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RESEARCH ARTICLE

Apparent downwind depletion of volcanic SO_2 flux—lessons from Masaya Volcano, Nicaragua

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Abstract A series of 707 measurements at Masaya in 2005, 2006, and 2007 reveals that SO_2 emissions 15km downwind of the active vent appear to be ~33% to ~50% less than those measured only 5km from the vent. Measurements from this and previous studies indicate that dry deposition of sulfur from the plume and conversion of SO_2 to sulfate aerosols within the plume each may amount to a maximum of 10% loss, and are not sufficient to account for the larger apparent loss measured. However, the SO_2 measurement site 15km downwind is located on a ridge over which local trade winds, and the entrained plume, accelerate. Greater wind speeds cause localized dilution of the plume along the axis of propagation. The lower concentrations of SO_2 measured on the ridge therefore lead to calculations of lower fluxes when calculated at the same plume speed as measurements from only 5km downwind, and is responsible for the apparent loss of SO_2. Due to the importance of SO_2 emission rates with respect to hazard mitigation, petrologic studies, and sulfur budget calculations, measured fluxes of SO_2 must be as accurate as possible. Future campaigns to measure SO_2 flux at Masaya and similar volcanoes will require individual plume speed measurements to be taken at each flux measurement site to compensate for dilution and subsequent calculation of lower fluxes. This study highlights the importance of a comprehensive understanding of a volcano's interaction with its surroundings, especially for low, boundary layer volcanoes.

Keywords Masaya volcano · Persistent volcanic degassing · Sulfur dioxide · Topographic effects · Volcano monitoring · FLYSPEC

Introduction

Volcanic gas emissions play an important role in the understanding of volcanic processes and the forecasting of volcanic eruptions (e.g., Stoiber et al. 1983; Zapata et al. 1997; Williams-Jones et al. 2003). Sulfur dioxide is the gas most commonly monitored due to (1) the relative abundance of SO_2 in volcanic emissions in comparison to background concentrations, and (2) the fact that SO_2 also absorbs radiation in the ultraviolet range, making it easily detectable through solar remote sensing techniques (Stoiber et al. 1983). Campaigns to measure SO_2 emissions using ground-based UV-spectrometers have been undertaken at volcanoes worldwide since the 1970s (e.g., Stoiber and Jepsen 1973; Stoiber et al. 1983; Elias et al. 1998). Recent advances in spectroscopic technology have led to the development of small, low cost spectrometers that allow SO_2 monitoring campaigns to be conducted with greater ease at an increasing number of volcanoes worldwide (e.g., Galle et al. 2003; Horton et al. 2006; Nadeau and Williams-Jones 2008).

In making SO_2 measurements, it is important to note the reactivity of the species and the potential for loss of SO_2 from the plume that could lead to underestimates of the

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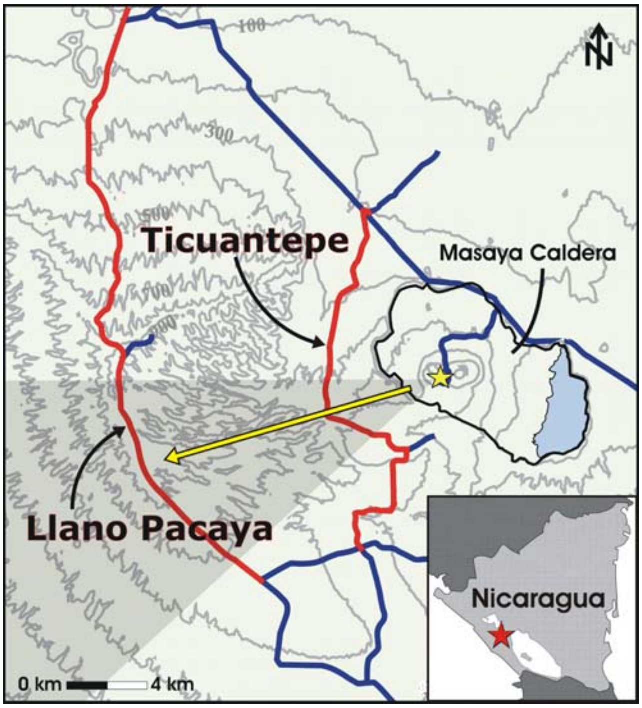
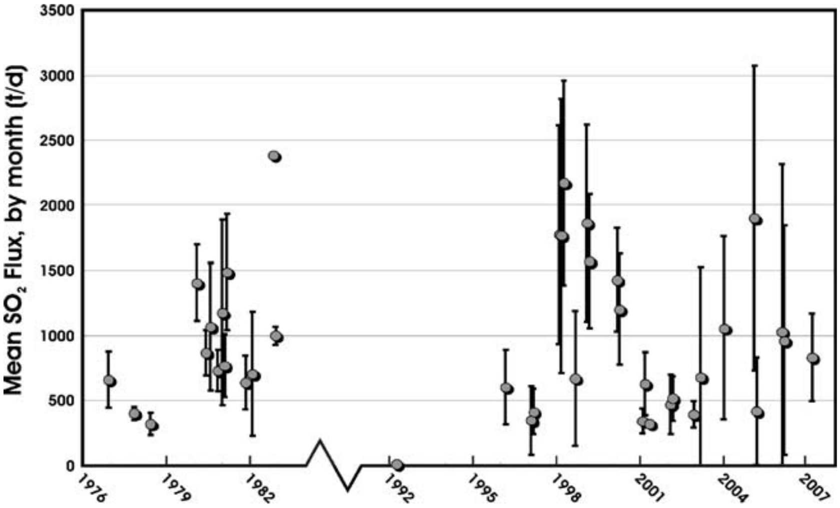


Fig. 1 Map of road network in the vicinity of Masaya volcano, with inset map of Masaya's location in Nicaragua. The Ticuantepe and Llano Pacaya roads, utilized for measuring SO_2 flux, are shown. *Yellow star* indicates the location of the active vent; *yellow arrow* indicates usual plume direction during measurements; *shaded area* shows sector over which plume direction generally varies in dry season

actual flux. SO_2 may convert to sulfate aerosols in the atmosphere, be adsorbed onto ash particles within an ash-laden plume (Witham et al. 2005 and references therein), and scavenged from the airborne plume by means of wet or dry deposition (Delmelle et al. 2001, 2002). Recent studies have reported a range of SO_2-sulfate conversion rates from those that are negligible for the typical timescales of SO_2 measurements (McGonigle et al. 2004) to near 100% depletion of a volcanic plume's SO_2 content (Oppenheimer et al. 1998). These studies, however, relied upon plume speed estimates obtained through methods with associated uncertainties of 10–100% (Williams-Jones et al. 2006). More recently, methods to better constrain plume speed have been developed, increasing the accuracy and precision of SO_2 flux measurements (McGonigle et al. 2005a, b; Williams-Jones et al. 2006, 2008). Further, the use of sun photometers as a means to measure volcanic aerosols has grown more commonplace (e.g., Watson and Oppenheimer 2000, 2001; Porter et al. 2002; Mather et al. 2004). Measurements of aerosols themselves (as opposed to a plume speed proxy) used in combination with more accurate estimations of SO_2 flux (by means of improved plume speed measurement techniques), can offer a more comprehensive understanding of the behavior of volcanic SO_2. In light of these new developments, it was felt that the issue of SO_2 loss in volcanic plumes should be revisited.

Masaya volcano, ~20km southeast of Managua in western Nicaragua, provides an ideal natural laboratory to study potential SO_2 loss. Masaya (Fig. 1), a basaltic complex consisting of nested calderas, cones, and pit craters (McBirney 1956; Rymer et al. 1998; Girard and van Wyk de Vries 2005), though persistently active, rarely experiences eruptive activity. Rather, the volcano has undergone a series of episodes of quiescent degassing for over 150 years, with intermittent gas "crises" associated with periods of elevated SO_2 output (Stoiber et al. 1986 and references therein; Stix 2007). One thousand four hundred thirty seven individual measurements of SO_2 flux reveal that over the period from 1972–2007, Masaya emitted an average of ~1,100 metric tonnes/day (t/d) of SO_2 (Stoiber and Jepsen 1973; Stoiber et al. 1986; Rymer et al. 1998; Galle et al. 2003; McGonigle et al. 2002; Williams-Jones et al. 2003; Williams-Jones, unpublished data; Fig. 2). Current

Fig. 2 Mean SO_2 fluxes grouped by month. *Error bars* represent 1 SD of 1 month of measurements. Note the break in the *x*-axis. Data from this study, Stoiber and Jepsen 1973; Stoiber et al. 1986; Rymer et al. 1998; Galle et al. 2003; McGonigle et al. 2002; Williams-Jones et al. 2003; and Williams-Jones, unpublished data



activity is marked by the persistence of a gas crisis that began in 1993 (Rymer et al. 1998; Delmelle et al. 1999; Williams-Jones et al. 2003; Smithsonian Institution 2006). During the dry season in Nicaragua (December to April), easterly trade winds typically blow the volcanic SO_2 plume from Masaya towards the Pacific Ocean. A well-developed road network exists in the region downwind of the volcano despite the irregular terrain marked by steep ridges and valleys. The Ticuantepe and Llano Pacaya roads are roughly perpendicular to the plume's normal propagation direction at distances of ~5 and ~15km to the west of the vent, respectively (Fig. 1). The combination of consistent degassing, well-developed infrastructure at two distances downwind of the active vent, and general accessibility of the volcano make it a prime location for the study of the plume's evolution through time and space. This paper reports the results of intensive, month-long field campaigns at Masaya volcano aimed at utilizing the latest field methods to better evaluate the presence or absence of significant depletion of SO_2 in volcanic plumes.

Methodology

SO_2 measurements were made between February 25 and March 16, 2005, and February 16 and March 12, 2006, with one additional day of measurements on March 8, 2007. Measurements were made only on days when the consistent easterly trade winds prevailed; days dominated by strong on-shore breezes (as determined by low wind speeds, wide plumes, and eastward motion of clouds) were not utilized for data collection.

SO_2 flux

In order to make simultaneous measurements on the two downwind roads, SO_2 data were collected by conducting multiple automobile traverses beneath the volcanic plume using small UV spectrometers known as FLYSPECs (Horton et al. 2006). In 2005, traverses were made using one FLYSPEC; later data were often collected simultaneously by two FLYSPECs each traversing at different distances downwind of Masaya's degassing vent. Possible diurnal effects were mitigated in 2005 by alternating the roads traversed in the morning and afternoon. Instrument bias in 2006 was determined to be negligible by a six-traverse comparison in which both FLYSPECs were used for the same traverses and yielded nearly identical data. Further, instrument location was varied such that neither FLYSPEC was used solely on the Llano Pacaya or Ticuantepe roads.

The total number of traverses was 707, or approximately 20 measurements per day. Spectra were captured at intervals of 1, 2, or 3 scans per second, and then averaged to one measurement per second in order to coincide with the frequency of the GPS data collection. The spectra captured along a traverse beneath the plume were representative of an integrated cross-section of the SO_2 in the plume (integrated column amount, ICA), which was multiplied by a plume speed in order to determine a flux of SO_2 (e.g., Casadevall et al. 1981; Stoiber et al. 1983; Williams-Jones et al. 2008). As many uncertainties are associated with the accurate determination of plume speed (e.g., Stoiber et al. 1983; Doukas 2002; Williams-Jones et al. 2006), data are also reported as ICAs of SO_2 (in ppm·m^2) to omit the largest source of uncertainty in the measurements.

Plume speed

Plume speeds were most often measured using the multiple-spectrometer method described by Williams-Jones et al. (2006), typically at a single location on either the proximal or the distal road. Data from two time-synchronized FLYSPECs aligned along the axis of propagation of the plume were iteratively fitted to determine the best correlation and therefore the speed of the plume. In 2007, plume speeds were measured on both roads in a near-simultaneous fashion with two pairs of FLYSPECs. Hardware problems and environmental conditions limited the number of dates on which this method could be used. For example, excessively fast winds (e.g., a value in m/s greater than the product of the spectrometer separation in m and the sampling frequency in Hz) prohibited plume speed measurement using the standard instrument arrangement, and increasing the instrument separation was not always logistically feasible. For all problematic dates, in cases when hand-held anemometer data were available, they were substituted for plume speeds derived from spectrometer data. However, as ground-level winds are often substantially less than those aloft (Table 1), it is important to note that estimates of flux relying on such ground-level wind data are likely significantly misrepresenting the true flux (uncertainties of 10–100% versus <15% with the dual-spectrometer method; e.g., Stoiber et al. 1983; Doukas 2002; Williams-Jones et al. 2006, 2008). Some dates lacked both adequate spectrometer-based and hand-held anemometer wind data; on these dates, only ICAs of SO_2 were calculated.

Results

Results of this study's 707 measurements of SO_2 emissions at Masaya are reported in Table 2 and Table 3. Figure 3 gives a graphical representation of ICA data divided into two subsets according to measurement location. For the two month-long periods over which measurements were made,

Table 1 Comparison of simultaneous measurements of ground-level wind speed by hand-held anemometer and plume speed measurements made using the dual-spectrometer method

Date	Road	Anemometer wind speed (m/s)	Anemometer maximum gust (m/s)	Dual-spectrometer plume speed (m/s)
2/25/2005	Llano Pacaya	3.7	7	10.3
2/26/2005	Llano Pacaya	2.8	5.9	9
3/5/2005	Ticuantepe	1.4	4.4	3.4
3/6/2005	Ticuantepe	1.7	4.1	2.1
3/7/2005	Ticuantepe	2.2	5.2	12
3/11/2005	Ticuantepe	3.6	8.5	2.1
3/12/2005	Ticuantepe	2.6	7.5	3.5
3/15/2005	Ticuantepe	1.1	2.1	12.4
3/16/2005	Ticuantepe	1.1	2.9	10.5
2/23/2006	Llano Pacaya	7.6	12.5	12.1
2/26/2006	Llano Pacaya	6.5	9.9	22.5
2/27/2006	Llano Pacaya	5.6	12.4	12.4
2/28/2006	Llano Pacaya	9.3	13.2	19
3/1/2006	Llano Pacaya	7.2	10.2	20.6
3/3/2006	Llano Pacaya	4.9	8.3	7.3
3/7/2006	Llano Pacaya	6.1	10.9	7
3/12/2006	Llano Pacaya	6.1	10.2	16.8

the average daily ICA was approximately $5.2 \times 10^5 \pm 4.7 \times 10^5$ppm·m^2 in 2005 and $5.7 \times 10^5 \pm 2.4 \times 10^5$ppm·m^2 in 2006 as measured on the Ticuantepe road. ICAs on the Llano Pacaya road were $6.7 \times 10^5 \pm 5.1 \times 10^5$ppm·m^2 and $3.1 \times 10^5 \pm 1.3 \times 10^5$ppm·m^2 in 2005 and 2006, respectively. The single day of measurements in 2007 yielded an average ICA of $10.5 \times 10^5 \pm 2.6 \times 10^5$ppm·m^2 on the Ticuantepe road and $6.9 \times 10^5 \pm 3.4 \times 10^5$ppm·m^2 on Llano Pacaya. The maximum ICA on Ticuantepe was on February 27, 2005 at $18.4 \times 10^5 \pm 1.9 \times 10^5$ppm·m^2, while the minimum was $2.3 \times 10^5 \pm 0.56 \times 10^5$ppm·m^2, measured on March 5, 2005. On the Llano Pacaya road, the maximum ICA was $13.0 \times 10^5 \pm 4.2 \times 10^5$ppm·m^2 on February 26, 2005. The minimum ICA on Llano Pacaya was $1.9 \times 10^5 \pm 0.55 \times 10^5$ppm·m^2 on March 14, 2005. However, there were also a number of dates in 2005 on which SO_2 was below detection levels on the Llano Pacaya road.

Using the dual spectrometer plume speed method, it was determined that plume speeds ranged from 2.1 to 22.5m/s on days for which measurements were made. Overall, winds during the measurement periods were weaker in 2005 than in 2006, with a 2005 average measured plume speed (calculated using 5-min moving windows; see Williams-Jones et al. 2006) of 6.8 ± 4.4m/s, as compared to an average of 12.2 ± 6.4m/s in 2006. The single day of plume speed measurements in 2007 yielded plume speeds of 3.2 and 5.4m/s (calculated using 3-min moving windows) for Ticuantepe and Llano Pacaya measurement sites, respectively. Taking into account only dates with accurately measured, spectrometer-based plume speeds, daily fluxes ranged from 115 ± 30 to 3,552 ± 1,980t/d, with average values of 1,690 ± 1,480t/d on Ticuantepe and 1,140 ± 770t/d on Llano Pacaya.

Discussion

Apparent loss of SO_2 with increasing distance from vent

In previous SO_2 monitoring campaigns at Masaya (e.g., Stoiber et al. 1986; Williams-Jones et al. 2003; CCVG-IAVCEI 2003; McGonigle et al. 2004), it was implicitly assumed that, while dispersion would inevitably occur as the plume propagated further downwind, no measurable mass loss would occur. Any vertical dispersion is accounted for by the fact that the spectrometers (COSPEC, FLYSPEC, or mini-DOAS) measure concentrations over the total vertical column of atmosphere, while lateral dispersion in the cross-wind direction was assumed to affect measurements only in that profiles downwind would be wider than those made at more proximal locations (Williams-Jones et al. 2008). Dispersion along the axis of the plume's propagation is not an issue due to the relatively continuous nature of the plume. However, inspection of the SO_2 data from 2005 and 2006 indicated that there is a significant discrepancy between the magnitudes of the SO_2 integrated column amounts calculated for the Ticuantepe and Llano Pacaya roads. Regardless of the overall magnitude of SO_2 output, ICAs calculated for the traverses on the more distal Llano Pacaya road are generally ~33% to ~50% less than those calculated for the proximal Ticuantepe road (Fig. 3, Tables 2 and 3).

Possible sources of ICA discrepancy

Deposition of sulfur

Loss of SO_2 by deposition of S on the earth's surface was initially thought to be one possibility in accounting for the

Table 2 Summary of SO_2 emission data as measured on the Ticuantepe road

Date	Number of traverses	Plume speed (m/s)	Mean Daily SO_2 ICA (x 10^5 ppm·m^2)	SD (x 10^5 ppm·m^2)	Mean daily flux at measured plume speed (t/d)	SD (t/d)
2005						
2/25/05	6	10.3 LP	7.1	2.0	1,684	485
2/26/05	8	9.0 LP	15.2	4.1	3,153	846
2/27/05	5		18.4	1.9		
3/3/05	7	2.4 T	6.1	1.8	339	100
3/5/05	10	3.4 T	2.3	0.56	182	44
3/6/05	15	2.1 T	2.8	1.1	136	53
3/7/05	9	12.0 T	2.9	1.0	811	282
3/11/05	11	2.1 T	2.8	1.1	137	53
3/12/05	9	3.5 T	3.1	0.80	249	65
3/14/05	12	3.0 T[a]	3.7	1.5	254	104
3/15/05	7	12.4 T	3.4	1.0	965	294
3/16/05	10	10.5 T	5.0	2.1	1,217	518
Average[#]	9	6.4	5.2	4.7	713	879
2006						
2/16/06	3	6.5 LP[a]	4.3	1.5	646	221
2/17/06	14	3.0 T[a]	4.9	1.5	340	102
2/18/06	11	2.2 T[a]	3.7	1.1	189	56
2/19/06	12	1.4 T[a]	3.6	1.3	115	43
2/20/06	10	2.5 T[a]	3.7	1.4	211	80
2/21/06	14	1.1 T[a]	4.6	1.2	115	31
2/23/06	7	12.1 LP	7.1	1.6	1,983	458
2/24/06	11	2.4 T[a]	5.6	2.4	311	132
2/26/06	23	22.5 LP	6.9	3.8	3,552	1,976
2/27/06	20	12.4 LP	4.2	2.1	1,212	595
2/28/06	13	19.0 LP	6.6	1.7	2,876	734
3/1/06	23	20.7 LP	6.8	2.3	3,224	1,115
3/2/06	12	8.0 LP[a]	7.2	2.0	1,321	377
3/3/06	25	7.3 LP	6.7	2.0	1,127	340
3/4/06	29	7.9 LP[a]	5.2	1.8	943	330
3/6/06	8	9.6 LP[a]	4.5	1.4	989	303
3/7/06	6	7.0 LP	5.2	1.5	837	242
3/8/06	24	4.5 LP[a]	5.1	1.7	528	174
3/9/06	12		7.0	1.4		
3/10/06	9		7.6	2.2		
3/12/06	7	16.8 LP	7.8	2.5	3,014	972
Average[#]	14	8.8	5.7	2.4	1,348	1,369
2007						
3/8/07	2	3.2 T	10.5	2.6	771	195
Ticuantepe Average[#]	12	7.8	5.6	3.2	1,165	1,277

Superscripts T and LP are indicative of the road on which the plume speed (derived from 5-min windows of full plume speed scan, except in 2007, which used 3-min windows) utilized for flux calculation was measured. *Blank line* in 2005 dataset denotes a landslide in Santiago crater, which blocked the vent, lowering SO_2 fluxes

[#] All averages were determined using individual measurements from the entire 707-measurement dataset.

[a] Plume speed data in which handheld anemometer data have been substituted for spectrometer-based measurements.

discrepancy. Delmelle et al. (2001) estimated that approximately 10% of the total SO_2 flux from Masaya is lost to soils and vegetation through dry deposition of S. However, this estimate is based on SO_2 flux measurements conducted solely on the Llano Pacaya road. Given our observations that ICAs measured on Llano Pacaya are up to 50% less than those measured on the more proximal Ticuantepe road, the volume of dryly deposited sulfur measured by Delmelle et al. (2001)

Table 3 Summary of SO_2 emission data as measured on the Llano Pacaya road

Date	Number of traverses	Plume speed (m/s)	Mean daily SO_2 ICA (x 10^5 ppm·m^2)	SD (x 10^5 ppm·m^2)	Mean daily flux at measured plume speed (t/d)	SD (t/d)
2005						
2/25/05	6	10.3^{LP}	8.9	1.7	2,098	396
2/26/05	7	9.0^{LP}	13.0	4.2	2,688	863
2/27/05	6		10.9	2.3		
3/7/05	2	12.0^{T}	2.3	1.2	636	322
3/12/05	6	3.5^{T}	2.0	0.47	161	38
3/14/05	6	3.0^{Ta}	1.9	0.55	128	38
3/15/05	4	12.4^{T}	2.3	0.63	663	181
Average[#]	5	8.4	6.7	5.1	1,063	1,110
2006						
2/16/06	2	$6.5^{LP,a}$	2.9	1.3	436	193
2/17/06	10	$7.9^{LP,a}$	2.4	1.0	445	185
2/18/06	12	$7.8^{LP,a}$	1.9	0.39	346	71
2/19/06	11	$9.3^{LP,a}$	2.1	0.55	446	117
2/20/06	8	$6.3^{LP,a}$	2.4	0.58	342	85
2/21/06	12	$5.2^{LP,a}$	2.2	0.58	264	69
2/23/06	6	12.1^{LP}	3.7	1.7	1,035	486
2/24/06	12	$9.4^{LP,a}$	3.1	0.92	676	199
2/26/06	8	22.5^{LP}	4.3	1.8	2,228	946
2/27/06	11	12.4^{LP}	2.7	0.82	778	233
2/28/06	10	19.0^{LP}	2.6	0.72	1,144	317
3/1/06	8	20.7^{LP}	3.2	0.76	1,524	362
3/2/06	23	$8.0^{LP,a}$	4.1	1.4	749	262
3/3/06	25	7.3^{LP}	4.3	0.95	727	159
3/4/06	24	$7.9^{LP,a}$	3.4	1.3	622	234
3/6/06	31	$9.6^{LP,a}$	2.4	1.0	523	220
3/7/06	9	7.0^{LP}	2.9	0.59	466	95
3/8/06	20	$4.5^{LP,a}$	2.8	0.78	287	80
3/9/06	5		3.7	0.51		
3/10/06	6		5.8	1.1		
3/12/06	9	16.8^{LP}	3.6	0.70	1,381	271
Average[#]	13	10.5	3.1	1.3	691	485
2007						
3/8/07	4	5.4^{LP}	6.9	3.4	861	418
Llano Pacaya Average[#]	10	9.8	3.6	2.5	741	610

Superscripts T and LP are indicative of the road on which the plume speed (derived from 5-min windows of full plume speed scan, except in 2007, which used 3-min windows) utilized for flux calculation was measured. *Blank line* in 2005 dataset denotes a landslide in Santiago crater, which blocked the vent, lowering SO_2 fluxes.

[#] All averages were determined using individual measurements from the entire 707-measurement dataset.

[a] Plume speed data in which handheld anemometer data have been substituted for spectrometer-based measurements.

may amount to only 5% of the total SO_2 emissions at Masaya. In reality, the total loss of S to dry deposition could be even less than 5%; Ticuantepe is 5km downwind of the active vent and fluxes measured there may also be underestimates of actual SO_2 emissions. Accordingly, dry deposition of S from the SO_2 plume is not sufficient to fully explain the difference in measured fluxes at Masaya.

Conversion of SO_2 to sulfate aerosols

During daytime conditions, the principal oxidant in the conversion of SO_2 to sulfate aerosols is recognized as the hydroxyl radical, such that the net atmospheric reaction for sulfate generation (and subsequent regeneration of hydroxyl) is as follows (Eatough et al. 1994 and references therein):

$$OH + SO_2(+O_2, H_2O) \rightarrow H_2SO_4 + HO_2 \quad (1)$$

Should such conversion occur downwind of the degassing volcano, integrated column amounts and fluxes of SO_2 measured by spectrometers may underestimate the actual emissions from the volcano's vent.

To directly assess aerosol conversion rates between the two roads directly, of the 707 FLYSPEC traverses, approximately 60 incorporated the use of Microtops II sun

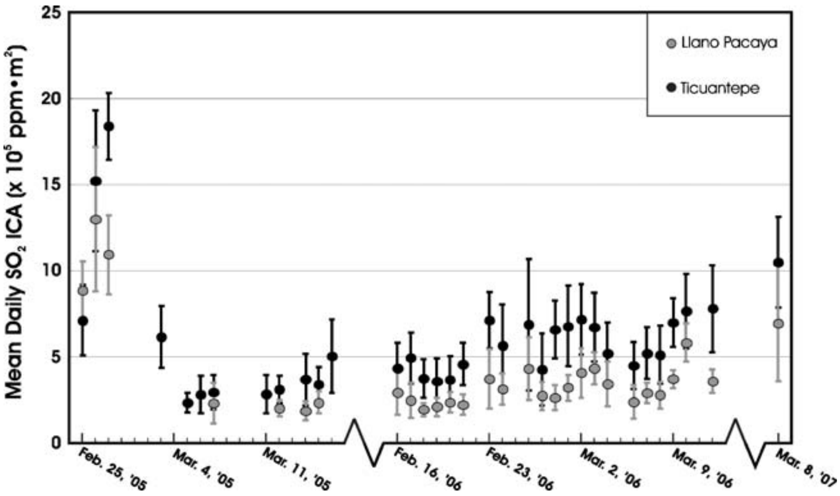


Fig. 3 Mean daily SO_2 integrated column amount (ICA) as measured on each of the two roads downwind of Masaya's active vent. *Error bars* represent 1 SD of 1 day of measurements. Note the breaks in the *x*-axis. See Tables 2 and 3

photometers to measure aerosol optical depths (e.g., Morys et al. 1996; Porter et al. 2001). As SO_2 data were being captured over the course of a single traverse, the field vehicle stopped at intervals of ~300m to allow for a Microtops II measurement. Raw data in the 500nm channel were re-processed using software after Watson and Oppenheimer (2000) to obtain aerosol ICAs (for more detailed methodology see Watson and Oppenheimer 2000; Mather et al. 2004). Of the approximately 60 traverses that incorporated aerosol measurements, only 5 pairs were sufficiently close in time to be utilized in the assessment of sulfate conversion between the two roads. For the five pairs of traverses, the minimum particle ICA on Ticuantepe was 1.1 × 10^{19} particles/m, while the maximum was 1.5 × 10^{19} particles/m. The corresponding range for Llano Pacaya was 0.8 × 10^{19} particles/m to 2.4 × 10^{19} particles/m (Table 4).

The particle ICAs calculated for the five pairs of traverses are all of the same order of magnitude, with no more than a twofold difference in the magnitudes seen on the Ticuantepe versus Llano Pacaya roads (within the margin of error of the measurements). Some traverses show particle column densities following the same general trend as SO_2 concentration path-length within the plume (Fig. 4), possibly indicating that variations in aerosol content within the plume merely correspond to equivalent variations in the overall concentration of the plume as a whole.

Table 4 Plume particle content for five pairs of aerosol traverses. T and LP in traverse name indicate Ticauntepe and Llano Pacaya roads, respectively

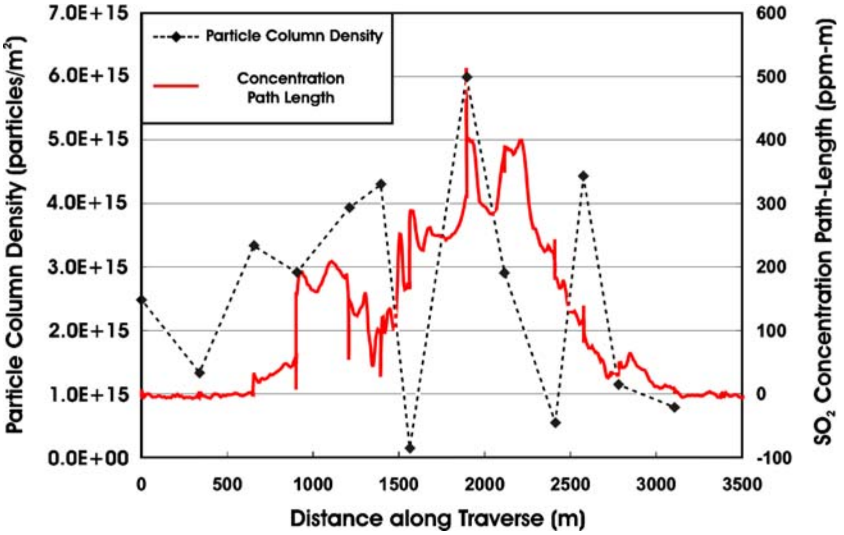
Date and traverses	Ticuantepe ICA of particles (x 10^{19} particles/m)	Llano Pacaya ICA of particles (x 10^{19} particles/m)
3/1/2006—T20 and LP6	1.5	2.4
3/6/2006—T2 and LP5	1.3	1.7
3/6/2006—T6 and LP9	1.3	1.3
3/8/2006—T4 and LP4	1.1	1.2
3/8/2006—T6 and LP8	1.3	0.80

Previous studies of aerosol conversion in volcanic plumes have quoted conversion rates ranging from negligible (e.g., McGonigle et al. 2004) to close to 100% (e.g., Oppenheimer et al. 1998). Conversion of SO_2 to sulfate in dry, summer conditions like those at Masaya have been found to be approximately 5–10% per hour (Eatough et al. 1994), and conversion rates at Masaya are reported to be close to 0% (McGonigle et al. 2004). Based on plume speeds measured with the dual-spectrometer method, plume travel times over the ~10km separation between the Ticuantepe and Llano Pacaya roads range from 7 to 79min. For conversion rates expected at Masaya, even 79min is not sufficient to account for the ~33% to ~50% SO_2 ICA discrepancy measured. It is probable that most, if not all, aerosols in the plume are due to high-temperature, near-vent conversion (Allen et al. 2002; Mather et al. 2003) and maintain a relatively constant concentration over the spatial scope of this study.

Topographic modification of winds

Another possible reason for the discrepancy in SO_2 measurements between the proximal and distal roads is the effect of topography. Despite a number of previous studies of volcanic gas at Masaya (e.g., Stoiber et al. 1986; Horrocks et al. 1999; CCVG-IAVCEI 2003; Williams-Jones et al. 2003), all have failed to consider the geometry of the roads with respect to elevation as well as location. The Llano Pacaya ridge, ~15km downwind, at its highest point, is more than 400m higher than the degassing summit of Masaya. A series of secondary ridges and valleys branches off the main ridge in the direction of the volcano. The regional trade winds generally blow northeast to southwest, almost directly over the highest points on the Llano Pacaya

Fig. 4 Example of simultaneous particle and SO_2 column measurements from March 8, 2006



ridge. The potential for interaction of the trade winds with the complex topography cannot be ignored. Wind field modifications by topography at other volcanoes have been previously noted (e.g., Graziani et al. 1997; Favalli et al. 2004), however no investigation of wind speed variations has been conducted at Masaya as yet.

Oke (1987) gives the following equation as a simple, first-order means to calculate the likely acceleration factor of winds over a two-dimensional ridge:

$$V_{\max}/V_{up} = 1 + b(H/X) \quad (2)$$

where $V_{\max}/V_{\mathrm{up}}$ is the actual acceleration factor, or the ratio of the maximum wind velocity relative to the velocity of the wind upwind of the ridge; b is the theoretical maximum acceleration factor for the topography in question and is equal to 2 for a two-dimensional ridge, 1.6 for a three-dimensional hill, and 0.8 for a step-up (Taylor and Lee 1984; Oke 1987); H is the height of the ridge; and X is the distance from the peak of the ridge to the point where the elevation is equal to $H/2$. In general, actual maximum acceleration factors, $V_{\max}/V_{\mathrm{up}}$, for this topographic geometry range from 1.6 to 1.8 (Oke 1987). Winds are perturbed to a lesser degree within an envelope ranging from just upwind of the ridge to just downwind of the ridge, and up to an altitude approximately equivalent to X.

The ~400m elevation difference over a horizontal distance of ~15km from Masaya's summit to the Llano Pacaya road is sufficient to cause orographic acceleration of winds (Oke 1987). For the topography at Masaya, an expected range of acceleration factors, as determined by Eq. 2, over the Llano Pacaya ridge is at least 1.2 to 1.4. Actual acceleration factors likely exceed those estimated by Eq. 2, as the topography is more complex than can be represented by the simplistic Eq. 2 (D. Steyn, personal communication, 2006). As such, a given parcel of the plume not only will be diluted across the width of the plume as it propagates away from the vent, but also along the axis of the plume, most noticeably at the highest elevation, where acceleration is greatest (Hunt and Simpson 1982; Oke 1987). Should winds be faster over the Llano Pacaya road than over the Ticuantepe road, SO_2 column abundances and, therefore, derived fluxes, would vary between the two measurement sites.

The degree of the topographic acceleration's effect on the plume and its propagation speed will depend largely on the height of the plume and ambient atmospheric conditions. The region surrounding Masaya is prone to the development of a nocturnal temperature inversion (Delmelle et al. 2002), which can interfere with the plume's ability to propagate over the Llano Pacaya ridge, sometimes forcing it to spread laterally along the windward side of the ridge. Heating of the surface during daylight hours generally dissipates the capping inversion, which allows the plume to clear the ridge. Depending on the height to which the plume rises, it will either be near ground-level and, therefore, be affected by orographic acceleration, or it will rise above the envelope influenced by the acceleration and continue over the ridge unaffected. Persistence of an atmospheric inversion may also enhance the orographic acceleration, as the accelerating layer is constricted between the ridge top and the base of the inversion (Oke 1987). Smaller topographic features may complicate the issue further, causing localized interaction with and acceleration of the plume.

Field measurements to investigate the effects of topographic acceleration of winds at Masaya were conducted in March of 2007. Plume speed measurements were conducted on both the Ticuantepe road and the Llano Pacaya road in a near-simultaneous fashion, with a total of four spectrometers, in order to assess the difference in magnitude of plume speeds at the different locations. Over an hour-long time span, the plume was determined to be moving over the Ticuantepe measurement site at an average speed of 3.2m/s. A 40-min measurement period on the Llano Pacaya road indicated that the plume's average speed over the ridge was 5.4m/s. This confirmed that SO_2 loss between the two roads is apparent (due to the assumption of a uniform plume speed in calculations of SO_2 flux); wind acceleration factors on the order of 1.7 affecting Masaya's plume are sufficiently large to account for all of the ~33 to ~50% apparent losses measured in this study.

Fig. 5 Photographs of Masaya volcano's plume as seen from the space shuttle, with the active vent indicated by a star. The portion of the plume over the Llano Pacaya ridge is visibly less concentrated than other portions of the plume. Photos are from November 9, 1984 (*top photo*; NASA image STS 051a-32-066) and January 13, 1986 (*bottom photo*; NASA image STS061c-37-076). Images courtesy of the Image Science and Analysis Laboratory, NASA-Johnson Space Center

Photographs of Masaya's plume taken from the space shuttles in the mid-1980s support the finding that topographically induced wind acceleration causes dilution of the plume over the Llano Pacaya ridge (Fig. 5). In each of the images, there appears to be a visible dilution of the plume beginning immediately adjacent to the windward side of the ridge, and a subsequent semi-transparent section of the plume directly over the ridge. Leeward of the ridge, the plume appears to regain characteristics similar to those prior to encountering the ridge, becoming more concentrated and opaque. Also of note in support of the dilution due to acceleration is the fact that, while results from the 2006 field campaign generally indicated an apparent loss of ~33 to ~50%, data from March 10, 2006 showed only a 24% apparent loss between the Ticuantepe and Llano Pacaya measurements. The winds had shifted that day, becoming more southerly. In turn, the plume was blown farther north, over a lower-altitude portion of the Llano Pacaya ridge than is normally the case, and at a more oblique angle to the ridge as well. The topographically induced plume acceleration would be subdued under such conditions, which is consistent with the observed apparent loss of only 24%.

In general, acceleration factors up to two are likely to be the cause of the apparent loss of SO_2 over the 10km from the Ticuantepe road to the Llano Pacaya road. The discrepancy between SO_2 integrated column amounts measured on the two roads will persist as long as one single plume speed is applied to measurements made at different localities. It is important to recognize that a single plume speed measurement location, which may or may not be the same location as SO_2 measurements, is often the norm for volcanic SO_2 flux studies. Plume speeds may be derived from hand-held anemometer (e.g., Williams-Jones et al. 2001) or weather station (e.g., Elias et al. 1998) measurements of ground wind speed, multi-spectrometer measurement of plume speed/velocity (e.g., McGonigle et al 2005b; Williams-Jones et al. 2006), or normalization to an arbitrary speed of 1m/s (Zapata et al. 1997). However, at volcanoes with complex topography and the possibility of topography-wind interactions, as at Masaya, plume speed measurements must be conducted in the same locality as the SO_2 measurements themselves.

The findings in this study have implications beyond field protocol for making SO_2 flux measurements. SO_2 fluxes from Masaya have been used in calculating worldwide volcanic SO_2 input to the atmosphere (Andres and Kasgnoc 1998), the majority of which were measurements made on the Llano Pacaya road. True SO_2 fluxes are conceivably twice those used in such calculations, depending on the method for determination of plume speed utilized. As Masaya was already one of the largest non-eruptive emitters of SO_2, a twofold increase in reported SO_2 fluxes from Masaya could significantly alter the estimated budget of volcanic SO_2. Similarly, remotely sensed SO_2 fluxes are quoted with respect to the 'excess sulfur problem' (e.g., Andres et al. 1991; Wallace et al. 2003). Volumes of SO_2 released by volcanoes are often more than can be accounted for by petrologic estimates of magmas' pre-eruptive sulfur contents. If erroneously low SO_2 fluxes, as with this study's Llano Pacaya measurements, are referenced with respect to the 'excess sulfur,' true SO_2 fluxes will exacerbate the 'excess sulfur problem.'

Conclusions

Three decades of SO_2 flux measurements at Masaya volcano, Nicaragua have consistently resulted in coefficients of variation of approximately 30% over the short time periods associated with individual field campaigns (Stoiber and Jepsen 1973; Stoiber et al. 1986; Rymer et al. 1998; Galle et al. 2003; McGonigle et al. 2002; Williams-Jones et al. 2003; Williams-Jones, unpublished data). The 707 measurements from this study exhibit the same natural variability, and also reveal a significant discrepancy between ICAs measured at two different distances downwind of Masaya's active vent. Fluxes measured on the Llano Pacaya road, ~15km downwind of the vent, were ~33 to ~50% lower than those recorded on the Ticuantepe road, only ~5km from Masaya.

To account for the apparent loss over 10km, dry deposition of sulfur, conversion of sulfur to sulfate aerosols, and topographic interactions were considered. Previous estimates of losses to dry deposition were approximately 10% (Delmelle et al. 2001). Accordingly, dry deposition cannot be solely responsible for the measured SO_2 discrepancy. Likewise, estimates of the plume's aerosol content in this study do not indicate sufficient variation to account for a ~33 to ~50% apparent loss of SO_2. Further, published rates of conversion of SO_2 to sulfate would lead to degrees of conversion much smaller than those needed to explain the losses seen at Masaya. Most sulfate aerosols present in Masaya's plume are likely to be of near-source, high temperature origin (Allen et al. 2002; Mather et al. 2003).

The complex topography surrounding the low-lying Masaya volcano is interpreted to be at the root of the apparent losses of SO_2 with distance downwind. Simple first-order calculations indicate that the Llano Pacaya ridge is likely modifying the persistent trade winds that have made Masaya an ideal site for SO_2 measurements; field measurements of plume speeds in 2007 confirm that the plume can be at least 1.7 times faster over the distal Llano Pacaya road than over the proximal Ticuantepe road. Up to 400m higher than the summit of Masaya, the Llano Pacaya ridge forces winds and, therefore, the entrained plume, to accelerate. Consequently, the plume is diluted along its axis of propagation over the Llano Pacaya road relative to the Ticuantepe road. This dilution results in smaller SO_2 integrated column amounts over Llano Pacaya, and when these ICAs are multiplied by a single plume speed, it results in a misleading discrepancy between fluxes recorded on the two roads. As a consequence of the acceleration of local winds, Llano Pacaya fluxes routinely appear ~33 to ~50% lower than those measured on Ticuantepe, when only one plume speed is used for all Masaya measurements. Distinct plume speed measurements for each distance downwind will remedy the problem, with faster winds measured over Llano Pacaya compensating for the lower column thicknesses.

It is important to note that orographic modification of winds may occur at other volcanoes. One must be wary of using one blanket plume speed value for all data collected at different locations, as it can result in misleading variations within the SO_2 flux dataset, either by creating non-existent 'losses' or exacerbating the true discrepancies between values from different measurement locations. Single plume speeds or normalizing factors may still be useful in comparing year-to-year datasets for individual measurement locations, but should not be used in comparing measurements from different distances downwind. Use of erroneous fluxes of SO_2 may result in flawed estimations of both global volcanic SO_2 emissions and volumes of degassed magma at individual volcanoes.

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