SO\textsubscript{2} depletion in tropospheric volcanic plumes

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[1] Ground based remote sensing techniques are used to measure volcanic SO\textsubscript{2} 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 SO\textsubscript{2} to sulphate aerosol (conversion rates are dependent on meteorological conditions), complicating interpretation of observed SO\textsubscript{2} flux trends. In contrast to anthropogenic plumes, SO\textsubscript{2} lifetimes are poorly constrained for tropospheric volcanic plumes, where the few previous loss rate estimates vary widely (from \(<1\) to \(>99\%) per hour). We report experiments conducted on the boundary layer plume of Masaya volcano, Nicaragua during the dry season. We found that SO\textsubscript{2} fluxes showed negligible variation with plume age or diurnal variations in temperature, relative humidity and insolation, providing confirmation that remote SO\textsubscript{2} flux measurements (typically of \(\sim 500\) – \(2000\) s old plumes) are reliable proxies for source emissions for ash free tropospheric plumes not emitted into cloud or fog.


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] SO\textsubscript{2} 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 SO\textsubscript{2} 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 SO\textsubscript{2} to sulphate aerosol in the atmosphere prior to measurements (typically a few km downwind of the source). The in-plume SO\textsubscript{2} 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 SO\textsubscript{2} oxidation (which occurs primarily via reaction with OH) than for power station plumes, where emitted NO\textsubscript{x} concentrations are higher, acting to reduce the available OH concentrations [Hewitt, 2001]. Other potential SO\textsubscript{2} removal mechanisms, which remain poorly constrained in volcanic contexts, are wet and dry deposition [Aiuppa et al., 2001; Delmelle et al., 2001; Delmelle, 2003].
Assuming first order kinetics, loss rates ($k$) of volcanic SO$_2$ can be characterised by:

$$I = I_0 e^{-kt}$$

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 SO$_2$ depletion in tropospheric volcanic plumes, $k$ values ranging from $2 \times 10^{-7}$ to $5 \times 10^{-3}$ 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 $\leq 1\%$ $I_0$ and $>99\%$ $I_0$, for the typical ages ($\approx 500$–$2000$ s) of plume sampled during remotely sensed measurements. Thus there remains large uncertainty concerning how much SO$_2$ depletion can cause underestimations of source strength, and whether changes in meteorology can complicate volcanological interpretation of flux time series trends.

For reference, Möller [1980] reported $k$ values of $\approx 0.12 \times 10^{-3}$ s$^{-1}$, $\geq 5 \times 10^{-3}$ s$^{-1}$, and $\approx 0.1$–$10 \times 10^{-3}$ s$^{-1}$, respectively for SO$_2$ oxidation via gas phase, aqueous phase, and particle surface reactions (important for particle loading $>100$ µg 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 $20^\circ$C, and $\approx 8\%$ h$^{-1}$ at $30^\circ$C, for 50% R.H.) for gas phase reactions during daylight. They also report diurnal variations in SO$_2$ loss via gas phase oxidation, with maxima at noon ($\approx 7\%$ h$^{-1}$, vs. 2% h$^{-1}$ daily mean, for $25^\circ$C and 50% R.H.) when OH concentrations are highest. Aqueous phase SO$_2$ 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].

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 SO$_2$ depletion on remotely sensed SO$_2$ flux measurements of tropospheric plumes. In particular, the extent to which SO$_2$ 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

SO$_2$ column amount measurements were made using a laptop PC controlled OceanOptics Inc. USB2000 spectrometer (245–400 nm spectral range, $\approx 0.5$ 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 SO$_2$ 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 Ticuantepe highway, $\approx 6$ 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 SO$_2$ cells was used [Horton et al., 2002]. The two spectrometers were inter-calibrated to ensure data compatibility.

For each spectrum, the SO$_2$ 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 SO$_2$ 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

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...
SO$_2$ output order to obtain a representative assessment of a volcano’s averaging flux measurements from multiple traverses, in the plotted data, by analogy with the standard procedure of best-fit serves to average out the aforementioned scatter in about a near horizontal axis for the best-fit lines of the cross 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 SO$_2$ 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 SO$_2$ output [Stoiber et al., 1983].

[10] It is clear from Figure 2 that SO$_2$ depletion causes negligible systematic reduction in measured flux with increasing plume age: the gradient of the best fit line is $-1 \pm 2 \times 10^{-3}$ s$^{-1}$. For typical remotely sensed plume ages (up to $\approx$2000 s), this corresponds to negligible SO$_2$ losses of 0–6%, prior to measurement. For such low levels of SO$_2$ 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 SO$_2$ 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 SO$_2$ 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$4% per hour) reported for our study is within the range of values reported for power station plumes (1–10% per hour) [Eatough et al., 1994], not emitted into fog or cloud, indicating that the more exotic physico-chemical environment of this volcanic plume causes no major perturbation to SO$_2$ loss rates. Of the few other depletion rates reported for tropospheric plumes most are in agreement with this report that SO$_2$ 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: $\approx$99% loss per hour [Oppenheimer et al., 1998], and $\approx$97% loss per hour [Oppenheimer et al., 1998; Jaeschke et al., 1982]. However, a later survey of the same volcano (Mt. Etna) studied by Jaeschke et al. [1982] found lower SO$_2$ loss rates (average of 7% per hour) [Martin et al., 1986]. This more recent investigation used Si and Po$^{210}$ as tracers for plume dispersion, as opposed to CO$_2$ in the former case. Due to high variability of background CO$_2$ concentrations and Etna’s degassing of CO$_2$ 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 SO$_2$ 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 SO$_2$ depletion in tropospheric volcanic plumes does not significantly alter mea-
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, contributing to the high \( k \) values reported by Oppenheimer et al. [1998] (high plume particle density of \( >400 \text{ mg m}^{-3} \)) and Jaeschke et al. [1982]. In contrast, we estimate the ash loading of the Masaya plume to be considerably below the 100 \( \text{ mg m}^{-3} \) threshold, at which such reactions become significant, based on the visual observation that the non-condensed plume was not discolored by ash. The effects of these phenomena upon SO\( _2 \) 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

In this study we report results of an experiment at Masaya volcano, Nicaragua, aimed at determining the effect of in-plume SO\( _2 \) depletion upon remotely sensed flux measurements of tropospheric volcanic plumes. We find that SO\( _2 \) 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 volcanic 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 SO\( _2 \) oxidation in volcanic plumes could be obtained by using the USB20000 to monitor in-plume ozone concentrations, in parallel with SO\( _2 \).

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