared with those calculated assuming SO_4 to be 100% H_2SO_4 (Table I vs Table VI), acidity was lower than expected by 0.2 to 1.3 (mean 0.6) pH units. This seems to call for the conclusion that more alkaline than acidic materials must have been deposited during the 1986–87 sample year over the SW Rift, but not during the 1985–86 sample year.

In spite of the elevated pH found during sample year 1986–87, at least one more non-sulfate source might exist in the precipitation at the SW Rift. This conclusion was made evident after oxidation when data from sequential samples with and without H_2O_2 (Table I vs Table II) were compared. With only three exceptions out of 12, reactions with H_2O_2 lowered rain sample pH by 0.5 to 1.0 units. The major non-sulfate acid is weaker than H_2SO_4 but produces it upon oxidation. H_2SO_3 (pk_1 = 1.81, pk_2 = 6.91), of course, fits that description, as subsequent SO_4

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TABLE VI

Calculated pH values assuming that sulfate content is 100% H_2SO_4 before and after oxidation

Sample period	Upwind-visitor center				Downwind-SW rift			
	$-H_2O_2$	$+H_2O_2$	Δ calc	found	$-H_2O_2$	$+H_2O_2$	Δ calc	found
1	>5.3	>5.3	–	–	3.7	3.3	-0.4	-0.9
2	>5.3	>5.3	–	–	3.5	3.1	-0.4	-0.9
3	>5.3	>5.3	–	–	4.0	3.8	-0.2	-0.2
4	>5.3	>5.3	–	–	4.0	3.8	-0.2	0
5	4.1	4.1	0	0	3.8	3.3	-0.5	-0.7
6	>5.3	>5.3	–	–	3.5	3.5	0	-0.8
7	4.0	3.7	-0.3	-0.4	3.6	3.4	-0.2	-0.8
8	>5.3	>5.3	–	-0.5	3.7	3.3	-0.4	-0.5
9	>5.3	>5.3	–	+0.1	3.7	3.2	-0.5	-0.9
10	>5.3	>5.3	–	+0.1	4.0	3.5	-0.5	-0.9
11	>5.3	>5.3	–	-0.2	4.0	3.6	-0.4	-0.6
12	3.9	3.9	0	0	3.7	3.4	-0.3	-1.0

determinations reveal. The calculated decrease in pH of 0 to 0.4 units (Table VI), in 9 out of 12 of the 2 weekly samples, falls short of the measured values (means are respectively: 0.33 and 0.68). Therefore, the combination of SO_4 and oxidizable sulfite cannot account for the total lowering of pH after oxidation.

The upwind acidity data presents a different picture and poses a problem distinct from that seen on the rift zone. In these examples, the SO_4 content did not exceed 0.5 ppm, our analytical limit. Therefore, the contribution of deposited SO_4, if assumed to be 100% H_2SO_4, cannot account for a pH lower than 5.3 (Table VI). These upwind samples when collected in H_2O_2, exhibit neither a reduction in pH nor an increase in SO_4. Obviously, the fact that upwind precipitation fell below pH 5.0 in 58% of the samples and below 4.5 in 42%, cannot be accounted for by any sulfur compounds.

Eliminating local contributions of HCl and NO_x, Miller et al. (1984) concluded that 33% of the June 1984 acid precipitation in the city of Hilo (medium pH 4.7) 50 km ENE of Kilauea was organic in nature. They further observed that samples collected over remote forested areas upslope on Mauna Loa contained up to 80% organic acids. Our samples, collected at approximately 1300 m on the Kilauea plateau, are consistent with significant contributions of non-mineral (organic) acids downwind in spite of the high rate of SO_2 emission. The upwind acid precipitation, in a number of cases, can be best accounted for by attributing most of the acidity to organic compounds.

Of 28 papers in a 1985 symposium concerned with acidic precipitation rain or snow (Martin, 1986), not one, recognized a significant organic source of protons. More recent reports on rain composition (Bridges and Summers, 1989; Diaz-Canejo et al., 1989) fail to address the contribution organic acid components.

It is interesting to speculate that the easily recognized organic component in acid precipitation in Hawaii and not in North America or Europe is a reflection of its continuous emission from highly productive tropical rainforests.

Although Abelson (1983) has named formic acid as a signature compound over remote forested areas, the specific nature of the acidic components of Hawaiian precipitation remains to be determined. In their 1984 study, Miller *et al.* questioned the significance of local volcanism as a source acid and, proposed alternatively that the major source is oceanic.

We suggested that neither marine emissions nor local introductions into the atmosphere from volcanoes and forests can be dismissed as plausible sources of acid rain in Hawaii. A more accurate determination of the respective roles of local and remote sources should be greatly assisted by identification of the organic acids deposited around Kilauea.

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