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KALAPANA CIVIL DEFENSE DEPARTMENT
HILO, HAWAII

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SUMMARY

A Health Hazard Evaluation (HHE) request was received in 1990 by the National Institute for Occupational Safety and Health (NIOSH) from the Director of the Hawaii County Civil Defense Agency concerning intermittent exposures to volcanic emissions received by civil defense workers stationed near active lava flows from the Hawaii Volcanoes National Park. A site visit was conducted between July 30 to August 2, 1990, a time period which coincided with a lava flow from the nearby Kilauea Volcano reaching the ocean. Personal and general area air samples for various inorganic acids and sulfur dioxide (SO_2) were collected at various locations surrounding the former village of Kalapana, Hawaii and near the Kaimu black sand beach recreational area. The air sampling was conducted to assess the potential exposures of the civil defense personnel to contaminants found in the *laze*, the acidic steam cloud formed by the interaction of lava with sea water, and to other possible volcanic emissions (such as SO_2).

Short-term colorimetric detector tubes (sampling periods of approximately 5 minutes) measured hydrochloric acid (HCl) concentrations in the dense *laze* near the shoreline of up to 10 to 15 parts per million (ppm). Air samples collected over longer time periods (up to eight hours) measured HCl concentrations up to 3.6 ppm. However, samples collected at the civil defense road block locations, and in areas where the general public or community residents had access measured concentrations which were significantly lower, ranging from not detectable to 1.1 ppm. Both the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) and the NIOSH Recommended Exposure Limit (REL) for HCl are 5 ppm (equivalent to 7 milligrams per cubic meter [mg/m^3]) for a 15-minute ceiling exposure.

Concentrations of hydrofluoric acid (HF) ranged from not detectable to 0.4 ppm, levels which were well below the OSHA PEL and NIOSH REL for this substance of 3 ppm for an 8-hour time-weighted average exposure and 6 ppm for a 15-minute ceiling exposure. Analyses for nitric, phosphoric, and hydrobromic acids were performed but none of these acids were detected. Sulfur dioxide was not detected in any of the general area air samples collected during this survey.

Based on these results, the civil defense personnel, community residents, and the general public were not being exposed to concentrations of HCl, HF, or other inorganic acids in excess of any occupational standards in the unrestricted areas of Kalapana/Kaimu during this survey. Long-term HCl concentrations ranging from 0.5 to 3.6 ppm were measured on the lava flow in an area from which the general public was restricted. These levels suggest that the use of protective equipment for all individuals who may be downwind of the *laze* is recommended. Appropriate personal protective gear (e.g., a chemical cartridge respirator for protection against acid gases, and eye goggles) is recommended when exposure to the lava/sea water aerosol, near its origin, is unavoidable. This group would include not only the civil defense workers but also photographers, geologists, and other individuals authorized to be in the restricted areas of the lava flow.

KEYWORDS: SIC 9229 (Public Order and Safety, Not Elsewhere Classified), hydrochloric acid, hydrofluoric acid, sulfur dioxide, volcanic emissions, civil defense.

INTRODUCTION

A health hazard evaluation request was received in 1990 from the Director of the Hawaii County Civil Defense agency and a site visit was conducted between July 30 to August 2, 1990. This site visit was scheduled to coincide with when the lava flow from the nearby Kilauea Volcano reached the ocean. Personal and general area air samples for various inorganic acids and sulfur dioxide (SO_2) were collected at various locations surrounding the former village of Kalapana, Hawaii and near the Kaimu black sand beach recreational area. The air sampling was conducted to assess the potential exposures of the civil defense personnel to contaminants found in the *laze*, the acidic steam cloud formed by the interaction of lava with seawater, and to other possible volcanic emissions (such as SO_2).

BACKGROUND

The Hawaiian Volcanoes National Park (HVNP) located on the island of Hawaii is home to Kilauea and Mauna Loa, two of the largest and most active volcanoes on earth. These volcanoes, located within the HVNP boundaries, have been continuously "active" since 1983. Volcanic activity is quite variable and the direction and quantities of lava and volcanic gas emissions can fluctuate hourly, daily, weekly, etc. The recent lava flows in 1990 have been on the southeast side of the island, outside the park boundary, in the Kalapana area, and are part of the continuing eruptive series from the Pu'u O'o rift. To date, several roads and trails have been covered by the lava, and over 166 structures/homes have been destroyed by lava, the majority of which were private residences in Kalapana. The lava flow has continued to flow in an easterly direction toward the ocean, across private and county land, toward the village of Kaimu.

The U.S. Geological Survey has studied the explosive plume/steam clouds (*laze*) which are created when lava from the east rift zone of the Kilauea Volcano enters the ocean near Kupapa'u Point, Hawaii. In a journal abstract published in
October 24, 1989, entitled "Acid Rain from the Heating and Evaporation of Seawater by Molten Lava: A New Volcanic Hazard," it was determined that the acid rain formed from this plume cloud is derived from HCl gas formed primarily by the hydrolysis reaction of steam with magnesium chloride salts, precipitated locally where magma (lava) evaporates seawater to dryness. In addition, calculations based on irreversible mass transfer indicate that evaporation of one liter of seawater to dryness at temperatures of 100-300 ^{o}C will produce about a liter of hydrochloric acid condensate with a Ph of 1.0.

EVALUATION METHODS

General area air samples at various locations in the Kalapana and Kaimu black sand beach areas were collected for inorganic acids (such as HCl and HF) and for SO_2, a gas present in volcanic emissions. It should be noted that although sampled for in this evaluation, SO_2 concentrations along the coastline were expected to be very low considering the distance that the lava had travelled from its point of eruption. For the acid gas samples both short-term (approximately 5 minutes) and long-term (up to
8-hours) colorimeter detector tubes sensitive to HCl were used. Short-term detector tubes for SO_2 were also used to periodically monitor for this gas.

In addition to the direct-reading detector tubes, air samples for acid gases (such as HCl and HF) were collected on silica gel adsorbent tubes (ORBO 53 sorbent tubes, manufactured by Sulpelco) using flow rates ranging from 20 to 200 cubic centimeters per minute following the NIOSH

sampling and analytical method no. 7903.[1] Both long-term (up to 7 hours) and short-term (15 minutes) air samples were collected. These air samples were subsequently analyzed by ion chromatography.

EVALUATION CRITERIA

The following evaluation criteria suggest levels of exposure that most workers can be exposed, day after day, for a working lifetime without adverse health effects. Because of variation in individual susceptibility, a small percentage of workers may experience health problems or discomfort at exposure levels below these existing criteria. Since these occupational exposure levels are intended to protect workers (presumably healthy adults) they may not be adequate for young children or people with certain health problems. They may also not be appropriate for evaluating community health risks.

1. **Hydrogen Chloride**

Hydrogen chloride and hydrochloric acid (HCl) are strong irritants to the eyes, mucous membranes, and skin. The major effects of acute exposure are usually limited to the upper respiratory tract and are sufficiently severe to encourage prompt withdrawal from a contaminated atmosphere. Exposures can also cause cough, burning of the throat, and a choking sensation. Effects are usually limited to inflammation and occasionally ulceration of the nose, throat, and larynx. Acute exposures causing significant trauma are usually limited to people who are prevented from escaping; in such cases, laryngeal spasm or pulmonary edema may occur. High concentrations of the gas cause eye irritation and may cause prolonged or permanent visual impairment. Exposure of the skin to a high concentration of the gas or to a concentrated solution of the acid will cause burns; repeated or prolonged exposure to dilute solutions may cause dermatitis. Erosion of the exposed teeth may occur from repeated or prolonged exposure.[2,3] Both the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) and the NIOSH Recommended Exposure Limit (REL) for HCl are 5 parts per million (ppm, equivalent to 7 milligrams per cubic meter [mg/m^3]) for a 15-minute ceiling exposure.[4,5]

2. **Hydrofluoric Acid**

Hydrogen fluoride (HF) liquid or vapor causes severe irritation and deep-seated burns of the eye and eye lids if it comes in contact with the eyes. If the chemical is not removed immediately, permanent visual defects may result.[2,3] When lower concentrations (20% or less) come into contact with the skin, the resulting burns do not usually become apparent for several hours. Skin contact with higher concentrations is usually apparent in a much shorter period, if not immediately. The skin burns may be very severe and painful. Hydrofluoric acid is a severe irritant to the nose, throat, and lungs. Severe exposure causes rapid inflammation and congestion of the lungs, including pulmonary edema. Breathing difficulties may not occur until some hours after exposure has ceased. Prolonged or repeated exposure to lower concentrations of hydrogen fluoride vapor may cause changes in the bones. The fluoride ion readily penetrates skin and deep tissue, causing necrosis of soft tissues and decalcification of bone. Exposure to low concentrations of vapors of hydrogen fluoride may also cause chronic irritation and congestion of the nose, throat, and bronchial tubes.[2,3] The OSHA PEL for HF is 3 ppm (equivalent to 2 mg/m^3) for an eight hour time- weighted average (TWA) exposure and 6 ppm for 15-minute short-term

exposure limit (STEL), whereas, the NIOSH REL is 2.5 mg/m^3 for up to a 10-hour workshift, with a 15-minute ceiling level of 5 mg/m^3.[4,5,6]

3. **Sulfur Dioxide**

Sulfur dioxide (SO_2) is a colorless, water-soluble gas which forms sulfurous acid (H_2SO_3) on contact with moisture. This reaction may occur on the mucous membranes lining the respiratory tract following inhalation, causing immediate irritation of the respiratory tract and constriction of the respiratory air passages.[2] This presents as cough, breathlessness, a choking sensation, and chest tightness or discomfort. Such effects are usually reversible on removal from further exposure. Sulfur dioxide is also a severe irritant of the eyes and skin.[2]

In 1974 NIOSH recommended that occupational exposures to SO_2 not exceed 2 ppm (equivalent to 5.2 mg/m^3) for up to a 10-hour TWA exposure over a 40-hour workweek.[7] NIOSH revised this recommendation of the basis of four epidemiological studies that became available after publication of the 1974 NIOSH criteria document. Based on these more recent studies, NIOSH has lowered its original exposure limit from 2 ppm to 0.5 ppm, TWA.[8] The OSHA Permissible Exposure Limit (PEL) for SO_2, revised in 1989, is 2 ppm for an 8-hour TWA. OSHA also has established a 15-minute Short-Term Exposure Limit (STEL) of 5 ppm.[4]

In addition to the occupational exposure criteria of NIOSH and OSHA, the Environmental Protection Agency (EPA) promulgates national primary and secondary ambient air quality standards for SO_2. This standard was designed to protect public health and welfare and, as previously mentioned, would be more appropriate than occupational criteria to evaluate public exposure risks. The national primary and secondary ambient air quality standards for SO_2 are as follows: primary standards of 0.03 ppm (annual arithmetic mean) and 0.14 ppm (minimum 24-hour concentration not to be exceeded more than once a year); secondary standard of 0.5 ppm (3-hour concentration not to be exceeded more than once a year).

RESULTS

Short-term colorimetric detector tubes (sampling periods of approximately 5 minutes) measured HCl concentrations in the dense *laze* near the shoreline of up to 10 to 15 ppm. All of the short-term detector tube measurements for HCl were made using Drager® brand detector tubes. These indicator tubes have a measurement range of zero to 10 ppm for HCl. High humidity conditions (which existed in several "worse case" measurements made directly in the *laze* plumes) may have caused the tubes to underestimate the HCl concentration since aerosols, which could exist in the humid conditions, may not be measured by the detector tube. Results from these short-term samples are shown in Table 1.

Air samples collected over longer time periods (up to eight hours) measured HCl concentrations up to 3.6 ppm. However, samples collected at the civil defense road block locations, and in areas where the general public or community residents had access measured concentrations which were significantly lower, ranging from not detectable to 1.1 ppm. These long-term (up to eight hours) air samples for HCl and other inorganic acid mists were collected using two different collection techniques:

(1) Drager long-term direct reading detector tubes; and (2) solid sorbent tubes which

required laboratory analysis (NIOSH Analytical Method No. 7903). The results of these samples are reported in Tables 2 and 3, respectively.

DISCUSSION

The referenced evaluation criteria for the acid gases suggest levels of exposure that most workers can be exposed day after day for a working lifetime without adverse health effects. Because of variation in individual susceptibility, a small percentage of workers may experience health problems or discomfort at exposure levels below these existing criteria. Thus, it is important to understand that these evaluation criterion are guidelines, not absolute limits between safe and dangerous levels of exposure. The evaluation criteria referenced in the tables, NIOSH RELs, the ACGIH TLVs, and the OSHA PELs, are intended for occupational health settings and may not be appropriate for evaluating community health risks. There are no NIOSH recommended exposure criteria which cover community health standards when evaluating HCl exposure risks for the general population. Considering that there is a greater age range and variation in overall health status to consider with the general public, community exposures should definitely not exceed the 15-minute ceiling limit for HCl of 5 ppm, and a lower exposure limit may be more appropriate.

Short-term detector tubes (sampling periods of approximately 5 minutes) measured HCl concentrations in the dense *laze* near the shoreline of up to 10 to 15 ppm. Air samples collected over longer time periods (up to eight hours) measured HCl concentrations up to 3.6 ppm. However, samples collected at the civil defense road block locations, and in areas where the general public or community residents had access, were significantly lower, ranging from not detectable to 1.1 ppm.

Conflicting results were obtained from samples situated at the Route 130 road block where both civil defense workers and the public had access. Hydrochloric acid concentrations at this location ranged from 0.7 to 1.1 ppm when measured using long-term detector tubes over three consecutive days of sampling. However, side-by-side samples at this location, using a different collection method (NIOSH Method No. 7903 using ORBO 53 sorbent tubes and subsequent laboratory analysis for HCl and other inorganic acids), measured HCl levels of only 0.1 ppm. While some of the differences in these measured concentrations may be explained by the different sampling and analytical methods, the fact that HCl was detectable at this road block location (approximately one-third of a mile downwind of where the *laze* was being formed at the shoreline) suggests that levels of HCl may occasionally exceed 1 ppm.

CONCLUSIONS

Based on these results, the civil defense personnel, community residents, and the general public were not being exposed to concentrations of HCl, hydrofluoric, or sulfuric acids in excess of any occupational standards in the Kalapana/Kaimu area during this survey. Long-term HCl concentrations ranging from 0.5 to 3.6 ppm were measured over a four-hour period at the former Harry K. Brown park in Kalapana (a point approximately one-half mile downwind from the shoreline where the *laze* was being created).

RECOMMENDATIONS

The following recommendations were made to ameliorate existing or potential hazards in the Kalapana and Kaimu coastal areas of Hawaii. Action has been taken on these recommendations by the Hawaii County Civil Defense Agency.

1. All individuals living in the areas near the lava/sea water interaction should be informed about potential exposures to acid gases such as HCl. Personnel required to work in these areas should be informed about the potential for acid gas exposure near the ocean and instructed on the potential health risks. While the results of the initial sampling collected from July 30 to August 2 in the Kalapana and Kaimu coastal areas showed that civil defense personnel, community residents, and the general public were not being exposed to concentrations of HCl, hydrofluoric, or sulfuric acids in excess of any occupational standards, the use of protective equipment for all individuals who may be downwind of the *laze* is recommended. Appropriate personal protective gear (e.g., a chemical cartridge respirator for protection against acid gases and eye goggles) is recommended when exposure to the lava/sea water aerosol, near its origin, is unavoidable. This group would include not only the civil defense workers but also photographers, geologists, and other individuals authorized to be in the restricted areas of the lava flow. Considering that long-term HCl concentrations ranging from 0.5 to 3.6 ppm were measured at locations over one-quarter mile downwind of where the *laze* was being formed, respirators should continue to be worn even in areas not immediately adjacent to the shoreline.

2. Warning signs should be posted along nearby roads and at blockades to alert visitors to the area about the potential for exposure to acid gases. Written warning should be given to residents and tourists in the areas near the lava/sea water interaction to provide health effects information and emphasize the increased exposure risk for young children, the elderly or individuals with cardiopulmonary problems. A warning siren, or other appropriate warning device, may be appropriate to alert area residents when the lava/sea water aerosol is directed towards nearby villages by prevailing winds.

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Copies of this report have been sent to:

1. Hawaii County Civil Defense Agency
2. Superintendent, Hawaii Volcanoes National Park
3. Hawaii State Health Department
4. Hawaii Department of Health
5. National Park Service

6. U.S. Geological Survey, Hawaii Volcanoes National Park
7. OSHA, Region IX
8. NIOSH, Region VIII

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

TABLE 1
RESULTS OF SHORT-TERM AIR SAMPLES FOR HYDROCHLORIC ACID
SAMPLING METHOD: DRAGER SHORT-TERM DETECTOR TUBES

Kalapana Civil Defense Agency
HETA 90-317
July/August, 1990

Date	Time	Location	Concentration
7/31	1800	In *laze* plume, on the shore and near actively flowing lava. Public was restricted from this area.	7 ppm
7/31	1822	On shoreline, but not in the *laze* plume. Public was restricted from this area.	1 ppm
7/31	1830	Directly in *laze* plume. Active lava flow visible from this position, approximately 50 feet away. Very dense *laze* periodically drifted through this location. Public was restricted from this area.	10 ppm
7/31	1845	At the black sand beach civil defense road block. Trace discoloration detected on the tube but not in the measurement section. Prevailing trade winds carried the *laze* away from this location and the viewing public.	Trace
8/1	1200	Directly in the *laze*, approximately 10 feet from active lava flow and approximately 30 to 40 feet from the tide line where the *laze* was being formed.	>10 ppm
8/1	1230	At the Black Sand Beach Drive-In restaurant. No color change detectable on the tube.	None
8/1	1235	At the black sand beach road block (new location on 8/1/90). Prevailing trade winds carried the *laze* from this area.	None
8/2	1015	Downwind of the *laze* and approximately 100 yards from the Black Sand Beach Drive-In restaurant. Air sample collected by the roadway. Dense *laze* periodically drifted through this area. Active lava flows into the ocean were visible from this location.	2 ppm

TABLE 1 (Cont.)
RESULTS OF SHORT-TERM AIR SAMPLES FOR HYDROCHLORIC ACID
SAMPLING METHOD: DRAGER SHORT-TERM DETECTOR TUBES

Kalapana Civil Defense Agency
HETA 90-317
July/August, 1990

Date	Time	Location	Concentration
8/2	1150	At the Route 130 roadblock No detectable color change, although a "burning" odor was detectable, possibly from burning brush.	None
8/2	1305	Along the roadway in the black sand beach area. The public was restricted from this area. Active lava flows were visible along the shoreline from this location. Dense *laze* occasionally drifted through this location.	2 ppm
8/2	1440	On the black sand beach approximately 20 feet from active lava flows. Dense *laze* periodically drifted through this area.	5 ppm

TABLE 2
LONG-TERM GENERAL AREA AIR SAMPLES FOR ACID MISTS
SAMPLING METHOD: DRAGER LONG-TERM DIRECT READING DETECTOR TUBES

Kalapana Civil Defense Agency
HHE 90-317
July/August, 1990

Location	Date	Time	Concentration
Road Block on Road 130	7/31	1616 - 2100	1.1 ppm
	8/1	0927 - 1725	1.0 ppm
	8/2	0953 - 1553	0.7 ppm
Road Block, Black Sand Beach area	7/31	1639 - 2040	0.6 ppm
	8/1	1030 - 1655	Trace*
	8/2	0935 - 1624	0.1 ppm**
Black Sand Beach Drive-In	7/31	-	No sample
	8/1	1003 - 1636	None detected
	8/2	1013 - 1644	0.3 ppm
At Harry K. Brown park (downwind of *laze*)	7/31	-	No sample
	8/1	1148 - 1542	3.6 ppm
	8/2	-	No sample

* Trace describes a very slight color change noted on the detector tube sample but the discoloration was too slight to accurately quantify.

** There was some discoloration observed on this detector tube sample but the color change was not correct, suggesting that it was not HCl which was contributing to the reading on the detector tube. Because of the uncertainty with this sample, the minimum amount which could have been read by this sample has been reported.

Comments:

All of the long-term detector tube samples for sulfur dioxide were negative (no detectable amounts).

TABLE 3
LONG-TERM PERSONAL AND GENERAL AREA AIR SAMPLES FOR ACID MISTS
SAMPLING METHOD: ORBO 53 SORBENT TUBES

Kalapana Civil Defense Agency
HHE 90-317
July/August, 1990

Sample No.	Date	Time	Location	Concentration[a]		
				HCl	H_2SO_4	HF
GB-1	7/31	1616 to 2100	Route 130 civil defense road block. Sample situated on shelter.	(0.1)[b]	ND	ND
GB-4	7/31	1639 to 2040	Blacksand beach civil defense road block. Sample located on the shelter.	0.1	ND	ND
GB-7	7/31	1713 to 2023	In restricted area, on the beach. Near *laze*.	1.0	(0.11)	ND
GB-12	8/1	0945 to 1119	Personal sample on geologist mapping the lava flow.	(0.3)	ND	ND
GB-17	8/1	1148 to 1542	Harry K. Brown park. General public was restricted from this area. The park had been covered in an earlier lava flow.	0.5	(0.1)	0.4
GB-22	8/2	0938 to 1624	At the black sand beach civil defense road road block (new location). Sample located on the shelter.	0.2	(0.1)	ND
GB-24	8/2	0953 to 1553	Civil defense road block on Route 130.	0.1	ND	ND

TABLE 3 (Cont.)
LONG-TERM PERSONAL AND GENERAL AREA AIR SAMPLES FOR ACID MISTS
SAMPLING METHOD: ORBO 53 SORBENT TUBES

Kalapana Civil Defense Agency
HHE 90-317
July/August, 1990

Sample No.	Date	Time	Location	Concentration[a] HCl	H_2SO_4	HF
GB-26	8/2	1013 to 1644	Area air sample at the Black Sand Beach Drive-In restaurant. Local residents were allowed access to this area.	0.1	ND	ND
GB-28	8/2	1300 to 1720	On the beach in an area not accessible to the general public. Dense *laze* periodically drifted through this location.	1.5	(0.1)	(0.01)
Evaluation Criteria:						
OSHA Permissible Exposure Limits (PELs)				5[c]	1[d]	3[d]/6[c]
NIOSH Recommended Exposure Limits (RELs)				5[c]	1[d]	3[d]/6[c]
ACGIH Threshold Limit Values (TLVs)				5[c]	1[d]	-- /3[c]

Comments:

a. All concentrations except for sulfuric acid are expressed in parts of contaminant per million parts of air and are time-weighted over the period sampled. Sulfuric acid is expressed in milligrams per cubic meter.
HCl = hydrochloric acid
H_2SO_4 = sulfuric acid
HF = hydrofluoric acid

b. The values shown in brackets indicate that the measured concentration for that sample was between the reported limit of detection and limit of quantitation. This means that the contaminant in question was present but in an amount too low to reliably measure.

c. 15 minute ceiling limit. (Also called a short-term exposure) limit.

d. 8 to 10 hour time-weighted average exposure limit.

Analytical Comment: Analyses for nitric, phosphoric, and hydrobromic acids were performed on these samples. None of these acids were detected.