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Acid gas hazards in the crater of Villarrica volcano (Chile)

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ABSTRACT

The atmospheric concentrations of the acid gases SO_2, HCl, and HF were measured during austral summer 2001 in the summit crater area of Villarrica volcano using 'filter packs'. These data were collected in order to assess the acid gas hazards to tourists who ascend the volcano. The authors compared their acid gas concentration results with exposure limits outlined by the National Institute of Occupational Safety and Health (NIOSH-United States of America). The authors conclude that tourists who visit the summit crater of Villarrica may be exposed to non-lethal concentrations of SO_2 and HCl that exceed the recommended exposure limits defined by NIOSH, while atmospheric concentrations of HF do not exceed the recommended exposure limits.

Key words: Volcanic gases, Hazards, Sulfur dioxide, Villarrica volcano, Chile.

RESUMEN

Peligros de gases ácidos en el cráter del volcán Villarrica (Chile). Las concentraciones atmosféricas de los gases ácidos SO_2, HCl y HF se midieron durante el verano austral de 2001 en el área del crater somital del volcán Villarrica, usando paquetes de filtro, para evaluar los peligros de gases ácidos para los turistas que ascienden el volcán. Los autores compararon los resultados de los gases ácidos con límites de exposición delineados por el 'National Institute of Occupational Safety and Health' (NIOSH-Estados Unidos de Norteamérica). Los autores concluyeron que los turistas que visiten el cráter somital del volcán Villarrica pueden estar expuestos a concentraciones no letales de SO_2 y HCl que exceden los límites de exposición recomendados por NIOSH, en tanto las concentraciones atmosféricas de HF no exceden los límites de exposición recomendados.

Palabras claves: Gases volcánicos, Peligros, Dióxido de sulfuro, Volcán Villarrica, Chile.

INTRODUCTION

Villarrica volcano is a 2,847 m high, subduction zone stratovolcano located in the southern Chilean Andes (39.5°S), that has been continuously degassing from its summit crater since the end of the last eruption in 1985. Like other volcanoes, the volcanic gas plume emitted from Villarrica is dominated by water vapor; however, noxious, acid gases (*e.g.*, SO_2, HCl, and HF) are also released (Witter, 2003). The occasional presence of an active lava lake in the summit crater (Calder *et al.*, 2004) combined

with a relatively easy ascent make climbing to the top of Villarrica an attraction for many tourists. During the summer months, up to 100 tourists per day ascend to the summit of the volcano to look into the degassing crater (mountain guide M. Bustamante and CONAF park ranger M. San Martin, oral communication, 2001). Park rangers at Villarrica National Park require tourists to climb with local mountain guides to ensure their safety during ascent and descent of the volcano. However, there exist no regulations that require tourists to wear gas masks to protect themselves from the potential dangers of breathing noxious volcanic gases in the summit region. Therefore, many of the tourists who approach the summit crater may expose their respiratory systems to the acid gases SO_2, HCl, and HF that are emitted by the volcano. At low concentrations, SO_2, HCl, and HF cause irritation to the eyes, mouth, throat, and nasal passages. At high concentrations, these acid gases cause burns to the skin, mouth, throat, and nasal passages and can even result in death (Williams-Jones and Rymer, 2000; NIOSH Pocket Guide to Chemical Hazards, http://www.cdc.gov/ niosh/npg/npg.html). In this study, the authors set out to quantify the range in concentrations of the acid gases SO_2, HCl, and HF that tourists may be exposed to in the summit crater area of Villarrica volcano. The authors compared their results with exposure limits for these gases recommended by the National Institute of Occupational Safety and Health (NIOSH–United States of America).

ANALYTICAL METHODS

SAMPLE COLLECTION

The authors used a gas filtration method called 'filter packs' to measure the atmospheric concentrations of acid gases (S, Cl, and F) in the summit crater area of Villarrica volcano in January and February 2001. This method collects trace gases in the atmosphere using impregnated filters. It is analogous to gas filtration methods used at Masaya (Stoiber *et al.*, 1986), Erebus (Zreda-Gostynska *et al.*, 1993), and Etna (Pennisi and LeCloarec, 1998). We filtered ambient gases (a mixture of atmospheric air and volcanic gases) while standing within Villarrica's billowing volcanic gas plume on the innermost, accessible rim of the actively degassing summit crater. The filter pack instrument (Fig. 1) consists of a small vacuum pump which sucks the ambient gases through a series of three paper filters (Whatman 2.2 cm diameter ashless Grade 42 filters) each impregnated with a saturated sodium bicarbonate solution. The gases were pre-filtered with a 10 μm Teflon mesh to minimize intake of airborne aerosols and ash particles. The average flow rate of ambient gases through the pump was measured (in liters per minute) using a flow meter with ball float. Total filtration time varied from 3 to 46 minutes. Filtration time was chosen so that nearly all of the acid gases were absorbed by the first two filters in the filter stack. In this manner, we avoided problems of oversaturation of the three filters that results in inaccurate

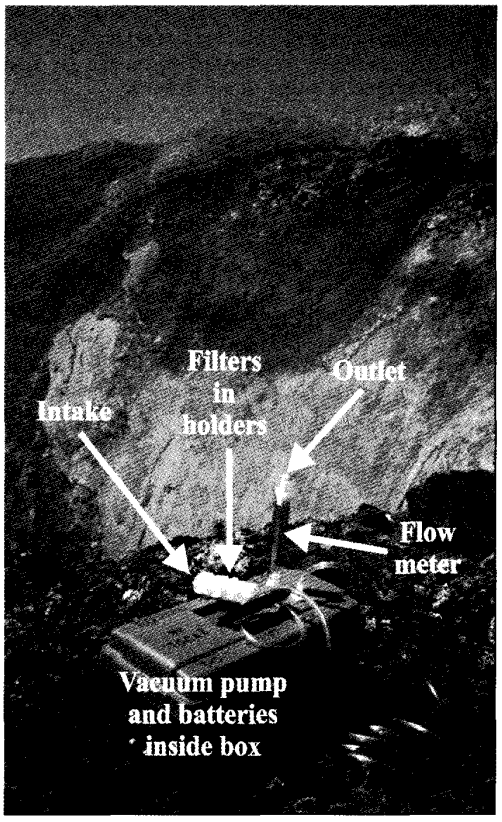

FIG. 1. 'Filter pack' instrument situated on the edge of the summit crater of Villarrica volcano.

measurements. From the flow rate measurements and total filtration time, we calculated the total volume of filtered air. Twenty-two gas measurements were made using filter packs on eight separate summit days over the course of one month.

LABORATORY ANALYSES

After gas filtration at the volcano, the filters were soaked in 10 mL of deionized water to extract S, Cl, and F in the forms of sulfate, sulfite, chloride and fluoride anions. The total mass of the acid gas species (mg of SO_2, Cl, and F) absorbed onto the filter paper were determined by ion chromatography at Département des sciences du Sol, Université Catholique de Louvain of Belgium (P. Delmelle, analyst). The oxidation of sulfite to sulfate during the analysis was blocked by adding a few μL of formaldehyde to all samples. Total sulfur (as SO_2) was obtained by summing the concentrations of sulfite and sulfate. The error on sulfate, sulfite, chloride and fluoride determinations is less than 5%.

RESULTS

The total mass of acid gases absorbed onto the filters (in mg), divided by the total volume of air filtered (in m^3) gives the atmospheric concentration of acid gases in mg/m^3 at the ambient pressure and temperature conditions in the Villarrica summit crater area. Measurements of atmospheric acid gas concentrations made on the same day varied widely as did measurements made on different days. Measured sulfur dioxide concentrations range from 3.7-38.2 mg/m^3 SO_2. Hydrochloric acid concentrations range from 1.2–8.3 mg/m^3 HCl. Lastly, hydrofluoric acid concentrations have the range 0.1-1.0 mg/m^3 HF (Table 1).

The authors compared their measurements of acid gas concentrations (Table 2) with exposure limits for SO_2, HCl, and HF outlined in the NIOSH Pocket Guide to Chemical Hazards (http://www.cdc.gov/niosh/npg/npg.html). According to NIOSH, gas concentration levels that should not be exceeded at any time are termed Recommended Exposure Limits (REL). NIOSH outlines a higher exposure limit which is considered Immediately Dangerous to Life and Health (IDLH). None of the atmospheric acid gas concentration measurements that the authors made at Villarrica volcano exceed the IDLH limit for SO_2, HCl, or HF. In addition, measured atmospheric HF concentrations in the Villarrica crater area were found to be consistently lower than the REL for HF. However, out of the 22 measurements of atmospheric acid gas concentrations, eleven exceed the REL for SO_2 and one exceeds the REL for HCl.

The authors' results show that, during the study period, SO_2 and HCl were present in sufficient concentrations to pose a non-lethal health hazard to individuals breathing ambient air in the summit crater area of Villarrica volcano. If the authors use the frequency with which measurements from this study exceed the REL for SO_2 and HCl, then the relative health hazard from SO_2 was greater than that from HCl. Measured atmospheric gas concentrations of HF were consistently low and posed no short-term health hazard.

DISCUSSION

The atmospheric concentrations of acid gases encountered in and around the summit of Villarrica are a function of the total flux of acid gases out of the summit crater, the direction of travel of the gas plume after emission from the crater, and the rate of mixing and dilution of the acid gases with ambient air. As a result, we can expect that atmospheric acid gas concentrations vary widely with the acid gas emission rate, azimuth around the crater, distance from the actively degassing crater, and wind conditions. The large range in the atmospheric acid gas concentrations measured in this study is likely dominated by variations in the acid gas emission rate. The authors attempted to minimize the influence of the other effects by collecting the filter pack samples while standing in the gas plume at the

TABLE 1. VILLARRICA VOLCANO FILTER PACK DATA FOR JANUARY AND FEBRUARY 2001.

ANALYTICAL DATA									FIELD DATA			
				Raw Data (mg)[b]		Total mass acid airflow rate			Average time	Filtration air filtered	Volume of (mg/m³)[d]	
(mg/l)[a] Date	Sample No.	F	Cl	SO_3	SO_4	F	Cl	SO[c]	(L/min)	(min)	(liters)	HF
1/20/01	A	0.4	3.5	3.8	20.0	0.004	0.028	0.150	4.5	3	13.5	0.3
1/20/01	B	1.3	8.3	20.0	47.5	0.013	0.076	0.464	3.3	12.25	39.8	0.3
1/25/01	A	3.2	22.6	90.3	62.0	0.032	0.218	1.122	3.6	30	108.8	0.3
1/25/01	B	1.9	15.7	46.0	39.4	0.019	0.150	0.617	1.9	46.5	88.4	0.2
1/25/01	C	0.4	4.7	4.9	14.6	0.004	0.039	0.123	2.1	15.5	33.2	0.1
1/28/01	A	5.1	39.5	160.9	101.6	0.051	0.388	1.952	2.2	32	71.3	0.8
1/28/01	B	2.9	20.1	81.3	46.5	0.029	0.193	0.948	3.4	15	50.6	0.6
1/28/01	C	1.3	11.8	41.5	31.0	0.013	0.111	0.526	1.4	10	13.8	1.0
2/2/01	A	4.5	30.2	145.4	82.6	0.045	0.295	1.701	3.4	37.5	128.3	0.4
2/2/01	B	3.3	20.3	88.3	54.0	0.033	0.196	1.053	5.6	15.5	86.2	0.4
2/2/01	C	3.3	19.6	78.4	51.7	0.033	0.189	0.958	5.6	11	61.1	0.6
2/8/01	A	2.4	19.8	67.8	54.1	0.024	0.191	0.890	2.8	25	68.8	0.4
2/8/01	B	1.9	15.1	52.6	44.3	0.019	0.143	0.703	2.8	15	41.3	0.5
2/8/01	C	0.7	6.1	14.0	18.7	0.007	0.054	0.224	1.8	7	12.3	0.6
2/13/01	A	2.4	21.6	64.9	53.7	0.024	0.209	0.864	1.9	20	37.5	0.7
2/13/01	B	1.4	10.9	25.7	37.3	0.014	0.102	0.442	1.8	11	19.3	0.8
2/13/01	C	0.6	5.6	9.3	17.8	0.006	0.049	0.180	2.3	5	11.3	0.6
2/17/01	A	0.8	11.3	32.9	35.0	0.008	0.106	0.484	1.8	20.5	35.9	0.2
2/17/01	B	0.7	6.1	15.0	18.9	0.007	0.054	0.233	1.8	10	18.0	0.4
2/17/01	C	0.2	3.1	3.7	11.5	0.002	0.023	0.093	1.6	4.8	7.8	0.3
2/21/01	A	0.8	9.2	26.7	28.5	0.008	0.085	0.391	2.1	20	41.6	0.2
2/21/01	B	0.5	5.2	13.6	14.7	0.005	0.045	0.193	1.8	10	17.5	0.3

Blank No.	F (mg/L)	Cl (mg/L)	SO_3 (mg/L)	SO_4 (mg/L)
Blank No. 1	0.0	0.8	0.0	2.2
Blank No. 2	0.0	0.7	0.0	2.0
Blank No. 3	0.0	0.7	0.0	1.8
Blank Average	0.0	0.7	0.0	2.0

[a] Filters soaked in 0.01 L of deionized water to extract S, Cl, and F.

[b] Total Mass Acid = (Raw Data - Blank) * 0.01 L.

[c] Convert SO_3 and SO_4 raw data to SO_2 (using ratios of molecular weights) t

[d] Concentration = Total Mass Acid / Volume of Air Filtered.

Note: 1,000 Liters = 1 m^3.

Gas samples were collected through a stack of three filters impregnated with a sodiumbicarbonate solution. S, Cl, and F were extracted from the filters a and F were analyzed by ion chromatography.

TABLE 2. COMPARISON OF ATMOSPHERIC ACID GAS CONCENTRATIONS MEASURED IN THIS STUDY WITH EXPOSURE LIMITS RECOMMENDED BY THE NIOSH.

NIOSH	HF	HCl	SO_2
REL	5	7	13
IDLH	25	75	262
This study	HF	HCl	SO_2
Minimum	<1	1	4
Maximum	1	8	38

All data are in units of mg/m^3. The acid gas exposure limit which NIOSH recommends is not to be exceeded at any time is denoted REL. A higher limit (IDLH) is regarded as immediately dangerous to life and health. REL = Recommended Exposure Limit. IDLH = Immediately Dangerous to Life and Health; NIOSH= National Institute of Occupational Safety and Health, USA.

edge of the summit crater where acid gas concentrations are likely to be the highest.

Individuals caught within the gas plume, breathing air with dangerous acid gas concentrations can easily find safer air to breathe by moving away from and upwind of the summit crater or by donning a respirator outfitted with acid gas filtration cartridges. Acid gas concentrations that are higher than the range of values reported here are likely to be encountered only when individuals approach very close to the vent by climbing down into the summit crater and/or under degassing conditions characterized by total acid gas emission rates that are higher than those encountered during the study period (100-700 ton/day SO_2; Witter, 2003).

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