

Article

Exposure to Acid Aerosols in the Visiting Areas of the Poás Volcano National Park, Costa Rica

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Abstract: Poás Volcano made a magmatic eruption in April 2017. The volcanic outburst resulted in an ash and vapor column towering over three kilometers high. Since that time, there has been a continual release of gases, aerosols, and more recently, ash, posing potential issues for visitors and park rangers. In this work, the potential for exposure to acid gases and aerosols faced by park rangers, officials, and visitors to the Poás Volcano National Park was evaluated, and the concentrations found were compared with the exposure limits established by the Occupational Safety and Health Administration (OSHA). The study was conducted between October 2021 and November 2022. The concentrations of HCl(g), HNO₃(ac), HF(g), and H₂SO₄(ac) were determined at three strategic points: the ranger station, the visitor center, and the main crater viewpoint. The maximum concentrations obtained were (7.0 ± 1.6) ppb for HCl(g), (6.2 ± 2.8) ppb for HNO₃(ac), and (0.029 ± 0.044) ppm for H₂SO₄(ac). There were no concentration values above the detection limit (0.94 µg/m³) for HF(g). By comparing the data obtained with similar studies, it is concluded that the measured values in Poás Volcano National Park are low and only show similarities to the results found in volcanoes within the national territory. The exposure limit established by OSHA (0.02 ppm) was only surpassed by H₂SO₄(ac), and could be the cause of health effects experienced over the years by park rangers. To minimize these risks, the use of personal protective equipment and air quality monitoring is essential.

Keywords: acid aerosols; Poás volcano; exposure limits; chemical risk



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1. Introduction

Volcanic eruptions serve as a mechanism for the release of chemicals into the atmosphere. Among the main substances released are water vapor, carbon dioxide (CO₂), hydrogen sulfide (H₂S), sulfur dioxide (SO₂), hydrogen chloride (HCl), and hydrogen fluoride (HF) [1]. However, the release of substances does not only occur during volcanic eruptions, but some volcanoes remain active in gas and material emissions, such as the Poás Volcano. This volcano has a crater lake that undergoes cyclical evaporation depending on the season and the rainwater gathered during the rainy season [2,3]. This continuous emission has a presence of acidic gases and aerosols. In this area, the impact on vegetation is noticeable and directly linked to the acidic gases and aerosols created from the combination of solid material with liquid sulfuric acid (H₂SO₄) and nitric acid (HNO₃) particles enveloped in the expelled material from the crater. The aerosols have the ability to travel long distances, forming corridors of acidification throughout the surrounding region [4,5].

Near the National Park, there is an acidification alley heading west towards the Bajos del Toro area. Some effects associated with this exposure have been observed over the years, such as the fact that vegetation does not grow, and strong odors are perceived by residents of

the Grecia and Sarchí areas. This region is located near many communities in the province of Alajuela, including San Miguel, Poasito, San Pedro de Poás, San Roque, San Rafael, Sabana Redonda, and Fraijanes. Therefore, there is a latent risk for the residents, animals, and vegetation of these communities in the event of heightened volcanic activity [6].

The Poás Volcano National Park (Figure 1) is one of the 158 protected wildlife areas of the National System of Conservation Areas (SINAC). Over the years, it has become one of the most important tourist attractions nationwide. It brings economic benefits to both the country and the local trade of neighboring populations [7]. This volcano is known for its active state and its significant volcanic eruptions. By 2017, the activity intensifies with volcano–tectonic earthquake swarms. It leads to a first internal explosion on 28 March. Subsequently, the volcano continued its activity with the emission of gases and ash, as well as particulate material, and strong explosions of over 500 m in height between 13 April and 19 April. During that explosion, the structure of the dome located in the crater experienced a disappearance of approximately 90%. The infrastructure of the main viewpoint was also affected, and it suffered damage due to the expelled material [8,9].



Figure 1. Photograph of the Poás volcanic crater in the province of Alajuela, Costa Rica. taken by José Pablo Sibaja Brenes.

In April 2017, the volcano activity led the authorities to decide on the temporary closure of the national park to visitors, due to the imminent danger posed by the release of volcanic material [7,10]. This had consequences for the communities of Poasito, San Pedro de Poás, San Rafael, Sabana Redonda, and Fraijanes, because the visitation to the park decreased significantly, reducing the economic income of SINAC and local merchants [7,11].

During the initial phase of reopening, following a year and four months, the volcano's activity decreased, prompting authorities to implement a security protocol. This protocol involved shifts with time limits, restrictions on the number of visitors, the construction of protective buildings for visitors, and the mandatory use of safety equipment. These measures facilitated the reopening of the national park [7,12]. In a second phase, on 3 July 2022, the national park enabled the trail that connects the main crater with Laguna Botos. The entry of tourists was also increased with a maximum capacity of up to 1500 people, extending the stay time with a maximum of 20 min in the crater area.

Among the main components expelled during a volcanic eruption are gases such as sulfur dioxide (SO_2), which can interact in the atmosphere and produce sulfuric acid (H_2SO_4). Other compounds with acidic properties, like hydrogen fluoride (HF) and hydrogen chloride (HCl), are also released, which, together with the expelled particulate matter, form acid aerosols [6,13].

The study of these gases and acidic aerosols generated in eruptions allows for evaluating the effects on the fauna and flora of a location and neighboring communities. For example, the deterioration of water quality, damage to crops, the destruction of vegetation, death, or impact on local fauna. If rain or very high humidity occur around the volcano, a process of dragging the gases and acidic aerosols towards the water matrix can occur, leading to the phenomenon of acid precipitation or acid rain [14]. The pH of acid rain can reach values of 3.0 or less [15]. However, pH values ranging between 2.50 and 5.22 have been reported for rainwater samples taken at the overlook for visitors in the Poás Volcano National Park [16,17]. Additionally, there are health effects such as respiratory system problems, eye irritation, and skin irritation in park rangers, visitors of the National Park, or residents of the nearby communities [3,18].

Currently, the measures established to ensure the safety and health of people located at the volcano consider factors such as the precipitation of gases and aerosols on the surface, the smell of sulfur, and the concentration of SO_2 and H_2S in the environment, but do not ponder the levels of acidic components [7]. The objective of this study is to monitor the emissions of acidic gases and aerosols (H_2SO_4 , HNO_3 , HF, and HCl) in the Poás Volcano National Park. The goal is to establish technical criteria that will assist the SINAC authorities in decision-making processes related to estimating the daily times of stay in visitation areas and the exposure of park rangers who are in the area. For such a purpose, we are comparing the values obtained with the reliable exposure limits set by the Occupational Safety and Health Administration (OSHA) in the United States [19], which establishes the average exposure limits within any 8 h work shift.

2. Materials and Methods

2.1. Study Site Description

The study was carried out in the Poás Volcano National Park, Alajuela, Costa Rica. To collect the samples, 3 sampling points were established (Figure 2), specifically in areas where park rangers and visiting tourists spend most of the time: the ranger station, the visitor center (main entrance to the national park), and the main crater viewpoint.



Figure 2. Map of Poás Volcano National Park showing the geographical location of the defined sampling points.

2.2. Data Collection

For the sampling of HNO₃, HCl and HF denuders were used. They were placed at an approximate height of 1.5 m above the ground and had rain protection to prevent interference with the measurement [20–22]. A denuder is a device used in the sampling and analysis of atmospheric aerosols, designed to separate and collect specific gases from an air stream while removing particles before analysis. Denuders operate by absorbing gases onto surfaces coated with appropriate chemical reagents, in this case, with sodium carbonate and ethanol. In addition, another sampling method described in the “NIOSH Manual of Analytical Methods (NMAM) 4th Edition” was used for the measurement of HF, HCl, HNO₃, and H₂SO₄, for which a volume of air was passed through glass cartridges containing silica gel [23].

For transportation, the denuders were sealed at the ends of the glass with paraffin and the respective septum, then they were stored in a tube holder for protection. The samples contained in the glass cartridges with silica were transported in sealed envelopes with their respective caps. All samples were carried out under the protection of atmospheric conditions and light.

In the Laboratory of Atmospheric Chemistry (LAQAT) at the National University (UNA), the samples were stored under refrigeration (0 °C–4 °C) until the moment of analysis. An aqueous extraction was carried out on the denuders with 3 mL of deionized water, while the glass cartridges were extracted with 3 mL of a solution of sodium carbonate/sodium bicarbonate (NaHCO₃/Na₂CO₃).

The analysis of the samples was carried out using a Thermo Scientific (Sunnyvale, CA, USA) DIONEX[®] ion chromatograph, model ICS-5000 DUAL, with an anionic pre-column IonPac AG23 (4 mm × 50 mm), an anionic analytical column IonPac AS23 (4 mm × 50 mm), an electric conductivity detector, and a mobile phase of NaHCO₃/Na₂CO₃ following the procedure established in the “Standards Methods for the Examination of Water and Wastewater 23rd edition”. Concentrations for fluoride, chloride, nitrate, and sulfate ions were obtained from the acidic substances collected [24,25].

The data obtained were compared to reports from other volcanic parks (Popocatepetl in Mexico, Majkjsaya in Nicaragua, Kilauea Volcano in the Hawaii region, Mount Yasur in Vanuatu, and Villarrica Volcano in Chile, as well as a case study on Poás Volcano and Turrialba Volcano). Finally, a comparison was made against the limits set by OSHA for the acid aerosols studied to assess the level of exposure by visitors and workers in the national park.

2.3. Data Analysis

The concentration of acid aerosols acquired was related to location of the sampling sites in the volcano park and the environmental conditions that can directly affect the dispersion of acid aerosols into visitation areas. For this purpose, the statistical processing software MINITAB 1.4.0. was used.

The data obtained from the sampling campaigns was interpreted through a mean comparison against OSHA exposure limits to determine the effects that a person may experience when visiting the three study points within Poás Volcano National Park.

These interpretations generated a technical criterion with a scientific basis, allowing for the determination of whether the concentrations of acid aerosols in the area are below or exceed OSHA limits. This information is crucial to establish visitation times, aiming to project responsible tourism in the area.

3. Results and Discussion

Figures 3 and 4 show the concentration found for H₂SO₄ at the sampling points during the daytime and nighttime. The concentration increases as it approaches the emission point (main crater). At the park ranger’s house, maximum values of (0.0019 ± 0.0022) ppm were found during the day and (0.012 ± 0.019) ppm at night. At the visitor center, this analyte reached a maximum of (0.0062 ± 0.0085) ppm during the day and (0.012 ± 0.022) ppm at

night. At the crater viewpoint, a maximum concentration of (0.0030 ± 0.0045) ppm was reported during the day, with one exception on 26 October 2021, where a concentration of (0.023 ± 0.037) ppm was recorded. During the nighttime, values were higher, ranging from (0.021 ± 0.032) ppm to (0.029 ± 0.044) ppm.

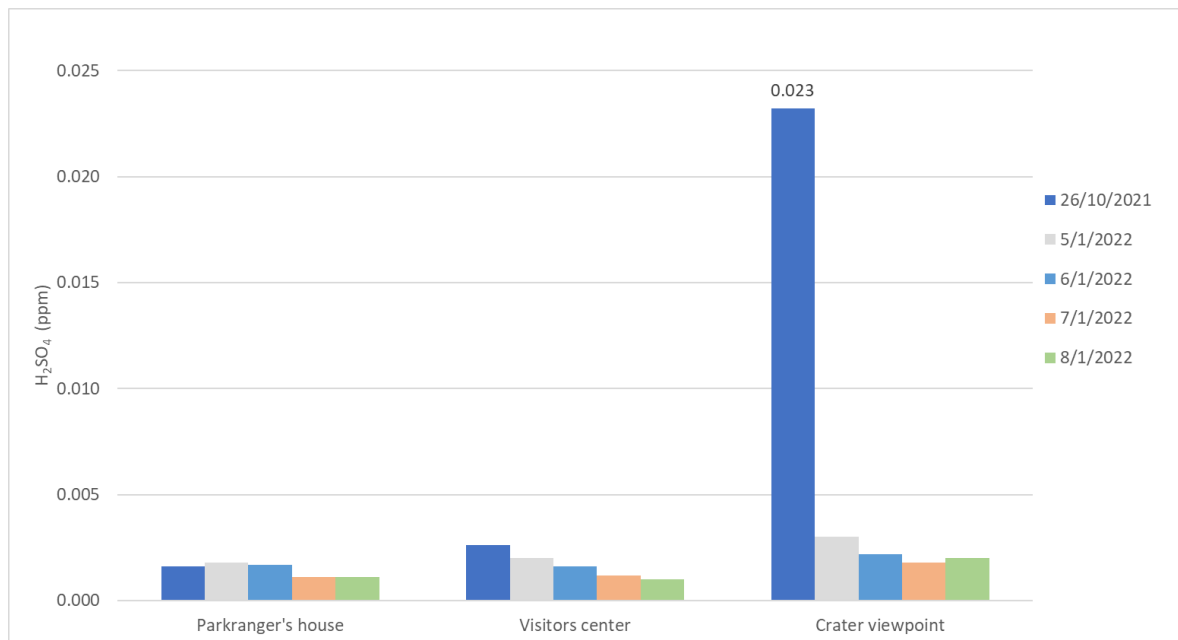


Figure 3. Concentration of H₂SO₄ in parts per million, according to daytime sampling points and dates.

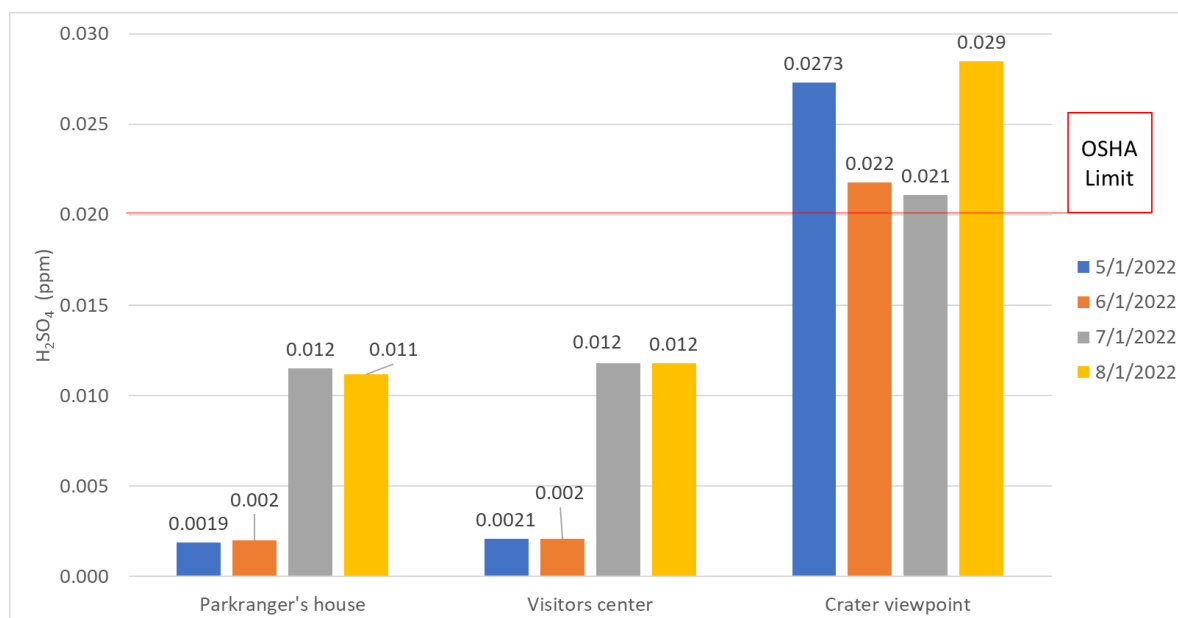


Figure 4. Concentration of H₂SO₄ in parts per million, according to nighttime sampling points and dates.

HCl concentrations below the established detection limit of $0.89 \mu\text{g}/\text{m}^3$ were obtained for the days 26 October 2021, 11 December 2021, and 29 November 2022. During the week of 5–8 January 2022, extremely low values were obtained with a maximum of (7.0 ± 1.6) ppb (Figure 5).

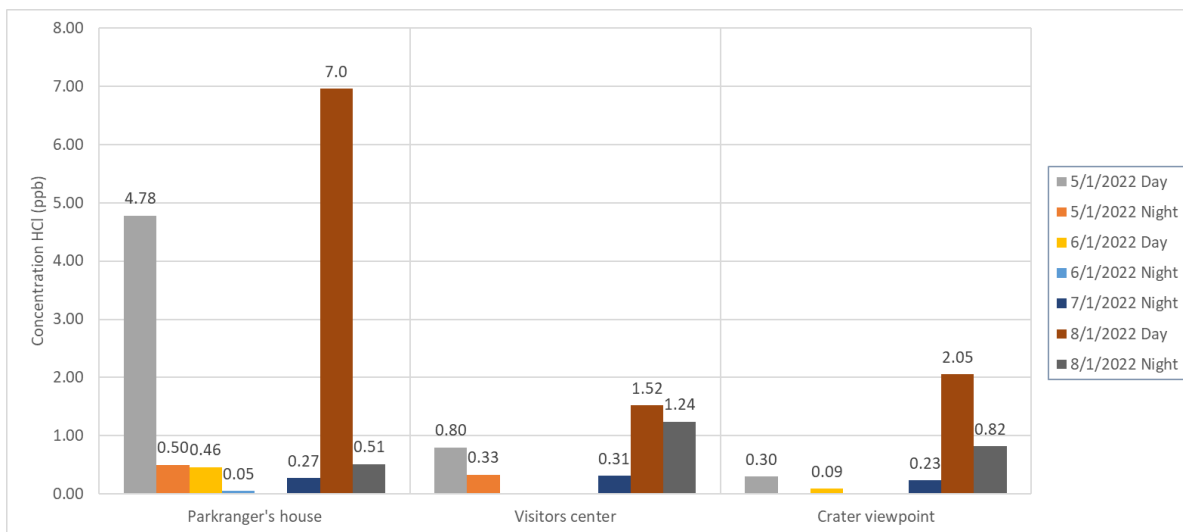


Figure 5. Concentration of HCl in parts per million, according to the sampling points and dates.

Figure 6 shows the concentrations obtained for HNO₃. The highest value for this analyte was (6.2 ± 2.8) ppb on 26 October 2021, at the main crater viewpoint.

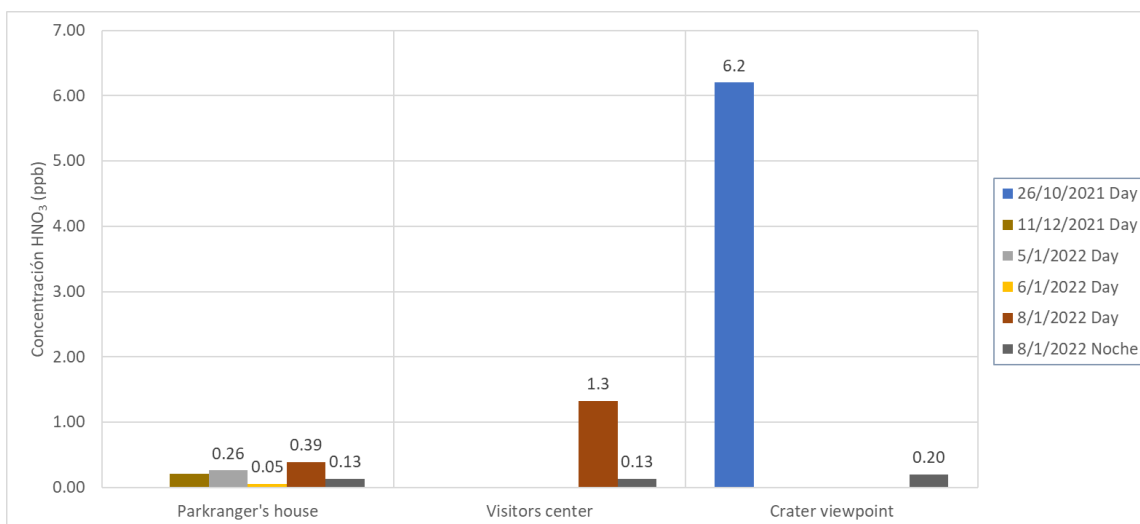


Figure 6. Concentration of HNO₃ in parts per million, according to sampling points and dates.

In general terms, the results obtained for HF, HCl, and HNO₃ show extremely low or undetectable values compared to the limits under study. The high solubility of these compounds, along with the high cloudiness and relative humidity present in Poás Volcano National Park, can cause these substances to be carried by the water in the atmosphere. This has been reported in previous studies at the site through the collection of rainwater between 2017 and 2019 [16,17]. During the time, the study was in place, the pH level of rainwater showed a variation between 2.50 and 5.22, evidencing the acidity level of rainwater near the emission source of gases and acid aerosols. The concentrations of anions reported by Bolaños et al. (2024) were up to (239 ± 5) mg/L for the sulfate ion, (301 ± 7) mg/L for chloride, and (66 ± 2) mg/L for the fluoride ion.

3.1. Weather Station Data

According to the data from the station of the Foundation for the Development of the Central Volcanic Range (FUNDECOR) during the sampling days, a constant airflow was observed heading northwest. This airflow could have prevented higher levels of pollutants

from reaching the visitation area at the Poás Volcano [17]. However, this may change during the day or throughout the year, as shifts in the wind direction towards the south or southwest have occurred within periods of up to 30 min to 3 h, prompting alerts to the visitors, reducing the time spent in the areas, and even leading to site closures.

The weather station data show temperatures ranging between 14 to 17 °C during the day, while at night, temperatures between 5 °C and 8 °C were recorded [26]. When air is heated, its density decreases, leading to the elevation of air columns within the troposphere. This phenomenon disperses gases and acidic aerosols to higher altitudes, making their sampling at the surface level difficult. During night samplings, the absence of solar radiation causes gases and aerosols in the troposphere to concentrate in the lower layers of the atmosphere [27].

Out of the gases studied, HF did not have values above the detection limit of 0.94 µg/m³. So the presence of the gas does not present a critical concentration in the study area.

3.2. Limits Established by OSHA

The maximum value recommended by OSHA over an 8 h period for H₂SO₄ is 0.02 ppm, a quantity that was not exceeded at the sampling points except on 26 October 2021, with a value of (0.023 ± 0.037) ppm. In contrast, during the night measurements, it was observed that, in the four consecutive samplings that were carried out, the OSHA limit value was exceeded with values in the range of (0.021 ± 0.032) ppm to (0.029 ± 0.044) ppm. Exposure during the night should be considered by park rangers and decision makers in the health area, as the acidic aerosols reach the rest area at concentrations that exceed the recommended levels for occupational exposure.

The limit established by OSHA for HCl is 300 ppb, and the highest concentration obtained in the study was (7.0 ± 1.6) ppb in the park ranger's house. This result represents 2.32% of the limit, allowing the results to be considered insignificant regarding the exposure to this gas. For HNO₃, the highest concentration obtained was (6.2 ± 2.8) ppb on 26 October 2021, at the main crater viewpoint. This result is much lower than the established exposure limit of 2000 ppb, representing only 0.31% of this value.

The park staff has automatic SO₂ and H₂S meters, which are used 24 h a day to quantify and generate a warning (alarm, vibration, and lights) in the event of an increase in the concentration of the two gases measured. Acid aerosols are not detectable by the current meters, so it is recommended to develop a possible health plan for people that considers acidic substances, especially for H₂SO₄.

3.3. Comparison with Other Volcanic Places

It is noticeable in the literature there is little information about events and measurements of acidic gases and aerosols in relation to their exposure to people. Usually, the episodes are isolated for each compound and exposure analyses focus on measuring the concentration of SO₂, and to a lesser extent that of H₂S. This is because SO₂ and H₂S are gases that are emitted in greater quantity by the volcano, making their analysis methodology simpler compared to determining acidic aerosols.

Regarding reports on gases and acidic aerosols, a study was carried out at Popocatepetl volcano, Mexico, where in 1997 concentrations of approximately 0.3 ppm of HF and 1 ppm of HCl were reported. These data were obtained around the crater, 1 km from the emission source [28]. In Masaya, Nicaragua, measurements were taken with variable times between 12 min and 110 min, at 200 m from the edge of the crater. The concentrations of HF found in 1999 were greater than 4 ppm and those of HCl were greater than 23 ppm. The measurements for HF in 2001 were 0.567 ppm and for HCl 0.902 ppm [29]. In 1990, on the Kilauea volcano in Hawaii, due to the interaction between lava and seawater, a concentration of HF that was less than 1 ppm was released near the site in one of the cones. By 2004, concentrations ranged from 3 ppm to 15 ppm of HF [30]. On Mount Yasur, Vanuatu, concentrations between 3 ppm and 9 ppm for HCl were obtained in 1988 [31]. In Villa Rica, Chile, measurements were also taken with times ranging from 3 min to 46 min at

200 m from the crater edge. Occasionally, concentrations greater than 5 ppm of HCl have been measured at this volcano, depending on the activity found [32].

Similar studies conducted in Costa Rica report on the Poás volcano, measurements of acid aerosols in the air for a period of 4 h at the ranger station, toll booth, and park viewpoint. Concentrations of HCl ($<30 \mu\text{g}/\text{m}^3$), HF ($<30 \mu\text{g}/\text{m}^3$), and HNO_3 ($<10 \mu\text{g}/\text{m}^3$) were obtained [17]. Measurements of acid aerosols in the air were also taken at the Turrialba volcano for a period of 4 h, at the La Central Farm School, ranger station, and park viewpoint, reporting concentrations of HCl (LD = $30 \mu\text{g}/\text{m}^3$), HF (LD = $30 \mu\text{g}/\text{m}^3$), and HNO_3 (LD = $10 \mu\text{g}/\text{m}^3$) [17].

Currently, there is a scarce number of measurements published by volcanic institutions around the world, which makes this study important to provide a perspective regarding other acidic substances that can affect life and structures in a volcanic park. When comparing the results of the acids found in other volcanic parks with the values measured at the Poás Volcano, it is evident how the values obtained in this study are extremely low. However, international reports in the literature were carried out directly in the volcanic plume, where the concentrations are maximum as it is the emission source. In this study, the concentrations evaluated are for occupational exposure, and the closest sampling point (the main crater overlook) is located at 720 m in a straight line to the emission zone, so air currents and temperature can generate effects that deflect the trajectory of the acidic gases and aerosols from the sampling system.

Other studies carried out in Costa Rica by [17] in 2017 and 2018 involved measurements which were taken over a period of 4 h during the day, and the quantities found were consistently below the detection limit of the method. These studies revealed that the concentrations of the substances of interest are low and that a 4 h period would not be sufficient for sampling. When comparing the values with those reported in 2022 [33], it is demonstrated that 8 h measurements are just enough to quantify acidic aerosols, with the impact of acids in the air being low but not negligible.

4. Conclusions

Concentrations of gases and acidic aerosols were measured in the Poás Volcano National Park, whereas for HF, values above the detection limit ($0.94 \mu\text{g}/\text{m}^3$) were not obtained. For HCl, the maximum concentration obtained was (7.0 ± 1.6) ppb; in the case of HNO_3 , the maximum value obtained was (6.2 ± 2.8) ppb, and for H_2SO_4 , the maximum concentration obtained was (0.029 ± 0.044) ppm. Contrasting the air quality during the day and night, the concentrations recorded during the nighttime were up to 10 times higher than those registered during the day in the national park. The concentrations of acidic aerosols were very low compared to the values found in other volcanic environments internationally, as measurements of these substances have not been carried out in workplaces or visitation areas. Only at the Poás Volcano and the Turrialba Volcano, during 2018 and 2019, were aerosol samples taken, but with values below the detection limit, for a 4 h daytime period. Thus, this work represents a pioneering study where for the first time, acid measurements were made in the air for an 8 h period, both day and night. Only in the case of H_2SO_4 did the values obtained exceed the OSHA limit, which could be the cause of health effects experienced over the years by park rangers, leading to skin irritations and respiratory system effects. To minimize these risks, the use of personal protective equipment and air quality monitoring is essential.

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