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Measurements of volcanic SO_2 and CO_2 fluxes by combined DOAS, Multi-GAS and FTIR observations: a case study from Turrialba and Telica volcanoes

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Abstract Over the past few decades, substantial progress has been made to overcome the technical difficulties of continuously measuring volcanic SO_2 emissions. However, measurements of CO_2 emissions still present many difficulties, partly due to the lack of instruments that can directly measure CO_2 emissions and partly due to its strong atmospheric background. In order to overcome these difficulties, a commonly taken approach is to combine differential optical absorption spectroscopy (DOAS) by using NOVAC scan-DOAS instruments for continuous measurements of crateric SO_2 emissions, and electrochemical/NDIR multi-component gas analyser system (multi-GAS) instruments for measuring CO_2/SO_2 ratios of excerpts of the volcanic plume. This study aims to quantify the representativeness of excerpts of CO_2/SO_2 ratios measured by Multi-GAS as a fraction of the whole plume composition, by comparison with simultaneously measured CO_2/SO_2 ratios using cross-crater Fourier transform infrared spectroscopy (FTIR). Two study cases are presented: Telica volcano (Nicaragua), with a homogenous plume, quiescent degassing from a deep source and ambient temperature, and Turrialba volcano (Costa Rica), which has a non-homogeneous plume from three main sources with different compositions and temperatures. Our comparison shows that in our "easier case" (Telica), FTIR and Multi-GAS CO_2/SO_2 ratios agree within a factor about 3 %. In our "complicated case" (Turrialba), Multi-GAS and FTIR yield CO_2/SO_2 ratios differing by approximately 13–25 % at most. These results suggest that a fair estimation of volcanic CO_2 emissions can be provided by the combination of DOAS and Multi-GAS instruments for volcanoes with similar degassing conditions as Telica or Turrialba. Based on the results of this comparison, we report that by the time our measurements were made, Telica and Turrialba were emitting approximately 100 and 1,000 t day^{-1} of CO_2, respectively.

Keywords DOAS · FTIR · Multi-GAS · Volcanic SO_2 and CO_2 fluxes

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Introduction

The increase of atmospheric CO_2 emissions leads to higher temperatures via the greenhouse effect, a natural process that has played a critical role during the different stages of

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the earth's temperature record. After the industrial revolution, anthropogenic emissions became the dominant source of atmospheric CO_2 (IPCC 2007), leading to an increase of the global average temperature (Solomon et al. 2009). Despite the importance of estimating the budget of atmospheric CO_2, natural CO_2 emissions are still poorly constrained, thus making it difficult to quantify the extent of the anthropogenic signature in the atmosphere (e.g. Burton et al. 2013; Hazen and Schiffries 2013). Volcanoes constitute an important source of natural CO_2 emissions in the atmosphere; therefore, quantifying volcanic emissions is crucial in order to improve our knowledge of the atmospheric CO_2 budget.

In addition to their role in the atmospheric composition, quantifying volcanic gas emissions are an important parameter to quantify for evaluating magma-degassing processes, thus contributing to volcanic hazard assessment (e.g. Casadevall et al. 1983; Burton et al. 2007; Symonds et al. 1994). Water vapour, CO_2 and SO_2 are the most abundant volcanic gases (Symonds et al. 1994). In general, measuring volcanic gases is not a straightforward task; however, the difficulties for measuring SO_2 emissions have been successfully reduced with ground-based remote sensing techniques such as the correlation spectrometer (COSPEC) (Hoff and Millan 1981), mobile/scan differential optical absorption spectroscopy (DOAS) (Galle et al. 2002, 2010; Edmonds et al. 2003; Burton et al. 2009) and SO_2 cameras (Mori and Burton 2006). In contrast, volcanic CO_2 and water vapour are still hard to determine with similar techniques, partly due to the lack of suitable spectroscopic features in the ultraviolet (UV) spectral region and partly due to their abundant atmospheric background concentrations, which makes it difficult to distinguish the volcanic contribution from the standard atmospheric composition.

The volcanic CO_2 budget is still unconstrained for a number of degassing volcanoes (Burton et al. 2013), including Turrialba and Telica, two active volcanoes in Costa Rica and Nicaragua, respectively. Here, we present the results of a multidisciplinary experiment carried out in March 2013 with the aim of characterizing the gas composition of both volcanic plumes, with a particular focus on CO_2 and SO_2 emissions ratios. To overcome the difficulties of CO_2 flux measurements, we estimate the CO_2/SO_2 ratio of the volcanic plume by applying the Multi-GAS technique (Aiuppa et al. 2007; Shinohara 2005). Hence, the CO_2 flux is inferred by multiplying the CO_2/SO_2 ratio by parallel SO_2 flux measurements, which were made by using NOVAC scan-DOAS instruments (Galle et al. 2010). However, the CO_2/SO_2 ratio obtained by the stationary Multi-GAS instruments corresponds to an excerpt of the whole volcanic plume. In order to estimate how representative this ratio is compared to the bulk plume composition, cross-crater open-path (OP) Fourier transform infrared spectroscopy (FTIR) measurements (Oppenheimer et al. 1998; Sawyer et al. 2011; Duffell et al. 2003) were also made in parallel to stationary and mobile Multi-GAS measurements. The plumes of Turrialba and Telica volcanoes are easily accessible and are situated in regions with relatively stable wind direction and are therefore excellent test sites to apply and validate the combination of OP-FTIR, Multi-GAS and scan-DOAS techniques. This study represents the first systematic attempt to our knowledge to quantitatively compare results of two independent and widely used volcanic gas sensing techniques (Multi-GAS and OP-FTIR).

Turrialba volcano

Turrialba volcano is a basaltic-to-dacitic stratovolcano located approximately 15 km north of the city of Turrialba at 10.03°N 83.77°W (Fig. 1). It has an altitude of 3,340 m.a.s.l and is the easternmost of Costa Rica's Holocene volcanoes. The south-western end of the Turrialba edifice comprises an area of 800 m by 2,200 m, hosting three craters.

Historical natural hazards at Turrialba include landslides, pyroclastic flows, surges, lahars and ash falls and acidic volcanic gases. Reports from the 1864 to 1866 VEI 2 eruptions suggest ash fell as far as 125 km from the source (Reagan et al. 2006), which implies fallout from ash emissions may have been a problem in the Central Valley, the most populated and important economic area of Costa Rica. After 150 years of quiescence, a phreatic eruption, preceded by a gradual increase of activity, opened a new vent on the south-western side of the west crater on 5 January 2010 (Vaselli et al. 2010; Martini et al. 2010). The resulting new vent (Boca 2010) became the main contributor to the Turrialba plume. During the rainy season of 2011, the vent Boca 2011 opened. In 2012, another vent (Boca 2012) opened, emitting non-juvenile material on January 12 and 18 (OVSICORI-UNA 2012). Although Boca 2010 remained the main contributor to the Turrialba plume, the pair Boca 2011 and Boca 2012 added substantial additional gas input. The recent increase of activity of Turrialba has been accompanied by an increment of SO_2 emissions in the range of about 2,000–3,000 metric tonnes per day (t day^{-1}) at the onset of the eruptive event in January 2010 (Campion et al. 2012; Conde et al. 2013).

Telica volcano

Telica volcano is a basaltic-andesitic volcano located at 12.602°N 86.85°W. It has an altitude of 1,061 m.a.s.l. and is located north-west of the volcanic chain of Nicaragua. Telica features a typical stratovolcano shape; its summit is the highest point near the city of León and has a crater 700 m in diameter and 120 m deep (Smithsonian-Institution

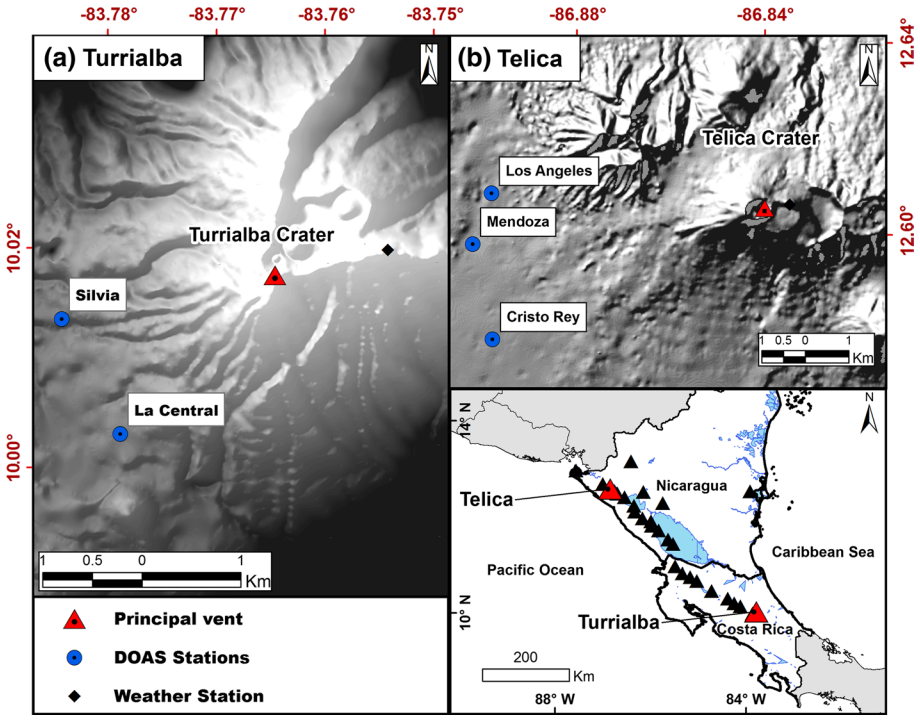

Fig. 1 Map showing the location of the NOVAC instruments surrounding the studied volcanoes **a** Turrialba volcano (Costa Rica). **b** Telica volcano (Nicaragua)

2013). The past eruptive story of Telica comprises at least ten important eruptions of vulcanian and strombolian styles since 1527, including the 1982 eruption that emitted a 3.7–4.3-km high column, from which ash fallout covered a distance of 37 km from the crater to the city of Corinto (Novák and Přichystal 2006). Currently, small explosive events are expected to take place every 1–5 years (Rodgers et al. 2013). For the past 5 years, SO_2 emissions have remained rather low, ranging between 70 and 200 t day^{-1}. This degassing rate has remained steady even during the last eruptive event, in May 2011 (Smithsonian-Institution 2011).

Measurements and methods

SO_2 flux measurements

Sulphur dioxide measurements were made by using NOVAC scan-DOAS instruments. This instrument acquires spectra which radiation source is UV-scattered sunlight in a vertical plane of 180° from one horizon to the other in angular steps of 3.6°. The spectra acquisition implemented by the NOVAC instrument consists of a motor-driven mirror or prism that redirects the scattered light from the sky collected through a telescope defining a field of view (FOV) of 8 mrad. From the telescope, light is redirected to a spectrometer (Ocean Optics®, S2000) by an optical fibre. More details about the NOVAC instruments can be found in Galle et al. (2010).

The instrument runs during daylight hours, adding 15 spectra in each step, and therefore improving the signal-to-noise ratio. The exposure time is automatically adjusted in order to avoid light saturation in the spectrometer detector. In view of the variable local weather conditions, this exposure adjustment is made every time a new scan measurement starts. Under clear sky conditions, a scan can be completed in <3 min. The SO_2 column amount was retrieved from the spectra for each angular step, applying DOAS (Platt and Stutz 2008). The spectra was evaluated in the wavelength region of 310–322 nm, which is less sensitive to scattering and stray light (Johansson 2009; Galle et al. 2010). The plume elevation, speed and direction are needed to determine the SO_2 flux. The SO_2 flux was obtained by multiplying the integrated gas columns by the plume (wind) speed.

At Turrialba, two NOVAC instruments were installed in the west flank of the volcanic edifice according to the predominant easterly wind direction, at a radial distance of about 2.3 km from the crater and a mean altitude of 2,600 m.a.s.l (Fig. 1). Similarly, a temporary installation of three NOVAC instruments was made at Telica, near a locality called Cristo Rey; this site is located at a radial distance of 6 km from the crater on the west side of the volcanic edifice and a mean altitude of 250 m.a.s.l. Plume direction and plume height were determined by triangulation, using the direction to the plume centre as simultaneously recorded by two instruments.

At Turrialba, during 18 and 19 March, plume speed was measured using an additional Dual-beam DOAS

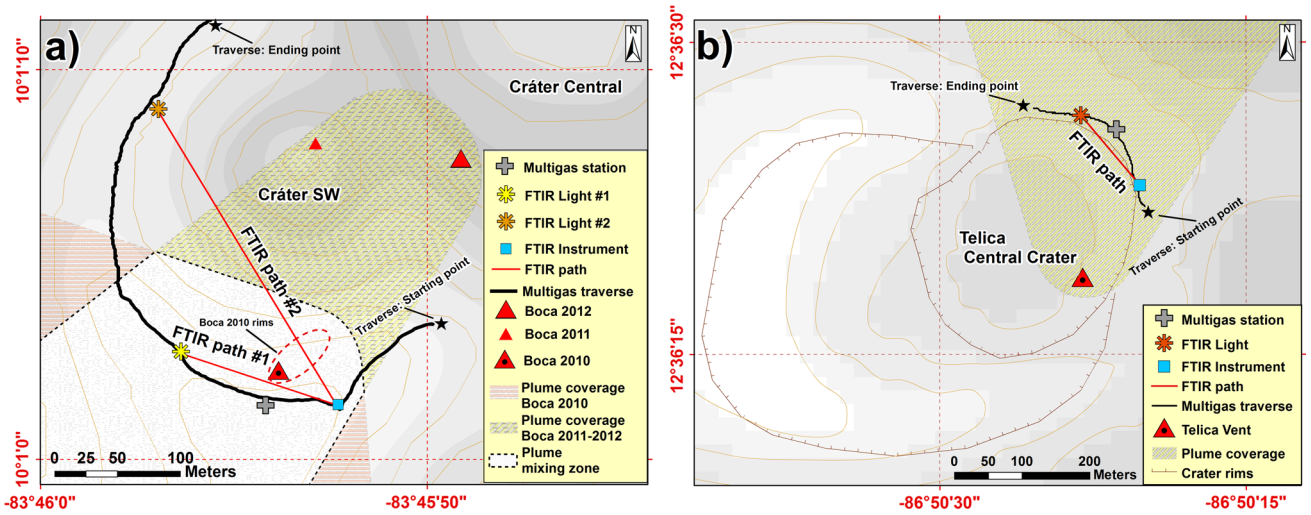

Fig. 2 Map of the area showing the spatial distributions of the volcanic plume, the location of the FTIR, the light sources and the stationary Multi-GAS stations. **a** Turrialba volcano. **b** Telica volcano

instrument located under the plume at a distance of about 3 km from the crater. This instrument measures simultaneously and with high time resolution the total column of SO_2 in the centre of the plume in a direction upwind and downwind. By correlating the time series, the time lag between different features in the plume can be determined and a plume speed can be derived. The method is described in detail in Johansson et al. (2009). The average plume speed was determined to be 5.3 and 5.9 m/s for 18 and 19 March, respectively, while for 17 March, the average of the two previous days, 5.6 m/s, was used. The plume direction and height averaged 260° and 3,340 m.a.s.l., respectively. At Telica, the plume speed was obtained from a meteorological station located on top of Telica, about 500 m east of the crater, and averaged 3 m/s. Although the plume at Telica typically hit the north wall of the crater rim, it was then typically dispersed further to the west, following the predominant wind direction, which during our field work averaged 268° with a height of 1,150 m.a.s.l.

FTIR measurements

FTIR allows to measure the columns of volcanic gas species that have spectral signatures in the infrared region (e.g. CO_2, SO_2, HCl, HF, CO, COS and H_2O). However, this study will be confined only to CO_2 and SO_2, since they can also be measured in parallel with a Multi-GAS instrument. The OP-FTIR measurements were made in the south-west sector of the crater of Turrialba from 17 to 19 March 2013, and north-east sector of Telica on the afternoon of 23 March 2013 using a FTIR spectrometer manufactured by Bruker, which has a Peltier cooled MCT detector and a ZnSe beam splitter. Spectra were collected in the range of 1,850–5,000 cm^{-1} with a resolution of 0.5 cm^{-1}. The spectrometer is equipped with an electric cooler, which avoids the difficulties of cooling down the detector by using liquid nitrogen. In order to reduce the signal-to-noise ratio, 16–64 spectra were averaged for every individual measurement, yielding a time resolution between 75 s and 5 min. An incandescent lamp stabilized with a DC/DC converter placed across the crater provided the source of artificial infrared radiation.

At Turrialba, the lamp was placed at two different positions, leading to two different light paths: path 1 and path 2, with lengths of 136 and 275 m, respectively (Fig. 2a). Each light path assesses the contribution of the main vents (Boca 2010 and the pair Boca 2011 and Boca 2012) to the total volcanic plume composition as shown in Fig. 3b. At Telica, the plume has a single origin; thus, the lamp remained fixed during the period of measurements (Fig. 2b).

The spectra were recorded in a portable computer and later evaluated using the software MALT (Multiple Atmospheric Layer Transmission) (Griffith 1996), which retrieves gas concentrations by implementing a nonlinear least square (NLLS) fitting of the measured spectra with a modelled synthetic spectrum retrieved from the molecular spectroscopy database HITRAN (Rothman et al. 2009), jointly with the estimated values of the atmospheric pressure and plume temperature. These last two parameters were obtained from the Multi-GAS instruments as explained in the following section. Different spectral regions were selected in order to retrieve the gas species: 2,100–2,248 cm^{-1} for CO_2 and 2,470–2,535 cm^{-1} for SO_2. In addition, other ambient species, N_2O, CO and H_2O, were included in the NLLS fitting.

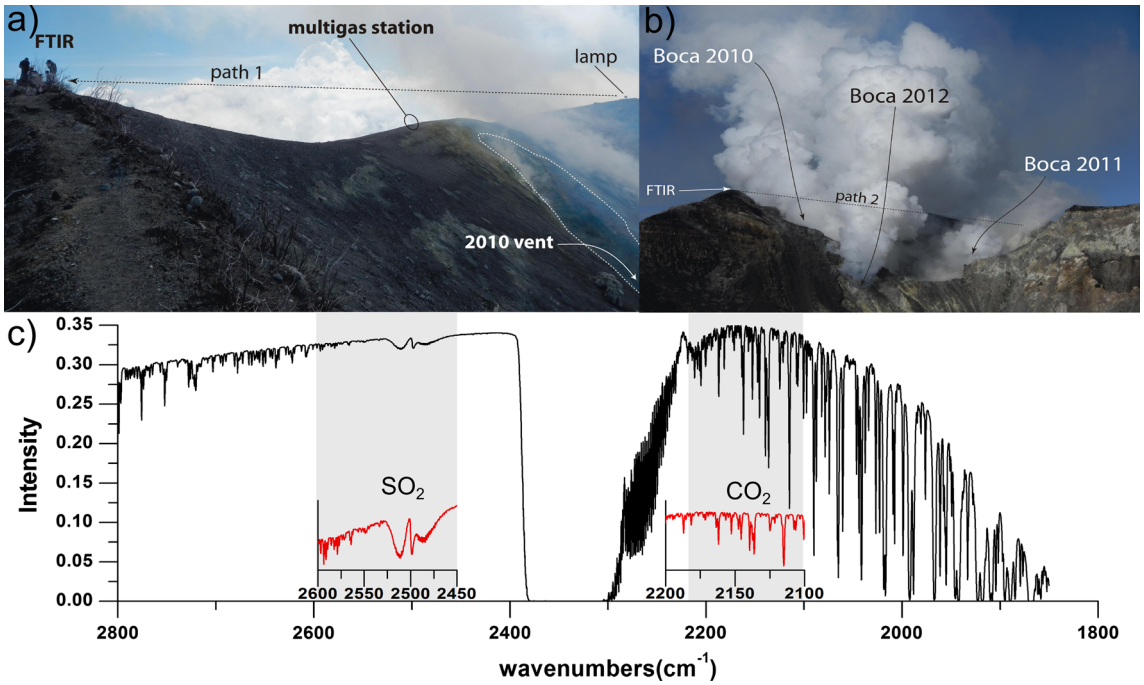

Fig. 3 Measurements at Turrialba and Telica volcano. **a** Location of the FTIR, incandescent lamp (path 1) and Multi-GAS at Turrialba. **b** Path 2 of Turrialba, through the main vents (Boca 2010, Boca 2011 and Boca 2012). **c** Example of a FTIR spectrum measured at Telica volcano on 23 March 2013

Due to the relatively short distance of the light paths and fairly high intensity of the incandescent light, good quality spectra were acquired at both volcanoes, for example the spectrum shown in Fig. 3c. Spectra with zero-base offset around the line 2,350 cm^{-1} and/or strong attenuation due to the occasional heavy condensation were discarded; however, only 20 % of the total spectra were considered to be of bad quality. The continuous background spectrum was modelled by using a fourth-order polynomial both for CO_2 and SO_2.

In addition to the gas concentration retrieval, the spectrum analysis also reports an evaluation fitting error; however, it has been demonstrated that the reported error largely underestimates actual measurement errors (Smith et al. 2011). Independent studies quantifying the error budget of the gas concentration retrievals have estimated that for a SO_2 concentration of 250 ppm, the choice of the background polynomial and inaccuracies in the instrumental line shape account for an uncertainty of 1.2 and 1.5 %, respectively (Horrocks et al. 2001). Similarly, Smith et al. (2011) estimated that for a CO_2 concentration of 280 ppm, the choice of the polynomial and FOV variations of the instrument account for an uncertainty of 1.7 and 5.2 %, respectively. All these uncertainties can be critical when measuring absolute gas columns/concentrations, while for measuring ratios between two gases, these uncertainties tend to cancel out and become less significant. Nevertheless, in a typical field situation with variable ambient conditions, the measured ratios may be significantly affected by an incorrect assumption of the plume temperature and pressure.

Multi-GAS measurement

The concentrations of major volcanic gas species (H_2O, CO_2, SO_2, H_2S) were also characterized using a multi-component gas analyser system (Multi-GAS) (Aiuppa et al. 2005, 2007; Shinohara 2005). A fully automated Multi-GAS instrument, developed at the Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Palermo, was temporarily deployed from 17 to 19 March 2013 at a fixed site on the southern rim of the active west crater of Turrialba, about 10 m south-west from Boca 2010. A similar deployment was made on the north rim of the active crater of Telica on March 23 and during the period from March 27 to April 8.

The instrument integrates an infrared spectrometer for CO_2 measurement (Gascard II, calibration range 0–3,000 ppmv; accuracy ±2 %; resolution, 0.8 ppmv), along with specific electrochemical sensors for the measurement of SO_2 (CityTechnology, sensor type 3ST/F; calibration range, 0–200 ppmv; accuracy, ±5 %; resolution, 0.1 ppmv) and H_2S (SensoriC, sensor type 2E; calibration range, 0–200 ppmv; accuracy, ±5 %; resolution,

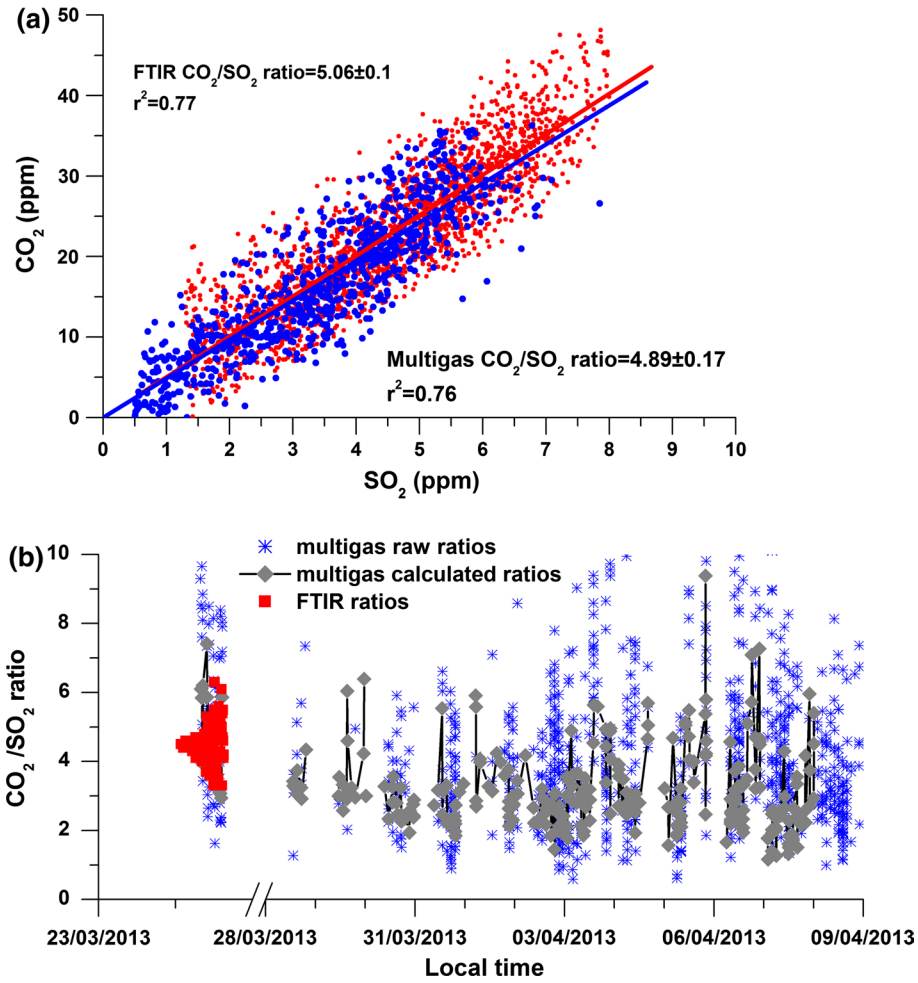

Fig. 4 Scatter plots of the CO_2/SO_2 ratios measured by FTIR (*red*) and Multi-GAS (*blue*) at Telica. The CO_2 concentration background has been removed from both data sets. **a** FTIR and Multi-GAS measurements on March 23 (13:00–19:00, local time). **b** CO_2/SO_2 ratio measured by Multi-GAS (*blue* and *grey dots*) and FTIR (*red dots*) on 23 March and from 17 March to 8 April 2013

0.1 ppmv). H_2O concentrations were also calculated from records of temperature and relative humidity (Galltec sensor; measuring range, 0–100 % Rh; accuracy, ±2 %), using a time-average pressure of 670 mBar at Turrialba and 912 mbar at Telica.

The Multi-GAS was set to perform measurements during sampling periods of 30 min to 2 h. During each measurement, the plume gas was steadily pumped into the sensor's housing and a data-logger board captured the output signals from the sensors at a rate of 0.1 Hz. The Multi-GAS was powered by a 12-V lead battery connected to a photovoltaic module, and the main box with sensors was protected inside a waterproof wallet (30 × 20 × 15 cm). At the end of each cycle, the data are automatically transferred via a radio link from the remote Multi-GAS to a temporary base station on the flank of the volcano.

In addition to the static measurements, a small, compact, portable version of the Multi-GAS instrument was used to perform sequences of walking transects around the outer rim of the western Turrialba Crater. During the walking traverses, the inlet tube of the Multi-GAS was kept 50 cm from the ground to capture plume gas while avoiding any soil contribution. In total, 12 traverses were done between March 9 and 19.

The acquired concentration data (from both fixed and portable Multi-GAS instruments) were processed using custom-made Ratiocalc software (Tamburello 2013), which automatically runs the retrieval methodology described in Aiuppa et al. (2005, 2006, 2009). Air-background-corrected concentrations were first calculated by subtracting ambient air concentrations of ~25,000 ppmv for H_2O and ~390 ppmv CO_2 from the raw data. Any temperature-dependent sensors' baseline drift was also removed by simple baseline fitting with polynomial functions. These corrected data were then used to derive gas–gas scatter plots and finally to derive CO_2/SO_2 molar ratios in the plume by taking the gradient of the best-fit regression lines (e.g. Fig. 4a). To explore the time variability of plume compositions, a number of such scatter plots were sequentially created by Ratiocalc (by scanning the available data set), each from data acquired during individual time windows of a few minutes. A time series for such "time-averaged" CO_2/SO_2 gas ratios is shown in Figs. 4e and 6b. Measurement intervals were discarded (e.g. no

ratio was calculated) when CO_2 and SO_2 concentrations were below fixed threshold values (e.g. air-corrected $CO_2 < 300$ ppmv; $SO_2 < 3$ ppmv). In such diluted plumes, the error in gas ratios has been observed to be larger than the error typically (±20 %) obtained in denser plumes (Aiuppa et al. 2006, 2009). The short-term (0.1 Hz) variability of CO_2/SO_2 ratios was also explored by calculating the point-to-point ratio between simultaneously measured CO_2 and SO_2 concentrations (e.g. Métrich et al. 2011). While the error in such higher frequency measurements can be as high as 20 %, we still observe an overall good match between point-to-point and time-averaged results (e.g. Figs. 4e, 6b). Overall, the instrument acquired a total of 12.5 h of observations, in ~20 % of which the plume was dense enough at the measurement site to allow accurate retrieval of plume composition.

Results

Comparison of CO_2/SO_2 ratio between Multi-GAS and FTIR at Telica

The simultaneous CO_2/SO_2 measurements made with FTIR and Multi-GAS at Telica are shown in the scatter plot of Fig. 4a. Both data sets exhibit linear trends that can be modelled as a simple regression line:

$$Y_k = rX_k + b \tag{1}$$

where the pair X_k and Y_k correspond to the fitted SO_2–CO_2 data points, while r and b correspond to the concentration ratio and the background CO_2 concentration, respectively.

In order to quantify the alikeness between FTIR and Multi-GAS, it is necessary to calculate independently their concentration ratios while taking into account their most significant uncertainties, which normally can be made with a simple least-squares line fitting. However, SO_2 and CO_2 measurements contain independent uncertainties; thus, fitting a line is not straightforward. Although several methods have been proposed to deal with this problem (e.g. Deming 1943; Reed 1989; Pearson 1901; York et al. 2004), the approach considered in this study is the one formulated by Deming (1943), as shown in Eq. (2):

$$S^2 = \sum_{k=1}^{N} \left[\left(\frac{x_k - X_k}{\sigma_{xk}} \right)^2 + \left(\frac{y_k - Y_k}{\sigma_{yk}} \right)^2 \right] \tag{2}$$

Equation (2) assumes that the best fitted lines X_k and Y_k (Eq. 1) are those minimizing the sum of the orthogonal distances (S^2) of the N pairs of SO_2–CO_2 (x_k and y_k) measurements with their respective uncertainties σ_{xk} and σ_{yk}.

The main source of FTIR retrieval uncertainties is the inability to obtain accurate values of atmospheric pressure and temperature for each spectrum. However, during the measurement period at Telica, the pressure was rather invariable with an average of 914 ± 1.5 mbar; thus, its contribution to the measurements' uncertainties can be assumed to be negligible (Smith et al. 2011; Horrocks et al. 2001). On the other hand, it was estimated that plume temperature ranged more widely (21–25 °C) and was, therefore, the predominant source of uncertainties in the gas concentration retrievals.

In Eq. (2), x_k and y_k correspond to the retrieved CO_2 and SO_2 concentrations assuming the mean temperature value (23 °C). Their uncertainties σ_{xk} and σ_{yk} were constrained by repeatedly retrieving the concentrations, assuming temperatures varying in the 21–25 °C range in steps of 1 °C, and further calculating the standard deviation:

$$\sigma(x_{23}) = \sigma_k(x_{23}) = \sqrt{\frac{\sum_{k=1}^{N} \sum_{T=\mathrm{ti}}^{\mathrm{tf}} \left(x_{23,k} - x_{T,k} \right)^2}{N(\mathrm{tf} - \mathrm{ti} + 1) - 1}} \tag{3}$$

whereas $x_{T,k}$ is the kth gas concentration data point assuming a temperature T; ti and tf are the limits of the considered temperature range (21–25 °C). Hence, σ_{xk} and σ_{yk} are estimated to be ±0.05 and ±4.65 ppm for SO_2 and CO_2, respectively. At first glance, these values appear to be of minor importance; nevertheless, their contribution to the uncertainty of the concentration ratios is significant, as will be further discussed.

The chosen procedure for minimizing Eq. (2) is based on a weighted total least-squares (WTLS) algorithm, which has been proved to be robust, and considers the orthogonal distance between the fitting line and the data points, by taking into account the reciprocal of the uncertainties as a "weight" (Krystek and Anton 2008). Hence, the estimated FTIR CO_2/SO_2 ratio (r_F) is 5.06, with a standard deviation (σ_F) of 0.1.

A similar procedure was followed in order to obtain the Multi-GAS parameters, but in this case, the main source of uncertainties σ_{xk} and σ_{yk} are linked to the sensors' accuracy, which, as described in the previous section, is proportional to the individual measured concentrations by a fraction of 2 % for CO_2 and 5 % for SO_2. From Eq. (2) and applying a WTLS fitting to the measurements and its uncertainties, the estimated Multi-GAS concentration ratio (r_M) is 4.89, with a standard deviation (σ_M) of 0.17.

Finally, the alikeness between FTIR and Multi-GAS ratios is statistically tested by measuring the 95 % confidence interval (CI) of the difference of both ratios relative to the Multi-GAS ratio:

$$\mathrm{CI}\,[\%] = \frac{(r_F - r_M) \pm t_{\alpha/2} \sqrt{\sigma_F^2 + \sigma_M^2}}{r_M} \times 100 \tag{4}$$

whereas $t_{\alpha/2}$ (1.96) is the 95 % T.

Table 1 Comparison of the CO_2/SO_2 ratio obtained by FTIR and Multi-GAS at Telica

Measurement period	Technique	CO_2/SO_2 ratio	R^2	95 % confidence interval (CI) of the ratio differences (%)
23 March 2013, 12:30–19:30	FTIR	5.06 ± 0.1	0.77	−4.11
	Multi-GAS	4.89 ± 0.17	0.76	

The CI of the measurements at Telica (Table 1) has an overlap of −4 to 11 %, which indicates that both ratios are statistically equivalent, with a typical discrepancy between Multi-GAS and FTIR of a factor ~3.5 %. Considering the scatter plot of the simultaneous measurements (Fig. 4a), the statistical alikeness between both techniques was expected.

Comparison of CO_2/SO_2 ratio between Multi-GAS and FTIR at Turrialba

The simultaneous measurements of CO_2/SO_2 ratios made with Multi-GAS and FTIR through the path 1 (March 17, 18) at Turrialba are shown in the scatter plot of Fig. 5a, b. The atmospheric pressure did not vary during the two measurement periods (664 ± 2 and 680 ± 4 mbar), while temperature, which ranged 30–40 °C with a mean value of 35 °C, remained as the main source of uncertainties. The alikeness between both techniques was quantified by applying the same procedure described in the previous section. From Eq. (2), x_k and y_k correspond to the SO_2 and CO_2 concentrations measured either with FTIR or Multi-GAS. For FTIR, the concentrations were retrieved by assuming the mean temperature value (35 °C), while their uncertainties (σ_{xk} and σ_{yk}) were calculated as shown on Eq. (3), with ti = 30 and tf = 40. On March 17, the estimated σ_{xk} and σ_{yk} are ±1.107 and ±8.72 ppm, respectively, while on March 18, σ_{xk} and σ_{yk} are ±1.35 and ±8.54 ppm, respectively. For Multi-Gas, the uncertainties were calculated based on the accuracy of the sensors (2 % for CO_2 and 5 % for SO_2). The concentration ratios and their standard deviations both for FTIR and Multi-GAS were calculated by applying WTLS fitting, yielding the results shown in Table 2.

From Eq. (4), the 95 % CI of the difference between the ratios on March 17 ranges between 20 and 30 %. On March 18, the 95 % CI of the difference between the ratios is found to be between 11 and 16 %. The results of these statistical tests suggest that in comparison with the general agreements observed at Telica volcano, the Multi-GAS and FTIR measurements at Turrialba differ by factors of 25 and 13 %, respectively.

The FTIR measurements through the path 2, corresponding to the secondary vents (Boca 2011 and 2012), were made on the afternoon of March 18 and the morning of March 19. The estimated CO_2/SO_2 ratios are 1.19 and 1.11 (Fig. 5c, d), which are approximately half of the ratio measured through path 1. The systematically lower ratios at Boca 2011 and Boca 2012, relative to the bulk plume (essentially contributed by Boca 2010; see Fig. 5), demonstrate a chemical vent-to-vent heterogeneity of gas emissions at Turrialba. This vent-to-vent variability likely reflects different vent temperatures, which were ~800 °C (Boca 2012) and ~400 °C (Boca 2010) during our survey (OVSICORI-UNA 2013). High temperatures at Boca 2012 likely resulted in larger extents of sulphur(S) remobilization (and consequently, in lower CO_2/SO_2 ratios).

SO_2 emissions

By the time of our measurements, NOVAC instruments measured the average SO_2 flux from Turrialba to be 840 ± 120 t day^{-1}, as shown in Fig. 6a and Table 3. These results are within the range of variability of the SO_2 flux since 2012 (OVSICORI-UNA 2012). Similarly, the SO_2 flux from Telica averaged 64 ± 34 t day^{-1}, within the range of typical values expected for this volcano (Smithsonian-Institution 2011).

Discussion

Our results are the first to our knowledge for the CO_2/SO_2 compositions of the volcanic plumes issuing from two persistently degassing volcanoes in Central America. Our inferred CO_2/SO_2 ratios for Telica and Turrialba (Tables 1, 2) compare well with the compositional signature of volcanic arc gases, the majority of which typically exhibit CO_2/SO_2 ratios in the 1–5 range (Hilton et al. 2002; Fischer et al. 2009). More specifically, our results are qualitatively consistent with the CO_2/SO_2 ratio of 2.7, proposed by Hilton et al. (2002) as representative of volcanic gas emissions in the Central American Volcanic Arc (CAVA). A slightly lower CO_2/SO_2 ratio (1–2.2) was proposed for CAVA by (Mather et al. 2006), which is still within the range of variation of our results.

Apart from adding a new piece to the puzzle of the still-growing database of volcanic gas emissions, our results pave the way to the first quantitative intercomparison between Multi-GAS- and FTIR-derived CO_2/SO_2 ratios, as detailed below.

CO_2/SO_2 ratios: FTIR and Multi-GAS matching

The statistically good match between CO_2/SO_2 ratios measured at Telica, as shown by the 95 % CI statistical test, results from favourable measuring conditions at this crater. At Telica, the plume is emitted by only one major vent

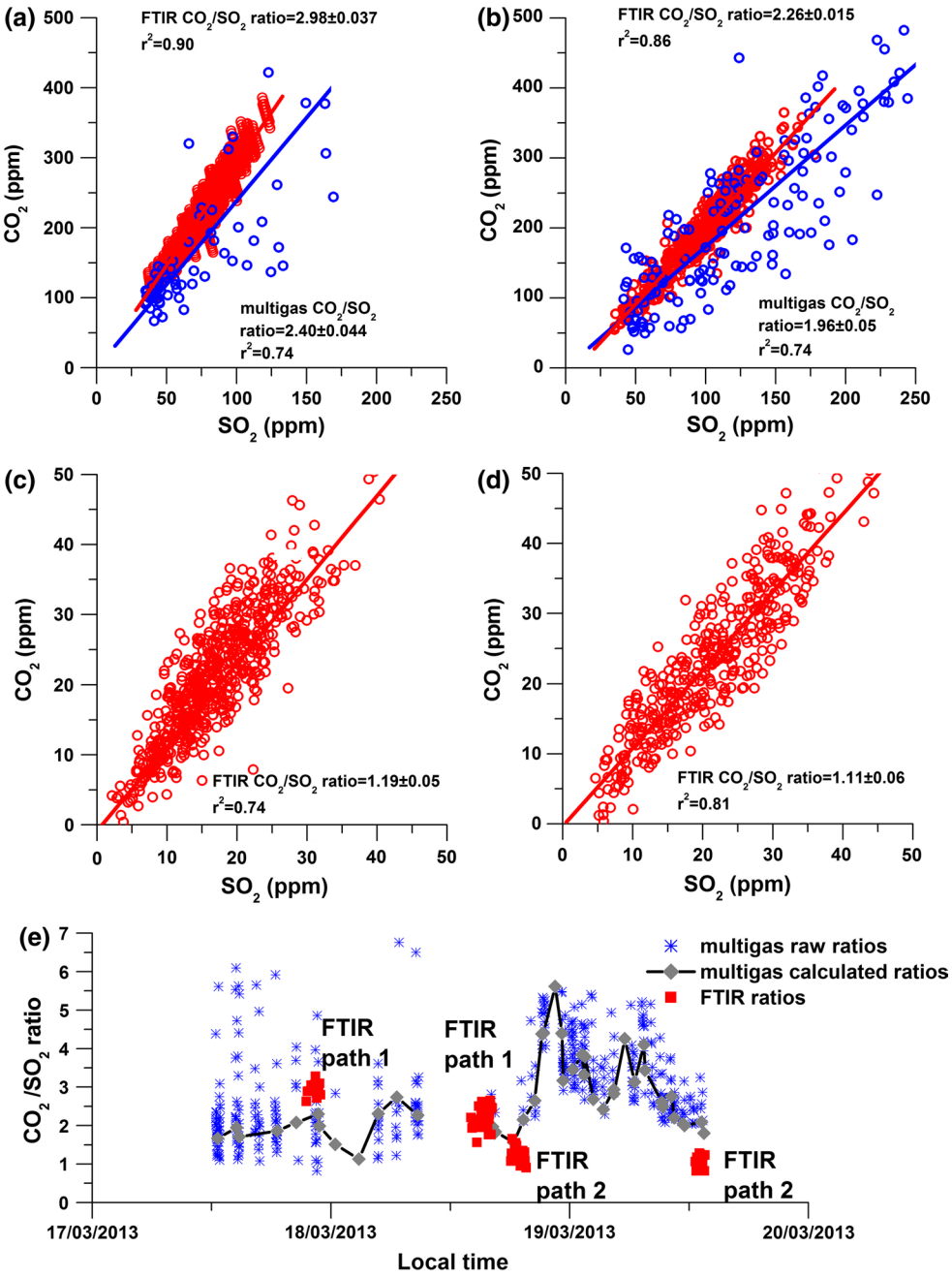

Fig. 5 Scatter plots of the CO_2/SO_2 ratios measured simultaneously by FTIR (*red*) and Multi-GAS (*blue*) at Turrialba in March 2013. The CO_2 concentration background has been removed from both data sets. **a** FTIR and Multi-GAS measurements through the vent Boca 2010 (path 1) on March 17 (21:30–23:00, local time). **b** FTIR and Multi-GAS measurements through the vent Boca 2010 (path 1) on March 18(14:30–16:00, local time). **c** FTIR measurements through the vents Boca 2011 and Boca 2012 (path 2) on March 18 (18:00–20:00, local time). **d** FTIR measurements through the vents Boca 2011 and Boca 2012 (path 2) on March 19 (12:30–13:30, local time). **e** CO_2/SO_2 ratio measured by Multi-GAS (*blue* and *grey*) and FTIR (*red*) during 17–19 March 2013. The measured FTIR ratios through path 2 are approximately half of the ratio measured through path 1

Table 2 Comparison of the CO_2/SO_2 ratio obtained by FTIR and Multi-GAS at Turrialba

Measurement period	Technique	CO_2/SO_2 ratio	R^2	95 % confidence interval (CI) of the ratio differences (%)
17 March 2013, 21:30–23:00	FTIR	2.98 ± 0.037	0.9	20.30
	Multi-GAS	2.40 ± 0.044	0.76	
18 March 2013, 14:30–16:00	FTIR	2.26 ± 0.015	0.86	11.16
	Multi-GAS	1.96 ± 0.05	0.74	

that is ≈120 m deep inside the crater. Because of transport through the atmosphere to the rim, the temperature of the plume was approximately the same as the ambient temperature, further supporting thorough mixing and homogeneity.

At Turrialba volcano, on the other hand, there is still reasonable correspondence of CO_2/SO_2 ratios observed by the two independent techniques, although to a lower degree than at Telica. The CO_2/SO_2 ratio measurements, made with the mobile Multi-GAS for traverses, indicate a distinct lateral heterogeneity of the Turrialba plume (Fig. 7). In all these traverses, made perpendicular to the plume transport

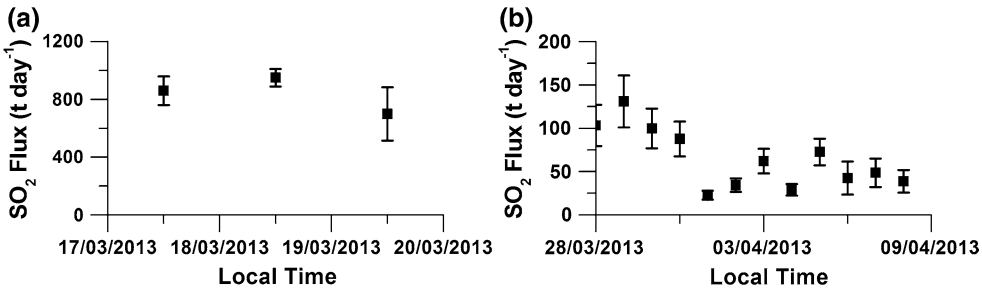

Fig. 6 Daily SO_2 emissions measured at Turrialba and Telica volcano by the NOVAC instruments. **a** Turrialba: 17–19 March 2013. **b** Telica: 27 March–8 April 2013. The error bar indicates the daily variability

Table 3 Daily average of SO_2 and CO_2 emissions at Turrialba during 17, 18 and 19 March

Day	Mean SO_2 flux (t day^{-1})	Standard deviation SO_2 flux (t day^{-1})	Mean CO_2 flux (t day^{-1})	Standard deviation CO_2 flux (t day^{-1})
17 March 2013	860	100	1,000	150
18 March 2013	950	60	1,350	150
19 March 2013	700	185	1,000	511

direction, the ratios are systematically higher (a factor of 10–40 %) in the centre of the plume than on its boundary. The variation of the ratio, observed along such relatively short distance (~10 m), is comparable to the differences estimated by the previous statistical tests. In the light of our FTIR results (Fig. 5), we suggest these deviations reflect gas contributions to the plume that come from three compositionally distinct sources (Boca 2010, Boca 2011 and Boca 2012). The FTIR measurements made through path 2 allow characterizing the gas contributions from Boca 2011 and Boca 2012 vents and indicate a CO_2/SO_2 ratio that is approximately half of the ratio measured through path 1. The CO_2-richer gas columns measured through path 1 instead are more likely to have their prevalent contribution from the Boca 2010 gas, due to the proximity of this vent to the south-west sector of the crater rim (≈25 m). In contrast, the boundaries of the plume are more likely to contain a mixed contribution of gas concentrations from the three vents, justifying the CO_2-poorer compositions observed during Multi-GAS traverses. The implication of these results is that a fixed Multi-GAS instrument is fairly sensitive to slight angular variations of the plume/wind direction, as can be observed by the broad dispersion of individual measurements in the time series and the scatter plots shown in Fig. 4.

CO_2 fluxes

Synchronized SO_2 flux and Multi-GAS measurements allowed monitoring of CO_2 flux emissions at Telica and Turrialba during our campaign. At Telica, these measurements were made continuously during a period of 13 days, and at Turrialba, for a period of 3 days (Figs. 4b, 5d). Combining the Multi-GAS CO_2/SO_2 ratios with the NOVAC-based SO_2 fluxes, the first estimates of CO_2 emission rates for Turrialba

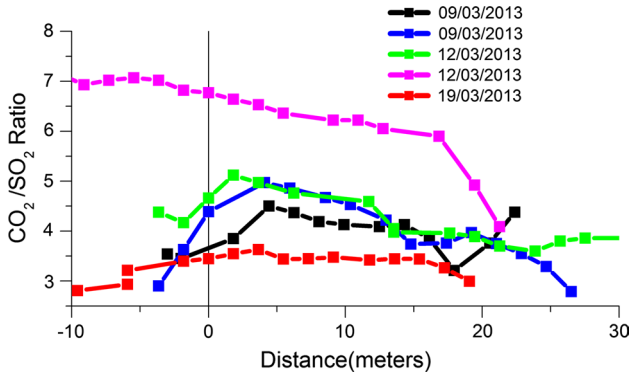

Fig. 7 Multi-GAS CO_2/SO_2 ratios measured by walking transects on the southern sector of the crater rim of Turrialba. The distance 0 is the reference point, where the walking transect was closest to the fixed Multi-GAS instrument

and Telica were derived, as shown in Fig. 8a, b, respectively. The averaged CO_2 emissions rates are 1116 ± 164 t day^{-1} for Turrialba and 166 ± 76 t day^{-1} for Telica.

When compared to the typical levels of CO_2 emissions from subaerial volcanoes, which range from 18 to 52,000 t day^{-1} (Burton et al. 2013), our derived CO_2 outputs can be ranked as moderate (Turrialba) to low (Telica). Our results indicate that along with Masaya volcano in Nicaragua (Burton et al. 2000; Martin et al. 2010), Turrialba is the strongest punctual source of volcanic CO_2 in the Costa Rica–Nicaragua segment of the CAVA.

Conclusions

The aim of this study was to determine CO_2 emissions from the volcanoes Turrialba and Telica and to compare CO_2/

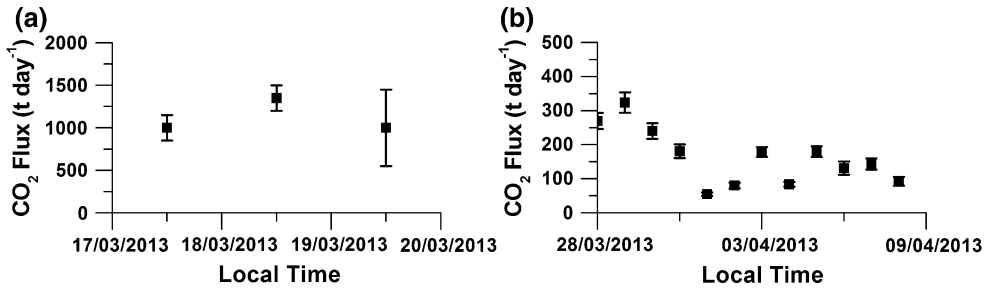

Fig. 8 Daily CO_2 emissions at Turrialba and Telica volcanoes, estimated by the product of the SO_2 flux with the calculated mass ratio measured by Multi-GAS. **a** Turrialba: 17–19 March 2013. **b** Telica: 27 March–8 April 2013. The error bar indicates the daily variability

SO_2 ratios obtained from two independent measurement techniques, FTIR and Multi-GAS, with a focus on their different spatial resolutions. The active OP-FTIR technique provides concentration averages across the entire plume, while the Multi-GAS instrument provides measurements from a fixed point in the plume. Telica volcano, with only one deep vent providing a well-mixed plume at the measurement site, represents an easy case of Multi-GAS–FTIR intercomparison. Results demonstrate a very good match between the two techniques, with the independently estimated CO_2/SO_2 ratios differing by only 3 %. This is within the calibration errors of the two methods. However, at Turrialba volcano, instead, the presence of 3 distinct active vents, for which there is FTIR evidence of CO_2/SO_2 ratio diversity, makes results of the intercomparison more difficult to interpret. The Multi-GAS instrument showed large fluctuations in the CO_2/SO_2 ratio over shorter time scales, while the FTIR showed a more constant ratio. This reflects the fact that the plume composition varied over its cross-section. Over time scales of several hours, the Multi-Gas ratio stabilized at a CO_2/SO_2 ratio 13–25 % lower than the FTIR average.

Our results show that for well-mixed plumes and single-vent emissions, the Multi-GAS instrument gives representative values of the CO_2/SO_2 ratio. For more complex cases, the method can still give representative results, but additional care should be taken in locating the instrument in the core of the plume and farther downwind from the vents (where the plume will be more mixed). Long-term deployments might also be required to obtain robust estimates of time-averaged CO_2/SO_2 ratios. Finally, this study demonstrates that CO_2/SO_2 ratios measured by the Multi-GAS instrument provide an acceptable representation of the bulk volcanic plumes' composition, and its combination with NOVAC instruments is a suitable strategy for measuring crateric CO_2 emissions at volcanoes with similar degassing styles. In the specific case of Turrialba and Telica, typical CO_2 emissions of 1,100 and 160 t day^{-1} are estimated, respectively, in the field studies reported here.

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