





U. S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

ANNOTATED BIBLIOGRAPHY

VOLCANIC GAS EMISSIONS AND THEIR EFFECT ON AMBIENT AIR
CHARACTER

By A. J. Sutton and T. Elias¹

OPEN-FILE REPORT 93-551-E

Prepared in cooperation with the
U.S. Department of Energy

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¹ Hawaiian Volcano Observatory, Hawaii National Park, Hawaii 96718

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Introduction

This bibliography was assembled to service an agreement between Department of Energy and the USGS to provide a body of references and useful annotations for understanding background gas emissions from Kilauea volcano. The current East Rift Zone (ERZ) eruption of Kilauea releases as much as 500,000 metric tonnes of SO₂ annually, along with lesser amounts of other chemically and radiatively active species including H₂S, HCl, and HF. Primary degassing locations on Kilauea are located in the summit caldera and along the middle ERZ. The effects of these emissions on ambient air character are a complex function of chemical reactivity, source geometry and effusivity, and local meteorology. Because of this complexity, we organized the bibliography into three main sections: 1) characterizing gases as they leave the edifice; 2) characterizing gases and chemical reaction products away from degassing sources; and 3) Hawaii Island meteorology.

Acknowledgements

Many thanks to Tom Wright and Jane Takahashi for their creation of the EndNote bibliographic data base on Hawaiian volcanism. Their extremely useful database was an important tool in our work on this document.

Sections

- I. Characterization of gas emissions from Kilauea Volcano point-sources
 - A. Fumarole studies
 - B. Volcanic gas plume studies
 - C. Other gas studies on and near Kilauea Volcano
- II. Characterization of ambient air away from the Kilauea Volcano point-sources
 - A. Volcanic smog (vog) and Lava haze (laze)
 - B. Compliance monitoring, previous EIS, and related interpretive reports
- III. Meteorology

I. Characterization of gas emissions from Kilauea Volcano point-sources

A. Fumarole studies

Fumarole studies are those in which samples of gas, aerosols, or condensates are taken directly from a fumarole, usually through a sampling tube. Fumaroles on Kilauea are holes, cracks or fissures, from which volcanic gas escapes. Cool fumaroles, those with temperatures less than 200°C, are not always connected directly to the magma supply. Hotter fumaroles, with temperatures > 500°C, are better for collecting eruptive gases, often from directly above the degassing magma. The collected samples are analyzed in the laboratory by instrumental and/or wet chemical techniques. Volcanic gases from Kilauea are characterized by oxidized conditions, with SO₂ as the predominate sulfur gas. This is in contrast to the reduced conditions characteristic of Hawaiian geothermal gas emissions, where H₂S dominates and SO₂ is not present. Results from fumarole studies provide detailed chemical and physical information about specific vent gas compositions for a specific time.

Ault, W.U., 1960, Geochemical research during the 1959-60 activity of Kilauea Volcano: The Geochemical News, p. 1-12.

The 1959-60 activity at Kilauea Volcano provided a graphic sequence of summit eruption, flank eruption, and summit collapse. The eruption was also a unique laboratory for geochemical studies. Varied techniques for sampling lava and gases were used to follow changes in erupted materials. Volcanic gases highly diluted by air show oxidized conditions represented by CO₂ (up to 6.3%) and SO₂ (up to 1.0%) in the high-temperature interior of the newly formed pumice cone (760°C near the surface). SO₂ is oxidized to SO₃ in the iron oxide-rich environment and forms H₂SO₄ at the surface.

This early study on eruptive gases diluted by air gives general constraints on SO₂ concentrations.

Barnard, W.M., Halbig, J.B., and Fountain, J.C., 1990, Geochemical study of fumarolic condensates from Kilauea Volcano, Hawaii: *Pacific Science*, v. 44, no. 3, p. 197-206.

Results of a geochemical study based on 20 samples of condensates obtained between late December 1987 and early January 1989 at five fumarole sites on the summit and upper east rift zone of Kilauea Volcano are presented. Concentrations of 28 chemical elements in these samples were quantified by neutron activation/gamma-ray spectroscopy and were statistically analyzed. Tabulated results show that 11 elements (Al, Ca, Cl, Co, I, La, Mn, Na, S, V, and Zn) exhibited significant variation.

Condensates can indicate the characteristics of fumarolic gases and aerosols that enter into the Earth's exchangeable reservoirs. Fumarole products have a potentially harmful impact on health and the environment through release of toxic materials and creation of acidic precipitation and vog. Although the authors of the report pose some important fundamental questions, this paper basically presents data from a short-term, limited study.

Casadevall, T.J., and Hazlett, R.W., 1983, Thermal areas on Kilauea and Mauna Loa Volcanoes, Hawaii: *Journal of Volcanology and Geothermal Research*, v. 16, p. 173-188.

High-temperature fumaroles on Kilauea are found in the upper East Rift Zone (Mauna Ulu summit fumaroles, 562°C), middle east rift zone (1977 eruptive fissure fumaroles), and in the summit caldera. Solfataric activity that has continued for several decades occurs along border faults of Kilauea caldera and at Sulphur Cone on the southwest rift zone of Mauna Loa. Solfataras that are only a few years old occur along recently active eruptive fissures in the summit caldera and along the rift zones of Kilauea. Steam vents and hot-air cracks also occur at the edges of cooling lava ponds, on the summits of lava shields, along faults and graben fractures, and in diffuse patches that may reflect shallow magmatic intrusions.

This information is the most recent (though not necessarily complete) published inventory of thermal features on Kilauea.

Darzi, M., 1981, Fumarolic aerosols from Kilauea Volcano, Hawaii: *Nuclear Instruments and Methods*, v. 181, p. 359-365.

As part of a geochemical survey of Kilauea, an active Hawaiian volcano, aerosol samples were collected in February 1979, a quiescent period, from several fumaroles within the caldera and along border faults. Portable and self-contained equipment, including pumps, batteries and cascade impactors, was used for the aerosol collection. Results are reported here for 16 samples analyzed at the Florida State University using particle induced X-ray emission for a dozen or more elements, including Si, P, S, Cl, and Fe.

These analyses are among the first for size fractionated particles during volcanic degassing activity. The six size fractions (from <0.25 to >8.0 µm particle diameter) collected by single orifice cascade impactors enable differentiation to be made between primary aerosols converted from gases and reentrained particles from the ground that are swept into the plume.

Finlayson, J.B., Barnes, I.L., and Naughton, J.J., 1968, Developments in volcanic gas research in Hawaii, in Drake, C.L., Hart, P.J., and Knopoff, L., eds., *The crust and upper mantle of the Pacific area*:

Washington, D.C., American Geophysical Union, Geophysical Monograph 13, p. 428-438. [based on the Upper Mantle Project Symposium, Tokyo, Aug. 1966]

Gases were collected from the surface and drill holes in Makaopuhi lava lake during recent eruptions (1965). Samples were taken using chromatographic adsorbents in sealed sampling tubes. Samples were analyzed by gas chromatography for eight gases, including H₂S and SO₂. These samples showed significant air contamination, SO₂ concentrations between 0.01 and 8.13 mole percent, and H₂S concentrations from 0.04 to 3.88 mole percent, though it appeared less frequently than did SO₂. Reasons for the variability in sample composition were investigated, and the relationship of the sample collected to primary magmatic gases is discussed.

These are some of the only reported analyses for chemistry of Makaopuhi lava lake gases.

Gerlach, T.M., 1980, Evaluation of volcanic gas analyses from Kilauea Volcano: *Journal of Volcanology and Geothermal Research*, v. 7, no. 3/4, p. 295-317.

An examination of early gas analyses (by Jaggar) at Kilauea suggests that these samples contain varying amounts of contamination by meteoric water. The results from the restored analyses reflect a spectrum of concentrations ranging from an "early" magmatic gas containing 35% H₂O, 50% CO₂, and 15% SO₂, to a more evolved gas with 70% H₂O, 10% CO₂ and 20% SO₂. The common presence of hydrocarbons and anomalously low atomic S/C in several Kilauea gas analyses is due to contamination of erupting lavas with organic materials. A similar origin also applies to above-background levels of environmentally hazardous organohalogens in volcanic gases. Thermodynamic calculations indicate these compounds would be virtually absent in gases erupted from lavas at temperatures above 500-600°C.

These "restored" gas analyses reflect vent compositions for early (1918-1919) summit eruption samples.

Gerlach, T.M., 1986, Exsolution of H₂O, CO₂, and S during eruptive episodes at Kilauea Volcano, Hawaii: *Journal of Geophysical Research*, v. 91, no. B12, p. 12,177-12,185.

A model for the exsolution of H₂O, CO₂, and sulfur from Kilauea magma as it rises from a shallow crustal reservoir predicts that vigorous exsolution occurs only after magma has ascended to shallow depths (≤150 m lithostatic) where pressures are < 3 MPa (30 bars). Most CO₂ is exsolved above 10 MPa, whereas most S, like H₂O, is exsolved below 2-3 MPa (< 100-150 m lithostatic). The critical condition for major outgassing and disruption of magma into spray is reached at 1.0-0.6 MPa (< 40-25 m lithostatic).

Gases do not vigorously exsolve until magma is close to the surface; then, sequentially under reducing pressure, CO₂ is exsolved, followed by SO₂ and water.

Gerlach, T.M., 1993, Oxygen fugacity of Kilauea volcanic gases and the oxygen fugacity of Kilauea basalt: *Geochimica et Cosmochimica Acta*, v. 57, p. 795-814.

This paper reports chemical analyses for a suite of relatively uncontaminated type II (CO₂ depleted) gases collected from episode 1 of the Pu'u 'O'o eruption. This study demonstrates that Kilauean lavas buffer oxygen fugacities of both type I (CO₂ rich) and type II volcanic gases, and that this buffering is consistent with mechanisms that transfer oxygen from gas to lava during cooling. It is further shown that these buffering effects control fugacities of minor and trace species in the gas phase. An extensive appendix covers sample collection, analysis, contamination and disequilibrium effects and their corrections.

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

The volatile content of magma in the reservoirs of active volcanoes has an important bearing on problems of petrogenesis, magma degassing, eruption mechanisms, eruption forecasting and monitoring, and the environmental impact of eruptions. Volcanic gas compositions and the sulfur content of glasses are used to infer the volatile

content and the degassing systematics of magma from the Kilauea Volcano. The authors' results are combined with data for Kilauea's magma supply and distribution over the past 27 years to calculate the volatile budget of the volcano.

CO₂ and SO₂ "pollution" from Kilauea is, on average, small, compared with global anthropogenic pollution. For example, the rate of anthropogenic CO₂ pollution ($2 \times 10^{16} \text{gyr}^{-1}$) corresponds to ~15,000 Kilaueas operating on budgets similar to the estimated budget from 1956-1983. Likewise, anthropogenic SO₂ pollution levels ($6.5 \times 10^{13} \text{gyr}^{-1}$) are equivalent to 380 Kilaueas.

Gerlach, T.M., Graeber, E.J., and Krumhansl, J.L., 1983, Gases from the 1983 east rift eruption, Kilauea Volcano [abs.], in AGU fall meeting, San Francisco, Calif., Dec. 5-9, 1983, Program and abstracts: Eos, Transactions, American Geophysical Union, v. 64, no. 45, p. 904.

Gases collected in association with active phases of the 1983 East Rift eruption indicate the erupting lavas are depleted in CO₂ and have O₂ fugacities well above QFM. Gases were sampled in 1/83, 2/83, and 8/83 at T > 900°C. Ten samples from 1/83 were free of direct atmospheric contamination (N₂ + O₂ + Ar < 0.05 mole %) and correspond to equilibrium compositions at T = 950 to 1035°C. Contamination by meteoric H₂O was apparent in one sample. Typical 1/83 gas compositions (mole %) were 79.7 H₂O, 0.93 H₂, 3.5 CO₂, 0.06 CO, 13.7 SO₂, 1.2 H₂S, 0.6 S₂, 0.002 COS, 0.16 HCl, and 0.18 HF. Gas compositions are similar at the peak fountaining temperature (1140°C) except for greater SO₂/H₂S.

These results are representative of modern analyses of east rift eruptive gases.

Gerlach, T.M., Hinkley, T.K., Briggs, P., and Stokes, J.B., 1991, Fumarole gases of Halemaumau pit crater and summit magma chamber degassing models for Kilauea Volcano, in AGU fall meeting, San Francisco, Calif., Dec. 9-13, 1991, Program and Abstracts: Eos, Transactions, American Geophysical Union supp., v. 72, no. 44, p. 562

Models by Greenland and others. (1985) and Gerlach and Graeber (1985) predict C/S of 14.6 and 7.7, respectively, for the gases emitted from the summit magma chamber of Kilauea Volcano. Both predictions are inconsistent with data from 200-300°C fumarole gases discovered recently inside Halema'uma'u pit crater and presumed to contain emissions from the summit chamber. The fumaroles inside the crater have C/S of 2, whereas Halema'uma'u rim fumaroles from the same systems have C/S of 5 to 16. The Greenland et al. model fails to predict the C/S of 2 in the crater fumarole gases because it assumes that the summit plume SO₂ flux equals the summit magma chamber flux and that SO₂ is not lost in transit to the surface. The author's observations contradict this assumption. They interpret the higher C/S of rim fumaroles as reflecting oxidation and loss of SO₂ as H₂SO₄ during cooling and condensation of the gases migrating to the surface. The Gerlach-Graeber model permits SO₂ loss during passage to the surface, but this model fails to predict crater fumarole C/S because it requires parental magma that is too CO₂-rich to be consistent with the present-day crater fumarole C/S of 2.

Based on this study of several fumaroles within Halema'uma'u, previous estimates of SO₂ dissolved in the magma (by Greenland) may be too low.

Giggenbach, W.F., and Matsuo, S., 1991, Evaluation of results from second and third workshops on volcanic gases, Mt. Usu, Japan, and White Island, New Zealand: Applied Geochemistry, v. 6, p. 125-141.

This paper summarizes the results from an international study of fumaroles on the two volcanoes. The aim of this workshop was to develop improved and standardized techniques for collection and analysis of volcanic gases. This paper is relevant to the study of Kilauean gases in the following way: gases from White Island are representative of a system that is principally a volcano but has an active hydrothermal system, as does Kilauea. One section of the paper discusses the important chemical reactions responsible for the observed composition of

gases being discharged from active vents. In particular, the reactions of S, SO₂, and H₂S are discussed. The authors report that, especially for low temperature fumaroles (<400°C), the H₂S present reacts quantitatively with available SO₂ to form elemental solid sulfur, or sulfur vapor, effectively scrubbing H₂S from the ambient air.

Conversion of H₂S to sulfur by reaction with SO₂ is especially important at Kilauea where H₂S is present to a much lower extent than SO₂, resulting in nearly quantitative conversion (removal) of H₂S from the ambient air.

Graeber, E.J., Gerlach, T.M., Hlava, P.F., and Bernard, A., 1983, Metal transport and deposition by high-temperature gases of the 1983 east rift eruption, Kilauea Volcano [abs.], in AGU fall meeting, San Francisco, Calif., Dec. 5-9, 1983, Program and abstracts: Eos, Transactions, American Geophysical Union, v. 64, no. 45, p. 904.

A 29-cm fused quartz tube of 3 cm i.d. was inserted into a fumarole vent at Kilauea, Hawaii, during the January 1983 East Rift eruption. Temperatures in the tube ranged from 865° to 618°C throughout the 100-hr exposure period. Gas collections were made before insertion and after removal of the tube from the same fumarole. Deposits inside the tube were analyzed by optical microscopy, energy dispersive analysis, electron microprobe and x-ray diffraction. The deposits were zoned with cristobalite and iron oxides occurring at high temperatures (850°-800°C); sphalerite and wurtzite with variable FeS and CdS at intermediate temperatures (800°-750°C); and wurtzite and KNaSO₄ predominating at lower temperatures (750°-625°C).

This study shows qualitatively, the emission and deposition of several metals as sulfates, sulfides and chlorides.

Greenland, L.P., 1984, Gas composition of the January 1983 eruption of Kilauea Volcano, Hawaii: *Geochimica et Cosmochimica Acta*, v. 48, p. 193-195.

Gas collections were made from a ~900°C vent, both by conventional evacuated-bottle/wet-chemical techniques and by manual pumping of flow-through bottles. The two sampling techniques yielded analytical data in mutual agreement. The author suggests that the very low C/S ratio is due to degassing of CO₂ during storage of the magma in a shallow reservoir before eruption.

These are some of the earliest analyses characterizing gases from the current east rift eruption. The comparison of sampling techniques is important for evaluating utility of later L.P. Greenland studies.

Greenland, L.P., 1986, Gas analyses from the Pu'u 'O'o eruption in 1985, Kilauea Volcano, Hawaii: *Bulletin of Volcanology*, v. 48, p. 341-348.

Volcanic gas samples were collected from July to November 1985 from a lava pond in the main eruptive conduit of Pu'u 'O'o from a two-week-long fissure eruption and from a minor flank eruption of Pu'u 'O'o. The uniformly carbon-depleted nature of these gases is consistent with previous suggestions that all east rift eruptive magmas degas during prior storage in the shallow summit reservoir of Kilauea.

This study indicates that eruptive gas compositions remained essentially constant over the first three years of the episodic east rift eruption of Kilauea.

Greenland, L.P., 1987, Hawaiian eruptive gases, chap. 28, in Decker, R.W., Wright, T.L., and Stauffer, P.H., eds., *Volcanism in Hawaii*: U.S. Geological Survey Professional Paper 1350, v. 1, p. 759-770.

Analysis of eruptive gases began at Kilauea Volcano in 1912. After the classic gas collections of 1917-19, there was a lapse of 40 years until sampling of eruptive gases recommenced in 1960. This paper summarizes results of gas analyses from Kilauea for the 1912-19 and 1968 Halema'uma'u eruptions, two summit eruptions in 1982, the 1960, 1965, 1977, and 1983-84 east-rift eruptions, and a shallow southwest-rift intrusion in 1981. Also included are results from the 1919 and 1984 eruptions of Mauna Loa. These data show the following: (1) Hawaiian eruptive gases predominantly have one of two compositions, defined by an atomic carbon/sulfur ratio (C/S) of

~0.2 for gases exsolving from magma that has had even brief storage in shallow summit reservoirs, and (much less commonly) a C/S ratio of ~2 for gases associated with eruptions of magma directly from the mantle.

This paper is an excellent historical summary for relevant gas studies that characterize vent compositions.

Greenland, L.P., 1988, Gases from the 1983-84 east-rift eruption, chap. 4, in Wolfe, E.W., eds., The Pu`u `O`o Eruption of Kilauea Volcano, Hawaii: Episodes 1 through 20, January 3, 1983, through June 8, 1984: U.S. Geological Survey Professional Paper 1463, p. 145-153.

Gases emitted during the January 1983-March 1984 eruptive period of the east rift of Kilauea Volcano had a very low C/S atomic ratio (0.17). This low atomic ratio is attributable to pre-eruptive degassing in the shallow summit storage reservoir before transport of the magma to the east rift zone. The volatile contents (in weight percent) of the eruptive magma are estimated as follows: H₂O, 0.42; S, 0.11; and CO₂, 0.02.

This paper points out the carbon depleted nature of rift eruptive gases, also implying that sulfur-bearing volatiles remain dissolved until they are erupted on the rift zone.

Greenland, L.P., 1987, Composition of gases from the 1984 eruption of Mauna Loa Volcano, chap. 30, in Decker, R.W., Wright, T.L., and Stauffer, P.H., eds., Volcanism in Hawaii: U.S. Geological Survey Professional Paper 1350, v. 1, p. 781-790.

The very low atomic C/S ratio (0.2, similar to Kilauea) is attributed to pre-eruption degassing of the magma during storage in Mauna Loa's shallow (3-4 km) summit reservoir. This study suggests that Hawaiian magmas degas in stages: CO₂ from 3-4-km depth long before the start of eruption, SO₂ as the eruptive magma begins its ascent from the reservoir, and H₂O and halogens only as the magma nears the surface. An implication of this hypothesis is that gas samples collected from eruptive vents do not reflect the gas composition of the original magma and may not even reflect the gas composition of the erupting magma.

Mauna Loa gases are examined in the larger context of Hawaiian gases. Competing reactions of gases as they exsolve from the melt are discussed in some detail. These reactions affect actual measured vent compositions.

Greenland, L.P., and Aruscavage, P., 1986, Volcanic emission of Se, Te, and As from Kilauea Volcano, Hawaii: Journal of Volcanology and Geothermal Research, v. 27, p. 195-201.

The Se, Te, and As content of the eruptive gas and of sulfur sublimates from the current (January 1983 through March 1985) east-rift eruption of Kilauea Volcano, Hawaii, have been determined. These data, in combination with previous data, suggest that most of the Se and Te in eruptive plumes occur in the particulate fraction while most of the As is in the gas phase. Eruptive emissions to the atmosphere have been estimated at 10 metric tonnes each of Se and As and 2 tonnes of Te over the first 14 months of the eruption. Material balance calculations suggest 0.28 ppm Se and 0.017 ppm Te for the initial Kilauean magma content of these elements. Only one-third of the original Se and Te is lost from the magma by degassing.

In addition to giving an estimation of concentrations, emission rates and fate for these metals, this paper discusses the role of particulate sulfur in mechanically removing Se and Te in close proximity to the eruptive vent.

Greenland, L.P., Okamura, A.T., and Stokes, J.B., 1988, Constraints on the mechanics of the eruption, chap. 5, in Wolfe, E.W., eds., The Pu`u `O`o eruption of Kilauea Volcano, Hawaii: Episodes 1 through 20, January 3, 1983, through June 8, 1984: U.S. Geological Survey Professional Paper 1463, p. 155-164.

Data from gas emissions and inflation/deflation of Kilauea's summit are used to estimate the gas content and rise rate of magma at Pu`u `O`o. Most degassing of the magma occurs in the depth interval 500-900 m of the conduit. Repose-period gas emissions represent previously exsolved gases migrating upward; these emissions may be the source of continuous repose-period tremor.

This paper describes magma effusion process. This process controls the majority of gas release and other attendant physicochemical processes.

Hinkle, M.E., and Stokes, J.B., 1990, Tabulation of CO₂, SO₂, and He concentrations in summit fumarole gases and wind and rainfall data at Kilauea Volcano, Hawaii, for the period June 1987-February 1989: U.S. Geological Survey Open-File Report 90-507, 27 p.

Gas chromatographic analyses for CO₂ and SO₂, and mass spectrometer analyses for helium were performed for samples taken from two boiling point solfataras.

Measurements were made several times weekly. These tabular data show time-series variations for the three species. No interpretations are made.

Jaggard, T.A., 1940, Magmatic gases: American Journal of Science, v. 238, p. 313-353 [includes plates].

Analyses of the gaseous constituents of Hawaiian lava are arranged in order of abundance of each gas. Progressing from poor to good collections, the author found that H₂O, SO₃, and Cl decrease, while CO₂, CO, SO₂, S₂, H₂, N₂, and Ar increase.

These analyses are historically important as some of the earliest gas studies done on Hawaiian volcanic gases. They form the basis for later gas vent characterization studies and are reinterpreted by Gerlach (1980).

Le Guern, F., Nohl, A., and Bicocchi, P., 1982, Field measurements of volcanic gases: Vulcano Island (Italy), Kilauea (Hawaii, U.S.A.), Merapi (Java, Indonesia): Bulletin Volcanologique, v. 45, p. 229-233.

A field gas chromatograph, built in 1978, was used in the field to directly analyze volcanic gases before water vapor condenses. Tested in Vulcano (Italy), Kilauea (Hawaii) and Merapi (Indonesia), this field measurement technique provides the actual composition of the volcanic gas mixture.

This paper highlights the low temperature reaction between H₂S and SO₂ to form sulfur and water. This reaction is important for scrubbing H₂S from volcanic emissions.

Modreski, P.J., and Graeber, E.J., 1976, Fumarolic gases from Kilauea Volcano, Hawaii [abs.], in Geological Society of America annual meeting, Denver, Colo., Nov. 8-11, 1976, Abstracts with programs: Boulder, Colo., Geological Society of America, v. 8, no. 6, p. 1014-1015.

Gases from fumaroles on former eruptive fissures in Kilauea caldera have been collected in Naughton-type evacuated tubes containing silica gel and analyzed by gas chromatography and wet chemical analysis. Representative analyses (mole %) are given here for the August 1971, September 1974, and November 29, 1975 fissures. Gas collection by pumping from a Teflon tube inserted several meters into a fumarole ('74, '75 samples) minimizes air contamination, but condensation of water in the tube complicates the technique. Measured vent compositions are as follows:

Vent name	1971 Fissure	1974 Fissure	1975 Fissure
date	11/7/75	12/5/75	12/4/75
T ° C	122°	94°	237°
CO ₂	1.81	14.5	53
SO ₂	039	99	< .002
SO ₃	51	23	.13
HCl	.013	.003	.012
HF	< .0003	< .0004	.0007
H ₂ O	94.6	83.9	95.0

Oxygen fugacities calculated for equilibrium between SO_2 and condensed sulfur (observed at all fumaroles) are slightly more oxidizing than hematite-magnetite. Calculated $f(\text{H}_2\text{SO}_4)$ is low, 10^{-9} bars or less at collection temperatures. Calculated $f(\text{H}_2\text{S})$ is around 10^{-4} to 10^{-2} bars, consistent with sulfur formation by oxidation of H_2S by SO_2 or O_2 upon cooling or mixing with air at the vent.

Murata, K.J., Ault, W.U., and White, D.E., 1964, Halogen acids in fumarolic gases of Kilauea Volcano [abs.]: Bulletin Volcanologique, v. 27, series 2, p. 367-368.

The water-rich condensates of fumarolic gases, obtained from degassing lavas of the 1959-60 eruption of Kilauea Volcano, contain unexpectedly high concentrations of hydrofluoric and hydrochloric acids, and thereby suggest that halogens are significant constituents of basaltic magmas. Vents on the pumice hill of Kilauea Iki yielded one sample that contained, in parts per million, 21,000 HF (1.1 N) with 2,920 HCl, and another sample, 20 HF with 70,500 HCl (2.0 N). Samples from vents elsewhere on the volcano had from one-fortieth to one-thousandth as much of the two acids.

These early measurements made at Kilauea's summit show anomalously high halo-acid contents, which could affect local environment.

Naughton, J.J., 1980, Composition of some components in gas collected during the 1977 eruption at Kilauea, Hawaii: Journal of Volcanology and Geothermal Research, v. 7, no. 3/4, p. 319-322.

Two each gas and condensate samples were collected and analyzed from a site along the primary fissure zone (temperature, 900°C) of the September 1977 eruption on the southeast rift of Kilauea. Samples contained $> 70\%$ air, and were analyzed for 13 gas and aqueous species, including SO_2 , but not H_2S . Carbon dioxide/ SO_2 ratios were 19 and 33 for the two gas samples. Condensate pHs were 1.5 and 2.1.

The CO_2/SO_2 ratios reported are uncharacteristic of eruptive gases, possibly reflecting sample deterioration prior to analysis.

B. Volcanic gas plume studies

These studies characterize gases or aerosols after they leave the vent or fumarole. Correlation spectrometer (COSPEC) measurements provide direct information on emission rates for SO_2 . Other gas plume studies measure particle-size, load and chemistry using special filtering and/or lab-analytical techniques.

Andres, R.J., Kyle, P.R., Stokes, J.B., and Rose, W.I., 1989, SO_2 from episode 48A eruption, Hawaii: Sulfur dioxide emissions from the episode 48A east rift zone eruption of Kilauea Volcano, Hawaii: Bulletin of Volcanology, v. 52, p. 113-117.

An SO_2 flux of 1170 ± 400 (1σ) tonnes per day was measured with a correlation spectrometer (COSPEC) along Chain of Craters Road in October and November 1986 from the continuous, non-fountaining, basaltic East Rift Zone eruption (episode 48A) of Kilauea Volcano. This flux is 5-27 times less than that of high-fountaining episodes, three to five times greater than that of contemporaneous summit emissions or interphase Pu'u 'O'o emissions, and 1.3-2 times the emissions from Pu'u 'O'o alone during 48A. Measurements made along the Chain of Craters road permit calculation of an emission rate of SO_2 that integrates both obvious and subtle degassing sources along the east rift zone. Calculations based on the SO_2 emission rate resulted in a magma supply rate of 0.44 million m^3 per day and a 0.042 wt % sulfur loss from the magma upon eruption. Both of these calculated parameters agree with determinations made previously by other methods.

COSPEC measurements are currently the best constraint on total SO_2 emission rates for Kilauea. Emission rates measured in this study predicted a lava extrusion rate consistent with independent geologic observations.

Cadle, R.D., and Frank, E.R., 1968, Particles in the fume from the 1967 Kilauea eruption: *Journal of Geophysical Research*, v. 73, no. 14, p. 4780-4783.

The fume from Halema`uma`u Crater of Kilauea Volcano was sampled in 1965 and 1966 during the absence of eruption. The particles consisted largely of dilute H_2SO_4 droplets containing ammonium ions. The 1967 eruption of Halema`uma`u Crater provided an opportunity to sample and identify particles in the actual eruption fume. Samples were collected from various points about the crater's edge on November 14 and 15.

This paper points out the acidic nature of fume, as well as the important conversion of SO_2 to sulfate that occurs close to the vent.

Cadle, R.D., Wartburg, A.F., and Grahek, F.E., 1971, The proportion of sulfate to sulfur dioxide in Kilauea Volcano fume: *Geochimica et Cosmochimica Acta*, v. 35, p. 503-507.

Particles collected from the fume of Kilauea Volcano are largely dilute H_2SO_4 droplets containing dissolved salts. The concentrations of salts in the droplets vary markedly depending on the volcanic conditions where collection occurs. A technique has been developed for determining the proportion of sulfate to SO_2 in such fume. Very large variations in these proportions have also been found. All of these variations can be explained as being due to varying degrees of oxidation of H_2S , S and SO_2 at high temperatures by atmospheric oxygen.

While these measurements were made several years ago, they point out the important conversion of SO_2 to sulfate that occurs close to the vent.

Cadle, R.D., Wartburg, A.F., Pollock, W.H., and Gandrud, B.W., 1973, Minor constituents of particles in Kilauea Volcano fume [abs.],: *Eos, Transactions, American Geophysical Union*, v. 54, no. 4, p. 511.

We have now determined the relative concentrations of a large number of trace constituents in particles collected from the fume above the active lava lake of the Mauna Ulu Crater of Kilauea and from the fume from the presently dormant Halema`uma`u Crater of Kilauea. Strongly emitted fume from a sink hole on the active floor of Mauna Ulu had an unusually low $\text{SO}_4^{2-}/\text{Cl}^-$ ratio. The order of decreasing concentration, for the sample most completely analyzed (from Halema`uma`u) was $\text{SO}_4^{2-} > \text{Ca} > \text{Si} > \text{Cl} > \text{NH}_4^+ > \text{Fe} > \text{Na} > \text{Mg} > \text{Cu} > \text{Mn} > \text{Cr} > \text{Sb} > \text{Br} > \text{Pb} > \text{Hg} + \text{Se} > \text{Cd} > \text{As} > \text{Co} > \text{Sc}$. The ratio of the concentrations of chloride to bromide, about 30, was similar to that found in the stratospheric "sulfate" layer. The particles were collected on filters and analyzed by wet chemical, atomic absorption, neutron activation, and x-ray fluorescence techniques.

This study presents some of the only data on relative abundances for particulate emissions from the Mauna Ulu eruption.

Casadevall, T., Greenland, P., and Furukawa, B., 1981, Gas studies of the March 10-12, 1980, intrusion of Kilauea Volcano, Hawaii [abs.], in *American Geophysical Union fall meeting, San Francisco, Calif, Dec. 7-11, 1981, Program and abstracts: Eos, Transactions, American Geophysical Union*, v. 62, no. 45, p. 1072.

The intrusive event of March 10-12, 1980 near Mauna Ulu on the upper east rift zone of Kilauea produced large amounts of magmatic gases, which indicate that magma was emplaced near the surface. Sulfur dioxide and H_2S were detected during the first few hours of seismic activity. The two sources of gas emission were the summit crater of Mauna Ulu and a 300-m-long, $\text{N}60^\circ\text{E}$ fracture located midway between Mauna Ulu and Kane Nui O Hamo. Measurements of SO_2 emission by COSPEC technique from March 11 to April 17 indicate that the flux of SO_2 gas decreased from about 550 t/d (tonnes per day) on March 11 to less than 50 t/d within two weeks. A total of 2,200 tonnes of SO_2 was produced from March 11 to early April. H_2S was smelled on March 10 and 11 but could not be measured using PbAc detectors with a sensitivity of 3 ppb.

A near-surface intrusive event produced fleeting albeit unmeasurable H₂S anomalies in ambient air, and produced a 10-fold spike in SO₂ emission from an individual vent.

Casadevall, T.J., Stokes, J.B., Greenland, L.P., Malinconico, L.L., Casadevall, J.R., and Furukawa, B.T., 1987, SO₂ and CO₂ emission rates at Kilauea Volcano, 1979-1984, chap. 29 in Decker, R.W., Wright, T.L., and Stauffer, P.H., eds., *Volcanism in Hawaii*: U.S. Geological Survey Professional Paper 1350, v. 1, p. 771-780.

Since June 1979 regular measurements were made of SO₂ emission rates from Kilauea. In 1983 and 1984, measurements of CO₂ emission rates were also made for Kilauea. The average daily SO₂ emission rate from 1979 through 1982 was 170 ± 50 t/d; from 1983-1984, the average daily emission rate had increased to 260 ± 90 t/d. The 1979-1982 rate occurred during a time when no major eruptive activity occurred at Kilauea summit. The increase in 1983 is coincidental with the start of major eruptive activity at the Pu`u `O`o vent on the east rift zone and probably reflects an increase in the rate of magma supply. The 1983-1984 episodes of the Pu`u `O`o eruption produced about 370,000 tonnes of SO₂, or as much as 3% of the global annual volcanic contribution.

This paper is the most recent detailed summary of SO₂ emission rates for Kilauea. It describes COSPEC technique and associated uncertainties.

Chartier, T.A., Rose, W.I., and Stokes, J.B., 1985, SO₂ emission rates at Pu`u `O`o vent, Kilauea between east rift zone phases 33 and 34 [abs.], in AGU fall meeting, San Francisco, Calif., Dec. 8-13, 1985, Program and abstracts: *Eos, Transactions, American Geophysical Union*, v. 66, no. 46, p. 1132.

SO₂ emission rates at Pu`u `O`o were measured from 6/12/85 to 7/6/85 by a ground-based tripod survey method, 775 m norththwest of the vent. The objective was to obtain data to reveal the degassing pattern during repose. The mean rate of SO₂ emission was 166 ± 83 tonnes/day (t/d). The average daily flux decreased from 240 to 130 t/d during the first 20 days of repose. The emission rate often varied markedly (factors of 2-4) in periods of a few minutes. Data was collected on 17 out of 24 repose days averaging 38 runs/day. The number of individual flux determinations made was 909, which corresponds to 313 of the suitable daylight hours in the 24-day period. The total SO₂ released during the repose period of 24 days was 4,000 t or about 160 ± t/d.

This study puts constraints on SO₂ emission rates during eruptive interphase periods.

Cruikshank, D.P., and Morrison, D., 1980, Spectroscopy of volcanic flames and fume: Research Reports, National Geographic Society, v. 12, p. 117-123.

An emission spectrograph was used to study the spontaneously combusting flames produced during a summit eruption at Kilauea. Strong emission lines were identified for water, with the conclusion that the lines were due to the combination of hydrogen and admixed oxygen to form water.

Several components in volcanic gases are combustible, including H₂S, carbon monoxide, and hydrogen. Combustion products affect chemistry of gases found near the volcano.

Greenland, P., Rose, W.I., and Stokes, J.B., 1985, An estimate of gas emissions and magmatic gas content from Kilauea Volcano: *Geochimica et Cosmochimica Acta*, v. 49, p. 125-129.

Emission rates of CO₂ have been measured at Kilauea Volcano, Hawaii, in the east-rift eruptive plume, and CO₂ and SO₂ have been measured in the plume from the non-eruptive fumaroles in the summit caldera. These data yield an estimate of the loading of Kilauean eruptive gases to the atmosphere and suggest that such estimates may be inferred directly from measured lava volumes. These data, combined with other chemical and geologic data, suggest that magma arrives at the shallow summit reservoir containing (wt. %) 0.32% H₂O, 0.32% CO₂, and 0.09% S. Magma is rapidly degassed of most of its CO₂ in the shallow reservoir before transport to the eruption site. Because this summit degassing yields a magma saturated and in equilibrium with volatile species and because transport of the magma to the eruption site occurs in a zone no shallower than the summit reservoir, the authors

suggest that eruptive gases from Kilauea characteristically should be one of two types: a "primary" gas from fresh magma derived directly from the mantle and a carbon-depleted gas from magma stored in the summit reservoir.

This paper gives what are still considered modern general constraints on degassing for Kilauea.

Hinkley, T.K., 1991, Distribution of metals between particulate and gaseous forms in a volcanic plume: Bulletin of Volcanology, v.53, p. 395-400.

The air-diluted gas plume of the Pu'u 'O'o vent of Kilauea was sampled during a non-eruptive period using a pumping system, filter system and aqueous trapping system. The study produced data on abundances of metal particles, including Tl, Bi, Cd, Pb, Cd, and Cu.

Particle masses of the several metals are tabulated, along with total volume sampled, permitting calculation of metal concentration in the sampled air.

Naughton, J.J., Derby, J.V., and Glover, R.B., 1969, Infrared measurements on volcanic gas and fume: Kilauea eruption, 1968: Journal of Geophysical Research, v. 74, no. 12, p. 3273-3277.

Infrared spectra from Halema'uma'u overlook of Kilauea Volcano show absorption by volcanic and atmospheric gases. The gases were measured using erupting fountain as the light source, and measuring infrared absorbance spectra from 2.5 to 14.5 microns. The composition of the main volcanic gaseous components within the primary fountain is estimated to be H₂O, 95%; CO₂, 4%; and SO₂, 1%.

These measurements from several years ago indicate a somewhat higher proportion of carbon to sulfur than characteristic of current middle east rift eruptive gases.

Naughton, J.J., Finlayson, J.B., and Lewis, V.A., 1975, Some results from recent chemical studies at Kilauea Volcano, Hawaii: Bulletin Volcanologique, v. 39, no. 1, p. 64-69.

Fume samples from Halema'uma'u Crater in Kilauea caldera and from a fissure eruption that occurred nearby on the floor of the caldera during August 1971 were examined for their halogen (Cl and F) and sulfur content. The ratio of chloride to fluoride ranged from 0 to 3, and for chloride to sulfate, the ratios ranged from 8 to 30. on a weight/weight basis. Chloride/fluoride ratios increased one month prior to eruption.

The exact nature of the samples is unclear, some came from near-eruptive fissures, some from fume in ambient air. Complete analyses are not shown. Data may be useful for comparing with other more complete analyses.

Naughton, J.J., Lewis, V.A., Hammond, D., and Nishimoto, D., 1974, The chemistry of sublimates collected directly from lava fountains at Kilauea Volcano, Hawaii: Geochimica et Cosmochimica Acta, v. 38, p. 1679-1690.

Collections were made on quartz wool held within open-ended quartz tubes and, for silica detection, on stainless steel wool in a stainless steel tube. The main components in the sublimate were, in order of decreasing concentration for the best sample, Na, Ca, Al, Fe, Mg, K, B, Si, Ti, Zn, H⁺, NH₄⁺, Cu and Ni in the form of sulfates, chlorides and fluorides. Particulate sulfates appear under the increasing oxidizing conditions caused by the access of air.

This earlier work using an independent method of investigation indicates the sulfur species gas-to-particle conversion that is evidenced in later studies.

Naughton, J.J., Lewis, V., Thomas, D., and Finlayson, J.B., 1975, Fume compositions found at various stages of activity at Kilauea Volcano, Hawaii: Journal of Geophysical Research, v. 80, no. 21, p. 2963-2966.

Fume in ambient air was collected at Kilauea Volcano with equipment patterned after that used in industrial pollution studies, using impingers containing aqueous solutions for absorbing acid gases. Particulates and some of the gases present were separated. The fume analyzed was collected from Halema`uma`u Crater in a noneruptive state, from Mauna Ulu lava lake with mild lava fountaining, and from vigorous but short-lived fountaining from fissures across the floor of Kilauea caldera. Data show SO₂/sulfate ratio of 3.1 at rim of Halema`uma`u and 1.6 measured 0.5 km downwind, reflecting air oxidation. In general, SO₂ comprised most of the fume (excluding air), followed by hydrochloric acid. Sulfate comprised 50% to 90% of the particulate portion of the fume. Data tables are presented.

Olmez, I., Finnegan, D.L., and Zoller, W.H., 1986, Iridium emissions from Kilauea Volcano: Journal of Geophysical Research, v. 91, no. B1, p. 653-663.

During May 1983, gas and particulate samples were collected at the cooling vents of Kilauea. Three vents on the southeast rift zone were sampled using base-treated filter packs to absorb acidic gases and Teflon filters for particles. The samples were analyzed for 40 elements by nondestructive neutron activation analysis. Unlike the case with other volcanoes, iridium was observed to be highly enriched (10⁵ fold) at the higher temperature vents. Estimates of iridium emission rates during eruptions of Kilauea yield an emission rate of 3 grams of iridium per million cubic meters of magma. This rate amounts to only about 0.3% of the iridium present in the magma being released by the volcano. Concentrations and enrichment factors for the 40 elements, relative to a standard Hawaiian basalt, are presented.

Siegel, S.M., and Siegel, B.Z., 1984, First estimate of annual mercury flux at the Kilauea main vent: Nature, v. 309, no. 5964, p. 146-147.

Mercury is the principal metal emitted in vapor form by volcanoes and other natural geothermal sources. Direct evidence for the release of mercury at volcanic, fumarolic and hydrothermal sites has been obtained in Hawaii, Iceland, Antarctica and the Pacific northwest. From 1971 to 1980, mercury and sulfur dioxide analyses were carried out on air samples collected immediately downwind of Halema`uma`u, the Kilauea main vent in Hawaii. From these measurements, a Hg/SO₂ ratio of 0.51×10^{-3} was derived. As reported here, applying this ratio to the recently determined sulfur dioxide mass output of Halema`uma`u, yields a calculated mercury flux of 2.6×10^8 g annually.

Note that the estimated total mercury emission rates are based on normalization to SO₂, and assume that the ratio of the two species is constant.

Stoiber, R.E., Malinconico, L.L., Jr., and Casadevall, T.J., 1979, SO₂ monitoring by remote sensing at Kilauea Volcano, Hawaii [abs.], in Hawaii Symposium on Intraplate Volcanism and Submarine Volcanism, Hilo, Hawaii, July 16-22, 1979, Abstract Volume: Hilo, Hi., U.S. Geological Survey and University of Hawaii, p. 174.

SO₂ emissions were monitored using a remote-sensing correlation spectrometer. Any SO₂ oxidized to other sulfur species or dissolved in water is effectively lost to the spectrometer. Twenty-two traverses were made during the five-day period of the investigation. Traverses were made completely around the crater and down the Chain of Craters Road. The volcano was in a "quiet" state of activity at the time. Over a six-day period in February 1975 an average of 280 metric t/d of SO₂ was measured by Stoiber and Malone. In February 1975 and October 1978, the volcano was in a state of quiescence, so it seems reasonable to assign an average emission level of 200 to 400 metric tonnes of SO₂ gas per day to a quiescent Kilauea.

These are some of the earliest reported COSPEC measurements at Kilauea and are within a factor of two of more recently measured emission rates. Although the authors assign an average emission level to a quiescent Kilauea, they do not explicitly state the measured 1978 SO₂ flux.

C. Other gas studies on and near Kilauea Volcano

Cox, M.E., 1980, Ground radon survey of a geothermal area in Hawaii: *Geophysical Research Letters*, v. 7, no. 4, p. 283-286.

Rates of ground radon emanation, in the Puna geothermal area on the lower east rift of Kilauea Volcano were measured by alpha particle sensitive cellulose nitrate films. This type of survey was found suitable for the basaltic island environment characteristic of Hawaii and is now used in Hawaii as a routine geothermal exploration technique.

Data from this study indicate that radon emission varies in space and time, being controlled by geologic structure and emplacement of magma beneath the monitoring site. Data indicate concentration in the ground, not emission rate, or ambient air concentration.

Cox, M.E., 1981, Radon monitoring on Kilauea summit [abs.], in *Arc Volcanism, Tokyo and Hakone, Japan, Aug. 28-Sept. 9, 1981, Abstracts: Tokyo, the volcanological Society of Japan and International Association of Volcanology and Chemistry of the Earth's Interior (IAVCEI)*, p. 68-69.

Cox, M.E., Cuff, K.E., and Thomas, D.M., 1980, Variations of ground radon concentrations with activity of Kilauea Volcano, Hawaii: *Nature*, v. 288, no. 5786, p. 74-76.

Concentrations of radon (Rn), predominantly the isotope ^{222}Rn , were monitored at 10 stations on the summit of Kilauea Volcano and its upper rift zones. The technique uses α -particle sensitive cellulose nitrate films housed in inverted 250 ml containers buried at 40 cm depth, and changed approximately every three weeks. The first 18 months and data for four stations (T1-T4) are discussed.

Data from these studies indicate that radon emission, which is controlled by geologic structure and emplacement of magma beneath the monitoring site, varies in space and time. Data indicate concentration in the ground, not emission rate, or ambient air concentration.

Franczyk, K.J., Gibson, E.K., and Tilling, R.I., 1987, Sulfur and carbon abundances in Hawaiian tholeiite lavas: 1972-1975 eruptions of Kilauea and 1975 eruption of Mauna Loa, chap. 31, in Decker, R.W., Wright, T.L., and Stauffer, P.H., eds., *Volcanism in Hawaii: U.S. Geological Survey Professional Paper 1350*, v. 2, p. 791-803.

Analysis of sulfur and carbon abundances in 135 samples of fresh Hawaiian basalts erupted subaerially during 1972-1975 indicates that the different degassing behavior of sulfur and carbon volatiles and the ease of contamination by atmospheric carbon explain the different relationships observed between the sulfur and carbon contents in the samples and their density, flowage distance, and type of eruptive material.

Sulfur abundances in erupted basaltic lava range from 37 to over 15,000 ug/g (median value 153 ug/g). Decreases in sulfur abundance in the lava away from the vent further document previous findings that sulfur is progressively lost by degassing during lava fountaining and flowage. The greatest loss occurs within about 2 km of the active vent.

Thomas, D.M., 1982, A geochemical case history of the HGP-A well, 1976-1982, in *Pacific Geothermal Conference, Auckland, N.Z., 1982, Proceedings: Auckland, N.Z., University of Auckland Geothermal Institute and cooperating agencies*, p. 273-278.

The Hawaii Geothermal Project Well-A was completed in 1976 to a depth of 1966 meters. The bottomhole temperature, under shut-in conditions, was 360°C and at full discharge, capable of producing about 45,500 kg/hr of mixed fluid composed of 48% steam and 52% liquid. Non-condensable gas compositions from the period 1977-1982 show H_2S concentrations ranging from 112 to 1435 mg/kg of steam and CO_2 from 445 to 4431 mg/kg of steam.

Thomas, D.M., Cuff, K.E., and Cox, M.E., 1986, The association between ground gas radon variations and geologic activity in Hawaii: *Journal of Geophysical Research*, v. 91, no. B12, p. 12,186-12,198.

Soil gas radon activities were recorded at 10 stations on Kilauea Volcano for approximately five years. Long-term average radon activities were found to vary by a factor of more than 25. Spatial variations appear to be controlled predominantly by near-surface hydrothermal activity, thickness and permeability of soil-cover, and presence of subsurface fracturing. Magmatic intrusions were associated with contemporaneous changes in radon concentration. Time-series plots of track-densities for the five-year study period are presented. Data were collected as alpha track-etch densities, rather than as volumetric concentrations (pico-curies/liter).

II. Characterization of ambient air away from Kilauea Volcano point-sources

A. Volcanic smog (vog) and lava haze (laze)

Volcanic smog or "vog" is a locally-used term, referring to air pollution produced by the volcano. The principal components of vog are the reaction products of SO₂ and aerosols mixed with the gas plume. These reaction products include H₂SO₃ and H₂SO₄, alkali and alkali-earth metal-sulfates. Lava haze, or "laze," is another locally-used term that refers to the plume produced by the interaction of molten lava and sea water. Laze is principally composed of HCl and entrained sea water brine. Vog and laze are of concern in Hawaii because they are carried by prevailing winds, creating a variety of environmental effects that impact areas of the island as far as 100 miles away.

Anderson, B., and Higa, D., 1991, Concentrations of lead in water from cisterns on the island of Hawaii [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagued.

The State of Hawaii Department of Health analyzed over 2,000 water samples for lead from water cisterns on the island of Hawaii. Lead concentrations ranged from less than the level of detection (5 ug/l) to over 3,300 ug/l. Altogether, about 24% (544 samples) of the water samples collected exceeded the Maximum Contaminant Level (MCL) proposed by the U.S. Environmental Protection Agency for public water systems of 20 ug/l; 11% of the cisterns exceeded the current MCL of 50 ug/l. The highest percentage of systems with lead levels above the MCL was found in West Hawaii, where about 23% of the water systems sampled exceeded the 50 ug/l standard. Acid rain resulting from volcanic emissions is believed to cause the leaching of leaded building materials, such as solder, nails, flashing, and leaded coatings, all of which may contribute to elevated lead levels in cistern water.

Cisterns are an important source of domestic drinking water. The leaching of lead into cisterns is a secondary volcanogenic environmental effect.

Casadevall, T.J., Rye, R.O., and Morrow, J.W., 1991, Sources of sulfur in volcanic haze: preliminary report of isotopic results [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagued.

This study analyzes sulfur isotopes of sulfate on high-volume air filter samples collected at Kalapana and Captain Cook on the island of Hawaii in order to determine the source of sulfur in volcanic haze. Preliminary data indicate two distinct sources of sulfur in these samples. Sea water sulfate (+20 per mil $\delta^{34}\text{S}$) is indicated for low-yield samples collected in November 1990 at the Kalapana site (upwind from degassing lava) during normal trade wind conditions.

Sulfate of dominantly magmatic origin (+2 to +5 per mil $\delta^{34}\text{S}$) is indicated for higher-yield samples collected during the same period at the downwind site at Captain Cook.

Chuan, R.L., 1991, The production of hydrochloric acid aerosol from the eruption of Kilauea Volcano [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagued.

Two mechanisms have been observed to produce hydrochloric acid aerosol from the eruption of Kilauea Volcano. Both mechanisms create hydrochloric acid aerosol as a result of a secondary process. One mechanism is the flash evaporation of sea water, along with salts, which occurs when lava from the volcano enters the ocean, as first observed by Gerlach. The other is the reaction of the H_2SO_4 aerosol with sea salt as the plume from the Pu'u 'O'o vent is transported over the ocean. The reaction yields sodium sulfate and hydrogen chloride, which then hydrolyzes to HCl aerosol. Evidence of this mechanism is found in aerosol samples taken from the west coast of the island of Hawaii at Kona, about 100 km from the vent, in a populated area that has been experiencing the deleterious effects of vog. Whereas H_2SO_4 constitutes over 80% of the total aerosol mass from the Pu'u 'O'o vent, in the Kona samples it only constitutes about 50%, the balance being silicates and sodium chloride (30%) and sodium sulfate and aqueous HCl (20%).

Elias, T., 1992, The effect of volcanic emissions on ambient air quality in Hawaii Volcanoes National Park [abs.], in Earthquake, Tsunami, and Volcano Hazards Seminar, Hilo, Hawaii, Aug. 6, 1992, Abstracts: Hilo, Hi., Center for the Study of Active Volcanoes, University of Hawaii at Hilo, unpagued.

The National Park Service has been monitoring air quality at the summit of Kilauea Volcano in Hawaii Volcanoes National Park since October 1986. Concentrations of SO_2 , wind speed, wind direction, temperature, dewpoint, solar radiation, and rainfall are automatically recorded at this site. Fine-particle (<2.5 micron) and PM-10-particle (<10 micron) samples are collected on stacked filter units. The fine particles are analyzed for total mass, concentrations of the elements sodium to lead, hydrogen ion, the coefficient of optical absorption, organic and light-absorbing carbon, nitrate, sulfate, and SO_2 .

Data gathered from 1987-1990 show that SO_2 levels exceeded the Ambient Air Quality Primary (24-hr) standard established by the EPA 50 times. An analysis of meteorological parameters shows that Kona winds and very low speed trade winds accompany periods of high SO_2 concentration at this site. During these wind conditions, EPA SO_2 standards are more likely to be exceeded.

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.], in AGU fall meeting, San Francisco, Calif., Dec. 4-8, 1989, Program and abstracts: Eos, Transactions, American Geophysical Union supp., v. 70, no. 43, p. 1421.

Continuous eruption on the east rift zone of Kilauea Volcano since July 1986 has established a subsurface lava tube system that frequently permits lava to enter the ocean near Kupapa'u Point, Hawaii. The flows produce spectacular steam explosions and a large plume cloud. Acid rain from the plume creates local environmental and health problems. Analyzed samples of the plume rain show that it is a brine with a salinity 2.3 times that of sea water and a pH of 1.75. The authors propose that the acid derives from HCl gas formed primarily by the hydrolysis reaction of steam with magnesium chloride salts precipitated locally where magma evaporates sea water to dryness. Dissolution of this acid in brine droplets formed by ejection of disrupted, boiled sea water to the atmosphere produces the observed acid rain with a slightly higher pH resulting from dilution effects and reactions with lava fragments.

Irreversible mass transfer calculations predict that the evaporation of 1 liter of sea water to dryness at temperatures of 100-300°C will produce a liter of hydrochloric acid condensate with a pH of 1. Prevailing trade winds carry these products as far away as Kona, on the west side of the island, 100 miles away.

Gill, T.E., Tanada, T.N., and Cahill, T.A., 1990, Effect of Kilauea's ongoing eruption on the air quality of Hawaii [abs.], in International Volcanological Congress, Mainz, Germany, Sept. 3-8, 1990, Abstracts:

Mainz, Germany, International Association of Volcanology and Chemistry of the Earth's Interior (IAVCEI), unpagged

In order to quantify the effect of the ongoing eruption of Kilauea on the overall air quality of the island of Hawaii, particulate sampling and/or SO₂ monitoring was performed at seven sites on the island in spring 1988. Samples were taken from a site upwind of the vent, from a site adjacent to the surface outbreak of lava very near the coast, from the lava-covered visitor center, and at sites across the island at various elevations and distances from the vent. Volcanic aerosols and gases are emitted directly by the vent and lava and are also extensively formed by the vaporization of sea water by lava flows. Samples were analyzed for mass, elemental composition, and SO₂ concentration. Sulfur compounds (SO₂ and sulfates) are the dominant emissions.

These processes combine to become a major source of air pollution on the Kona coast. Due to material emitted by Kilauea, particulate concentrations on Hawaii are often greater than those in rural areas of continental North and South America. Other compounds, including potentially toxic elements such as Se, As, Pb and Hg, are also seen in aerosols emitted by Kilauea. The concentrations of these materials, by themselves, do not seem to present a significant risk to the health of the island's residents, but particulate levels, especially of acidic species, could be detrimental to those working and living closest to the vent.

Halbig, J.B., and Barnard, W.M., 1991, Atmospheric geochemistry at windward and leeward locations in the island of Hawaii during the early eruptive phases of Pu`u `O`o [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagged.

A study funded by the State of Hawaii, Department of Business and Economic Development, was conducted in 1983 and in early 1984 to characterize the atmospheric geochemistry at windward (Panaewa) and leeward (Kawaihae) locations on the island of Hawaii. A variety of data was collected on air and rain water chemistry and on meteorological conditions. This paper particularly addresses the results of chemical determinations of the acidic components (with emphasis on sulfate ion) in air and rain water.

In a few cases, relatively high sulfate concentrations were measured at the Kawaihae site during or immediately following an eruptive phase of Pu`u `O`o, but such correlation was not apparent for the entire set of data.

Hallenborg, C.P., 1991, Respiratory effects to man by volcanic eruption in Hawaii [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagged.

Respiratory complaints are associated with volcanic eruption by patients and health care workers. The existence of such claims, as well as the cause, is being examined by the author. The respiratory health of 50 healthy children and adults upwind from the volcano (Hilo) was compared to 50 subjects downwind (Kona) during the study period 1989-1990. Daily peak flow and spirometric data were compared to certain pollutants, particulates, and sulfates known to cause respiratory illness.

Sulfate and particulate pollution do not reach levels known to cause respiratory illness in controlled situations. A few subjects apparently suffered from even mild elevation in pollution. An over-all downward trend in pulmonary function is noted in both children and adults.

Luria, M., Boatman, J.F., Harris, J., Ray, J., Straube, T., Chin, J., Gunter, R.L., Herbert, G., Gerlach, T.M., and Van Valin, C.C., 1992, Atmospheric sulfur dioxide at Mauna Loa, Hawaii: Journal of Geophysical Research, v. 97, no. D5, p. 6011-6022.

Measurements of SO₂ were made at the National Oceanic and Atmospheric Administration's Mauna Loa Observatory in Hawaii during a 12-month period beginning in December 1988. Concentrations of SO₂ varied from background levels of less than 0.05 ppbv to a maximum of 50 ppbv, during episodes that lasted from two to 24 hrs. Kilauea caldera, located approximately 35 km southeast of the Hawaiian Volcano Observatory at an

elevation of about 1,000 m ASL and the current eruption at Pu'u O'o 50 km east-southeast of the observatory, are the most likely sources of the elevated SO₂ measured during these episodes. These episodes occurred 10-25 times each month, mostly during the day; peak concentrations were usually recorded at mid-day.

Emissions from Kilauea have a measurable effect on ambient SO₂ concentrations at Mauna Loa Observatory, especially during southerly or southeasterly winds.

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.

Daily or biweekly precipitation samples have been collected at various sites on the island of Hawaii since 1974. The elevations of the sites ranged from sea level to 3,400 m. Samples were analyzed on the day of collection for pH and conductivity. Detection of major anions, such as sulfate and nitrate, were made on selected samples during the period.

The pH data show a progressive increase of acidity with elevation. The sea level site averaged pH 5.2, in contrast to the sites above 2,500 m, which averaged pH 4.3. It is postulated that the increase in acidity at higher levels is due to acidic materials, either natural or man-made, transported over long distances in the mid-troposphere and being scavenged in the rain of the Hawaiian Islands.

Morrow, J.W., 1991, Effects of Hawaiian volcanic gases on human health: an overview [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagued.

The eruptions of Kilauea Volcano are accompanied by increased emissions of a number of gaseous compounds, some of which are potentially hazardous to human health. These include H₂O, CO₂, SO₂, H₂, CO, HCl, HF, and Hg. The first three normally comprise well over 90% of the gaseous emissions on a mole-percent basis. Sulfur dioxide emissions which average 1,000-2,000 t/d, but which have reached the equivalent of 32,000 t/d, are capable of producing ambient SO₂ concentrations in excess of public health standards. Its ultimate conversion in the atmosphere to a secondary acid aerosol further magnifies and complicates the potential adverse health effects. Sulfur dioxide and its acidic reaction products are irritants with demonstrated adverse effects on the respiratory system. The odorous H₂S is also a highly toxic gas, but its relatively low emission rate (approximately 1.0 mole-%) renders it much less important than SO₂; furthermore, it is eventually oxidized and follows SO₂ pathways. HCl and HF emissions from volcanic vents, while very low relative to SO₂, also contribute to the acidic nature of the atmosphere downwind of the volcano. Both are strong irritants capable of causing lung injury. In addition, molten lava flowing into the ocean generates very high HCl concentrations (> OSHA standards), thus creating a localized hazard.

This study qualifies effects of Kilauean volcanic emissions on human health, taking into consideration levels found near the volcano and influence of wind conditions on these emissions.

Morrow, J.W., 1991, The atmospheric fate of sulfur gases from Kilauea Volcano [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagued.

Kilauea is currently in the eighth year of an eruptive phase that began in January 1983. SO₂ emissions over this period have been variable and, at times, massive. On December 4, 1984, for example, an emission rate equivalent to 32,000 t/d continued for 15 hrs. This rate may be further put into perspective when one considers that U.S. EPA regulations define a "major source" as one which emits 100 t/yr. Despite these significant emissions, ambient air monitoring on the island of Hawaii has not detected high SO₂ levels. Routine monitoring by the Department of Health (DOH) at Hilo averaged < 5 ug/m³, or 2 parts per billion by volume (ppbv) over the 1972-1985 period with maximum 24-hr concentrations not exceeding 45 ug/m³ (17 ppbv), well under the 24-hr National Ambient Air Quality Standard (NAAQS) of 365 ug/m³ (139 ppbv). A special study conducted by the DOH over the June 1985-August 1986 period at Kealahou also averaged < 5 ug/m³, with a 24-hr maximum of 12 ug/m³ (5 ppbv).

In the case of Hilo, we attribute the failure to detect high SO₂ levels to (1) its generally upwind location and (2) the infrequent sampling (once every six days). At Kealahou in West Hawaii, the findings are attributed to (1) dispersion due to distance from the source and (2) conversion of SO₂ to SO₄²⁻ particles during transport from the source and trapping behind the Mauna Loa mountain mass. In order to begin testing the hypothesis of SO₂-to-SO₄²⁻ conversion, air sampling at Hilo and Captain Cook was conducted during the July 1989-June 1990 period. A PM-10 sampler was installed at each location and programmed to collect day (0700-1900 HST) and night (1900-0700 HST) samples. Samples were analyzed by XRF and ion chromatography. Wind data were collected on site at Captain Cook and obtained from the National Weather Service for Keahole and Hilo Airports. Results revealed very low SO₄²⁻ levels at Hilo most of the year but clearly showed episodes during southerly (kona) wind conditions when the plume from the volcanic vents was carried toward the city. In Captain Cook, the annual mean SO₄²⁻ was 4.7 ug/m³, while Hilo was 1.9 ug/m³, a significant difference ($p < 0.01$), but 12-hr maxima at the two sites were comparable (13-15 ug/m³). No diurnal variation was found at either site, but significant seasonal differences were observed. Hilo experienced higher winter-time SO₄²⁻ levels ($p < 0.01$) while Captain Cook had higher levels in the summer ($p < 0.10$). This is attributed to the northeast trade wind regime which is more dominant in the summer. On an annual basis, SO₄²⁻ also comprised a large portion of the PM-10 mass at Captain Cook (38%) versus Hilo (15%), but both sites experienced similar maxima during episodes (51-67%). The findings of this work provide support for the original hypothesis of SO₂-to-SO₄²⁻ conversion.

This study shows significant evidence for conversion of SO₂ to sulfate, and that much of this converted SO₂ is transported to the leeward side of the island by trade winds.

Morrow, J.W., 1991, Volcanic effects on the elemental composition of inhalable particulates in Hilo and Captain Cook [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagued.

The author proposes that vog is an aerosol composed of primary and secondary particulate matter. Historical Department of Health (DOH) air monitoring data, however, do not seem to support this particulate nature of vog. Routine total suspended particulate (TSP) monitoring conducted at Hilo during the 1972-1985 period averaged only 14 ug/m³ and the highest 24-hr concentration of 169 ug/m³ was still well under the 24-hr primary National Ambient Air Quality Standard (NAAQS) of 260 ug/m³. The DOH special study conducted from June 1988 - August 1986 at Kealahou also averaged 14 ug/m³ with a 24-hr maximum of 28 ug/m³. In the case of Hilo, the author attributes the failure to detect high TSP levels to (1) its generally upwind location (2) the infrequent sampling (once every six days), and (3) the inadequacy of the TSP sampling method to detect changes in fine particulate matter. At Kealahou the findings are attributed to (2) and (3) above, as well as to dispersion due to distance from the source. Results from air sampling conducted at Hilo and Captain Cook during the July 1989-June 1990 period reveal low PM-10 levels relative to the current NAAQS. Fossil-fuel related elements (Ni, V, and Pb) were significantly ($p < 0.01$) higher in Hilo. Of 37 elements identified, only Se showed a weak, positive correlation ($R^2 = 0.47$) with sulfur, the best indicator of vog infiltration at Captain Cook.

Both TSP and PM-10 sampling indicated a low over-all burden of particles in both Hilo and Captain Cook. This work suggests that, with the exception of S, the volcano has little long-term impact on the elemental composition of inhalable particulates.

Morrow, J.W., Morgan, E.J., Furuike, A.N., Peters, T.A., and Badgett-West, C.R., 1991, Characterization of volcanic aerosol in two populated areas on the island of Hawaii: First year finding of a 3-year investigation [abs.], in AWMA annual meeting, 84th, Vancouver, B.C., June 16-21, 1991, Abstract volume: Vancouver, B.C., Air & Waste Management Association, 16 p.

Morrow, J.W., 1992, Volcanic air pollution in Captain Cook, Hawaii [abs.], in Earthquake, Tsunami, and Volcano Hazards Seminar, Hilo, Hawaii, Aug. 6, 1992, Abstracts: Hilo, Hi., Center for the Study of Active Volcanoes, University of Hawaii at Hilo, unpagued.

Both of these papers report on the results of the Hilo/Captain Cook particulate/SO₄²⁻ studies begun in 1989. The 1991 report includes graphics showing time-series PM-10 and sulfate data for the two populated areas, along with

XRF analyses for 12-hr particulate collection samples. The 1992 study reports average H_2SO_4 levels of about 1.5 $\mu\text{g}/\text{m}^3$.

Resing, J.A., and Sansone, F.J., 1991, Lava-sea water interactions and the resultant steam plume at Wahaula, Hawaii [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagued.

Chemical, physical, and visual observations were made of lava entering the ocean near Waha`ula Heiau. The site under study included the coastal ocean and the near-shore littoral environment. Land- and ocean-based samples were taken at this site to determine the chemical and physical effects on the near-shore environment. Important chemical processes include water/lava and water/hot-rock reactions that cause the formation of acid and produce aerosol particles that are entrained in the steam. Precipitation samples collected on land had pH value of 1.7, with salinities nearly twice that of the local sea water. Coastal ocean samples showed depletions in alkalinity, total CO_2 , and pH, each showing a strong inverse correlation with increase in water temperature. Temperatures in excess of 70°C were measured in the coastal ocean.

This study supports the findings of Gerlach et al. (1991) and, in addition, examines the effects of lava on sea water.

Robinson, E., 1991, Atmospheric circulation of Hawaiian volcanic gases [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagued.

This report describes both the large-scale and local wind patterns which affect the island of Hawaii from the standpoint of the distribution of Kilauea eruption effluents. Large-scale winds are part of the global trade wind regime. Along with the wind patterns, the vertical mixing of the effluents is important, or, more exactly, the lack of vertical mixing in the Hawaii-Kona area. Considering these several factors together leads to a logical explanation of why Kilauea effluents can affect the Kona side of Hawaii without passing over the summit of Mauna Loa but, rather, by moving around the south end of the island and then northerly along the Kona coast.

Wind patterns on the island affect where volcanic gas and particle emissions are blown.

Stokes, J.B., 1991, How vog is made: a photographic perspective [abs.], in Vog and Laze Seminar, University of Hawaii at Hilo, July 29, 1991, Proceedings: Hilo, Hi., University of Hawaii at Hilo, unpagued.

HVO has accumulated nearly a decade of geochemical information about Kilauea from extensive monitoring of both the chemistry and total amounts of gases emitted from vents of the ongoing eruption on Kilauea's East Rift Zone. The current eruption causes vog, originating from volcanic vents, and laze, produced when lava enters the ocean, both of which affect human health. The prevailing winds from the northeast usually carry the vog toward the southwest, around the southern tip of the island; frictional forces cause it to turn northward into a convergence behind Mauna Loa, where they are effectively capped by trade winds or inversion layers. During kona wind conditions, when wind blows from the southwest to the northeast, the vog impacts population centers on the eastern side of the island, including Hilo.

B. Compliance monitoring, previous EIS, and related interpretive reports

Much of the air quality data that has been published for the Puna district is incorporated in this section. In general, compliance monitoring projects provide the basic data for use in writing EIS and other interpretive reports. In this bibliography, we have included information *derived* from compliance monitoring projects, by abstracting the related interpretive reports or EIS, rather than abstracting the compliance monitoring reports themselves. This is true with one exception. The results from Measurement Technologies (1991), which are reported exclusively as raw data monthly summaries, are reviewed and extracted by the authors of this

bibliography. Listed below are the main baseline compliance monitoring studies and the interpretive reports that draw on their results. It is not always clear exactly who was responsible for the various monitoring projects; thus, this list may contain omissions or redundancies.

Lower east rift studies:

The monitoring associated with the HGP-A project (May 1975-June 1976) was interpreted by Kamins (1976-1978).

The monitoring in the vicinity of HGP by Environmental Analysis Lab and possibly others, (three sites, 1982-1983, and one site 1981-1986), was interpreted by Morrow (1988), Carter (1984), and Dames and Moore (1984).

Middle east rift studies:

The monitoring by Houck/NEA, Inc. (1982-1984), was sponsored by Hawaii State Department of Planning and Economic Development (1984-1985), was sponsored by Kahauale'a Geothermal Project (1984), and was sponsored by National Park Service. These data were interpreted by Houck (1985, 1986) and the Kahauale'a Environmental Impact Statements (1986).

Carter, L.S., 1984, An analysis of ambient atmospheric hydrogen sulfide concentrations to determine the effect of the HGP-A geothermal plant on air quality in the Puna district; report to the American Lung Association of Hawaii, April 12, 1984: Hilo, Hi., American Lung Association of Hawaii, 30 p.

This analysis covers the period from January 1 to December 31, 1983. Raw data used are also included in Morrow, Thomas, and Burkards' 1988 paper. This report, however, includes analysis of data from two additional meteorological stations.

Wind data may be useful for interpreting possible volcanogenic influences. The author concludes that not all measured H₂S is coming from the geothermal plant.

Dames and Moore, 1984, Report; evaluation of BACT for and air quality impact of potential geothermal development in Hawaii: Santa Barbara, Calif., Dames and Moore, unpagged [approximately 120 p.].

This report focuses on possible ambient air quality effects around the Hawaii Geothermal Project at Puna, Hawaii. This includes descriptions of existing meteorology and air quality in the Puna district and estimated air quality impacts resulting from the proposed development. The data from the Environmental Analysis Lab's 1981 H₂S monitoring program are presented and discussed. Total suspended particulate (TSP) levels are presented, as well. This report notes, as did Morrow (1988), that average and maximum concentrations of H₂S at all monitoring sites are substantially less in 1983 than in 1982. The authors state that the source of these H₂S concentration anomalies could not be determined from the available data.

Dames and Moore, 1988, Puna geothermal zone development cumulative air quality impact analysis; a report prepared for Department of Business and Economic Development, Energy Division: Goleta, Calif., Dames and Moore, unpagged.

This report provides information regarding potential ambient air quality impacts related to geothermal power plant development in Puna. The study assesses potential H₂S impacts, utilizing a model which employs scaled emission rates and emission control data.

Department of Land and Natural Resources, 1984, Environmental impact analysis of potential geothermal resource areas: Honolulu, Department of Land and Natural Resources, Division of Water and Land Development, State of Hawaii, Circular C-106, 120 p.

This report summarizes the major environmental impacts, including ambient air quality, that may result from geothermal development. A short section (4 p.) on meteorology describes general wind patterns of the island. Ambient H₂S concentrations along the east rift before development (summarized from Houck, v. 1, 1984) are presented, along with ambient SO₂ concentrations. In general, this report relies almost exclusively on Houck's work for reporting on air quality.

Fluor Technology Inc., 1987, EIS for Puna Geothermal Venture project: Irvine, Calif., Thermal Power Company, unpagged [approximately 300 p.].

This document is the most recent EIS available for the lower Puna area. Section five of this EIS includes meteorology and air quality information. The section on air quality is based on the compliance monitoring carried out in the vicinity of HGP from 1981-1986. Data from the Schraeder, Hess, Gillman and Woods sites associated with this monitoring are incorporated in the presentation.

Houck, J.E., Pritchett, L.C., 1985, Baseline air quality, Kilauea East Rift, Puna and Ka`u Districts, County of Hawaii: Honolulu, Department of Planning and Economic Development, State of Hawaii, 130 p.

This report summarizes the results of five baseline air quality studies:

Houck, J.E., 1983, Environmental baseline survey, Kilauea East Rift, Puna and Ka`u districts, County of Hawaii- December 1982 through December 1983 study period; report to Hawaii Department of Planning and Economic Development, 3 v.: Beaverton, Ore., NEA, Inc., 122 p. plus appendices.

Houck, J.E., 1984, Environmental baseline survey, Kilauea East Rift, (year two), Puna and Ka`u districts, County of Hawaii, January 1, 1984 through December 31, 1984 study period; report prepared for Department of Planning and Economic Development, State of Hawaii, v. 1, 2: Beaverton, Ore., NEA, Inc., unpagged.

Houck, J.E., 1985, Remote environmental baseline monitoring, Hawaii Volcanoes National Park, 1984; final report: Beaverton, Ore., NEA, Inc., 13 p.

Houck, J.E., 1984-1985, Ambient air quality monitoring survey, Kahuale'a geothermal project; quarterly reports to True/Mid-Pacific Geothermal Venture, 4 v.

Houck, J.E., 1985, Ambient air quality monitoring survey, Puna Forest Reserve; report to True/Mid-Pacific Geothermal Venture, 23 p. plus appendices.

This report includes data and discussion of monitoring networks and methods used for studying atmospheric particles, SO₂ and H₂S gas, rain water chemistry, mercury vapor, radon activity, other air pollutants and meteorology. Also incorporated is a survey of data from relevant research and monitoring projects conducted by a variety of agencies, including the Hawaiian Volcano Observatory, Mauna Loa Observatory, Hawaii Department of Health, National Weather Service, National Park Service, Thermal Power Company.

This comprehensive summary draws together much of the air quality data available on the middle east rift zone of Kilauea and presents it in a concise, tractable format.

Houck, J.E., and Pritchett, L.C., 1986, Baseline air quality of Kilauea East Rift Zone, Hawaii: Geothermal Resources Council Transactions, v. 10, p. 267-272.

Baseline air quality along the Kilauea East Rift Zone has been documented by a series of environmental studies. Baseline concentrations of particles, SO₂, H₂S, mercury, and radon have been monitored. The chemical content of particles and rain water has been measured. From the chemical data, the sources of particles and pollutants contained in the rain water were determined. This paper is an interpretive summary of a study quantifying pre-

development concentrations of environmentally hazardous pollutants. In general, the air quality along the Kilauea East Rift was determined to be very good, with the exception of short periods of volcanic eruptions or at locations downwind of fumaroles. Ambient H₂S concentration near eruptive vents, as measured by continuous flame photometric detector, gave maximum values of 5-12 ppbv, and SO₂ 150-500 ppbv. Ambient H₂S concentrations near a poorly drained, organic rich soil were 2 to 9 ppbv indicating generation of H₂S by decay of organic matter. For most of the time of study, ambient H₂S concentrations were less than 0.5 ppbv and never exceeded 30 ppbv.

Kamins, R.M., Chun, M.J., Berger, A.J., Bonk, W.B., Siegel, B.A., Siegel, S.M., Speitel, T., Lau, L.S., Buddemaier, R.W., Kroopnick, P., Hufen, T., 1976, Environmental baseline study for geothermal development in Puna, Hawaii: Honolulu, Hawaii Geothermal Project, University of Hawaii, 42 p.

Kamins, R.M., Tinning, K.J., 1977, An assessment of geothermal development in Puna, Hawaii: Honolulu, Hawaii Geothermal Project, University of Hawaii, 103 p.

Kamins, R.M., 1978, Revised Environmental Impact Statement for the Hawaii Geothermal Research Station utilizing the HGP-A well at Puna, Island of Hawaii: Honolulu, Center for Science Policy and Technology Assessment, Department of Planning and Economic Development, unpagged [approximately 130 pages].

These three reports discuss environmental baseline data collected as background for drilling for the Hawaii Geothermal Project in Puna. Additional tests of the water and air were conducted at the site after the drilling was completed but before the well was blown to free it of debris. The results of all tests, before and after the drilling, are summarized in the 1976 and 1977 report and included in the 1978 EIS.

The EIS includes rain water pH, mercury, SO₂ and H₂S data from pre-drilling through flashing experiment of HGP-A (May 1975 to July 1976). Sulfur gas values are reported to be at or below the project's instrumentation detection thresholds in spite of the proximity (25 miles) of natural vents in Volcanoes National Park continuously supplying these sulfurous gases. Detection thresholds for SO₂ and H₂S were <0.5 ppm and <0.2 ppm respectively. Measurements made at unspecified fumarole areas during 1971-76 yielded peak values as high as 25 ppm for SO₂ and 5 ppm for H₂S. The authors observe that these toxic emissions do not reach the HGP drill site area, or do so only infrequently and for brief periods. Airborne mercury concentrations are reported at approximately 1 microgram/m³ for pre-drilling and preliminary testing environments and 9.9 microgram/m³ during the flashing experiment.

Rain water pH values reported here are substantially higher than those reported in other studies.

Measurement Technologies, 1991, Ambient air and meteorological monitoring, Kilauea Middle East Rift Zone, island of Hawaii, November 1989-January 1991; report prepared for True Geothermal Energy Company, San Luis Obispo, Calif.: Measurement Technologies, unpagged [approximately 500 p.]

Measurement Technologies was contracted by True Geothermal Energy Company to conduct an air quality and meteorological monitoring program to support incremental exploration and development of the Kilauea's Middle East Rift Zone Geothermal Resources Subzone (GRS) in the Puna District. The monitoring program consisted of two sites, from which the following parameters were collected: H₂S, SO₂, meteorological data, rain water chemistry, total suspended particulates (TSP), inhalable particulates (PM-10) and radon. The data from this monitoring project are presented as monthly and quarterly reports which include quality assurance/quality control activities, operations narrative, raw data with graphical presentations, and data capture summaries. The monthly summaries show insignificant loading of particulate filters, radon levels below detection limits a majority of the time, and only occasional detectable concentrations of H₂S (except during geothermal maintenance activities at the nearby PGV plant). Windrose data shows a predominance of north-northwest wind at the site located in the Kaohe Homesteads area.

There appear to be occasional discrepancies between monthly summary narratives and raw data presented in the tables. Maps of site locations and monitoring equipment are not included.

Morrow, J.W., Thomas, D.M., Burkard, H.D., 1988, Ambient hydrogen sulfide monitoring in the vicinity of Hawaii's first geothermal power plant [abs.], in Annual Meeting of the APCA, 81st, Dallas, Texas, June 19-24, 1988, Abstract volume: Dallas, Texas, 16 p.

Data from two one-year periods during 1981-1983 are presented for two ambient air sites, one each up-trade wind and down-trade wind. In addition to the continuous gas monitoring, wind conditions were characterized by weather monitoring instrumentation at the upwind site. Data are summarized from these instruments in tables and windrose diagrams.

The wind data for the two sites were used to help identify H₂S sources. Among other conclusions, the authors attribute higher H₂S concentrations to downslope winds from the direction of unspecified fumaroles. The (current) east rift eruption started during the second year of the study and coincided with *lower* measured H₂S concentrations during downslope wind conditions. The authors suggest that highly oxidizing conditions produced by the eruptive gases, SO₂ in particular, may be responsible for scrubbing H₂S.

Research Corporation of the University of Hawaii, 1983, Report on Hawaii geothermal power plant project: Honolulu, Research Corporation of the University of Hawaii, unpagged [approximately 100 p.]

In March 1981, Environmental Analysis Lab activated a monitoring program to measure environmental impact surrounding the Hawaii Geothermal Program's HGP-A power plant. The monitoring program focused on the effects of H₂S emission from the plant on the ambient air. Mercury, arsenic and lead were also monitored. The monitoring results are presented in tabular form in Appendix C of the document. Analyses of the H₂S data are presented by Carter (1984) and Morrow and others (1988).

Siegel, S.M., and Siegel, B.Z., 1980, The impact of geothermal resource development in Hawaii (including air and water quality): Honolulu, Hi., University of Hawaii, Hawaii Energy Resource Overviews, v. 4, Geothermal, the environment: 3. Impact, 163 p.

This study discusses environmental consequences of natural processes in a volcanic-fumarolic region, using HGP-A as a site-specific model. Ecological effects (physical, chemical); toxic gas emissions during non-eruptive stage (sulfur compounds, mercury compounds) and effects on plant and animal life were considered in the study, along with environmental setting prior to geothermal development.

True/Mid-Pacific Geothermal Venture, 1986, Final supplemental environmental impact statement to the revised environmental impact statement for the Kahauale`a Geothermal Project, in coordination with the estate of James Campbell: Honolulu, True/Mid-Pacific Geothermal Venture and James Campbell Estate, unpagged [approximately 240 p.]

Included in this EIS is the characterization of ambient air quality along the middle East Rift Zone, as determined by three air quality monitoring programs. The first, sponsored by the Hawaii State Department of Planning and Economic Development, covered 1982-1984 and included monitoring stations from Hawaii Volcanoes National Park to Pohoiki. The second program, sponsored by the Kahauale`a Geothermal Project, included generally much of the same area and spanned the period from February 1984-March 1985. The third survey, conducted in 1984, was sponsored by the National Park Service and covered the area generally along the boundary between the Hawaii Volcanoes National Park and Kahauale`a. The six environmental pollutant categories examined were atmospheric particles, SO₂, H₂S, rain water chemistry, radon activity and mercury vapor. Highlights of the results of the surveys are extracted from the summary report by Houck (1985).

III. Meteorology

Meteorological conditions have an impact on the dispersion and concentration of emission-source products. The geographical fate of these products is dependent on wind speed and direction relative to emission sources. It is especially important on the island of Hawaii to scrutinize the microclimate wind characteristics that may override

generalized theoretical wind conditions when examining the potential impact of emissions on an area. References listed here are not exhaustive, but give a basic overview of Hawaii Island meteorology.

Blumenstock, D. I., Price, S., 1967, Climatology of the United States - State of Hawaii: Environmental Science Services Administration, U.S. Department of Commerce

A short but informative section on wind characteristics describes the complexity of Hawaii's wind conditions. Distortion and disruption of relatively uniform trade wind flow is caused by mountains, hills and valleys. Local wind regimes, which may be inconsistent in direction or speed, play an important role in defining wind conditions at a given location. Average windspeed values are informative only in a broad, descriptive sense.

Haraguchi, Paul, 1979, Weather in Hawaiian Waters: Honolulu, Hawaii, Pacific Weather, Inc., 107 p.

Although this is a general reference on marine weather elements, discussions of trade wind and local wind patterns are highlighted. A table of the mean monthly frequency of trade winds (p. 14), as well as a brief discussion of wind speeds off eastern Hawaii and winds other than trades, is presented.

Leopold, L.B., 1949, The interaction of trade wind and sea breeze, Hawaii: Journal of Meteorology, v. 6, p. 312-320.

This paper is the first significant published work on winds for the island of Hawaii. Local sea-breeze and land-wind regimes in Hawaii meet and interact with the prevailing trade wind to create local microclimates. Leopold suggests that the diurnal cycle of winds (daytime up-slope/night time down-slope), rainfall, and clouds are linked to an island-scale thermally driven circulation independent of the large scale trade wind flow.

Nash, A.J., 1992, Diurnal surface weather variations on the island of Hawaii: Honolulu, Master's thesis, Department of Meteorology, University Hawaii, 127 p.

This study examines the diurnal cycle of surface weather on the island of Hawaii, using data from the Hawaiian Rainband Project (HaRP), the largest field experiment to date on the island of Hawaii. The majority of data for this study were collected from 50 portable automated mesonet (PAM) stations situated around the entire island, with three located in lower Puna (Pahoa, Cape Kumukahi, and Paradise Park). The seven variables measured by the PAMs and used in this study are pressure, temperature, wet-bulb temperature, horizontal and vertical wind components, rainfall and long-wave radiation. This study also used data from aircraft soundings, tethersondes and National Weather Service Hilo radiosonde launches. The narrative on surface wind patterns in chapter 4 is of particular interest. Wind flow on the island of Hawaii is grouped into four general conditions: daytime/onshore, nighttime/offshore, and morning and evening transition periods. Daytime surface flow on the windward side of the island is an onshore and trade wind mix, not a pure up-slope flow. Examining the division of strong and weak trade wind conditions shows that surface winds may exhibit important differences during strong and weak wind cases. The data are presented as a comprehensive collection of figures, including, but not limited to, wind direction, velocity and steadiness averaged through the diurnal cycle for each PAM site; average resultant surface winds for daytime/nighttime conditions; surface streamline analysis for average winds; and average resultant wind and streamline analysis during strong and weak trade wind days.

This study highlights the many factors that can affect surface winds. Although the HaRP data is limited to six weeks of observations during July and August 1990, it is used here to provide, for the first time, an accurate depiction of surface wind and precipitation patterns associated with the diurnal cycle of weather on the island.

Nickerson, E.C., Dias, M.A., 1981, On the existence of atmospheric vortices downwind of Hawaii during HAMEC project: Journal of Applied Meteorology v. 20 p. 868-873.

A NOAA research aircraft made six flights over and around the island of Hawaii, studying winds during 1980, as part of the Hawaii Mesoscale Energy and Climate project (HAMEC). This paper discusses the June 1980 aircraft observations.

Nickerson, E.C., and Magaziner, E.L., 1976, A three-dimensional simulation of winds and non-precipitating orographic clouds over Hawaii: NOAA Technical Report, ERL 377-APCL 39 p.

Smolarkeiwicz, P.K., Rasmussen, R.M., Clark, T.L., 1988, On the dynamics of Hawaiian cloud bands: Island forcing: Journal of the Atmospheric Sciences, v. 45, p. 1872-1905.

These two papers present numerical models which simulate the winds around the island of Hawaii. The first includes the Kona convergence, while the second deals mainly with the windward side of the island.

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