

SO₂ loss rates in the plume emitted by Soufrière Hills volcano, Montserrat

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Abstract. To improve interpretation of volcanic SO₂ flux data, it is necessary to quantify and understand reactions involving SO₂ in volcanic plumes. SO₂ is lost in volcanic plumes through a number of mechanisms. Here we report SO₂ measurements made with miniature ultraviolet spectrometers at Soufrière Hills volcano, Montserrat; a low altitude volcano (~1000 m above sea level) whose plume entrains humid marine air in the planetary boundary layer. Traverses very near (<400 m) beneath the ash-free plume were made at various distances from the source (from ~2 km to ~16 km), thereby spanning plume ages of about 6 to 35 minutes with minimal attenuation. We find average SO₂ loss rates of ~10⁻⁴ s⁻¹ (e-folding time of ~2.78 hours), slightly lower than estimated previously for Soufrière Hills. These are in the fast end of the range of loss rates measured at other volcanoes (10⁻³ – 10⁻⁷ s⁻¹, e-folding times of 0.28-2778 hr), indicating that Montserrat plumes have short SO₂ lifetimes. This work is more detailed and precise than previous work and is likely to represent the general case at Montserrat. SO₂ flux measurements made >2 km downwind from Soufrière Hills volcano significantly underestimate at-source SO₂ emission rates, on the order of 70-146%, when not accounting for the decay rate. Similar SO₂ loss is likely to occur in plumes from other tropical low altitude volcanoes under conditions of high relative humidity (~20% of active volcanoes worldwide). These results suggest that the global volcanic SO₂ emission rate may be underestimated as the estimates are based on measurements taken downwind of volcanoes, by which time significant loss of SO₂ may have taken place. The loss rates calculated here could be used, in conjunction with downwind SO₂ fluxes, to estimate at-source SO₂ emission rates from volcanoes with similar environmental conditions to those at Soufrière Hills volcano.

Keywords:

sulfur dioxide; loss rate; plume chemistry; DOAS; Soufrière Hills

1. Introduction

It is important to understand volcanic SO₂ reactions in different meteorological environments, because uncertainties in near-source plume chemistry can complicate interpretations of gas plume measurements, which are used for volcanic monitoring purposes and in atmospheric and environmental impact studies. Sulfur dioxide is typically the third most abundant volcanic gas (Symonds et al., 1994), and is a trace constituent of the Earth's atmosphere, mainly present in the troposphere (Vandaele et al., 1994). It is an environmentally significant species associated with direct and indirect (acidification) damage to ecosystems (Delmelle, 2003) and is potentially harmful to human health (WHO Air quality guidelines, 2006; Hansell and Oppenheimer, 2006). Sulfur emissions are also relevant to the radiative transfer of the atmosphere, particularly through the action of sulfate aerosol (Lacis et al., 1992).

The difficulties inherent in the measurement of continuous, persistent emission of relatively small concentrations of gases, occurring between and during long-lived eruptions from volcanoes, have meant that few studies have been conducted to look at their impact on the troposphere. However, the contribution of quiescent, continuous emissions of SO₂ and sulfate aerosols from volcanoes is significant and must be known when attempting to quantify anthropogenic emissions and their effects on climate (Robock, 2003). Anthropogenic emissions contribute about 78 Tg S yr⁻¹ to the atmosphere (Bates et al., 1987; 1992), which is ~76% of the global S emissions (Bates et al., 1992; Spiro et al., 1992; Andres and Kasgnoc, 1998). The uncertainties in the measurements of passive emissions are caused by (1) the study of only a fraction of passive degassing volcanoes, (2) errors arising from measurement techniques (Rodríguez

et al., 2004), and (3) factors unique to each volcano that can make measurements logistically difficult and less accurate (e.g., access, meteorology, volcanic activity). Even at volcanoes that are intensively monitored, there are often uncertainties in some of the parameters needed to calculate the emission rates accurately. Uncertainties in measurements from ground-based (correlation spectrometer, UV spectrometers) studies of passive emissions propagate throughout global volcanogenic SO₂ budgets. Most studies are based on a low percentage of the total number of active volcanoes (e.g., 20%, Andres and Kasgnoc, 1998). Andres and Kasgnoc (1998) calculated a time-averaged flux of ~13.4 Tg yr⁻¹ SO₂, based on gas data between 1970 and 1997. Previous studies estimate a range in global volcanic emission of 1.5 and 50 Tg yr⁻¹ SO₂ (from Table 5, Andres and Kasgnoc, 1998), which includes both passive and explosive degassing. The range in the estimates is an indication of the uncertainty in calculating the annual global volcanic SO₂ emissions.

Volcanic SO₂ emission rates are commonly measured using ground-based spectroscopic techniques (e.g., Galle et al., 2002; McGonigle et al., 2002; Edmonds et al., 2003). The column concentration of SO₂ is integrated across a traverse of the plume, perpendicular to the transport direction, at some distance downwind of the volcano. Traverses are generally not exactly perpendicular to the plume transport direction; therefore they have to be corrected for this effect. The corrected column concentration is then multiplied by the plume speed to yield the SO₂ flux. This is assumed to be equal to the emission rate from the source. Typically, the measurements are undertaken a few kilometers downwind from the volcano and perhaps up to several kilometers away from the plume, depending in the most part on access and safety. This allows time for SO₂ to

interact with other volcanogenic gases, particles and droplets of volcanogenic and/or meteoric origin, as well as atmospheric gases and aerosols, and for the possibility of attenuation of SO₂ signal by airlight or scattering. The processes leading to SO₂ loss during transport downwind include oxidation (conversion to sulfate aerosol), dry and wet deposition, absorption, and dissolution. The effects of one process versus another are challenging to separate and, for this work, we will assume that the loss of SO₂ is dominated by in-cloud mechanisms.

Local meteorology affects the fate of tropospheric plumes initially by dispersion and transport downwind and secondly through factors such as humidity, temperature, the amount of sunlight reaching the plume (solar radiation), cloud cover, fog, and precipitation (Oppenheimer et al., 1998; Horrocks et al., 2003). An important SO₂ depletion process is the conversion of SO₂ to SO₄⁻² (sulfate). This conversion can proceed by both homogeneous and heterogeneous mechanisms to form particulate sulfate in the atmosphere (Eatough et al., 1994). In the gas phase, oxidation occurs by reaction with hydroxyl radicals to form sulfuric acid, while aqueous-phase oxidation (multiphase reaction) of SO₂ involves reaction with H₂O₂ or O₃ to form sulfate (Eatough et al., 1994).

The processes mentioned above, among others, can remove or mask the SO₂; therefore the measured SO₂ flux may not represent the at-source SO₂ emission rate. SO₂ loss rates ranging from 10⁻⁷ (e.g., Mount St. Helens) to 10⁻³ (e.g., Soufrière Hills) s⁻¹ have been estimated for tropospheric volcanic plumes at various altitudes (e.g., Martin et al., 1986; Oppenheimer et al., 1998; McGonigle et al., 2004). The loss rates were estimated using a number of different techniques (ground and satellite-based), including the correlation spectrometer (COSPEC), UV spectrometers, photometry, the Total Ozone

Mapping Spectrometer, and filters (e.g., Martin et al., 1986; Oppenheimer et al., 1998; McGonigle et al., 2004). Each technique has advantages and disadvantages, and the results may not be comparable directly, however, this also justifies the need to determine more accurately the range in SO₂ loss rates in volcanic plumes. Recent studies have shown variation on the order of at least two orders of magnitude for volcanoes with similar conditions (e.g., meteorological, SO₂ emission rates): Soufrière Hills volcano (SHV) and Masaya volcano, Nicaragua. Very fast loss rates ($\sim 10^{-3} \text{ s}^{-1}$, e-folding times ~ 17 minutes) were calculated by Oppenheimer et al. (1998) at SHV in 1996 (using a COSPEC), while McGonigle et al. (2004) determined very slow to negligible loss ($\sim 10^{-5} \text{ s}^{-1}$, e-folding times ~ 28 hours) at Masaya in 2003 (using UV spectrometers).

This work aims to quantify SO₂ depletion rates in volcanic plumes injected into the boundary layer, from the SHV, Montserrat, using ground-based remote sensing techniques. SHV is a low altitude volcano in a humid environment (conditions typical of $\sim 20\%$ of active volcanoes worldwide; Smithsonian's Global Volcanism Program, Summary Lists). In order to address potential underestimates on global emission rates, SO₂ fluxes were measured near to the eruptive vent and at various distances downwind of the SHV (Fig. 1). The two main reasons for choosing SHV were: (1) it is one of the world's most heavily monitored volcanoes, with a continuous gas monitoring network (ultraviolet (UV) spectrometers) since 2002 (Edmonds et al., 2003) and (2) previous measurements of SO₂ loss indicated fast loss rates, in the order of 10^{-3} s^{-1} (Oppenheimer et al., 1998). The summit of SHV is at <1100 m asl and its average relative humidity is generally $>75\%$. The current eruption began in July 1995 and has been characterized by periods of lava dome growth, dome collapses with pyroclastic density currents, and

episodes of explosive activity. The mean SO₂ emission rate for the entire period from 1995-2005 is ~500 t d⁻¹ (5.8 kg s⁻¹); with higher emission rates occurring during periods of high extrusion rate and immediately after large dome collapses (MVO data). The volcanic plume typically is at ~1000 m above sea level or lower, many times close to the ground. It typically enters the tropical, marine boundary layer and drifts towards the west under the influence of the trade winds. The location of Montserrat in the trade winds belt represents an unusually constant meteorological environment which mitigates the issue of misinterpretation of downwind SO₂ data because of meteorology (Fig. 1).

Fig. 1.

2. Methodology

2.1 Mini-UV Spectrometer

A commercial UV spectrometer (here called Mini-UV Spectrometer or MUSE) and the principles of Differential Optical Absorption Spectroscopy (DOAS) form the basis of the technique (Platt, 1994), similar to that used in previous experiments (Galle et al., 2002; McGonigle et al., 2002; Edmonds et al., 2003). UV light from the Sun, scattered by aerosols and molecules in the atmosphere, is collected by a telescope. The observational geometry is similar to that used for correlation spectrometer (COSPEC) measurements in the past. Automated COSPECs have been used at Mt. Erebus, Antarctica, achieving high temporal resolution (Kyle et al., 1994). Together with full automation and high temporal resolution, however, the MUSE has the advantage that the equipment is much more compact, cheap, and provides high spectral resolution. The

spectrometer's optics, detector, and electronics are built into a unit of 8.91 x 6.33 x 34.4 cm dimensions, and are powered via the USB-port of a laptop computer, which also supports data transfer (Galle et al., 2002). Details on the characteristics of the mini-UV spectrometer and on the DOAS technique are discussed elsewhere (Platt, 1994; Galle et al., 2002; Edmonds et al., 2003).

Two Ocean Optics USB2000 spectrometers (Fig. 2) were used to measure SO₂ column amounts at SHV. The data reported here are from one MUSE, however data were acquired simultaneously with two, in the case a computer or spectrometer became faulty during the time of measurements. Characteristics of the spectrometer/telescope systems are: (a) wavelength range: 220-390 nm (ultraviolet), (b) limit of detection: 5-10 ppm m (Edmonds et al., 2003), (c) spectral resolution: ~0.32-0.44 nm, and (d) field-of-view: ~27.4 mrad (~1.57°). A temporal resolution of less than 1 second is possible, depending on the integration time (exposure time of an individual spectrum) and number of co-added spectra used. On March 26, April 13, and April 22, 2004, traverses were carried out by helicopter, and on April 12, by boat. Traverses were at a range of distances downwind from the vent and therefore measured plume of different ages. The azimuths of the plumes during the measurements are shown in Fig. 1.

Fig. 2.

SO₂ emission rates from SHV are routinely measured by three automated, telemetered, scanning UV spectrometers, which acquire data continuously from 8 AM to 4 PM (Edmonds et al., 2003). These are located at Air Studios, ~5.7 km from vent (~120

m above sea level), at Lovers Lane, ~4.7 km from vent (~60 m above sea level), and at Brodericks, ~4.3 km from vent (~35 m above sea level) (Fig. 1). The distance from these instruments to the plume will depend on the plume's azimuth, but it will be <3 km for Brodericks and Air Studios, and a few hundred meters for Lovers Lane, more than 85% of the time (the wind direction in Montserrat is predominantly to the west). Vertically they are at most times <800 m from the plume. Data from these continuous sites, together with those collected as part of this study enable determination of SO₂ column amounts at different distances downwind in the plume. This will allow comparison between the results obtained with the traverses and those obtained by the scanning spectrometers and reported by the Montserrat Volcano Observatory (MVO). A weather station at the top of St. Georges Hill (Fig. 1) provides continuous meteorological data pertaining to the conditions prevailing within the volcanic plume (e.g., wind speed and direction, relative humidity, temperature, pressure). The station is ~308 m above sea level, which is about 600 m lower than the vent. It is ~3.9 km from the vent, in the area of prevalent wind direction in Montserrat. The results are therefore not truly representative of the in-plume meteorology. However, the station is the only means to at least acquire data close to the plume and to understand some of the environmental conditions.

2.1.1. Data acquisition and processing

Data were acquired with the OOIBase32TM (version 2.0.0.1) software, supplied by Ocean Optics, Inc. The processing program used to retrieve SO₂ total column amounts was written in IDL Version 6.1 Win32TM. The basis for the processing program is the

Beer-Lambert Law ($I(\lambda) = I_0(\lambda)\exp(-L\sigma(\lambda)c)$), which describes the absorption of radiation ($I_0(\lambda)$ and $I(\lambda)$) as it passes through a layer of a thickness L , where the species (in this case SO_2 , with an absorption cross section $\sigma(\lambda)$) to be measured is present at a concentration c (Platt, 1994; Finlayson-Pitts and Pitts, 2000). After removal of instrumental noise (“dark spectrum”), each spectrum is normalized by a clear-sky spectrum acquired outside the plume (“background spectrum”), thus eliminating absorption and scattering due to non-volcanic sources. The negative logarithm of each spectrum is then calculated; the result is the absorbance spectrum and contains absorption due to volcanic gases only. The absorbance spectra are filtered following standard DOAS evaluation procedures (Platt, 1994). Experimental variables (e.g., degree of water vapor within the plume, sun-plume-instrument geometry, concentration of non-water aerosols in the plume) are dealt with by the retrieval by removing the high and low frequency noise (Platt, 1994; Edmonds et al., 2003). The spectra are then fitted against a reference spectrum for SO_2 using a non-linear least squares algorithm (Galle et al., 2002). The SO_2 reference spectrum is derived from a high-spectral resolution laboratory spectrum of SO_2 (Vandaele et al., 1994) convolved with the spectrometer’s line shape function.

Vertical SO_2 column amounts (in ppm m) are measured along a traverse perpendicular to the plume transport direction and integrated, to yield the total amount of SO_2 in a 2-dimensional section of the plume (in ppm m^2). Often exact perpendicular traverses are difficult to conduct and angular relationships between the plume azimuth and the position of the instrument are used to adjust for the non-perpendicular orientation.

The SO₂ emission rate, in kg s⁻¹ or t d⁻¹, is obtained by multiplying the integrated amount by the plume speed (in m s⁻¹).

2.2 Calculation of SO₂ loss rates

As traverses were acquired at increasing distance from the vent (from ~2 km to ~16 km), while attempting to track individual pulses of gas, it is possible to calculate an SO₂ loss rate from the difference between traverses. The SO₂ fluxes calculated for the individual traverses were used to obtain the loss rates k , using

$$\varphi_{t_1} = \varphi_{t_2} e^{k_1(t_2-t_1)} \quad (1)$$

where φ_t represents an SO₂ flux at a given time t (Oppenheimer et al., 1998).

One issue when determining loss rates in a plume is that the plume does not result from a constant emission rate; therefore it is important to try to repeatedly measure the same parcel as it travels downwind. It is, of course, possible to calculate a loss rate between any two traverse measurements. In practice, some sort of data selection process is required to determine which down-plume traverses pertain to which pulse. Two criteria were used to determine which traverses to use in the calculation of loss rates.

1. In a hypothetical example (Fig. 3) a plume is traveling in a determined direction (plume azimuth), and traverses (T1-T7) are made by the helicopter in a quasi-perpendicular direction to the plume. Therefore, the helicopter track (the helicopter has a constant speed) intersects the plume center seven times downwind from the vent. Using the plume azimuth and speed (assumed to be constant), together with the helicopter track, we can determine the position of these intersections and the times (t_1 - t_7) in which they occur. A portion of the

plume, representing a period of constant emission, at the intersection with T1 can therefore be tracked downwind using the plume speed. The time difference (time difference = position difference/wind speed) between the location of a given plume portion and its intersection with the track of the helicopter for traverses T2 to T7 is determined. The criterion used to decide which fluxes to use in the calculation of the SO₂ loss rates was to use those traverses where this time difference was less than 70 seconds. This criterion was based on the data; there was a cluster with values below 70 seconds, the remaining data were mostly significantly higher (>100 s) and 70 seconds is a reasonable approximation of the time it takes to make a traverse. In the example of Fig. 3, loss rates would be calculated using fluxes at T1, T3, T5, and T6. Fluxes from T2, T4, and T7 do not represent the same portion of the plume tracked from T1, and therefore would not be used in the calculation of SO₂ loss rates. The same method was applied to plume portions with starting points at each of the other intersections (traverses T2-T7), in order to track the portions of the plume downwind.

Fig. 3.

2. The second criterion was based on the distances of the traverses from the vent. During the measurements on April 13 and 22, there was at different times a geographical overlap between the traverses, causing a traverse that was conducted later in time to be actually closer to the vent in distance. The traverse closer to the

vent but measured later in time was discarded, as it did not represent the same plume portion as the remaining traverses.

The calculation of loss rates for each day was based on the traverses that followed the criteria explained above. For March 26, we used traverses 3, 4, and 5 to calculate the loss rates. As the plume speeds were very accurate for this day (calculated from the helicopter at plume height), we chose the cluster of traverses with the lowest time difference, based on criterion 1. In this case, the time difference for the cluster was less than 30 seconds. On April 13, most of the traverses were used in the calculation of loss rates. Traverse 1 was eliminated as it did not follow the second criterion; it was made first but it was actually at a greater distance from the vent than traverse 2. Traverse 8 was eliminated because it did not follow the first criterion. Finally, for the measurements on April 22, we chose the traverses for the calculations based mainly on the second criterion. Consequently, we calculated two loss rates, based on two sets of traverses (1-3-5-6 and 4-7).

2.3 Errors

2.3.1. Sources of error

The MUSE and optical assembly used here are subject to most of the same sources of error as the COSPEC, including uncertainty in the plume speed, scattering and absorption of ultraviolet light by other plume constituents (multiple scattering effects), and errors in the calculation of plume geometry (plume width and azimuth). Additional sources of error are the DOAS method (errors related to the smoothing, filtering and

more importantly to the spectral fitting routine) and signal-to-noise changes (determining plume edges accurately when the concentrations are low) (Edmonds et al., 2003).

The error on plume speed is the largest for this type of measurement. We estimated plume speed using two methods: using the wind speed measured in the helicopter at the altitude of the plume (on March 26), and using that measured at the permanent weather station located at St. Georges Hill (Fig. 1). For our measurements on March 26 we compared the weather station estimates (average for time of measurements, 0.84 m s^{-1} standard deviation) with the wind speed measured from the helicopter. Measurements from the ground station were less than 40% lower than those observed from the helicopter. Differences between our estimates of plume direction and those of the permanent weather station (STGH w.s.) were also quantified. These were 63% different for March 26, 30% different for April 13, and 19% different for April 22. However, the plume azimuths used by the MVO are calculated based on the signal structure (using Brodericks and Lovers Lane data) and the difference between them and our estimates is <10%.

A second major source of error is scattering. It is difficult to establish the effective path through the volcanic plume when measuring with passive optical techniques such as DOAS (Millán, 1980; Edner et al., 1994). This is because the source of light cannot be considered to be completely above the volcanic plume, as light is scattered within and under it as well (Edner et al., 1994). Multiple scattering can therefore influence the column amounts retrieved, potentially resulting in overestimated fluxes. The scattering within and below the plume can cause a decrease in the spatial resolution of the measured profile, which is enhanced if the plume contains more aerosols

(e.g., condensed water vapor). Edner et al. (1994) conducted measurements of SO₂ flux at Vulcano, Stromboli, and Etna volcanoes in 1992, using both Light Detection and Ranging (LIDAR, an active remote sensing technique) and DOAS. They found that DOAS SO₂ flux measurements were 5-33% higher than those obtained simultaneously with LIDAR. The low end of this corresponds to overestimates of 5% for measurements at Stromboli (plume 2-2.5 km wide and 1 km above sea level). These conditions are similar to those at SHV.

We acquired GPS data continuously during the flights, using a hand-held GPS (Garmin eTrex[®]), which continuously tracks and uses up to 12 satellites to compute and update positions. The position accuracy of the instrument is 15 m (49 ft) RMS (Garmin eTrex owner's manual, February 2003). The GPS data and the helicopter speed were used to calculate the plume width and azimuth. Maps of the helicopter track were constructed for each day, and after analysis of the data the centers of the plumes were determined in order to calculate the plume direction (see Figs. 4a, 5a, and 6a). The error related to calculation of plume geometry in the case of our helicopter traverses is <1%, and therefore is regarded as insignificant.

2.3.2. Error analysis

Stoiber et al. (1983) and Williams-Jones et al. (in press) calculated errors in the COSPEC measurements to range between $\pm 13\%$ to $\pm 42\%$. McGonigle et al. (2003) estimated $\pm 15\%$ to $\pm 50\%$ error for DOAS measurements, while Edmonds et al. (2003) estimated a total error of -20% to $+36\%$ for the same technique. The total error in the measurements presented here is the square root of the sum of the squares of the

individual errors, for positive and negative errors. Individual errors are: (a) processing errors in the DOAS method (e.g., smoothing, filtering, and fitting) are $\pm 5\%$ (up to $\pm 10\%$) (based on this research and Edmonds et al., 2003), (b) signal-to-noise changes cause errors of $\pm 5\%$ (based on Edmonds et al., 2003), (c) multiple scattering effects cause an error of -5% (Edner et al., 1994, using data from Stromboli volcano), (d) the error on wind speed calculated at helicopter altitude is around $\pm 5\%$ and that estimated from the weather station data is -5% $+30\%$ (based on this research and Edmonds et al., 2003), (e) variable aircraft speed during traverses causes an error of $\pm 5\%$ (Williams-Jones et al., in press), and (f) errors related to the determination of plume width and direction are deemed negligible (± 0.3 - 1.2%). The total error for measurements carried out on March 26 is therefore -11% $+10\%$, and on April 13 and April 22 it is -11% $+31\%$.

3. Results

The SO_2 depletion rates and residence times, calculated from emission rates measured with the mini-UV spectrometer at SHV on March 26, April 13, and April 22, 2004, are shown in Table 1, together with the number of traverses used to calculate the loss rates each day. Weather conditions for each day are also described. Figs. 4a, 5a, and 6a show the track of the helicopter on March 26, April 13 and April 22. The traverses are labeled with the approximate location of the plume centers for each traverse and the plume azimuths. The measured SO_2 fluxes as a function of age of the plumes are plotted in Figs. 4b, 5b, and 6b. Best-fit exponential curves yield an estimate of “at-source” emission rates of SO_2 . The SO_2 fluxes calculated from the MVO continuous scanning spectrometer system during the time of our measurements are also plotted. For this, we

chose the flux closest in time to when the traverses were carried out. These were corrected using our plume azimuth and speed, but were not used for the calculation of loss rates. Measurements on April 12 were not used in the calculation of loss rates, as plume portions could not be tracked from one traverse to the next (criterion 1), because the boat speed was slow relative to the plume speed.

Several assumptions are made for these loss rate calculations. First, we assume there is a constant SO₂ emission rate for these short term measurements (one set of traverses in a day), as we are attempting to measure a single portion of the plume as it travels downwind. However, previous studies have shown that the emission rate can vary in short time scales (e.g., Sutton et al., 2001; Edmonds et al., 2003; Rodríguez et al., 2004). The second assumption is that there is no formation of SO₂ in the plume. One of the processes that can cause this is the chemical conversion of H₂S to SO₂. However, no H₂S has been detected in the plume during Fourier Transform Infrared Spectrometer (FTIR) measurements in Montserrat. The third assumption is that we do not consider the emission of primary sulfate from the SHV.

Fig. 4.

Fig. 5.

Fig. 6.

The SO₂ loss rates calculated for Montserrat are not absolute. In order to propagate the flux errors to the loss rates, we used two methods, which will be discussed here. An example, using the data from March 26, 2004, can be found in Fig. 7. In the

case of Montserrat, the largest source of error in the flux measurements is the wind speed. In order to propagate this effect to the loss rates, we calculated a range in plume ages and fluxes, based on those errors. Trendlines were then created for the minimum and maximum loss rate, based on the minimum and maximum plume ages and fluxes. This resulted in parallel trendlines to the average loss rate presented in Figs. 4b, 5b, and 6b. The second method also uses the calculated ranges in plume age and flux, but trendlines are created from the maximum flux at the youngest plume age to the minimum flux at the oldest plume age, and from the minimum to the maximum fluxes, respectively. In the case of Montserrat, because of the low errors and the precision of the measurements, we conclude that the more realistic errors are those obtained using the first method. The results from the second method will represent the worst case and will produce a wide range when the data is not very precise. Table 2 shows the range in the loss rate measurements, as well as the resultant at-source emission rates, for the three days of measurements in 2004, using both methods.

Fig. 7

The calculated SO₂ depletion rates ranged from $3.0 \times 10^{-4} \text{ s}^{-1}$ to $1 \times 10^{-3} \text{ s}^{-1}$ (Figs. 4-6). Data from the three days of measurements were also plotted together and the fluxes were normalized from 0 to 1, for each individual day (Fig. 8). Normalizing the data reduces daily variability issues. The trends observed show the consistency of the data, even when using every traverse measured. Data collected on March 26 display the least amount of scatter, consistent with the lower calculated error for this day.

Fig. 8.

4. Discussion

The data presented in the previous section clearly show that SO₂ fluxes measured at progressively larger distances (and hence plume ages) downwind from SHV decrease at a predictable rate. The transition between homogeneous gas phase oxidation of SO₂ and heterogeneous and multiphase reactions has been previously studied by Eatough et al. (1994), Thornton et al. (1996), and Oppenheimer et al. (1998). Based on these relationships, the loss rates calculated for the SHV can be ascribed primarily to heterogeneous oxidation of SO₂. The rates of transformation and removal of gas species depend on the availability of condensed water and solid particles within the plume, on the UV flux, on the availability of oxidants (e.g., H₂O₂, O₃, OH) (Horrocks et al., 2003), and on the evolution of the aerosol in terms of size distribution, pH, etc. The relative humidity (RH) ranged from 68-78% during the days of measurements. Because the troposphere contains suspended liquid and solid particles, heterogeneous and multiphase (in droplet) reactions are usually more important in controlling concentrations of soluble gases than slower homogeneous gas phase reactions (Ravishankara, 1997). As discussed in the introduction, many mechanisms can contribute to the removal of SO₂ and the effects of one versus another are difficult to separate. However, oxidation is probably the major one in the case of Montserrat. If deposition processes were more important, we would expect to see a greater loss at other low altitude volcanoes with more surrounding

topography (i.e. Masaya volcano, Nicaragua). Based on studies by McGonigle et al. (2004) this is not the case (see 4.4).

4.1 Loss rates

The loss rate on March 26 was $4.7 \times 10^{-4} \text{ s}^{-1}$ (Fig. 4). Three traverses were used to calculate the loss rate, after tracking portions of the plume downwind from each traverse. Since the plume speed was determined at plume height, the loss rate for this day is the one we are most confident about. There is a variation in the depletion rates as we move downwind, when taking into account every traverse. Traverse 1 was associated with a lower SO_2 flux than traverse 2, opposite to the expected trend. These first traverses correspond to the approximate area of the shoreline. This apparent increase in SO_2 flux may be due to the influence of sea salt-particles, which may be important media for reactions (Ravishankara, 1997), to a shallow daytime sea-breeze circulation (Allen et al., 2000), or to secondary SO_2 maxima caused by turbulence and intense fumigation events (Allen et al., 2000; Delmelle, 2003). Sea-salt particles in the marine boundary layer are an example of available suspended matter in the troposphere which provide potential exchange surfaces for atmospheric constituents (Ravishankara, 1997). The same apparent increase was observed on April 13 and 22, also influenced by the possible occurrence of plume puffing, as the plume speeds were not measured at plume height and we could be reaching a different plume section to the one being tracked.

The loss rate on April 13 was $3.0 \times 10^{-4} \text{ s}^{-1}$ (Fig. 5). Six traverses were used for the calculation of this loss rate, which was the higher number of traverses used to calculate loss. The conditions on this day were of clear skies close to the vent and

downwind. This was the lowest loss rate measured in the campaign, which would be expected when comparing the meteorological conditions during the three days of measurements. It supports the idea of slower loss rate in the absence of clouds.

The loss rates on April 22 averaged $7.0 \times 10^{-4} \text{ s}^{-1}$ (Fig. 6) and it is the fastest loss rate observed in this study. Two loss rates were calculated, because when tracking the portions of the plume with starting points at each of the traverses, two different plume tracks were observed. The first one ($1.0 \times 10^{-3} \text{ s}^{-1}$) included four traverses, while the second one ($4.0 \times 10^{-4} \text{ s}^{-1}$) included only two. The confidence in the second loss rate, however, is lower, as it is based only on two traverses and the accuracy is probably orders of magnitude higher when having two more contributors to the line of best fit. The results from this day are the ones in which we are least confident, mainly because the first five traverses were close together in distance, even overlapping at times. This can also be confirmed by the wide range in loss rates (Table 2) obtained using the second method to propagate the flux errors to the loss rates.

4.2 Comparison to MVO results

Extrapolation of our data back to time zero gives us an idea of the at-source emission rate at the time of our measurements, based on an exponential decay of SO_2 . We compared these to the SO_2 fluxes reported by the MVO both for the time of measurement (average of results from scanning spectrometer closest to plume azimuth) and for the day (8 AM – 4 PM). In the three days of measurements, the results reported by the MVO, using the scanning spectrometer data, were significantly lower than those reported here, which take into account SO_2 loss (Table 3). Some care must be taken

when comparing the two data sets, as they are acquired with different spectrometers, using different methodologies and processed with similar, but not identical, retrieval programs. It is a valid exercise, however, as a first order estimate of the amount by which the SO₂ emitted from SHV might have been underestimated.

These results illustrate that the SO₂ fluxes routinely measured at SHV, ~4.5 km downwind from the vent, underestimate at-source SO₂ emission rates by significant and variable amounts (based on the % difference between fluxes). For March 26, when using the daily average reported by the MVO, the at-source emission rates are underestimated by ~130%, while they are underestimated by ~85% when comparing to the average results reported during the time of measurements. On April 13, the at-source emission rates are underestimated by ~70% and ~25%, respectively. Since there were no emission rates calculated during the time of measurements on April 22, an underestimate of ~146% was calculated based on the daily average. These differences (ranging between 70%-146% for the daily average) are all estimates and should be considered the highest possible differences, especially since the comparisons were not side-by-side. However, the trend observed indicates the need to take into account loss rates when reporting SO₂ emissions from volcanoes with similar conditions to the SHV, by developing a decay curve to correct the SO₂ emission rates. This loss rate correction should be based upon the time it takes for the plume to get to the MVO scanning spectrometer and a regular loss rate measurement.

We also compared the SO₂ fluxes measured using the method described here and those derived from the MVO scanning spectrometer system, by calculating the % difference between the flux corresponding to the traverse passing over the site of the

scanning spectrometer and the flux from the scanning spectrometer closer in time to the traverse (<3 min). This is not a direct comparison, as we cannot be sure that the same plume portion was measured. However, it does partly explain why the variation between the fluxes calculated with the two methods (previous paragraph) may be larger than the actual decrease in SO₂ attributed to SO₂ removal. The difference ranged from as low as 5% (April 13) to as high as 66% (March 26). Other than the effects of not measuring the same plume portion, the difference is also due to the difference in instrumentation, method, assumptions and processing inherent in the two spectrometer methods. Further validation and comparison between techniques would be of value.

4.3 Comparison to 1996 results

In 1996, Oppenheimer et al. (1998) conducted a similar study in Montserrat (through boat traverses) and determined loss rates in the order of 10^{-3} s^{-1} , an order of magnitude faster than the average rates obtained here (Table 1). They inferred that in-cloud scavenging of SO₂ by liquid-coated ash particles and aqueous aerosol was the primary removal mechanism. We made significantly more traverses than Oppenheimer et al. (1998) over a longer period. This improves the accuracy and reliability of the results, as trends are based on more data points, in cases spanning distances from a couple of kilometers from the vent to distances of up to 16 km away. Also, the conditions differ in that we measured ash-free plumes during the dry season, while Oppenheimer et al. (1998) measured ash plumes during the peak of the rainy season (greater concentration of available condensed atmospheric water). Removal rates dramatically increase in the presence of liquid water or when the RH is greater than 75%

(Horrocks et al., 2003). Finally, the criteria used to choose the traverses for the calculation of loss rates in this research improves the chances of tracking a portion of the plume from one traverse to another.

Based on these, the loss rates reported here are definitely an improvement from previous work; however, we expect these rates to be faster during the rainy season or in the presence of ash-laden plumes. With respect to the accuracy of previous loss rate calculations, we think their observations could be taken as an example of the fastest loss, but in the general case of Montserrat, the results reported here should be used.

4.4 Comparison to Masaya results

McGonigle et al. (2004) conducted a study at Masaya volcano (a 600 m high basaltic shield volcano in Nicaragua) during the dry season (March 2003), when it was emitting ash-free plumes to the boundary layer. These conditions are similar to those encountered during this study at SHV. Vehicular traverses were carried out using a road ~6 km downwind of the volcano throughout the day and at different plume speeds, in order to determine SO₂ flux as a function of plume age. Their results show very slow to negligible loss ($k = -1 \pm 2 \times 10^{-5} \text{ s}^{-1}$). They concluded that SO₂ flux measurements are reliable indicators of at-source emission rates for ash-free tropospheric plumes not emitted into cloud or fog. However, we are not very confident in their methodology: (1) all the measurements were made from one road, using average plume speeds to calculate different plume ages; this does not allow us to see the variation at different distances (closer to the vent and at longer distances), (2) it assumes a constant emission rate from Masaya for the campaign (several days), which is unlikely, (3) the trends shown include

all the data collected during different days; therefore it does not enable us to see variation in the trends for the individual days, (4) effects of the topography are not taken into consideration; recent studies have demonstrated that the topography at Masaya has a significant effect on the wind speeds calculated and can lead to errors in the flux calculations (Tricia Nadeau, pers. comm., August 1, 2007).

The loss rates obtained at Masaya (McGonigle et al., 2004) are within the range of values reported for plumes produced by power stations (Eatough et al., 1994), which are between 1-10% per hour. However, the significant difference in the results between the SHV and Masaya is difficult to understand because of the similarities in their environmental conditions: altitude (~1 km versus ~600 m asl), SO₂ emission rates (~6-18 kg s⁻¹ for SHV versus ~7-23 kg s⁻¹ for Masaya), relative humidity (68-78% versus 40-100%), and temperature (24-26 °C versus 20-32 °C). We believe that the differences in the methodology are the main factor causing the SO₂ loss at Masaya to be almost negligible. However, there are other possible conditions that could contribute to the variation in the loss between the two areas: (1) the effect of marine aerosols in Montserrat (coastline is ~4 km from vent), (2) the possible presence of very small amounts of ash in the plume from SHV, and (3) differences in the HCl concentrations in the plumes which should reduce the uptake of SO₂ in the aqueous phase. The latter is not an important factor given the high abundance of HCl in the SHV plume (Edmonds et al., 2003), because we would expect as a consequence to have slower loss at SHV. With respect to the influence of marine aerosols, Allen et al. (2000) found much sodium and chloride in the aerosols emitted from the dome at SHV, indicating the entry of seawater to the magmatic-hydrothermal system. They also determined that neutralization of the aerosol

occurred rapidly during transport. On the other hand, Allen et al. (2002) determined that aerosols at Masaya were highly acidic ($\text{pH} < 1.0$ in the fine aerosols). This lower pH at Masaya potentially supports the slower loss of SO_2 in the plume.

5. Conclusions

We found that SO_2 flux measurements made downwind (at distances of 2-16 km, which represent plume ages of ~6-35 minutes) from SHV, using a mini-UV spectrometer during three days in the dry season of 2004, significantly underestimate at-source SO_2 emission rates, in the order of 70-146%. This is based on comparison between our measurements and the SO_2 emission rates reported daily by the MVO. Similar SO_2 loss is likely to occur in plumes from other volcanoes (with low altitude, high RH, boundary layer emissions). The results obtained here are applicable to about one fifth of the active volcanoes in the world (Global Volcanism Program summaries), which share the conditions of altitude and humidity.

The extent to which downwind flux measurements underestimate SO_2 at-source emission rates varies widely; the discrepancy between the observed fluxes and the at-source emissions can be large or almost negligible. Conditions such as seasonality and ash content will cause the discrepancy to be larger in volcanoes which emit to the boundary layer. On the other hand, we expect that at volcanoes that emit to the free troposphere the discrepancy will be very low and in most cases negligible.

Based on the “at-source” SO_2 emission rates determined here (by extrapolation of traverse flux results) and their comparison to those reported by the MVO, we conclude that the fluxes measured at 3-5 km downwind underestimate the at-source emission rate

three to eleven times. Therefore, decay curves should be developed periodically to validate the scanning method and be able to use the results obtained to extrapolate to an at-source emission. This loss rate correction should be based upon the time it takes for the plume to get to the MVO scanning spectrometer and a regular loss rate measurement.

Another important conclusion to this research is its application to current estimates of SO₂ fluxes from volcanoes. Based on the results obtained here, the contributions of volcanoes similar to SHV to the global SO₂ budget are underestimated several times. Although a numerical underestimate is difficult to calculate with these data alone, we can make some calculations, based on the available loss rate data (from Table 1 in Oppenheimer et al., 1998; Guo et al., 2004; McGonigle et al., 2004; Bluth and Carn, in press; this research). In order to calculate an underestimate, we need an emission rate, a loss rate, and a time between the at-source emission and the actual measurement downwind. The global SO₂ emission estimate from volcanoes is 13.4 Tg SO₂/year (Andres and Kasgnoc, 1998), of which the passive degassing volcanoes contribute about 5.36 Tg SO₂ per year (~40%; Stoiber et al., 1987; Halmer et al., 2002). Averaging the volcanoes with plume altitudes above 1 km and below 3 km (representative of more than 50% of passive degassers), we used an average loss rate of $3.6 \times 10^{-4} \text{ s}^{-1}$. We used plume ages (for the time) of 10 minutes, 20 minutes, 40 minutes, and 60 minutes. These represent different distances from the vent, and therefore an estimate of when the measurements are taken in volcanoes worldwide. Using these times, we get underestimates on the order of 22% to 114%. The range is due to the distance of measurement to vent, which will vary from one volcano to the next.

However, this shows that the underestimate could be significant, and therefore, should be considered.

Future studies on SO₂ loss in volcanic plumes should include a better understanding of other removal processes, including dry and wet deposition. It would be advantageous also to include a quantitative description of the aerosol particle distributions in order to complement the data on SO₂ fluxes and correctly estimate the SO₂ oxidation in volcanic plumes.

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Figure captions

Fig. 1. Map of Montserrat. The typical plume dispersion is shown (solid lines), along with plume transport azimuths during our measurements (arrows). The locations of MVO's scanning spectrometers (BR-Brodericks, LL-Lovers Lane, AS-Air Studios) and the permanent weather station (St. Georges Hill - STGH w.s.) are also shown.

Fig. 2. (a) Mini-UV spectrometer, optical assembly and laptop computer used for the measurements. (b) Telescope setup during helicopter traverses.

Fig. 3. Diagram showing the method to determine which traverses to use in the calculation of SO₂ loss rates, based on the first criterion. Helicopter traverses T1-T7 intersect the plume as it travels downwind, at times t₁-t₇. A portion of the plume at the intersection with T1 is tracked downwind, and the time difference between the location of that portion and its intersection with the track of the helicopter (<70 seconds) was used to determine which fluxes to use in the calculation of loss rates. In the example, loss rates would be calculated using fluxes at T1, T3, T5, and T6.

Fig. 4. (a) Track of helicopter from and back to MVO, on March 26, 2004. Shaded region represents Montserrat's coastline. Traverses are labeled (1-7), as well as the plume centers at each one. Plume azimuths (see also Fig. 1) are shown, as plume changes direction after traverse 5. Plume centers are 2.1 to 11.9 km from the vent (coastline at plume azimuth is ~4.2 km from vent). (b) SO₂ flux vs. plume age. Fluxes for each traverse (1-6) are plotted. A best-fit exponential curve yields the flux at t=0 s. The fluxes at traverses labeled with larger symbols were used in the calculation of the loss rate (k). Error bars are -11% +10%. The average emission rate for the MVO

scanning spectrometer BR (during the time of measurements) is also included (error bar is -20% +36%).

Fig. 5. (a) Track of helicopter from and back to MVO, on April 13, 2004. Shaded region represents Montserrat's coastline. Traverses are labeled (1-8), as well as the plume centers at each one. The plume azimuth (see also Fig. 1) is shown. Plume centers are 4.3 to 16.2 km from the vent (coastline at plume azimuth is ~4.4 km from vent). (b) SO₂ flux vs. plume age. Fluxes for each traverse (1-8) are plotted. A best-fit exponential curve yields the flux at t=0 s. The fluxes at traverses labeled with larger symbols were used in the calculation of the loss rate (k). Error bars are -11% +31%. The average emission rate for the MVO scanning spectrometer BR (during the time of measurements) is also included (error bar is -20% +36%).

Fig. 6. (a) Track of helicopter from and back to MVO, on April 22, 2004. Shaded region represents Montserrat's coastline. Traverses are labeled (1-7), as well as the plume centers at each one. The plume azimuth (see also Fig. 1) is shown. Plume centers are 5.0 to 7.7 km from the vent (coastline at plume azimuth is ~5.2 km from vent). (b) SO₂ flux vs. plume age. Fluxes for each traverse (1-7) are plotted. Best-fit exponential curves yield fluxes at t=0 s for plume portions with starting points at traverse 1 (solid, traveling downwind through traverses 3, 5, and 6) and traverse 4 (dashed, traveling downwind to traverse 7). The loss rates are labeled k(1) and k(4), respectively. Error bars are -11% +31%. No emission rate for the MVO continuous scanning spectrometers was reported during the time of measurements.

Fig. 7. SO₂ flux vs. plume age for March 26, 2004. The fluxes at traverses labeled with larger symbols were used in the calculation of the loss rate (k). Best-fit exponential

curves yield the flux at $t=0$ s (see Table 2). The trendline for the average loss rate is labeled k_{ave} (solid line). The dashed trendlines parallel to k_{ave} represent the maximum and minimum loss rates obtained using the first method of calculating loss rate errors. The two dashed lines that intersect each other represent the range in loss rate errors obtained using the second method. Flux error bars are -11% +10%.

Fig. 8. Normalized SO_2 flux vs. plume age for each day of measurement (the y intercept for the trendlines is 1, which represents the highest flux measured each day). All trendlines are exponential and the SO_2 loss rate (k) for each day is shown.

Table 1. Results of measurements and conditions during each day of helicopter traverses.

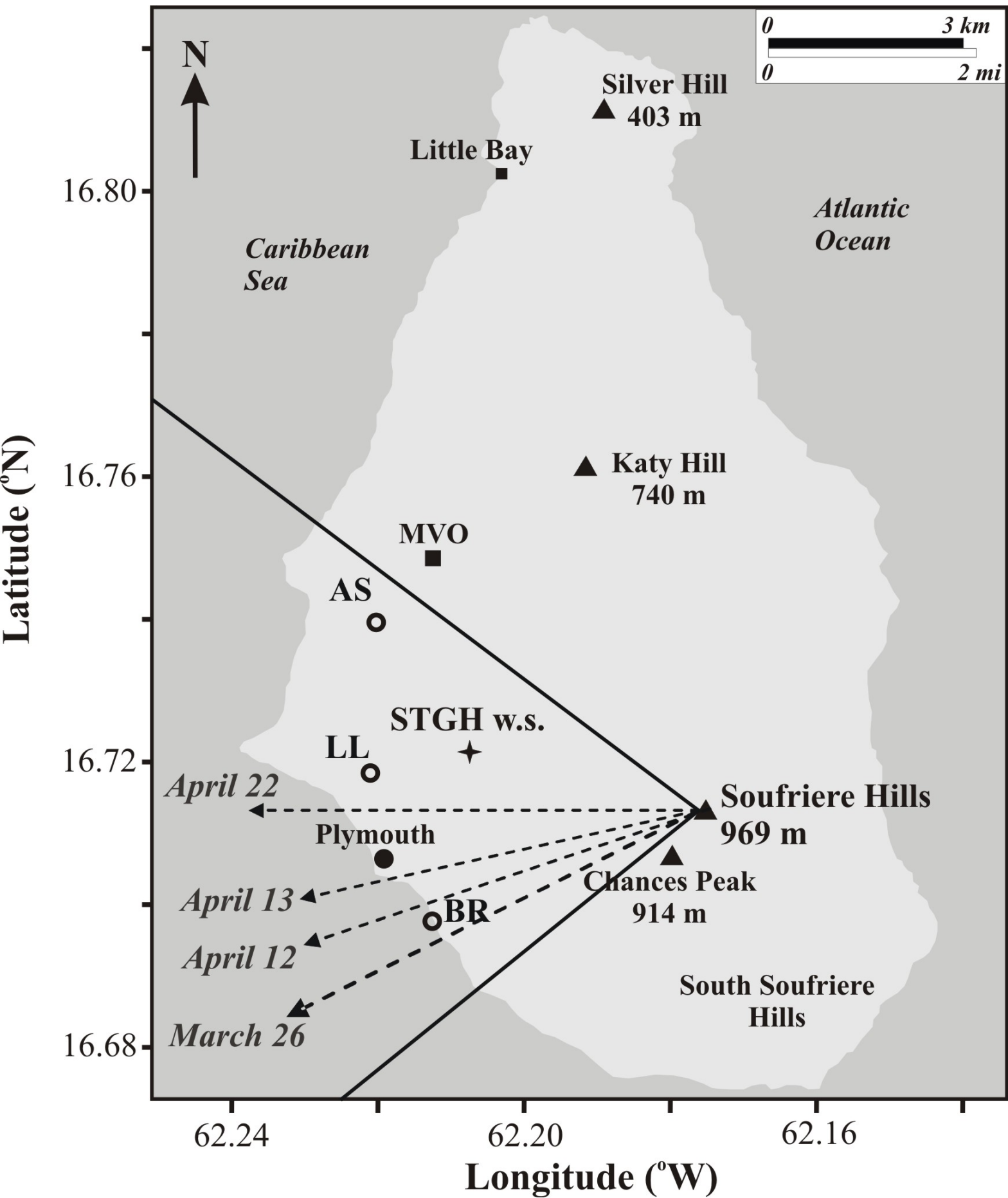
	Weather conditions	Plume speeds (m/s)	Average loss rates (k) (s⁻¹)	Average residence times (τ=1/k) (minutes)
March 26 (Fig. 4)	- RH ~ 72% - T ~ 24.4 °C - Plume is entrained directly into clouds	6.2 Calculated at plume elevation, from the helicopter	4.7 x 10 ⁻⁴ (3 traverses)	35
April 13 (Fig. 5)	- RH ~ 68% - T ~ 25 °C - clear skies	8.8 Plume speeds are an average of wind speeds from weather station at St. George's Hill (STGH – 308 m asl)	3.0 x 10 ⁻⁴ (6 traverses)	56
April 22 (Fig. 6)	- RH ~ 78% - T ~ 25.6 °C - Plume is entrained directly into clouds	7.1 Plume speeds are an average of wind speeds from weather station at STGH	1.0 x 10 ⁻³ (4 traverses) 4.0 x 10 ⁻⁴ (2 traverses)	17 42

Table 2. Range in loss rates (k) calculated for the three days of measurements in 2004, together with the resultant at-source emission rates. The methods are labeled 1 and 2.

Day of measurement	# of traverses used in calculation	Range in k (s⁻¹)	Range in SO₂ at-source emission rates (kg s⁻¹)
March 26 - 1	3	$4 \times 10^{-4} - 5 \times 10^{-4}$	27 – 24
March 26 - 2	3	$2 \times 10^{-4} - 1 \times 10^{-3}$	40 – 19
April 13 - 1	6	$2 \times 10^{-4} - 3 \times 10^{-4}$	17 – 12
April 13 - 2	6	$2 \times 10^{-4} - 5 \times 10^{-4}$	8 – 19
April 22 (I) - 1	4	$7 \times 10^{-4} - 1 \times 10^{-3}$	28 – 20
April 22 (I) - 2	4	$3 \times 10^{-4} - 6.9 \times 10^{-3}$	14 – 8550
April 22 (II) - 1	2	$3 \times 10^{-4} - 4 \times 10^{-4}$	22 – 16
April 22 (II) - 2	2	$3 \times 10^{-4} - 1.2 \times 10^{-2}$	10 – 1×10^6

Table 3. Comparison of at-source emission rates calculated in this study to the emission rates reported by the MVO based on the scanning spectrometer system.

Day of measurement	At-source emission rates (kg s⁻¹)	MVO daily average (kg s⁻¹)	MVO emission rate during time of measurements (kg s⁻¹)
March 26	25	5.1	10.1
April 13	13	6.2	10.0
April 22 (I)	22	2.9	not calculated
April 22 (II)	16	2.9	not calculated

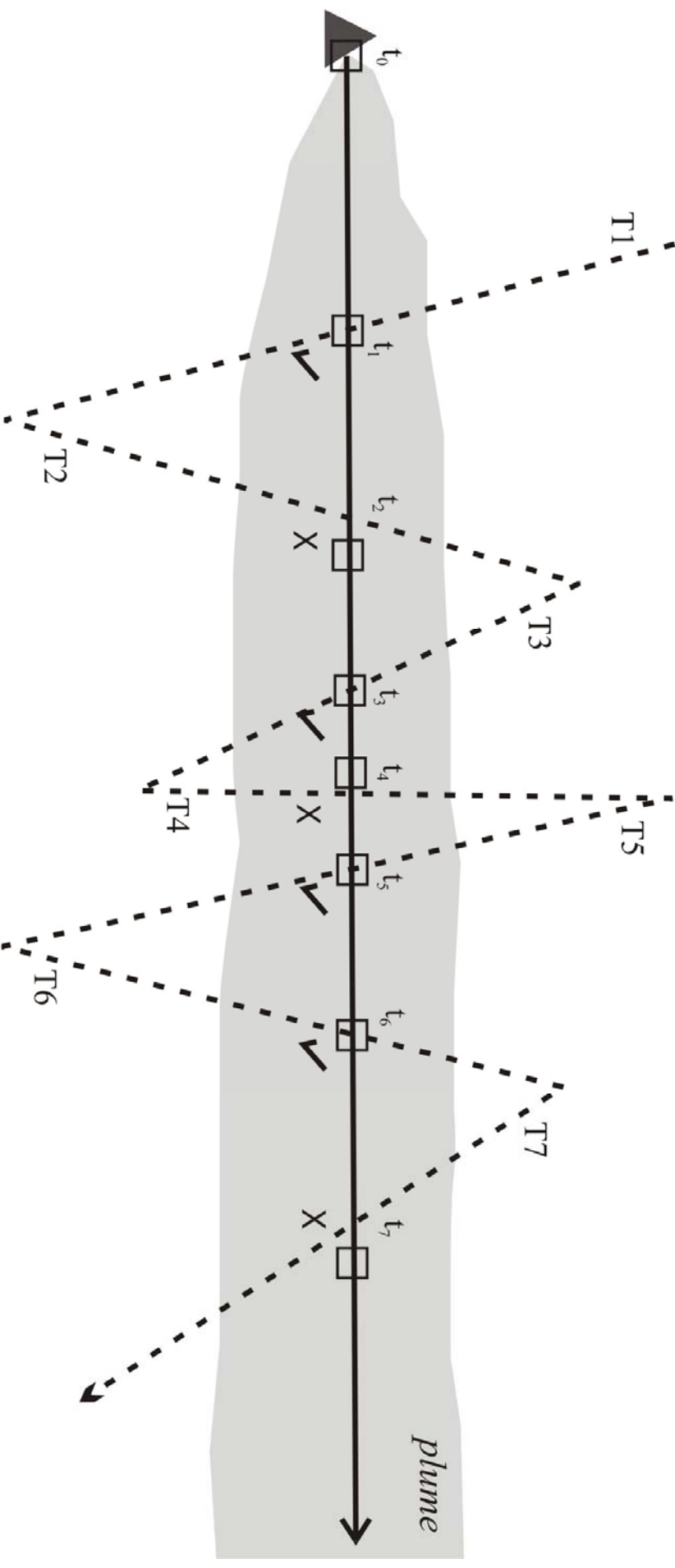


(a)



(b)





▲ Vent (plume portion at time t_0)

→ Plume azimuth (wind speed = $x \text{ m s}^{-1}$)

- - → Helicopter track

□ Plume portion traveling downwind (intersections between helicopter track and plume azimuth)

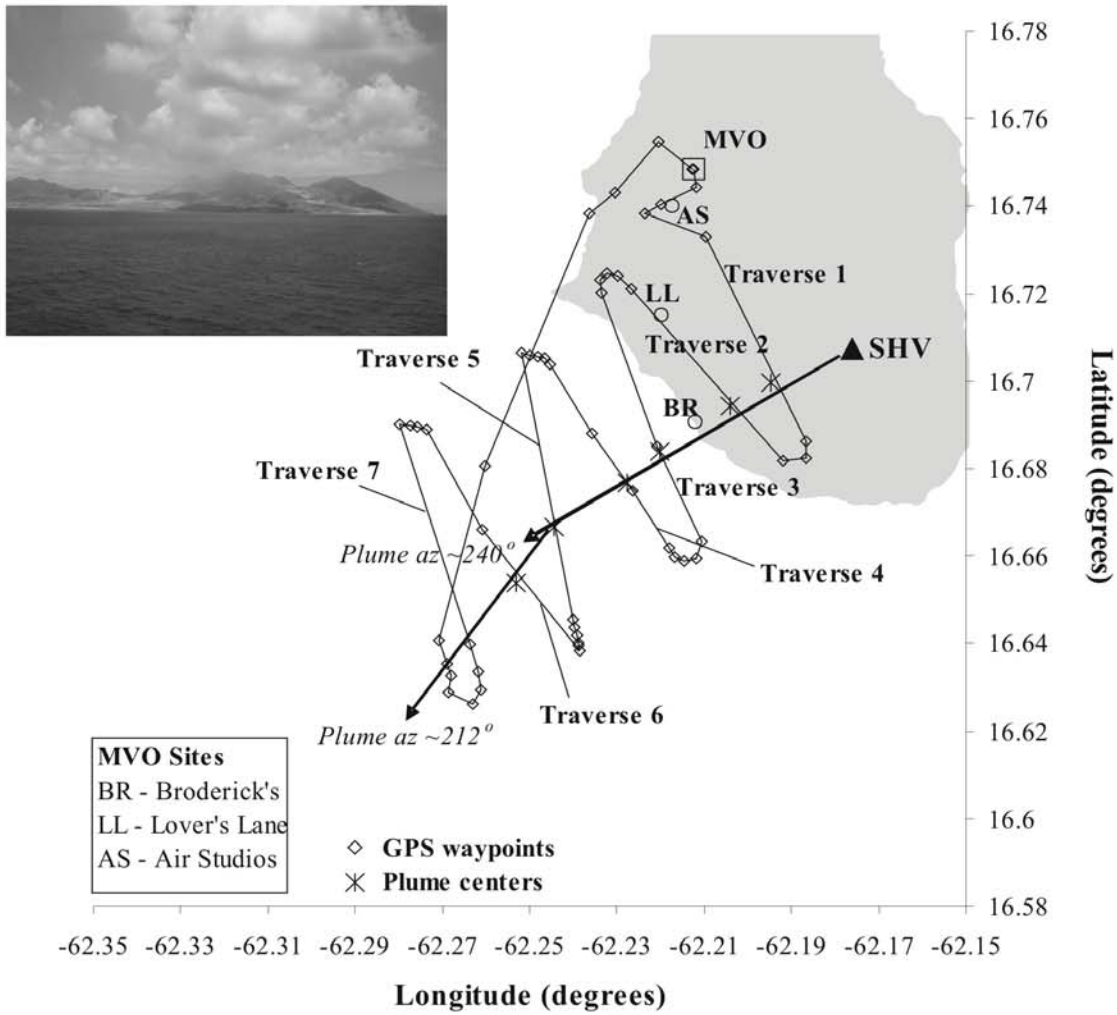
Tx Traverse number

t_x Time of intersection between helicopter track and plume azimuth

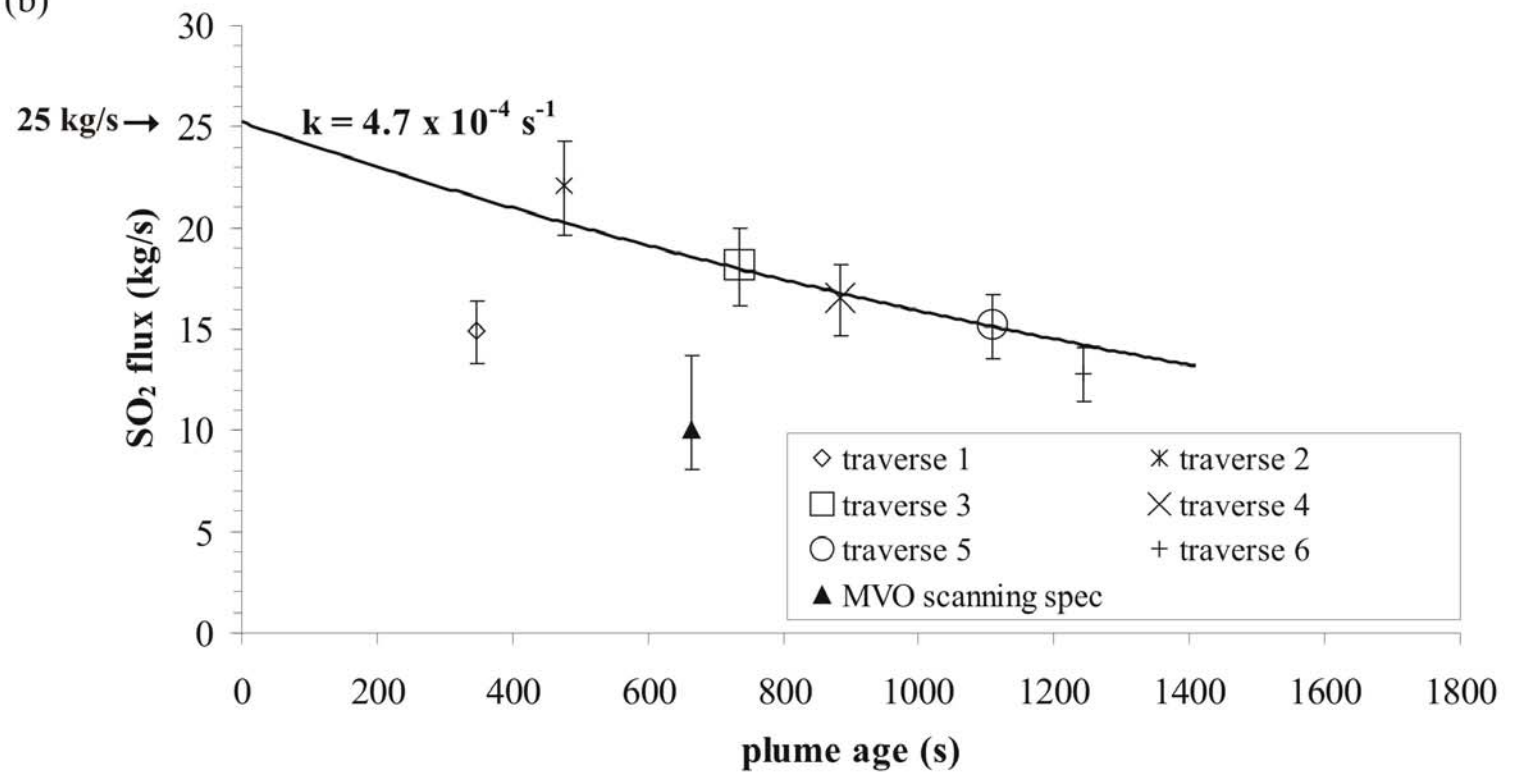
✓ SO_2 fluxes used to calculate loss rates for a plume portion traveling from T1

✗ SO_2 fluxes not used for loss rate calculation

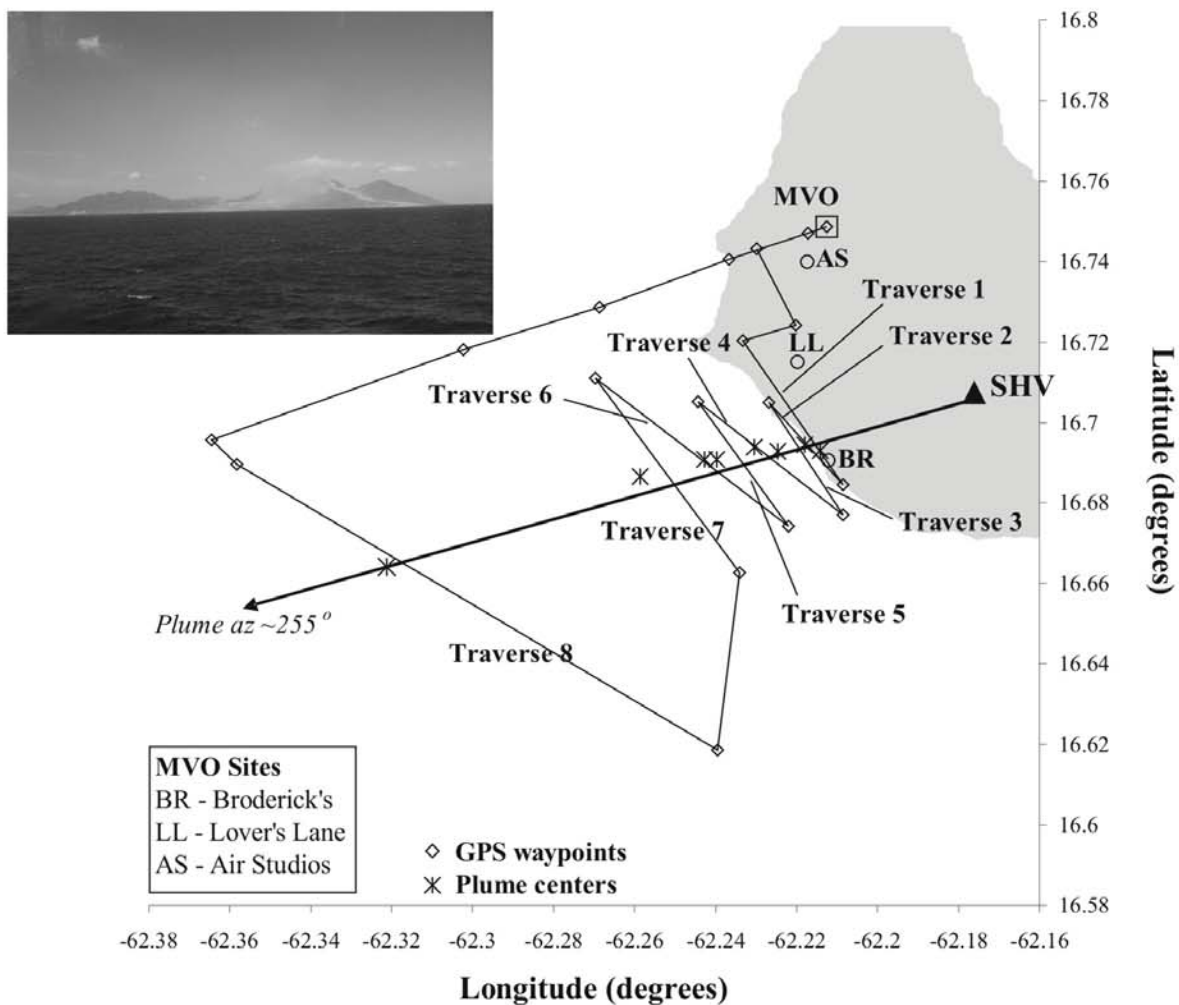
(a)



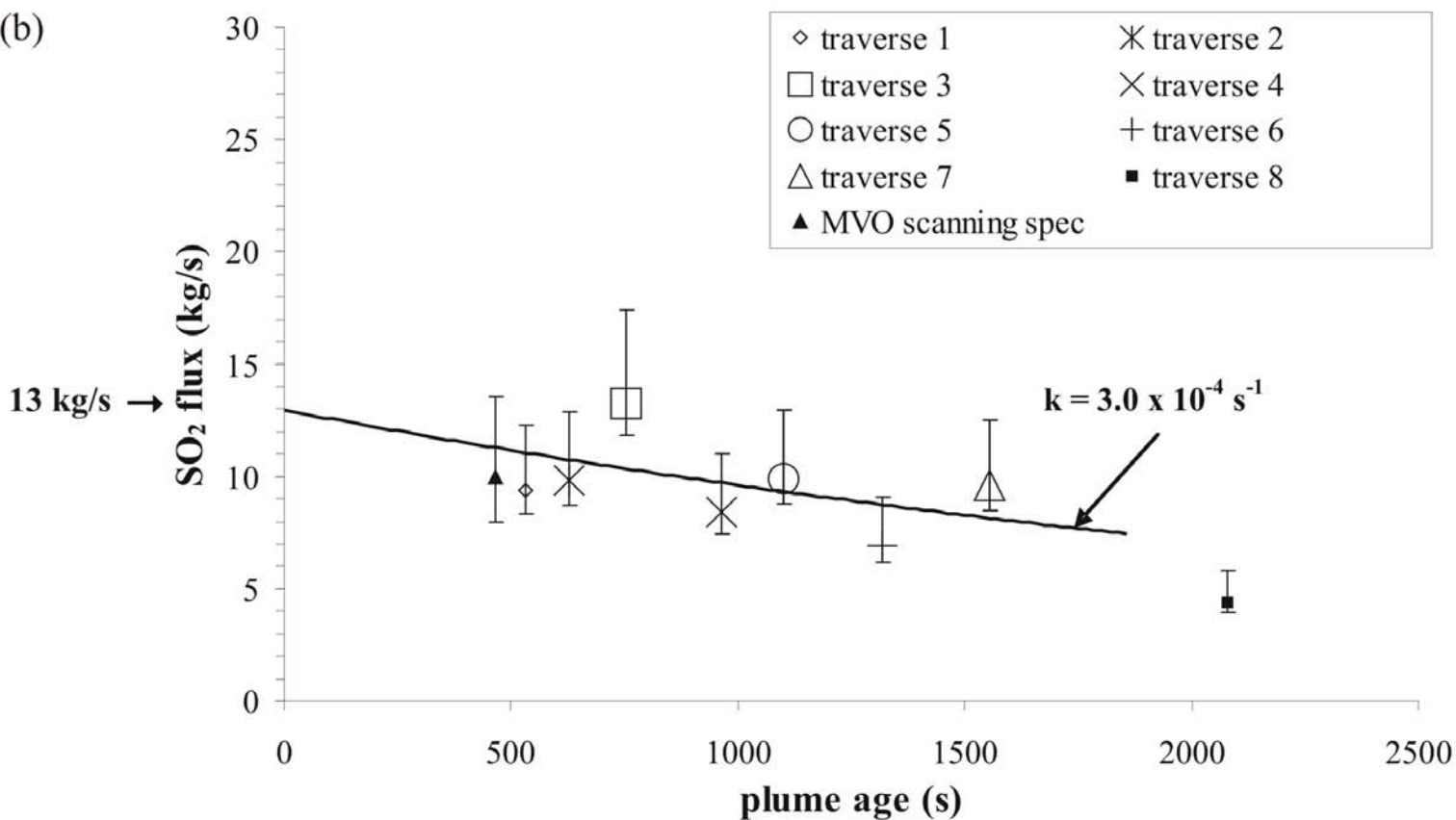
(b)



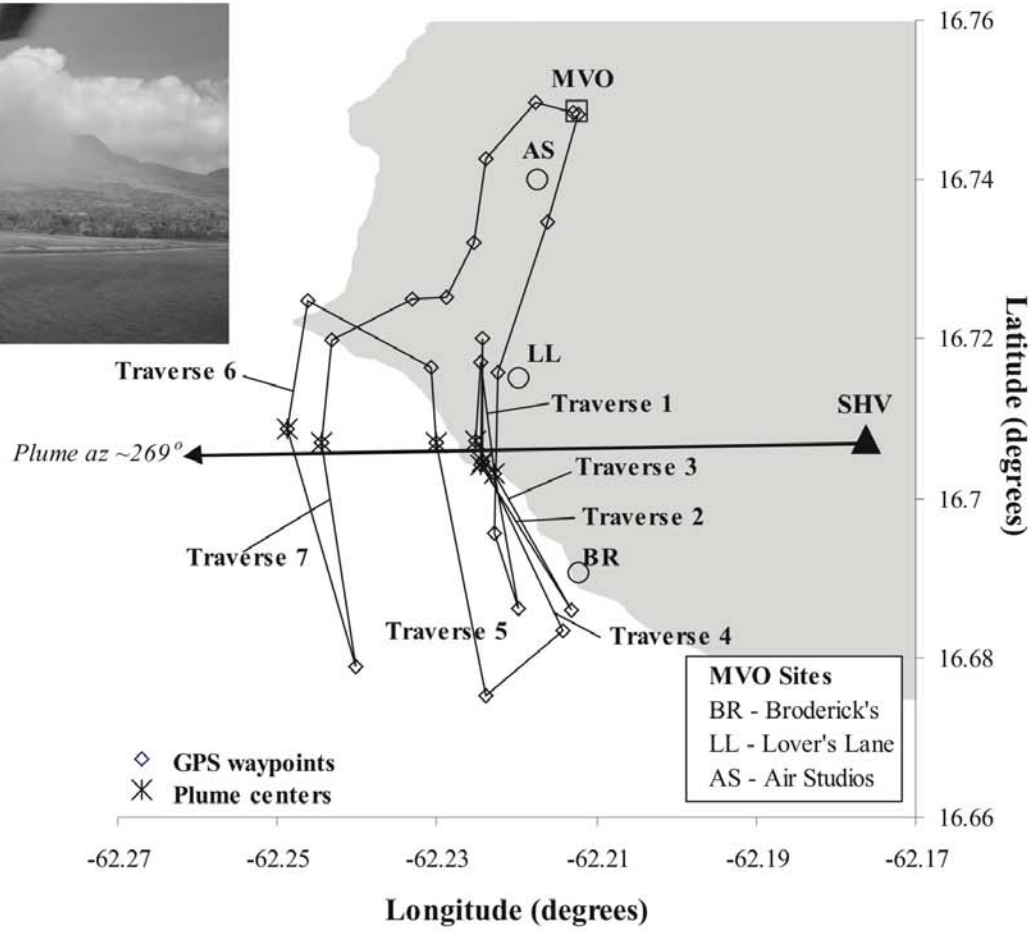
(a)



(b)



(a)



(b)

