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NATIONAL PARK SERVICE
HAWAII VOLCANOES NATIONAL PARK
HILO, HAWAII

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SUMMARY

In March 1990, the National Institute for Occupational Safety and Health (NIOSH) received a request for a health hazard evaluation (HHE) from the National Park Service to evaluate park employees' exposures to volcanic emissions (both gases and particulates) within the Hawaii Volcanoes National Park (HVNP). An industrial hygiene study was conducted at HVNP during March 25-30, 1990, which also included the administration of a symptoms questionnaire to all park employees.

Park personnel were concerned about their exposures to sulfur dioxide (SO_2) emissions, to the asphalt decomposition products (generated when the lava covers the roadways and burns the pavement), to acid mists when lava enters the ocean, to volcanic-caused smog (termed VOG), and to *Pele's* hair (a fibrous glass-like material which is formed when lava enters the ocean and is rapidly cooled and also during periods of high lava fountaining). None of these conditions, with the exception of SO_2 emissions, were present during the NIOSH evaluation in March 1990 either within the national park boundaries or outside the park.

Long-term colorimetric detector tube samples, used to characterize HVNP workers' personal full-shift exposures to SO_2, revealed no detectable levels. General area air samples taken at various locations within the national park where employees occasionally worked had SO_2 concentrations ranging from 0.8 to 5.0 parts per million (ppm). Direct reading, short-term detector tube samples collected near a naturally occurring sulfur vent showed SO_2 levels of 1.2 ppm. The current NIOSH Recommended Exposure Limit (REL) for SO_2 is 0.5 ppm for up to a 10-hour time-weighted average (TWA). The Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) for SO_2 is 2 ppm for an 8-hour TWA. OSHA has also established a 15-minute Short-Term Exposure Limit (STEL) of 5 ppm.

Symptoms questionnaires were distributed to all park workers on March 25-30, 1990. Forty-three (approximately half) of the park employees returned the symptoms questionnaire before May 1, 1990. Work-related symptoms reported by more than 50% of the respondents included headache, eye irritation, throat irritation, cough, and phlegm. Chest tightness or wheezing and shortness of breath were also frequently reported.

A separate, but related, NIOSH evaluation was conducted in response to a request submitted in 1990 by the Hawaii County Civil Defense Agency.[1] This study was conducted to measure the acidic contaminants generated by the interaction of lava and sea water (an acidic steam cloud termed *laze*). Personal breathing-zone and general area air samples were collected for hydrochloric acid (HCl) and hydrofluoric acid (HF) at various locations surrounding the former village of Kalapana, Hawaii, and near the Kaimu Black Sand Beach recreational area. These sampling locations, which were outside of the HVNP boundaries, were situated within restricted areas, at civil defense road block locations, and in areas accessible to the general public or community residents. During the survey, conducted from July 30 to August 2, 1990, HCl concentrations of up to 15 ppm were measured in short-term samples (approximately 5 minutes) collected near the ocean. Area air samples collected for up to 8 hours had HCl concentrations ranging up to 3.6 ppm. The NIOSH REL and OSHA PEL for HCl are 5 ppm for a 15-minute ceiling exposure.

Another NIOSH evaluation was conducted on March 13-19, 1990, in response to a request submitted by the Hawaii Department of Health.[2] During this evaluation air samples were collected to measure levels of inorganic acids, respirable dust, respirable crystalline silica, various metals and elements, mineral fibers, and hydrocarbon vapors which may be present in *laze*. Sampling locations were directly downwind of the *laze* and at points within approximately 500 yards of the lava/sea water interaction. The inorganic acids HCl and HF were present in the highest concentrations, ranging up to 12 and 1.0 ppm, respectively. Airborne particulates in the *laze* plume were comprised largely of chloride salts. Crystalline silica concentrations in respirable dust samples were below detectable limits. Airborne fibers, comprised largely of a hydrated calcium sulfate similar to the mineral gypsum, were detected at quantifiable levels in one of 11 samples, at a concentration of 0.16 fibers per cubic centimeter (f/cc). Glass fibers were also detected in some air samples although concentrations did not exceed the occupational exposure criteria of OSHA, ACGIH, or NIOSH. Concentrations of the other substances were below either their limits of detection or their respective exposure limits.

The results of the general area air samples indicate that excessive exposures to SO_2 gas can occur at some locations within the Hawaii Volcanoes National Park, e.g. at the Sulphur Bank area and the Halemaumau Trail area. All current and any new park employees should be made aware of this fact. Workers with preexisting respiratory conditions such as asthma, chronic bronchitis, and emphysema may be particularly susceptible to the effects of SO_2. We recommended that park administrators inform visitors of the potential for exposure to volcanic emissions within the park via brochures and/or warning signs.

Keywords: SIC 7999 (Amusement and Recreation Services, Not Elsewhere Classified), sulfur dioxide, hydrochloric acid, hydrofluoric acid, volcano, asthma, respiratory problems.

INTRODUCTION

In March 1990, the National Institute for Occupational Safety and Health (NIOSH) received a request from the National Park Service to evaluate park employees' exposures to volcanic emissions (both gases and particulates) at the Hawaii Volcanoes National Park (HVNP), located on the island of Hawaii in the state of Hawaii. In response to this request, an industrial hygiene study was conducted at HVNP during March 25-30, 1990. Results obtained from the air and drinking water samples were provided to the HVNP Superintendent and other interested parties via interim reports dated May 22 and June 20, 1990, respectively.

In addition to the HVNP request, two other requests were received in 1990, one from the Hawaii County Civil Defense Agency and the other from the Hawaii State Health Department, to assess the potential exposures of civil defense personnel and the general public to airborne contaminants from volcanic emissions. The results from these surveys are summarized in this report.[1,2]

BACKGROUND

Hawaii Volcanoes National Park

Designated a national park in 1916, HVNP covers approximately 250,000 acres on the island of Hawaii. The volcanoes within the national park have been continuously "active" (lava flowing either above or below ground and/or steam and gas emissions) since 1983. In 1990 park personnel perceived an increase in the amount of lava flowing above the ground and in the volcanic gas emission. The primary responsibility for the 70 park personnel is the safety and control of the approximately 4000 to 5000 tourists who visit HVNP daily. The park workers' mandate is to allow tourists to get as close to the volcanoes as possible without endangering their lives. Park service personnel include interpreters, law enforcement officers, maintenance personnel, resource management personnel, and volunteers.

The exposure concerns which prompted the HVNP Health Hazard Evaluation (HHE) request were multifaceted. Park personnel were concerned about their exposures to sulfur dioxide (SO_2) emissions, to the asphalt decomposition products (when the lava covers the roadways and burns the pavement), to acid mists when lava enters the ocean, to volcanic-caused smog (termed VOG), and to *Pele's* hair (a fibrous glass-like material which is formed both when lava enters the ocean and is rapidly cooled and also during periods of high lava fountaining). None of these conditions, with the exception of SO_2 emissions, were present during the NIOSH evaluation in March 1990 either within the national park boundaries or outside the park.

It has been estimated that the Kilauea Volcano naturally emits approximately 270 tons of mercury (Hg) annually, almost all in vapor form.[3] Previous monitoring within the HVNP has measured average airborne Hg concentrations of almost 10 micrograms per cubic meter ($\mu g/m^3$) at the Sulphur Bank fumaroles near the Kilauea vent.[4] Because of the possibility of employee exposures resulting from the natural venting of elemental Hg within the park boundaries, personal breathing-zone and general area air samples were also collected for elemental mercury vapor during this evaluation.

Drinking Water Contamination

Although not part of the original HHE request, concern was expressed to NIOSH investigators by the HVNP management of an apparent perchloroethylene contamination problem in the water supply of the park. Water samples were collected during the March 1990 survey to assist the Park Service in evaluating the apparent contamination problem in the water supply.

The HVNP obtains its potable water from three sources. During dry weather conditions, water is brought into the park via tanker trucks. The Park Service owns a water tanker truck and hauls water from the Keaau County standpipe on an as-needed basis. The well site for this standpipe is located between Hilo and Volcano, Hawaii. When conditions warrant, the Park Service contracts to have water hauled from nearby Pahala, Hawaii, to the park. In addition, the park has its own rain water catchment and filtrations systems. Collected rain water is filtered through sand filters and is chlorinated prior to distribution throughout the park.

NIOSH investigators learned that ambient volcanic emissions common to the HVNP area contribute to the formation of acid rain and considered the possibility that the acid rain might leach lead and other metals from metal roofs and gutters of homes and/or buildings into the rain water catchment systems. For this reason the water samples collected during this evaluation were also analyzed for pH[*] and lead.

RELATED NIOSH EVALUATIONS

Hawaii County Civil Defense Agency

A separate HHE request was received in 1990 from the Hawaii County Civil Defense Agency to assess the potential exposures of civil defense personnel to airborne contaminants from volcanic emissions.[1] The civil defense agency was especially concerned about the hydrochloric acid mist (HCl) present in *laze* (a term describing the acidic steam cloud created when lava reacts with sea water.) A NIOSH evaluation was conducted from July 30 to August 2, 1990. Personal breathing-zone and general area air samples were collected for HCl and hydrofluoric acid (HF) at various locations surrounding the former village of Kalapana and near the Kaimu Black Sand Beach recreational area.

Hawaii State Health Department

Another related NIOSH evaluation was conducted in March 1990 in response to a request submitted by the Hawaii Department of Health.[2] During this evaluation air samples were collected to measure the various contaminants found in *laze*, including inorganic acids (especially HCl and HF), respirable dust, respirable crystalline silica, various metals and elements, mineral fibers, and hydrocarbon vapors. Area sampling stations were used to measure air contaminants formed by the lava and sea water. The following sampling locations were selected based on conversations with Hawaii State Health Department and Hawaii Civil Defense.

- Beach areas - sampling stations positioned in the visible clouds of *laze* at distances from 10 to 400 yards from the lava/sea

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[*] pH is a value taken to represent the acidity or alkalinity of a solution. Pure water, the standard used in arriving at this value, is assigned a pH of 7. The pH range extends from 1 (acidic) to 14 (alkaline).

water source.

- Roadblock - sampling station positioned on Highway 130 roadblock west of Kalapana. This station was positioned near the *laze* formation point.
- Kalapana - 2 sampling stations.
    1. Papaya Plant - near the intersection of Highway 130 and Highway 137.
    2. Village Residence - on Highway 130 approximately 1/2 mile east of the tourist roadblock.
- Background - sampling station located at the fire station in Keaau, Hawaii, near the intersection of Highways 130 and 11.
- Hawaii Volcanoe's National Park - two sampling stations positionedapproximately 2.5 and 4.5 miles downwind from the *laze* origin.

These air samples were collected during Kona wind conditions when the *laze* was directed into Kalapana and surrounding areas. Samples were collected during March 13-15 and March 18, 1990.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest limits of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these limits. A small percentage may experience adverse health effects because of individual susceptibility, a preexisting medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the limit set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are the following: 1) NIOSH Recommended Exposure Limits (RELs)[5], 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs)[6], and 3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs)[7]. The OSHA PELs may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH RELs, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure concentrations and the recommendations for reducing these concentrations, it should be noted that the lowest exposure criteria was used in this report; however, industry is legally required to meet those limits specified by the OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits (STELs) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

The following criteria suggest concentrations to which most workers can be exposed, day after day, for a working lifetime without adverse health effects. Because of variations in individual susceptibility, a small percentage of workers may experience health problems or discomfort at exposure concentrations below these existing criteria. Additionally, since OSHA PELs and NIOSH RELs are intended to protect workers (presumably healthy adults), these exposure limits may not be adequate to protect the general population.

Sulfur Dioxide

Sulfur dioxide (SO_2) is a colorless, water-soluble gas which is severely irritating to the eyes, mucous membranes, and skin. On contact with moist membranes, it rapidly forms sulfurous acid (H_2SO_3). Acute exposures to SO_2 above 10 parts per million (ppm) are irritating to the eyes, nose, and throat, and can cause choking, cough, and increased mucus secretion. Repeated exposure to 10 ppm have caused nosebleeds among exposed workers.[8] Acute inhalation of large amounts of sulfur dioxide can result in death from asphyxia.[9] Bronchial asthma can also result following acute exposure to SO_2.[10]

There is varying sensitivity among different individuals to the broncho-constricting effects of SO_2. Experimental studies on healthy human volunteers at rest exposed to 1 ppm SO_2 have shown that airway resistance is not generally affected after short-term exposure, but decreases in Forced Expiratory Flow (FEF_{25-75}, a measure of airflow) have been found in some individuals after prolonged exposure.[11] Deep breathing, which can occur during heavy work, has been found to increase airway resistance at exposures of 1 ppm.[12] At exposures of less than 1 ppm, persons with mild asthma exhibited increased airway resistance during moderately heavy exercise.[13]

In 1974 NIOSH recommended that occupational exposures to SO_2 not exceed 2 ppm for up to a 10-hour time-weighted average (TWA) exposure over a 40-hour workweek.[13] NIOSH subsequently revised this recommendation on the basis of results of four epidemiological studies that became available after publication of the 1974 recommendation. Based on these more recent studies, NIOSH has lowered its exposure limit from 2 ppm to 0.5 ppm for a 10-hour TWA.[14]

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.[7]

In addition to the occupational exposure criteria of NIOSH and OSHA, the Environmental Protection Agency (EPA) promulgated 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 exposures to the general public. 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).

Hydrogen Chloride

Hydrogen chloride gas 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 inhalational exposures causing significant trauma are usually limited to people who are prevented from escaping; in such cases, laryngeal spasm or pulmonary edema may occur.[12] High concentrations of the gas cause eye irritation and the resulting tissue damage may cause prolonged or permanent visual impairment. Exposure of the skin to a high concentration of the gas will cause burns; repeated or prolonged exposure to dilute solutions may cause dermatitis. Erosion of exposed teeth may occur from repeated or prolonged exposure.[11] The NIOSH REL and OSHA PEL for HCl are both 5 ppm (equivalent to 7 mg/m^3) for a 15-minute ceiling exposure.[5,7]

Perchloroethylene

Perchloroethylene, also known as tetrachloroethylene, is a clear, colorless, nonflammable liquid with an ethereal odor. The major uses of perchloroethylene are for commercial dry cleaning and metal degreasing; however, it also is formulated into a variety of products used in the home. While very insoluble in water, perchloroethylene is miscible with most organic solvents and oils.[15]

The Environmental Protection Agency (EPA) recommends a maximum contaminant level (MCL) of 5 parts per billion (ppb) of perchloroethylene in drinking water, effective July 30, 1992.[16] There are no NIOSH or OSHA criteria for perchloroethylene in drinking water.

Lead in Drinking Water

Lead, a very soft and malleable metal, is slightly soluble in water in the presence of nitrates, ammonium salts, and carbon dioxide.[9] The currently enforceable MCL for lead in drinking water (an EPA primary pollutant) is 50 ppb. The EPA has adopted an action level for lead in drinking water (which replaces the MCL) of 15 ppb, effective December 7, 1992.[17]

pH

The term pH is used to express the degree of acidity or alkalinity of a solution in reference to pure water (assigned a neutrality of 7.0 pH). If the pH is less than 7.0, the solution is acidic. Correspondingly, if the pH is higher than 7.0, the solution is alkaline. The pH scale is logarithmic (not linear), meaning that a solution with a pH of 1 is ten times as acidic as a solution with a pH of 2. Some examples of approximate pH values for common substances include lemon juice (pH ≈2.3), vinegar (pH ≈2.9), rainwater (pH ≈6.2), seawater (pH ≈8.5), and household ammonia (pH ≈11.5).[18]

The EPA does not have an enforceable maximum or minimum level for pH in drinking water but rather considers pH value as a secondary pollutant. The EPA lists a drinking water pH range of 6.5 to 8.5 as "acceptable" and considers pH values outside this range as "aesthetically displeasing."[19]

EVALUATION DESIGN AND METHODS

Sampling Locations

On March 26-27, 1990, exposures to SO_2, elemental Hg, and hydrogen sulfide within the park were measured by collecting personal breathing-zone and general area air samples. Personal samples were collected on park employees whose job assignments required them to be at the following locations for varying lengths of time on March 26, 1990:

- Kamoamoa Campground & Picnic area.
- Both outside and inside the Hawaiian Volcano observatory/Jaggar Museum.
- Kilauea Military Camp.
- Devastation Trail, Crater Rim Drive, Crater Rim Road, and the Chain of Craters Road near the Resource Management offices.
- Inside the Kilauea Visitor's Center & Museum.
- Adjacent to the park maintenance shop and the gravel pit area.

Air Sampling Methodology

The following sampling and analytical methods were used for the personal and area air monitoring performed within the park.

Sulfur dioxide

Direct reading colorimetric detector tubes were used to measured both short- and long-term SO_2 concentrations at various sites within the park. Both personal breathing-zone and general area air samples were collected for SO_2. Long-term detector tube samples were collected for 4 hours using a sampling rate of 20 cubic centimeters per minute (cc/min). Short-term detector tubes were used to measure peak SO_2 exposures occurring over 2 to 3 minutes.

Personal breathing-zone and area air samples were also collected for sulfates and SO_2 following NIOSH Method 6004.[20] This method does not quantitate SO_2 directly, but rather measures sulfate and sulfite ion concentrations by ion chromatography. Samples were collected on two 37-mm diameter cassette filter holders connected in series. The front cassette contained a 0.8 micrometer (µm) pore size cellulose ester membrane filter with backup pad; the backup filter cassette contained a cellulose filter (Whatman 40) which had been saturated with potassium hydroxide. The filters were connected via Tygon® tubing to battery-powered sampling pumps calibrated to a flow rate of 1.0 liter per minute (lpm). Sulfur dioxide is collected on the backup (treated) filter. Sulfuric acid, sulfate salts, and sulfite salts are collected on the front filter and may be quantitated as total particulate sulfate and sulfite. The filters were desorbed and analyzed for SO_2 and sulfate ion concentrations by ion chromatography. The analytical limit of detection (LOD) and limit of quantitation (LOQ) for both sulfate and SO_2 in this sample set were 2 and 4 micrograms (µg) per sample, respectively.

Hydrogen Sulfide

Personal breathing-zone and area air samples were collected for hydrogen sulfide (H_2S) using long-term colorimetric detector tubes. Air samples were collected over periods ranging up to 6 hours using a sampling rate of 20 cubic centimeters per minute (cc/min).

Mercury

Personal breathing-zone and area air samples for Hg were collected on SKC Hydrar® solid-sorbent tubes connected via Tygon® tubing to battery-powered sampling pumps calibrated to a flow rate of 1.5 lpm. Analysis of the Hydrar solid-sorbent tube samples was conducted via Cold Vapor Atomic Absorption (**AA**) Spectroscopy according to NIOSH Method No. 6009.[21] The analytical LOD and LOQ for this sample set were 0.02 and 0.056 µg of Hg per sample, respectively.

Hydrochloric Acid

No personal breathing-zone or general area air monitoring was conducted for HCl during the HVNP survey since exposure to this inorganic acid was considered unlikely. However, air samples for HCl and other inorganic acids at several shoreline locations adjacent to the national park were collected in related NIOSH investigations and are summarized in this report. In these evaluations, short-term exposures to HCl exceeding 10 ppm were measured in the dense *laze* formed along the shoreline.

Review of Records and Questionnaires

Park records were reviewed to gather information concerning incidents in which tourists and/or park employees were exposed to volcanic emissions (gases/vapors and particulates) and were reported to experience some health effects as a result of these exposures. A noteworthy finding was a 1987 park report of a tourist (who was later reported to be asthmatic), who collapsed and died in the Halemaumau Trail area. Seventy-nine self-administered symptom questionnaires were given to park administrative representatives for distribution among the entire park work force.

Drinking Water Evaluation

Water samples were collected from cold water taps at 15 locations within the park. Samples were collected after the water had been flowing for one minute or more, using one-liter glass jars with Teflon®-lined lids. All water samples were collected by filling the jars as full as possible to avoid leaving any headspace within the container.

Perchloroethylene Analysis

Five milliliters (ml) of each water sample were placed in a sparging unit coupled to a Hewlett-Packard model 5890 gas chromatograph (GC) equipped with an electroconductivity detector as well as a photoionization detector. The analytes were purged out of the water onto a charcoal trap and the trap was then heated to a final temperature of 180° C to liberate the trapped analytes which were then transferred to the GC.

The presence of perchloroethylene was determined by comparison with standard solutions. Quantitation was performed by comparing peak areas of several standards to the area of the peak in the samples.

Lead in Water Analysis

The water samples were analyzed for lead using a modification of NIOSH Method 7802. The graphite furnace atomic absorption (AA) spectroscopy method used consisted of taking a 25 ml aliquot of each sample and washing it with concentrated nitric acid and hydrogen peroxide. The sample aliquots were then quantitatively transferred to 25 ml volumetric flasks prior to aspiration of the samples into the AA.

pH Measurements

The water samples were analyzed for pH by electrometric measurement following EPA Method 150.1 (revised March 1983). The pH of the samples was measured on three successive volumes of approximately 20 ml each until the values differed by less than 0.1 pH units.

RESULTS FROM THE HVNP EVALUATION

Environmental

Sulfur Dioxide

The direct reading, long-term colorimetric detector tube samples collected on March 26, 1990, to characterize HVNP workers' personal full-shift exposures to SO_2 revealed no detectable levels. On March 27, 1990, stationary air samples were collected in the park at the following locations:

- Halemaumau Trail
- Sulphur Bank area
- Steam Vent area

Three long-term detector tube area samples for SO_2, taken on March 27, 1990, at the Halemaumau Trail, measured ambient concentrations of 0.8, 1.7, and 5.0 ppm, with the highest concentration measured at the parking lot. An area air sample, collected at the Sulphur Bank with a long-term detector tube positioned on top of a 3-foot high rock pile that covered a vent, measured SO_2 concentrations of 4.1 ppm at the vent source. Direct reading, short-term detector tube samples for SO_2 collected approximately three feet from a rock pile vent source measured ambient SO_2 levels of 1.2 ppm. The OSHA PEL and ACGIH TLV for SO_2 as an 8-hour TWA is 2 ppm. Both organizations have also established a 15-minute Short-Term Exposure Limit (STEL) of 5 ppm for SO^2. The NIOSH REL for SO_2 is 0.5 ppm for up to a 10-hour TWA.

Sulfur Dioxide, Sulfates, Sulfuric Acid (Using NIOSH Sampling and Analytical Method 6004)

Concentrations of SO_2 in general area air samples ranged from not detected (ND) to 6.7 ppm. Results from two personal breathing-zone air samples (collected on a photographer crossing an old lava flow and an employee working near the Kamoamoa Campground/Picnic area) ranged from ND to 0.5 ppm. The area sampling locations where the highest SO_2 concentrations were measured are listed in the following chart. The OSHA PEL and ACGIH TLV for SO_2 is 2 ppm for an 8-hour TWA. The NIOSH REL for SO_2 is 0.5 ppm for a 10-hour TWA.

LOCATION	SAMPLE DURATION (Military Time)	SO_2 CONCENTRATION
Sulfur Bank (turn around point)	1437 to 1838	5.6 ppm
Sulfur Bank (turn around point)	1132 to 1432	6.7 ppm
Halemaumau Crater Trail (near parking lot)	1600 to 1855	5.4 ppm
Halemaumau Crater Trail (between lookout and parking lot)	1220 to 1624	1.4 ppm

Since there is no existing evaluation criteria for sulfate particulates, sulfuric acid (H_2SO_4) was chosen as a possible "worst case," or "most toxic," exposure criteria for the sulfate particulates. Assuming that all of the sulfate measured was present as H_2SO_4, the concentrations for the personal breathing-zone and general area air samples ranged from ND to 0.05 milligrams per cubic meter (mg/m^3), well below the OSHA, ACGIH, or NIOSH exposure criteria for sulfuric acid of 1 mg/m^3 for an 8- to 10-hour TWA.

Mercury and Hydrogen Sulfide

Mercury was not detected in any of the air samples collected during this evaluation. Hydrogen sulfide concentrations ranged from ND to 4.1 ppm, concentrations below the OSHA PEL of 10 ppm for an 8-hour TWA and the NIOSH REL of 10 ppm for a 10-minute short-term exposure.

Questionnaires

Symptom questionnaires were distributed to all park workers during the initial visit of March 25-30, 1990. Forty-three (approximately half) of the HVNP employees returned the questionnaire before May 1, 1990. Work-related symptoms reported by more than half the respondents included headache, eye irritation, throat irritation, cough, and phlegm. Chest tightness or wheezing and shortness of breath were also frequently reported. Other reported symptoms included dizziness or lightheadedness, skin rash or itching, nausea, nasal irritation, and to a lesser extent, nose bleeds. Employees often attributed the symptoms to VOG, *laze*, sulfur compounds, and burning asphalt.

Water Samples

On March 29-30, 1990, 15 water samples were collected from various locations within and near the park. Table 1 lists the locations, collection times, and the laboratory analytical results for perchloroethylene, lead, and pH for each sample.

Levels of perchloroethylene ranged from ND to 7.6 ppb. Only three of the 15 water samples (3.3, 6.5, and 7.6 ppb) contained perchloroethylene above the LOQ for this sample set of 2.0 ppb. Two of these 3 samples were in excess of the EPA's drinking water criteria of 5 ppb. The 2 elevated samples were collected at the Hawaii Volcano Observatory (wash tub in the janitor's closet) and at the Namakani Paio Campground (sink in the men's restroom), respectively.

Analysis of the water samples for lead content showed concentrations ranging from ND to 13 ppb, concentrations well below the EPA maximum contaminant level for lead in drinking water of 50 ppb.

The pH of the water samples ranged from 4.5 to 7.8. Four of the 15 samples (4.5, 5.1, 6.3, and 6.4) were less than the EPA's recommended pH criterion of 6.5 to 8.5. Three of the 4 samples were collected at the park's water treatment plant while the fourth sample was collected at the Visitor's Center.

DISCUSSION

Hawaii Volcanoes National Park

Air Monitoring and Employee Questionnaires

Area air samples collected for SO_2 within the HVNP boundaries had concentrations which exceeded the NIOSH REL (O.5 ppm) and the OSHA PEL (2.0 ppm), most notably in the Sulfur Bank and Halemaumau Crater Trail areas of the national park. These evaluation criteria, however, are for personal exposures and, as noted, the personal breathing-zone samples had no detectable SO_2. This may be due to the fact that the park employees and volunteers generally spend only a small fraction of their workday near these high exposure areas (conducting tours, for example.) Another factor influencing the low personal SO_2 exposures may be that during this survey numerous park employees reported that they perceived ambient volcanic emissions (gases/vapors) within the park to be minimal. Therefore, the SO_2 concentrations measured on March 27, 1990, could be considered minimal values and typical of low volcanic emission periods.

The responses to the questionnaires suggest that many park employees are experiencing acute irritant symptoms which are consistent with exposures to known irritants (e.g., SO_2 from volcano emissions or related to lava flows). However, symptoms of chest tightness, wheezing, and shortness of breath may be manifestations of bronchospasm and may indicate the possibility of more serious and potentially long-term respiratory impairment in some employees.

Drinking Water Samples

The lead concentrations were all below the new EPA action level for drinking water. The source of the perchloroethylene in the water cannot be conclusively identified from the information gathered during this evaluation. Several plausible explanations for the presence of the perchloroethylene in the water include the following:

- Residual contamination present in the tanker trucks used to haul water to the park.
- Inadvertent use of some product and/or minor leaks from some equipment used or stored near the park's water collection or filtration system.
- Perchloroethylene leaching from some unidentified material used in the water collection or filtration system.
- Contamination of the water collection system by a park visitor. This is mentioned since access to the water system was unrestricted at the time of this evaluation.

A comparison of the NIOSH perchloroethylene water sample results with the last set of data the park obtained from the Hawaii State Health Department showed the concentrations of this solvent in the park's water system have declined. According to the Hawaii State Health Department, the perchloroethylene concentrations measured in the drinking water were not believed to be "an imminent health threat to the public." However, a recommendation made by the Hawaii State Health Department that further attempts should be made to identify the source of perchloroethylene in the drinking water by taking additional samples and by testing materials used in the water system (or to treat the water) which may be a source for the perchloroethylene seems reasonable.

Four of the 15 water samples fell outside the pH range of what the EPA considers aesthetically pleasing. Rain water in the vicinity of the HVNP has a potential for being acidic due to the daily, naturally occurring SO_2 emissions from the volcanic vents. Guidance as to the use of buffering agents in the water to bring the pH levels within the acceptable EPA range should be sought from the Hawaii State Health Department.

Other Sampling Results

Air concentrations of mercury, hydrogen sulfide, and sulfuric acid were well below their respective occupational evaluation criteria during this evaluation.

Related HHE: Hawaii County Civil Defense Agency[1]

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 in restricted-access areas over longer time periods (up to 8 hours) measured HCl concentrations ranging up to 3.6 ppm. Area air samples, with sampling times of approximately 8 hours, were also collected at various civil defense road block locations and in areas where the general public or community residents had access. These HCl concentrations were significantly lower, ranging from ND to 1.1 ppm.

Related HHE: Hawaii State Health Department[2]

The results of general area air monitoring are shown in Table 2. The only notable concentrations measured either in or near the *laze* was HCl (short-term concentrations measured up to 12 ppm). The *laze* cloud, with a pH of 1.3, was also highly acidic. Hydrofluoric acid mist was also detected in some of the samples, but at concentrations below existing occupational health standards. It should be noted that at distances of approximately 400 yards or greater, HCl concentrations (directly downwind from the lava/sea water interaction) were generally less than 1 ppm and HF concentrations were near background (ND) levels.

Airborne fibers were detected in samples collected from the *laze* plume. The fiber concentrations in air samples analyzed by transmission electron microscopy (TEM) concentrations ranged from ND to 0.16 fibers per cubic centimeters (f/cc). Airborne fibers were only detected in the samples collected from the beach sampling stations. Three of the 4 samples with detectable fiber concentrations had low fiber densities on the filters, and the reported concentrations, 0.004 to 0.01 f/cc, should be considered approximate. Energy dispersive x-ray analysis suggests a large portion of these fibers were comprised of calcium and sulfur with a morphology characteristic of gypsum; however, 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 comprised largely of calcium. Glass fibers were also detected on some of the air samples. Gypsum and fibrous glass particles can cause irritation to the eyes, skin, and upper respiratory tract.

CONCLUSIONS

The results of the area air sample measurements indicate that excessive exposures to SO_2 gas can occur at some locations within the national park (e.g. the Sulphur Bank area and the Halemaumau Trail). All current and any new park employees should be made aware of this fact. Workers with preexisting respiratory conditions, such as asthma, chronic bronchitis, and emphysema, may be particularly susceptible to the effects of SO_2.

In other NIOSH evaluations, concentrations of HCl and HF were measured in the Kalapana and Kaimu areas near the shoreline where the *laze* was being created.[1,2] Potential exposure to inorganic acids, such as HCl and HF, presents the most significant health risk from *laze*. Hydrochloric acid concentrations, highest in dense plumes of *laze* within approximately 12 yards of the sea, exceeded the OSHA 15-minute ceiling limit of 5 ppm (for personal exposures) in several instances. However, these high exposures were measured in areas which were off-limits to the general public. Concentrations of these inorganic acids decreased with distance from the source. At distances of approximately 400 yards or greater, HCl concentrations directly in the diluted plume were less than 1 ppm.

Although inorganic acid sampling was not conducted at the park locations where the SO_2 sampling was conducted, it is reasonable to conclude that the HCl and HF concentrations measured near the shore will rapidly diminish as distance from the source increases. NIOSH investigators consider it unlikely that HCl or HF concentrations at the Kamoamoa Campground, the Hawaiian Volcano observatory/Jaggar Museum, the Kilauea Military Camp, and locations along Devastation Trail, Crater Rim Drive, Crater Rim Road, and the Chain of Craters Road would exceed applicable OSHA or NIOSH exposure limits.

RECOMMENDATIONS

The following recommendations were made to ameliorate existing or potential hazards at the Hawaii Volcanoes National Park and the Kalapana and Kaimu coastal areas of Hawaii. Action has been taken by the management of the Hawaii Volcanoes National Park on most of these recommendations.

1. Future development of new trails, paths or parking lots in the Sulphur Bank area and the Halemaumau Crater Trail area should be reviewed in light of the excessive SO_2

exposures which have been measured. Further monitoring of these areas to more fully characterize SO_2 concentrations is warranted. Unless subsequent SO_2 air monitoring results indicate that concentrations are consistently below the NIOSH REL of 0.5 ppm, public access to some locations on the Halemaumau Crater Trail area and in the Sulphur Bank area should be restricted to short visits.

Since NIOSH REL's are intended to protect workers (presumably healthy adults), these exposure limits may not be adequate for young children or people with certain health problems. Therefore, even if SO_2 levels in the Sulphur Bank and Halemaumau areas are below the NIOSH REL, warning signs should be posted. An example of the wording for these signs follows:

> "Caution, volcanic gases present
> in this area may be harmful
> to young children or people with
> respiratory or heart disorders."

Park administrators should also consider distribution of brochures, which contain a similar warning, to all park visitors.

2. Park employees performing maintenance activities (e.g. replacing trail posts, painting lines on the paved roadways or in the parking lots, etc.) in these areas may be exposed to high SO_2 levels. Ideally, in the industrial environment the reduction of employee overexposures to contaminants is accomplished by the installation of engineering controls. This approach is not a practical nor feasible option at the park. While respirators are generally not recommended for use on a long-term basis, the use of respirators is the only logical alternative other than avoiding working in the Sulfur Bank and Halemaumau Trail areas of HVNP. Because of the potential adverse health effects resulting from exposure to SO_2, park management should provide employees required to work in these areas with respirators that have adequate protection factors (such as NIOSH approved half-face piece chemical cartridge respirators).

3. In the event that park employees' exposures to SO_2 exceed 0.5 ppm (8-hour TWA), NIOSH recommends that pre-placement and annual medical examinations should be done. These examinations should be directed toward complaints of mucus membrane irritation, cough, and shortness of breath. Persons with a history of asthma or with subnormal pulmonary function should be monitored closely. Basic pulmonary function tests should be a part of the examinations. These can be used to determine whether a person's pulmonary function is declining at a faster than normal rate. Such determinations are much more sensitive when pooled data from a number of individuals are used. The forced expiratory volume at 1 second and the maximal mid-expiratory flow rate (FEF_{25-75}) appear to be the most useful of the simple pulmonary function tests for monitoring the effects of SO_2.[14]

4. For respirator users, OSHA 29 CFR Part 1910.134 states that no one should be assigned a task requiring use of respirators unless found physically able to do the work while wearing the respirator. This general industry standard declares that a physician should determine what health and physical conditions are pertinent, and that respirator wearers' medical status should be reviewed periodically.

Pre-placement medical examinations should identify those who are physically or psychologically unable to wear respirators safely. As another part of this examination, medical tests pertinent to the respiratory hazards that workers may encounter should be made to get baseline data against which to assess physiological changes in respirator wearers. In addition, the workers' previous medical and employment history should also be considered.[22]

5. An ongoing water monitoring program should be established at the HVNP to address the current perchloroethylene contamination in the drinking water and any potential future water quality problem. This program should be developed and administered by personnel familiar with the appropriate water collection techniques, analytical methods, and evaluation procedures. Park service management officials should consider requesting assistance from the Hawaii State Health Department in establishing a water monitoring program.

6. Access to the park's water catchment and treatment areas should be restricted to park employees only.

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

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Table 2
Characterization of Contaminants Generated by the
Interaction of Lava from the Kilauea Volcano and Sea Water*
Hawaii Volcanoes National Park
HETA 90-179

ANALYTE	**CONCENTRATION**	**NIOSH REL**	**ACGIH TLV**	**OSHA PEL**
Respirable Dust	0.12 to 1.3 mg/m^3	None	None	5 mg/m^3
Respirable Crystalline Silica	None detected (ND)	0.05 mg/m^3[a]	0.1 mg/m^3[b]	0.05 mg/m^3
Calcium	ND to 0.03	None	None	None
Copper (both dust and fume)	ND to 0.005	0.1 mg/m^3[c] 1.0 mg/m^3[d]	0.2 mg/m^3[c] 1.0 mg/m^3[d]	0.1 mg/m^3[c] 1.0 mg/m^3[d]
Iron (both dust and fume)	ND to 0.005	5 mg/m^3	5 mg/m^3[c]	10 mg/m^3
Magnesium	0.01 to 0.13	None	None	None
Sodium (as sodium chloride)	0.12 to 1.0	None	10 mg/m^3[e]	15 mg/m^3[e]
Hydrochloric acid	LOQ to 9.1 ppm[f] 0.45 to 12 ppm[g] 0.2 to 8.0 ppm[h]	5 ppm	5 ppm	5 ppm
Hydrofluoric acid	ND to 0.5 ppm[f] ND[g] LOQ to 1.0 ppm[h]	3 ppm[i] 6 ppm[j]	3 ppm[j]	3 ppm[i] 6 ppm[j]

* = These sampling results are from a related NIOSH HHE (RDHETA 90-200) conducted in 1990 at the request of the Hawaii State Health Department. All criteria are time-weighted averages over the work shift unless otherwise noted.

ND = Non-detectable
mg/m^3 = milligrams per cubic meter
ppm = parts per million
ACGIH = American Conference of Governmental Industrial Hygienists (Threshold Limit Values)
NIOSH = National Institute for Occupational Safety and Health (Recommended Exposure Limits)
OSHA = Occupational Safety and Health Administration (Permissible Exposure Limits)

Footnotes:

a NIOSH considers crystalline silica to be a suspect human carcinogen and exposures should be reduced to at least 0.05 mg/m^3.
b Crystalline silica, expressed as quartz.
c When present as a fume.
d When present as a dust.
e Particulate matter not otherwise classified.
f Collection method for inorganic acids using silica gel tubes.
g Collection method for inorganic acids using sodium hydroxide-filled impingers.
h Collection method for inorganic acids using distilled water-filled impingers.
i Time-weighted average over an eight- to ten-hour work shift.
j Short-term exposure limit (15 minutes).

Table I
RESULTS OF WATER SAMPLE ANALYSES FOR PERCHLOROETHYLENE, LEAD, AND pH
Hawaii Volcanoes National Park
HETA 90-179
March 29-30, 1990

			Concentration, (ppb)[2]		
Date	Time	Sample Location[1]	Perchloroethylene	Lead	pH
3/29/90	0915	Research Center: Wash tub outside pesticide storage area	(1.1)	ND[2]	7.8
3/29/90	0923	Spigot outside Maintenance Foreman's Office	(1.8)	ND	6.8
3/29/90	0936	Sample from horizontal pipe outside of Pump House	ND	13	4.5
3/29/90	0943	Filter Plant: Slow Sand Filter, Spigot alongside 20,000 gallon tank	3.3	(2.0)	5.1
3/29/90	0950	Filter Plant: Chlorinator Room, Spigot next to exterior wall	(0.6)	(2.0)	6.3
3/29/90	1005	Park Headquarters/Visitor's Center: Wash tub in janitor's closet	(1.1)	4.7	6.4
3/29/90	1018	Namakani Paio Campground: Sink in Men's Restroom	6.5	5.3	6.7
3/29/90	1053	Downtown Pahala: Fire hydrant at Ohia and Kamani Streets	ND	ND	7.5
3/29/90	1122	Volcano House Hotel: The kitchen sink alongside the food preparation tables (directly below No Smoking Sign)	(1.5)	ND	6.7
3/29/90	1143	Thurston Lava Tube area: Drinking fountain near parking lot	(1.4)	6.5	6.6
3/29/90	1210	Hawaii Volcano Observatory: Wash tub in janitor's closet	7.6	ND	6.9
3/30/90	0906	Kamoamoa Campground & Picnic area: Sink in Men's Restroom	ND	ND	7.6
3/30/90	1014	Kilauea Military Camp: Ice Maker in cafeteria	ND	(3.0)	6.7
3/30/90	1030	Volcano Golf Course Restaurant: Sink in the food preparation area	ND	ND	7.6
3/30/90	1106	Keaau County Standpipe: HVNP water meter on Pahoa Road Adjacent to St. Rd. #130	ND	ND	7.5
Evaluation Criteria:			**5.0**	**50**	**6.5-8.5**
Laboratory Analytical Limit of Detection (LOD)			**0.5**	**2.0**	**±0.1**
Laboratory Analytical Limit of Quantitation (LOQ)			**2.0**	**3.5**	

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1. All water samples were collected from the cold water tap after the water had been flowing from one to two minutes
2. ppb = parts per billion
3. ND = non-detectable concentration