

Characterization of Air Contaminants Formed by the Interaction of Lava and Sea Water

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We made environmental measurements to characterize contaminants generated when basaltic lava from Hawaii's Kilauea volcano enters sea water. This interaction of lava with sea water produces large clouds of mist (LAZE). Island winds occasionally directed the LAZE toward the adjacent village of Kalapana and the Hawaii Volcanos National Park, creating health concerns. Environmental samples were taken to measure airborne concentrations of respirable dust, crystalline silica and other mineral compounds, fibers, trace metals, inorganic acids, and organic and inorganic gases. The LAZE contained quantifiable concentrations of hydrochloric acid (HCl) and hydrofluoric acid (HF); HCl was predominant. HCl and HF concentrations were highest in dense plumes of LAZE near the sea. The HCl concentrations at this sampling location averaged 7.1 ppm; this exceeds the current occupational exposure ceiling of 5 ppm. HF was detected in nearly half the samples, but all concentrations were <1 ppm. Sulfur dioxide was detected in one of four short-term indicator tube samples at approximately 1.5 ppm. Airborne particulates were composed largely of chloride salts (predominantly sodium chloride). Crystalline silica concentrations were below detectable limits, less than approximately 0.03 mg/m³ of air. Settled dust samples showed a predominance of glass flakes and glass fibers. Airborne fibers were detected at quantifiable levels in 1 of 11 samples. These fibers were composed largely of hydrated calcium sulfate. These findings suggest that individuals should avoid concentrated plumes of LAZE near its origin to prevent over exposure to inorganic acids, specifically HCl. *Key words:* airborne fibers, hydrochloric acid, hydrofluoric acid, lava, sea water, sulfur dioxide. *Environ Health Perspect* 102:478–482(1994)

Lava flow from the eruption of Hawaii's Kilauea volcano produces large clouds of mist (lava and sea emissions; LAZE) on interaction with sea water (Fig. 1). Island wind patterns (Kona winds) occasionally move this LAZE toward populated areas in the adjacent village of Kalapana and into the Hawaii Volcanos National Park. The potential for both occupational and community exposure to this mist led to health concerns due to the absence of environmental health information on the chemical composition of LAZE. Some local residents and workers had complained of irritation after exposures to LAZE. In March 1990,

The National Institute for Occupational Safety and Health (NIOSH) provided technical assistance to the Hawaii State Health Department in characterizing the LAZE air contaminants. Environmental samples were collected on 13–18 March 1990 to quantify air contaminants formed through the interaction of lava and sea water. This information was needed to evaluate potential exposure risks and develop public health policy.

Background

The Hawaiian Archipelago includes eight major islands: Niihau, Kauai, Oahu, Molokai, Lanai, Kahoolawe, Maui, and Hawaii. These islands are the tops of a large mountain range built up from the ocean floor by numerous volcanic eruptions and lava flows. Theory suggests that these islands are formed as the earth's Pacific plate moves across a fixed hot spot (or hole) in the earth's mantle during the northwest plate drift (1–3).

Hawaii is the newest island and has the most volcanic activity. The island was formed by lava flows from five volcanos. Among these, Mauna Loa and Kilauea, the two southernmost volcanos, are considered active and are among the most active volcanos in the world. Kilauea, currently the most active Hawaiian volcano, began the longest sustained eruption of any Hawaiian volcano in recorded time starting in January 1983 (1,2).

Molten rock from volcanic eruptions is a complex solution of silicates and oxides associated with water vapor and possibly other gases. Lavas can vary in composition. Hawaiian lavas have a lower silica content and are rich in iron, magnesium, and calcium. Olivine basalt is the most common lava from recent eruptions of Kilauea and Mauna Loa volcanos (1). Hawaiian lavas are more viscous, with a lower gas content, resulting in milder, less explosive volcanic eruptions. Hawaiian volcanos erupt not only at their summits but also along rift zones, which are heavily fractured zones of weakness in the volcano (1–3). Lava flows can occur on the surface or within lava tubes beneath the surface of lava that has cooled and crusted. The interaction of the molten lava with sea water produces large clouds of LAZE (1,2). These LAZE clouds move in various directions depending on

prevailing wind patterns. Kona conditions, winds moving from the southeast to the northwest, can direct the LAZE over land and into the Hawaii Volcanos National Park and other populated island areas, creating the potential for both occupational and community exposure. Park employees, Hawaii civil defense workers, tour guides, geologists, or other scientists studying the volcano would be at increased risk for LAZE exposure; park visitors and individuals living in communities proximate to the LAZE formation would also be at increased risk.

Methods

We conducted environmental sampling to characterize the air contaminants formed by the interaction of lava and sea water. Air samples were collected for several environmental analytes including respirable dust, respirable crystalline silica and other minerals, fibers, trace metals, inorganic acids, and organic and inorganic gases. Table 1 describes the sampling and analytical methods used during the survey.



Figure 1. Lava and sea emissions (LAZE), March 1990, near Kalapana, Hawaii.

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Area sampling stations were used to measure the air contaminants formed by the lava and sea water. The following sampling locations were selected based on conversation with local health officials (Fig. 2): 1) Beach areas. These sampling stations were positioned in visible clouds of LAZE; samples were collected at distances from approximately 10–400 yards from the LAZE source as determined by the terrain and wind direction during sampling. 2) Roadblock. This sampling station was positioned at the highway 130 roadblock west of Kalapana, Hawaii; the highway was closed at this location from past lava flows. This station was one of the closest points of public access to the LAZE formation. 3) Kalapana, Hawaii. Two sampling stations were positioned in Kalapana at separate village locations. 4) Hawaii Volcanos National Park. Two sampling stations were positioned in the park approximately 2.5 and 4.5 miles downwind from the points of LAZE origin. 5) Background. This sampling station was located in Kaaui, Hawaii, approximately 20 miles from the LAZE origin. This station was near the intersection of highways 130 and 11.

We collected samples during 4 days: 13–15 March and 18 March 1990. Difficult terrain, active lava flows, and varying wind patterns influenced the sampling dates, beach sample station position, and the number of samples collected. By design, samples were to be collected during Kona wind conditions when the LAZE was directed into Kalapana, Hawaii, and surrounding areas. Wind patterns during the

survey did not direct the LAZE toward sampling stations in Kalapana or the highway 130 roadblock; although, on four of seven scheduled sampling dates, wind carried mists directly over land, providing the opportunity to collect samples from the LAZE plume at the beach sampling stations and at stations positioned downwind in the Hawaii Volcanos Park. NIOSH scientists used respiratory protection and eye protection when sampling in concentrated LAZE plumes at beach sampling stations.

Results and Discussion

Environmental measurements show that the LAZE is highly acidic. A 6.4 ml sample of condensate, collected in dense clouds of LAZE approximately 10–12 yards from its origin, had a pH of approximately 1.3. This reading is consistent with pH readings obtained by placing strips of pH paper directly in the LAZE. The condensate sample, analyzed for inorganic acids by ion chromatography, contained hydrochloric acid (11 mg); hydrofluoric acid (0.25 mg), and sulfate anion (SO_4 ; 0.8 mg). (Analysis of this condensate sample by ion chromatography and ion-pair chromatography failed to give a clear separation of sulfate and perchlorate anions. Thus, the presence of perchlorate anion can neither be confirmed nor rejected, and a portion of the sulfate anion response may be due to perchlorate anion. Mineralogical results suggest that the sulfate ion in this sample may have been present as a mineral complex similar to gypsum.) Other anions (bromide, nitrate, and phosphate) were not detected

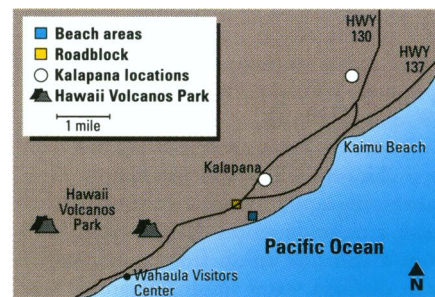


Figure 2. Sampling locations: Kalapana, Hawaii, and vicinity.

in this sample. These measurements show that the acidic nature of the LAZE is primarily a function of HCl content. These findings are consistent with research data from the U.S. Geological Survey indicating that HCl can be formed by the steam hydrolysis of magnesium chloride salts precipitated when sea water is evaporated to dryness by molten lava (6,7).

Time-weighted average (TWA) air samples collected to measure inorganic acid concentrations show HCl as the predominant acid in LAZE. We collected these samples using several sampling methods (Table 1). The HCl concentration from the two types of impinger samples were also in agreement, ranging from below detectable limits (ND = approximately 0.004–0.04 depending on impinger method) to 12 ppm. The HCl concentrations measured using the silica-gel sorbent tubes were in also agreement with the impinger results. HCl concentrations were highest in the beach sampling stations

Table 1. Environmental sampling methods

Analyte	Sampler	Media	Air sampling rate		Sample analyses
			(l/min)	Sampling time	
Respirable dust and crystalline silica	Respirable cyclone	Polyvinyl chloride filter (37 mm)	1.7	2–8 hr	1) Gravimetric, 2) X-ray diffraction, NIOSH method 7500 (4)
Metals/elements	Total dust cassette	Mixed cellulose ester filter (37 mm)	2.0	2–8 hr	1) Inductively coupled argon plasma, atomic emission spectroscopy, NIOSH method 7300 (4)
Minerals/fibers	Total dust cassette	Mixed cellulose ester or polycarbonate filter	2.0	0.25–2 hr	1) Transmission electron microscopy, NIOSH method 7402 (4), 2) polarized light microscopy (4), 3) scanning electron microscopy
Particulate (settled dust)					1) Polarized light microscopy, 2) scanning electron microscopy
Hydrocarbon vapors	Solid sorbet tube	Charcoal and silica gel	0.05	2–8 hr	1) Gas chromatography (4)
Inorganic acids	Solid sorbet tube	Silica gel	0.2	2–8 hr	1) Ion chromatography, NIOSH method 7903 (4)
	Midget impinger	Sodium hydroxide solution	1.0	2–8 hr	1) Ion chromatography
	Midget impinger	Deionized water	1.0	2–8 hr	1) Ion chromatography, 2) metals inductively coupled plasma-atomic emission spectroscopy (4)
	Glass condenser	—	—	2 hr	1) Ion chromatography (4), 2) pH measurements
Gases (inorganic)	Direct reading indicator tubes	—	—	5 min	1) Colorimetric—length of stain in sample tube proportional to the air contaminant concentration—a direct measure (5)

positioned directly in the LAZE. The mean HCl concentration from 10 samples collected using impinger methods was 3.5 ppm and, with the sorbent tube method, 2.9 ppm (Table 2).

These HCl concentrations are based on total chloride (Cl) anion per sample. (Ion chromatography analysis cannot distinguish a chloride anion derived from HCl from a chloride anion from ocean salts.) Each distilled water impinger sample was analyzed for metals commonly bound as chloride salts to estimate the chloride anion potentially contributed to the impinger samples by ocean salts. Chloride anion potentially bound as salts of calcium, magnesium, or sodium may have reduced HCl concentration to an estimated 87% of the reported concentration in impinger samples collected in the concentrated LAZE plume near its origin and to 36% of reported concentration in less dense LAZE plumes approximately 400 yards from origin.

HCl concentrations were the highest in those sampling stations positioned directly in the LAZE plume near the point of origin (Fig. 3). The eight TWA samples (impingers and sorbent tubes) collected in dense mists within approximately 12 yards of a tubular LAZE source had a mean concentration of 7.1 ppm (SD = 2.9). Four direct-reading indicator tube samples collected at this same location had an average concentration of 6.4 ppm. As indicated in Figure 3, HCl concentrations declined with distance from the source. At approximately 100 yards, the average TWA HCl concentrations from eight samples was 0.69 ppm (SD = 0.51). The nine direct-reading indicator tube samples collected at this distance had an average concentration of 0.3 ppm. Four TWA samples collected at approximately 400 yards from the LAZE source on March 18 had an average concentration of 0.39 ppm (SD = 0.11). The three indicator tubes collected at this distance had an average concentration of 0.4 ppm. Samples collected within the LAZE plume at distances of approximately 2.5 and 4.5 miles from the origin were below quantifiable limits for HCl. HCl concen-

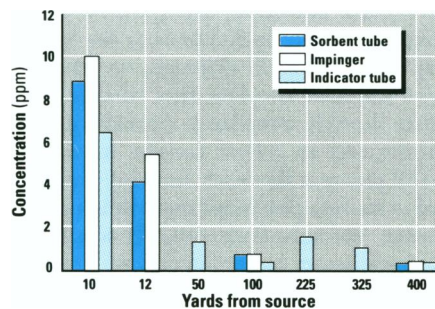


Figure 3. Effect of distance from source on concentrations of HCl in air.

tration from all other sampling locations were outside of the LAZE plume and generally below detectable limits, reflecting ambient or background conditions. HCl concentrations measured in the dense LAZE plume within 12 yards of the source were in excess of the permissible exposure limits (PELs) enforced by Occupational Safety and Health Administration (OSHA), 5 ppm as a ceiling level. These area HCl concentration also exceeded NIOSH recommended exposure limits (RELs) and the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) exposure recommendations (both 5 ppm as a ceiling exposure value) (8–11).

We also analyzed the impinger and silica-gel sorbent tubes for anions of other inorganic acids including bromide, fluoride, nitrate, perchloric, phosphate, and sulfate. Of these, fluoride, nitrate, perchloric, and sulfate were identified in some samples collected from the sampling stations within the plume. Nitric and perchloric acids were below quantifiable levels in all samples. Hydrofluoric acid (HF) was detected in 9 of 20 samples from the beach sampling stations. Four of these samples had quantifiable HF concentrations; these samples were collected from beach areas at distances of 10–100 yards from the source. The highest HF concentration, 0.99 ppm, was measured in a dense LAZE plume approximately 12 yards from the source. Fluoride anion was also detected at quantifiable levels in four samples collected from other sampling

locations separate from the beach and outside of the LAZE plume. The presence of fluoride anion in these background, ambient samples may possibly be attributed to vent gas emissions from Kilauea. None of the area HF concentrations exceeded the personal occupational exposure standards/criteria of OSHA and ACGIH (3 ppm as a TWA) or NIOSH (3 ppm as a TWA and 6 ppm as a STEL), although HF exposures would have an additive health effect in combination with HCl exposures (10).

Sulfate anion was detected in 14 of 20 samples from the beach sampling station, with concentrations ranging from below detectable limits to 1 mg/m³. It is unlikely that this anion was present as sulfuric acid (H₂SO₄) because indicator tube samples for sulfuric acid, collected in dense LAZE, were below detectable limits. A more probable source of the SO₄ in these samples is a mineral, similar to gypsum (CaSO₄•2H₂O), that was identified in many airborne samples by transmission electron microscopy analysis.

Volatile organic compounds were not detected in any of the 13 high-volume charcoal and silica-gel tube samples analyzed qualitatively. Direct-reading indicator tube samples, taken to evaluate potential presence of a number of chemical substances in LAZE, were below detectable levels for ammonia, carbon disulfide, carbon monoxide, chlorine, hydrofluoric acid, hydrogen sulfide, nitrogen dioxide, and sulfuric acid. Carbon dioxide, hydrochloric acid, and sulfur dioxide were measured at detectable levels with indicator tubes. The two carbon dioxide measurements, 400 and 450 ppm, were close to expected ambient levels. Sulfur dioxide was detected in one of four short-term samples at a concentration of 1.5 ppm. This sample was below the OSHA PEL (5 ppm as a TWA), ACGIH TLV, and NIOSH REL (both 2 ppm as a TWA and 5 ppm as a short-term exposure limit) (8–11).

Respirable dust concentrations ranged from below detectable levels (limit of detection = approximately 0.01 mg/m³) to a high of 1.3 mg/m³ (Table 3). The five samples collected from beach sampling stations, within the LAZE plume, had the highest concentrations, with an average of 0.5

Table 2. Hydrochloric acid concentrations by sampling location (ppm in air)^a

	Impinger methods			Sorbent tube methods		
	N	Mean	Range	N	Mean	Range
Beach	10	3.5	0.2–12	10	2.9	LOQ–9.1
Roadblock	3	LOQ	ND–0.002	4	LOQ	ND–LOQ
HVP	2	LOQ	ND–LOQ	4	ND	ND
Kalapana	2	0.03	ND–0.06	4	LOQ	ND–LOQ
Keaau	1	0.02	—	2	LOQ	ND–LOQ

^aThe concentrations are based on total chloride anion; interference from chloride salts may have reduced the reported HCl concentrations (see Results and Discussion). HVP, Hawaii Volcanoes Park. ND, below the limit of detection, approximately 0.004–0.04 depending on the impinger method and approximately 0.08 ppm for the sorbent tube method. LOQ, below the limit of quantification, approximately 0.01–0.04 ppm depending on the impinger method and 0.23 ppm for the sorbent tube method.

Table 3. Respirable dust concentrations by sampling location (mg/m³ in air)^a

	N	Mean	SD	Range
Beach	5	0.5	0.49	0.12–1.3
Roadblock	2	0.03	0	None
HVP	2	0.025	0.007	0.02–0.03
Kalapana	1	0.01	—	—
Keaau	1	ND	—	—

HVP, Hawaii Volcanoes Park. ND, below the limit of detection, approximately 0.01 mg/m³.

mg/m³ (SD = 0.49). Respirable dust concentrations from other sampling stations out of the plume were ≤ 0.03 mg/m³ and reflect ambient or background conditions. Crystalline silica (alpha-quartz, cristobalite, or tridymite) was not detected in any of the samples. The limit of detection for crystalline silica is 0.015 mg/sample or approximately 0.03 mg/m³ given the average volume of air sampled.

Calcium, copper, iron, magnesium, sodium, and zinc were the predominant metals detected in airborne total dust samples collected using open-face filter cassettes. Metal concentrations were highest in the beach sampling stations positioned in the LAZE plume. Sodium and magnesium were the most abundant metals. Sodium was detected in each sample collected from the beach sampling stations at concentrations ranging from 0.03 mg/m³ to 1.0 mg/m³. Magnesium was detected in four of the five samples from this area at concentrations ranging from ND (<0.003 mg/m³) to 0.13 mg/m³. Sodium and magnesium salts make up more than 90% of the total ocean salts (by weight), and their presence is consistent with particulate formed from boiled/evaporated sea water (12). Exposures to sodium, magnesium, and the other metals identified in these samples were below existing occupational exposure standards/criteria of OSHA, ACGIH, and NIOSH (8–11).

The nature of the particulate formed by the interaction of lava and sea water was evaluated in several ways. By visual inspection of the LAZE plumes, particulate fall-out could be observed on occasion. These particles, thin sheets or flakes measuring up to approximately 10 cm in diameter, have been recently described as Limu'o Pele or Pele's seaweed. They are composed largely of amorphous silicon dioxide. This material, as well as fibrous glass particles, could be observed in the crevices of hardened lava flows near the ocean (Fig. 4). The aerosolization of this amorphous glass results from the explosive interaction of lava and sea water.

Microscopic analysis of air samples collected on filter media or by suspending a microscope slide directly in the LAZE plume showed a predominance of cubic crystals (Fig. 4). Further observation of these particles by polarized light microscopy indicated that they were isotropic, which suggests NaCl. Confirmation was obtained by scanning electron microscopy with X-ray analysis.

Airborne fibers were also detected in samples collected from the LAZE plume using transmission electron microscopy. Only one of the five LAZE plume samples had a quantifiable fiber concentration, 0.16 fibers/cm³. Energy dispersive X-ray analysis suggests a large portion of these

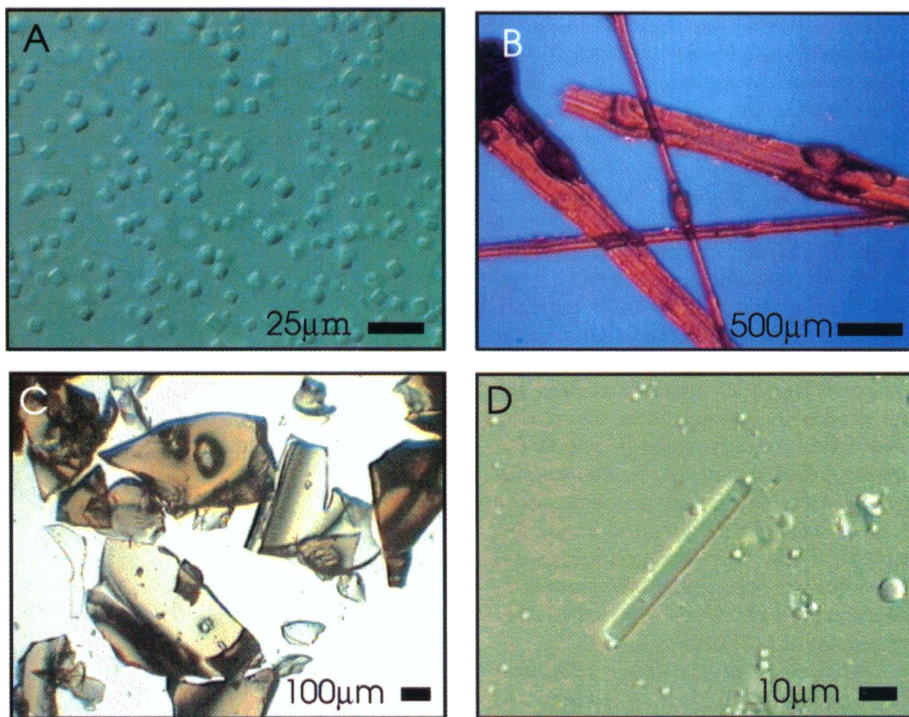


Figure 4. Digital images of (A) air sample collected in plume showing cubic crystals (differential interference contrast illumination); (B) settled dust sample showing glass fibers (Rheinberg illumination); (C) settled dust sample showing glass fragments (brightfield illumination); and (D) air sample collected in a plume showing a glass fiber (differential interference contrast illumination).

fibers was composed of a hydrated calcium sulfate with a morphology characteristic of gypsum, although the calcium-to-sulfur ratios were variable, and exact fiber identity (as gypsum) could not be verified in all instances. Some of the airborne fibers appeared to be composed largely of calcium. Glass fibers were also detected on some of the air samples. Figure 4 shows a digital image of an air sample observed under the microscope, showing one of these isotropic glass fibers. Exposures to gypsum and fibrous glass particles could cause irritation to the eyes, skin, and upper respiratory tract (13,14). There are no occupational exposure standards specifically for gypsum fibers, although the OSHA standard for total gypsum dust is 15 mg/m³ as a TWA. NIOSH and ACGIH recommend occupational exposure to total gypsum dusts be maintained below 10 mg/m³ and respirable gypsum dusts below 5 mg/m³ as a TWA. Concentrations of gypsum dusts (including gypsum fibers) were well below these occupational exposure standards. Airborne fiber concentrations were also low by comparison to existing occupational exposure standards/criteria for fibrous glass. NIOSH recommends a TWA exposure limit of 3 fibers/cm³ (for glass fibers ≤ 3.5 μm in diameter and ≥ 10 μm in length) and 5 mg/m³ as total fibrous glass. ACGIH recommends a TLV limit of 10 mg/m³ for fibrous glass as a TWA exposure. Concentrations of airborne fibers (including fibrous glass) were below these occupational criteria (8–11).

Conclusions

The interaction of lava and sea water generated quantifiable concentrations of HCl and HF; HCl was predominant. Condensate samples of LAZE were highly acidic, with a pH of 1.3. The potential for exposure to inorganic acids (HCl and HF) presents the most significant health risk from LAZE. HCl and HF concentrations were highest in dense plumes of LAZE within approximately 12 yards of the sea. The HCl concentrations measured at those sampling locations exceeded the 5 ppm ceiling standard and presented an occupational health hazard according to occupational exposure criteria of OSHA, ACGIH, and NIOSH (8–11). HF concentrations were below existing occupational exposure standards, although HF would produce additive exposure effects in combination with HCl (9,15,16). HCl and HF concentrations decreased with distance from the source. At distances of approximately 400 yards or greater, HCl concentrations, measured directly in the diluted plume, were less than 1 ppm.

The exposure criteria referenced in this report are derived from occupational health research settings and are not an appropriate tool for evaluating community health risks. Community exposures to HCl should not exceed the 5 ppm ceiling standard used for occupational settings; a lower exposure limit may be appropriate to protect the public.

Sulfur dioxide was detected in one of four short-term detector tube samples at a concentration of approximately 1.5 ppm, demonstrating the potential for intermittent SO₂ exposure near areas of volcanic activity and active lava flow. Airborne particles in the LAZE plume were composed largely of sodium chloride crystals. Crystalline silica concentrations in TWA air samples were all below detectable limits (less than approximately 0.03 mg/m³). This is consistent with the basaltic nature of Hawaiian lavas (1-3). Airborne fibers, composed largely of hydrated calcium sulfate similar to gypsum, were detected at quantifiable concentrations in one of five samples collected from the beach sampling stations. Glass fibers were also detected in some samples collected from beach sampling stations. These fiber concentrations did not exceed the occupational exposure standards/criteria of OSHA, ACGIH, or NIOSH for gypsum or fibrous glass (8-11).

Our findings indicate that individuals should avoid exposure to the concentrated LAZE near its origin to prevent overexposure to acid gases, specifically HCl. Elderly persons, young children, and individuals with cardiopulmonary problems may be at increased risk and should avoid all exposure to this mist (15,16). Appropriate personal protective gear (including a chemical cartridge respirator for acid gases and eye

goggles or a full facepiece chemical cartridge respirator) is recommended, as part of a formal respiratory protection program, in those occupational settings when exposure to the LAZE, near its origin, is unavoidable (17).

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