



Tunable diode laser measurements of hydrothermal/volcanic CO₂ and implications for the global CO₂ budget

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Abstract. Quantifying the CO₂ flux sustained by low-temperature fumarolic fields in hydrothermal/volcanic environments has remained a challenge, to date. Here, we explored the potential of a commercial infrared tunable laser unit for quantifying such fumarolic volcanic/hydrothermal CO₂ fluxes. Our field tests were conducted between April 2013 and March 2014 at Nea Kameni (Santorini, Greece), Hekla and Krýsuvík (Iceland) and Vulcano (Aeolian Islands, Italy). At these sites, the tunable laser was used to measure the path-integrated CO₂ mixing ratios along cross sections of the fumaroles' atmospheric plumes. By using a tomographic post-processing routine, we then obtained, for each manifestation, the contour maps of CO₂ mixing ratios in the plumes and, from their integration, the CO₂ fluxes. The calculated CO₂ fluxes range from low ($5.7 \pm 0.9 \text{ t d}^{-1}$; Krýsuvík) to moderate ($524 \pm 108 \text{ t d}^{-1}$; La Fossa crater, Vulcano). Overall, we suggest that the cumulative CO₂ contribution from weakly degassing volcanoes in the hydrothermal stage of activity may be significant at the global scale.

1 Introduction

The chemical composition of volcanic gas emissions can provide hints concerning the mechanisms of magma ascent, degassing and eruption (Allard et al., 2005; Burton et al., 2007; Oppenheimer et al., 2009, 2011), and can add useful information for interpreting the dynamics of fluid circulation at dormant volcanoes (Giggenbach, 1996; Chiodini et al., 2003, 2012).

Carbon dioxide (CO₂) is, after water vapour, the main constituent of volcanic (Giggenbach, 1996) and hydrothermal (Chiodini et al., 2005) gases, and has attracted the attention of volcanologists because it can contribute to tracking magma ascent prior to eruption (Aiuppa et al., 2007, 2010). The volcanic/hydrothermal CO₂ flux sustained by diffuse soil degassing can be measured relatively easily during surveys (Chiodini et al., 1996, 2005; Favara et al., 2001; Hernández, 2001; Cardellini et al., 2003; Inguaggiato et al., 2005, 2012; Pecoraino et al., 2005; Mazot et al., 2011) or with permanent installations (Brusca et al., 2004; Carapezza et al., 2004; Werner and Cardellini, 2006; Inguaggiato et al., 2011). In contrast, the volcanic CO₂ flux contributed by open vents and/or fumarolic fields is more difficult to measure, since the volcanic CO₂ gas signal is diluted – upon atmospheric transport – into the overwhelming background air CO₂ signal. Such volcanic CO₂ flux emissions have been quantified for only ~30 volcanic sources, based upon simultaneous measurement of SO₂ fluxes (via UV spectroscopy) and CO₂/SO₂ plume ratios (via direct sampling, Fourier transform infrared (FTIR) spectroscopy, or the Multi-GAS; see

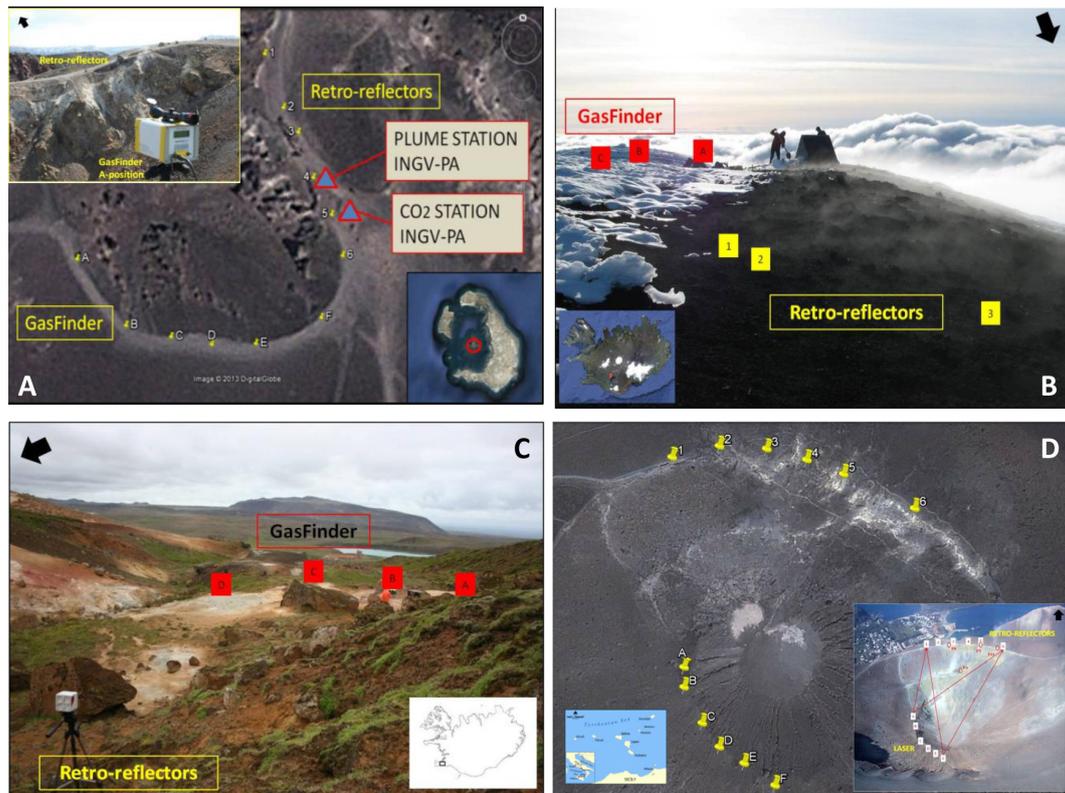


Figure 1. The study areas. (a) Nea Kameni summit crater (Greece), (b) Hekla summit (Iceland), (c) Krýsuvík hydrothermal field, and (d) La Fossa crater (Vulcano Island). In each picture, the positions of GasFinder and retro-reflectors are shown with letters and numbers, respectively.

Burton et al., 2013). This methodology is however not applicable to the countless number of quiescent volcanoes with low-temperature (SO₂-free) emissions (Aiuppa et al., 2013). As a consequence, the available data set of volcanic CO₂ fluxes is still incomplete, making estimates of the global volcanic CO₂ flux inaccurate (Burton et al., 2013).

In this paper, we discuss the use of tunable diode laser spectrometers (TDLs) for estimating volcanic/hydrothermal CO₂ fluxes from quiescent volcanoes. TDLs are increasingly used in air monitoring (Gianfrani et al., 1997a) and, more recently, for volcanic gas observations (Gianfrani et al., 1997b, 2000; De Natale et al., 1998; Richter, 2002). Pedone et al. (2014) recently reported on the first direct observation of the volcanic CO₂ flux from the fumaroles of the Campi Flegrei (the Phlegraean Fields, southern Italy), by using a portable tunable diode laser (TDL) system. Here we extend this previous work, discussing the results of TDL observations at four additional quiescent volcanoes: Nea Kameni (Santorini, Greece), Hekla and Krýsuvík (Iceland), and Vulcano Island (Aeolian Islands, Italy) (Fig. 1). We selected these volcanoes because they display a range of fumarolic activity from weak (Krýsuvík, Hekla) to moderate (Vulcano Island). While there is strong argument for the global volcanic CO₂ budget

being dominated by a relatively small number of strong emitters (Shinohara, 2013), weakly degassing volcanoes dominate – at least in number – the population of historically active volcanoes on Earth. This study contributes to better characterizing the typical levels of CO₂ emission from such feeble volcanic point sources.

2 Background

Santorini, the site of the famous Minoan eruption ~ 3600 yr ago (Druitt et al., 1999), is an island located in the Aegean Sea, part of the Cyclades Archipelago. Santorini has a surface of 75.8 km² and is presently made up of five islands (Thera, Therasia, Aspronisi, Palea Kameni and Nea Kameni) that constitute the active intra-caldera volcanic field (Dominey-Howes and Minos-Minopoulos, 2004). Four periods of unrest in the 20th century have culminated into small-scale eruptions in 1925–1926, 1928, 1939–1941 and 1950 (Fyticas et al., 1990). Outside the caldera, volcanic activity has been recorded in AD 1649–1650, in the Kolumbo submarine volcano (Vougioukalakis et al., 1994). Since the last eruption in 1950, the volcano has remained quiescent (Tsapanos et al., 1994; Papazakos et al., 2005; ISMOSAV, 2009). In early 2011, geodetic monitoring revealed a new

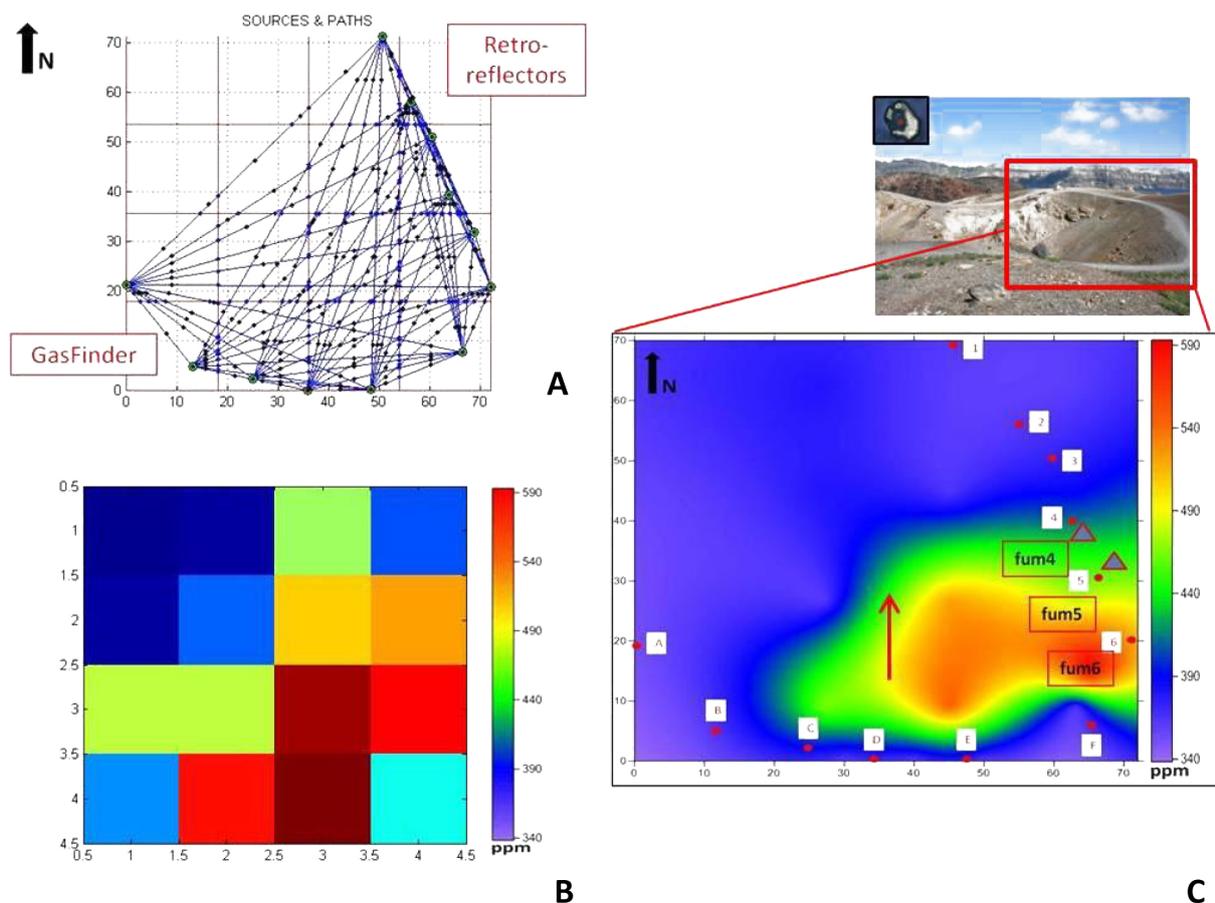


Figure 2. Output of the tomographic algorithm, and example for the Nea Kameni campaign, 9 April 2013 is shown. (a) Geometric reconstruction of the field experimental set-up and (b) tomographic matrix. The script uses a data inversion procedure to assign an averaged CO₂ mixing ratio (in ppm) to each cell of the matrix. (c) CO₂ mixing ratios (ppm) contour map. GasFinder and retro-reflectors positions are shown with letters and numbers, respectively. “Fum4”, “Fum5” and “Fum6” are the positions of main degassing vents; blue triangles are the permanent INGV-PA stations; the red arrow depicts the principal direction of plume dispersal.

stage of caldera-wide uplift (Newman et al., 2012; Parks et al., 2012), accompanied by swarms of shallow earthquakes. This unrest lasted from January 2011 to April 2012 (Parks et al., 2013). Degassing activity at Santorini is currently concentrated in a small, hydrothermally altered area on top of Nea Kameni islet (Parks et al., 2013), where a number of weakly fuming fumaroles (mostly CO₂, water vapour and air-derived gases; temperatures of 93–97 °C) are concentrated (Tassi et al., 2013). A recent survey carried out by Parks et al. (2013) indicated increased diffuse CO₂ emissions between September 2010 and January 2012; this period was characterized by a change in the degassing pattern, with an increase in soil CO₂ emissions peaking at $38 \pm 6 \text{ t d}^{-1}$ in January 2012 (Parks et al., 2013). Tassi et al. (2013) examined the response of fumarole composition to the 2011–2012 unrest, and reported increasing CO₂ concentrations (and decreasing $\delta^{13}\text{C-CO}_2$) from May 2011 to February 2012, suggesting increased mantle CO₂ contribution. During the survey on 9 April 2013, we investigated the central portion

of the soil CO₂ degassing structure identified by Parks et al. (2013), right on top of the most actively degassing Nea Kameni summit crater (Figs. 1a and 2).

Hekla is one of the most active volcanoes in Europe. Its historical volcanic activity, petrology and geochemistry of volcanic rocks have been the subject of several studies (e.g. Thorarinnsson, 1967; Sigmarsson, 1992). Hekla (63.98° N, 19.70° W; 1490 m a.s.l) is located in the southern part of Iceland at the intersection of the South Iceland Fracture Zone and the Eastern Volcanic Zone (Thordarsson and Larsen, 2007 and references therein). Five Plinian eruptions have been identified in the historical record, most recently in AD 1104 (Thorarinnsson, 1967; Larsen et al., 1999). In recent decades, Hekla has erupted frequently, at an average rate of one eruption per decade, and most recently in 2000 (Höskuldsson et al., 2007). Gas information has long remained missing, because Hekla appears to be only degassing during eruptions. Very recently, Ilyinskaya et al. (2014) identified a weakly degassing, warm ground on the summit of

Table 1. CO₂ fluxes (in t d^{-1}) and standard deviation (1σ) calculated in this study. The survey duration (in h), the number of CO₂ readings (with $R^2 > 0.95$), and the plume vertical transport speed (in m s^{-1}) are also given for each site.

Volcano	Date	Survey duration (h)	Number of readings	Gas speed (m s^{-1}) ($\pm 1 \sigma$)	CO ₂ flux (t d^{-1}) ($\pm 1 \sigma$)
Nea Kameni	9 April 2013	4	1070	1.20 ± 0.4	63 ± 22
Hekla	2 July 2013	1	985	1.00 ± 0.5	15 ± 7
Krýsuvík	5 July 2013	1.5	1150	1.17 ± 0.18	5.7 ± 0.9
Vulcano	11 March 2014	2	1757	1.00 ± 0.20	524 ± 108

the Hekla 1980–1981 crater (Fig. 1b), and studied the composition of this gas using data from a permanent Multi-GAS instrument and field campaigns using an accumulation chamber installed by INGV-PA (Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo) and IMO (Icelandic Meteorological Office) in 2012. These authors provided evidence for this gas spot being the only current surface manifestation at Hekla. This degassing field was therefore the site of our measurement survey with the TDL on 2 July 2013 (see Fig. 1b).

Krýsuvík (Fig. 1c) is one of five presently active geothermal areas on the Reykjanes Peninsula, in Iceland (Markússon and Stefansson, 2011). Geothermal activity at Krýsuvík includes hot grounds, steaming vents, steam-heated hot springs and mud pots, and pervasive surface alteration. The most important surface manifestations are confined to the Sveifluháls area, including Austurengjahver and the small areas of Seltún and Hveradalur (Markússon et al., 2011). On 5 July 2013, we performed TDL observations in Hveradalur ($63^{\circ}53$, $449'$ N, $22^{\circ}4$, $190'$ W; Fig. 1c). This area included two major fumarolic manifestations (indicated as “FumA” and “FumB” in our study. The fumarolic vent “FumA” is monitored by a permanent Multi-GAS instrument deployed in a joint monitoring program led by the British Geological Survey (BGS), INGV and IMO.

Vulcano is a volcanic island belonging to the Aeolian Islands in the southern Tyrrhenian Sea (Italy). Since the last eruption in 1888–1990, this closed-conduit volcanic system has been characterized by intense fumarolic activity concentrated on the summit of La Fossa crater (Fig. 1d), a small (391 m a.s.l.; 2 km in diameter) < 5 ka old pyroclastic cone. Degassing activity has shown signs of intensification in the last few decades, including increased fumarole temperatures (Badalamenti et al., 1991; Chiodini et al., 1995; Capasso et al., 1997), and episodic variations of gas/steam ratios (Chiodini et al., 1996; Capasso et al., 1999; Paonita et al., 2002, 2013). The CO₂ flux from the La Fossa fumarolic field has been measured previously by Aiuppa et al. (2005, 2006), McGonigle et al. (2008), Tamburello et al. (2011) and Inguaggiato et al. (2012). On 11 March 2014, we measured the CO₂ emissions from La Fossa using the measurement configuration of Fig. 1d.

3 Methods

The tunable diode laser spectroscopy technique (TDLS) relies on measuring the absorbance due to the absorption of IR radiation (at specific wavelengths) by a target gas. Like in previous work at Campi Flegrei (Pedone et al., 2014), we used a GasFinder 2.0 Tunable Diode Laser (produced by Boreal Laser Inc.), a transmitter/receiver unit that can measure CO₂ mixing ratios over linear open paths of up to 1 km distance, operating in the 1.3–1.7 μm wavelength range. Radiation emitted by the IR laser transmitter propagates to a gold plated retro-reflector mirror, where it is reflected back to the receiver and focused onto a photodiode detector. Incoming light is converted into an electrical waveform, and processed to determine in real-time the linear CO₂ column amount (in $\text{ppm} \times \text{m}$) along the optical path, using the procedure described in Tulip (1997). CO₂ column amounts are converted into average CO₂ mixing ratios (in ppm) along the path by knowledge of path lengths (measured with an IR manual telemeter, 1 m resolution). A portable meteorological station was continuously recording (frequency = 1 Hz) during the measurements to restrict post-processing to sampling intervals characterized by similar meteorological conditions. Instrumental accuracy is evaluated using a correlation coefficient (R^2), which is a measure of the similarity between the waveforms of the sample and reference signals. According to the manufacturer’s data sheets, an accuracy of $\pm 2\%$ is achieved for $R^2 > 0.95$ (Trottier et al., 2009).

In the field, the GasFinder was set to measure CO₂ mixing ratios at a 1 Hz rate (Pedone et al., 2014). Alignment between the laser unit and the retro-reflector mirror was optimized using a red visible aiming laser and a sighting scope. The size of the retro-reflector mirror was chosen as to adjust the returning light level to a desired value, depending on the path length and the expected amount of absorbed radiation.

4 Results and discussions

4.1 Field operations

The GasFinder operated for more than 10 h during the four field campaigns (more than 4 h at Nea Kameni on 9 April 2013; 1 h at Hekla on 2 July 2013; 1.5 h at

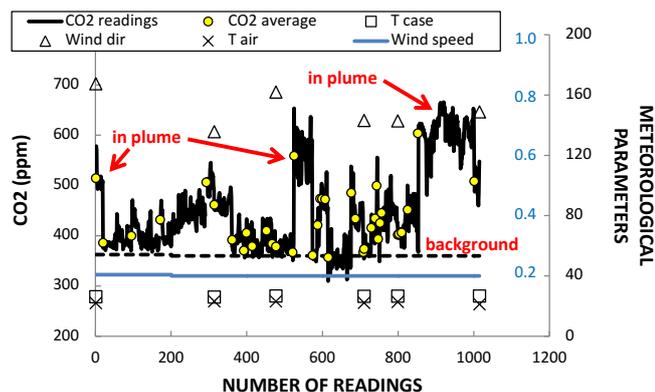


Figure 3. Time series of CO₂ mixing ratios (ppm) and meteorological conditions for the Nea Kameni example (~ 4 h of observations). The meteorological measurements were acquired from the INGV-type station temporarily installed on the summit crater (except wind speed, which was measured using a portable weather station). T case: temperature inside the station (°C); T air: outside air temperature (°C); Wind dir: wind direction (°N); Wind Speed: average wind speed (0.2 m s^{-1} , blue line) during field operation; dashed black line: CO₂ background average. CO₂ measurements at plume margins, oscillating close to the background values, are plotted. In-plume cross sections (CO₂ mixing ratios peaking at ~ 600 ppm) are shown. CO₂ average values (ppm) for each laser-mirror path are also given. The right vertical axis refers to the meteorological parameters (blue units, range of 0–1, for the wind speed; black units, range of 0–200, for the air and case temperature, and wind direction).

Krýsuvík on 5 July 2013; and more than 2 h at Vulcano on 11 March 2014, Table 1). Measuring at 1 Hz, the GasFinder acquired more than 9000 readings of path-integrated CO₂ mixing ratios. However, we concentrate here onto a subset of data (1070 readings for Nea Kameni; 985 readings for Hekla; 1150 readings for Krýsuvík; and 1757 for Vulcano Island, Table 1), extracted from the original data set based on data quality criteria (the same described in Pedone et al., 2014): we selected readings characterized by high accuracy (R^2 values > 0.95, optimal light values), and taken during phases of stable wind direction and speed.

The environmental parameters were monitored using a portable weather station, equipped with a data logger, that was temporarily installed in each of the survey sites. As an example, Fig. 3 shows time series of CO₂ mixing ratios (acquired by the TDL) and ambient parameters (air temperature, temperature inside the station, and wind speed/direction) recorded by the meteorological station, during 4 h of acquisition at Nea Kameni (Fig. 3, Table 1). Wind was nearly absent and stable (mean speed, $\sim 0.2 \text{ m s}^{-1}$; blue line in Fig. 3) during the time covered by TDL observations, making conditions ideal for TDL operations (especially for accurate quantification of plume transport speed; see below). Northern trending winds prevailed during the field campaign at Nea Kameni (red arrow in Fig. 2); southern trending winds

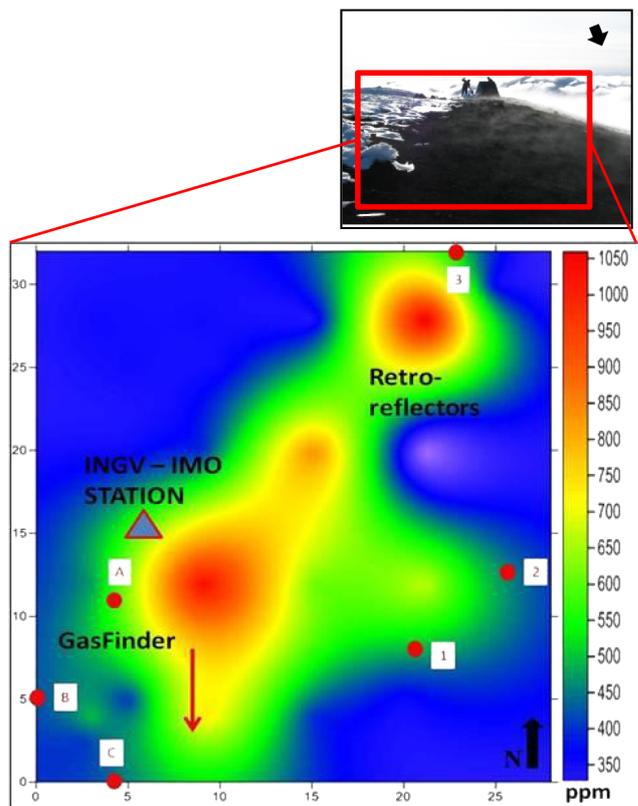


Figure 4. Contour map of CO₂ mixing ratios (ppm), Hekla campaign of 2 July 2013. GasFinder and retro-reflector positions are shown with letters and numbers, respectively. Blue triangle: INGV-PA/IMO station; red arrow: principal direction of plume dispersal.

at Hekla (red arrow in Fig. 4); and north-western trending winds at both Krýsuvík (red arrows in Fig. 5) and La Fossa crater at Vulcano Island (red arrow in Fig. 6).

Figure 1 shows the GasFinder operational field set-up at the four volcanoes. In each picture, the GasFinder unit positions are expressed by letters; while retro-reflectors positions are expressed by numbers (Fig. 1). During each campaign, and at each of the degassing areas, the position of the GasFinder unit was sequentially moved (e.g. from positions A to F in Fig. 1a) so as to scan the plume from different viewing directions and angles. We acquired along each single GasFinder–retro-reflector path (e.g. path A-1 in Fig. 1a) for ~ 4–5 min, before rotating the instrument head to measure along the subsequent path (e.g. A-2). The number of operated paths ranged from 9 (Hekla) to 36 (Nea Kameni and Vulcano), and the entire measurement grid (i.e. the total number of possible GasFinder–retro-reflector paths) was covered in a few h at most.

4.2 CO₂ mixing ratios and plume transport speed

The highest CO₂ mixing ratios (~ 1050 ppm) were measured at Hekla (Fig. 4), while the lowest mixing ratios values were

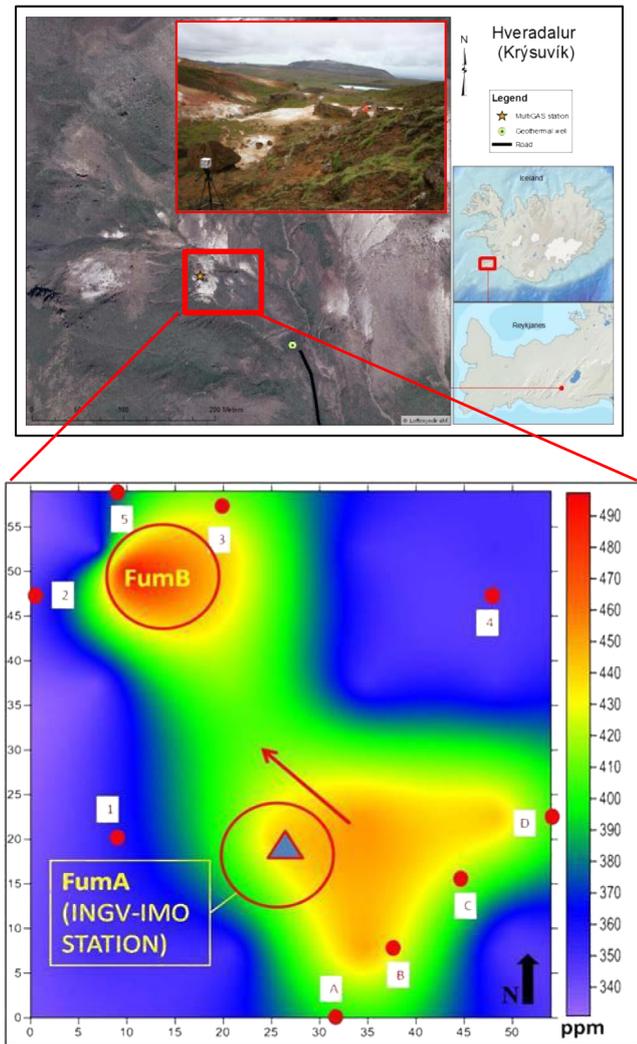


Figure 5. CO₂ Contour map of CO₂ mixing ratios (ppm), Krýsuvík campaign of 5 July 2013. GasFinder and retro-reflectors positions are shown with letters and numbers, respectively. “FumA” and “FumB”: positions of main degassing vents; blue triangle: INGV-PA/IMO station; red arrow: principal direction of plume dispersal.

detected at Nea Kameni and Krýsuvík (peaking at 590 ppm and < 500 ppm, respectively, see Figs. 2 and 5). Intermediate CO₂ mixing ratios (~ 900 ppm) were detected at La Fossa crater at Vulcano Island (Fig. 6), reflecting gas contributions from fumarolic vents located on the rim and in the inner wall of the crater.

Background readings were obtained in each of the measurement sites by pointing the laser beam toward a mirror, positioned upwind of the fumarolic area (Pedone et al., 2014). Background values of < 400 ppm were observed in all the analysed areas (Figs. 2–6).

During each campaign, the vertical plume transport speed was measured by a video camera pointing toward the fumarolic vents, and acquiring sequences of images of each

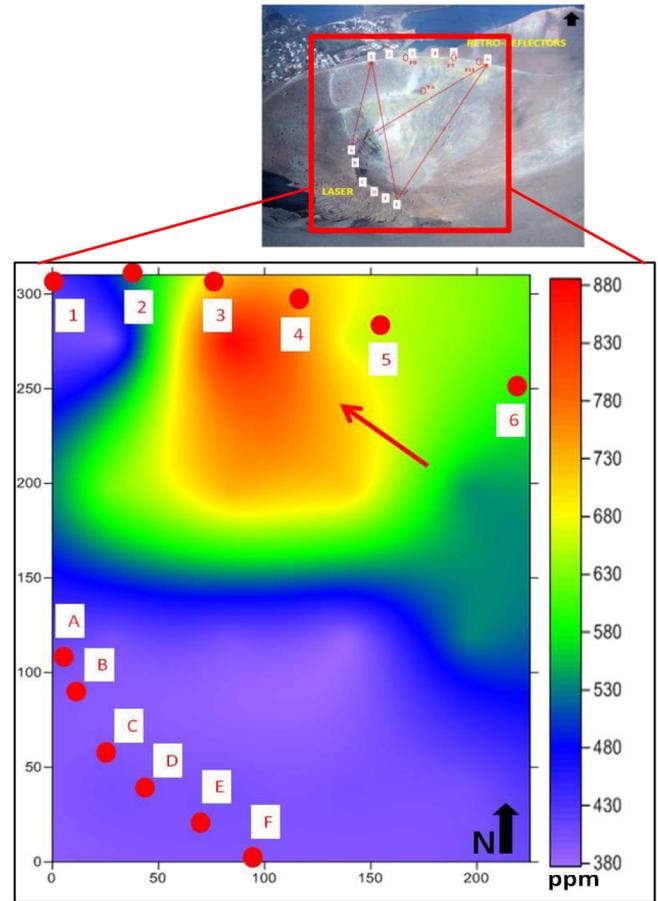


Figure 6. Contour map of CO₂ mixing ratios (ppm), La Fossa campaign, Vulcano Island, 11 March 2014. GasFinder and retro-reflectors positions are shown with letters and numbers, respectively. Red arrow: principal direction of plume dispersal.

visible rising plume at 25 frames per second (see Aiuppa et al., 2013; Pedone et al., 2014). The sequences of frames were later post-processed to calculate the time-averaged plume transport speed, after converting camera pixels into distances (using a graduated pole, positioned close to the vent). Plume transport vertical speeds are reported in Table 1, and converge at 1–1.2 m s⁻¹ at all volcanoes.

4.3 Contouring of in-plume CO₂ mixing ratios

At each of the four volcanoes, we combined the available set of path-integrated mixing ratio data to derive a two-dimensional reconstruction of CO₂ distribution (in ppm) in the plume cross section, between the GasFinder position(s) and the retro-reflectors.

In order to achieve this, we used a Matlab script (released by the authors, and available on request; see Pedone et al., 2014 for more details), to (i) create a matrix containing information on the geometry of the experimental setup (an example is given in Fig. 2 for Nea Kameni) and (ii) use this matrix

to obtain a bi-dimensional reconstruction of CO₂ concentrations in a cross section of the atmospheric plumes, starting from the raw GasFinder data set. In order to start the calculations, the Matlab script was initialized with the coordinates of the laser and retro-reflectors positions. The additional input data was a column vector, containing the mean CO₂ column amount (in ppm × m) obtained for the different GasFinder–retro-reflector paths. With these inputs, the script performed a data inversion using a least-squares method, previously described by Pedone et al. (2014). The geometric matrix (Fig. 2a) generated by the Matlab algorithm, is a geometric reconstruction of the experimental set-up (the explored space was divided into 16 equally sized cells; the cells separated by the red lines in Fig. 2a). The scripts used the data inversion procedure to assign an averaged CO₂ mixing ratio (in ppm) to each cell of the 4 × 4 matrix (the same 16 cells as Fig. 2a). Using sets of synthetic data to test the algorithm, we estimated an error of ≤ 3 % associated with these individual cell mixing ratios.

The so-called tomographic matrix (Fig. 2b) was then interpolated with the Surfer software to obtain the contour maps of Figs. 2c and 4–6. We used the point Kriging geo-statistical method to interpolate the available data and produce an interpolated grid (Isaaks and Srivastava, 1989). Figure 2c is the contour map of CO₂ mixing ratios obtained at Nea Kameni. This map (obtained by interpolation of the tomographic matrix of Fig. 2b) shows the distribution of CO₂ mixing ratios in the roughly horizontal atmospheric cross section, covering the area between the GasFinder (A–F) and retro-reflector (1–6) positions (Fig. 1a). The figure shows that, in spite of the feeble degassing activity present, a CO₂ plume is imaged by our observations on the eastern, inner rim of the Nea Kameni crater. Low CO₂ mixing ratios (~390 ppm) are outputted by the Matlab routine on the north-western portion of the investigated area, while higher CO₂ mixing ratios (from 490 to ~540 ppm) are identified on the east, where the main gas emission vents are located. The peak CO₂ mixing ratio of ~590 ppm is located in correspondence to one principal gas vent (marked as “Fum6” in Fig. 2c).

Similar results have been obtained at Hekla, Krýsuvík and Vulcano. Figure 4 is a contour map of CO₂ mixing ratios at the Hekla measurement site (Fig. 1b). Given the positioning of GasFinder and retro-reflectors, the Matlab-derived contour map is here relative to an hypothetical horizontal cross section, taken at about 1 m height above the warm degassing ground identified by Ilyinskaya et al. (2014) on the rim of the 1980–1981 summit crater of Hekla (Figs. 1b and 4). In this area, the background CO₂ mixing ratio was evaluated at around 400 ppm. The peak CO₂ mixing ratio (~1050 ppm) was detected in the central portion of the investigated area, in the same sector where the highest soil CO₂ fluxes have been observed (Ilyinskaya et al., 2014).

The CO₂ contour map obtained at Krýsuvík is shown in Fig. 5. In this area, CO₂ mixing ratios ranged from 350–380 ppm at the periphery of the exhaling area, and up

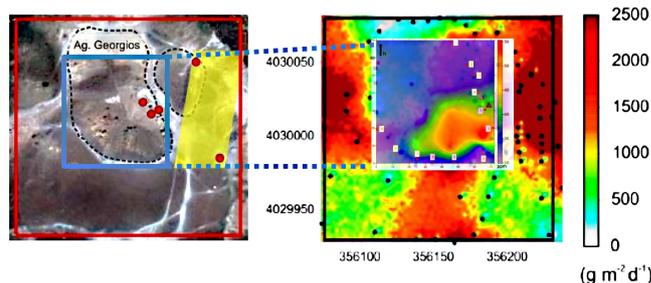


Figure 7. Our TDL CO₂ map for Nea Kameni volcano (same as Fig. 2) compared with the soil CO₂ flux map of Parks et al. (2013). The study of Parks et al. (2013) covered a wider exhaling area that contributes a diffuse CO₂ output of $38 \pm 6 \text{ t d}^{-1}$ (in January 2012), or ~60 % of our $63 \pm 22 \text{ t d}^{-1}$ fumarolic CO₂ output. Left, (modified from Parks et al., 2013): red square: survey area investigated from Parks et al. (2013); blue square: our survey area; red dots: position of fumaroles (from Tassi et al., 2013); yellow box: the area with elevated diffuse degassing (Parks et al., 2013 and Chiodini et al., 1998); black dashed circles: summit craters.

to ~500 ppm near the two main fumarolic vents (“FumA” and “FumB” in Fig. 5).

The CO₂ distribution map of La Fossa crater at Vulcano Island is shown in Fig. 6. The highest CO₂ mixing ratios (up to 880 ppm; Fig. 6) were detected in correspondence of the principal fumaroles (“F0”, “F5” and “F11”) of the crater rim and the “FA” fumarolic field in the inner wall of the crater.

4.4 Calculation of the CO₂ flux

The ability of the TDL to contour CO₂ mixing ratios in a volcanic gas plume cross section (Figs. 2–6) opens the way to quantification of the fumarolic CO₂ output from each of the studied areas. In order to calculate the CO₂ output from each fumarolic area, we integrated each set of CO₂ mixing ratio values in each CO₂ contour map (Figs. 2, and 4–6), to obtain a CO₂ integrated column amount (ICA) over the entire plume cross section. This ICA was then multiplied by the vertical plume transport speed, yielding a CO₂ flux. The calculated CO₂ fluxes are listed, for each site and each campaign, in Table 1. The accuracy (1σ) of the mean flux estimates are calculated from error propagation theory applied to both ICA and plume transport vertical speed.

Applying this procedure to the contour map of Fig. 2, we estimate a CO₂ flux from Nea Kameni fumaroles of $63 \pm 22 \text{ t d}^{-1}$. This fumarolic output is ~4 times higher than the total diffuse discharge from the soils of 15.4 t d^{-1} reported by Chiodini et al. (1998), and ~1.5 times higher than the soil CO₂ output of $38 \pm 6 \text{ t d}^{-1}$ estimated (in January 2012) by Parks et al. (2013). One of the advantages of using the Tunable Diode Laser is the possibility to capture simultaneously the CO₂ contributions from both diffuse soil degassing and concentrated emissions (fumaroles). Our CO₂ concentration map of Fig. 2, and the CO₂ output we derive

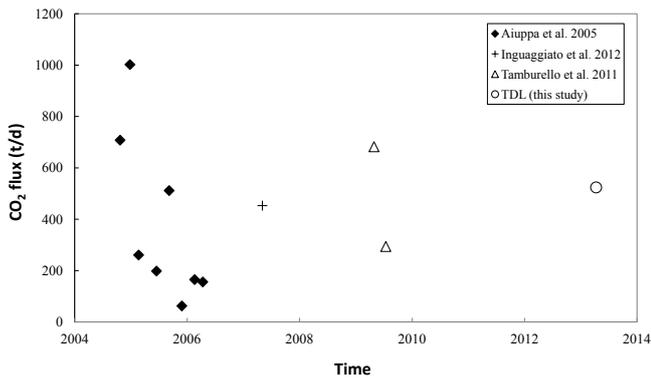


Figure 8. Time series of CO₂ flux values (t d⁻¹) for La Fossa crater (Vulcano Island). Previous studies shown are: Aiuppa et al. (2005, 2006), Tamburello et al. (2011) and Inguaggiato et al. (2012). The flux value of 524 ± 108 t d⁻¹, obtained in this study, is also shown.

from it, allows us to capture a cross section through whole areas of CO₂ degassing, that includes both diffuse and concentrated (fumaroles) forms of emission. To make the case more clear, we compare in Fig. 7 the spatial distribution of our CO₂ anomaly with that detected (in January 2012) in the diffuse CO₂ flux map of Parks et al. (2013). The study of Parks et al. (2013) covered a wider (than studied here) exhaling area that nonetheless contributed diffusively only a fraction (~60%) of the diffuse and fumarolic CO₂ output we estimate in our study. From this comparison, we argue that persistent fumarolic activity on top of Nea Kameni's central crater dominates the CO₂ degassing budget over more peripheral weakly degassing soils.

For Hekla, we estimated a CO₂ flux of about 15 ± 7 t d⁻¹ (Table 1). The large error in our flux estimate (±46%) reflects the poor quality of our plume transport speed measurement, the determination of which was complicated by the strong winds blowing across the top of Hekla at the time of our measurements. We still observe, however, that our 15 ± 7 t d⁻¹ estimate matches closely the recently reported CO₂ flux for Hekla summit (13.7 ± 3.7 t d⁻¹), obtained using conventional (accumulation chamber) soil survey techniques (Ilyinskaya et al., 2014).

For the Hveradalur fumarolic field of Krýsuvík, we estimate a CO₂ flux of 5.7 ± 0.9 t d⁻¹ (Table 1). This is the first CO₂ output estimate for this area, at least to our knowledge.

Finally, on March 2014 we evaluate the CO₂ flux at La Fossa crater at 524 ± 108 t d⁻¹ which is in the same range of those estimated in previous studies, obtained with other techniques (e.g. CO₂/SO₂ ratio + SO₂ flux), by Aiuppa et al. (2005) (420 ± 250 t d⁻¹), Tamburello et al. (2011) (488 t d⁻¹, average of two campaigns in 2009), and Inguaggiato et al. (2012) (453 t d⁻¹) (see Fig. 8).

4.5 Implications for the global volcanic CO₂ flux

Our CO₂ observations were taken at four volcanoes displaying a range of fumarolic activity, from weak (Hekla) to moderately strong (La Fossa of Vulcano). As such, our results add novel information on the CO₂ degassing regime of quiescent volcanoes in the solfatara stage of activity (for which the fumarolic CO₂ contribution was undetermined until the present study), and on their potential contribution to the global volcanic CO₂ budget.

The current state-of-the-art of volcanic CO₂ flux research has recently been summarized in Burton et al. (2013). The authors (2013) presented a compilation of 33 subaerial volcanoes for which CO₂ flux observations were available at that time. These “measured” emissions totalled a cumulative CO₂ output of 59.7 Mt yr⁻¹. The same authors used linear extrapolation, from the measured 33 to the 150 plume-creating, passively degassing volcanoes on the GVP catalogue (Siebert and Simkin, 2002), to obtain an extrapolated global volcanic CO₂ flux of ~271 Mt yr⁻¹.

The linear extrapolation approach of Burton et al. (2013) is based on the implicit assumption that the measured 33 volcanoes represent a statistically significant sub-set of the volcanic CO₂ flux population. However, we argue that past volcanic CO₂ observations have been prioritized at strongly degassing volcanoes during periods of unrest; therefore, the 33 volcanoes population may be biased towards the category of top gas emitter, implying the linear extrapolation technique may be incorrect. The low CO₂ output associated with “quiet” volcanoes, as reported in our present work, corroborates this conclusion.

The alternative extrapolation approach used to quantify CO₂ emissions from “unmeasured” volcanoes assumes that the distribution of volcanic CO₂ fluxes obeys a power law (Brantley and Koepenick, 1995), as other geophysical parameters do (Marret and Allmendinger, 1991; Turcotte, 1992). If volcanic emissions follow a power-law distribution, then the number of volcanoes (N) with an emission rate $\geq f$ are given by:

$$N = a f^{-c}, \quad (1)$$

where a and c are constants that can be derived from linear regression on measured CO₂ emission data sets. In the power-law assumption, the global volcanic CO₂ flux (f_{tot}) was extrapolated to 88–132 Mt yr⁻¹ (Brantley and Koepenick, 1995) using the relation:

$$f_{\text{tot}} = f_1 + f_2 + f_3 + f_N \left[\frac{c}{1-c} (N+1) \left(\frac{N}{N+1} \right)^{\frac{1}{c}} \right], \quad (2)$$

where f_N refers to the N th largest measured flux. This 88–132 Mt yr⁻¹ estimate is a factor of 2–3 lower than that obtained with the linear extrapolation technique (Burton et al., 2013). On the same basis, the volcanic plus metamorphic

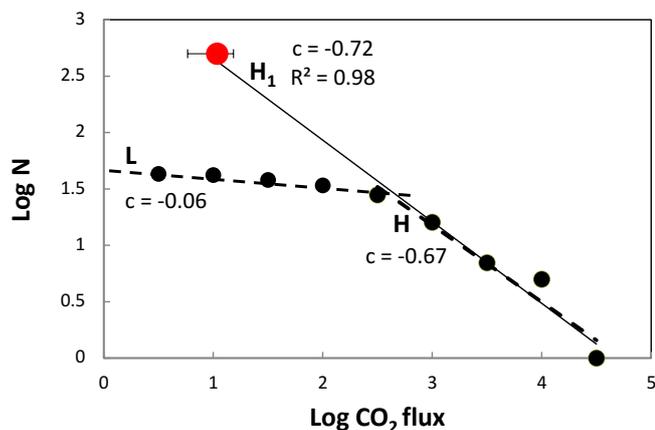


Figure 9. Cumulative frequency of the number of volcanoes (N) emitting CO₂ flux (logarithmic scale). The diagram is based on the data set of Burton et al. (2013), implemented with new results from this study and additional data (see text). The red point, with coordinates $\log f = 1$ (CO₂ flux = 10 t d⁻¹) and $\log N = 2.69$ (500 volcanoes), lies right above the linear regression line of the high CO₂ flux ($\log f > 2.5$) population (dashed line H). The regression line (line H₁; $R^2 = 0.98$) is obtained considering the high CO₂ flux volcanoes ($\log f \geq 2.5$) plus this new $\log f = 1$ point.

CO₂ flux was evaluated at ~ 264 Mt yr⁻¹ (Brantley and Koepnick, 1995).

The power-law distribution assumption has extensively been used to extrapolate volcanic gas fluxes at both the global and individual-arc scale (Hilton et al., 2002). However, concerns have recently been raised on its validity. For example, Mori et al. (2013) demonstrated that the SO₂ flux distribution of Japanese volcanoes noticeably diverges from a simple power law distribution. The case of the global volcanic CO₂ flux population is illustrated in Fig. 9. The figure is a log–log plot of the cumulative number of volcanoes (N) having measured CO₂ flux of $\geq f$. The diagram is based upon the data set of Burton et al. (2013), implemented with new results from this study (Table 1) and additional data for Turrialba (1140 t d⁻¹; Conde et al., 2014) and Poás (24.7 t d⁻¹; Aiuppa et al., 2014) in Costa Rica, Telica (132 t d⁻¹; Conde et al., 2014) and San Cristóbal (523 t d⁻¹; Aiuppa et al., 2014) in Nicaragua, Lastarria (973 t d⁻¹) and Láscar (534 t d⁻¹) in Chile (Tamburello et al., 2013, 2014), and La Soufriere volcano in Guadeloupe, Lesser Antilles (14.9 t d⁻¹; Allard et al., 2014). This implemented CO₂ flux population (43 volcanoes in total) clearly departs from a linear trend, as would be expected for a power-law distribution (see Eq. 1). The observed distribution shows, instead, a clear inflection point at $\log f \sim 2.5$ – 2.8 (i.e. a CO₂ flux of ~ 300 – 600 t d⁻¹), which appears to divide high (> 600 t d⁻¹) from low (< 300 t d⁻¹) CO₂ flux volcanoes (L and H regression lines in Fig. 9).

In view of our novel results (listed in Table 1), we propose that the non-linear behaviour of the volcanic CO₂ flux population may (at least in part) reflect the scarcity of CO₂ flux in-

formation on weakly fuming, quiescent volcanoes. The case of Hekla is emblematic in this context: the volcano has remained in a very active state in the last century (it violently erupted only fourteen years ago; Höskuldsson et al., 2007), but shows today a very weak diffuse gas emission. Yet our data suggest the volcano may contribute daily ~ 15 t of CO₂ to the atmosphere in a not distinctly visible, but probably persistent form. Similarly, no plume is distinctly seen on top of Nea Kameni in Santorini, nonetheless its weak fumaroles release 63 ± 22 t of CO₂ every day (in addition to a sizeable diffuse contribution from the soil), and 5.7 ± 0.9 t of CO₂ are released daily by quiet hydrothermal activity at Krýsuvík (whose most recent activity probably dates back the 14th century; Smithsonian Institute, 2013). While the individual contribution of each of the above volcanoes is negligible globally, the cumulative contribution of all feebly degassing volcanoes on Earth may not be, and may in fact impact the global CO₂ flux distribution of Fig. 9.

To explore the latter argument further, we consider that, of the 1549 volcanic structures listed in the GVP catalogue, around 500 are considered to have been active in the Holocene (Smithsonian Institution, 2013), and thus still potentially degassing. For the sake of illustration, we assume that all such 500 volcanoes have a CO₂ flux equal to or higher than 10 t d⁻¹ (the mean of our measured Krýsuvík and Hekla fluxes). This yields a new point on Fig. 9, with coordinates $\log f = 1$ (CO₂ flux = 10 t d⁻¹) and $\log N = 2.69$ (500 volcanoes), which lies right above the linear regression line of the high CO₂ flux ($\log f > 2.5$) population (see dashed line H in Fig. 9). The regression line (line H₁; $R^2 = 0.98$) obtained considering the high CO₂ flux volcanoes ($\log f \geq 2.5$) plus this new $\log f = 1$ point has slope $c = -0.72$. Using this value in Eq. (1), and with $N = 500$, we calculated an extrapolated CO₂ flux of 67 Mt yr⁻¹.

From these preliminary calculations, we conclude that the power-law distribution may be an appropriate representation of the population of CO₂ flux data, provided the output of the several hundreds of weakly degassing, quiescent/hydrothermal/dormant volcanoes is considered. We caution, however, that a large number of potentially strong volcanic CO₂ emitters remain to be measured (specifically, in poorly explored areas such as Papua New Guinea, Indonesia and nearby countries), and that these have the potential to strongly impact the distribution and regression shown in Fig. 9.

5 Conclusions

We have investigated the fumarolic CO₂ output from four quiescent volcanoes in a hydrothermal state of activity, using an infrared TDL. At each of the studied volcanoes, the acquired TDL results have been used to produce contour maps of CO₂ mixing ratios in the plumes' cross sections, and consequently to quantify the fumarolic CO₂ output.

The highest output ($524 \pm 108 \text{ t d}^{-1}$) is obtained at La Fossa of Vulcano Island, the only volcano of the four where a persistent atmospheric plume is observed. The lowest CO₂ output ($5.7 \pm 0.9 \text{ t d}^{-1}$) is associated with hydrothermal activity at Krýsuvík, with intermediate emissions at Hekla ($15 \pm 7 \text{ t d}^{-1}$) and Nea Kameni ($63 \pm 22 \text{ t d}^{-1}$). The latter three volcanoes all currently display weak exhalative activity rather than predominant plume emission. We therefore suggest that a $5.7\text{--}63 \text{ t d}^{-1}$ CO₂ output range may be characteristic of many of the ~ 500 volcanoes active in the Holocene, in spite of the majority lacking obvious surface manifestations of degassing. Assuming a representative CO₂ output of 10 t d^{-1} for such 500 Holocene volcanoes, we argue that the global population of CO₂ emissions may approach a simple power-law distribution. This conclusion will remain somewhat speculative, however, until new measurements become available for the several potentially strong volcanic CO₂ point sources (e.g. Papua New Guinea, Indonesia) that are missing from the global CO₂ data set.

Our results here suggest that the TDL technique can assist CO₂ output determinations at volcanoes covering a range of activities and surface degassing manifestations. Compared to other more consolidated gas sensing techniques (e.g. FTIR), the TDL has the disadvantages that only one species (CO₂ in our case) can be measured at same time (against multi-species simultaneous detection by FTIR), and that no passive measurement is possible (FTIR uses passive sources such as the sun or hot rocks/magma). Advantages include, however, lower cost (a commercial TDL is a factor of 2–3 cheaper than FTIR), user-friendly operation and processing, and robustness for use in harsh/aggressive volcanic environments. Our results and that of Pedone et al. (2014) indicate, in particular, that the GasFinder can operate in a variety of volcanic conditions, provided the plume is not condensing and/or optically thick (fog and/or other obstacles within the laser-mirror path can reduce its functionality during field operations). Such versatility and robustness, and the availability on the market of pan-tilt units that can be interfaced to the GasFinder to rapidly scan a target gas emission from a fixed position, open new prospects for semi-continuous, automatic CO₂ flux observations. We suggest that, although measurements will remain restricted to periods with stable meteorological conditions and good visibility, semi-permanent TDL volcano installations may pave the way to acquisition of volcanic CO₂ output time series with temporal resolution of 10 s of minutes.

Author contributions. M. Pedone carried out the field campaigns in the study areas and drafted the manuscript. A. Aiuppa enabled the realization of the study and actively contributed to drafting the manuscript. G. Giudice participated and provided technical support during field campaigns. F. Grassa provided important suggestions during data processing. V. Francoforte provided technical assistance during the field work. B. Bergsson and E. Ilyinskaya partici-

pated and provided technical support during field campaigns in Iceland. All authors read and approved the final manuscript.

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