

# Preliminary studies of acid and gas contamination at Poas volcano, Costa Rica

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**Abstract:** Primary volcanic phenomena are potentially catastrophic, whilst those of a secondary nature may be merely considered as background activity but may be of sufficient intensity to cause long-term suffering to indigenous populations. The latter is the case at Poas volcano in Costa Rica, where a change in the quiescent state of the volcano has been shown by increasing activity during the last decade. Acid gases are apparently now being emitted more intensely than before, particularly during the dry season, to the detriment of the health of people and domestic livestock living in the surrounding countryside. Damage to crops and farm buildings is also evident.

A pilot geochemical study has been undertaken at Poas volcano to determine the principal constituents of the gas emissions, the form in which they are most likely to be transported and the extent of the area within which they can be easily measured.

The results obtained indicate that emissions of mixed volatile acids contribute to the problems encountered, and that, as might be expected, seasonal changes and distance from the source also exert control. Rainfall effectively scrubs the acid gases during the wet season, thereby considerably ameliorating the immediate effects of the emissions.

Poas is a composite stratovolcano rising 1400 m above its surroundings in the populated Cordillera Central of Costa Rica (Fig. 1). The last major eruptions occurred in 1952/53, when phreatic activity resulted in the loss of the crater lake and culminated in the growth of a 45 m high

pyroclastic cone, which subsequently became the focus of continuous fumarolic activity. A new lake had formed by 1967 and reached a depth of about 50 m, circulating mildly acidic brines at about 40°C. Apart from minor fluctuations in level and temperature, and a brief period of

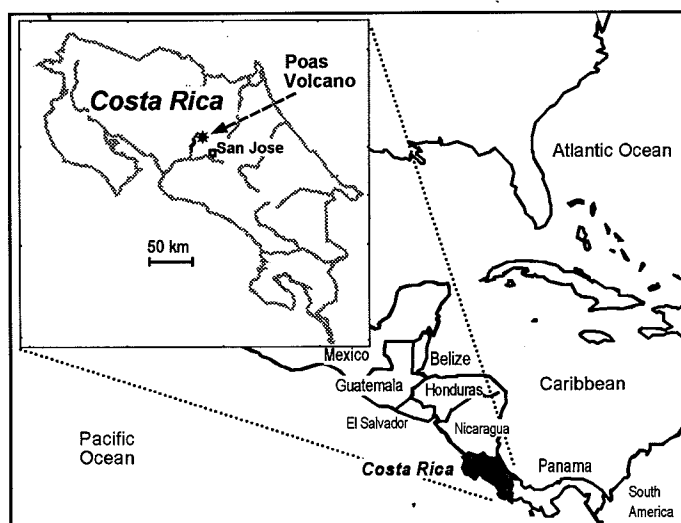


Fig. 1. Location of Poas Volcano, Costa Rica.

**Table 1.** Sulphur dioxide concentrations from long-term diffusion tubes (24 hour average)

Location	1991 ( $\mu\text{g SO}_2/\text{m}^3$ )	1992 ( $\mu\text{g SO}_2/\text{m}^3$ )
	Wet season conditions	Dry season conditions
Control tubes (Bajos del Toro)	0.4	4
Cajon	250	249
San Luis	299	730*
Trojas	60	124
Farm near summit	314	499*
Public viewpoint	117	156

Sample locations shown on Fig. 2.

\*Approximate data only due to normal tube capacity being exceeded.

geyser activity during 1978/79, the system appeared stable until early 1986 when a long-term decrease in the lake level and increase in acidity commenced. Intense geysering again occurred from June 1986 to July 1987, and these events heralded the start of a new magmatic cycle which has been studied by a variety of geophysical and geochemical techniques (Brown *et al.* 1989; Barquero & Fernández 1990; Rowe *et al.* 1992a,b). However, the environmental hazards posed by the escape of high temperature volcanic gases and aerosols are only now becoming apparent. The effects of acid gases can be seen on the western flank of Poas, which is completely denuded of vegetation on the inner-facing slopes for *c.* 1 km downwind, and only supports low scrub elsewhere.

### Gas monitoring

A preliminary visit to Poas took place in late 1991 towards the end of the wet season in Costa Rica, during which the proposed sampling was curtailed because of the danger of slope instability in parts of the crater induced by heavy rain (Nicholson *et al.* 1992). As Poas volcano comprises andesitic lavas separated by layers of unconsolidated volcanoclastic materials, periods of exceptional rainfall cause some areas to be liable to spontaneous collapse. During 1991, parts of the crater area were therefore considered inaccessible for safety reasons, and it was decided to repeat the sampling exercise when drier conditions would be encountered. This would also allow comparison of analytical data obtained during wet and dry seasons. During this initial visit long-term diffusion tubes were emplaced for approximately two weeks to determine sulphur dioxide gas concentrations around the volcano. Figure 2 indicates the approximate locations of these sample sites in relation to the active crater.

A second visit took place a few months later

in early 1992, when a marked difference was noted between the conditions encountered and those experienced at the end of 1991. Little or no rain fell throughout the entire visit, and there was only light precipitation from persistent afternoon cloud-cover. However, acid fall-out from the volcanic plume appeared to be more intense in the drier air, and this was evident by personnel experiencing dry throats and being able to smell 'sulphurous' fumes in the atmosphere. Brief interviews with local people confirmed this as typical of the dry season effects of the volcano (Nicholson *et al.* 1993).

### Results

In the populated areas downwind, several kilometres from the summit, acid gases were detected in the atmosphere, although the highest concentrations of sulphur dioxide ( $\text{SO}_2$ ) measured did not exceed 0.3–0.5 ppm over periods of a few minutes. These measurements were carried out using an MEI (Survey Plus) toxic gas monitor equipped with an electrolytic sensor for the detection of  $\text{SO}_2$ . Data subsequently obtained from the long-term diffusive gas samplers showed comparable values (Table 1).

During a visit to the crater rim on the north-western side of the volcano (Fig. 2) in 1992, the highest temporal  $\text{SO}_2$  concentration recorded using the toxic gas monitor was *c.* 35 ppm (Short Term Exposure Limit 5.0 ppm; HSE 1995). Stinging sensations caused by acid precipitation on exposed skin were pronounced. The acid gases present at this location were later confirmed by collecting the acid fall-out on filter papers impregnated with sodium formate, and measuring the sulphate and fluoride contents. On this later occasion low cloud within the crater obscured the view and variable air circulation ensured that the volcanic plume was constantly changing direction, and therefore levels of  $\text{SO}_2$  measured with the toxic gas

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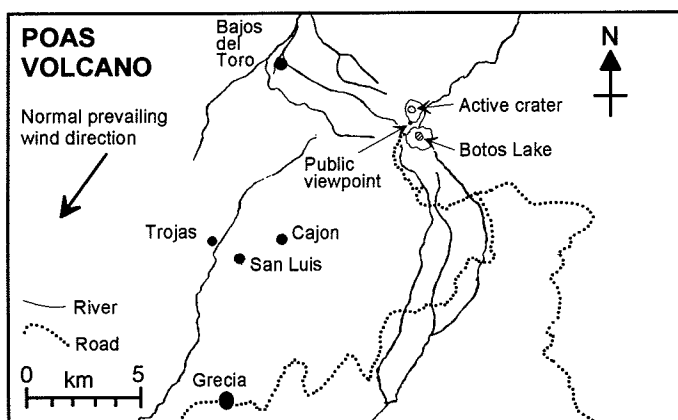


Fig. 2. Sampling locations, Poas Volcano.

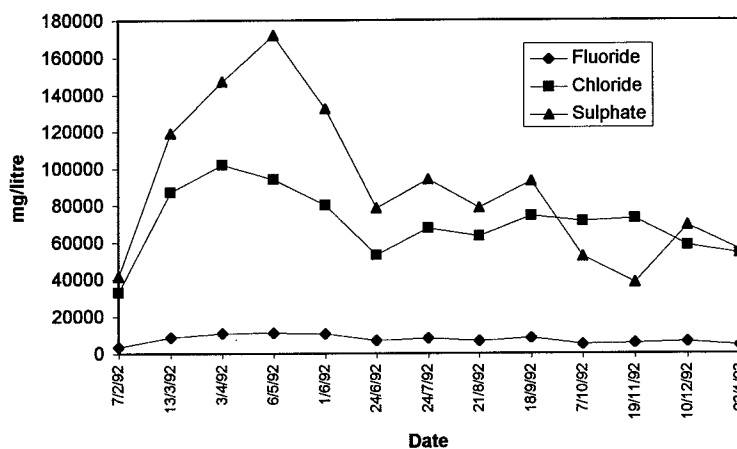


Fig. 3. Fluoride, chloride and sulphate concentrations measured in crater lake waters between February 1992 and January 1993.

monitor did not exceed 0.2 ppm at any one time. However, Draeger chemical diffusion tubes emplaced above open ground showed a total flux of 10 ppm  $\text{SO}_2$  over a four-hour period, i.e. 2.5 ppm per hour. The use of similar tubes confirmed that there was no hydrogen chloride or hydrogen sulphide at this location. Studies carried out at the public viewing platform on the southern side of the main crater, which is much closer to the source but normal to the prevailing wind direction, did not detect measurable concentrations of any of the three acid gases, even after five hours of exposure.

In the crater bottom, values of 2.5 and 5.0 ppm per hour for hydrogen chloride and  $\text{SO}_2$  respectively were obtained with the Draeger

chemical diffusion tubes; there was no indication of hydrogen sulphide. However, atmospheric  $\text{SO}_2$  concentrations measured using the toxic gas monitor ranged between 20 and 70 ppm. The wind direction was highly variable, and although positioned only 100 m–300 m from the source of the gases, it was often possible to work for prolonged periods without a respirator, because the gas plume was impacting throughout the caldera. This effect is very localized due to the nature of the terrain, and in no way affects the general southwesterly flow of the plume away from the crater (Fig. 2). It was not possible to approach any of the high temperature fumaroles venting through the remnants of the crater lake, due principally to the presence of acid waters

and thixotropic sediments, but it was possible to collect lake water samples.

#### *Crater lake water chemistry*

Major and trace elements in the water samples were determined by a combination of ICP/AES, ion chromatography, flow injection analysis, selective ion electrode and titrimetric techniques.

The pH of the crater lake water samples was not determined but previous investigations have shown that acid concentrations were generally high, with pH values of *c.* -0.5 being common (Rowe *et al.* 1992b).

Under such highly acid conditions it would be expected that any uncomplexed anionic species will be present as the free acids. Figure 3 shows the distribution of fluoride, chloride and sulphate in the lake waters throughout 1992/93, although practical difficulties associated with sampling from exactly the same location on each occasion may have slightly affected the overall results. These samples were collected by staff of OVSICORI-UNA (Observatorio Vulcanológico y Sismológico de Costa Rica-Universidad Nacional) as part of their routine sampling programme. In general much higher concentrations prevail throughout the drier months (December-April) indicating the gradual depletion by evaporation or drainage of the remnants of the lake, followed by dilution with rain water during the wet season. It was reported by local scientists that rainfall was much heavier than usual during the latter months of 1992 and early 1993. This obviously affected the concentrations of dissolved ions (Fig. 3), which would normally be expected to start increasing as the lake waters either evaporated or drained away (Brown *et al.* 1991).

#### *Gas geochemistry*

*Diffusion samplers.* To corroborate data on acid precipitation around the volcano, long-term diffusion tubes were emplaced at sites near the summit, and also at several locations on the downwind side, to collect SO<sub>2</sub>. The village of Bajos del Toro some 6 km from Poas summit (Fig. 2) was chosen as the background location because there is no record of gases having impacted on this area on a regular basis, and it was also readily accessible by road. Other areas could equally have served as background monitoring sites, but were either more difficult to approach or records of gas dispersion were incomplete. The other diffusion samplers were placed in villages where they would receive constant exposure to the volcanic gases, subject

to the prevailing winds. During the 1991 survey, tubes were emplaced for between 336 and 430 hours and during the 1992 survey for *c.* 600 hours. The tubes were subsequently returned to the UK for analysis; all data are shown in Table 1 calculated as an average exposure time over 24 hours.

At some locations measurements indicated significantly increased levels of SO<sub>2</sub> during the dry season in early 1992, compared to those obtained under much wetter conditions in 1991. However, the order of magnitude increase shown by the control tubes placed in the Bajos del Toro is well within the unexposed control variation of the tubes. The release of acid gases and aerosols into the environment is much greater during the drier months, due principally to the loss of the scrubbing effects of rainfall near the summit source.

*Impregnated papers.* Simple chemical absorption techniques were used to monitor the short-term variation of gas dispersion at different locations around the crater (Fig. 2). During the 1992 visit, a site was chosen on the crater rim, due north of the public viewpoint and directly under the 'normal' direction of the gas plume. One litre volumes of air were pumped through individual filter papers impregnated with sodium formate, at predetermined intervals over a period of almost four hours, during which time the aerial SO<sub>2</sub> concentration was monitored using the toxic gas monitor. The papers were then sealed in polyethylene bags and returned to the laboratory for analysis. Each paper was cut into two pieces, one being leached with distilled water for sulphate determination, and the other with a special buffer solution to extract the fluoride. The results are shown in Table 2, and for comparison, also include data for 1 litre volumes of air sampled on the top of the lava dome within the crater, at atmospheric SO<sub>2</sub> concentrations of 10-20 ppm. These latter samples are significantly higher due to greater exposure to high gas concentrations. It is to be expected that there would be a general increase in both fluoride and sulphate content, with the accompanying temporal increase in the measured aerial SO<sub>2</sub> concentration.

#### **Environmental and health effects**

It has been shown that there is a wide variation in the amounts of acid contaminants dispersing into the air from Poas crater lake. The damage to vegetation is readily visible immediately downwind of the volcano, but there are undoubtedly potentially more serious effects at

Table 2. Acid ion and SO<sub>2</sub> data from impregnated papers (1 l pumped samples)

Sample no.	Time	F <sup>-</sup> (mg l <sup>-1</sup> )	SO <sub>4</sub> <sup>-</sup> (mg l <sup>-1</sup> )	SO <sub>2</sub> (ppm)
1	12:15	0.15	0.64	3.0
2	13:00	0.11	0.53	0.4
3	13:15	0.10	0.42	0.4
4	13:30	0.09	0.87	0.6
5	13:45	0.10	0.54	0.2
6	14:00	0.10	0.66	0.2
7	14:15	0.15	0.54	0.4
8	14:30	0.22	0.56	0.3
9	14:45	0.20	0.55	0.6
10	15:00	0.25	1.79	1.5
11	15:15	0.31	1.63	1.0
12	15:30	0.29	1.76	0.8
13	15:45	0.32	1.99	1.8
Lava Dome		0.40	3.65	10.0
Lava Dome		0.50	7.87	15.0-20.0

During the 1991 survey, between 336 and 430 1992 survey for c. 600 subsequently returned to data are shown in Table exposure time over 24 measurements indicated levels of SO<sub>2</sub> during the survey, compared to those under conditions in 1991. A magnitude increase was placed in the Bajos where the unexposed control showed the release of acid gases into the environment is much more pronounced in 1992 months, due principally to the effects of rainfall

The chemical absorption method was used to monitor the short-term concentrations of SO<sub>2</sub> at different locations. During the 1992 visit, samples were taken from the water rim, due north of the crater rim, directly under the gas plume. One litre of water was passed through individual filter papers impregnated with sodium formate, and the other with a solution of sodium hydroxide. The samples were sealed and returned to the laboratory where each paper was cut into strips and placed in a beaker with distilled water, and the other with a solution of sodium hydroxide. The results are shown in Table 2, and for comparison with data for 1 litre volumes of water taken from the top of the lava dome in 1991. The atmospheric SO<sub>2</sub> concentrations in these latter samples are generally lower, due to greater exposure to the plume. It is to be expected that there will be a general increase in both SO<sub>2</sub> and F<sup>-</sup> content, with the accompanying increase in the measured

### Health effects

There is a wide variation in the concentrations of contaminants dispersing from the crater lake. The damage to vegetation is visible immediately after the eruption, but there are no serious effects at

greater distances from the summit, caused by the long-term low concentrations of these contaminants. The principal agricultural problems are likely to arise from general acid precipitation comprising halogen and sulphur acids, which readily disperse from the source during the dry season. Sulphur species measured as SO<sub>2</sub> have been monitored at least 7 km from the summit, and may cause health problems such as respiratory tract irritation and asthma attacks in susceptible people. The SO<sub>2</sub> results from higher strength sulphur acids being formed through evaporation of water during vapour transport (Nicholson *et al.* 1993). The formation of acid aerosols is suspected, and these preliminary measurements have indicated that although the amounts may be very small, they are a potential pathway through which acid gases escape to the environment. Further studies are needed to substantiate this.

The enhanced levels of SO<sub>2</sub> measured at some localities indicate the problems of acidic components in the atmosphere near the volcano, and are very conspicuous through visible damage to vegetation. This emphasizes the environmental problems created when a change in wind direction alters the fallout zone of the volcanic plume. During the wet season, many areas seem to be protected from the effects of the acidity, presumably because rainfall effectively scours the main acid components of the plume close to their source. The release of acid gases and aerosols into the environment is therefore apparently much greater during the drier months. Local farmers complained of aggravated respiratory problems during the dry season, and also damage to important (for

Costa Rica) cash crops such as coffee. WHO guideline exposure values for SO<sub>2</sub> are 30 µg/m<sup>3</sup> for plants and 50 µg/m<sup>3</sup> for humans (annual average), and 100 µg/m<sup>3</sup> for plants and 125 µg/m<sup>3</sup> for humans (24 hour average). Therefore by reference to Table 1 it can be seen that the recommended exposure levels to SO<sub>2</sub> are being routinely exceeded, in some locations by substantial margins. Visible foliar damage to coffee plantations and other vegetation several kilometres from the summit of Poas was indeed apparent on each of the field trips, and therefore invisible damage to soil profiles may also be expected, with obvious consequences for plant health. It is hoped to undertake further studies at Poas involving health studies of the local population and air monitoring of SO<sub>2</sub> and airborne particulates with the objective of assessing the health impacts of gaseous emissions from Poas volcanic crater lake.

Only a few of the contributors to this work can be acknowledged individually. Special mention should be made of Eduardo Malavassi, Jorge Barquero and Erick Fernández from OVSICORI-UNA, Costa Rica, all of whom gave either assistance with field investigations and/or helpful advice. We also thank colleagues in the BGS Analytical Geochemistry Group who undertook many chemical determinations, and Martin Williams, Glen Campbell and Clare Downing of Warren Spring Laboratory who provided the SO<sub>2</sub> diffusion tubes and also carried out the subsequent analyses. The late Professor Geoff Brown, and his colleague Dr Hazel Rymer, from the Open University also assisted with an introduction to the field area, and by providing geological information based on their personal experiences over many years working at Poas.

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