TOTAL AND NON-SEASALT SULFATE AND CHLORIDE

MEASURED IN BULK PRECIPITATION SAMPLES FROM THE

KILAUEA VOLCANO AREA, HAWAII

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U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 95-4001

Menlo Park, California
1995

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CONVERSION FACTORS

Multiply	by	To obtain
meter (m)	3.281	feet
square meter (m^2)	10.764	square feet
kilometer (km)	0.6214	mile
gram (g)	0.0353	ounce
megagram (Mg)	1.1023	ton
liter (L)	0.2642	gallon

For conversion of degrees Celsius (°C) to degrees Fahrenheit (°F), use the formula:

$$°F = 1.8°C + 32$$

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Martha A. Scholl and Steven E. Ingebritsen

ABSTRACT

Six-month cumulative precipitation samples provide estimates of bulk deposition of sulfate and chloride for the southeast part of the Island of Hawaii during four time periods: August 1991 to February 1992, February 1992 to September 1992, March 1993 to September 1993, and September 1993 to February 1994. Total estimated bulk deposition rates for sulfate ranged from 0.12 to 24 grams per square meter per 180 days, and non-seasalt sulfate deposition ranged from 0.06 to 24 grams per square meter per 180 days. Patterns of non-seasalt sulfate deposition were generally related to prevailing wind directions and the proximity of the collection site to large sources of sulfur gases, namely Kilauea Volcano's summit and East Rift Zone eruption. Total chloride deposition from bulk precipitation samples ranged from 0.01 to 17 grams per square meter per 180 days. Chloride appeared to be predominantly from oceanic sources, as non-seasalt chloride deposition was near zero for most sites.

INTRODUCTION

Kilauea Volcano emits large quantities of sulfur dioxide, with smaller amounts of hydrogen sulfide, hydrogen chloride, and hydrogen fluoride. Household catchment systems for drinking water supply are prevalent in the southeast part of the Island of Hawaii, and a significant portion of the land is devoted to agricultural use. Therefore, the volcanic gas emissions cause concern about acid deposition and subsequent effects, such as crop damage and leaching of roofing metals into drinking water (Sutton and Elias, 1993).

In the course of a study of the ground-water system, a network of precipitation collectors was established in a 4,200 km^2 area surrounding Kilauea volcano (fig. 1), and cumulative samples were collected at approximately 6-month intervals. The cumulative samples were analyzed for stable isotopes and selected major cations and anions. The samplers were designed primarily to obtain isotope samples, and collected both wet and dry deposition. The data reported here provide an estimate of bulk atmospheric deposition of sulfate and chloride in the study

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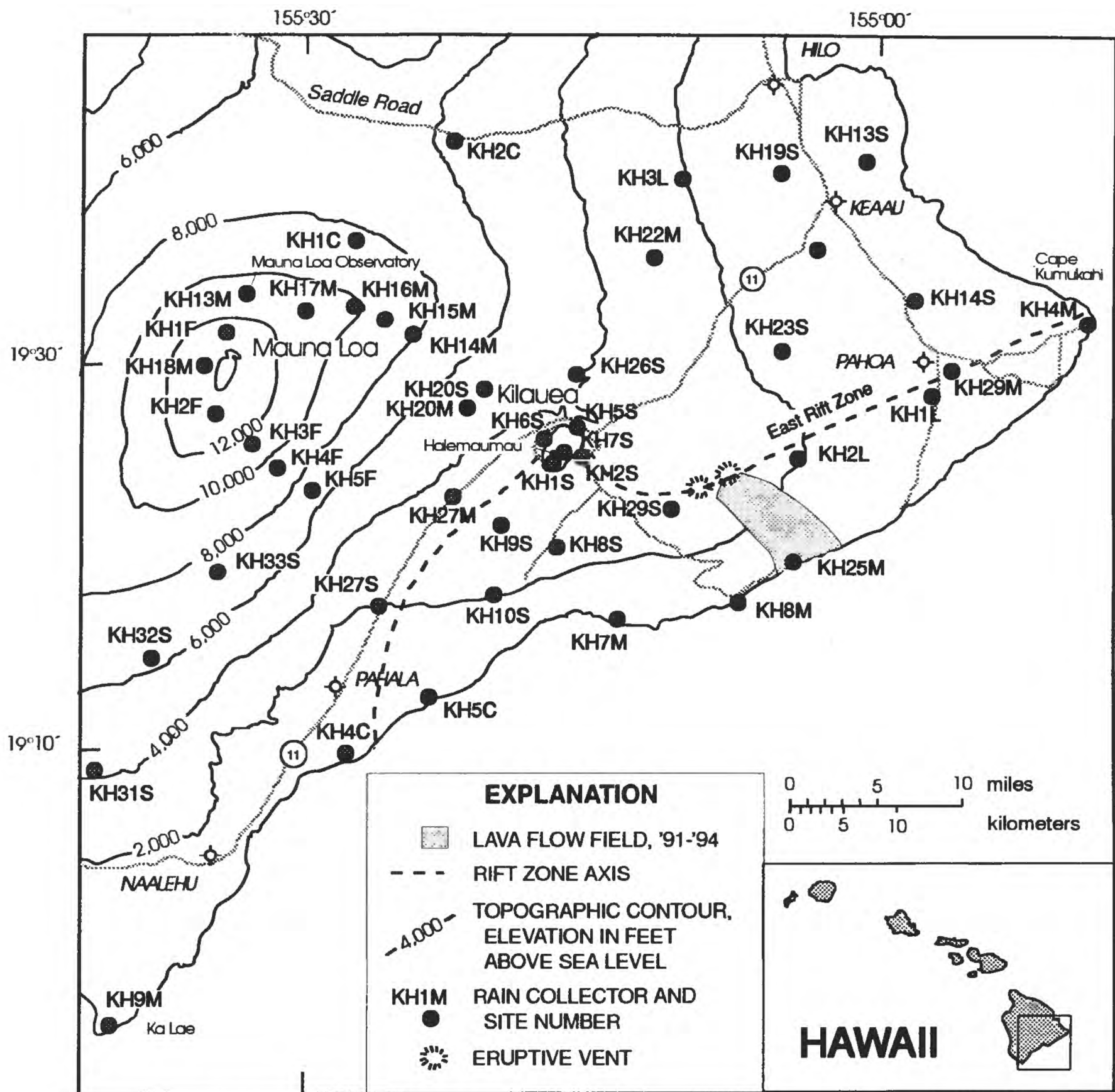
Figure 1. Location map of the study area in southeast Hawaii.

area. However, they do not accurately represent the composition, pH, and chemical speciation of the precipitation. To obtain an accurate representation of precipitation chemistry, samples would need to be collected weekly or on an event basis, and dry deposition should be excluded (Galloway and Likens, 1976; NADP Annual Summary, 1991, p. 2). Bulk precipitation collectors of the type used in this study can lead to underestimation of dry deposition of certain species, including sulfate (Lindberg, et al, 1989).

Purpose and Scope

This report includes estimates of the bulk (wet and dry) atmospheric deposition of sulfate (SO_4) and chloride (Cl) for the southeast part of the Island of Hawaii for four time periods, August 1991 to February 1992, February 1992 to September 1992, March 1993 to September 1993, and September 1993 to February 1994. Estimates of total and non-seasalt (nss) deposition of sulfate and chloride are presented, and the spatial patterns of deposition are discussed. The samples collected in this study cover a larger area than any previously published rain chemistry study. These estimates of sulfate and chloride deposition are useful for indicating spatial patterns, but individual values should not be regarded as highly accurate, as the methods of collection were not standard. Although the data are sparse in the western part of the study area, the patterns of nss sulfate deposition suggest that areas other than those immediately adjacent to Kilauea's summit and East Rift Zone may be affected by volcanic emissions. The data in this report can be used to determine specific areas in the southeast part of Hawaii in which to concentrate sampling efforts for a study of possible acid deposition effects.

Previous Studies

There are no published regional-scale studies of atmospheric deposition for the Island of Hawaii. Several smaller-scale precipitation chemistry studies focused on chemical composition (Eriksson, 1957; Miller and others, 1984), pH (Miller and Yoshinaga, 1981), and acid rain and the effect of Kilauea emissions on rain chemistry (Harding and Miller, 1982; Nachbar-Hapai and others, 1989; Siegel and others, 1990).

Miller and Yoshinaga (1981) summarized pH values for precipitation collected at 9 sites from Cape Kumukahi to Mauna Loa Observatory (2 to 3,400 m elevation). All sites were upwind of Kilauea summit during prevailing east-northeast tradewind conditions, and the data were collected before the 1983-to-present eruption of Kilauea began. The data from that study showed that rainfall pH decreased (acidity increased) with elevation. The authors postulated that the

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acidity at higher elevations might be due to long-range atmospheric transport of acidic compounds. They also noted that, during a major eruption, volcanic emissions would increase rain acidity locally. Miller and others (1984) later reported results from a 14-day study in June 1980, with samples collected at many of the same sites as in the previous work. They found that seasalt-derived ions (Na, Mg, Cl) decreased most with increasing elevation, while H^+ and SO_4 decreased to a lesser extent. Sulfate concentrations more than 100 percent in excess of those expected from seawater ratios were found in the precipitation samples.

Harding and Miller (1982) collected precipitation in the area around Kilauea's summit and compared upwind and downwind samples. They concluded that the effect of Kilauea emissions on the acidity of rain during noneruptive periods was local (within 10 km of the summit), that sulfate was the major anion in the rain, and that much of the acidity of the rain was due to sulfuric acid (H_2SO_4). Nachbar-Hapai and others (1989) collected precipitation in the same area around Kilauea summit. This group found no correlation between sulfate content and pH of rain samples, and questioned whether H_2SO_4 was the major source of acidity. In a follow-up study (Siegel and others, 1990), duplicate rain collectors were deployed at each site; one collector was untreated and one collector contained peroxide solution to oxidize sulfur species to SO_4. The oxidized duplicates had higher measured sulfate content than the untreated samples at sites downwind of the caldera, but not at sites upwind of the caldera. In all samples, the calculated amount of H_2SO_4 was not sufficient to account for the acidity of the sample. The authors concluded that organic acids, as well as H_2SO_4, were a likely source of rainfall acidity in the Kilauea area.

Acknowledgments

SOURCES OF SULFUR AND CHLORIDE

Sulfur

In the study area, possible sources for sulfate and sulfur compounds that can oxidize to sulfate include (1) Kilauea volcano summit and eruptive vents, (2) sea-salt aerosols, (3) volatile sulfur compounds such as dimethyl sulfide, carbonyl

sulfide and hydrogen sulfide emitted from the ocean, wetlands, and soils and plants (Andreae, 1985), (4) power plants and automobile exhaust, and (5) Asian dust storms (Darzi and Winchester, 1982). The sulfate collected in our bulk precipitation collectors could have originated as wet or dry deposition. In near-shore areas, wet deposition may include sea spray, or rain or heavy fog droplets which have nucleated around sea salt particles. Precipitation can also scavenge sulfur compounds (SO_2, SO_3, S^-) from the air, which eventually oxidize to sulfate. The dry deposition input to our collectors may have been particulate sea salt, sulfur dioxide (SO_2), or (for collectors near the caldera area) dust from fumarolic sulfur deposits that deposited on the funnel surface and were washed into the collector.

Recent sulfur-dioxide emissions from Kilauea volcano were summarized by Elias and others (1993) and Sutton and others (1994). Until late 1991, SO_2 emissions from the current (1983 - present) eruption on Kilauea's East Rift Zone (ERZ) were from point sources at Kilauea's summit and from eruptive vents (fig. 1). From late 1991 to the present (late 1994), degassing has occurred from many sources along the lava flow field between the eruptive vents and the ocean. Estimates of current SO_2 emissions from the ERZ eruption are 280-1,500 megagrams per day (Mg/d). Current SO_2 emissions from Kilauea summit are significantly smaller, ranging from 125 to 250 Mg/d. The mid-1994 estimate of total SO_2 emissions from Kilauea's summit and ERZ is 400 to 1,850 Mg/d (Sutton and others, 1994).

Chloride

The major chloride sources in the study area are probably sea salt and emissions from Kilauea volcano, either in the form of hydrochloric acid (HCl) emitted directly from fumaroles and eruptive vents or HCl generated when molten lava contacts seawater (Gerlach and others, 1989). HCl constitutes 0.163 percent by volume of the gaseous emissions from Kilauea's sustained East Rift Zone eruption, whereas SO_2 makes up 13.6 percent by volume; estimated degassing from Kilauea over a 322-month period from July 1956 to April 1983 totaled 2×10^{10} g Cl and 4.6×10^{12} g S (Gerlach and Graeber, 1985).

SAMPLE COLLECTION AND DATA ANALYSIS

Precipitation Collection Methods

Precipitation collectors were 13- or 19-liter high-density polyethylene buckets with o-ring sealed lids, with 5, 8 or 14 cm diameter polyethylene funnels set in the lid, depending on the anticipated rainfall for the site. Collectors were placed on the ground in open-sky and throughfall (forested) sites, and were sampled at approximately 6-month intervals for stable isotopes and major cations and anions. Sample condition was variable, with most open-sky collectors yielding fairly clean-looking samples, whereas throughfall collectors in some cases contained large amounts of algae, leaves, twigs, and insects. Because of variable type and surface area of vegetative canopy, we considered the throughfall samples to contain unquantifiable amounts of atmospheric deposition. The throughfall data were not used in the sulfate and chloride deposition analysis.

Several of our open-sky rain collectors were sited either next to or within about 1 km of a standard rain gauge. Comparison of the amount of rain in our collectors with the amount of rain reported at the rain gauge over the same time period (Climatological Data, 1991 to 1993) resulted in apparent collector efficiency of 54 to 116 percent for our rain collectors (table 1). Percentages more than or less than 100 percent may be due to splashing of rain into the funnel from the bucket lid during heavy rain, to local differences in rainfall, or to errors in measured volume in the collectors.

Table 1. Apparent collection efficiencies for selected precipitation collectors in the southeast portion of the Island of Hawaii

[Collectors used in this study were compared with nearby standard rain gauges that were read daily. Rainfall from standard gauges was obtained from NOAA Climatological Data reports, the U.S. Geological Survey's Hawaiian Volcano Observatory, and the University of Hawaii Waiakea Agricultural Experiment Station. Diameter refers to funnel diameter; percent efficiency is relative to the standard gauge; do., ditto; cm, centimeters.]

Site (fig. 1)	Collection period	Diameter (cm)	Rain-fall (cm)	Rain gauge	Rain-fall (cm)	Percent efficiency
KH14S	8/2/91-2/14/92	5.3	141	Pahoa 65	135	104%
do.	2/14/92-9/14/92	"	181	do.	156	116
do.	3/23/93-8/27/93	"	123	do.	143	86
KH19S	8/2/91-2/17/92	5.3	164	Waiakea Ag. Ex. Sta.	168	98
do.	2/10/92-9/21/92	"	200	do.	213	94
do.	9/21/92-3/24/93	"	193	do.	201	96
do.	3/24/93-8/25/93	"	152	do.	166	92
KH27S[a]	8/4/91-2/13/92	5.3	61	Kapapala Ranch 36	98	62
do.	2/13/92-9/18/92	8.3	35	do.	48	73
do.	9/20/92-3/25/93	"	70	do.	83	84
do.	3/25/93-9/1/93	"	39	do.	49	80
KH6S	7/31/91-2/7/92	5.3	50	Volcano Observatory	81	62
do.	9/18/92-3/27/93	8.3	87	do.	110	79
do.	3/27/93-8/26/93	8.3	38	do.	71	54
KH1C	8/2/91-2/17/92	15	20	Kulani Mauka[b]	24	83
do.	2/17/92-9/20/92	14	34	do.	31	110
do.	9/20/94-3/27/94	"	39	do.	41	95
do.	3/27/93-8/25/93	"	30	do.	26	115

[a]Collector about 1 kilometer from standard gauge. Other collectors were within 15 meters of a standard gauge.
[b]Collector not always read daily.

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For the first collection period (August 1991 to February 1992), most rain collectors had 5.3-cm diameter funnels and contained a layer of silicone oil to retard evaporation. However, there was some degree of evaporation from these collectors (estimated at 0 to 30 percent of total volume, with most less than 10 percent). For subsequent collection periods, larger (8 or 15 cm) funnels were used in areas with lower rainfall and most collectors were designed without silicone oil, but had a floating ball in the funnel which covered the opening during dry periods. During these collection periods evaporation did not exceed 2 percent. At the end of 1993, the network of rain collectors was decreased to 14, with 10 open-sky sites; hence the smaller data set for the last collection period.

At the end of each collection period, the precipitation samples were weighed, passed through quantitative filter paper (Whatman 54) to remove oil and (or) debris, then passed through a 0.45 µm filter. Cation samples were acidified with high-purity nitric acid. Samples from the first two collection periods were analyzed within 6 months of collection and samples from the latter two periods were analyzed within 2.5 months of collection. There was a 6-month hiatus (September 1992 to March 1993) between the first two and the last two collection periods; no chemistry samples were taken for this period.

Chemical Analyses

The first set of samples was analyzed for chloride by the mercuric thiocyanate/ferric nitrate colorimetric method (Franson, 1985). Sulfate analyses were done by the automated methylthymol blue method (Franson, 1985), with a detection limit of 2 mg/L. Because some of the first set of samples were visibly colored, subsequent anion samples were analyzed for chloride and sulfate by ion chromatography. Cation analyses for the first set of samples were done using inductively coupled plasma - atomic emission spectroscopy (ICP-AES). For subsequent sets, Ca and Mg were analyzed using ICP-AES and Na and K were analyzed using flame atomic absorption. Samples for each time period were analyzed only if the collector was not damaged or missing, so the number of sample analyses reported for particular sites differs (table 2).

Table 2. Chemical analyses for bulk precipitation samples from the vicinity of Kilauea Volcano

[Analyses are from undamaged open-sky collectors. Analyses for the first sample set were done by the authors, and for the last 3 sample sets, by D. Counce and P. Trujillo of Los Alamos National Laboratory. All concentration values are in milligrams per liter (mg/L). Diameter refers to funnel diameter, Volume refers to sample volume collected. Dashes indicate the absence of data.]

Sample ID	Latitude	Longitude	Date placed	Date sampled	Diameter (cm)	Volume (L)	Mg	Ca	K	Na	Cl	SO4
										----mg/L----		
KH1S-1	19.401	155.284	7/31/91	2/7/92	5.3	0.89	0.39	1.5	0.07	1.0	1.4	64
-4			3/21/93	8/26/93	8.3	2.20	0.17	--	--	1.0	1.3	8.3
KH2S-1	19.408	155.256	7/31/91	2/7/92	5.3	1.90	0.26	0.94	0.29	0.89	1.2	6.8
-2			2/7/92	9/11/92	5.3	1.47	0.10	0.71	0.10	0.62	1.1	2.5
-4			3/21/93	8/26/93	5.3	1.36	0.11	--	--	0.62	0.97	1.4
KH5S-1	19.432	155.261	7/31/91	2/7/92	5.3	2.06	<0.15	0.69	0.20	0.66	1.3	5.5
-2			2/7/92	9/10/92	5.3	1.70	0.10	0.89	0.09	0.69	1.6	4.1
-4			3/24/93	8/26/93	5.3	1.92	<0.10	--	--	0.59	1.1	1.7
KH6S-1	19.423	155.290	7/31/91	2/7/92	5.3	1.10	<0.15	0.99	0.24	0.58	0.9	7.1
-4			3/27/93	8/26/93	8.3	2.06	0.13	0.41	0.55	0.73	1.2	3.6
-5			8/26/93	2/10/94	8.3	8.41	0.32	--	0.13	1.47	2.5	6.0
KH7S-1	19.411	155.273	8/1/91	2/7/92	5.3	1.10	<0.15	1.0	0.32	0.88	1.5	13
-2			2/7/92	9/9/92	8.3	2.84	0.17	1.4	0.20	1.1	1.7	6.7
KH8S-1	19.344	155.276	8/1/91	2/12/92	5.3	1.65	<0.15	0.21	0.85	<0.15	1.4	<2.0
-4			3/26/93	8/26/93	8.3	1.96	0.12	--	--	0.81	1.5	2.7
KH9S-1	19.358	155.316	8/1/91	2/12/92	5.3	1.10	0.32	1.3	0.17	0.79	1.3	20
-2			2/12/92	9/15/92	8.3	2.46	0.23	1.4	0.16	0.95	1.3	8.4
-4			3/26/93	8/30/93	8.3	1.43	0.47	--	--	2.6	1.1	12
KH10S-1	19.289	155.327	8/1/91	2/12/92	5.3	1.75	<0.15	0.55	0.21	1.4	2.2	5.6
-4			3/26/93	8/26/93	8.3	2.22	0.14	--	--	1.2	2.0	4.1
KH13S-1	19.661	155.011	8/2/91	2/10/92	5.3	2.41	0.24	0.42	0.33	2.4	3.9	<2.0
-2			2/10/92	9/20/92	5.3	3.28	0.21	0.39	0.22	1.8	3.5	1.4
-4			3/24/93	8/27/93	5.3	2.44	0.29	--	--	2.6	4.4	1.3
KH14S-1	19.541	154.975	8/2/91	2/14/92	5.3	3.12	0.18	0.33	0.31	2.2	3.9	<2.0
-2			2/14/92	9/14/92	5.3	4.00	0.23	0.49	0.11	1.8	3.5	1.3
-4			3/23/93	8/27/93	5.3	2.71	0.30	0.72	0.19	2.9	4.9	1.3
KH19S-1	19.647	155.083	8/2/91	2/10/92	5.3	3.62	0.28	0.39	0.49	1.9	3.5	<2.0
-2			2/10/92	9/21/92	5.3	4.41	0.20	0.40	0.08	1.6	3.2	1.2
-4			3/24/93	8/25/93	5.3	3.36	0.20	--	--	2.3	4.0	0.62
KH20S-1	19.462	155.344	8/2/91	2/8/92	5.3	1.10	0.28	1.0	0.37	2.6	1.4	6.7
-2			2/8/92	9/12/92	8.3	10.02	0.13	0.50	0.27	0.61	0.79	5.2
-4			3/30/93	8/31/93	8.3	2.64	0.11	--	--	0.48	0.56	2.3
-5			8/31/93	2/11/94	7.0	7.40	0.13	--	0.49	0.57	1.3	5.2

Sample ID	Latitude	Longitude	Date placed	Date sampled	Diameter (cm)	Volume (L)	Mg	Ca	K	Na	Cl	SO$_4$
									—mg/L—			
KH23S-1	19.496	155.080	8/4/91	2/9/92	5.3	3.47	0.24	0.52	0.78	1.9	3.3	<2.0
-4			3/27/93	8/30/93	5.3	4.18	0.30	--	--	2.0	4.3	1.3
KH26S-1	19.476	155.264	8/4/91	2/9/92	5.3	1.60	<0.15	0.55	0.16	0.66	1.0	<2.0
-2			2/9/92	9/24/92	5.3	2.07	<0.10	0.44	0.18	0.62	1.5	1.9
-4			3/24/93	8/27/93	5.3	2.08	<0.10	--	--	0.51	0.85	1.2
KH27S-1	19.277	155.434	8/4/91	2/13/92	5.3	1.35	0.46	0.88	0.48	1.5	3.1	3.0
-2			2/13/92	9/18/92	8.3	1.89	1.0	2.2	0.79	2.5	5.2	6.9
-4			3/25/93	9/1/93	8.3	2.08	0.22	--	--	4.1	5.3	14
KH29S-1	19.364	155.176	8/5/91	2/11/92	5.3	2.61	<0.15	0.33	0.19	1.4	2.6	5.6
-2			2/11/92	9/15/92	5.3	2.24	0.16	0.71	0.23	1.1	2.5	3.4
-4			3/26/93	8/30/93	5.3	1.75	0.17	0.87	0.10	1.4	3.7	4.3
-5			8/30/93	2/9/94	5.3	5.04	0.31	--	0.14	2.4	5.4	6.3
KH31S-1	19.140	155.703	8/6/91	2/14/92	5.3	0.89	0.15	1.7	0.20	1.1	1.5	6.6
-4			3/31/93	9/3/93	8.3	2.02	0.27	--	--	1.9	3.0	7.5
KH32S-1	19.233	155.635	8/6/91	2/14/92	5.3	1.10	<0.15	0.80	0.10	0.36	0.5	5.2
-4			3/31/93	9/3/93	8.3	2.74	<0.10	--	--	0.68	1.1	3.8
KH33S-2	19.308	155.574	2/14/92	9/22/92	8.3	3.36	<0.10	0.61	0.12	0.28	0.47	2.5
KH4M-1	19.519	154.814	8/3/91	2/14/92	5.3	1.90	0.73	1.0	0.34	5.4	10	2.1
-2			2/14/92	9/14/92	5.3	2.28	0.57	0.85	0.24	4.4	9.2	1.8
-4			3/23/93	8/27/93	5.3	1.38	0.69	1.5	0.23	6.8	12	2.4
-5			8/27/93	2/9/94	5.3	3.21	0.46	--	0.40	4.1	7.2	1.6
KH7M-1	19.271	155.233	8/6/91	2/19/92	5.3	1.10	0.32	0.51	0.96	2.4	5.8	2.7
-4			9/23/92	7/1/93	8.3	4.84	0.27	--	--	2.2	3.7	0.73
KH8M-4	19.286	155.124	3/21/93	8/26/93	8.3	1.36	2.2	2.2	0.65	18	34	9.8
-5			8/26/93	2/9/94	7.0	3.12	0.63	--	0.49	5.5	10	3.4
KH9M-5	18.920	155.670	8/31/93	2/7/94	7.0	1.53	13	--	4.8	103	205	39
KH13M-1	19.538	155.579	8/12/91	2/17/92	14	*0.75	<0.15	<0.04	0.19	<0.15	0.4	2.0
-2			2/17/92	9/20/92	14	4.94	<0.10	0.12	0.07	0.09	0.12	0.64
-4			3/27/93	8/25/93	14	2.16	<0.10	--	--	0.10	0.14	0.86
KH14M-1	19.517	155.411	8/13/91	2/25/92	5.3	0.56	<0.15	1.7	0.11	0.21	0.9	<2.0
-2			2/25/92	9/12/92	8.3	2.08	<0.10	0.87	0.15	0.12	0.24	1.2
-4			3/30/93	8/31/93	8.3	2.28	<0.10	--	--	0.10	0.23	1.3
-5			8/31/93	2/11/94	7.0	4.23	<0.10	--	0.17	0.23	0.28	2.8
KH15M-1	19.022	155.438	8/13/91	2/25/92	5.3	0.54	<0.15	1.6	0.17	0.24	0.6	5.6
-4			3/30/93	9/4/93	8.3	2.13	<0.10	--	--	0.10	0.26	1.4
KH16M-1	19.533	155.468	8/13/91	2/25/92	14	4.36	<0.15	<0.04	0.06	0.14	0.1	<2.0
-2			2/25/92	9/11/92	14	3.79	<0.10	0.06	0.13	0.06	0.10	0.74
-4			3/30/93	9/4/93	14	4.30	<0.10	--	--	0.07	0.14	0.83
KH17M-1	19.527	155.503	8/13/91	2/24/92	14	3.62	<0.15	<0.04	0.15	0.17	0.1	<2.0

Sample ID	Latitude	Longitude	Date placed	Date sampled	Diameter (cm)	Volume (L)	Mg	Ca	K	Na	Cl	SO$_4$
									mg/L			
-2			2/24/92	9/12/92	14	3.55	<0.10	0.07	0.01	0.04	0.08	0.73
-4			3/30/93	9/4/93	14	4.87	<0.10	--	--	0.05	0.20	0.76
KH18M-1	19.478	155.608	8/12/91	3/2/92	14	1.28	<0.15	0.23	0.51	0.55	0.6	4.8
KH20M-1	19.462	155.351	9/12/91	2/8/92	5.3	0.59	0.17	1.0	0.18	<0.15	0.7	5.6
-2			2/8/92	9/10/92	8.3	7.24	0.15	0.76	0.22	0.81	1.4	6.5
KH22M-1	19.576	155.195	9/14/91	2/10/92	5.3	2.41	0.27	0.89	0.78	1.7	3.4	5.8
-2			2/10/92	9/19/92	5.3	2.98	0.24	0.74	2.19	1.7	3.7	3.1
-4			3/24/93	8/25/93	5.3	5.04	<0.10	0.33	0.05	0.87	1.4	0.94
-5			8/25/93	2/10/94	5.3	4.94	<0.10	--	0.12	1.1	2.0	2.0
KH25M-1	19.320	155.071	9/15/91	2/13/92	5.3	1.25	0.22	0.84	0.30	2.0	4.2	3.4
-2			2/13/92	9/15/92	5.3	1.32	0.32	2.3	0.20	2.5	7.8	1.1
KH27M-1	19.372	155.370	9/16/91	2/10/92	5.3	0.64	0.11	1.5	0.12	0.97	2.1	5.3
-2			2/10/92	9/18/92	8.3	9.20	0.18	0.51	0.07	1.2	1.7	6.9
-4			3/25/93	9/1/93	8.3	1.72	0.13	--	--	0.72	1.3	5.7
-5			9/1/93	2/7/94	8.3	1.87	0.20	--	0.12	0.83	1.4	5.1
KH29M-2	19.442	154.947	2/18/92	9/14/92	5.3	3.45	0.20	0.32	0.11	1.9	4.0	0.62
KH1F-1	19.499	155.589	8/13/91	3/3/92	14	0.72	<0.15	0.06	0.22	0.29	0.2	5.4
-2			3/3/92	9/20/92	14	3.74	<0.10	0.10	0.06	0.07	0.07	0.49
KH2F-1	19.440	155.580	8/13/91	3/3/92	14	2.28	<0.15	<0.04	0.25	0.20	0.1	<2.0
-2			3/3/92	9/20/92	14	5.00	<0.10	0.07	0.12	0.12	0.13	0.59
KH3F-1	19.420	155.552	8/13/91	3/4/92	14	2.41	<0.15	<0.04	0.63	0.22	0.1	<2.0
KH4F-1	19.401	155.533	8/14/91	3/4/92	14	0.54	<0.15	1.4	0.46	0.42	0.9	<2.0
KH5F-1	19.380	155.504	8/14/91	3/4/92	14	1.14	<0.15	0.66	0.33	0.44	0.4	<2.0
KH1C-1	19.586	155.457	8/2/91	2/17/92	15	3.52	<0.15	<0.04	0.13	0.22	0.1	<2.0
-2			8/2/91	2/17/92	14	5.23	<0.10	0.10	0.06	0.09	0.09	0.47
-4			3/27/93	8/25/93	14	4.64	<0.10	--	--	0.06	0.18	0.70
KH2C-1	19.671	155.372	8/2/91	2/17/92	5.3	1.10	<0.15	0.83	0.37	0.37	0.5	<2.0
-2			2/17/92	9/13/92	5.3	1.68	<0.10	0.65	0.06	0.24	0.58	0.82
-4			3/27/93	8/25/93	5.3	2.14	<0.10	0.49	0.10	0.24	0.34	0.58
KH4C-1	19.156	155.463	8/7/91	2/23/92	5.3	0.44	0.90	3.2	0.74	7.9	12	14
-2			2/23/92	9/23/92	8.3	1.45	0.85	2.6	0.31	7.6	13	6.5
KH5C-1	19.201	155.391	8/13/91	2/19/92	5.3	0.79	3.8	3.6	1.4	31	51	15
KH1L-2	19.456	154.969	2/19/92	9/17/92	5.3	4.28	0.18	0.46	0.14	1.7	3.0	0.77
-4			3/23/93	9/7/93	5.3	3.19	0.30	0.39	0.36	2.5	4.4	1.5
-5			9/7/93	2/9/94	5.3	3.76	0.24	--	0.38	2.4	4.0	1.1
KH2L-2	19.406	155.068	2/18/92	9/16/92	5.3	3.33	0.18	0.47	0.12	1.6	3.1	1.2
-4			4/1/93	9/2/93	5.3	2.90	0.19	0.46	0.26	1.9	3.2	1.0
KH3L-2	19.642	155.176	2/17/92	9/13/92	5.3	5.64	0.17	0.33	0.18	1.2	2.2	0.83

* estimated volume; collector spilled while sampling

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Comparison of Precipitation Chemistry With Other Studies

As noted in the introduction, several precipitation-chemistry studies have been done in the study area but have been short-term and (or) of limited areal extent. Eriksson (1957) reported complete chemical analyses for composite precipitation samples from a two-day period on the eastern slope of Mauna Loa. Harding and Miller (1982) collected rain samples biweekly using plastic funnel/bottle collectors at six sites around Kilauea caldera, and reported weighted-average anion concentrations for each of their sites. Siegel and others (1990) reported unoxidized and oxidized sulfate concentrations in precipitation from samples around Kilauea caldera. In addition, the National Oceanic and Atmospheric Administration (NOAA) has carried out long-term studies of precipitation chemistry at particular localities. The NOAA Mauna Loa Observatory has been monitoring long-term trends in precipitation chemistry for the National Acidic Deposition Program since 1980 (NADP Annual Summary, 1991). R.S. Artz (NOAA, Air Resources Laboratory, Silver Spring, Maryland, written commun., 1994) provided several years of sulfate concentrations for bulk precipitation samples collected at 3 to 18-day intervals, for two sites on the eastern side of the island. Comparisons of these various rain chemistry analyses with data from our nearby collectors are shown in table 3.

Table 3. Chemical analyses of precipitation samples from current and previous studies

[Data sources are: 1. NADP, 1992; 2. this study (table 2); 3. Eriksson, 1957; 4. Artz, R.S., NOAA-ARL, written communication, 1994; 5. Harding and Miller, 1982; 6. Siegel and others, 1990, a. unoxidized samples, b. oxidized samples. Abbreviations are: vwa, volume-weighted average; m, meter (elevation above sea level); km, kilometer; UH Ag. Ex. Sta., University of Hawaii Agricultural Experiment Station; Do, ditto; --, no data. Concentrations are in milligrams per liter (mg/L)].

Site name	Collection dates	Type	Collection period	Data source	Ca	Mg	K	Na	NO_3	Cl	SO_4
High elevation, east side of Hawaii											
Mauna Loa Observatory	1991 vwa	wet	event	1	0.01	0.006	0.004	0.047	0.08	0.07	0.47
Mauna Loa Obs. (KH13M-2)	2/92-9/92	bulk	6-month	2	0.12	0.02	0.07	0.09	--	0.12	0.64
Mauna Loa Obs. (KH13M-4)	3/93-8/93	bulk	do.	2	--	<.01	--	0.10	--	0.14	0.86
Saddle Rd. (1700 m)	10/19-20/54	bulk	2-day	3	0.18	0.15	0.04	0.19	<0.01	0.28	0.08
Saddle Rd. (1700 m, KH2C-2)	2/92-9/92	bulk	6-month	2	0.65	0.04	0.06	0.24	--	0.58	0.82
Saddle Rd. (1700 m, KH2C-4)	3/93-8/93	bulk	6-month	2	0.49	0.03	0.10	0.24	--	0.34	0.58
Saddle Rd. 22-mile (1800 m)	1981-85 vwa	bulk	3-10 day	4	--	--	--	--	--	--	0.60
Low elevation, east side of Hawaii											
Club 299 (SE of Hilo)	10/54	bulk	storm	3	0.36	0.94	0.40	6.3	0.05	11	0.69
Mauna Loa Mac. Nut (KH13S-2)	2/92-9/92	bulk	6-month	2	0.39	0.21	0.22	1.8	--	3.5	1.4
Mauna Loa Mac. Nut (KH13S-4)	3/93-8/93	do.	do.	2	--	0.29	--	2.6	--	4.4	1.3
Kumukahi	1978, 81-84 vwa	bulk	3-18 day	4	--	--	--	--	--	--	1.6
Cape Kumukahi (KH4M-2)	2/92-9/92	bulk	6-month	2	--	--	--	--	--	--	1.8
Cape Kumukahi (KH4M-4)	3/93-8/93	do.	do.	2	--	--	--	--	--	--	2.4
Cape Kumukahi (KH4M-5)	8/93-2/94	do.	do.	2	--	--	--	--	--	--	1.6
Kilauea summit area, upwind (N or NE) of Kilauea Crater											
Golf course, Volcano	5/78-2/79 vwa	bulk	2-week	5	--	--	--	--	--	0.7	0.9
National Park visitor center	12/86-6/87 vwa	bulk	2-week	6a	--	--	--	--	--	--	2.5
Do.	do.	do.	do.	6b	--	--	--	--	--	--	<3.9
UH Ag. Ex. Sta., Volcano (KH26S-2)	2/92-9/92	bulk	6-month	2	--	--	--	--	--	1.5	1.9
UH Ag. Ex. Sta., Volcano (KH26S-4)	3/93-8/93	do.	do.	2	--	--	--	--	--	0.85	1.2
Kilauea summit area, downwind (S or SW) of Kilauea Crater											
0.8 km SW of Halemaumau	5/78-2/79 vwa	bulk	2-week	5	--	--	--	--	--	0.9	3.5
0.8 km SW of Halemaumau	12/86-6/87 vwa	bulk	2-week	6a	--	--	--	--	--	--	18.5
Do.	do.	do.	do.	6b	--	--	--	--	--	--	38
6 km SW of Halemaumau (KH9S-1)	8/91-2/92	bulk	6-month	2	--	--	--	--	--	1.3	20
6 km SW of Halemaumau (KH9S-2)	2/92-9/92	do.	do.	2	--	--	--	--	--	1.3	8.4
6 km SW of Halemaumau (KH9S-4)	3/93-8/93	do.	do.	2	--	--	--	--	--	1.1	12
0.5 km S of Halemaumau (KH1S-1)	7/91-2/92	bulk	6-month	2	--	--	--	--	--	1.4	64
0.5 km S of Halemaumau (KH1S-4)	3/93-8/93	do.	do.	2	--	--	--	--	--	1.3	8.3

Comparison between chemical analyses of samples in this study and data from other studies points out some important differences. The nearly two- to tenfold difference in chemical content between our samples from Mauna Loa Observatory and their published data results from comparing their measurements of wet deposition with our measurements of bulk deposition (table 3). On the other hand, our 6-month cumulative bulk-deposition sulfate values for the Saddle Road and Cape Kumukahi sites agree fairly well with several-year volume weighted averages for bulk deposition from Artz (NOAA-ARL, written comm., 1994).

In the Kilauea summit area, the sulfate values from our 6-month cumulative samples are generally higher than the volume-weighted averages from Harding and Miller (1982), and for most samples, somewhat lower than values obtained by Siegel and others (1990). This could be due to variations in volcanic output, as noted by Siegel and others (1990) when comparing their results with those of Harding and Miller (1982). The disparity in sulfate values could also be due to the longer collection period in our study. The fact that Siegel and others (1990) measured higher sulfate in their peroxide-treated samples suggests that there are some unoxidized sulfur species in fresh precipitation samples that were not measurable with the turbidimetric method they used. We did not add peroxide to our samples, but if oxidation requires a time scale of weeks to months, most sulfur species in our 6-month samples probably had sufficient time to oxidize to SO_4.

Sodium/chloride and Sodium/sulfate Ratios in Precipitation

Plots of sodium as related to chloride concentrations for the bulk precipitation samples from this study show that most samples have a Na/Cl ratio close to that of seawater (fig. 2). The appearance of excess sodium in low-concentration samples in the first set (fig. 2A) may be due to underestimation of chloride concentrations, which were very close to the detection limit of the colorimetric method used for that set of samples. In contrast to the Na/Cl plots, plots of sodium versus sulfate for the precipitation samples (fig. 3) show sulfate concentrations in excess of seawater ratios for most of the samples. These results are similar to the findings reported by Miller and others (1984).

Determination of Total and Non-seasalt Sulfate and Chloride Load

Bulk deposition of sulfate and chloride (sulfate load and chloride load in grams per square meter per day ($g/m^2{\cdot}day$)) was determined from sulfate and chloride concentrations in the cumulative rainfall samples. The non-seasalt (nss) sulfate and chloride deposition was then determined on the basis of the sodium concentration. Calculation of the nss sulfate load allows comparison with
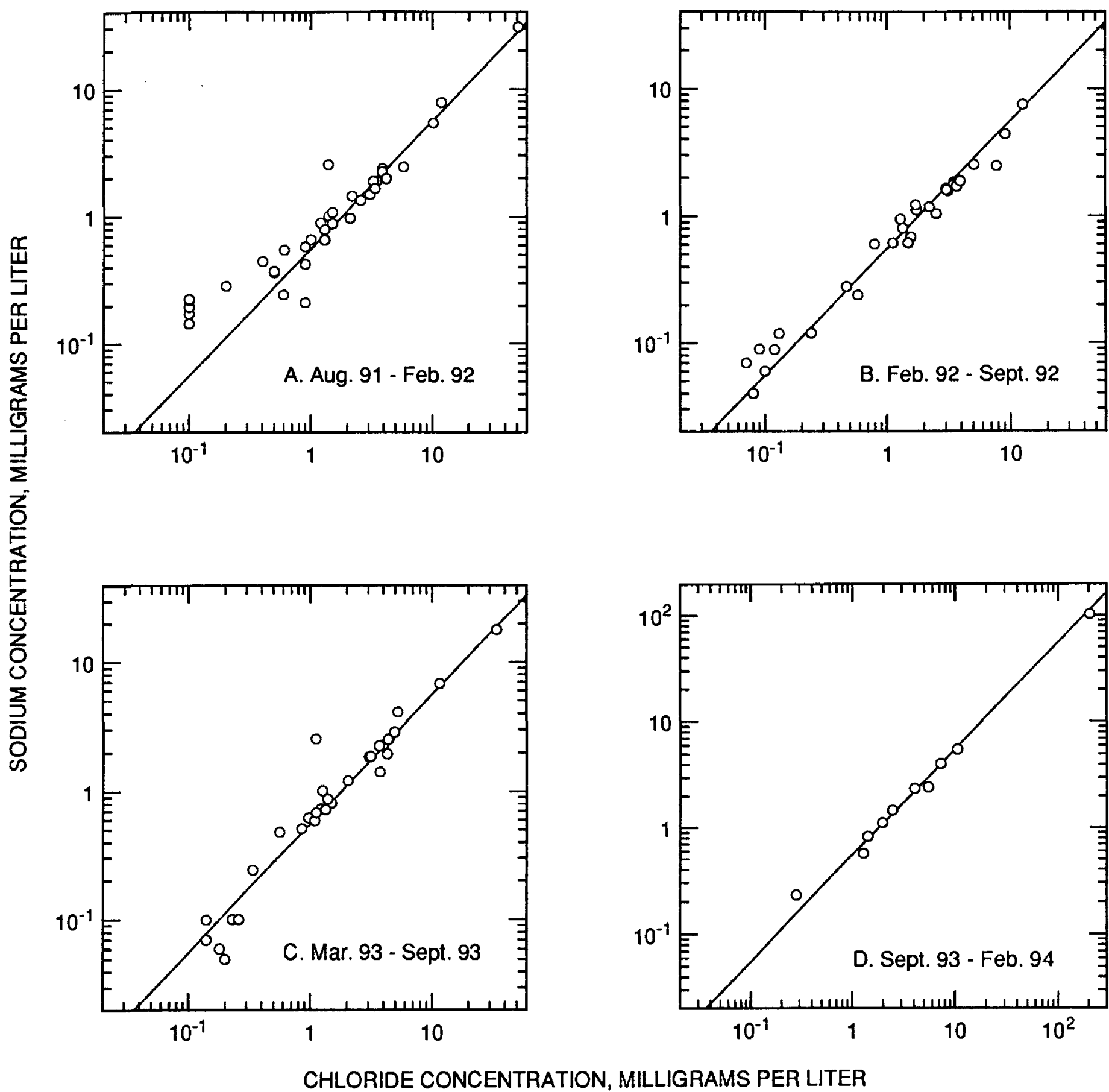
14

Figure 2. Relation between sodium and chloride concentration in precipitation samples from the Kilauea Volcano area for four time periods. Solid line is the seawater ratio of the two elements. Note extended scale for D.
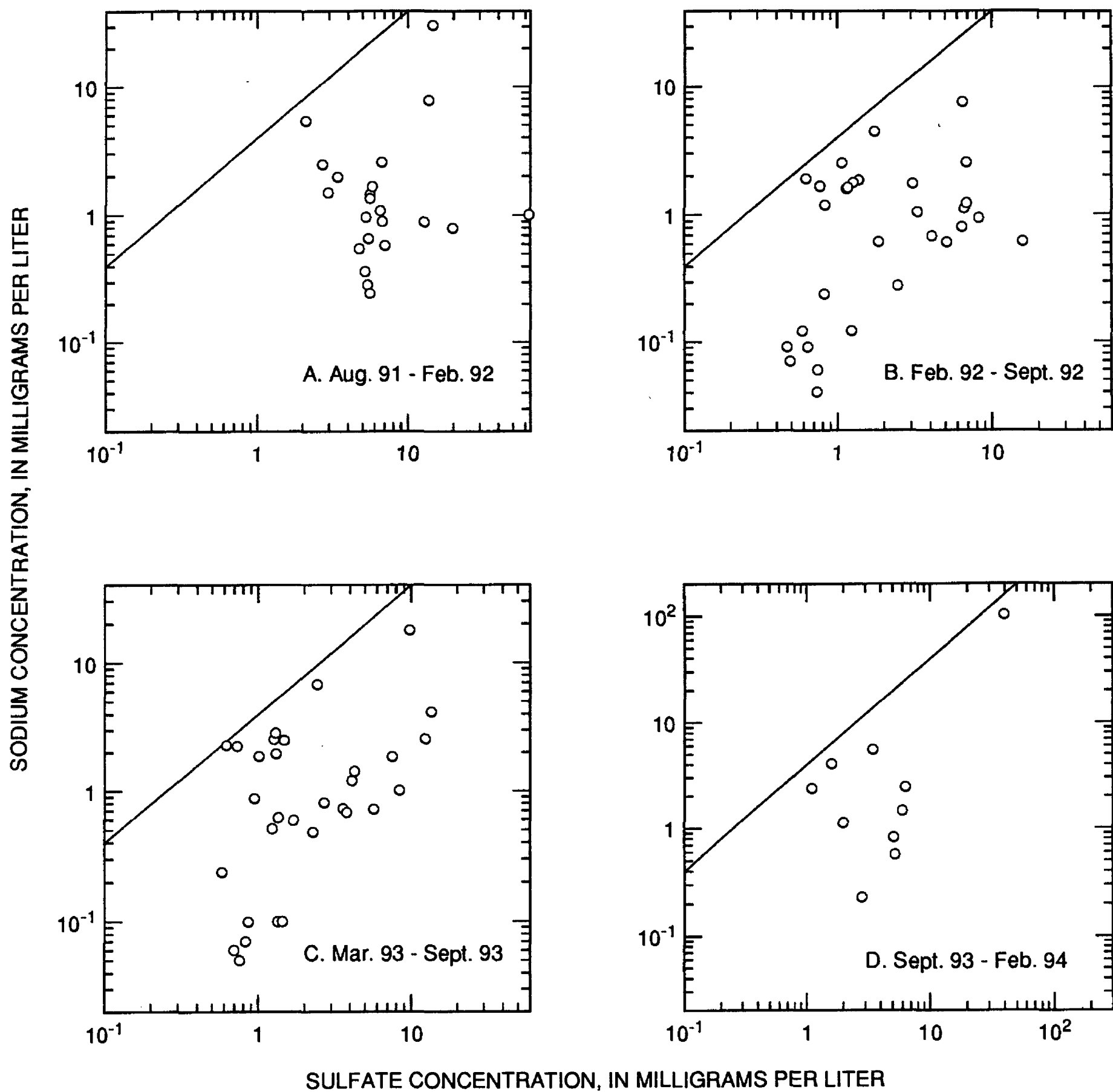
15

Figure 3. Relation between sodium and sulfate concentration in precipitation samples from the Kilauea Volcano area for four time periods. Solid line is the seawater ratio of the two elements. Note extended scale for D.

estimated outputs of sulfur from Kilauea volcano, which appears from these results to be the largest source of non-seasalt sulfate in the samples. We assume that the sulfate in the rain collectors originated in part as other sulfur species which eventually oxidized.

The total load of sulfate and chloride in $g/m^2{\cdot}day$ was determined as CV/At, where C is concentration of SO_4 or Cl in g/L, V is collected precipitation volume in liters (L), A is area of collection (funnel aperture area), and t is the number of days the collector was deployed. The samplers were deployed an average of 188 days for the first collection period, 216 days for the second period, 160 days for the fourth period, and 163 days for the fifth period. For purposes of comparison between the unequal collection periods, sulfate load in $g/m^2{\cdot}day$ for each set was multiplied by 180 to represent the total load for a 6-month period.

The method for determining nss sulfate or chloride (Keene and others, 1986) involves subtracting the seasalt-derived sulfate or chloride from the total amount measured, based on a reference species (usually Mg^{2+} or Na^+) and the ratio of the two constituents in seawater. This method relies on three assumptions: 1) the reference species used must be entirely of sea-salt origin, 2) there is no fractionation of sea-salt species during sea-salt aerosol formation, and 3) there is no fractionation of sea-salt species as the aerosol is scavenged by precipitation. A fourth assumption is necessary with our 6-month collection interval; 4) there is no significant loss or transformation of the chemical species of interest in the collectors in the time between deposition and analysis.

Keene and others (1986) stated that assumptions 2 and 3 above are difficult to evaluate, as there is little information or published studies disagree on these points. Assumption 2 may be incorrect for the process occurring at the sea entry of the eruption (fig. 1), where molten lava vaporizes seawater instantly, producing a cloud of HCl-rich steam. Assumption 4 seems likely to be valid for Na and Cl, which are fairly non-reactive species. For Mg and SO_4, precipitation as solid compounds seems unlikely in dilute rainwater, and biological sulfate reduction is confined to anaerobic systems. Assumption 1, that the reference species used must be entirely of sea-salt origin, can be evaluated by comparing reference species ratios with seawater ratios.

Sodium was used as the reference element for seawater for all the data, with the exception of KH27S-3, which showed excess sodium when both Na/Mg and Na/Cl concentrations were plotted with the seawater ratio line for reference. Magnesium was used as the reference species for KH27S-3. For the other data, sodium was the preferred reference species, because the low concentration of magnesium in the samples resulted in measurements close to or below detection limits.

The Na/SO$_4$ and Na/Cl ratios of seawater (Drever, 1982, p. 234) were used to calculate the expected contribution of seasalt SO$_4$ or Cl (C$_{ss}$) to the concentration of each sample, using C$_{ss}$ = (C$_{sea}$/Ref$_{sea}$)Ref$_{samp}$, where C$_{sea}$ is the concentration of the constituent in seawater, and Ref$_{sea}$ and Ref$_{samp}$ are the concentration of the reference species in seawater and in the sample, respectively (Keene and others, 1986). The concentration of nss SO$_4$ or Cl is then determined by difference as C$_{nss}$ = C$_{total}$ - C$_{ss}$.

For the first set of sulfate data, the colorimetric method used to analyze the samples had a detection limit of 2 mg/L. For sites below this detection limit, total and nss sulfate loads were determined on the basis of a concentration of 2 mg/L SO$_4$, and are reported as being less than or equal to the value calculated on this basis. Contour lines in figures 4A and 5A were drawn using these maximum values. The ion-chromatograph method used for succeeding data sets resulted in better estimates for low-concentration samples.

For each data set, calculation of nss chloride resulted in a spread of values around zero. The three largest values of nss chloride from each sample set are reported in table 5; the other samples are reported as having zero nss chloride.

Variability of the 6-month Estimates of Sulfate and Chloride Load

The amount of SO$_4$ or Cl in each bulk precipitation sample depends on many interrelated factors, including the location of a collector with respect to the source areas, wind direction and speed, and the frequency and intensity of rain events. Less is known about controlling factors for processes such as the scavenging of sulfur compounds from air by rain or fog, production of sea salt aerosols, transformations of sulfur species in the air and in the collectors, and processes controlling dry deposition. Sources of uncertainty in the actual load calculations include the error in analyses of the SO$_4$, Cl, and reference species, errors in measurement of the sample volume, and sample contamination.

GEOGRAPHIC PATTERNS OF SULFATE AND CHLORIDE DEPOSITION

Sulfate Deposition

Total and non-seasalt (nss) sulfate deposition for the four collection periods are contoured in figures 4 and 5 and listed in table 4. Contour maps in this report were produced using a kriging method on a grid of 2 km by 2 km squares.
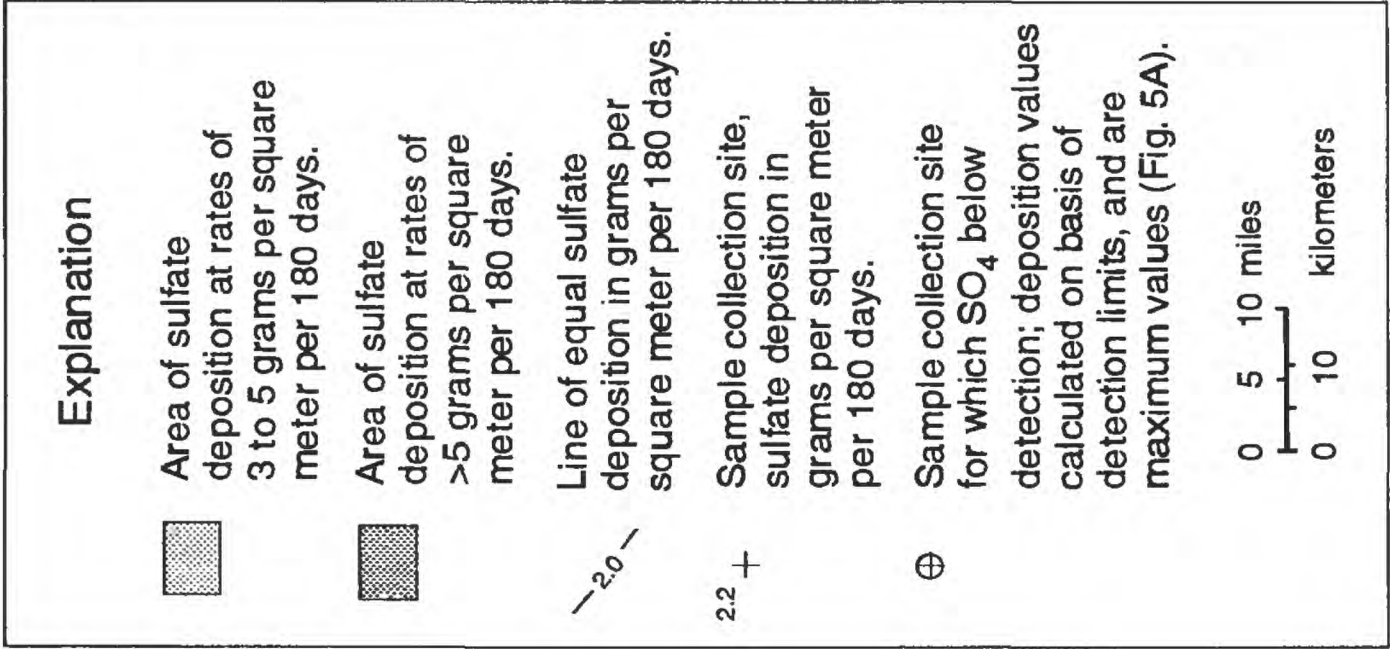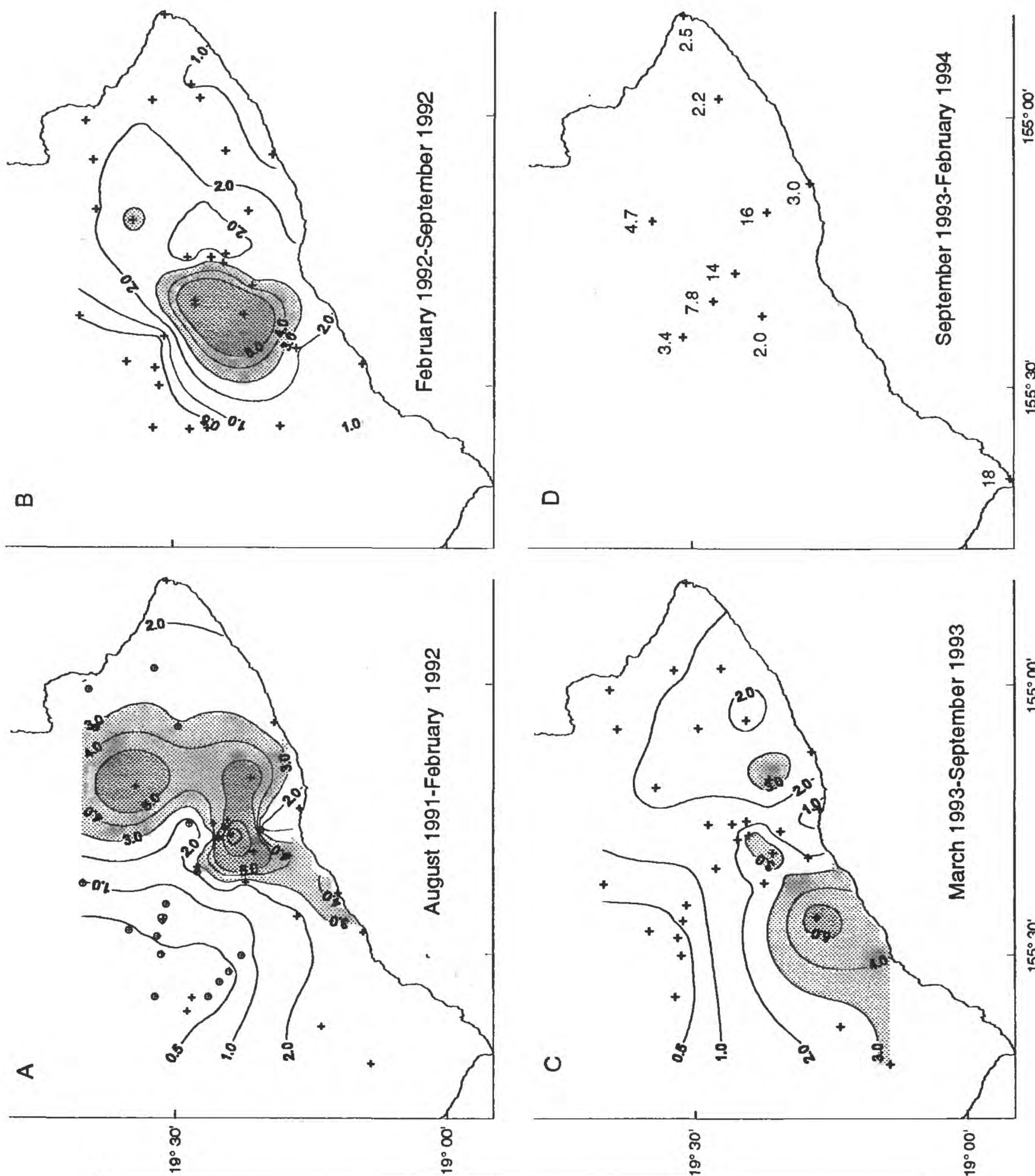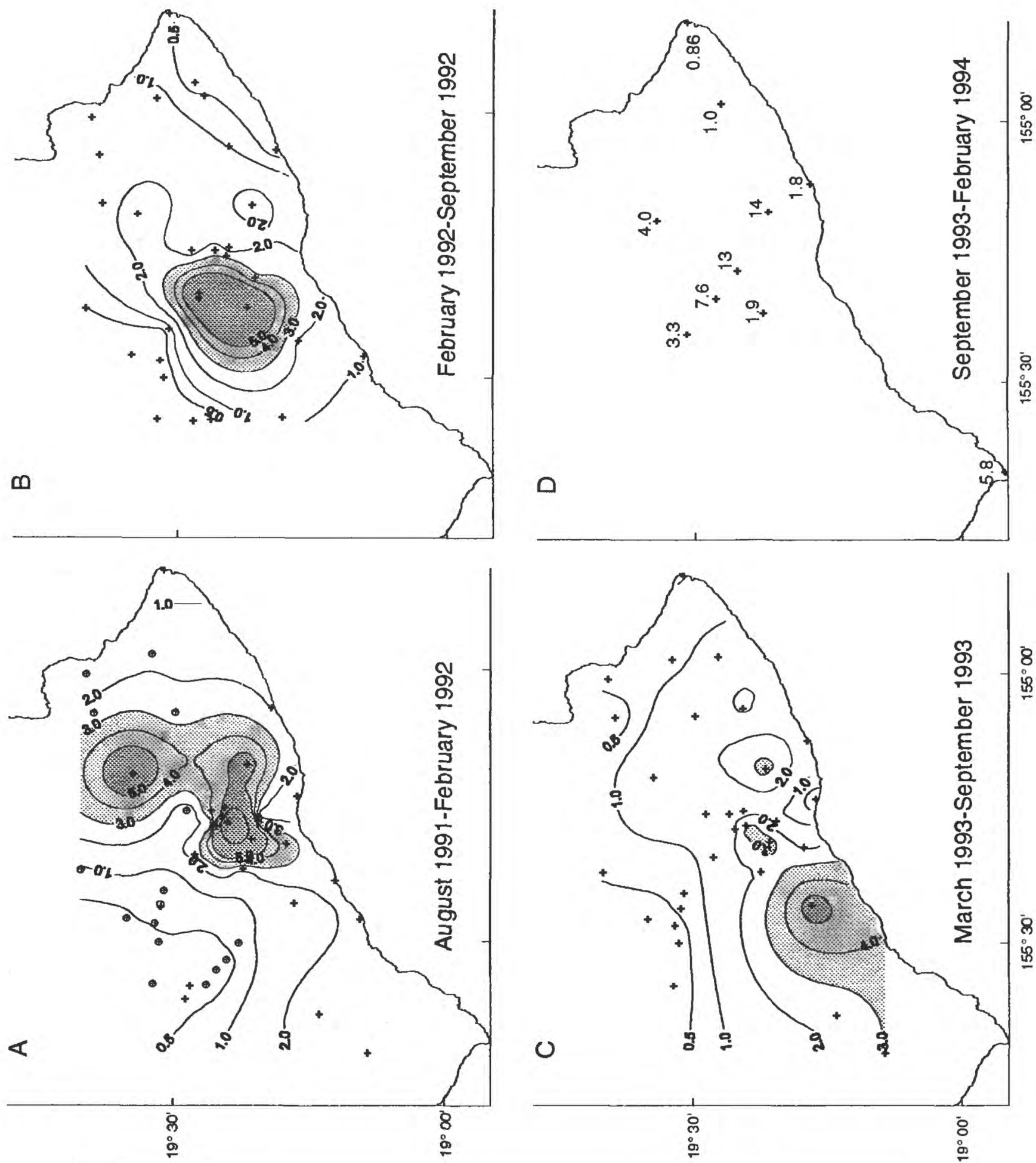
Figure 4. Total sulfate deposition in the Kilauea Volcano area.

Explanation

Area of sulfate deposition at rates of 3 to 5 grams per square meter per 180 days.

Area of sulfate deposition at rates of >5 grams per square meter per 180 days.

Line of equal sulfate deposition in grams per square meter per 180 days.

2.2 + Sample collection site, sulfate deposition in grams per square meter per 180 days.

⊕ Sample collection site for which SO$_4$ below detection; deposition values calculated on basis of detection limits, and are maximum values (Fig. 5A).

A August 1991-February 1992

B February 1992-September 1992

C March 1993-September 1993

D September 1993-February 1994

19

B

0.5

1.0

2.0

2.0

2.0

2.0

3.0

4.0

3.0

1.0

1.0

0.5

1.0

February 1992-September 1992

D

0.86

1.0

1.8

4.0

14

13

7.6

1.9

3.3

5.8

September 1993-February 1994

A

1.0

2.0

3.0

4.0

5.0

3.0

1.0

5.0

3.0

2.0

1.0

0.5

1.0

2.0

August 1991-February 1992

C

0.5

2.0

1.0

0.2

1.0

1.0

2.0

4.0

3.0

0.5

1.0

2.0

March 1993-September 1993

19° 30'

19° 00'

19° 30'

19° 00'

155° 30'

155° 00'

155° 30'

155° 00'

Figure 5. Non-seasalt sulfate deposition in the Kilauea Volcano area.

Explanation

Area of nss sulfate deposition at rates of 3 to 5 grams per square meter per 180 days.

Area of nss sulfate deposition at rates of >5 grams per square meter per 180 days.

Line of equal nss sulfate deposition in grams per square meter per 180 days.

—2.0—

Sample collection site, nss sulfate deposition in grams per square meter per 180 days.

2.2 +

Sample collection site for which Na and (or) SO_4 below detection; deposition values calculated on basis of detection limits, and are maximum values (Fig. 5A).

⊕

0   5   10 miles

0   5   10   kilometers

20

Although there were many sites where rain collectors were found broken after one or more of the collection periods, and the first data set had many analyses below detection limits, it is possible to compare patterns and amounts of total and nss sulfate deposition between time periods. The first and last data sets represent the fall-winter period, and the other two sets represent the spring-summer season. Wind directions during the summer season are dominated by strong tradewinds from the east-northeast, with a diurnal cycle of onshore and offshore winds (fig. 6; Nash, 1993). During the winter season, the tradewinds are weaker and winds blow from other directions more frequently. High SO_2 concentrations have been measured north-northeast of Kilauea summit when winds are from the southwest (Sutton and Elias, 1993; Sutton and others, 1993). These wind patterns may account for the higher nss sulfate deposition during the fall-winter periods at collection site KH22M, which is northeast of Kilauea and is also downwind of Hilo during tradewind conditions (figs. 5A and D, see also fig. 1 for location). This site may get contributions from both volcanic and anthropogenic sources in the fall-winter season.

In general, during each collection period the sites with highest nss sulfate deposition are near Kilauea summit and the ERZ eruption source. In the latter two collection periods (March 1993-February 1994), relatively high nss sulfate deposition was also seen in samplers in the western part of the study area (figs. 5C and D). This is likely due to the prevailing tradewind patterns (fig. 6); daytime winds from Kilauea summit and the ERZ eruption area converge on the area southwest of the summit. The sites with lowest nss sulfate deposition for each time period are at high elevations on the slopes of Mauna Loa (fig. 5).

The collection sites with the largest calculated proportion of seasalt sulfate deposition are in the eastern (windward) part of the study area and, in some cases, elsewhere along the coast. This is because the prevailing east-northeast tradewinds carry seasalt aerosols, and because sea spray is deposited on collector surfaces near the coast. Comparison of total and nss sulfate deposition for the 6 or 7 easternmost collectors in the study area shows that on the average, 55 percent of the sulfate in those samples originates from sea salt. In comparison, only about 5 percent of the sulfate in the 5 collectors around Kilauea summit and the 5 inland collectors southwest of the summit originates from sea salt.

EXPLANATION

TOPOGRAPHIC CONTOUR elevation in meters above sea level

WIND SPEED

= 0.5 meters per second

= 1 meter per second

= 5 meters per second

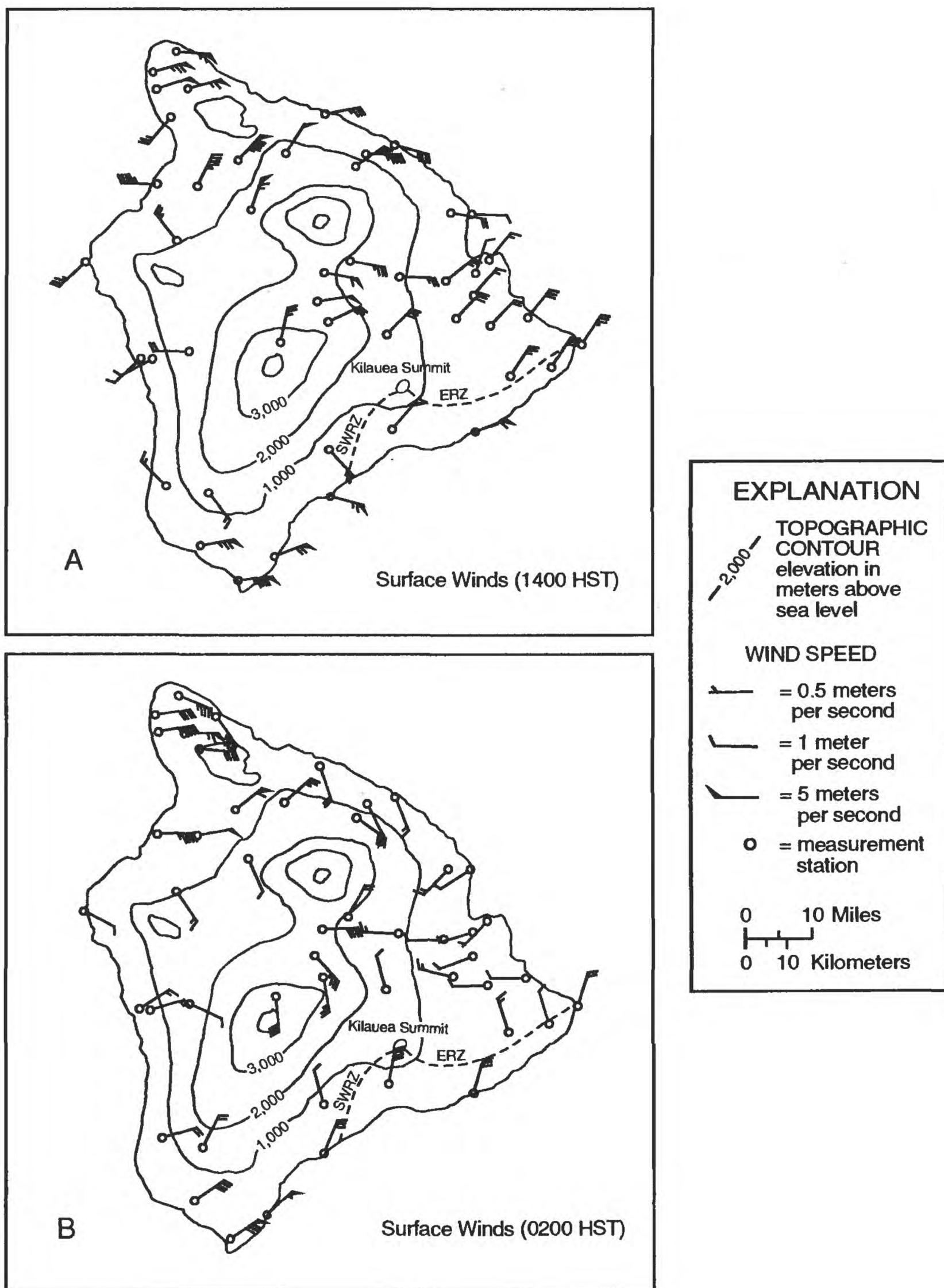o = measurement station

0   10 Miles

0   10 Kilometers

Figure 6. Average surface winds at A) 1400 HST and B) 0200 HST, measured during 6 weeks in July and August 1990 (modified from Nash, 1992). Abbreviations: ERZ, East Rift Zone; SWRZ, Southwest Rift Zone; HST, Hawaii Standard Time.

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Table 4. Total and non-seasalt sulfate deposition rates in the vicinity of Kilauea Volcano

[Values are in grams per square meter per 180 days, from precipitation collected during the periods August 1991-February 1992, February 1992-September 1992, March 1993-September 1993, and September 1993-February 1994. Dashes indicate lack of data, ND indicates not determined due to sodium being below detection limit. Nss, non-seasalt. Site locations are shown in fig. 1.]

Site (fig. 1)	8/91 to 2/92		2/92 to 9/92		3/93 to 9/93		9/93 to 2/94	
	Total SO_4	Nss SO_4	Total SO_4	Nss SO_4	Total SO_4	Nss SO_4	Total SO_4	Nss SO_4
KH1S	24	24	--	--	3.9	3.7	--	--
KH2S	5.6	5.4	1.4	1.3	0.96	0.84	--	--
KH5S	4.8	4.7	2.7	2.6	1.7	1.6	--	--
KH6S	3.3	3.2	--	--	1.6	1.5	14	13
KH7S	6.1	6.0	2.9	2.8	--	--	--	--
KH8S	<1.4	ND	--	--	1.1	1.1	--	--
KH9S	9.1	9.0	3.2	3.1	3.8	3.6	--	--
KH10S	4.1	3.8	--	--	2.0	1.8	--	--
KH13S	<2.0	<1.4	1.6	1.1	1.6	0.78	--	--
KH14S	<2.6	<1.9	2.0	1.3	1.8	0.81	--	--
KH19S	<3.1	<2.3	1.9	1.2	1.1	0.06	--	--
KH20S	3.1	2.8	7.9	7.7	1.3	1.2	7.8	7.6
KH23S	<3.0	<2.3	--	--	2.9	1.8	--	--
KH26S	<1.4	<1.3	1.4	1.3	1.4	1.2	--	--
KH27S	1.7	1.5	2.0	1.8	5.9	5.7	--	--
KH29S	6.3	5.9	2.8	2.6	3.9	3.6	16	14
KH31S	2.5	2.4	--	--	3.3	3.1	--	--
KH32S	2.8	2.8	--	--	2.2	2.1	--	--
KH33S	--	--	1.3	1.2	--	--	--	--
KH4M	1.7	0.54	1.5	0.54	1.7	0.48	2.5	0.86
KH7M	1.2	0.96	--	--	0.42	0.09	--	--
KH8M	--	--	--	--	2.8	1.5	3.0	1.8
KH9M	--	--	--	--	--	--	18	5.8
KH13M	<0.09	ND	0.18	0.18	0.15	0.15	--	--
KH14M	<0.48	<0.45	0.42	0.42	0.66	0.66	3.4	3.3
KH15M	1.3	1.3	--	--	0.66	0.63	--	--
KH16M	<0.51	<0.51	0.15	0.15	0.27	0.27	--	--
KH17M	<0.45	<0.42	0.15	0.15	0.27	0.27	--	--
KH18M	0.39	0.39	--	--	--	--	--	--
KH20M	1.8	ND	7.3	7.0	--	--	--	--
KH22M	7.6	7.0	3.4	2.9	2.5	1.9	4.7	4.0
KH25M	2.3	2.0	0.54	0.21	--	--	--	--
KH27M	1.9	1.8	9.6	9.1	2.0	2.0	2.0	1.9
KH29M	--	--	0.84	0.18	--	--	--	--
KH1F	0.21	0.21	0.12	0.09	--	--	--	--
KH2F	<0.27	<0.27	0.18	0.15	--	--	--	--
KH3F	<0.27	<0.27	--	--	--	--	--	--
KH4F	<0.43	<0.41	--	--	--	--	--	--
KH5F	<0.93	<0.87	--	--	--	--	--	--
KH1L	--	--	1.3	0.57	2.3	1.3	2.2	0.98
KH2L	--	--	1.5	0.96	1.6	0.81	--	--
KH3L	--	--	1.8	1.2	--	--	--	--
KH1C	<0.42	<0.39	0.12	0.12	0.24	0.24	--	--
KH2C	<0.90	<0.87	0.54	0.51	0.66	0.60	--	--
KH4C	2.5	2.1	1.5	1.0	--	--	--	--
KH5C	4.9	2.3	--	--	--	--	--	--

Chloride Deposition

Total chloride deposition for the four time periods is contoured in figure 7 and listed in table 5. Chloride deposition is highest near the coast and in the eastern part of the study area. Hydrochloric acid is one of the gases emitted from Kilauea's summit and at the ERZ eruption site. The sea entry of the eruption is also a primary source of HCl, because the molten lava entering the sea creates a steam plume of vaporized seawater containing HCl. However, plots of sodium/chloride ratios for the samples (fig. 2), as previously noted, do not show chloride concentrations in excess of seawater ratios for most samples.

In table 5, only the three samples for each collection period with the highest calculated nss chloride values are listed as having a nss chloride component. The collectors with highest apparent nss chloride do not all show a clear relation to volcanic sources. For example, collectors KH4M and KH29S had some of the highest nss chloride values (table 5). KH4M is at Cape Kumukahi on the eastern tip of the island, upwind of the volcanic sources, whereas KH29S is directly southwest (downwind) of the current eruptive vents (see fig 1 for locations).
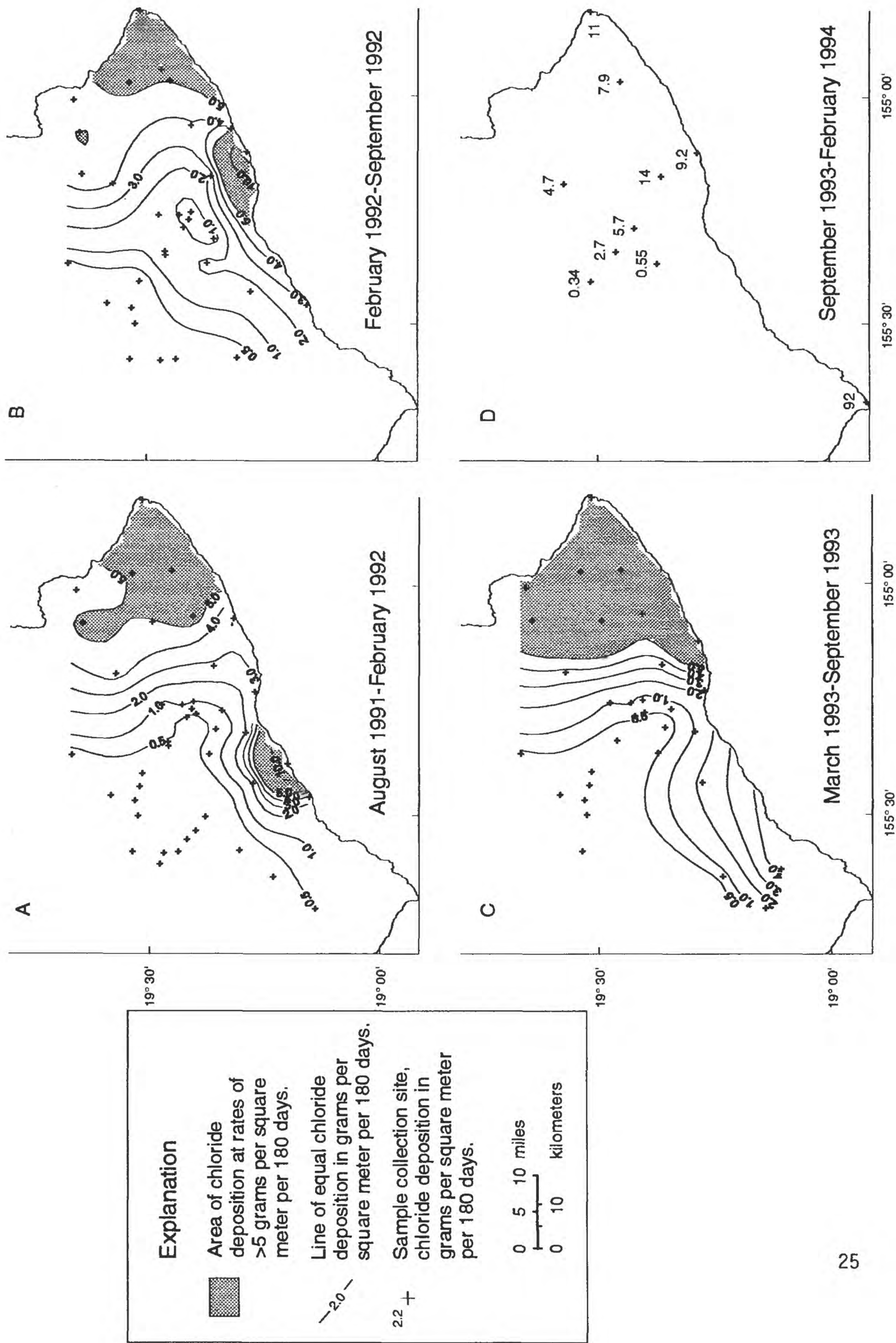
Figure 7. Total chloride deposition in the Kilauea Volcano area.

Explanation

Area of chloride deposition at rates of >5 grams per square meter per 180 days.

Line of equal chloride deposition in grams per square meter per 180 days.

Sample collection site, chloride deposition in grams per square meter per 180 days.

A — August 1991–February 1992

B — February 1992–September 1992

C — March 1993–September 1993

D — September 1993–February 1994

Table 5. Total and non-seasalt chloride deposition rates in the vicinity of Kilauea Volcano

[Values are in grams per square meter per 180 days, from precipitation collected during the periods August 1991-February 1992, February 1992-September 1992, March 1993-September 1993, and September 1991-February 1994. Only the three highest values for nss chloride in each time period are shown, other samples are shown as having nss chloride of 0. Dashes indicate lack of data. Nss, non-seasalt. Site locations are shown in fig. 1.]

Site (fig. 1)	8/91-2/92		2/92-9/92		3/93-9/93		9/93-2/94	
	Total Cl	Nss Cl	Total Cl	Nss Cl	Total Cl	Nss Cl	Total Cl	Nss Cl
KH1S	0.53	0	--	--	0.58	0	--	--
KH2S	0.9	0	0.62	0	0.68	0	--	--
KH5S	1.1	0	1.0	0	1.1	0	--	--
KH6S	0.42	0	--	--	0.55	0	5.7	0
KH7S	0.71	0	0.76	0	--	--	--	--
KH8S	0.97	ND	--	--	0.63	0	--	--
KH9S	0.60	0	0.49	0	0.34	0	--	--
KH10S	1.6	0	--	--	0.99	0	--	--
KH13S	4.0	0	4.2	0	5.6	0	--	--
KH14S	5.1	0	5.4	0	6.9	0	--	--
KH19S	5.4	0	5.1	0	7.1	0	--	--
KH20S	0.66	0	1.2	0	0.32	0	2.7	0.52
KH23S	4.9	0	--	--	9.4	1.7	--	--
KH26S	0.69	0	1.1	0	0.92	0	--	--
KH27S	1.8	0	1.5	0	2.3	0.87	--	--
KH29S	2.9	0	2.1	0	3.4	1.0	14	2.6
KH31S	0.57	0	--	--	1.3	0	--	--
KH32S	0.23	0	--	--	0.66	0	--	--
KH33S	0.11	0	0.24	0	--	--	--	--
KH4M	8.1	0.36	8.1	1.1	8.4	0	11	0
KH7M	2.6	0.62	--	--	2.1	0	--	--
KH8M	--	--	--	--	9.8	0	9.2	0
KH9M	--	--	--	--	--	--	92	8.3
KH13M	0.02	ND	0.03	0	0.02	0	--	--
KH14M	0.21	0	0.08	0	0.11	0	0.34	0
KH15M	0.13	0	--	--	0.12	0	--	--
KH16M	0.03	0	0.02	0	0.04	0	--	--
KH17M	0.02	0	0.02	0	0.07	0	--	--
KH18M	0.05	0	--	--	--	--	--	--
KH20M	0.23	ND	1.5	0	--	--	--	--
KH22M	4.5	0.52	4.1	0	3.7	0	4.7	0
KH25M	2.8	0	3.9	1.6	--	--	--	--
KH27M	0.75	0	2.4	0	0.48	0	0.55	0
KH29M	--	--	5.4	0.73	--	--	--	--
KH1C	0.02	0	0.03	0	0.06	0	--	--
KH2C	0.22	0	0.38	0	0.39	0	--	--
KH4C	2.1	0	2.9	0	--	--	--	--
KH5C	17	0	--	--	--	--	--	--
KH1L	6.1	0	5.0	0	6.8	0	7.9	0
KH2L	5.7	0	4.0	0	4.8	0	--	--
KH3L	--	--	4.9	0	--	--	--	--
KH1F	0.01	0	0.02	0	--	--	--	--
KH2F	0.01	0	0.04	0	--	--	--	--
KH3F	0.01	0	--	--	--	--	--	--
KH4F	0.03	0	--	--	--	--	--	--
KH5F	0.03	0	--	--	--	--	--	--

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Comparison of SO₄ and Cl Deposition Rates With Rates in Other Areas

Maps of SO_4 and Cl ion deposition for the continental United States are published yearly by the National Acidic Deposition Program. The 1991 maps (NADP, 1992) show sulfate deposition (wet deposition only) ranging from 0 to 3.4 g/m^2 per year; our results range from 0.2 to 36 g/m^2 per year for bulk (wet plus dry) deposition. Chloride deposition for 1991 (NADP, 1992) was 0 to 2.3 g/m^2 per year (wet deposition only); our results range from 0.02 to 184 g/m^2 per year (bulk deposition). It is difficult to compare these estimates; measurements of bulk deposition would be expected to be higher than wet deposition. In addition, the island of Hawaii is a marine and volcanic environment, so deposition of SO_4 and Cl is expected to be higher than at most continental stations. Galloway (1985, his fig. 8-1) estimated total wet and dry deposition of SO_4 in remote marine areas to be 0.52 g/m^2 per year, which is comparable to our lowest bulk deposition values, those from collectors above 2,740 m (9,000 ft) on Mauna Loa's slopes (0.2 to 0.8 g/m^2 per year).

Estimate of Total Non-seasalt Sulfate Deposition Rate

The nss sulfate deposition patterns show the highest spring-summer deposition to be in areas downwind of the volcanic sources during the prevailing tradewind conditions (figs. 5B and C). For the spring-summer periods of 1992 and 1993 total nss sulfate load was estimated by laying a grid of 10 km^2 squares over the maps of nss sulfate deposition and totaling the area within each contour interval. The total nss sulfate deposition was estimated for a 2,965 km^2 area in the northeast part of our study area where sufficient samples were collected during both time periods. The extent of this area is shown by the extent of the contours in figure 5B.

Table 6. Estimated non-seasalt sulfur bulk deposition rate for the eastern and central part of the study area

[Deposition rates are for the periods February - September 1992 and March - September 1993. Sulfur deposition rate is calculated on the basis of measured sulfate deposition. Abbreviations are: g, grams; d, day; km^2, square kilometers; m^2, square meters; Mg/d, megagrams per day.]

Deposition category (g SO_4/m² per 180 d)	Total area (km²)		Number of samplers in category		Average deposition (g SO_4/m² per 180 d)	Total deposition (g SO_4 per 180 d)	
	1992	1993	1992	1993		1992	1993
<1.0	1020	1240	13	13	0.5	5.1×10^8	6.2×10^8
<2.0	970	133	7	11	1.5	1.5×10^9	2.0×10^9
<3.0	520	270	4	1	2.5	1.3×10^9	6.8×10^8
<5.0	260	90	1	3	4.0	1.0×10^9	3.6×10^8
<10.0	195	35	3	1	7.5	1.5×10^9	2.6×10^8
					Total load over 180 days (g SO_4):	5.8×10^9	3.9×10^9
					Total load over 180 days (g S):	1.9×10^9	1.3×10^9
					Average estimated deposition rate (Mg/d S):	11	7

Kilauea's current summit emissions of SO_2 average 190 Mg/d, and East Rift Zone emissions average 900 Mg/d (Sutton and others, 1994). Although the summit source currently produces only about one-fifth the amount of SO_2 that the ERZ eruption produces, the tradewind patterns tend to carry the rift-zone emission plume out to sea or over the western part of the study area, where we had few samplers.

This estimate of total nss sulfate deposition is very approximate, because we are interpolating between collectors that are, in places, tens of kilometers apart. In addition, there are certainly other sources of nss sulfur for the island besides Kilauea's SO_2 output; for example, dimethyl sulfide emitted from the ocean contributes sulfate to precipitation in marine environments (Andreae and Raemdonck, 1983). The samples collected in different areas likely contained different proportions of volcanic and non-volcanic nss sulfur. Nevertheless, if we assume that all nss sulfur was from the volcano, the total deposition rate of nss sulfur measured in the eastern and central part of the study area (~9 Mg/d) amounts to about 10 percent of the average summit emissions (190 Mg/d SO_2, 95 Mg/d S) or 1-5 percent of the total summit and ERZ emissions (400 to 1,750 Mg/d SO_2, 200 to 875 Mg/d S). The very few data points in the southwestern part of the study area suggest that deposition of nss sulfate in that area may be higher.

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SUMMARY

Comparison of the chloride and sulfate deposition patterns for the southeast portion of the Island of Hawaii indicates that the two elements have very different sources. Chloride is nearly all of seasalt origin, and deposition patterns are controlled by proximity to the ocean and prevailing wind direction. In contrast, the patterns of total and nss sulfate deposition show a definite relation to sources of volcanic SO_2. Sulfate deposition is highest in areas that are downwind of the Kilauea summit and East Rift Zone sources under prevailing tradewind conditions. It must be emphasized that the geographic patterns of sulfate and chloride deposition are the major contribution of this report; the reported deposition amounts are very approximate, due to the non-standard sample collection procedure. The results from this study do not establish a correlation between high sulfate deposition and low rainfall pH, since six-month bulk samples do not provide representative rainfall pH values. However, the areas of high nss sulfate deposition identified in this report are areas where monitoring of air quality and precipitation chemistry may be needed to identify any detrimental effects of Kilauea's emissions. Any future acid deposition studies in this area need to focus on the areas west and southwest of Kilauea's summit and East Rift Zone SO_2 source areas, and also, but to a lesser extent, on areas north and northeast of the summit and ERZ, where volcanic nss sulfate deposition may be higher in winter months.

References

Andreae, M.O., 1985, The emission of sulfur to the remote atmosphere, in: Galloway, J.N. and others, eds., The biogeochemical cycling of sulfur and nitrogen in the remote atmosphere: Dordrecht, Holland, D. Reidel, 249 p.

Andreae, M.O., and Raemdonck, H., 1983, Dimethyl sulfide in the surface ocean and the marine atmosphere: A global view: Science, v. 221, p. 744-747.

Climatological Data, Hawaii and Pacific, National Oceanic and Atmospheric Administration, National Climatic Data Center, Asheville, North Carolina, v. 87, no. 8, 1991 through v. 89, no. 8, 1993.

Darzi, Michael and Winchester, J.W., 1982, Aerosol characteristics at Mauna Loa Observatory, Hawaii, after East Asian dust storm episodes: Journal of Geophysical Research, v. 87, no. C2, p. 1251-1258.

Drever, J.I., 1982, The Geochemistry of Natural Waters: Englewood Cliffs, New Jersey, Prentice-Hall, 388 p.

Elias, Tamar, Sutton, A.J., and Stokes, J.B., 1993, Current SO_2 emissions from Kilauea volcano: quantifying scattered degassing sources [abs.]: EOS, Transactions, American Geophysical Union, v. 74, no. 43, p. 670.

Eriksson, Erik, 1957, The chemical composition of Hawaiian rainfall: Tellus, v. 9, no. 4, p. 509-520.

Franson, M.A., ed., 1985, Standard Methods for the examination of water and wastewater, (16th edition): Washington, DC, American Public Health Association, 1268 p.

Galloway, J.N. and Likens, G.E., 1976, Calibration of collection procedures for the determination of precipitation chemistry: Water, Air and Soil Pollution, v. 6, p. 241-258.

Galloway, J.N., 1985, The deposition of sulfur and nitrogen from the remote atmosphere, in: J.N. Galloway and others, eds., The biogeochemical cycling of sulfur and nitrogen in the remote atmosphere: Dordrecht, Holland, D. Reidel, 249 p.

Gerlach, T.M. and Graeber, E.J., 1985, Volatile budget of Kilauea Volcano: Nature, v. 313, no. 6000, p. 273-277.

Gerlach, T.M., Krumhansl, J.L., Fournier, R.O., and Kjargaard, J., 1989, Acid rain from the heating and evaporation of sea water by molten lava: A new volcanic hazard [abs.]: EOS, Transactions, American Geophysical Union, v. 70, no. 43, p. 1421.

Harding, Duane and Miller, J.M., 1982, The influence on rain chemistry of the Hawaiian volcano Kilauea: Journal of Geophysical Research, v. 87, no. C2, p 1225-1230.

Keene, W.C., Pszenny, A.P., Galloway, J.N., and Hawley, M.E., 1986, Sea-salt corrections and interpretation of constituent ratios in marine precipitation: Journal of Geophysical Research, v. 9, no. D6, p. 6647-6658.

Lindberg, S.E., Harriss, R.C., Hoffman, W.A. Jr., Lovett, G.M., and Turner, R.R., 1989, Atmospheric chemistry, deposition, and canopy interactions, in: Johnson, D.W., and Van Hook, R.I., eds., Analysis of biogeochemical cycling processes in Walker Branch watershed: New York, Springer-Verlag, 401 p.

Miller, J.M,, Stensland, G.J., and Semonin, R.G., 1984, The chemistry of precipitation for the Island of Hawaii during the HAMEC project: National Oceanic and Atmospheric Administration Technical Memorandum ERL ARL-133, 33 p.

Miller, J.M. and Yoshinaga, A.M., 1981, The pH of Hawaiian precipitation: A preliminary report: Geophysical Research Letters, v. 8, no. 7, p. 779-782.

Nachbar-Hapai, Marlene, Siegel, B.Z., Russell, Christa, Siegel, S.M., Siy, Mei-Li and Priestly, Doris, 1989, Acid rain in the Kilauea Volcano area (Hawaii): Archives of Environmental Contamination and Toxicology, v. 18, p. 65-73.

Nash, A.J., 1992, Diurnal surface weather variations on the Island of Hawaii: Honolulu, University of Hawaii, M.S. Thesis, 127 p.

National Atmospheric Deposition Program, 1992, NADP/NTN Annual Data Summary, Precipitation Chemistry in the United States, 1991: Fort Collins, Colorado State University, Natural Resource Ecology Laboratory, 475 p.

Siegel, B.Z., Nachbar-Hapai, Marlene, and Siegel, S.M., 1990, The contribution of sulfate to rainfall pH around Kilauea volcano, Hawaii: Water, Air and Soil Pollution, v. 52, p. 227-235.

Sutton, A.J. and Elias, Tamar, 1993, Volcanic gases create air pollution on the Island of Hawaii: Earthquakes and Volcanoes, v. 24, no. 24, p. 178-196.

Sutton, A.J., Elias, Tamar, and Navarrete, Ramona, 1993, The effects of volcanic gas emissions on ambient air character at Kilauea Volcano, Hawaii [abs.]: EOS, Transactions, American Geophysical Union, v. 74, no. 43, p. 671.

Sutton, A.J., Elias, Tamar, and Navarrete, Ramona, 1994, Volcanic gas emissions and their impact on ambient air character at Kilauea Volcano, Hawaii: U.S. Geological Survey Open-File Report 94-569.