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Contribution of CO_2 and H_2S emitted to the atmosphere by plume and diffuse degassing from volcanoes: the Etna volcano case study

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Abstract Active subaerial volcanoes often discharge large amounts of CO_2 and H_2S to the atmosphere, not only during eruptions but also during periods of quiescence. These gases are discharged through focused (plumes, fumaroles, etc.) and diffuse emissions. Several studies have been carried out to estimate the global contribution of CO_2 and H_2S emitted to the atmosphere by subaerial volcanism, but additional volcanic degassing studies will help to improve the current estimates of both CO_2 and H_2S discharges. In October 2008, a wide-scale survey was carried out at Mt. Etna volcano, one the world's most actively degassing volcanoes on Earth, for the assessment of the total budget of volcanic/hydrothermal discharges of CO_2 and H_2S, both from plume and diffuse emissions. Surface CO_2 and H_2S effluxes were measured by means of the accumulation chamber method at 4075 sites, covering an area of

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about 972.5 km^2. Concurrently, plume SO_2 emission at Mt. Etna was remotely measured by a car-borne Differential Optical Absorption Spectrometry (DOAS) instrument. Crater emissions of H_2O, CO_2 and H_2S were estimated by multiplying the plume SO_2 emission times the H_2O/SO_2, CO_2/SO_2 and H_2S/SO_2 gas plume mass ratios measured in situ using a portable multisensor. The total output of diffuse CO_2 emission from Mt. Etna was estimated to be 20,000 ± 400 t day^{-1} with 4520 t day^{-1} of deep-seated CO_2. Diffuse H_2S output was estimated to be 400 ± 20 kg day^{-1}, covering an area of 9.1 km^2 around the summit craters of the volcano. Diffuse H_2S emission on the volcano flanks was either negligible or null, probably due to scrubbing of this gas before reaching the surface. During this study, the average crater SO_2 emission rate was ~2100 t day^{-1}. Based on measured SO_2 emission rates, the estimated H_2O, CO_2 and H_2S emission rates from Etna's crater degassing were 220,000 ± 100,000, 35,000 ± 16,000 and 510 ± 240 t day^{-1}, respectively. These high values are explained in terms of intense volcanic activity at the time of this survey. The diffuse/plume CO_2 emission mass ratio at Mt. Etna was ~0.57, that is typical of erupting volcanoes (mass ratio <1). The average CO_2/SO_2 molar ratio measured in the plume was 11.5, which is typical of magmatic degassing at great depth beneath the volcano, and the CO_2/H_2S mass ratio in total diffuse gas emissions was much higher (~11,000) than in plume gas emissions (~68). These results will provide important implications for estimates of volcanic total carbon and sulfur budget from subaerial volcanoes.

Keywords Mt. Etna · Carbon dioxide · Hydrogen sulfide · Gas budget · Diffuse degassing · Crater degassing

1 Introduction

Active subaerial volcanoes typically emit 0.1–2 Mt $year^{-1}$ of CO_2 at a global scale, with the highest emission rates being associated with alkaline volcanic systems. This is the case for Mt. Etna, Europe's largest active and most actively degassing volcano (Allard et al. 1991; D'Alessandro et al. 1997), characterized by high CO_2 contents in its alkaline magma (Gerlach 1991). At Etna, outgassing of CO_2 occurs not only as a plume from its open summit craters but also in diffuse form from its flanks, mainly through active faults (e.g., Allard et al. 1991; Giammanco et al. 1995; Aiuppa et al. 2004a; Giammanco et al. 2013). During the last two decades, numerous works have demonstrated that noneruptive, diffuse degassing may be the principal mode of gas release from many volcanoes (Aiuppa et al. 2004b; Hernández et al. 1998, 2001a, b, 2003, 2006; Chiodini et al. 1998, 2001, 2005, 2007; Giammanco et al. 1998; Fridriksson et al. 2006; Granieri et al. 2006; Lewicki et al. 2007; Padrón et al. 2003, 2008; Pérez et al. 2006, 2012, 2013).

Volcanic/hydrothermal discharges at active volcanoes occur both from diffuse degassing along active volcano-tectonic structures and by focused degassing through open vents (plume). During volcanic eruptions, large amounts of volcanic gases are injected into the atmosphere, thus having a significant short-term impact on the atmospheric CO_2 budget (Gerlach 2011). At present, however, there is no real consensus about the relative importance of this mode of degassing and its contribution to the global carbon budget (Burton et al. 2013; Hards 2005).

In recent years, significant efforts have been made to compute the amount of diffuse CO_2 released by volcanoes and by geothermal systems and the many studies published on this topic showed that this type of degassing can represent a significant portion of the total volcanic/geothermal CO_2 release to the atmosphere. Such computations were mostly made through mapping of the surface CO_2 efflux anomalies (Toutain et al. 1992.; Salazar et al. 2001), which also helped to reveal tectonic structures (particularly the hidden ones) that act as preferential pathways for the leakage of volcanic gas to the surface (e.g., Giammanco et al. 1998, 2007, 2010). Furthermore, since the emission rate of diffuse CO_2 can increase prior to a volcanic eruption (Hernández et al. 2001a; Carapezza et al. 2004; Pérez et al. 2012; Liuzzo et al. 2013; De Gregorio et al. 2014), it is important to estimate the potential range of variation in the output of this gas from active volcanoes at different levels of activity in order to have a better understanding of the ongoing processes within a volcano and to provide more refined and reliable data to the estimate of the global volcanic CO_2 budget.

An important issue regarding volcanic gas emission studies is to compare plume with diffuse emanations. Notsu et al. (2006) reported that high diffuse CO_2 efflux values are typically observed on volcanoes when active plume degassing is low, corresponding to a low-activity stage (i.e., Hakkoda in Japan, Hernández et al. 2003; Mammoth Mountain in USA, Gerlach et al. 2001; Teide in Spain, Mori et al. 2001; Sierra Negra in Ecuador, Padrón et al. 2012). On the other hand, some volcanoes exhibit weak diffuse CO_2 efflux and intense plume activity, as observed on White Island, New Zealand (Wardell et al. 2001), or Nisyros volcano, Greece. Considering the above observations, an attempt can be made to evaluate the level of volcanic activity by means of diffuse/plume CO_2 emission ratio, assuming that diffuse emission is a proxy of degassing from deep-seated magma and plume emission is a proxy of degassing from shallower magma. A similar reasoning was used by Liuzzo et al. (2013), who correlated the temporal evolution of diffuse CO_2 efflux with that of the CO_2/SO_2 ratio from crater gas emissions at Etna in order to discriminate between gas released directly from a rising magma batch and gas released from gas bubbles rising from depth without associated magma.

Another goal of this work was to estimate for the first time the total (plume and diffuse) H_2S emission from Mt. Etna. Jaeschke et al. (1982) were the first to carry out H_2S measurements at Mt. Etna, but only crater emissions were considered in that case. In general, very few data exist on the global H_2S volcanogenic contribution (Berresheim and Jaeschke 1983; Halmer et al. 2002; Aiuppa et al. 2005); thus, our work will provide important information on this issue.

The aims of this work, therefore, were (1) to quantify the total (plume and diffuse) CO_2 and H_2S output from Mt. Etna; (2) to estimate crater emissions of CO_2, H_2S, SO_2 and H_2O; (3) to compare plume with diffuse CO_2 emissions; and (4) to evaluate the implications of this study on the contribution of CO_2 and H_2S emitted to the atmosphere by plume and diffuse degassing from volcanoes.

2 Geological and volcanological settings

Mt. Etna (Fig. 1) is one of the world's most active volcanoes. The source of Mt. Etna magma is possibly connected with a mantle plume that Montelli et al. (2004) imaged above 1000 km depth using seismic tomography. Alternatively, the voluminous mantle melting under Mt. Etna may result from suction of asthenospheric material induced by the backward rolling of the descending Ionian slab (Gvirtzman and Nur 1999). Mt. Etna is constituted by several nested strato-volcanoes (Condomines et al. 1995; Branca et al. 2011). The ancient strato-volcanoes and the associated small scattered eruptive centers grew on a

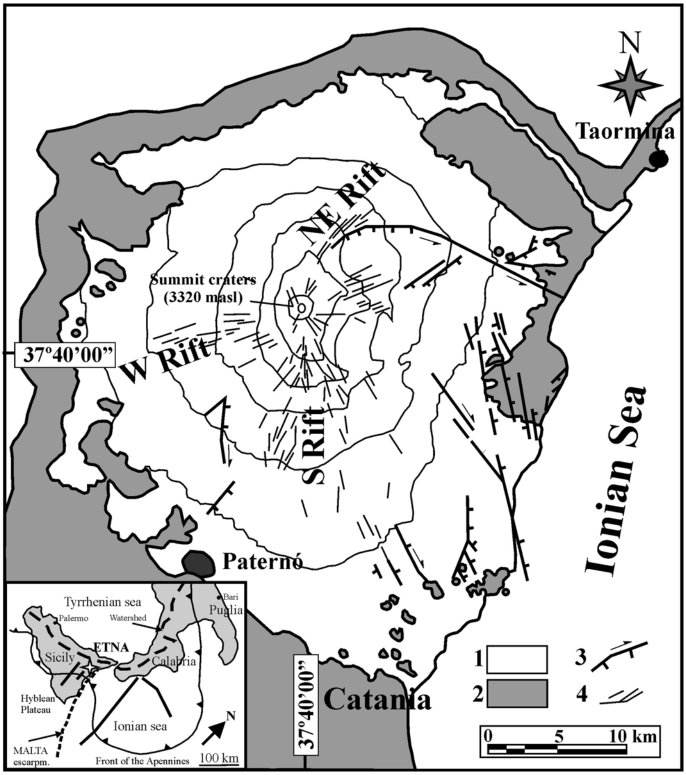

Fig. 1 Simplified volcano-tectonic map of Mt. Etna volcano (modified from Acocella and Neri 2003). *Legend*: *1* outcrops of volcanic products of Mt. Etna; *2* outcrops of sedimentary rocks of Etna basement; *3* faults; and *4* eruptive fissures

lava plateau, produced by fissural eruptions of tholeiitic/transitional lavas dated to about 0.5 Ma (Gillot et al. 1994; Corsaro and Cristofolini 1997).

The postplateau volcanic products show a composition ranging from picritic and alkalic basalt to trachytes, with hawaiites being the dominant rocks (D'Orazio 1995). The predominance of hawaiitic products in the recent activity of Mt. Etna is mainly explained as fractionation/mixing processes affecting a primary picritic magma in a relatively deep magma chamber (Armienti et al. 1996), whose existence has been suggested on the basis of seismological data (Sharp et al. 1980; Aloisi et al. 2002).

Throughout its evolution, Mt. Etna was essentially characterized by effusive activity, even though several pyroclastic sequences related to sub-Plinian and Plinian eruptions have been identified in the Holocene sequence (Coltelli et al. 1995, 1998). In the last decades, Etna's activity showed a marked increase both in the number of eruptions and in the yearly effusion rate (Behncke and Neri 2003).

Mt. Etna's summit today is occupied by a large cone complex including the original central crater (now nearly substituted by the two craters Bocca Nuova and Voragine), the northeast crater and the southeast crater (respectively, NE crater and SE crater in Fig. 2).

Apart from the main area of Mt. Etna, another smaller area considered in our study is located just outside of Mt. Etna boundaries, near the town of Paternò on the volcano lower

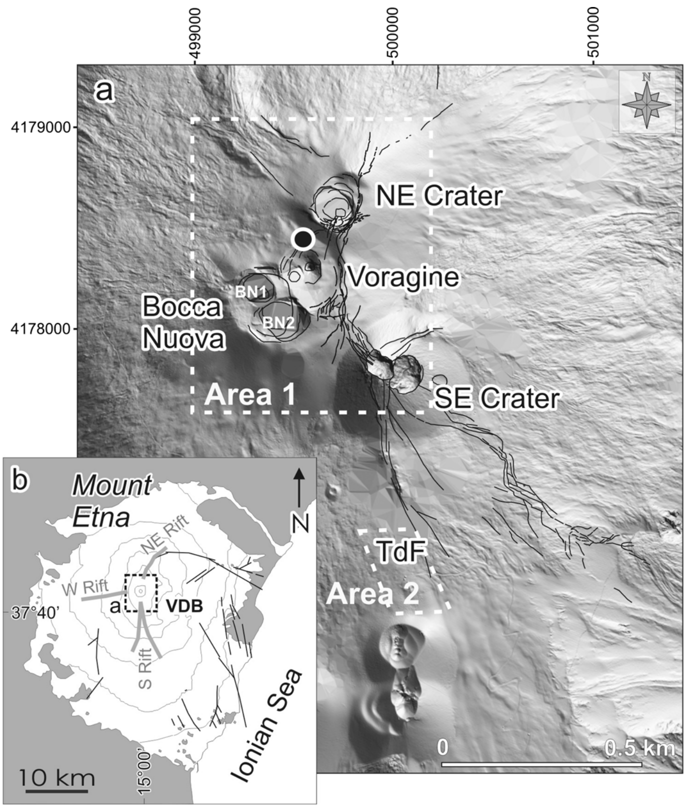

Fig. 2 **a** Digital elevation model of the summit area of Mt. Etna (courtesy of M. Pareschi research group, INGV Pisa) based on 2005 topographic data; *black lines* are the main dry and eruptive fissures developed between 1998 and 2006; BN1 and BN2 are the two pit craters inside the Bocca Nuova crater; *TdF* Torre del Filosofo. The location of the specific areas selected for intensive surveys is shown (*Areas 1* and *2* in the figure). Also shown is the location of the site (*filled black circle*) at the rim of Voragine summit crater, where a multisensory device was installed for the measurements of CO_2/SO_2, H_2O/CO_2, H_2S/SO_2 and H_2O/SO_2 molar ratios in the volcanic plume. **b** simplified structural map of Mt. Etna; *black lines* indicate main faults; *gray lines* represent the main rift zones; *VDB* Valle del Bove morphological depression

SW flank. This area is characterized by the presence of mud volcanoes, locally known as Salinelle, mofettes and several sites of high diffuse CO_2 degassing (Giammanco et al. 1995, 2007).

3 Methods

3.1 Surface CO_2 and H_2S efflux measurements

Sites for surface CO_2 and H_2S efflux measurements were selected in order to cover most of Mt. Etna's surface, after considering site accessibility and trying to intercept the main volcano-tectonic features of the volcano (Fig. 2). The study area included the most relevant morphological and volcanological features of Mt. Etna: rims of Bocca Nuova (BN) and

Voragine summit craters and floor of the summit cone, Torre del Filosofo (TDF) hydrothermal area, accessible areas of Etna flanks and surrounding active faults. A higher sampling density was used around the summit craters and at TDF, as well as near the towns of Zafferana Etnea, Santa Venerina and Paternò, due to their higher-than-normal diffuse or focused gas emissions (Aiuppa et al. 2004a).

In total, 4075 measurements were taken, covering an area of about 972.5 km^2 (Fig. 3), using the accumulation chamber method (Parkinson 1981). Of these measurements, 1443 were taken in the summit area (30.1 km^2) and 2633 in the rest of the volcano (942.4 km^2), thus giving average sampling densities, respectively, of 48.1 and of 2.8 points per square kilometer. Measurements of CO_2 and H_2S effluxes were taken in situ by means of four portable devices:

1. Two portable meters provided by a nondispersive infrared (NDIR) CO_2 analyzer (model LI-800, LI-COR) composed of a double-beam infrared carbon dioxide sensor compensated for temperature and atmospheric pressure, with full-scale range of 20,000 ppm, detection limit of 1 ppm, an accuracy of concentration reading of 2 % and a repeatability of ±5 ppm, and a H_2S electrochemical cell (model H2S-BH, Alphasense), with a full-scale range of 50 ppm, detection limit <0.1 ppm, precision of 3 % of reading and a resolution of 0.1 % of span, with a zero offset of 0.3 %.
2. An improved version of the classical West Systems portable flux meter, with a CO_2 detector Vaisala GP343 (full-scale range of 5000 ppm). The working principle is exactly the same than the classical LICOR LI-800-based portable flux meter. The only

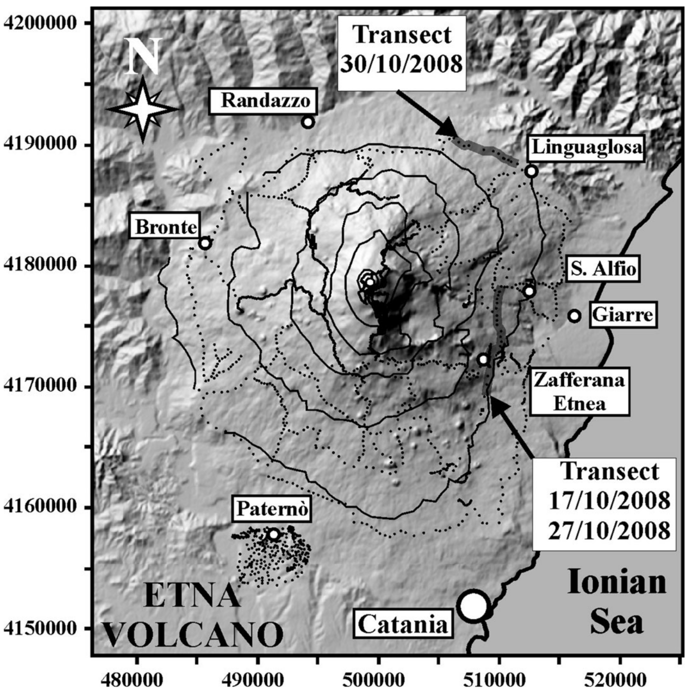

Fig. 3 Location of the sites where diffuse CO_2 and H_2S effluxes were measured on Mt. Etna during the present study. Transects (*thick gray lines*) surveyed for ground-based SO_2 flux measurements are also shown

significant difference consists of using a gas turbulence-based device instead of an electromechanical mixing device.

3. A portable meter provided by a nondispersive infrared (NDIR) CO_2 analyzer (model EGM-4, PPSystems) configured as an absolute absorption meter with microprocessor control of linearization, a measurement range of 0–10,000 ppm, an accuracy <1 % of span concentration over the calibrated range and a linearity drift <1 % throughout the measurement range.

Due to the use of different CO_2 efflux meters, before the beginning of field work, an inter-comparison measurement was carried out. A difference of 8–10 % between instruments was found, which is compatible with the usual error in this type of measurements (e.g., Giammanco et al. 2007). The GPS position of each measurement point was recorded with a resolution of ±5 m. At each point, soil temperature was measured at 20–40 cm depth by means of a thermocouple.

3.2 SO_2 plume emission measurement

Measurements of plume SO_2 emissions were taken using a car-borne mini-DOAS (Differential Optical Absorption Spectroscopy) instrument on October 17, 27 and 30, 2008. The mini-DOAS was based on an Ocean Optics USB2000 spectrometer, which collects the light caught by the telescope and guided by the optical fiber (telescope's diameter of 3 cm; focal length of 25 cm; field-of-view of 20 mrad) toward the spectrometer (Galle et al. 2002; Barrancos et al. 2008). This detector is provided with a CCD array of 2048 elements (each with width of 13 μm and height of 200 μm) treated for enhanced sensitivity below the 360-nm resolution, a 50-μm slit and spectral resolution of ~0.6 nm over a wavelength range of 245–380 nm (Galle et al. 2002).

Measurements were carried out along two transects kept as perpendicular as possible to the main plume direction (Fig. 3). The position of the car was continuously fixed by a GPS and recorded every 5 s. Drawing the time vs. the GPS position of the vehicle, the measured SO_2 concentration values and the wind speed (we assumed that the plume moved at the same speed along each transect), and integrating the results along the whole route, we obtained the value of SO_2 flux following the method of Stoiber et al. (1983). Wind speed data used for the above SO_2 flux calculation were taken from http://www.arl.noaa.gov/ready/amet.

3.3 Molar ratios of major volcanic gas components

Molar ratios of major volcanic gas components were measured at the Voragine crater rim by a portable multisensor device developed by West Systems, following the method described by Shinohara (2005). The Voragine crater was chosen because in recent years it has been by far the vent with the highest plume CO_2 emission rate among the four summit craters of Mt. Etna (Aiuppa et al. 2006, 2008; La Spina 2010). Furthermore, the location of our sensor was such that it allowed us to measure both the Voragine and the Bocca Nuova crater plumes, due to the prevailing wind direction during the period of our measurements, similarly to the work of Aiuppa et al. (2006).

The instrument pumped crater gases with a flow rate of 1 L/min during six hours on October 22, 2008, and it was equipped as follows:

1. CO_2 and H_2O were measured by means of a LI-840 spectrophotometer (LI-COR Inc.). This instrument was powered by 12 V batteries; it is portable (22 × 15 × 8 cm), light

(1 kg) and with low power consumption (3.6 W). This instrument works in concentration ranges between 0 and 3000 ppm for CO_2 and between 0 and 80,000 ppm for H_2O, with an error lower than 1 ppm at 370 ppm of CO_2 and lower than 10 ppm at 10,000 ppm of water vapor.

2. H_2S was measured using an Alphasense H_2S-BH Hydrogen Sulfide sensor, with a detection range between 0 and 50 ppm.
3. SO_2 was measured using a TOX-SO_2 electrochemical sensor with measurement range between 0 and 20 ppm.
4. Air temperature and relative humidity were measured using a silicon gauge. Plume water concentration (W, in ppm) was calculated following Padrón et al. 2012.

Data were stored in a hand-sized computer running data acquisition software.

4 Results

4.1 Diffuse CO_2 degassing

CO_2 efflux values ranged between nondetectable values from <0.25 g m^{-2} day^{-1} to 37.6 kg m^{-2} day^{-1}. Figure 4a shows the histogram of log CO_2 efflux values together with the distribution of their cumulated probability versus frequency. The distribution of CO_2 effluxes differs from a log-normal distribution, indicating that there are at least two different mechanisms of degassing. The probability-plot technique (Sinclair 1974) was applied to the entire CO_2 and H_2S efflux data sets to check whether the log of the data came from unimodal or polymodal distributions. A log-normal probability graph was constructed with the CO_2 efflux data to recognize the presence of overlapping different geochemical populations (Fig. 4b). The resulting probability graph allowed to distinguish two geochemical populations and to separate them from the original CO_2 efflux data set: i) a background population, representing 80.8 % of the total data, with a mean efflux of 6.3 g m^{-2} day^{-1} and ii) a peak population, representing 6.5 % of the total data, with a mean efflux of 1300 g m^{-2} day^{-1}. The rest of the data represents intermediate values between the background and peak populations. Background values represent pure biogenic contribution to the CO_2 efflux, while both the intermediate and the peak populations can be equally considered as contributions to the deep CO_2 diffuse emission. In these two populations, advection is probably the main transport mechanism to explain the observed relatively high CO_2 efflux values (Hernández et al. 2001a).

Surface CO_2 efflux data were treated using the sequential Gaussian simulation (sGs) method (Deutsch and Journel 1998) to construct a contour map in order to identify those areas characterized by anomalous diffuse CO_2 degassing. After mapping the results over the whole study area (Fig. 5a), it is evident that most of the volcano surface was characterized by background levels of CO_2 efflux. Peak values (>1300 g m^{-2} day^{-1}) were mainly detected around the summit craters and at TDF. Figure 5b shows an enlarged CO_2 efflux map of summit craters and TDF. Other zones with relatively high CO_2 efflux values were identified at Zafferana Etnea, Trecastagni-Viagrande and Paternò.

The sGs method was used also to compute the total CO_2 output and its relative uncertainties (Cardellini et al. 2003). To do so, 100 simulations were performed over an averaged grid of 261,792 squared cells (60 m × 60 m each) using a spherical variogram model. The obtained total output of CO_2 diffuse emission was 20,000 ± 400 t day^{-1}. This amount represents both the biogenic and the deep (magmatic/hydrothermal) CO_2 emission.

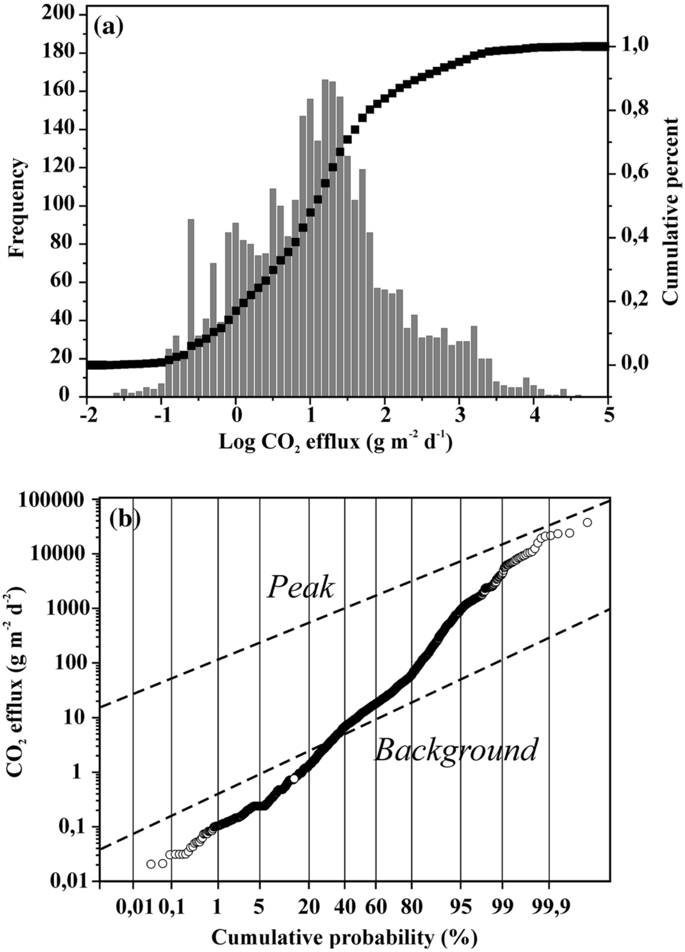

Fig. 4 **a** Histogram (with associated curve of cumulative percent of values) and **b** probability plot of CO_2 efflux data measured at Mt. Etna volcano during the present study. *Open circles* indicate original data; *dashed lines* separate background from peak populations

An attempt to isolate the deep contribution could be made based on the assumption that the intercept value between background and intermediate populations represents the threshold value between both contributions. To quantify the deep-seated CO_2 efflux from the studied area, we used the threshold value computed from the probability plot. We assumed the contribution of the deep-seated gas as the sum of the emission of the interpolated cells between the threshold and the maximum value. This threshold value was calculated at 16.9 g m^{-2} day^{-1}, which allowed us to estimate a deep CO_2 output of ~4500 t day^{-1} for Mt. Etna.

In order to better define the degassing pattern of Mt. Etna summit and TDF (respectively, areas 1 and 2 in Fig. 2), a more detailed survey was performed. Area 1 covers 2.9 km^2, and it was surveyed with 548 sampling sites distributed on all accessible areas. The spatial distribution of CO_2 efflux values showed an extensive anomaly in the southern

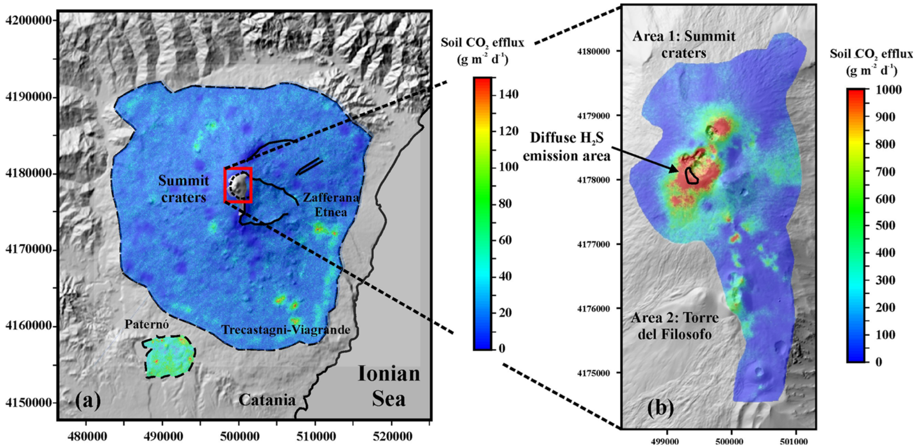

Fig. 5 **a** Average spatial distribution map obtained from 100 sequential Gaussian simulations of CO_2 efflux values measured at Mt. Etna volcano; **b** average spatial distribution map obtained from 100 sequential Gaussian simulations of CO_2 efflux values measured in *Area 1* (summit craters) and *Area 2* (TDF), on the summit of Mt. Etna volcano. The diffuse H_2S degassing area is delimited by a *solid black line*

part of the area, with some minor CO_2 efflux anomalies located in the north part of the summit and along the southern and southwestern flanks of the summit cone (Fig. 5b). High CO_2 efflux values measured in the summit area were strongly correlated with high soil temperatures, suggesting that heating of the ground is essentially due to condensation of the rising magmatic/hydrothermal fluids. On the contrary, the northern and northwestern flanks of the summit cone showed lower CO_2 efflux values. It must be underlined that at these locations there is no proper soil, since the ground is made of recent volcanic scoria deposits with a very high permeability, which favors strong mixing between volcanic gases and atmospheric air. As indicated in Fig. 5b, anomalous high CO_2 efflux values (i.e., values belonging to the peak population recognized by the probability-plot technique) were concentrated along several diffuse degassing structures (DDS), with the main CO_2 efflux anomalies occurring at the summit area, both on the inner slopes of the summit craters and on the northeast side of NE crater. Near the summit craters, the distribution of CO_2 effluxes showed a circular shape of the anomalous area, suggesting that the morphology of Mt. Etna's summit area plays a key role in determining the shape and the extension of local DDS, similar to what was observed at Vesuvius (Frondini et al. 2004). In particular, an important DDS near Mt. Etna's summit craters can be identified on the outer part of the southern margin of Bocca Nuova crater, where the highest CO_2 efflux values (>7 kg m^{-2} day^{-1}) were measured. This area is characterized by intense surface geothermal features such as fumaroles and steam discharges, suggesting the presence of a highly fractured zone where deep magmatic/hydrothermal fluids can migrate toward the surface. A second DDS was identified on the northeastern margin of the NE crater, where very high CO_2 efflux values (>7 kg m^{-2} day^{-1}) were measured as well. The very high CO_2 efflux values measured in those areas indicate a strong advective component in the transport of soil gas. The total output of CO_2 diffuse emission from this area was computed by performing 100 sGs simulations over an averaged grid of 181,467 squared cells (4 m $\times$ 4 m), following a spherical variogram model. The resulting calculated output was 1450 ± 240 t day^{-1}.

At TDF (Area 2 in Fig. 5b), a denser survey was performed in order to evaluate with great detail the spatial distribution of CO_2 and H_2S efflux anomalies and to estimate the total gas output from this fracture zone, characterized by stable fumarolic activity due to boiling of a shallow water table together with intense diffuse degassing related to active gas release from the central feeder system of the volcano (Pecoraino and Giammanco 2005). About 1103 sampling sites were selected over an area of 2.29 km^2. Also in this area, 100 sGs simulations were performed over an averaged grid of 46,795 squared cells (7 m × 7 m), following a spherical variogram model. The computed total output of CO_2 diffuse emission from this area was 90 ± 8 t day^{-1}.

Since this study is the first performed with a relatively high density of soil CO_2 efflux sampling points on the whole volcanic edifice of Mt. Etna, the estimated total diffuse CO_2 discharge from this volcano represents an important new contribution to the global carbon budget.

4.2 Diffuse H_2S degassing

H_2S efflux values ranged between nondetectable values from <0.08 g m^{-2} day^{-1} (i.e., the detection limit of the instrument used) to 190 g m^{-2} day^{-1}. H_2S was detected only at 62 sites out of 4075 (1.52 % of the total). Despite the low number of valid measures, we were able to construct a probability plot with the H_2S efflux data to identify the presence of overlapping different geochemical populations (Fig. 6). The results showed the existence of two distinct geochemical populations extracted from the original data set: a background population, representing 57.8 % of the total data, with a mean of 0.19 g m^{-2} day^{-1}, and a peak population, representing 4.3 % of the total data, with a mean of 170 g m^{-2} day^{-1}. The rest of the data represents intermediate values between the background and peak populations. The sGs method was not applied to the H_2S data because of the very large number of undetectable efflux values. Almost all of the anomalous H_2S efflux values at Mt. Etna were measured close to active thermal manifestations at the summit area, with background and peak values having a close correlation with the intensity of gas emanations. However, a relatively low positive correlation was found between soil temperature

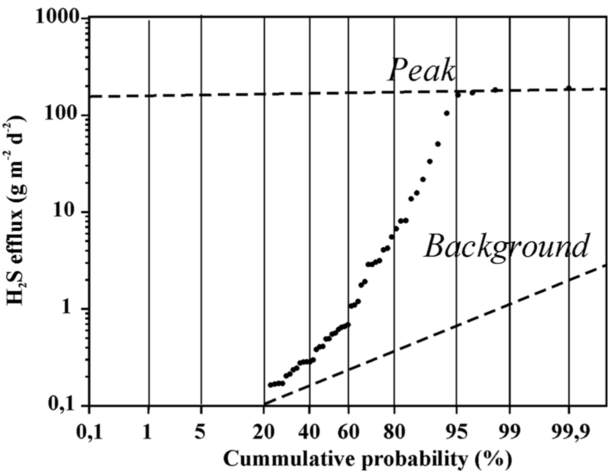

Fig. 6 Probability plot of H_2S efflux data measured at Mt. Etna volcano during the present study. *Open circles* indicate original data; *dashed lines* separate background from peak populations

and H_2S efflux ($R^2 = 0.33$). This would suggest that other mechanisms were controlling the transport of diffuse H_2S to the surface, although processes such as oxidation at high temperature and scrubbing of sulfur species (Symonds et al. 2001) cannot be ruled out. Giammanco et al. (1998) reported that at Mt. Etna's summit region diffuse degassing is mainly characterized by a low-temperature ($T < 100$ °C) CO_2-rich gas component, containing minor amounts of He, CH_4 and N_2. Among sulfur species in these discharges, H_2S is the most abundant (up to 23 ppmv H_2S; Aiuppa et al. 2005), since it dominates in low-temperature fumaroles and solfataras.

To quantify the total H_2S emission from the studied area, only the summit area of Mt. Etna volcano was considered, since no H_2S was detected along the lower flanks of the volcano. To this aim, 100 sGs simulations were performed over an averaged grid of 181,467 squared cells (4 m × 4 m), following a spherical variogram model. The obtained total output of H_2S diffuse emission from this area was 400 ± 20 kg day^{-1} over a surface area of 9.1 km^2.

4.3 Chemical composition of Etna volcanic plume

At the time of our survey, intense plume degassing from the summit craters of Mt. Etna was occurring, producing a plume emission that was dispersed over very long distances from the volcano summit. During the three days of measurements, SO_2 emission rates (Table 1) showed a total average output value of 2100 t day^{-1}, with a standard deviation (SD) of ±950 t day^{-1}. On October 27, an average SO_2 flux value of 3000 t day^{-1} with SD of ±700 t day^{-1} was measured, with peak value of 4200 t day^{-1}. The total average output value was lower than the average SO_2 flux value measured at Mt. Etna between January 1, 2005, and January 1, 2008, by Salerno et al. (2009). At that time, daily average of the SO_2 flux obtained during the traverses was 3250 t day^{-1}.

Molar ratios of major volcanic gas components measured in the volcanic plume by the portable multisensor are shown in Table 2. Relatively good correlation factors were obtained for all of the measured molar ratios, CO_2/SO_2, H_2O/CO_2, H_2S/SO_2 and H_2O/SO_2. Variations in the meteorological conditions affecting Mt. Etna's summit during the

Table 1 Measured values of SO_2 flux (t day^{-1}) on October 17, 27 and 30, 2008, at Mt. Etna volcano

	Date	SO_2 flux (t day^{-1})	Date	SO_2 flux (t day^{-1})	Date	SO_2 flux (t day^{-1})
	17/10/2008	2355	27/10/2008	4179	30/10/2008	1127
	17/10/2008	546	27/10/2008	3703	30/10/2008	2294
	17/10/2008	979	27/10/2008	2821	30/10/2008	1152
	17/10/2008	2817	27/10/2008	2613	30/10/2008	1882
	17/10/2008	1267	27/10/2008	2545	30/10/2008	1103
			27/10/2008	2474	30/10/2008	1545
			27/10/2008	2129		
Wind speed (m s^{-1})		7.7		15		21
Measurements		5		7		6
Average flux (t day^{-1})		1593		2923		1517
St Dev flux (t day^{-1})		956		738		489

The daily average of SO_2 flux was calculated based on the single flux values of the specific day of measurement

Table 2 Molar ratios measured by multisensor at summit of Etna volcano during October 2008

Peak	CO_2/SO_2	H_2O/SO_2	H_2S/SO_2	H_2O/CO_2
1	11.19	29.61	0.127	2.64
2	11.32	26.83	0.127	2.31
3	11.29	28.09	0.129	2.29
4	10.91	27.45	0.128	2.52
5	11.15	30.28	0.127	2.43
6	11.33	27.81	0.130	2.45
7	12.01	28.67	0.130	2.38
8	13.02	35.56	0.142	2.42
9	13.13	26.67	0.133	2.00
10	12.20	39.68	0.127	3.13
11	11.28	34.62	0.131	3.04
12	10.44	29.09	0.141	2.74
13	10.49	29.96	0.131	2.86
14	11.70	26.67	0.131	2.28

sampling period, variable contribution from different gas sources, including SO_2-poor low-temperature fumaroles, and mixing with air could be a possible explanation for the small variations observed in the measured ratios. In the case of SO_2, H_2S and CO_2 measurements, air contribution can be considered negligible or it can be subtracted easily. To do so, we followed the assumptions of Shinohara et al. (2008) that the SO_2 and H_2S concentrations in fresh air were zero and that the lowest CO_2 concentration among all measurements (411 ppm vol) was set as the CO_2 background concentration. However, in the case of H_2O, the atmospheric contribution cannot be neglected. In order to correct the atmospheric influence, a peak area method was applied to the time series of gas concentration data, as described in Shinohara et al. (2008).

The CO_2/SO_2, H_2O/CO_2, H_2S/SO_2 and H_2O/SO_2 molar ratios in the volcanic gas were calculated from the slopes of data on a scatter plot (Fig. 7). Estimated volcanic gas molar ratios showed small variations, ranging from 10.4 to 13.1 for the CO_2/SO_2 molar ratio, 26.7 to 39.7 for the H_2O/SO_2 molar ratio and 2.0 to 3.1 for the H_2O/CO_2 molar ratio. These molar ratios were similar to those measured by Shinohara et al. (2008) in 2005 and 2006 and by La Spina et al. (2010) during a survey carried out on July 21, 2008, thus only about one month before our measurements. According to those authors, Mt. Etna crater gas compositions can show large variations, which are dependent on the level of volcanic activity (Aiuppa et al. 2009; Edmonds et al. 2010; Arpa et al. 2013), in particular as regards the CO_2/SO_2 molar ratio. The continuous and large gas emissions from Mt. Etna suggest direct magmatic degassing with negligible influence from hydrothermal degassing.

The H_2S/SO_2 molar ratio ranged from 0.13 to 0.14. These values were much higher than those reported by Aiuppa et al. (2005, 2007), probably due to the higher level of volcanic activity at Mt. Etna during our sampling. Total CO_2, H_2O and H_2S emissions released by Etna's volcanic plume during this study have been calculated by multiplying the observed SO_2 emission rates (Table 1) by the average observed CO_2/SO_2, H_2O/SO_2 and H_2S/SO_2 mass ratios, respectively. Thus, the estimated H_2O, CO_2 and H_2S emission rates from Mt. Etna's volcanic plume were 220,000 $\pm$ 100,000 t day^{-1}, 35,000 $\pm$ 16,000 t day^{-1} and 510 $\pm$ 240 t day^{-1}, respectively.

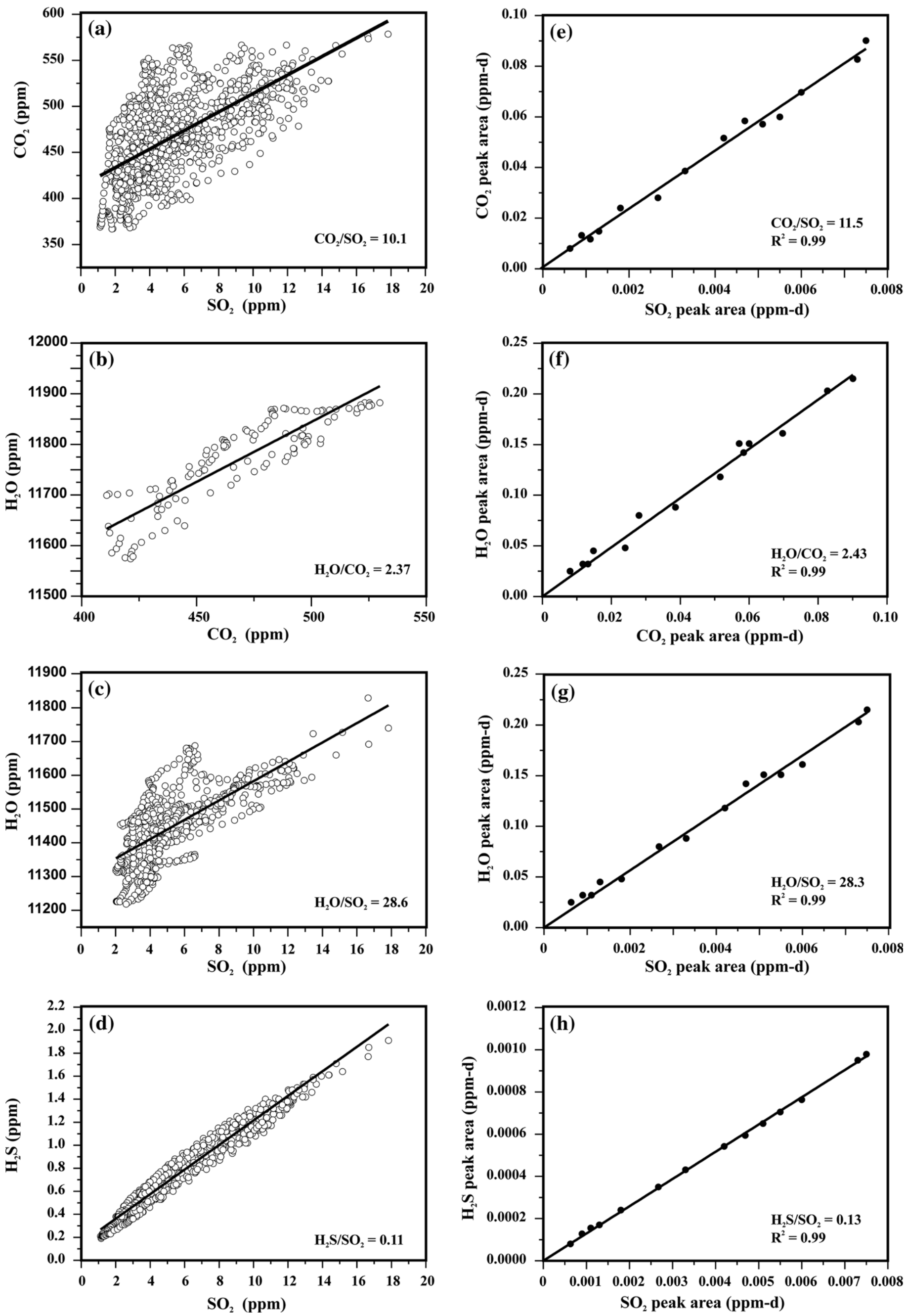

Fig. 7 Results of crater gas measurements at Voragine crater, Mount Etna, on October, 22, 2008. Correlations between **a** CO_2 and SO_2 concentrations, **b** H_2O and CO_2 concentrations, **c** H_2O and SO_2 concentrations, **d** H_2S and SO_2 concentrations, **e** CO_2 and SO_2 peak areas, **f** H_2O and CO_2 peak areas, **g** H_2O and SO_2 peak areas and **h** H_2S and SO_2 peak areas

5 Discussion

Allard et al. (1991) were the first to estimate both the plume and the diffuse CO_2 emissions from Mt. Etna. They found an extensive surface degassing of magma-derived CO_2 occurring in the upper part of the volcanic cone and reported a significant diffuse CO_2 flank degassing rate (55,000 t day^{-1} ± 30 %), which was in the same order of magnitude as that emitted from the crater plume (36,000 ± 7000 t day^{-1}; averaged value). However, D'Alessandro et al. (1997) later reported that the above diffuse CO_2 output was greatly overestimated, giving a new value of about 2800 t day^{-1}, after removal of the contribution from biogenic CO_2.

Even if the diffuse CO_2 efflux data presented herein are consistent with previous studies carried out at Mt. Etna (Allard et al. 1991; Burton et al. 2013), our estimated output of diffuse and plume CO_2 differs from previous studies. In this work, 20,000 ± 400 t·day^{-1} of diffuse CO_2 emission are computed for the entire studied area. This value is 37 % of that estimated by Allard et al. (1991) as representative of extensive surface degassing of magma-derived CO_2 from Mt. Etna. If we take into account only the diffuse CO_2 portion ascribed to a deep-seated origin (i.e., 4500 t day^{-1}), we find that this value is only 8 % of that reported by Allard et al. (1991), but it is in the same order of magnitude 1.65 times higher than the value reported by D'Alessandro et al. (1997).

Consistent with these studies, our results show that the amount of CO_2 released by crater degassing at Mt. Etna exceeds significantly that released by diffuse emissions. This is also in line with observations carried out at other volcanoes with strong and recent magmatic activity, such as Kilauea and Piton de la Fournaise, characterized by intense eruptive activity but weak diffuse degassing (Toutain et al. 2002). Taking into account the total diffuse CO_2 emission, the diffuse/plume CO_2 emission ratio at Mt. Etna is 0.57. However, considering only the endogenous fraction of CO_2 diffuse degassing, the diffuse/plume CO_2 emission ratio during the studied period is ~0.12. In any case, these values are similar to those calculated for volcanoes in frequent eruptive state (ratios lower than 1, Fig. 8). Conversely, much higher ratios were found at volcanoes with much lower eruptive rates: ~1.5 at Sierra Negra volcano (Galapagos Islands, Padrón et al. 2012); ~58 at Reykjanes (Iceland, Fridriksson et al. 2006). These findings allowed defining a relationship between the diffuse/plume ratio of CO_2 emissions at some basaltic volcanoes of the world and the time elapsed since their last eruption. Figure 8 shows the correlation between the two parameters, which confirms the plausible use of the diffuse/plume CO_2 ratio as indicator of the current state of volcanic activity.

The average CO_2 plume emission rate from Mt. Etna's crater degassing (35,000 t day^{-1}) fell in the range of the highest values recorded by Aiuppa et al. (2008) during the period 2005–2007 and ascribed by those authors to pre-eruptive degassing of a deep magma on its way to the surface. Lastly, the average crater H_2O emission rate (about 220,000 t day^{-1}) was more than an order of magnitude higher than that measured by Aiuppa et al. (2008). The explanation for the high values of CO_2 and H_2O emission rates measured during our survey probably is in the different location of the multisensor measuring device used in this work and/or to the different intensity of volcanic activity ongoing at the time of our measurements. In October 2008, actually, a sustained long-standing effusive activity was occurring from a flank fissure that was probably connected with a relatively large magma storage volume located deep beneath the central craters of the volcano (Aiuppa et al. 2010), as suggested also by the remarkable volume of erupted lava during the 2008–2009 eruption (68 × 10^6 m^3, Harris et al. 2011). Conversely, the data of Aiuppa et al. (2008) were collected during periods of quiescence (March 2005 to July

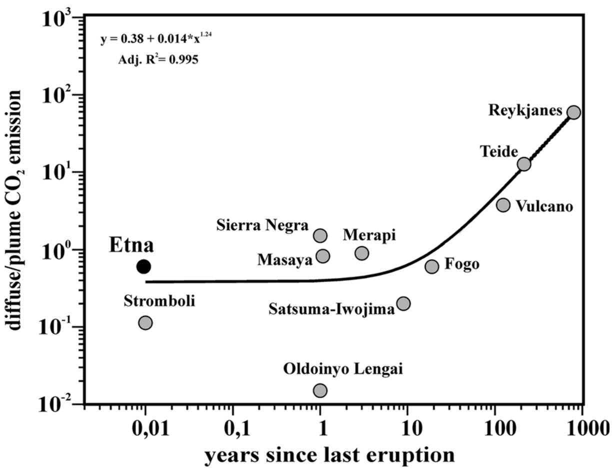

Fig. 8 Relationship between diffuse and plume CO_2 emission mass ratio versus years since the last volcanic eruption at several basaltic volcanoes of the world. Data from Burton et al. (2013), Carapezza et al. (2011), Mori et al. (2001), Padrón et al. (2012), Fridriksson et al. (2006) and this work. The plot shows that as time goes by since the last eruption, the diffuse fraction of total degassing from volcanoes increases until becoming dominant over plume degassing

2006, August 2006) alternated with short-lived or paroxysmal eruptions at the SEC (July 2006, September–December 2006), when small batches of magma (the total erupted volume of lava during 2006 was only 39 × 10^6 m^3, Harris et al. 2011) accumulated in a shallow storage volume just underneath this subterminal crater. This could imply release of magmatic H_2O mostly through the SEC, rather than through Mt. Etna's central craters.

Liuzzo et al. (2013) reported a stable degassing phase between the end of 2008 and July 2009. Aiuppa et al. (2008, 2010) reported volcanic gas plume CO_2/SO_2 ratio measurements during the 2006 and 2007–2008 activities of Mt. Etna. They found that low CO_2/SO_2 molar ratios (generally <7) were typically observed in the days prior, during and after the main paroxysmal episodes of the southeast crater. However, higher CO_2/SO_2 molar ratios characterized quiescent periods between paroxysmal episodes, with the highest ratios being recorded during pre-eruptive ascent of CO_2-rich magmas (Aiuppa et al. 2008). During our study, the average CO_2/SO_2 molar ratio was 11.5, reflecting relatively deep degassing of a magma batch stored beneath Mt. Etna.

Diffuse H_2S degassing at Mt. Etna was confined exclusively to the summit area of the volcano, where an intense plume emission was also present. The absence of measurable emission of H_2S in most of the study area is probably due to scrubbing processes affecting H_2S, such as dissolution into groundwater and/or precipitation from gas–water or gas–water–rock reactions (Symonds et al. 2001). Scrubbing of H_2S during its ascent toward the surface of the volcano is much more important and efficient through the flanks of the volcano than around active craters. In the latter, advective transport of volcanic gases minimizes their shallow interactions with the surrounding environment. In fact, the average CO_2/H_2S emission ratio (with deep CO_2 emission) shows a much higher value for diffuse degassing (~11,100) than for plume degassing (~68). Very few diffuse H_2S emission studies by direct measurements in volcanic/hydrothermal areas have been reported to date. Carapezza et al. (2012) studied the diffuse H_2S emission at two small areas (6400 and 8200 m^2, respectively) of Central Italy affected by permanent and high H_2S emissions from hydrothermal reservoirs, such that the health-risk threshold of H_2S in ambient air (10–15 ppm) was frequently exceeded. That study depicted very high normalized diffuse H_2S emission values (>5000 kg day^{-1} km^{-2}), but the geological and geochemical characteristics of the studied areas cannot be compared with those of Etna; thus, no direct correlation can be attempted with the data discussed in this work. Hernández et al. (2012) performed an extensive study at the Hengill volcanic system (Iceland) and found a very low normalized diffuse H_2S emission value ($\sim$0.05 kg day^{-1} km^{-2}). This value is lower than that reported here for the summit and the TDF areas at Mt. Etna ($\sim$45 kg day^{-1} km^{-2}, over a surface of 9.1 km^2), but the higher level of volcanic activity at Mt. Etna during our sampling was likely responsible for its higher diffuse H_2S emission rate as it was for its high crater H_2S emission rate. Actually, the value of about 510 t day^{-1} measured during our surveys is much higher than that previously reported for crater emissions on Mt. Etna (5–113 t day^{-1}, Jaeschke et al. 1982; Aiuppa et al. 2005). This apparent underestimation could be explained because our estimate is based on the total SO_2 crater flux, which includes the NE crater. However, according to Aiuppa et al. (2007), the SO_2/H_2S ratio measured at NE crater is much lower ($\sim$20) than that at the Voragine ($\sim$100), and because the SO_2 flux from NE crater was roughly 2/3 that of the Voragine on July 21, 2008 (La Spina et al. 2010), then the main contribution of H_2S to the total output of this gas measured near the time of our survey could be that of the NE crater, where we actually did not make H_2S measurements.

Notsu et al. (2006) proposed a five-stage evolutionary model for the release of volcanic gas based on the relationship between magma behavior (level of volcanic activity) and degassing pattern (diffuse vs. plume CO_2 emission). This model represents an important approach to estimate both plume and diffuse emissions from different volcanoes in a similar state of activity. Based on this model, Mt. Etna should be considered to be in Stage III during the period of our study: magma reaches the surface, and volcanic activity is high, with instantaneous release of a large amount of volcanic gas and ash as a plume from summit craters and low diffuse degassing throughout the volcanic edifice. However, Mt. Etna exhibited a high plume CO_2 emission (35,000 t day^{-1}) and relatively high diffuse CO_2 emission (20,000 t day^{-1}) even if we take into account only the endogenous contribution (4500 t day^{-1}). Other volcanoes in the same stage, like Popocatepetl, México, provide an extreme example of negligible diffuse CO_2 emissions of magmatic origin throughout its huge volcanic edifice (Varley and Armienta 2001) despite impressive peak emissions of up to 390,000 t day^{-1} of CO_2 from the summit crater (Goff et al. 2001). Figure 8 shows a good relation with the model proposed by Notsu et al. 2006. Volcanoes with a recurrent eruptive period shorter than 10 years (hence considered very active volcanoes) seem to show a diffuse/plume ratio close to 1, whereas those with a longer recurrent eruptive period (>100 years) show a clear exponential increase of this ratio. Assuming that timescales of volcanic events generally differ considerably among different volcanoes, because the recurrence time of eruptions ranges from several years to more than 100 years and the duration of each stage in an eruptive cycle varies case by case (Notsu et al. 2006), the diffuse/plume CO_2 emission ratio seems to be a good indicator of volcanic degassing stages and therefore of volcanic activity. However, differences in the CO_2 emission ratio between volcanoes that are in a similar volcanic stage suggest that other factors must be taken into account when estimating diffuse emissions. Apart from the specific geological and volcanic structural features of each particular volcano, such as type of magma (i.e., Oldoinyo Lengai, with magmas extremely rich in CO_2), undertaking extensive and detailed surveys all over a volcanic edifice seems to be a fundamental issue in order to constrain the extension and magnitude of diffuse degassing. It is well accepted that diffuse CO_2 degassing is an important contribution to the global geological CO_2 emission, but to obtain a realistic estimate of this process is difficult, due to the large areas to be surveyed and the large number of volcanoes to be studied (Burton et al. 2013). Although most of degassing volcanoes emit less gas than Mt. Etna, the observed differences between the estimated diffuse CO_2 emission rates in this study and previous reported data suggest that further surveys are needed also on other volcanoes than Mt. Etna in order to better assess whether diffuse CO_2 degassing can vary with time at a large scale.

Finally, to our knowledge, this study provides the first joint study to estimate at the same time diffuse and plume H_2S emission from a volcano. Our data show that diffuse H_2S emission (400 kg day^{-1}) is very small compared to H_2S plume emissions (510 t day^{-1}). This finding is reasonable since Mt. Etna is an open conduit persistently degassing basaltic volcano. If this is the case for most of volcanoes with crater plumes, diffuse H_2S emissions should be considered significant only in areas close to active summit vents, when estimating the total H_2S contribution from subaerial volcanoes.

6 Conclusions

The present work represents the first attempt to estimate the total budget of the main volcanic gas species emitted from Mt. Etna, with the inclusion of H_2S and considering also the diffuse degassing of CO_2 and H_2S. Actually, this work describes the largest diffuse CO_2 and H_2S degassing survey ever undertaken at Mt. Etna. Our results indicate that the summit area of Mt. Etna represents the main DDS and it is also the site of intense plume/fumarolic activity. This area was characterized by the highest CO_2 efflux values and by the only detectable values of H_2S efflux. Significant CO_2 effluxes were measured also in some limited areas of the eastern and southeast flanks of the volcano, as well as in some areas around the town of Paternò on its southwest flank, where mud volcano activity occurs (Giammanco et al. 2007). However, these emissions had a magnitude much lower than that of the diffuse emissions occurring in the summit area of the volcano. After removal of the biogenic contribution of CO_2 to the total diffuse degassing at Mt. Etna, the deep (volcanic/hydrothermal) CO_2 contribution was estimated at 4500 t day^{-1} over the entire surface of the volcano. The largest proportion of this degassing pertains to the summit area of Mt. Etna (1500 $\pm$ 200 t day^{-1} over a surface of 2.9 km^2), but smaller areas near the summit, characterized by marked fumarolic activity, also showed important diffuse CO_2 emissions. This is the case of the TDF area, where diffuse CO_2 output was estimated at 90 $\pm$ 8 t day^{-1} over a surface of 2.29 km^2.

These results allowed redefining in a more precise way the total budget of volcanic CO_2 from Mt. Etna: The summation of crater and deep diffuse CO_2 contributions was about 40,000 t day^{-1}, but almost 89 % of this amount was delivered by crater emissions.

The estimate of the H_2S budget here presented included, for the first time on Mt. Etna, also the diffuse H_2S contribution. The output of H_2S from diffuse emissions in the summit area of Mt. Etna (9.1 km^2), that is the only one with detectable values, was estimated at 400 $\pm$ 20 kg day^{-1}. Diffuse emissions of H_2S contributed about 0.08 % of the total H_2S budget, estimated at about 510 t day^{-1}.

The measured crater SO_2 emission rates during the study period (average of about 2100 t day^{-1}) were in the normal range of values detected on Mt. Etna after the 2001 flank eruption (Giammanco et al. 2013), whereas crater H_2O emissions were much higher than those previously estimated (Aiuppa et al. 2008). In general, the high values of gas output from Mt. Etna here reported were likely the effect of increased magmatic delivery to the volcanic system due to the 2008–2009 flank eruption, ongoing at the time of this survey.

The CO_2/H_2S emission ratio in volcanic plumes seems to be highly variable and depends both on the level of volcanic activity and on the redox state of the emitted fluids (Werner et al. 2013; Padrón et al. 2012; Carapezza et al. 2011; McGee et al. 2008). The value presented here ($\sim$68) was actually measured during an eruptive period.

This work produced new important data useful for the assessment of global volcanic gas budgets. The results here obtained stress the key role of monitoring total gas emissions from active volcanoes as a tool for the comprehension of the mechanisms of magmatic gas release at the surface, both in terms of interplay between tectonics and magmatism and in terms of time changes related to different levels of volcanic activity. The latter is a fundamental issue for the correct determination of volcanic gas budgets at active volcanoes, as it calls for long-term observation of volcanic degassing through different stages of volcanic activity in order to provide reliable estimates of gas output.

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