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Atmospheric dispersion, environmental effects and potential health hazard associated with the low-altitude gas plume of Masaya volcano, Nicaragua

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Abstract Masaya volcano (560 m a.s.l.), Nicaragua, resumed its degassing activity in mid-1993 with the continuous emission of SO₂ at rates increasing from 600 metric tons (t) day⁻¹ (7.0 kg s⁻¹) in 1995 to 1800 t day⁻¹ (21.0 kg s⁻¹) in 1999. The low-altitude gas plume is typically blown westward by the prevailing wind across the Masaya caldera and Las Sierras highlands, which are at a higher elevation than the gas vent. In this study, the areal distribution of atmospheric SO₂ concentrations was monitored within 44 km of the vent with a network of passive samplers. Measured SO₂ air concentrations ranged from <2 to 90 ppbv in 1998 and from <2 to 230 ppbv in 1999. The data suggest that the volcanic emissions influenced air quality across a 1,250-km² area downwind. Local topography exerts a strong control on plume dispersal, and hilltops are particularly prone to fumigation and thus, to high ambient SO₂ levels. In a zone 22 km² in size located within 15 km of the source, the response of vegetation to sustained exposure

to high atmospheric dose of volcanic SO₂ and HF resulted in a strong reduction in the number of plant communities. A transition zone of somewhat indefinite boundary surrounds the devastated zones and exhibits vegetation damage in the form of leaf injury. In addition to the environmental impacts of the volcanic emissions, both short- and long-term public health hazards may exist in areas most exposed to the plume. The harmful effects of the volcanic emissions on cultivated vegetation could be diminished by using windbreaks made of gas-tolerant trees and shrubs such as *Eugenia jambos*, *Brosimum utile* and *Clusia rosea*. The current gas crisis at Masaya volcano provides an unique opportunity for investigating the atmospheric, environmental and medical impacts of volcanic gases and aerosols.

Keywords Air pollution · Health hazards · Hydrogen fluoride · Sulphur dioxide · Vegetation damage

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Introduction

Recognition that gases and aerosols released to the atmosphere via eruptive and non-eruptive volcanic activity can affect the environment is long standing (e.g. Wilcox 1959; Lazrus et al. 1979; Thórarinnsson 1979). Although many studies have focused on the impact of plinian eruptions upon the chemical composition of the stratosphere (e.g. Hofmann and Solomon 1989; Wallace and Livingston 1992; McCormick et al. 1995), less is known regarding the fate of volcanic gas plumes emitted into the troposphere by eruptions with relatively low explosive force, or during persistent non-eruptive degassing. Yet, there is evidence that such emissions constitute an important agent of local and regional environmental changes. For example, the Lakagígar eruption, 1783–1784 A.D., released huge amounts of sulphur, chlorine and fluorine gases into the troposphere, which caused dramatic damage to vegetation, livestock and people of Iceland and Europe (e.g. Thórarinnsson 1979; Grattan 1994; Durand and Grattan 1999). Camuffo and Enzi (1995) also docu-

mented severe air pollution episodes in Italy between 1374 and 1819 associated with the activity of Mt Etna, Vesuvius, Vulcano and Stromboli volcanoes. In a similar manner, passively degassing volcanoes have been shown to affect the proximal environment. Notably, this was highlighted at Masaya, Kilauea, Mt Etna, Mt Sakurajima and Mt Erebus volcanoes (e.g. McBirney 1956; Kratky et al. 1974; Harding and Miller 1982; Johnson and Parnell 1986; Kawaratani and Fujita 1990; Parnell and Burke 1990; Zreda-Gostynska et al. 1997). Non-eruptive degassing also has been shown to contribute significantly to the tropospheric sulphur budget and acid deposition in some parts of the world (Arndt et al. 1997; Thornton et al. 1999).

The most important volcanogenic air pollutants are carbon dioxide (CO₂), sulphur dioxide (SO₂), hydrogen chloride (HCl) and hydrogen fluoride (HF). Similar to anthropogenic point source emissions, the extent to which these gases impact the proximal and distal environment depends on various factors. Once in the atmosphere, the gases are affected by physical and chemical processes (gas-phase reactions, reactions on, in, or with suspended solid and liquid particles), which may lead to their rapid or slow deposition, and favour or delay their conversion to aerosols. Importantly, the sensitivity of the soil and vegetation receptors to pollution also must be considered. Clearly, correct assessment of the environmental effects of volcanic gases requires multidisciplinary and time-integrated researches. Such studies are important because they will increase our ability to forecast and mitigate volcanic gas hazards.

The Masaya volcano in Central Nicaragua is currently undergoing an episode of strong gas emissions, with SO₂ emission rates in the range 800–1,800 metric tons (t) day⁻¹ (9.3–20 kg s⁻¹; Delmelle et al. 1999). Historical evidence suggests that at least five similar gas crises, lasting between 4 to 12 years, have occurred since 1852. Notably, the 1919–1927, 1949–1957 and the 1979–1984 events raised concerns about the effects of the gas emissions on vegetation and public health (McBirney 1956; Baxter et al. 1982; Johnson and Parnell 1986). During the 1979–1984 crisis, Johnson and Parnell (1986) attempted to determine how air pollution in the form of acid rain and bulk deposition varies from the source. More recently, Delmelle et al. (2001) monitored the dry deposition of SO₂ and HCl in relation to distance from the degassing crater. The primary objectives of the work reported here are (1) to characterise the dispersion of the gas emissions around the volcano, (2) to investigate the influence of these emissions on SO₂ air concentrations, (3) to delineate damaged vegetation areas and (4) to discuss potential hazards for human health. We also provide a brief overview of possible remedies to lessen the gas hazard.

The Masaya volcano

Masaya is an active basaltic volcano on the Central American volcanic front, situated about 25 km south-

east of Managua, Nicaragua (Fig. 1A). It consists of a 6×11.5 km caldera, which was formed by a series of major Plinian eruptions less than 6,000 years ago (Williams 1983). The complex has a broad low (~560 m above sea level) shield-like form, in contrast with the other volcanoes of Central America. The caldera is itself enclosed within a 25-km-wide older structure called the Las Sierras caldera (van Wyk de Vries 1993; Fig. 1B). The rim of this caldera is asymmetric in height, being ~900 m high in the west and ~250 m high in the east. The highest area of the Las Sierras caldera is locally known as Pacaya, a strongly dissected ridge, which is located approximately 15 km from the Masaya caldera. From here, the land slopes gently towards the Pacific Ocean coast (Fig. 1C).

Masaya has been the site of frequent periods of unrest since the time of the Spanish Conquistadors. These have taken the form of voluminous degassing, lava lakes and infrequent minor explosions from Santiago, one of its summit pit craters (McBirney 1956; Stoiber et al. 1986; Rymer et al. 1998). The current gas crisis began in June 1993 (Rymer et al. 1998; Delmelle et al. 1999). The emission rate of SO₂ from the Santiago summit crater, determined by correlation spectroscopy (COSPEC), averaged about 600 t day⁻¹ (6.9 kg s⁻¹) in March 1996, 390 t day⁻¹ (4.5 kg s⁻¹) in February–March 1997, 1,850 t day⁻¹ (21.4 kg s⁻¹) in February–April 1998 and 1,790 t day⁻¹ (20.7 kg s⁻¹) in February–March 1999 (Rymer et al. 1998; Delmelle et al. 1999).

Annual mean total precipitation at Masaya is ~1,100 mm, with approximately 85% of this falling during the rainy season. In the dry season (December–May), there are steady north-easterly winds that blow the volcanic plume across Masaya Caldera and Las Sierras highlands.

Methodology

Two surveys were conducted in 1998 (21 March–13 April) and 1999 (15 February–15 March) in the Masaya region. A network of passive (diffusion) samplers was established to measure the distribution of atmospheric SO₂ concentration downwind of the volcano. In March 1998, 32 monitoring stations were deployed within 15 km of Santiago crater, the emission source. In February 1999, the network was extended to 55 monitoring stations distributed within 44 km of the source. These also included background stations established to the east, upwind of the volcano. Seventeen stations installed within 15 km of Santiago crater were common to the 1998 and 1999 networks. Sites were selected to provide information on the spatial variability in ambient SO₂ level, and were located in open areas as much as possible and away from local sources of SO₂, such as from cooking stove flues. The sampling units were placed 1.5–2.5 m above the ground and the exposure times ranged from 17 to 20 days in 1998 and 21 to 27 days in 1999. The locations of the monitoring sites are shown in Fig. 1B, C.

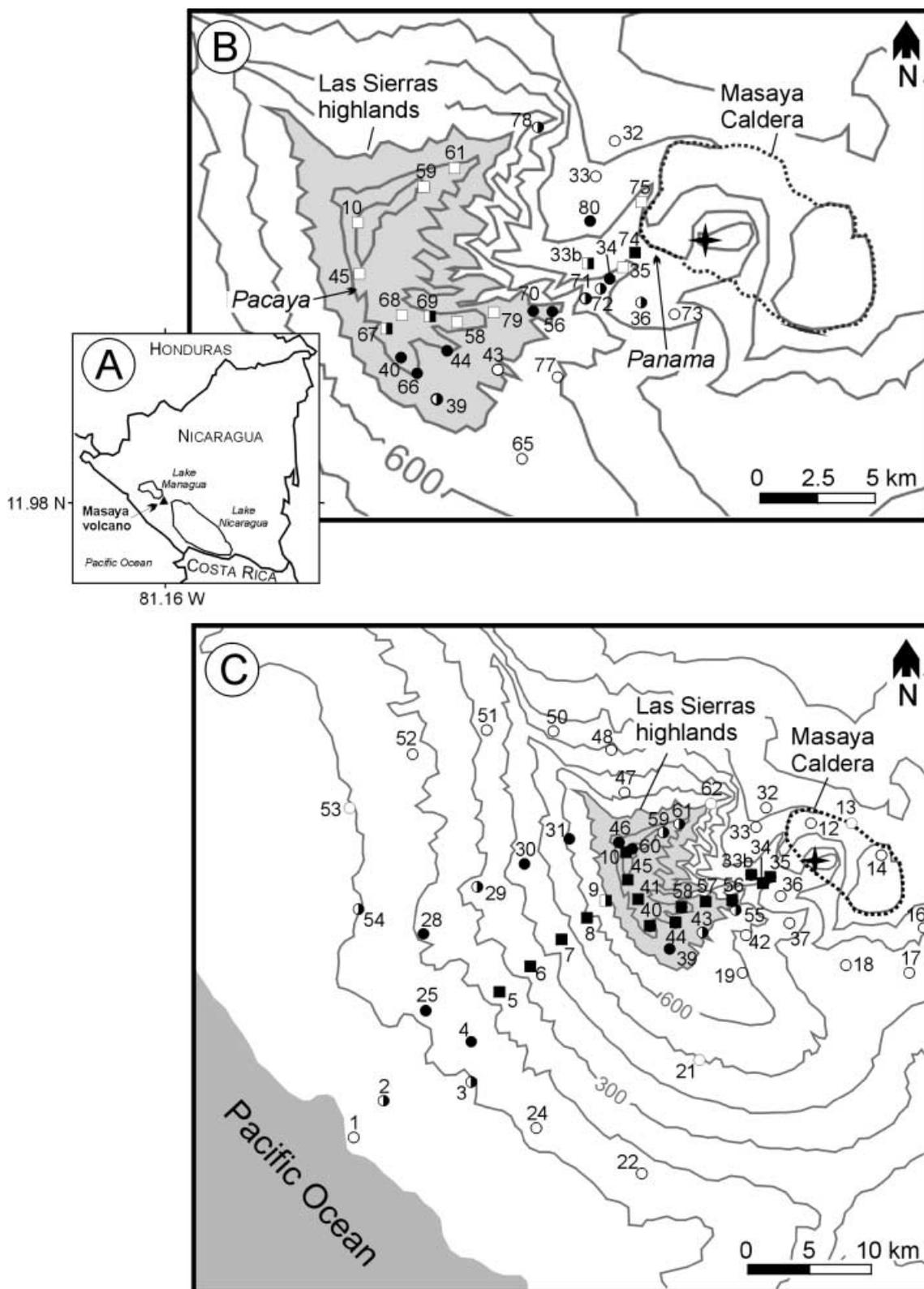


Fig. 1 A Map of Nicaragua showing Masaya volcano. B, C Maps showing the locations of the sites monitored in the vicinity of Masaya volcano over the periods March–April 1998 and February–March 1999, respectively. Each label indicates the site number. The symbol represents a concentration range (ppbv) according to filled circle <15; half-filled circle 15–29; filled circle 30–44;

empty square 45–59; half-filled square 59–74; filled square >75. Shaded area is the Las Sierras highlands topographic feature. The dotted ellipse and the black cross sketch Masaya's caldera rim and degassing vent (Santiago crater), respectively. Panama and Pacaya are local area names. Heights in metres

The diffusion samplers used in this study were developed by Downing et al. (1994). They offer a simple and low-cost means of obtaining weekly to monthly average atmospheric SO₂ concentrations over large areas. Testing in urban and volcanic environments has proven these samplers to be accurate and reliable (Downing et al. 1994; Downing 1996). The devices consist of a perfluoroalkoxy (PFA) tube, 7 cm long by 1 cm in diameter with two caps. A hole is made in the inlet cap where a porous polytetrafluoroethylene (PTFE) membrane is placed to prevent wind-driven shortening of the diffusion path (Ferm 1991; Downing et al. 1994). Atmospheric SO₂ is trapped on a potassium hydroxide (KOH)-impregnated stainless steel grid. The analysis of the diffusion tubes was performed by AEA Technology, UK. After exposure, the absorbent medium was removed and absorbed SO₂ extracted with a hydrogen peroxide solution. The amount of sulphate was analysed using suppressed ion chromatography. The SO₂ concentration was calculated from Fick's first law of diffusion assuming a diffu-

sion coefficient of SO₂ in air of $1.18 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. The mean value of nine travel blanks (i.e. diffusion tubes that were carried in the field, but not exposed) was $0.18 \pm 0.09 \text{ mg}$ of sulphate per tube. The detection limit of the method is defined as three times the standard deviation of the travel blank and is the equivalent of an exposure of the diffusion tube to approximately 2 ppbv of SO₂ for 30 days. The precision of the measurement was assessed by exposing diffusion tube pairs at 11 and 5 sites in 1998 and 1999, respectively. The mean relative deviation is 5.5%. A SO₂ concentration contour map was constructed from the irregularly-spaced diffusion tube measurements of 1999 using Surfer Software (Golden Software, Inc.).

Results

Results of the SO₂ surveys are presented in Table 1. Background SO₂ concentrations of <2 ppbv were ob-

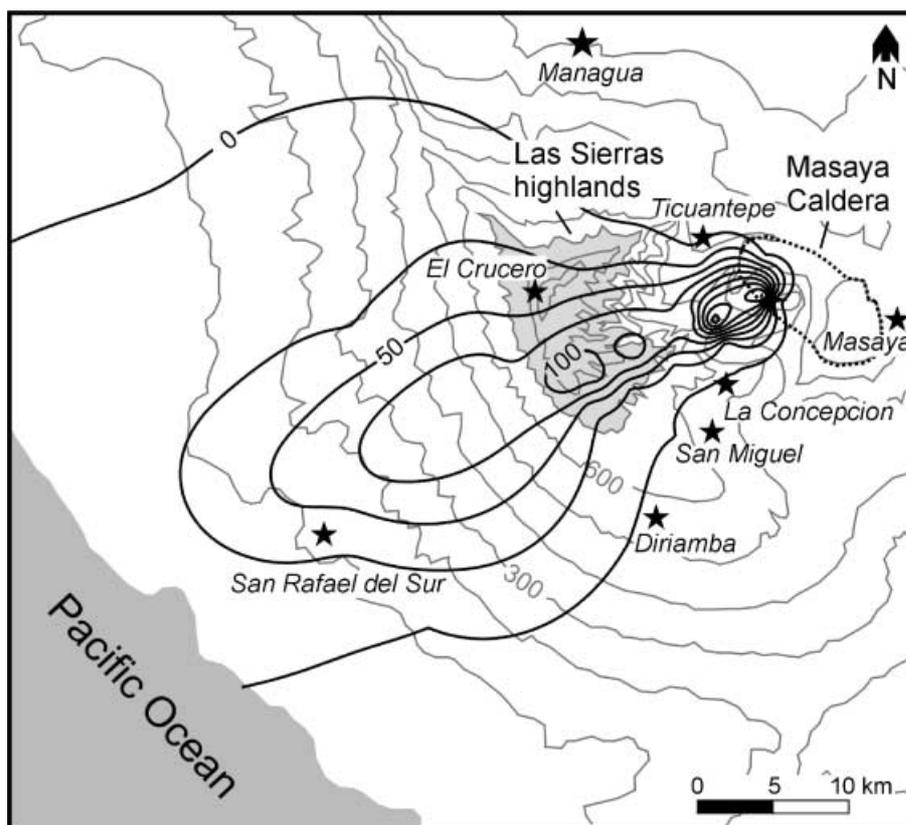
Table 1 Atmospheric SO₂ concentration and vegetation scale index (vsi^a) data for each site of the March–April 1998 and February–March 1999 monitoring networks

Site no.	SO ₂ (ppbv)		vsi	Site no.	SO ₂ (ppbv)		vsi
	1998	1999			1998	1999	
1		8.4	I	42		4.4	I
2		16.9	I	43	13.7	22.3	II
3		18.5	I	44	37.2	114.1	III
4		43.2	II	45	53.2	78.1 ^b	III
5		87.1	II	46		40.2	II
6		95.4	II	47		11.2	I
7		117.0	II	48		6.8	I
8		91.6	II	50		8.6	I
9		63.8	II	51		7.8	I
10	50.7	103.5	III	52		6.8	I
12		<2.0	I	53		5.2	I
13		<2.0	I	54		18.0	I
14		<2.0	I	55		67.8 ^b	II
16		<2.0	I	56	32.3	75.2	III
17		<2.0	I	57	44.3	119.6	III
18		<2.0	I	58	52.5	95.7	III
19		<2.0	I	59	46.3	24.2	II
21		<2.0	I	60		38.4	II
22		<2.0	I	61	54.6	15.9	II
24		<2.0	I	62		5.4	I
25		39.1 ^b	I	65	8.3		I
28		38.2	II	66	33.6		II
29		28.7	II	67	62.5		III
30		35.7	II	68	55.2		III
31		38.7	II	69	62.7		III
32	7.8	2.4	I	70	40.2		II
33	8.9	8.9	I	71	19.1		II
33b	66.2	83.2	II	72	27.4		II
34	40.3	145.9	II	73	6.6		I
35	53.8	230.0	III	74	90.8		III
36	20.4	6.9	II	75	46.0		II
37		<2.0	I	77	12.6		I
39	18.0	33.2	II	78	19.6		II
40	41.3	123.4	III	79	52.7		III
41		87.0	III	80	43.9		II

^a I No visible vegetation damage; II observable leaf injury to trees and shrubs; III vegetation is devastated and largely eliminated

^b Calculated from the corresponding sulphation rate value (see Delmelle et al. 2001)

Fig. 2 Atmospheric SO₂ concentration (ppbv) contour map based on measurements made during the February–March 1999 study period. The *black stars* sketch the main town and village locations. Other *symbols* as in Fig. 1



served systematically upwind of the volcano. In contrast, SO₂ varied greatly from <2 to 90 ppbv in 1998 and from <2 to 230 ppbv in 1999 at monitoring stations located south-west of the volcano. The highest SO₂ levels were found in the Panama area, within 4 km from the source. Secondary SO₂ maxima (60 and 100 ppbv in 1998 and 1999, respectively) also occurred in the Las Sierras highlands. Overall, there was a decrease in the SO₂ concentration with distance from the gas vent and away from the main plume direction.

The SO₂ concentration contour map constructed from the 1999 data highlights several important features of plume dispersion at Masaya (Fig. 2). The map confirms a dispersion pattern characterised by dilution of the plume during transport and by the occurrence of two concentration maximum zones at distances of about 4 and 15 km from the vent. The contour lines also reveals that the plume's south-eastern margin exhibited a sharp SO₂ concentration gradient (SO₂ increases from 20 to 90 ppbv over a distance of 3 km). The 1998 results suggest similar plume dispersion features within 15 km from the source.

Immediately adjacent to the vent, and for about 4 km distant in the Panama area, the effects of the volcano emissions on vegetation were obvious; there is no living trees and shrubs, and only a weedy grass composite subsists (Fig. 3A). The same situation also occurs further downwind in the Las Sierras highlands at distances between 7 and 17 km from the active vent (Fig. 3B). Cultivation is difficult or impossible in these devastated

zones. An exception to this strongly disturbed vegetation pattern are the deep valley bottoms of the Las Sierras topographic feature which appear to be partly sheltered from the noxious effects of the emissions (Fig. 3C).

Visible harmful effects to natural and cultivated vegetation also were noticed in a transition zone surrounding the devastated areas. However, these are less severe and typically consist of chlorotic and necrotic leaf symptoms and fruit injuries (Fig. 3D, E). Leaf damage is more pronounced on the windward side of the trees and shrubs. In this zone of intermediate damage, coffee planters noted decreases in the yield of coffee beans and in the normal growth of the plants. In the field, the change from severe to intermediate vegetation damage is relatively clear. In contrast, the outer boundary of the transition zone was somewhat indefinite. Overall, we estimate that the distance of vegetative impacts extended 32 km to the south-west of the volcano.

An attempt is made in Table 1 to summarise the above information by attributing a 'vegetation scale index' to each station of the 1998 and 1999 monitoring networks as follows: I = no visible vegetation damage; II = observable leaf injury to trees and shrubs; and III = vegetation is devastated and largely eliminated.

Other than vegetation, the principal effects were observed for metal roofs, fences, communication wires and antennas and machinery. According to inhabitants in the Panama and Pacaya areas most affected by the gas plume, galvanised metal roofs did not resist gas emissions for more than 6 months because the metal is rapid-

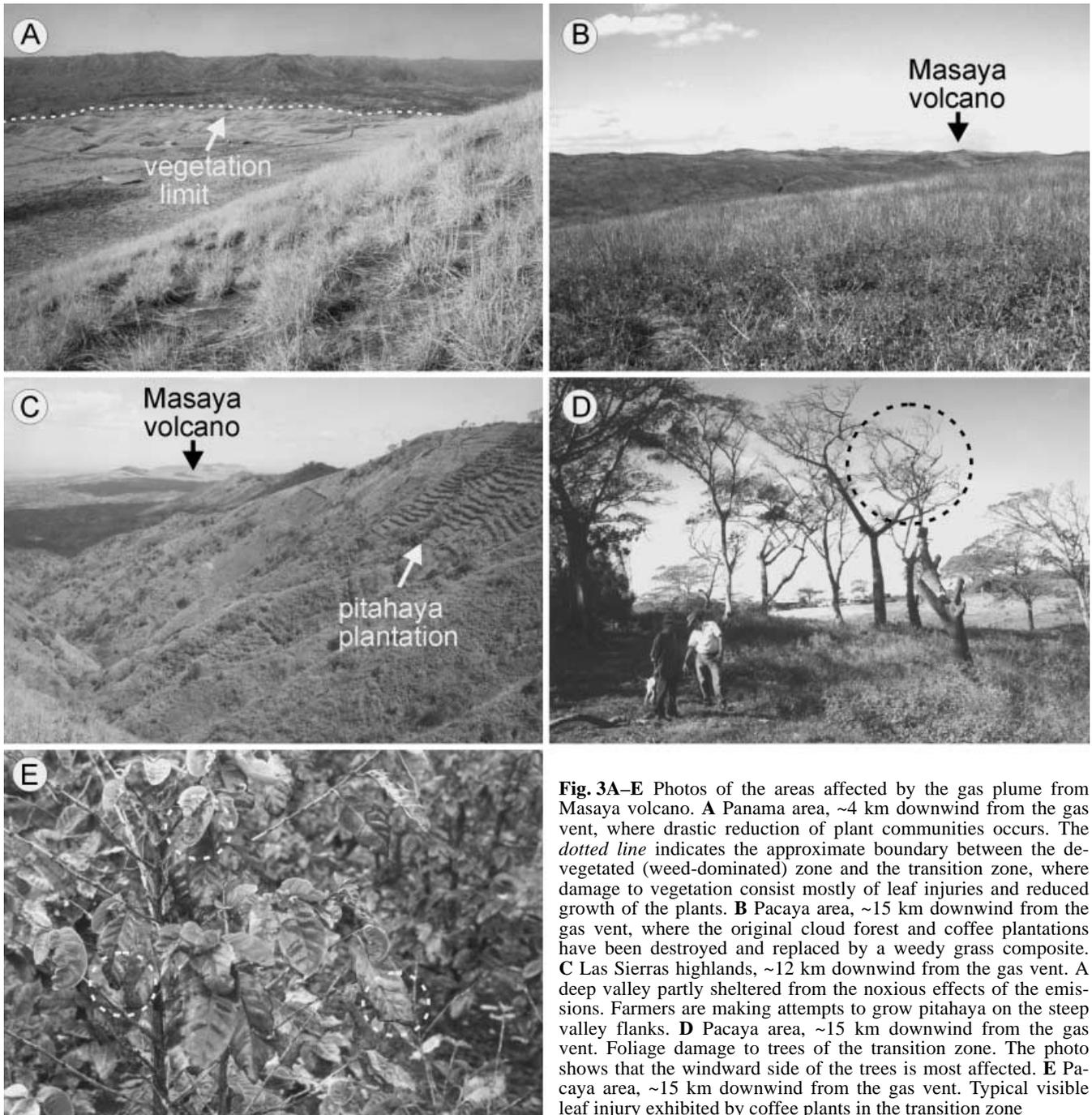


Fig. 3A–E Photos of the areas affected by the gas plume from Masaya volcano. **A** Panama area, ~4 km downwind from the gas vent, where drastic reduction of plant communities occurs. The *dotted line* indicates the approximate boundary between the de-vegetated (weed-dominated) zone and the transition zone, where damage to vegetation consist mostly of leaf injuries and reduced growth of the plants. **B** Pacaya area, ~15 km downwind from the gas vent, where the original cloud forest and coffee plantations have been destroyed and replaced by a weedy grass composite. **C** Las Sierras highlands, ~12 km downwind from the gas vent. A deep valley partly sheltered from the noxious effects of the emissions. Farmers are making attempts to grow pitahaya on the steep valley flanks. **D** Pacaya area, ~15 km downwind from the gas vent. Foliage damage to trees of the transition zone. The photo shows that the windward side of the trees is most affected. **E** Pacaya area, ~15 km downwind from the gas vent. Typical visible leaf injury exhibited by coffee plants in the transition zone

ly converted to a rusted, brittle porous material that cannot support its own weight. For the same reasons, communication antennas are regularly protected with special paints.

Discussion

Plume dispersion in a complex terrain

Masaya volcano behaves as a continuous point source of gas emissions into the atmospheric boundary layer. For

such types of sources, plume dispersion relates primarily to atmospheric motions and stratification (Arya 1999). In addition, local topography often complicates the situation. In the Masaya area, the combination of these different factors results in complex plume dispersion processes, some of which were detected by the SO₂ diffusion tube measurements. The SO₂ concentration contour map shows that the Masaya gas emissions affect ambient SO₂ levels over an area of ~1,250 km² (Fig. 2). This corresponds to an average dispersion of the gas plume by the north-easterly trade winds over a 80–85° sector, which is equivalent to average plume widths of about 9 and

29 km at distances of 5.5 and 15 km from the active crater, respectively.

The decreasing atmospheric SO₂ concentrations observed downwind of the gas vent is consistent with gradual dilution of the plume because of air entrainment and scavenging of SO₂ by surface deposition and oxidation to sulphate. According to Delmelle et al. (2001), about 10% of the total mass of the volcanic SO₂ emissions are returned to the ground by the process of dry deposition within 44 km from the volcano. The rate of SO₂ conversion to sulphate is not known. However, studies of smokestack SO₂ emissions indicate that plumes that lack fine ash particles (catalysts for the oxidation reaction) display low SO₂ oxidation rates, typically less than 10% per hour (e.g. Newman et al. 1975; Eathough et al. 1994). Thus, SO₂ scavenging through oxidation may not be important in the ash-free plume emitted by Masaya volcano. This is supported by the fact that the SO₂/HCl mass ratio of the gas plume measured at the summit of the volcano and downwind from the Panama and Pacaya localities showed similar values in the range 3.0–3.5 (Horrocks et al. 2002). In addition, the dry deposition measurements of Delmelle et al. (2001) suggest that SO₂ and HCl are removed at similar rates in the area directly exposed to the gas plume.

As mentioned above, SO₂ concentration maxima were measured in two distinct zones (i.e. Panama and Las Sierras highlands) downwind of the volcano. Both areas coincide with significant rises in the terrain. Because the gas plume is emitted from Santiago vent at a comparatively low altitude, this creates favourable conditions for fumigating the land, which, in turn, produces high SO₂ concentrations at ground levels. Visual observations made in 1998 and 1999 confirmed this hypothesis, and strong fumigation in the Pacaya area was reported during previous gas crises (McBirney 1956; Stoiber et al. 1986). The highest SO₂ dry deposition rates also were found in areas most exposed to gas fumigation (Delmelle et al. 2001). These observations suggest that the terrain topography strongly influences gas dispersion in the Masaya area.

The frequency and intensity of fumigation (and thus the degree of air pollution) of the land downwind of Masaya volcano depend on the height at which the plume is dispersed horizontally. In turn, this is controlled by degassing conditions at the vent (i.e. temperature and exit velocity of the emissions) and, more importantly, by atmospheric conditions (i.e. a stratified versus a well-mixed atmosphere). Typically, transitory fumigation events will occur after sunrise as heating of the surface dissipates the nocturnal temperature inversion and increases vertical mixing of air. Otherwise, persistent gas impingement on the ground will result when the volcanic plume is emitted into an unstable layer of air trapped between a temperature inversion and the ground, or when it is dispersed within a low-level capping temperature inversion. Combined with a complex topography that creates preferential wind channels, such conditions probably lead to severe plume confinement in the steep valleys

of the Las Sierras highlands. This phenomenon is believed to create the sharp SO₂ concentration gradient detected on the south-eastern margin of the plume in this area (Fig. 2).

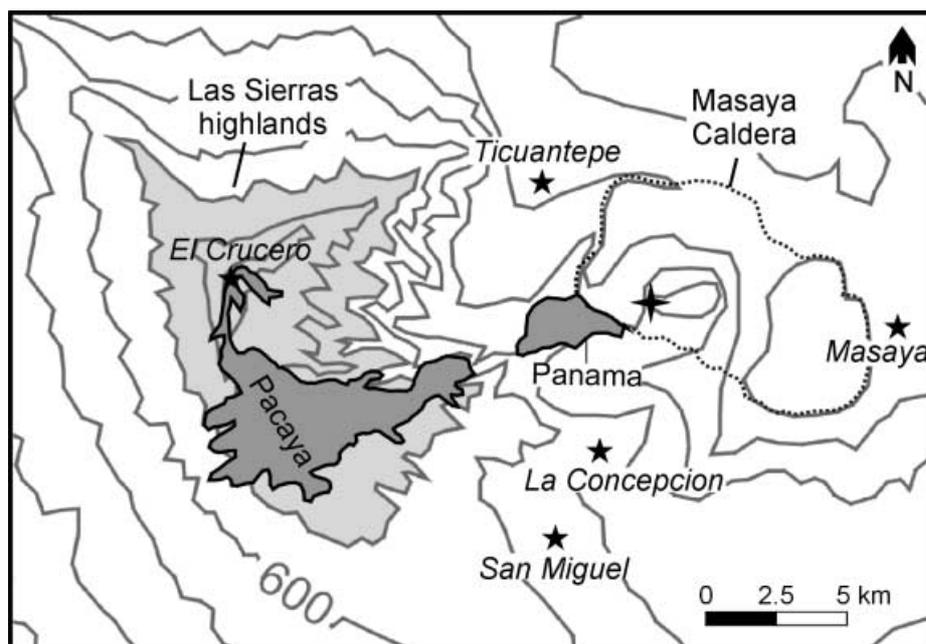
Clearly, concentrations of airborne SO₂ depend on the strength of the source and the dispersion behaviour of the plume. Wind is also of importance in determining air pollutant levels, with concentrations being inversely related to wind speed for ground level sources. Because Masaya was emitting SO₂ at the same rates in 1998 and 1999, the differences in SO₂ levels observed between the two periods of study may result from variations in local meteorological conditions rather than from changes in source strength. In general, ambient SO₂ levels tended to be higher in 1999 compared with 1998. This may be attributed to atmospheric conditions that favoured less dilution of the gas plume and more intense fumigation in 1999, thus leading to increased SO₂ concentrations. By contrast, three sites (36, 59 and 61), all located on the north-western side of the plume, showed significantly lower SO₂ concentrations in 1999 than in 1998. These may have been less exposed to the plume path, perhaps because of a slight shift in the mean wind direction during the 1999 period of study. Indeed, COSPEC measurements indicated that, on average, the plume direction in 1999 departed a few degrees to the south-east from the one deduced in 1998 (G. Williams-Jones, personal communication 2001).

Because local SO₂ concentration levels are sensitive to atmospheric conditions, the representativeness of our measurements with respect to other periods of the year cannot be assessed. In the Masaya region, the dry season runs from December to May and is usually characterised by relatively stable winds and temperatures and by low cloudiness (Instituto Nicaragüense de Estudios Territoriales, Dirección de meteorología, unpublished data 1998–1999). Thus, to the extent that the source strength does not change over the year, plume dispersion during this period should not differ significantly from the general pattern observed in March–April 1998 and February–March 1999. In contrast, atmospheric conditions during the rainy season may lead to significant differences in plume dispersion processes. Notably, a major effect is expected as a result of SO₂ removal from the plume by intermittent rainfalls. Also, areas normally not exposed to the plume path may be temporarily affected because of transient changes in the prevalent wind direction. At this stage, we cannot predict the trend followed by atmospheric SO₂ concentrations in the rainy season.

Environmental hazards

A 150-year history of gas release episodes at Masaya volcano has created strong perturbations in the ecosystems located downwind. McBirney (1956) reported on the dramatic vegetation damage in the Pacaya area associated with the 1924–1927 and 1947–1959 volcanic crises. Cultivation in this potentially rich coffee-growing

Fig. 4 Map sketching the zone (darker area) where vegetation is most impacted by Masaya's emissions. See text for explanation. Other symbols as in Fig. 1



zone has been rendered impossible since the mid-1940s (McBirney 1956; Johnson and Parnell 1986; Stoiber et al. 1986). Our field observations in the Las Sierras highlands agree with these reports. In addition, we have documented the severe vegetative impacts of the gas plume in the Panama area, closer to the volcano. Farmers reported to us that the detrimental effects of the gas plume are occasionally felt during the rainy season in the Arenal-San Marcos sector, which is to the south of the volcano. This is probably a consequence of transient changes in the plume direction.

In order to provide a sketch of the zones injured by the volcanic emissions, we used a set of 1:50,000 topographic map sheets made in 1987 from aerial photographs (Instituto Nicaragüense de Estudios Territoriales 1988). These allowed us to discriminate roughly between weed-dominated, forest and plantation (mainly coffee) zones. In support of our field observations, the maps show that a discontinuous, tongue-like weed-dominated enclave occurs within 15 km downwind from the source. The total surface area of this zone is ~ 22 km², and Fig. 4 shows its approximate boundaries. The important feature is that the weed-dominated zone corresponds to the highest ground level SO₂ concentrations (compare Fig. 4 with Figs. 1 and 2). Its shape also appears to be related to the average plume direction as well as to local topography (e.g. the broadening in the Pacaya ridge area). This is strong evidence that dispersal of the volcanic emissions has led to the destruction and reduction of the ecosystem diversity, as illustrated in Fig. 3A, B.

Although less spectacular, damage to vegetation in the transition zone (Fig. 3D, E) causes significant losses in the coffee production. The Nicaraguan Union of Coffee Planters (UNICAFE) concluded recently that about 57% of the total coffee-growing area ($\sim 5,180$ ha) in the Las Sierras highlands are suffering from the deleterious

influence of the volcanic fumes (Chamarro 1996). According to UNICAFE, coffee production for the period 1998–1999 dropped by almost 40% compared with the 1995–1996 period (J.F. Gutierrez, personal communication 2001). This decrease in coffee productivity may be a consequence of higher air pollutant levels associated with substantially stronger gas emissions in 1998–1999 (1,800 t SO₂ day⁻¹) than in 1995–1996 (600 t SO₂ day⁻¹). Besides coffee, we also observed that other types of cultivation (e.g. citrus, avocado, mango, papaya and banana) are affected to various degrees by the gas plume.

There are numerous examples where excessive SO₂ pollution by smelter and coal-power plants has resulted in strong ecosystem disruptions (e.g. Hogan and Wotton 1984; Smith 1990). It is commonly agreed that SO₂ causes direct damage once it is absorbed by the foliage (Smith 1990). However, SO₂ air concentrations alone are poor predictors of visible and invisible SO₂ damage in plants (Darrall 1989; Smith 1990). Apparently, plants respond differently to SO₂ depending on timing of exposure, atmospheric conditions and leaf type (e.g. Linzon et al. 1979; Winner and Mooney 1980; Smith 1990). Furthermore, differences in foliar sensitivity to SO₂ occur across species and provenance.

Thus, assignment of a single threshold SO₂ concentration above which damage to plant foliage occurs is difficult and misleading. Nevertheless, we accept that chronic exposures to SO₂ concentrations less than 500 ppbv can alter the composition of plant communities, decrease the productivity of agricultural systems and cause visible foliar injury such as chlorosis and necrosis (Winner and Mooney 1980). For example, light and severe foliar SO₂ injury symptoms were found downwind of smokestacks where the seasonal SO₂ average was 11 and 48 ppbv, respectively (Linzon et al. 1979). The average SO₂ levels measured in the weed-dominated and transition zones

downwind of Masaya volcano are similar to, or exceed these values and, therefore, may be considered detrimental to vegetation. Furthermore, direct foliage injury is augmented during periodic fumigation of SO₂ fumes at supra-lethal concentrations (>1,000 ppbv; e.g. Linzon et al. 1979; Smith 1990). We suspect that this phenomenon is largely responsible for the elimination of the trees and shrubs from the weedy zone. We noticed that vegetative impacts were generally more pronounced at sites on hill-tops than elsewhere, despite similar SO₂ air concentrations (Table 1). In general, hilltops are more susceptible to damage because of their topographic position (thinner, more poorly developed soils, more water stress, more wind damage, etc.). They also receive more direct fumigation. On the other hand, observations in the field suggested that long-term exposure to SO₂ concentration <15 ppbv may not pose a direct hazard to vegetation. However, we could not find lichens in the area surveyed. For forests and natural vegetation, the World Health Organisation (2000) recommends 6 ppbv as an annual mean concentration, and for lichens, 3 ppbv.

Besides SO₂, Masaya volcano also emits HCl and HF gases at substantial rates of 600–670 t day⁻¹ (7.0–7.8 kg s⁻¹) and 80–90 t day⁻¹ (0.9–1.0 kg s⁻¹), respectively into the troposphere (Burton et al. 2000). These emissions are carried downwind and may affect the ecosystems exposed to the plume path. A crude estimate of the ambient HCl and HF levels within 15 km of the source was made by hypothesising that, in the absence of rain, SO₂, HCl and HF behave conservatively in the plume. Combining the SO₂ diffusion tube measurements with the mean SO₂/HCl (2.9) and SO₂/HF (23.4) mass ratios measured at the gas vent during the same study periods (Burton et al. 2000) yielded HCl and HF concentration values in the ranges from <1 to 31 ppbv and from <1 to 3.9 ppbv, respectively in 1998; and HCl and HF concentration values in the ranges from <1 to 79 ppbv and from <1 to 10 ppbv, respectively in 1999. For comparison, Garrec et al. (1984) measured ground level HF concentrations of about 15 ppbv in the vicinity of the volcano during the 1979–1984 gas crisis. At these atmospheric levels, HCl is probably not a problem, but HF can cause direct symptomatic foliar injury for a large number of trees (Smith 1990). The World Health Organisation recommends that HF levels in the ambient air should be less than 1–2 ppbv to prevent effects on livestock and plants (and, coincidentally, humans). Furthermore, some authors believe that the presence of HF reduces the SO₂ thresholds of visible vegetation injury (e.g. Murray and Wilson 1988; Smith 1990). An opposite view is that the synergistic effects of the two pollutants may lessen the intensity of their impact (Mandl et al. 1975). In any case, it is likely that the volcanic HF emissions also contribute to vegetative damage in areas most exposed to the plume path.

Although the major impact of wet- and dry-deposited pollutants on vegetation is mediated mainly through the soil, there remains the possibility of direct effects of acidified rain or cloud droplets on foliage which add to

the impacts of high ambient SO₂ and HF levels (Cape 1993). In general, fog and cloud, which may contain solute concentrations up to ten times those found in rain, have a greater capacity for direct effects on vegetation. Thus, vegetation most at risk from direct effects caused by dissolved ions may be found in the Las Sierras highlands, which are regularly exposed to hill clouds. According to Cape (1993), visible injury to foliage in response to treatment with sulphate-rich acidic rain or mist requires pH values to be ≤3 and solute concentrations in the millimolar range. Johnson and Parnell (1986) encountered such wet-depositions in the Pacaya area during the 1979–1984 gas crisis at Masaya. These authors noted that HCl was the major acidifying compound in the precipitation in the vicinity of the volcano. We also collected waters with similar compositions during a short rainfall event in March 1999 (unpublished data).

Another potential volcanic source of atmospheric acidity in the Masaya area is the primary emission of coarse (>2.5 μm) and fine (<2.5 μm) sulphate aerosols from the gas vent (Allen et al. 2000). Aerosol particles were collected from the crater edge in May 2001. These measurements indicated high levels of acidity (pH <1.0) and sulphate (up to 160 μg m⁻³) in fine particles (C. Oppenheimer, personal communication 2002). The fine aerosols can be transported long distances without losing their acidity.

Finally, continuous exposure of the ecosystems around Masaya volcano to gas emissions may result in acidification and contamination of the soils through dry and wet-acid inputs. The quantities of SO₂ and HCl dry-deposited daily within 44 km of the volcano may generate an equivalent hydrogen flux ranging from <1 to 30 mg m⁻² day⁻¹ (Delmelle et al. 2001). These rates are one to ten times the highest acid deposition rates observed worldwide (Smith 1990). Prolonged acid loading at these rates may seriously impact the soil chemistry. Notably, Parnell (1986) found that the volcanic ash soils in the Pacaya area exposed to the gas plume exhibited low pH values and depressed base-saturation contents.

Public health hazards

The volcanogenic air pollution at Masaya may create a hazard for public health. This was first highlighted during the 1979–1984 gas crisis by Baxter et al. (1982). Sulphur dioxide is a highly reactive species and is an irritant when inhaled. This gas presents a respiratory health risk even at low ambient air concentrations, and so the plume hazard may persist for many kilometres away from the crater. Controlled studies with exercising subjects indicate that some asthmatic patients experience respiratory symptoms and falls in lung function after periods of exposure as short as a few minutes. To protect against this effect, the World Health Organisation recommends a guideline of 175 ppbv averaged over 10 min and 40 ppbv averaged over 24 h. The diffusion tube readings most closely represent 24-h average concentrations.

Evidently, our SO₂ measurements strongly suggest that conditions of poor air quality harmful to public health occur downwind of Masaya volcano. The areas potentially affected include Panama, Pacaya and El Crucero (Figs. 1 and 2). Importantly, peak exposures when the plume fumigates inhabited areas are likely to be much greater than the above figures, given the averages measured by the diffusion tubes, which continue to record when the plume is blowing in different directions. Levels over 1,000 ppbv are able to provoke asthma in fit exercising individuals, thus increasing the gas hazard. Although health records were not available, we often received complaints about eye sensitivity and inflammation, bronchitis, sore throats and headaches.

In addition to volcanic SO₂, people living in the vicinity of the volcano are exposed to airborne halide pollution. Hydrogen fluoride and HCl are both very water-soluble gases which are rapidly absorbed in the nose and upper respiratory tract. They are irritant gases of the same acute toxicity to the lung and do not pose a respiratory health hazard as great as SO₂. However, exposure to harmful fluoride contents may occur through the consumption of fluoridated drinking water and food. Rain water collected in April 1998 from roof catchments at sites 68 and 77 showed fluoride concentrations of 1.5 and 3.5 mg l⁻¹, respectively. According to the World Health Organisation (1993), concentrations of fluoride above 1.5 mg l⁻¹ carry an increasing risk of dental fluorosis.

Counteracting the effects of the volcanic emissions?

Air pollution at Masaya is a long-term recurrent problem. Remedies to reduce the emission rates at the vent, or to lessen the impacts of fumigation on vegetation, were proposed in the past (McBirney 1956, references therein). Some of them involved serious technical difficulties, whereas others were extravagant. Proposals to control the gas emissions at Santiago crater included sealing of the vent by dynamiting and bombing, diversion of the plume at high altitude by building a 300-m-tall chimney and capture of the emissions with pipes. The most spectacular efforts were conducted during the 1919–1927 gas crisis by Schönberg and Scharfenberg who attempted to cap the vent and collect the gases with the aim to convert them to marketable sulphuric acid (McBirney 1956, references therein). In February 1927, they succeeded in closing the vent orifice by blasting off portions of the crater walls so that gas emissions ceased abruptly. However, the two German engineers did not pursue their venture further. During the following activity at Masaya (1947–1959), the Nicaraguan Air Force dropped two bombs into the crater to block the vent, but this time without effect.

Rather than directly controlling the fumes at the Santiago vent, spraying of lime at the point of damage was suggested as an alternative method to protect vegetation from the noxious effects of the acidic gases (McBirney

1956). No tests were carried out in the field, but a difficulty of the method lies in the necessity to apply frequent sprayings during the wet season. Another solution to preserve coffee and other cultivated plants from the high air pollutants levels would be to construct wind-breaks of trees and resistant shrubs around the plantations located in the transition zones where light to moderate air pollution occurs. Indeed, vegetation acts as a sink for SO₂ and other airborne pollutants (Hill 1971). This requires the use of species that are tolerant to chronic SO₂ exposure from the volcanic emissions. McBirney (1956, references therein) reported that the evergreen *Eugenia jambos* species showed appreciable gas tolerance. Inhabitants also said that trees with waxy leaves such as *Brosimum utile* and *Clusia rosea* were particularly resistant. However, there remains the risk of acute fumigation events, which generate damaging gas concentrations to any tree species. Finally, farmers in areas strongly affected by Masaya's plume are making attempts to replace the coffee plants by pitahaya (*Acanthocereus tetragonus*), a fruit-bearing cactus (Fig. 3C). While this species seems to tolerate the high volcanic air pollutant levels, the harvest of its fruit depends strongly on the blooming period and, thus, on the extent of damage inflicted to flowers by the volcanic emissions. To a lesser degree, pineapple also presents a certain tolerance as it is found in areas where avocado, banana and citrus trees would be rapidly destroyed.

Conclusions

Monitoring of the atmospheric SO₂ concentrations has revealed that the degassing activity at Masaya creates air pollution in a 1,250 km² area downwind. This corresponds to dispersion of the volcanic emissions over a 80–85° sector to the west of the source. The spatial distribution of ambient SO₂ levels indicates the strong influence of topography on plume dispersion. Notably, the lower elevation of the gas vent relative to the Las Sierras highlands promotes fumigation in this area. As a result, zones of highest ambient SO₂ levels were detected up to 15 km from the volcano. Fumigation probably gains in intensity when an atmospheric temperature inversion impedes plume rise.

A 150-year history of gas release episodes at Masaya has produced severe damage to vegetation in the Panama and Las Sierras highlands areas. Intense environmental degradation is observed in a 22-km² zone where high SO₂ concentrations (typically above 50 ppbv) prevail, demonstrating the harmful effects of the volcanic fumes on the original vegetation. Cultivation has been rendered impossible in this zone since the late 1950s. Damage to vegetation also occurred in a less well-defined transition zone surrounding the devastated area. These take the form of leaf and fruit injury and cause important losses for coffee plantations. The disastrous effects of the volcanic emissions on vegetation result from chronic and acute exposure to volcanic SO₂ and possibly HF. At the

current rate of emission, atmospheric HCl concentration is not thought to be present at phytotoxic levels. In addition, vegetation in the Las Sierras highlands may suffer from detrimental acidified rains and mists. Indirect perturbations to the ecosystems also may arise through wet and dry volcanic acid inputs to the soil system.

The health hazards of the gas crises at Masaya have not been well documented. Our SO₂ measurements strongly suggest that people living in the main plume sector are exposed to a health hazard from this gas. Further work is needed to determine the adverse role of other gases and particulate matter, especially strong acid aerosols emitted from the crater.

Amongst the several countermeasures proposed in the past to diminish the environmental impacts of Masaya's gas emissions, those aimed at protecting plantations with resistant trees and shrubs acting as sinks for gases and as windbreaks appear to be the most realistic. A few endemic tree species could be tested for this purpose because these appear to show a certain tolerance to high volcanogenic air pollutant levels.

Improvements in our mapping techniques are required in the future to better delineate the area affected by Masaya's emissions and to estimate its temporal evolution. For example, aerial photography could be combined with remote sensing data to make use of vegetation indices (which are highly correlated with biomass and vegetation density). More extensive field and laboratory experiments also are needed for detailed analysis of the combined effects of volcanic SO₂, HCl, HF and their aerosols on the natural and cultivated vegetation of the Masaya area. This study has highlighted the range of potential environmental and health effects associated with sustained volcanic degassing in the troposphere. Masaya provides a fascinating opportunity to conduct research involving a diverse group of volcanologists, environmentalists (soil scientists, botanists), health professionals (toxicologists and epidemiologists) and physical scientists (pollutant dispersion modellers). Such data could support a detailed evaluation of potential strategies to mitigate the risks of volcanic pollution to health and the rural environment.

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