

SO₂ depletion in tropospheric volcanic plumes

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[1] Ground based remote sensing techniques are used to measure volcanic SO₂ fluxes in efforts to characterise volcanic activity. As these measurements are made several km from source there is the potential for in-plume chemical transformation of SO₂ to sulphate aerosol (conversion rates are dependent on meteorological conditions), complicating interpretation of observed SO₂ flux trends. In contrast to anthropogenic plumes, SO₂ lifetimes are poorly constrained for tropospheric volcanic plumes, where the few previous loss rate estimates vary widely (from $\ll 1$ to $>99\%$ per hour). We report experiments conducted on the boundary layer plume of Masaya volcano, Nicaragua during the dry season. We found that SO₂ fluxes showed negligible variation with plume age or diurnal variations in temperature, relative humidity and insolation, providing confirmation that remote SO₂ flux measurements (typically of ≈ 500 – 2000 s old plumes) are reliable proxies for source emissions for ash free tropospheric plumes not emitted into cloud or fog.

INDEX TERMS: 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0370 Atmospheric Composition and Structure: Volcanic effects (8409); 3307 Meteorology and Atmospheric Dynamics: Boundary layer processes; 3360 Meteorology and Atmospheric Dynamics: Remote sensing. **Citation:** McGonigle, A. J. S., P. Delmelle, C. Oppenheimer, V. I. Tsanev, T. Delfosse, G. Williams-Jones, K. Horton, and T. A. Mather (2004), SO₂ depletion in tropospheric volcanic plumes, *Geophys. Res. Lett.*, *31*, L13201, doi:10.1029/2004GL019990.

1. Introduction

[2] Sulphur dioxide is one of the most important magmatic volatiles for volcanic geochemical analysis [e.g., Symonds *et al.*, 1994]. Because of its abundance in volcanic plumes, low ambient concentrations and highly structured absorption features from 260–340 nm [Manatt and Lane, 1993] SO₂ is also well suited for volcano plume remote sensing [McGonigle and Oppenheimer, 2003]. During the last thirty years many studies have been conducted with correlation spectrometers [Stoiber *et al.*, 1983], and more recently compact charge coupled device (CCD) detector based instruments [McGonigle *et al.*, 2002, 2004; Galle *et al.*, 2003], to monitor remotely volcanic SO₂ fluxes for purposes of eruption prediction, and to investigate the environmental and atmospheric impacts of these emissions.

[3] However, volcanological interpretation of observed flux trends is potentially complicated by conversion of SO₂ to sulphate aerosol in the atmosphere prior to measurements (typically a few km downwind of the source). The in-plume SO₂ can be oxidised in the gas or aqueous phase and on the surface of solid particles, with reaction rates increasing with temperature, relative humidity (R.H.), insolation, and aerosol density [Eatough *et al.*, 1994]. Whilst these reactions are relatively well understood in the free atmosphere and for anthropogenic plumes, they are poorly characterised for tropospheric volcanic plumes. For instance, in the latter case, one might expect faster gas phase SO₂ oxidation (which occurs primarily via reaction with OH) than for power station plumes, where emitted NO_x concentrations are higher, acting to reduce the available OH concentrations [Hewitt, 2001]. Other potential SO₂ removal mechanisms, which remain poorly constrained in volcanic contexts, are wet and dry deposition [Aiuppa *et al.*, 2001; Delmelle *et al.*, 2001; Delmelle, 2003].

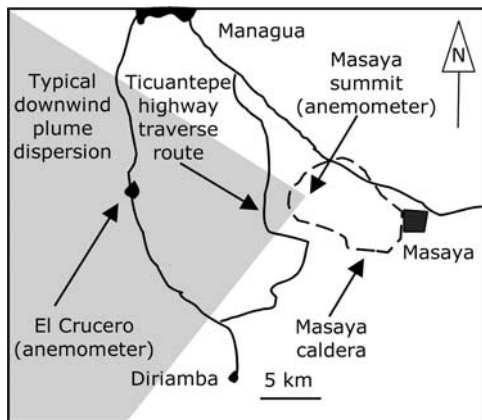


Figure 1. Map of the area surrounding Masaya volcano, Nicaragua showing the Ticuantepel highway route used during car traverses, the typical downwind plume dispersion (shaded area), and the locations of the two anemometers.

[4] Assuming first order kinetics, loss rates (k) of volcanic SO₂ can be characterised by:

$$I = I_0 e^{-kt} \quad (1)$$

where I_0 is the source flux and I is the flux measured after the plume has travelled for a time t [e.g., Möller, 1980]. In the few previous studies investigating SO₂ depletion in tropospheric volcanic plumes, k values ranging from 2×10^{-7} to $5 \times 10^{-3} \text{ s}^{-1}$ have been reported [e.g., Martin *et al.*, 1986; Oppenheimer *et al.*, 1998; Porter *et al.*, 2002]. These loss rates correspond to measured I varying between $\ll 1\%$ I_0 and $>99\%$ I_0 , for the typical ages (≈ 500 – 2000 s) of plume sampled during remotely sensed measurements. Thus there remains large uncertainty concerning how much SO₂ depletion can cause underestimations of source strength, and whether changes in meteorology can complicate volcanological interpretation of flux time series trends.

[5] For reference, Möller [1980] reported k values of $\approx 0.12 \times 10^{-5} \text{ s}^{-1}$, $\geq 5 \times 10^{-5} \text{ s}^{-1}$, and $\approx (0.1\text{--}10) \times 10^{-5} \text{ s}^{-1}$, respectively for SO₂ oxidation via gas phase, aqueous phase, and particle surface reactions (important for particle loading $>100 \mu\text{g m}^{-3}$) in the (non-volcanic) troposphere. In a detailed study of the effect of meteorological variables upon these processes, Eatough *et al.* [1994] documented that k varies from $<1\%$ h^{-1} to a maximum of around $\approx 10\%$ h^{-1} , with increasing temperature and R.H. (e.g., $\approx 3\%$ h^{-1} at 20°C , and $\approx 8\%$ h^{-1} at 30°C , for 50% R.H.) for gas phase reactions during daylight. They also report diurnal variations in SO₂ loss via gas phase oxidation, with maxima at noon ($\approx 7\%$ h^{-1} , vs. 2% h^{-1} daily mean, for 25°C and 50% R.H.) when OH concentrations are highest. Aqueous phase SO₂ conversion is more complex and loss rates can vary widely ($<2\%$ h^{-1} to $>500\%$ h^{-1}) depending upon oxidant concentrations, droplet size and composition [Eatough *et al.*, 1994].

[6] Here we report results of an experiment performed at Masaya, a 600-m-high basaltic shield volcano, situated 25 km southeast of Managua, Nicaragua, aimed at better constraining the effects of SO₂ depletion on remotely sensed SO₂ flux measurements of tropospheric plumes. In particular, the extent to which SO₂ flux varies diurnally, as

insolation, relative humidity and temperature change, was studied, for this boundary layer ash-free plume. At this time, as in previous years, gas was emitted passively from a vent on the floor of the active (Santiago) crater. Weak incandescence, visible at night, from the vent indicated “open-vent” degassing from a magma pond residing a few tens to hundreds of meters down. Masaya is an ideal site for this investigation given its network of downwind roads and steady-state (timescales of weeks-months) degassing regime [e.g., Delmelle *et al.*, 1999; Horrocks *et al.*, 2003].

2. Methodology

[7] SO₂ column amount measurements were made using a laptop PC controlled OceanOptics Inc. USB2000 spectrometer (245–400 nm spectral range, ≈ 0.5 nm resolution) fibre-coupled to a zenith-pointing telescope of 7-mrad field of view. The telescope was mounted to the side of a car, alongside a GPS receiver, and the vehicle was driven underneath Masaya’s plume. Time stamped spectra were continuously recorded with a time step of 1–3 s (depending on available skylight intensity). Each spectrum could then be located using the GPS datastream (logged at 1 Hz). Overhead SO₂ column amounts were evaluated in real time for each spectrum, using a differential optical absorption spectroscopy retrieval described by Galle *et al.* [2003] and McGonigle *et al.* [2002], to enable location of the plume boundaries. Between 24 and 29 March 2003 66 such traverses were completed on the Ticuantepel highway, ≈ 6 km downwind of the volcano, between 06:30 (just after sunrise) and 15:30 (see Figure 1). For twelve of the traverses, another USB2000, using a retrieval algorithm based on calibration with internal SO₂ cells was used [Horton *et al.*, 2002]. The two spectrometers were inter-calibrated to ensure data compatibility.

[8] For each spectrum, the SO₂ column amount was multiplied by the distance traversed perpendicularly to the plume transport direction, during the spectral acquisition and real-time evaluation. The plume direction was taken as the vector between the summit and the position corresponding to the weighted mean spectrum (weighted according to spectral concentration – typically close to the position at which the maximum gas concentration was recorded). By integrating these products across the entire plume the column cross section was found, which was multiplied by plume speed to derive fluxes. The plume speed was obtained by averaging readings from two anemometers: one located 3 m from the ground at Masaya’s summit, and the other situated 5 m above the ground, on a radio mast at El Crucero, locally the highest topographic point and close to the plume altitude (see Figure 1). In order to identify any variation of SO₂ flux with diurnal changes in meteorological conditions, temperature and relative humidity were recorded continuously using a weather station installed at the volcano’s summit.

3. Results and Discussion

[9] In Figure 2 the flux for each measurement (I) is plotted on a logarithmic scale, against the corresponding plume age (t) (the distance from the summit to the position corresponding to the weighted mean spectrum, divided by

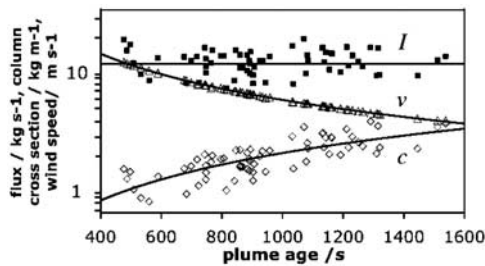


Figure 2. Plots of flux (I), column cross section (c), and plume speed (v) versus plume age for measurements made at Masaya, during March 2003. The exponential best-fit curve (a straight line for the logarithmic y axis) shows that SO₂ depletion was negligible over the range of plume ages encountered. This is highlighted by the mirror symmetry about a near horizontal axis for the best-fit lines of the cross section and plume speed plots.

the plume transport speed (v). The scatter in these data arose mostly from random errors in wind speed determination, the plume direction changing mid-traverse, and beading of the plume in transit, causing rapid changes in observed column cross section, not related to changes in wind speed. In the case of observable SO₂ depletion, the flux should decrease with decreasing wind speeds as the sampled plume's age increases. In order to determine whether there is any such systematic decrease in measured flux, a best-fit exponential curve was drawn through our data, which according to equation (1) is of the form $I_0 \exp(-kt)$, providing k (the first order loss rate). The line of best-fit serves to average out the aforementioned scatter in the plotted data, by analogy with the standard procedure of averaging flux measurements from multiple traverses, in order to obtain a representative assessment of a volcano's SO₂ output [Stoiber *et al.*, 1983].

[10] It is clear from Figure 2 that SO₂ depletion causes negligible systematic reduction in measured flux with increasing plume age: the gradient of the best fit line is $-1 \pm 2 \times 10^{-5} \text{ s}^{-1}$. For typical remotely sensed plume ages (up to ≈ 2000 s), this corresponds to negligible SO₂ losses of 0–6%, prior to measurement. For such low levels of SO₂ depletion, the observed fluxes were essentially independent of wind speed, such that the column cross section (c) multiplied by v (or $\ln(v) + \ln(c) = \ln(I)$) is near constant for our data, within the scatter described above. Plots of v and c against t are also included in Figure 2, along with lines of best fit (which are mirror images, for the logarithmic y axis, about a near-horizontal axis) to illustrate this effect.

[11] In order to investigate the degree to which meteorological conditions affect SO₂ depletion in tropospheric volcanic plumes, causing non-volcanogenic time variations in measured flux time series, flux was plotted against measurement time for each traverse (Figure 3). This figure also shows a typical trace of relative humidity and temperature versus time for the measurement period. According to Eatough *et al.* [1994], increases in temperature, insolation and relative humidity will all increase rates of conversion of SO₂ to sulphate via homogenous and/or heterogeneous processes. However, in our case it appears as though there is very little change in flux over the measurement period,

during which the typical temperature range was 12°C, R.H. ranged from 100% to $\approx 40\%$, and solar elevations were variable. In particular, the plume was highly condensed whilst passing over the traverse location before 08:00, becoming progressively more transparent as the relative humidity decreased (completely transparent by 09:00). Testing for variations in fluxes shortly after sunrise is pertinent, as flux measurements under such low light levels have only become possible with the recent advent of the USB2000's application within volcanology. In comparison, the USB2000's predecessor: the COSPEC, which is considerably less light sensitive, is only capable of measurements after 09:00 for illumination conditions at Masaya during April.

[12] The depletion rate ($\approx 4\%$ per hour) reported for our study is within the range of values reported for power station plumes (1–10% per hour) [Eatough *et al.*, 1994], not emitted into fog or cloud, indicating that the more exotic physico-chemical environment of this volcanic plume causes no major perturbation to SO₂ loss rates. Of the few other depletion rates reported for tropospheric plumes most are in agreement with this report that SO₂ depletion is negligible for typical plume sampling ages [e.g., Martin *et al.*, 1986; Porter *et al.*, 2002]. In contrast, there are two reports that offer considerably different k values: $\gg 99\%$ loss per hour [Oppenheimer *et al.*, 1998], and $\approx 97\%$ loss per hour [Oppenheimer *et al.*, 1998; Jaeschke *et al.*, 1982]. However, a later survey of the same volcano (Mt. Etna) studied by Jaeschke *et al.* [1982] found lower SO₂ loss rates (average of 7% per hour) [Martin *et al.*, 1986]. This more recent investigation used Si and Po²¹⁰ as tracers for plume dispersion, as opposed to CO₂ in the former case. Due to high variability of background CO₂ concentrations and Etna's degassing of CO₂ through its flanks, it is likely that the Jaeschke *et al.* [1982] study is the less reliable estimate of k . Likewise the two Oppenheimer *et al.* [1998] k values are based on only three traverses each, which may not enable sufficient averaging of plume beading affects, wind errors or changes in source strength to constrain SO₂ depletion (the volcano: Soufrière Hills Montserrat does undergo rapid changes in emitted gas flux [e.g., Edmonds *et al.*, 2003]).

[13] We therefore propose that SO₂ depletion in tropospheric volcanic plumes does not significantly alter mea-

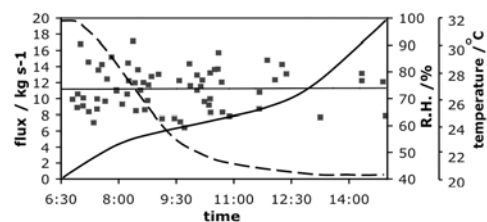


Figure 3. Plot of flux (dark squares), with straight line of best fit, versus time of day. Solid and dashed curves refer to typical traces of humidity and temperature throughout the measurement period, indicating that the observed flux was virtually invariant of these diurnal changes in meteorological conditions, during the just after sunrise to early afternoon measurement period. Note that the plume was highly condensed before 8:00, and completely transparent by 9:00.

sured fluxes for typical measurement locations for ash-poor plumes. However in the case of ash laden plumes or plumes entrained into cloud or fog, depletion rates may be much faster, possibly contributing to the high k values reported by Oppenheimer *et al.* [1998] (high plume particle density of $>400 \mu\text{g m}^{-3}$) and Jaeschke *et al.* [1982]. In contrast, we estimate the ash loading of the Masaya plume to be considerably below the $100 \mu\text{g m}^{-3}$ threshold, at which such reactions become significant, based on the visual observation that the non-condensed plume was not discoloured by ash. The effects of these phenomena upon SO₂ depletion in volcanic plumes have yet to be constrained, and may be difficult to quantify using UV spectroscopy for optically thick ash laden plumes or in fog. However, k values in excess of the highest ever reported for a volcanic plume ($5 \times 10^{-3} \text{ s}^{-1}$) have been found for power station plumes, emitted directly into cloud or fog [Eatough *et al.*, 1994].

4. Concluding Remarks

[14] In this study we report results of an experiment at Masaya volcano, Nicaragua, aimed at determining the effect of in-plume SO₂ depletion upon remotely sensed flux measurements of tropospheric volcanic plumes. We find that SO₂ removal rates are minimal, and similar to those reported for power station emissions, such that observed fluxes underestimate source strengths by insignificant amounts (up to a few percent). The diurnal variation in flux was also analysed and no significant change in flux was observed from just after sunrise (where the plume was highly condensed and relative humidity was $\approx 100\%$), to early afternoon (where the plume was completely transparent and relative humidity had dropped to $\approx 40\%$). These results affirm the value of remote sensed volcano fluxes as reliable proxies for source emissions, and that changes in meteorological conditions do not pose complications for volcanological interpretation of flux time series for ash-poor tropospheric volcanic plumes, not emitted into cloud or fog. Further information about SO₂ oxidation in volcanic plumes could be obtained by using the USB2000 to monitor in-plume ozone concentrations, in parallel with SO₂.

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