

SO₂ emissions from Popocatépetl volcano: emission rates and plume imaging using optical remote sensing techniques

M. Grutter¹, R. Basaldud¹, C. Rivera², R. Harig³, W. Junkerman⁴, E. Caetano¹, and H. Delgado-Granados⁵

¹Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Mexico

²Department of Radio and Space Science, Chalmers University of Technology, Sweden

³Technische Universität Hamburg-Harburg, Germany

⁴Institut für Meteorologie und Klimaforschung, Forschungszentrum Karlsruhe, Germany

⁵Instituto de Geofísica, Universidad Nacional Autónoma de México, Mexico

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Abstract. Sulfur dioxide emissions from the Popocatépetl volcano in central Mexico were measured during the MLAGRO field campaign in March 2006. A stationary scanning DOAS (Differential Optical Absorption Spectrometer) was used to monitor the SO₂ emissions from the volcano and the results were compared with traverses done with a COSPEC from the ground and a DOAS instrument on board an ultra-light aircraft. Daytime evolutions as well as day-to-day variation of the SO₂ emissions are reported. A value of 2.45 ± 1.39 Gg/day of SO₂ is reported from all the daily averages obtained during the month of March 2006, with large variation in maximum and minimum daily averages of 5.97 and 0.56 Gg/day, respectively. The large short-term fluctuations in the SO₂ emissions obtained could be confirmed through 2-D visualizations of the SO₂ plume measured with a scanning imaging infrared spectrometer. This instrument, based on the passive detection of thermal radiation from the volcanic gas and analysis with FTIR spectrometry, is used for the first time for plume visualization of a specific volcanic gas. A 48-h forward trajectory analysis indicates that the volcanic plume was predominantly directed towards the Puebla/Tlaxcala region (63%), followed by the Mexico City and Cuernavaca/Cuautla regions with 19 and 18% occurrences, respectively. 25% of the modeled trajectories going towards the Puebla region reached altitudes lower than 4000 m a.s.l. but all trajectories remained over this altitude for the other two regions.

1 Introduction

Volcanic emission of gases and particles can contribute significantly to the chemistry of the atmosphere, its aerosol budget and thus to the radiative forcing both in the regional and global scales. Depending on how far these emissions are transported prior to deposition, these emissions can have important environmental effects. 15–21 Tg of SO₂ are injected into the atmosphere every year due to active volcanoes worldwide (Halmer et al., 2002), either continuously by passive degassing or from short-lived eruptions. These emissions account for approx. 7.5–10.5% of the total global sulfur emission which has as major contributors the burning of fossil fuels, oxidation of oceanic dimethyl sulfide and biomass burning. SO₂ sinks are dominated by oxidation and deposition processes and its lifetime can range from a few days to a couple of weeks, reacting mostly with OH to form H₂SO₄ or being removed by clouds and aerosols. For volcanic plumes with high water vapor content or low-altitude volcanoes near the coast, this reaction might occur over hours and even tens of minutes. During large eruptions, however, SO₂ can be injected to higher altitudes and form longer-lived stratospheric aerosols.

Popocatépetl (19.02° N, 98.62° W, 5465 m a.s.l.) is a high emission rate, passively degassing active volcano located 60 km south-east of Mexico City. This stratovolcano is part of the Tran-Mexican volcanic belt. After being in a dormant period for nearly 70 years, it began significant fumarolic and seismic activity with a moderate eruption in December 1994 (Siebe et al., 1996). A new episode of activity began in March 1996 with pyroplastic flows and strong explosions that occurred in June of 1997. Ash columns reached 15 km a.s.l. In December of 2001, another strong eruption produced



Correspondence to: M. Grutter
(grutter@servidor.unam.mx)

lava flows reaching the timberline and ignited fires 4.5 km from the crater (Delgado-Granados et al., 2001; Macias and Siebe, 2005).

Frequent ash and gas emissions have continued irregularly since the reawakening of this volcano. SO₂ emission rates have been estimated beginning early February 2004 with several COSPEC instruments, averaging 2.2 and 3.4 Gg/d in studies performed during the 23 December 1994–28 January 1995 (Galindo et al., 1998) and 30 January 1995–30 June 1995 (Delgado-Granados et al., 2001) time periods. Other averages have been reported in the past: 2.0 Gg/d in 1994, 1.6 Gg/d in 1995, 15 Gg/d in 1996 and occasionally above 50 Gg/d in 1997 (Goff et al., 1998). As reported by these authors, the total discharge of volatile gases through November of 1996 was similar to yearly amounts released by Mount Etna.

The Mexican national inventory for the year 1999 reported annual emissions of 1871 and 735 Gg/y from the Popocatépetl and Colima volcanoes, respectively (INESEMARNAT, 2006), which can be translated into an average daily emission of 5.13 Gg/d from Popocatépetl alone. This value is comparable to 6.65 Gg, which is the amount of SO₂ emitted every year anthropogenically by the Mexico City Metropolitan Area from both point and mobile sources, as has been officially reported for 2004 (SMA-GDF, 2006). This value, however, does not include the emissions from important industries like power plants and refineries located just outside the metropolitan area. For example, the Tula industrial complex alone, located 60 km north of Mexico City and 130 km NW of the volcano, emits around 0.43 Gg/d (158 Gg/y) as estimated from optical remote sensing measurements carried out in 2003 (de Foy et al., 2007). Thus, the Popocatépetl volcano has been an important source of emissions during this past decade releasing similar or higher amounts of SO₂ than all the anthropogenic sources in the central region of Mexico.

The objective of this investigation was to study the emissions of SO₂ from the Popocatépetl volcano during the MILAGRO field campaign (Fast et al., 2007) and to examine its possible interaction with the Mexico City plume. The measurement of the emissions of SO₂ from Popocatépetl is important in the context of a megacity field study such as MILAGRO, where sulfate production and its radiative and chemical impacts are to be characterized in detail (Graf et al., 1997). More commonly, the monitoring of gases and their relative ratios in volcanic plumes has aimed at a better understanding and forecasting of eruptive processes since changes in the magmatic activity are reflected in both the quantity and chemical composition of the emissions. Particular emphasis has been placed on the relative abundances of emitted gases such as HCl, HF, H₂S, SiF₄, CO₂, BrO, ClO, among others. Both optical remote sensing methods employed in this investigation to characterize SO₂ in the infrared (FTIR) and ultraviolet (DOAS) wavelength regions have been used for this purpose before (Love et al., 1998; Oppenheimer et al.,

1998; Goff et al., 2001). The broad range of application of these methods as well as the ongoing work will be explained.

2 Methodologies

Out of the many techniques available to analyze the composition of volcanic plumes, the spectroscopic remote sensing methods are preferred due to the potential hazard in approaching an active volcano for sample taking. Other advantages include the high temporal and spatial resolution which can be achieved from the different measurement configurations and instrument platforms from which the spectroscopic analysis is performed (Oppenheimer et al., 1998). The COSPEC (Barringer Research correlation spectrometer) has been the most widely used instrument for volcanic plume surveillance. It is configured to measure SO₂ column concentrations using sky UV radiation and estimating emissions by combining plume cross-section and wind velocity information. The instrument has been widely described by many authors (see for example Stoiber et al., 1983) and is therefore not explained here. Differential Optical Absorption Spectrometers (DOAS) are now being implemented as more modern, light and versatile instruments. Possible platforms include ground-based measurements, aircraft and satellites (Eisinger and Burrows, 1998; Afe et al., 2004). The importance of complementing satellite observations with ground-based instrumentation has been made evident, particularly when attempting to quantify volcanic emissions from space (Matiella Novak et al., 2008).

2.1 DOAS

DOAS is a widely used technique for the continuous measurement of atmospheric gases both in active and passive configurations (Platt et al., 1979; Platt, 1994). It is based on the spectral analysis of the differential absorption by molecules in the ultraviolet and visible part of the spectrum. The broader extinction of UV light due to other processes such as scattering on air molecules and aerosol particles is cancelled during the DOAS retrieval and thus not taken into account. In this investigation, scattered sunlight was used as the radiation source and the differential absorption of the SO₂ gas was analyzed and used to obtain differential slant columns as has been described elsewhere (Bobrowski et al., 2003; Galle et al., 2003; Lee et al., 2005).

Passive DOAS measurements were made by collecting the scattered UV light with a narrow field-of-view (<20 mrad) telescope. This consists of a convex lens (f=100 mm), a bandpass optical filter (Hoya U330) blocking visible light with wavelengths higher than 360 nm to reduce stray light, and a 200 μm diameter quartz optical fiber. The light is analyzed with a spectrometer (Ocean Optics, model S2000), at a resolution of <0.6 nm between 280–420 nm. This device employs a UV holographic grating and a 2048 element CCD detector. The instruments described below use their own

acquisition and control interfaces, although the same spectral evaluation software DOASIS (Kraus, 2001) was used in both configurations.

2.1.1 Scanning DOAS

A scanning DOAS instrument was placed at Tlamacas station (19.06° N, 98.63° W, 4000 m a.s.l.), located on the northern flank of the volcano and 4.7 km from the crater. The instrument is equipped with a turning mirror and a housing holding a quartz window for environmental protection. A stepper motor turns the 45° mirror which is oriented so that the light coming from the quartz window is directed towards the focusing lenses and into the optical fiber. The elevation angle is scanned from a fixed position perpendicular to the direction of the plume propagation. A full scan of the plume is accomplished every 1–6 min from which an SO₂ emission rate is calculated using the slant column of every scanned position, plume height, wind direction and wind speed information. A detailed description of the instrument and spectra evaluation can be found in (Edmonds et al., 2003; Galle et al., 2003; McGonigle et al., 2003).

2.1.2 Airborne DOAS

The FZK-ENDURO Ultra-light aircraft (Junkermann, 2005) was used as the platform to perform downwind plume traverses with a portable DOAS instrument. The aircraft was stationed at Hermanos Serdán Airport (PBC at 19.16° N, 98.37° W, 2244 m a.s.l.) near Huejotzingo, Puebla. The telescope was mounted above the wing looking towards the zenith and the spectra were continuously recorded after take-off using a LabView® based interface that couples each acquisition with a longitude-latitude fix from a GPS receiver. The software is designed to automatically set the acquisition time of the spectrometer according to the light intensity. User defined parameters along with dark and background spectra are entered prior to each measurement along the trajectory. The traverses were planned so as to fly around the volcano with a radius of ~18 km, which is the permissible distance from the crater regulated by local aviation officials.

2.2 Scanning Imaging Infrared Spectrometry

A scanning imaging infrared spectrometer for visualizing the SO₂ plume was placed at Altzomoni (19.12° N, 98.65° W, 4000 m a.s.l.) which is 11 km NNW of Popocatépetl at the flanks of Iztaccíhuatl volcano. This location allows for an adequate view of the gas plume at a safe distance from the active volcano. The system (SIGIS) (Harig et al., 2002) is based on the combination of a modified Michelson interferometer (Bruker, Opag 22), a telescope (7.5 mrad), an azimuth-elevation-scanning mirror, a video camera and a computer for control, data analysis, and display of the results. The video image is used as reference and to control the position of the scanning mirror. For visualization of gas clouds,

the scanning mirror is sequentially set to all positions within the area of interest and both the video images and recorded spectra are graphically displayed on the PC. The size and the direction of the area of interest to be measured, as well as the step size (i.e. the angle between adjacent fields of view) can be varied by the operator. A complete description and specification of this system, which has been successfully deployed mostly for industrial pollution monitoring, can be found in (Harig and Matz, 2001; Harig et al., 2002; Grutter et al., 2008).

In the scanning mode, an area of interest within the video image as well as a step size is chosen. The instrument, capable of measuring 6 spectra/s at 4 cm⁻¹ resolution, will sequentially record a spectrum at each position such that an image of 45×30 pixels will take about 3 min to be completed. The radiation measured by the spectrometer contains the spectral signatures of the background atmosphere and the gas cloud and the atmosphere in each position in the area of interest.

The primary objective from these passive IR observations was to visualize the evolution of the SO₂ plume. This can be accomplished by analyzing the spectra and fitting the features of the expected atmospheric gases at each position. The procedure for identification of SO₂ within the area of interest follows the steps described in (Harig et al., 2002). In the first step, the spectra of the brightness temperatures of a field of view with and without the plume are calculated. The first spectrum of each row of the image is used as the background spectrum which is subtracted from the plume spectra. The reference spectra of the target gas, H₂O and other interfering gases are then fitted to the resulting spectrum using a least-squares fitting procedure. Reference spectra with different column densities are calculated by convolution of high-resolution transmittance spectra using the HITRAN database (Rothman et al., 2005) with an instrumental line function (Harig, 2004). The fitting procedure includes an approximation of the baseline. In the next step, the contributions of all fitted signatures (i.e. interferences, atmospheric species, and baseline) except the signature of the target compound are subtracted from the measured spectrum.

In this work, the spectral range between 1095 and 1250 cm⁻¹ was selected for the analysis of SO₂. Spectra of H₂O and ozone were used as interference species in the fitting procedure. The column densities of SO₂ that were used for the calculation of the reference spectra used in the fitting procedure were 800, 5000 and 18 000 ppm m. In order to decide if the target compound is present, the coefficient of correlation between the corrected spectrum, i.e. the result of the subtraction, and a reference spectrum is calculated. The calculation is sequentially performed for three different column densities of the target compound. In this final step, a color is assigned according to the maximum coefficient of correlation obtained in the fitting procedure and plotted at each position on top of the video image, as presented in Fig. 4.

Table 1. Occurrences of the wind direction at crater height from the NARR and radiosonde (RS) datasets classified by regions during March 2006.

Region	WDR range		% Occurrence		
	Degrees	NARR	Frw Trajectory	RS-500 HPa	
Mexico City Metropolitan Area	90–173	14.1	19.0	15.7	
Puebla, Tlaxcala	173–310	64.1	62.9	64.7	
Cuautla, Cuernavaca	310–90	21.8	18.1	19.6	

3 Results and discussion

Measurements of the SO₂ emissions from Popocatépetl were carried out during the month of March 2006. Apart from the scanning DOAS, which automatically measures slant column cross-sections of the plume from the Tlamacas fixed site, traverses done with COSPEC from the ground and a portable DOAS instrument on board the ultra-light aircraft were performed. Calculating the emission rates from any of these techniques requires knowing the plume velocity and direction at the time the measurement was done. This was derived from estimates of the wind speed at the altitude of the volcanic emission at ~5400 m a.s.l. The National Weather Service's National Center for Environmental Prediction (NCEP) runs a series of operational computer analyses and forecasts. Their North American Regional Reanalysis (NARR) products include meteorological fields such as u- and v- wind components, temperature and humidity on a 32 km grid 8 times a day (Mesinger et al., 2006). The three-dimensional wind data from NARR was used to calculate the propagation velocity of the plume and the forward trajectories starting from Popocatépetl at 500 hPa using the scheme proposed by (Krishnamurti and Bounoua, 2000). The terrain effects are taken into account in the trajectory computation through the eta vertical coordinate as well as the vertical velocity field in areas where there is convection. However, no other convection effects such as washout and wet deposition were considered for the 48-h forward trajectories that were generated for 00:00 to 21:00 UTC in three hour intervals.

Since the altitude of the volcanic plume varies and is not known with precision for every individual measurement, the 3-hourly model outputs for the 550 and 500 hPa layers, corresponding to approximate altitudes between 5100 and 5900 m a.s.l., were averaged and are shown in Fig. 1. This altitude range is thought to contain the plume above the measurement site at Tlamacas (4.7 km downwind) most of the time. Radiosonde data taken in Mexico City from the Servicio Meteorológico Nacional (SMN, station 76679 located at 19.4° N, 99.196° W, 2303 m a.s.l.) in this pressure range are also plotted in Fig. 1. For consistency and since the radiosonde data is assimilated by the NARR, the continuous dataset from NCEP was used for all emission calculations throughout this work.

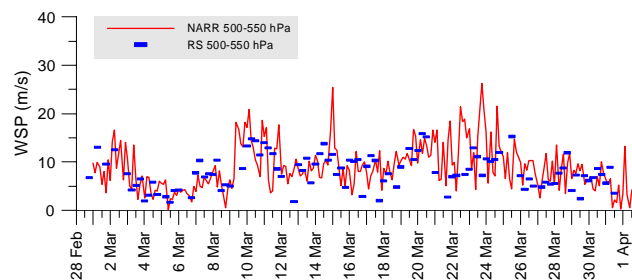


Fig. 1. 3-hourly wind speed data from NCEP (NARR) model output as well as 6 and 18 h (LST) radiosonde data (RS) from SMN for the month of March 2006. All data is averaged over the 550–500 hPa range.

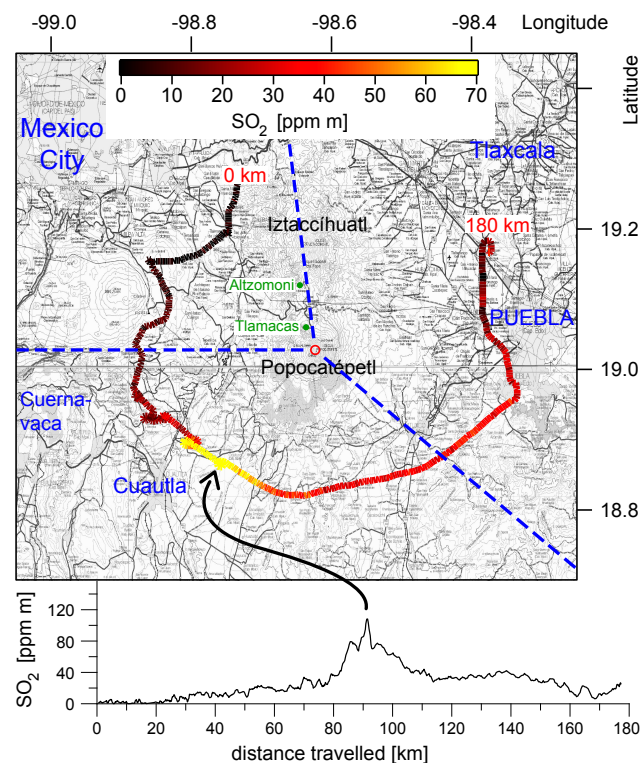


Fig. 2. Map of the region around the Popocatépetl volcano showing the results from a DOAS measurement made on board an ultra-light aircraft. The color scaled line represents the slant column of SO₂ (ppm × m) measured along the path flown on 18th March 2006. Blue dashed lines separate the main regions described in Table 1.

Evidence that the emissions of the Popocatépetl volcano can be influencing the particle formation in the Mexico City area has been presented elsewhere (Raga et al., 1999). In order to estimate the probability that volcanic emissions would affect neighboring urban areas during the MILAGRO field campaign, a frequency analysis was produced based on the NARR time series (500–550 hPa) for the month of March. A geographical division was established defining three major

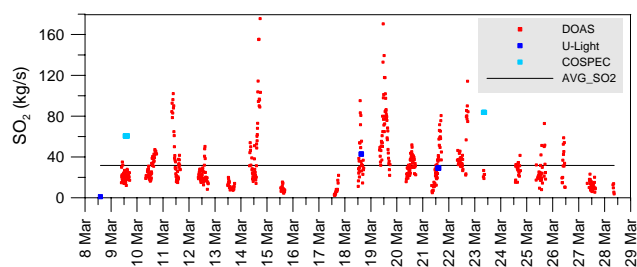


Fig. 3. Sulfur dioxide emission rates from the Popocatépetl volcano calculated from the ground-based scanning DOAS measurements (red dots), from traverses done with a mobile DOAS on board an ultra-light aircraft (dark blue) and with a COSPEC instrument (light blue) in 2006.

basins containing the largest nearby metropolitan areas: Mexico City Metropolitan Area (MCMA), Puebla/Tlaxcala and Cuautla/Cuernavaca. For this purpose, lines were drawn from the position of the crater in the directions 130, 270 and 353° as presented in Fig. 2, taking into account the surrounding mountains as physical barriers and major urbanized centers of the above-mentioned regions.

The corresponding wind direction ranges considered for this analysis are presented in Table 1. This table contains the percent occurrences from instantaneous wind direction datasets from NARR at the position of the crater, the final position of the forward trajectory calculated for 48 h and the radiosonde 500 hPa wind speed data which fall under this criterion. The results show that the volcanic plume was predominantly directed towards the Puebla/Tlaxcala region with an occurrence of about 63%, followed by the Mexico City and Cuernavaca/Cuautla regions with approximately 19 and 18%, respectively. Three dimensional plots generated for all trajectories during the month of March revealed that 25% of the modeled trajectories going towards the Puebla/Tlaxcala region reached altitudes below 4000 m a.s.l., while all the trajectories towards the other two regions remained above this altitude most of the time.

The March mean wind field at 500 mb is representative of the boreal winter over Central Mexico. The westerly winds are dominant from the middle to upper atmosphere. During the summer the weaker and moister easterly winds span the lower atmosphere up to 500 hPa due to northward displacement of the trade winds. The winter pattern is modified by cold fronts (northerly winds) and the summer patterns is modulated by the local convection and mesoscale convective systems.

3.1 Ultra-light aircraft measurements

SO₂ emissions were calculated from selected DOAS measurements performed on board an ultra-light aircraft in order to 1) compare them with the results from the ground-based instrument and 2) determine the plume position and width

Table 2. Daily averages and standard deviation of SO₂ emissions calculated from the ground-based DOAS instrument given the number of observations. COSPEC and airborne-DOAS emission calculations are instantaneous values from single traversals.

Date	Ground-based scanning DOAS		U-Light DOAS	COSPEC
	No. of samples	Daily Avg.	Std. Dev.	
2006				
			[Gg/d]	
4-Mar	18		0.09	
8-Mar				
9-Mar	44	1.84	0.42	5.23
10-Mar	48	2.53	0.82	
11-Mar	42	3.53	2.29	
12-Mar	46	1.94	0.73	
13-Mar	28	0.99	0.30	
14-Mar	51	4.42	3.42	
15-Mar	19	0.78	0.27	
17-Mar	18	0.63	0.46	
18-Mar	28	3.41	1.85	2.71
19-Mar	49	5.97	2.70	
20-Mar	48	2.70	0.74	
21-Mar	49	2.68	1.79	2.51
22-Mar	38	3.96	1.94	
23-Mar	5	1.93	0.26	7.23
24-Mar	18	2.36	0.61	
25-Mar	32	2.29	1.18	
26-Mar	15	2.74	1.42	
27-Mar	32	1.05	0.38	
28-Mar	5	0.79	0.38	

during a specific event. Data is presented from only three flights since not all the flight-patterns were relevant to this investigation and the instrument performance and weather conditions were not always favorable. The result from one of these experiments, corresponding to 18th March, is graphically presented in Fig. 2. The trajectory of the flight is marked with a colored line expressed in column density (ppm×m) of SO₂, starting south east of Iztaccíhuatl volcano and ending at the Puebla airport for landing after 180 km.

3.2 Ground-based DOAS measurements

An automated scanning DOAS was operated continuously from the Tlamacas site as described in Sect. 2.1. SO₂ emissions were calculated using the NARR dataset throughout the month of March for consistency. The emission results have been filtered so that only those data where the volcanic plume was completely crossed during a full scan of the instrument is included. These emission values from the ground-based DOAS instrument are plotted as red dots in Fig. 3 for the month of March 2006. It is important to note that since this method requires dispersed light from the sun, only daytime values are reported. Also in this plot, the emission calculations obtained from the three traverses done from the ultra-light aircraft (blue) and two emission calculations from the COSPEC instrument are included. Ground-based traverses with COSPEC are performed routinely twice a month by CE-NAPRED (Centro Nacional de Prevención de Desastres) in collaboration with the Instituto de Geofísica of UNAM. The

average of all measurements from the ground-based DOAS instrument, reported as 31.7 kg/s, is represented in the graph as a horizontal line.

The individual averages for every day measured during the month of March 2006 are presented in Table 2. Instantaneous emission determinations from traverses performed on selected days from the ground and from the air are also tabulated for comparison. Values obtained from the instrument on board the ultra-light aircraft agree with the daily averages from the ground based DOAS falling within their standard deviations on both days where the data is available. On the other hand, the emission calculation from the COSPEC measurements performed on the 9th and 23rd are 2.8 and 3.7 times higher than the daily average reported from the ground-based DOAS. Unfortunately, no direct comparison between the COSPEC and DOAS instruments was done in a single transect but a previous work aiming specifically at this (Elias et al., 2006) shows that the retrieved slant columns should not differ by more than 10% from properly calibrated instruments. Thus, a poor calibration of the COSPEC instrument is not discarded but more probable causes for the observed discrepancies are explained below.

It was observed from the wind trajectories calculated from NARR data, that often the wind direction changes and makes abrupt turns along the path of the plume. Although a geometrical correction is taken into account for the flux calculation, this considers a linear propagation between the origin of the emission and the position at which the SO₂-peak was observed. If, however, the wind direction at the position where the plume is crossed has changed and is considerably different from the one used for the correction, the cross-section and thus the flux will be overestimated. Another possibility would be for a difference in radiative transfer. It has been shown that measured SO₂ slant-column densities decrease with distance to the plume due to UV scattering (Mori et al., 2006). If the scanning DOAS is measuring a plume close to the horizon while the zenith-looking COSPEC measurement has a shorter distance to the plume, then the flux from the DOAS would be underestimated. The geometrical factor and thus overestimation of the COSPEC flux is, nevertheless, thought to be the most probable cause for the discrepancies. This is due to the fact that the traverses are performed at long distances (20–40 km) from the source and wind is expected to change directions as was commonly seen in the wind trajectories.

Two days with particularly high emission of SO₂ were the 14th and 19th, with daily averages reaching 4.42 and 5.97 Gg/d, respectively. The lowest activity was recorded on the 13, 15, 17 and 28th, all with emissions below 1 Gg/d.

3.3 Plume visualization

A large variability in the SO₂ emission is evident from the DOAS measurements shown above. A scanning imaging infrared spectrometer was deployed on selected days in order

to visualize the plume shape and monitor its temporal evolution. The instrument, described in Sect. 2.2, was placed at Altzomoni and was able to detect the SO₂ signature in the infrared spectra collected from a distance of 11 km from the crater. This detection is represented in a two-dimensional image according to the coefficient of correlation R with respect to a reference spectrum of SO₂ as seen in the example shown in Fig. 4 for 16 March.

These images include the black and white video image of the volcano at the beginning of each scan and the false color image of the SO₂ plume. For clarity, only spectra with R -values greater than 0.97 are plotted in order to better separate the plume shape from the background. In this particular case, the duration of each scan was 3 min and 14 s, although the scan time generally varied depending on the size of the area chosen. It is evident from these observations that the plume changes significantly from scan to scan. There are two potential reasons for this. The first reason is that changes in wind speed lead to a variability of the number of molecules present along the optical path if the emission rate is constant. The second reason is that the emission rate of the gas is not constant. The presence of these “puffs” or events of higher emission can be investigated by analysis of consecutive scans.

4 Conclusions

Knowing Popocatépetl's SO₂ emission source strength is important to assess its potential contribution to the atmospheric chemistry, aerosol formation and its radiative implications in the central region of Mexico. Optical remote sensing methods were deployed for this purpose during the MILAGRO international field campaign. An average of 2.45 ± 1.39 Mg of SO₂ were released every day to the atmosphere during the month of March 2006 as determined by a passive DOAS instrument continuously measuring from the ground and confirmed by traverses done with a similar instrument from an ultra-light aircraft. A frequency analysis of the 48-h forward trajectories suggests that the emissions from Popocatépetl were transported towards Puebla/Tlaxcala approximately 63% of the time during the month of March 2006. At this altitude the wind direction towards the Mexico City Metropolitan Area, located only 60 km NW of the crater, accounted for only 19% of the occurrence during this period and none of these trajectories crossed below 4000 m a.s.l. The observed mean wind field at 500 hPa is typical for the month of March (de Foy et al., 2008) and is representative only for the boreal winter over Central Mexico.

The SO₂ emitted by the volcano originates at an altitude well above the planetary boundary layer and is not expected to impact the metropolitan areas directly most of the time unless strong convective conditions are present. This could be observed only in the case of the Puebla/Tlaxcala direction, where 25% of the calculated trajectories cross at some point below an altitude of 4000 m a.s.l. However, sulfate

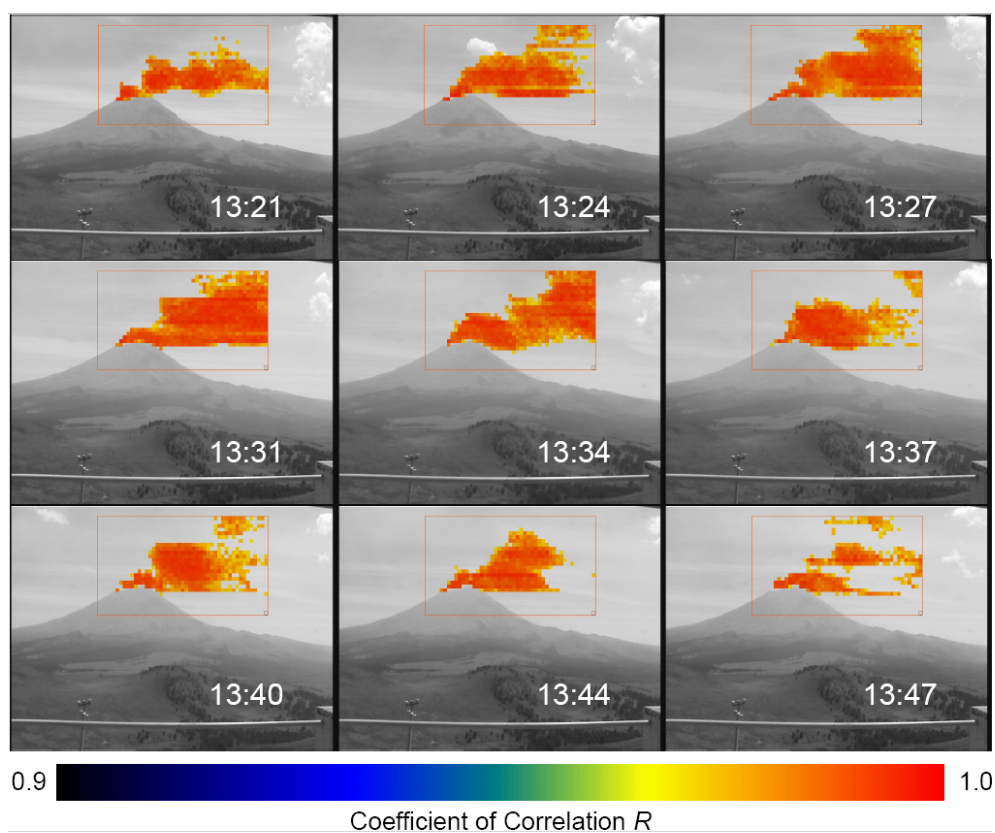


Fig. 4. SO₂ plume visualization of the Popocatépetl volcano by passive infrared spectroscopy during 17th March 2006. White numbers indicate the local time.

containing particles formed as a result of these emissions are more likely to interact with the urban pollution as found in a previous study (Raga et al., 1999). It would be important to further investigate the fate of these emissions by modeling not only their trajectories, but also the chemical and physical transformations along their path.

A scanning imaging infrared spectrometer was used to visualize the dispersion of the sulfur dioxide plume and investigate the large fluctuations observed in the emissions. The thermal infrared radiation of the emitted gases was collected and used to detect the SO₂ emission band from a distance of 11 km. Two-dimensional images of the detected SO₂ signature were generated to determine the plume shape and monitor plume evolution. These observations confirm that gaseous emissions from the volcano are not continuous but appear rather as “puffs”. This spectroscopic technique, used for the first time for plume visualization of a specific volcanic gas using its thermal radiation, represents important progress for the surveillance of volcanic activity since 1) it can operate day or night, 2) can handle cloudy conditions for gas detection as long as the clouds are not between the instrument and the plume, 3) can visualize shape, direction and evolution of a volcanic plume, 4) can allow for the determination of the plume’s velocity by analyzing sequential images (this

would eliminate much of the uncertainty in flux estimation) and 5) can be used to measure other gases like HCl, HF, SiF₄ (although at higher spectral resolutions) and report their relative abundances. Work is in progress to achieve this and also to determine column densities of SO₂ from the measured IR spectra which would provide an alternative method for estimating emissions.

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References

- Afe, O. T., Richter, A., Sierk, B., Wittrock, F., and Burrows, J. P.: BrO emission from volcanoes: A survey using GOME and SCIAMACHY measurements, *Geophys. Res. Lett.*, 31, 24, 2004.

- Bobrowski, N., Hönninger, G., Galle, B., and Platt, U.: Detection of bromine monoxide in a volcanic plume, *Nature*, 423, 273–276, 2003.
- de Foy, B., Fast, J. D., Paech, S. J., Phillips, D., Walters, J. T., Coulter, R. L., Martin, T. J., Pekour, M. S., Shaw, W. J., Kasten-deuch, P. P., Marley, N. A., Retama, A., and Molina, L. T.: Basin-scale wind transport during the MILAGRO field campaign and comparison to climatology using cluster analysis, *Atmos. Chem. Phys.*, 8(5), 1209–1224, 2008.
- de Foy, B., Lei, W., Zavala, M., Volkamer, R., Samuelsson, J., Melqvist, J., Galle, B., Martinez, A. P., Grutter, M., Retama, A., and Molina, L. T.: Modelling constraints on the emission inventory and on vertical dispersion for CO and SO₂ in the Mexico City Metropolitan Area using Solar FTIR and zenith sky UV spectroscopy, *Atmos. Chem. Phys.*, 7, 781–801, 2007, <http://www.atmos-chem-phys.net/7/781/2007/>.
- Delgado-Granados, H., Gonzalez, L. C., and Sanchez, N. P.: Sulfur dioxide emissions from Popocatepetl volcano (Mexico): case study of a high-emission rate, passively degassing erupting volcano, *J. Volcanol. Geoth. Res.*, 108(1–4), 107–120, 2001.
- Edmonds, M., Herd, R. A., Galle, B., and Oppenheimer, C. M.: Automated, high time-resolution measurements of SO₂ flux at Soufriere Hills Volcano, Montserrat, *Bull. Volcanol.*, 65(8), 578–586, 2003.
- Eisinger, M., and Burrows, J. P.: Tropospheric sulfur dioxide observed by the ERS-2 GOME instrument, *Geophys. Res. Lett.*, 25(22), 4177–4180, 1998.
- Elias, T., Sutton, A. J., Oppenheimer, C., Horton, K. A., Garbeil, H., Tsanev, V., McGonigle, A. J. S., and Williams-Jones, G.: Comparison of COSPEC and two miniature ultraviolet spectrometer systems for SO₂ measurements using scattered sunlight, *Bull. Volcanol.*, 68(4), 313–322, 2006.
- Fast, J. D., de Foy, B., Rosas, F. A., Caetano, E., Carmichael, G., Emmons, L., McKenna, D., Mena, M., Skamarock, W., Tie, X., Coulter, R. L., Barnard, J. C., Wiedinmyer, C., and Madronich, S.: A meteorological overview of the MILAGRO field campaigns, *Atmos. Chem. Phys.*, 7(9), 2233–2257, 2007.
- Galindo, I., Ivlev, L. S., Gonzalez, A., and Ayala, R.: Airborne measurements of particle and gas emissions from the December 1994 January 1995 eruption of Popocatepetl Volcano (Mexico), *J. Volcanol. Geoth. Res.*, 83(3–4), 197–217, 1998.
- Galle, B., Oppenheimer, C., Geyer, A., McGonigle, A. J. S., Edmonds, M., and Horrocks, L.: A miniaturised ultraviolet spectrometer for remote sensing of SO₂ fluxes: a new tool for volcano surveillance, *J. Volcanol. Geoth. Res.*, 119(1–4), 241–254, 2003.
- Goff, F., Janik, C. J., Delgado, H., Werner, C., Counce, D., Stimac, J. A., Siebe, C., Love, S. P., Williams, S. N., Fischer, T., and Johnson, L.: Geochemical surveillance of magmatic volatiles at Popocatepetl volcano, Mexico, *Geol. Soc. Am. Bull.*, 110(6), 695–710, 1998.
- Goff, F., Love, S. P., Warren, R. G., Counce, D., Obenholzer, J., Siebe, C., and Schmidt, S. C.: Passive infrared remote sensing evidence for large, intermittent CO₂ emissions at Popocatepetl volcano, Mexico, *Chem. Geol.*, 177(1–2), 133–156, 2001.
- Graf, H. F., Feichter, J., and Langmann, B.: Volcanic sulfur emissions: Estimates of source strength and its contribution to the global sulfate distribution, *J. Geophys. Res.-Atmos.*, 102, D9, 10727–10738, 1997.
- Grutter, M., Basaldud, R., Flores, E., and Harig, R.: Optical remote sensing for characterizing the spatial distribution of stack emissions, in: *Advanced Environmental Monitoring*, edited by: Kim, Y. J. and Platt, U., Springer Verlag, 107–118, 2008.
- Halmer, M. M., Schmincke, H. U., and Graf, H. F.: The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years, *J. Volcanol. Geoth. Res.*, 115(3–4), 511–528, 2002.
- Harig, R.: Passive remote sensing of pollutant clouds by Fourier-transform infrared spectrometry: signal-to-noise ratio as a function of spectral resolution, *Appl. Opt.*, 43(23), 4603–4610, 2004.
- Harig, R. and Matz, G.: Toxic cloud imaging by infrared spectroscopy: A scanning FTIR system for identification and visualization, *Field. Anal. Chem. Tech.*, 5(1–2), 75–90, 2001.
- Harig, R., Matz, G., and Rusch, P.: Scanning Infrared Remote Sensing System for Identification, Visualization, and Quantification of Airborne Pollutants, *Proc. SPIE*, 4575, 83–94, 2002.
- INE-SEMARNAT: Inventario nacional de emisiones de México 1999, Instituto Nacional de Ecología, SEMARNAT, 380 pp., 2006.
- Junkermann, W.: The actinic UV-radiation budget during the ESCOMPTE campaign 2001: results of airborne measurements with the microlight research aircraft D-MIFU, *Atmos. Res.*, 74(1–4), 461–475, 2005.
- Kraus, S.: The DOASIS Software, Chapter Presentation at the 1st International DOAS Workshop, Institut für Umweltphysik, University of Heidelberg, Germany, <http://www.iup.uni-heidelberg.de/bugtracker/projects/doasis/>, access: 7 November 2008.
- Krishnamurti, T. N. and Bounoua, L.: *An introduction to Numerical Weather Prediction Techniques*, 293 pp., CRC Press, Florida, USA, 2000.
- Lee, C., Kim, Y. J., Tanimoto, H., Bobrowski, N., Platt, U., Mori, T., Yamamoto, K., and Hong, C. S.: High ClO and ozone depletion observed in the plume of Sakurajima volcano, Japan, *Geophys. Res. Lett.*, 32, 21, 2005.
- Love, S. P., Goff, F., Counce, D., Siebe, C., and Delgado, H.: Passive infrared spectroscopy of the eruption plume at Popocatepetl volcano, Mexico, *Nature*, 396, 6711, 563–567, 1998.
- Macias, J. L. and Siebe, C.: Popocatepetl's crater filled to the brim: significance for hazard evaluation, *J. Volcanol. Geoth. Res.*, 141(3–4), 327–330, 2005.
- Matiella Novak, M. A., Watson, I. M., Delgado-Granados, H., Rose, W. I., Cárdenas-González, L., and Realmuto, V. J.: Volcanic emissions from Popocatepetl volcano, Mexico, quantified using Moderate Resolution Imaging Spectroradiometer (MODIS) infrared data: A case study of the December 2000–January 2001 emissions, *J. Volcanol. Geoth. Res.*, 170, 76–85, 2008.
- McGonigle, A. J. S., Oppenheimer, C., Hayes, A. R., Galle, B., Edmonds, M., Caltabiano, T., Salerno, G., Burton, M., and Mather, T. A.: Sulphur dioxide fluxes from Mount Etna, Vulcano, and Stromboli measured with an automated scanning ultraviolet spectrometer, *J. Geophys. Res.-Sol. Ea.*, 108(B9), 2003.
- Mesinger, F., DiMego, G., Kalnay, E., Mitchell, K., Shafran, P. C., Ebisuzaki, W., Jovic, D., Woollen, J., Rogers, E., Berbery, E. H., Ek, M. B., Fan, Y., Grumbine, R., Higgins, W., Li, H., Lin, Y., Manikin, G., Parrish, D., and Shi, W.: North American regional reanalysis, *Bull. Am. Meteorol. Soc.*, 87(3), 343, 2006.

- Mori, T., Mori, T., Kazahaya, K., Ohwada, M., Hirabayashi, J., and Yoshikawa, S.: Effect of UV scattering on SO₂ emission rate measurements, *Geophys. Res. Lett.*, 33, 17, 2006.
- Oppenheimer, C., Francis, P., Burton, M., Maciejewski, A. J. H., and Boardman, L.: Remote measurement of volcanic gases by Fourier transform infrared spectroscopy, *Appl. Phys. B-Lasers O.*, 67(4), 505–515, 1998.
- Platt, U.: Differential optical absorption spectroscopy (DOAS), in *Air monitoring by spectroscopy techniques*, edited by: Sigrist, M. W., Wiley Interscience, New York, USA, 27–83, 1994.
- Platt, U., Perner, D., and Pätz, H. W.: Simultaneous measurement of atmospheric CH₂O, O₃ and NO₂ by differential optical absorption, *J. Geophys. Res.*, 84, 6329–6335, 1979.
- Raga, G. B., Kok, G. L., Baumgardner, D., Baez, A., and Rosas, I.: Evidence for volcanic influence on Mexico City aerosols, *Geophys. Research Lett.*, 26(8), 1149–1152, 1999.
- Rothman, L. S., Jacquemart, D., Barbe, A., Benner, D. C., Birk, M., Brown, L. R., Carleer, M. R., Chackerian, C., Chance, K., Coudert, L. H., Dana, V., Devi, V. M., Flaud, J. M., Gamache, R. R., Goldman, A., Hartmann, J. M., Jucks, K. W., Maki, A. G., Mandin, J. Y., Massie, S. T., Orphal, J., Perrin, A., Rinsland, C. P., Smith, M. A. H., Tennyson, J., Tolchenov, R. N., Toth, R. A., Vander Auwera, J., Varanasi, P., and Wagner, G.: The HITRAN 2004 molecular spectroscopic database, *J. Quant. Spectrosc. Ra.*, 96(2), 139–204, 2005.
- Siebe, C., Abrams, M., Macias, J. L., and Obenholzner, J.: Repeated volcanic disasters in Prehispanic time at Popocatepetl, central Mexico: Past key to the future?, *Geology*, 24(5), 399–402, 1996.
- SMA-GDF: Inventario de emisiones DE LA zona metropolitana de México 2004 (Emission inventory for the Mexico City Metropolitan Area 2004), Secretaría del Medio Ambiente, Gobierno del Distrito Federal, Mexico City, online available at: www.sma.df.gob.mx/sma/index.php?opcion=26&id=421, access: 7 November 2008, 2006.
- Stoiber, R. E., Malinconico, L. L., and Williams, S. N.: Use of the correlation spectrometer at volcanoes, in *Forecasting volcanic events*, edited by: Tazieff, H. and Sabroux, J. C., Elsevier, Amsterdam, 425–444, 1983.