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Level of carbon dioxide diffuse degassing from the ground of Vesuvio: comparison between extensive surveys and inferences on the gas source

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ABSTRACT

An extensive campaign of diffuse CO_2 soil flux was carried out at the cone of Vesuvio in October 2006 with two main objectives: 1) to provide an estimation of CO_2 diffusely discharged through the soils in the summit area and 2) to evidence those sectors of the volcano where structural and morphological conditions could favour the gas output. The survey consisted of 502 measurements of soil CO_2 flux homogenously distributed over an area of about 1.8 km^2. Results of this survey were compared with those obtained during a similar campaign carried out by Frondini et al. in 2000, from which we have taken and reinterpreted a subset of data belonging to the common investigated area. Graphical statistical analysis showed three overlapping populations in both surveys, evidencing the contribution of three different sources feeding the soil CO_2 degassing process. The overall CO_2 emission pattern of 2006 is coherent with that observed in 2000 and suggests that a value between 120 and 140 t/day of CO_2 is representative of the total CO_2 discharged by diffuse degassing from the summit area of Vesuvio. The preferential exhaling area lies in the inner crater, whose contribution resulted in 45.3% of the total CO_2 emission in 2006 (with 62.8 t/day) and in 57.4% (with 70.3 t/day) in 2000, although its extension is only 13% of the investigated area. This highly emissive area correlated closely with the structural discontinuities of Vesuvio cone, mainly suggesting that the NW-SE trending tectonic line is actually an active fault leaking deep gas to the bottom of the crater. The drainage action of the fault could be enhanced by the "aspiration" effect of the volcanic conduit.

1. Introduction

Since early 1990s, geochemical surveys on soil diffuse degassing have been made at active and dormant volcanoes in several parts of the world, showing that, even during their quiescent state, volcanoes may release large quantities of gas to the atmosphere [Allard et al. 1991, Chiodini et al. 1996, 1998, Werner et al. 2000, Bergfeld et al. 2001, Brombach et al. 2001, Cardellini et al. 2003, Notsu et al. 2005]. Active faults or fractures act as preferential pathways for the escape of the fluids towards the surface [Sugisaki et al. 1983, Klusman 1993, Giammanco et al. 1997], being zones with higher permeability with respect to the unfractured surrounding rocks.

Carbon dioxide (CO_2) is the most common gas present with anomalous concentrations in the soils of active and quiescent volcanoes. In fact, CO_2 is the most abundant constituent of the non-condensable fraction of the magmatic gases and can be easily released by the magma for its low solubility in the magmatic melt at crustal pressure. Numerous studies have been focused on the soil CO_2 degassing from quiescent and active volcanoes with different aims of investigations: a) use of soil gas anomalies to detect active faults [Barberi and Carapezza 1994, Giammanco et al. 1997, Carapezza et al. 2009]; b) quantification of the CO_2 emission in the framework of the carbon budget emitted by a volcanic edifice [Baubron et al. 1990, Allard et al. 1991, Brantley and Koepenick 1995, Chiodini et al. 1996, 1998, 2001, Rogie et al. 2001]; c) association between high magnitude earthquakes and CO_2 emission [Salazar et al. 2002]; d) significance of the soil gas anomalies as pre-

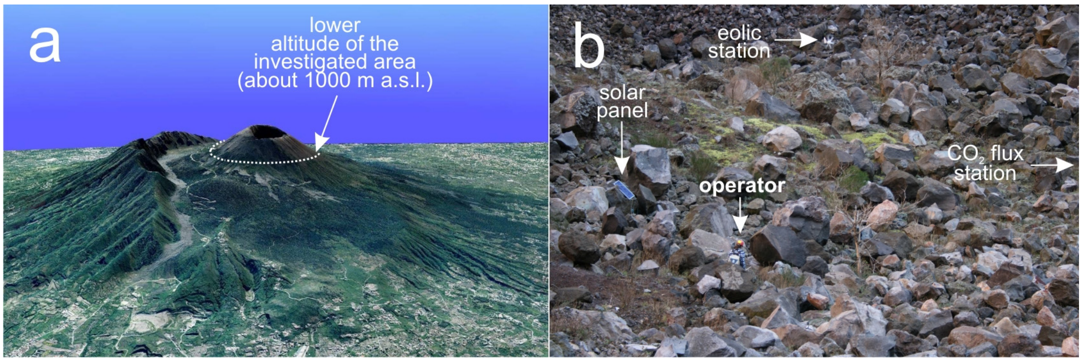

Figure 1. a) Perspective view (from NNE) of Vesuvio cone and Somma caldera (image elaborated by the Laboratorio di Geomatica e Cartografia of Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Vesuviano). Investigated area covers the summit cone, above the contour line of ~1000 m; b) bottom of Vesuvio crater, densely mantled by fallen lava blocks. Some devices forming the power system of the automatic CO_2 flux station (eolic power plant and solar panel) are also visible. Station is out of the picture.

cursor of volcanic eruptions [Carapezza et al. 2004]; e) estimation of the influence of environmental and meteorological parameters on CO_2 volcanic emissions [Granieri et al. 2003, Lewicki et al. 2007, Carapezza et al. 2009]; f) spatial and temporal variations of the diffuse CO_2 degassing process over an active volcano [Diliberto et al. 2002, Salazar et al. 2004, Granieri et al. 2006, 2010, Carapezza et al. 2011].

Independently from the goals of investigations, a geochemical survey on CO_2 soil degassing requires an appropriate number of field measurements and an adequate design of the sampling grid [Cardellini et al. 2003] in order to suitably estimate the total discharge of CO_2 and to define the spatial extension of the different degassing structures.

In a quiescent high risk volcano like Vesuvio, it is important to have a long data set of CO_2 soil flux data representing the background condition, in order to recognize any possible anomalous increase of CO_2 release reflecting an unrest possibly leading to volcano reactivation.

In this paper, we present a detailed study of CO_2 diffuse degassing from the whole cone of Vesuvio.

Vesuvio edifice has a regular conical shape truncated by a spectacular 450 m across and 330 deep summit crater (Figure 1a). External flanks of the cone are remarkably steep with average slopes ranging from 25° to 35°. In the upper part of the cone lavas and welded scoria are exposed, only covered by a thin layer of volcanic ash. Towards the lower part of the cone the unwelded pyroclastic cover thickens in correspondence of the gradual decrease in the slope. The presence of steep slopes, mantled by slippery products, and of natural obstructions (radial gullies and ravines) makes very difficult the practicability of the cone. Furthermore, the inner part of the crater is hazardous because of the frequent rock falls and occurrence of landslides from the subvertical walls, the removed large masses being recognizable on the bottom of the crater (Figure 1b). The rim only reveals a few narrow flat zones. Here, systematic measurements of CO_2 flux from the soil were carried out for monitoring purposes [Granieri et al. 2010]. Measurements along an array of 15 fixed points, encompassing roughly 1500 m^2 on the eastern sector of the rim, are repeated once a month since February 1998. In addition, in the bottom of the crater, an automatic soil CO_2 flux station was operational from August 1999 to November 2004, when it was definitely damaged by a large landslide.

Results of these long-term investigations are discussed in Granieri et al. [2010] and hereafter briefly summarized. Points inside the crater rim are characterized by high CO_2 flux with values progressively decreasing towards the rim. The spectral analysis of the 15-point array series has evidenced a dominant component with a period of about 19 months [Granieri et al. 2010] that is not a typical periodicity for any meteorological parameter. Indeed, CO_2 flux measured by the station at the bottom of the crater, is characterized by a dominant component with annual periodicity and flux values, on average, 5 times higher than those measured over the array of the rim [Granieri et al. 2010].

The first extensive diffuse CO_2 soil flux survey over the summit cone of Vesuvio was carried out in April-May 2000 and included 636 measurements [Frondini et al. 2004]. The study had the main objective to provide a first set of data on soil degassing at Vesuvio, to be used for the estimation of the total CO_2 emission from the cone and part of the Somma-Vesuvio caldera (~5.5 km^2). It also highlighted that CO_2 flux declines of three order of magnitude moving from the inner crater to the external flanks of the cone. During the same period (late winter-spring 2000) another investigation on the diffuse CO_2 degassing in the Vesuvian area was carried out by Aiuppa et al. [2004], but concentrated on the lower flanks of the Somma-Vesuvio down to the densely inhabited plain, thus excluding the summit cone.

In the present paper we present the results of a new

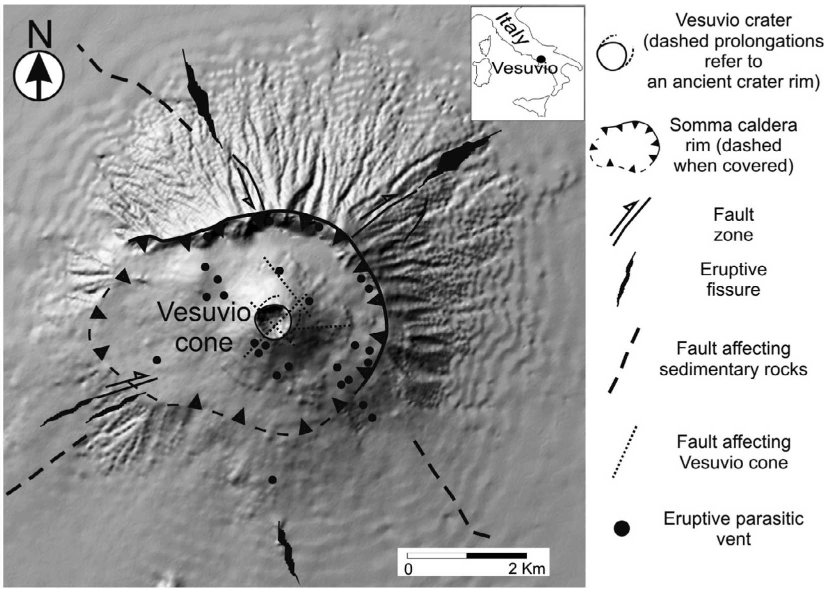

Figure 2. Structural sketch map of Somma-Vesuvio (modified from Bianco et al. [1998] and Ventura et al. [1999]).

extensive survey of CO_2 soil flux carried out on the summit cone of Vesuvio in October 2006. The campaign was carried out in the framework of the European civil protection exercise called MESIMEX (Major Event SIMulation EXercise) and it was integrated into a series of geological, geochemical and geophysical investigations to be carried out urgently on the volcano, following a simulated state of volcanic unrest, and aimed at checking how much time was needed to get reliable scientific results to complement the data provided by the permanent monitoring networks. Our survey was carried out in five days by four scientific teams of two operators each, using the same accumulation chamber methodology to measure the soil CO_2 flux. It consisted of 502 measurements covering an area of about 1.8 km^2 over the flanks of Vesuvio and in the bottom of the crater.

Flux data from October 2006 campaign are not directly comparable with those of April-May 2000, because of the different size of the investigated areas (5.5 km^2 in 2000 *vs* 1.8 km^2 in 2006). Then, a sub-set of 296 measurements was extracted from the April-May 2000 field campaign, in order to restrict the grid to the same area investigated in 2006.The two sets of measurements were processed with the same statistical and mapping approach.

2. Volcanological and structural setting of Somma-Vesuvio and geochemical background

The Somma-Vesuvio complex is a central composite volcano formed by the ancient stratovolcano of Mount Somma, topped by a multiple summit caldera, and by the more recent intracaldera cone of Vesuvio (Figure 2). Volcanic activity in the Somma-Vesuvio area began about 0.3-0.5 million years ago but the oldest outcropping products have an age lower than 39 ka [Santacroce et al. 2008]. The morphology of Mt. Somma is resulting from several collapses which caused the formation of the elliptical Somma caldera. The collapses occurred in several stages following four large plinian eruptions that occurred between 18 ka B.P. and A.D. 79 [Cioni et al. 1999]. The ring-fault scarps related to the collapses are well developed in the northern and eastern sector of the caldera whereas in the southern and western sectors of the volcano they are covered by the products of the post-A.D. 1631 activity [Santacroce and Sbrana 2003]. Mount Somma is basically constituted by lava flows and minor scoria fall/flow deposits. After the last A.D. 79 plinian eruption (the famous "Pompei" eruption), volcanism concentrated inside the Somma caldera, particularly in its southwestern sector. Here, the young cone of Vesuvio has grown after the A.D. 1631 sub-plinian eruption. Its most recent eruption occurred in 1944 after nearly 300 years of semi-persistent open-conduit activity. Vesuvio products include lava flows and pyroclastics emitted from the summit crater and lateral vents with a magma composition ranging from leucite tephrites to phonolitic tephrites [Santacroce et al. 2008]. At present, the cone is characterized by a few fumarolic emissions ($T<100°C$) and moderate seismicity [Del Pezzo et al. 2004].

Somma-Vesuvio complex lies on a main SW dipping NW-SE trending regional fault [Mostardini and Merlini 1986, Cassano and La Torre 1987], probably responsible for the dislocation of the sedimentary basement down to 6 km [Bianco et al. 1998]. A NE-SW trending regional fault system also affects the northeastern and the southwestern flank of the volcano (Figure 2), including the 1794 and 1861 'en enchelon' eruptive fractures and the submarine volcanic vents offshore Torre del Greco [Finetti and Morelli 1974]. On the sur-

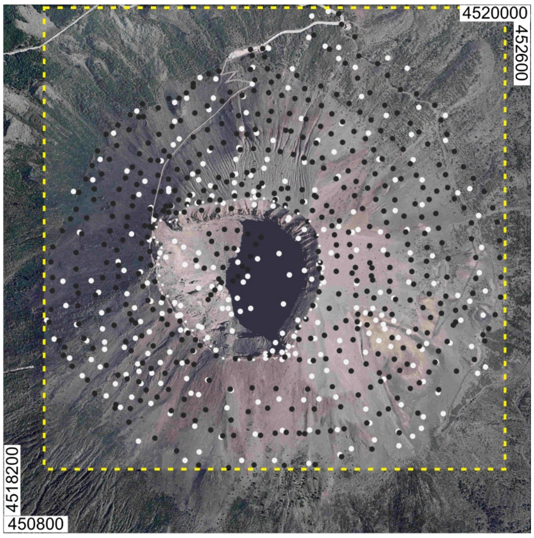

Figure 3. April-May 2000 (white dots) and October 2006 (black dots) measurements over the cone of Vesuvio. The simulation is defined over the squared area circumscribed about the circle of the more external samples (see text for explanation).

face, the NW-SE and NE-SW oriented structural discontinuities control the preferential alignment of faults, fissures, eruptive vents, valley floors [Santacroce 1987, Andronico et al. 1995]. Following some authors, the main NW-SE trending fault affects the recent cone of Vesuvio [Ventura et al. 1999], accounting for the morphological lowering of the southwestern side of the edifice [Bianco et al. 1998].

From a geochemical point of view, the present hydrothermal activity of Vesuvio is evidenced by a) large emissions of CO_2-rich groundwaters along the southern lower flanks of the cone [Federico et al. 2002, 2004, Caliro et al. 2005, Madonia et al. 2008]; b) fumarolic activity on the crater rim and at the bottom of the crater [Chiodini et al. 2001, Caliro et al. 2011]; c) soil diffuse discharge of CO_2 from some sectors of the recent cone [Granieri et al. 2003, Frondini et al. 2004, Granieri et al. 2010]. On the basis of a geochemical study of the bottom-crater fumaroles, Chiodini et al. [2001] suggested that these high-temperature surficial emissions are fed by a deep hydrothermal system characterized by the presence of NaCl brines. The total pressure estimation of the hydrothermal system (260 bar to 480 bar) is poorly constrained for the uncertainty in the salt content of the deep fluids [Chiodini et al. 2001]. Consequently, the depth of the hydrothermal reservoir would range from 2.5 to 5.0 km, assuming a hydrostatic regime. In any case, it is probably hosted within the carbonate sequence, which is present beneath Vesuvio at depth > 2.0 km [Cassano and La Torre 1987, Berrino et al. 1998]. The integrated indications of gas equilibria [Chiodini et al. 2001] and C-isotopic exchanges [Fiebig et al. 2004] leave little uncertainty on the thermal state of deep Vesuvio reservoir fluids, resulting in the interval between 450°C and 500°C.

3. Field work

In the October 2006 survey 502 measurements of CO_2 soil flux were carried out over an area of ~1.8 km^2, homogeneously covering the cone of Vesuvio. The field work was undertaken during a 5-day dry period (October 17 to 21) with no significant variation of the atmospheric conditions. CO_2 flux measurements were acquired with the accumulation chamber method [Chiodini et al. 1996, 1998, Carapezza and Granieri 2004]. The area investigated in October 2006 was only a restricted sector of the one investigated during the previous April-May 2000 campaign, when 636 measurements were made on Vesuvio cone and part of the Somma-Vesuvio caldera over an area of about 5.5 km^2 [Frondini et al. 2004]. Because of the different size of the investigated areas, the two data sets are not directly comparable. Therefore of the April-May 2000 survey, we considered hereafter only the 296 measurements made on the same 1.8 km^2 area investigated in 2006 (Figure 3).

4. Preprocessing and processing of CO_2 flux data

The measurement of the CO_2 flux is a function of the geometry between sensor and terrain surface. On a sloping terrain, the flux intercepted by a surface element is actually determined by the projection of the surface element on the horizontal plane (Figure 4a). Therefore, the measured flux (FCO_2^{meas}) should be normalized (FCO_2^{norm}) in order to remove the topographic effect of the terrain, according to the following formula:

$$FCO_2^{norm} = (A/A_o) * FCO_2^{meas} = [(A/(A\cos\alpha)] * FCO_2^{meas}$$

where A and A_o are the areas of the measured surface and of its projection on the horizontal plane, respectively, and α is the slope of the terrain.

The investigated sector of Vesuvio cone (Figure 4b) has an average slope of 30.6 degree, with some narrow flat zones on the crater rim and in the bottom of the crater (Figure 4b). The crater is delimited by subvertical walls (80°-85°) that are joined to the rim by remarkably steep slopes (from 50° to 75°). Actually, the measured flux at each location was divided by the cosine of the slope angle in that point, derived from a 10-m resolution digital elevation model [Tarquini et al. 2007]. The cosine correction yields an increase of the flux of 25.3% (corresponding to a mean slope of 28.8°) and the arithmetic mean of October 2006 measurements changes from 64.5 g m^{-2} d^{-1} to 80.8 g m^{-2} d^{-1}. Also the April-May 2000 measurements were corrected for the topography and the mean value changes from 68.2 g m^{-2} d^{-1} to 87.2 g m^{-2} d^{-1} (i.e. an increment of 27.8% for a mean slope of 29.6°). The main statistics of 2000 and 2006 surveys are summarized in Table 1.

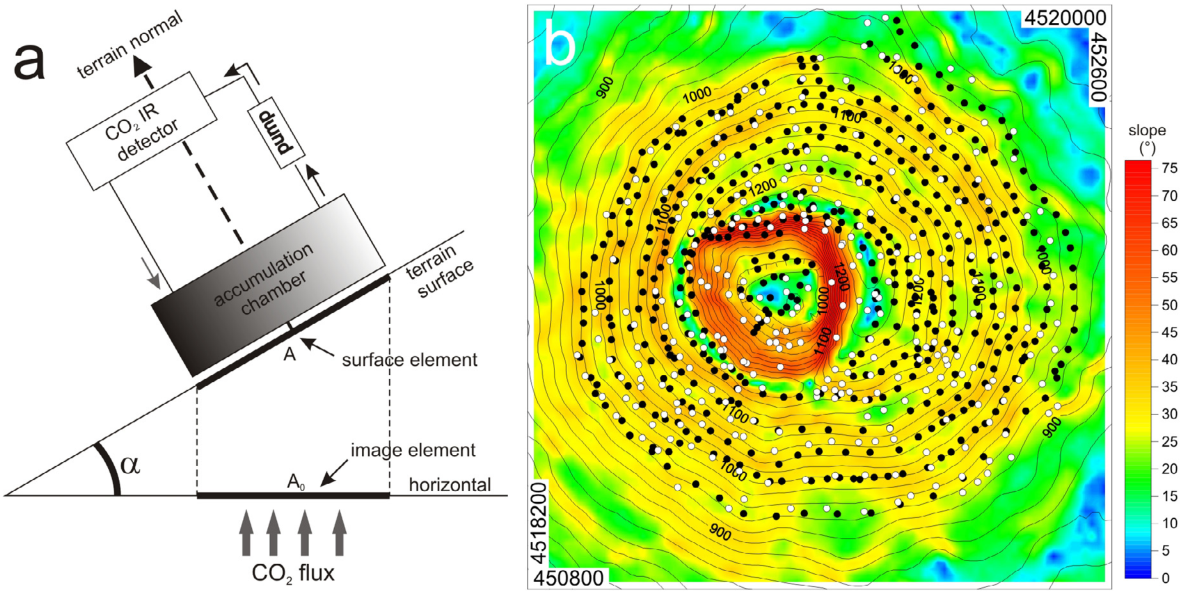

Figure 4. a) Effect of the topography on the accumulation chamber measurement for sloped terrain; b) slope of Vesuvio cone (degree) from the digital elevation model of Tarquini et al. [2007].

In order to recognize the unimodal or the polymodal distribution of measurements, the CO_2 flux data have been plotted on logarithmic probability plots. On such graphs a single population plots as a straight line, two log-normally distributed populations, partially overlapped, produce the typical z-shaped curve and *n* log-normal populations result on a more complex curve with *n-1* points of inflections [Sinclair 1974]. Afterwards the graphical statistical approach (GSA) [Chiodini et al. 1998] has been applied in order to partition the resulting complex distribution into the individual log-normal populations. Decomposing is a useful tool in the analysis of soil geochemical data for evidencing the presence of an anomalous high-value population, a low-value background population and, if exists, an intermediate group containing known proportion of the two end-member populations [Chiodini et al. 1998, Cardellini et al. 2003]. The proportion and the statistical parameters of each log-population have been computed by means of the Sinclair procedure [Sinclair 1974]. Finally, the Sichel's *t* estimator [David 1977] has been used to transform the mean and the standard deviation of the log-normal distributions into the corresponding arithmetic values, assigning to each population the mean and the range of the mean within the 95% confidence interval.

Survey	Meas. (#)	Invest. area (km^2)	Arith. mean ($g\ m^{-2}d^{-1}$)	Min-Max ($g\ m^{-2}d^{-1}$)
October 2006 *	502	1.80	80.8	0.1 – 10866
April-May 2000 *	296	1.80	87.2	0.1 – 7249

Table 1. Statistics of the CO_2 flux measurements on the Vesuvio cone. *: corrected for the topographic effect (see text).

For the mapping of the CO_2 flux data we used the sequential Gaussian simulation procedure (sGs) from SGSim software [Deutsch and Journel 1998], following the approach described by Cardellini et al. [2003]. The basic idea of such a procedure is the realization of a high number of spatial equiprobable representations of the studied parameter (soil CO_2 flux in this case), accounting for the basic statistics (histogram) and spatial features (semivariogram model) of the data. It is worth noting that the algorithm by SGSim software simulates the values of the parameter over a rectangular (or squared) area. In the case of roughly circular distribution of the samples, the simulation is defined over the squared area circumscribed about the circle of the more external samples (Figure 3). Considering that simulations are performed over a larger area, comprising four not sampled corners, the values of the estimations are higher than the actual ones and cannot be used as a measure of the total emission. Therefore, the estimation of the total CO_2 has been calculated by a volume integration algorithm applied over the contour grid derived by the sGs procedure and opportunely blanked in correspondence to the external measurements.

5. Results

5.1. Data statistical analysis

The distributions of October 2006 and April-May 2000 measurements are shown in Figure 5. On a logarithmic probability plot, both distributions produce a curve with two inflection points, deriving by the combination of three log-normal populations, A, B and C. Table 2 reports the proportion (percent) and the statistical parameters for each population, following the Sin-

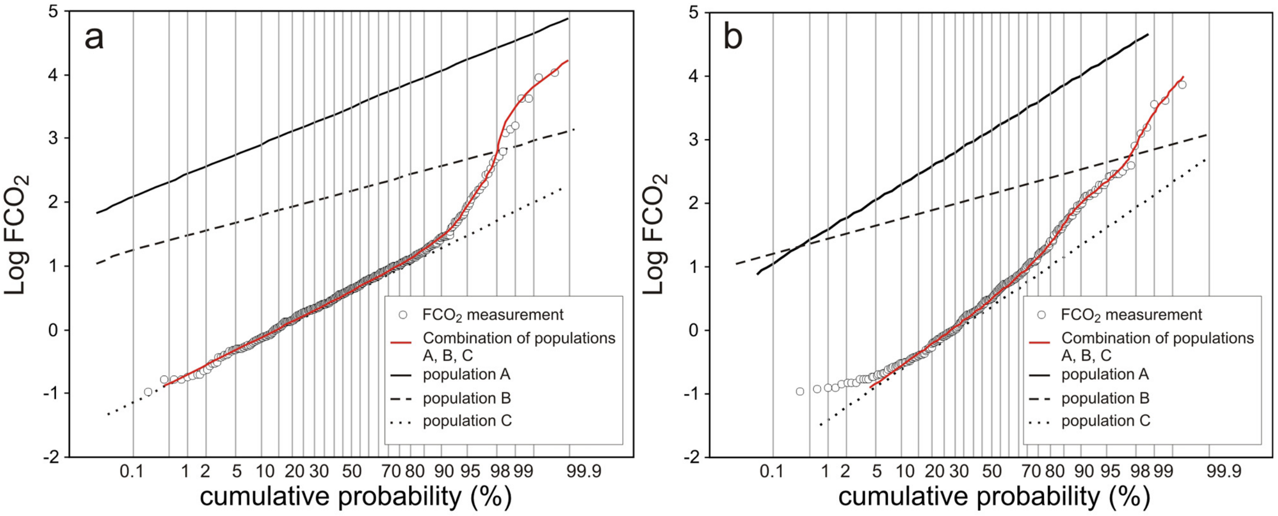

Figure 5. Probability plot of CO_2 flux for a) October 2006 and b) April-May 2000 survey. The figure shows the original samples (open dots), the portioned populations (straight lines) and the computed distribution from the combination of the theoretical populations (coloured lines).

Survey	Population	Proportion (%)	Arith. mean ($g\ m^{-2}d^{-1}$)	95% confidence interval ($g\ m^{-2}d^{-1}$)
October 2006	A	2	2043.8	1259.5 – 5440.5
(samples = 502)	B	3	121.3	91.4 – 191.6
	C	95	3.2	1.8 – 9.2
April-May 2000	A	3	747	306 – 4082
(samples = 296)	B	9	107	85 – 151
	C	88	1.7	1.2 – 2.8

Table 2. Statistical parameters of partitioned CO_2 flux populations.

clair procedure. The goodness of the estimates was checked by combining the calculated proportions of A, B and C populations into a ideal mixture to compare with measured data (Figure 5a,b, coloured lines). Ninety-five percent of October 2006 samples, population C, are characterized by a low CO_2 flux (mean value of 3.2 g $m^{-2}d^{-1}$), while only 2% of samples form the high-flux A population (mean value of 2043.8 g $m^{-2}d^{-1}$) and the remaining 3% of data, population B, are characterized by intermediate values of CO_2 flux (mean value of 121.3 g $m^{-2}d^{-1}$).

The distribution of the April-May 2000 samples is comparable to the one observed in the more recent campaign (Table 2). Three percent of the measurements belong to the high-flux population (mean value of 747 g $m^{-2}d^{-1}$), 9% form the intermediate population (mean of 107 g $m^{-2}d^{-1}$) and the remaining 88% form the low-value population (1.7 g $m^{-2}d^{-1}$).

The low values of the populations C are consistent with a degassing process deriving from the local weak biological activity of the soil [Granieri et al. 2010]. In contrast, the large CO_2 fluxes related to the populations A suggest a deep volcanic-hydrothermal source [Frondini et al. 2004, Granieri et al. 2010]. In addition, the intermediate populations B come out by the interaction between a deep CO_2-enriched source and air lightly enriched in CO_2 which enters laterally into the fractured cone [Chiodini et al. 2001, Granieri et al. 2010], as afterwards described.

5.2. Mapping and spatial pattern of the CO_2 flux

Sequential Gaussian simulation procedure was applied to map the CO_2 flux data of the two surveys. Simulations were performed over the investigated area of ~1.8 km^2, discretized into 12,547 squared cells (12×12 m) for October 2006 survey and 12,400 cells (12×12 m) for April-May 2000 campaign. Average maps resulting from 100 simulations are reported in Figure 6.

Despite the possible sources of data difference, the CO_2 flux maps show some correspondences between the October 2006 and April-May 2000 surveys. The maps indicate that the main area releasing CO_2 is the inner slope of the crater. Furthermore, the inner crater anomaly of October 2006 is limited to a very restricted

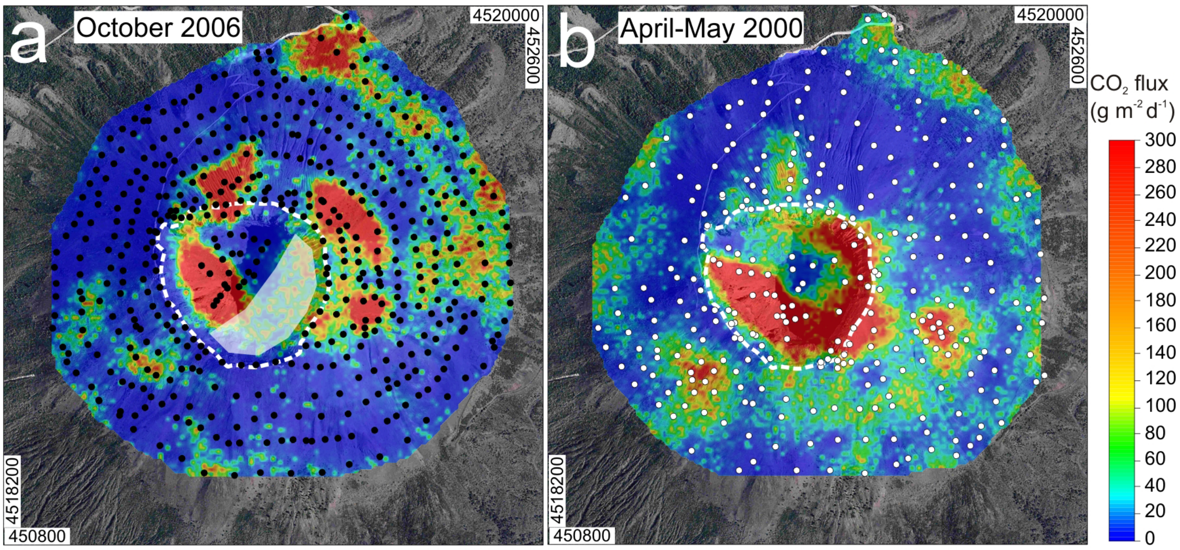

Figure 6. CO$_2$ flux maps of a) October 2006 and b) April-May 2000. Maps are the mean of 100 equiprobable representations. Dashed curve indicates the rim of the crater while the dots are the measurement point locations. White area in a) highlights the sector of the crater not covered by measurements during the October 2006 survey.

zone with a rough NW elongation (Figure 6a) that corresponds to the direction of the main fracture of the cone through which the deep gas probably rises to the surface [Frondini et al. 2004]. Indeed, the highly emissive ring-like zone of the April-May 2000 map mantles the whole inner slope of the crater, excluding the northern sector, and steps over the rim in limited sectors only (Figure 6b). Measured CO$_2$ fluxes as large as 100 g m^{-2}d^{-1} occurred in three localized areas on the external flanks of the cone, adjacent to the crater rim, in both maps, but with different extension and location (Figure 6). In contrast, the emissive area on the northern slope of the cone at relatively low altitude (around the 1000 m contour line) observed during October 2006 was not present in April-May 2000, when the CO$_2$ emission was there weak (Figure 6). The maps also reveal that the centre of the crater has a low level of CO$_2$ degassing, a behaviour observed also at La Fossa crater of Vulcano [Granieri et al. 2006], probably for the more impervious feature of the lavic infilling compared with the hosting rocks.

The areal CO$_2$ discharge was calculated by applying a volume integration algorithm over a file grid blanked in correspondence to the external measurements. The estimated CO$_2$ output was 122.5 t/day for April-May 2000 survey and 138.7 t/day for October 2006 campaign. The inner slope of the crater covers only 13% of the investigated area but contributed for 45.3% to the total CO$_2$ flux of the cone in 2006 (with 62.8 t/day) and for 57.4% (with 70.3 t/day) in 2000, with the major contribution from A1 (October 2006) and B1 (April-May 2000) high-CO$_2$ flux zones (Figure 7). On the external flanks of the cone, the A2, A3, and A4 (October 2006) emissive zones, close to the crater rim, emit 11.6 t/day, 16.6 t/day and 5.4 t/day, respectively (Figure 7). The contribution of the more external A5 (October 2006) emissive zone is 8.9 t/day. During April-May 2000 the contribution of the external flanks of the cone to the total CO$_2$ budget was lower than in October 2006 (42.6% or 52.2 t/day *vs* 54.7% or 75.9 t/day) with a modest contribution from B2 (0.5 t/day), B3 (5.0 t/day) and B4 (3.6 t/day) emissive areas.

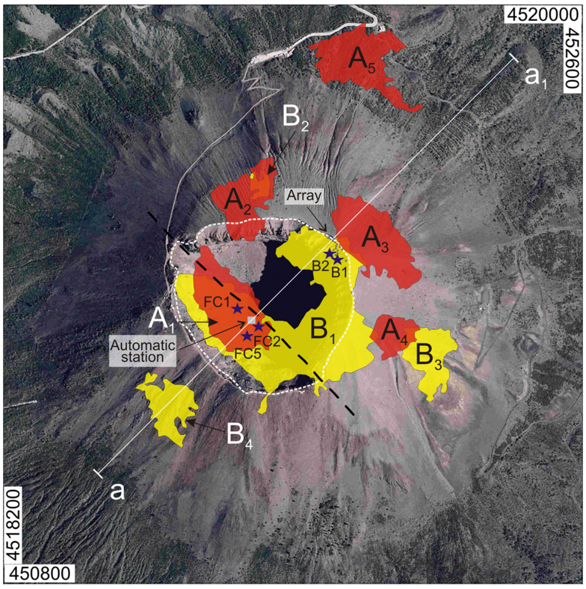

Figure 7. Sketch of the more emissive areas at Vesuvio cone. Each area contours the zone were CO$_2$ flux is higher than 100 g m^{-2}d^{-1}. Red colour refers to October 2006 survey (**A$_n$** areas), yellow colour to the April-May 2000 survey (**B$_n$** areas). The location of the fumaroles in the bottom of the crater (FC1, FC2 and FC5) and over the rim (B1 and B2) is also shown, such as the position of the automatic station and of the 15-point array. Bottom crater fumaroles have a temperature of about 95° (i.e. the T of the satured steam at the altitude of the crater), whereas rim crater fumaroles have temperature of 62°C to 75°C. Finally, a-a$_1$ line is the trace of the cross section reported in Figure 9.

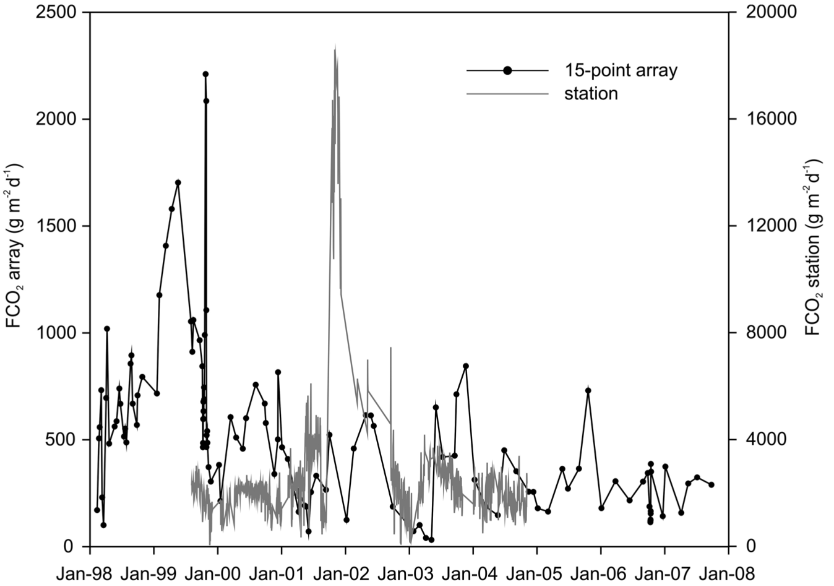

Figure 8. Soil CO_2 flux measured in the bottom of the crater (station series) and over the rim of the crater (15-point array series). Note the different scale on the left and on right axis (after Granieri et al. [2010]).

6. Discussion and conclusions

The results of the two CO_2 soil flux surveys of October 2006 and April-May 2000 indicate the occurrence of a large diffuse degassing from the soils of the volcano, with comparable values of the total CO_2 output estimated for the two campaigns but with different contribution from the more emissive sectors. In order to compare the results of the two investigations, it is important to keep in mind some factors that may have contributed to differences between the surveys. First of all: a) the different number of measurements made during the two investigations, and hence the different sampling density (2.78 samples/ha in October 2006 and 1.64 samples/ha in April-May 2000, where 1ha = 10000m^2); b) the different timeframe of the campaigns, as flux measurements were collected within a few days in October 2006 and during two months in 2000, with variations in weather conditions; c) the seasonal-dominant component in the soil CO_2 flux at Vesuvio [Granieri et al. 2003, 2010], mainly in the highly emissive bottom crater area, so that some fluctuations could be related to the different time of the year of the survey (spring of 2000 and autumn of 2006).

Despite the possible sources of data difference, both investigations provided a similar value of total CO_2 output, resulting in 122.5 t/day in April-May 2000 and 138.7 t/day in October 2006. Therefore, we consider a value between 120 and 140 t/day of CO_2 as representative of the total CO_2 discharge by diffuse degassing from the summit area of Vesuvio (1.8 km^2) in the present condition of rest of the volcano. We argue that this minor difference can be due to the natural temporal variability of gas flow (factors a-c, see above), rather than to significant variation in the overall degassing of the volcano. We estimated a total CO_2 output that is slightly lower than the previously published value referred to the same investigated area. In their study, Frondini et al. [2004] calculated a total CO_2 emission of 151 t/d by means of 291 CO_2 flux measurements. In our opinion, the disagreement could be explained by the different elevation model employed to correct the CO_2 flux data for the topographic effect. The cosine correction applied by Frondini et al. [2004] yielded an increase of the CO_2 flux from 69.1 g m^{-2}d^{-1} to 98.2 g m^{-2}d^{-1} (~ 42%) implying an average slope of the cone of 49°. This value seems too large for the flanks of Vesuvio, where the recent digital elevation model of Tarquini et al. [2007] indicates a mean slope of 30.6° (as mean of ~18000 cells, 10×10 m) that agrees with the mean slope of the 502 points of October 2006 (28.8°) and the 296 points of April-May 2000 (29.6°) surveys.

The existence of three overlapping populations for CO_2 flux in both surveys is clearly related to different sources feeding the degassing process in the volcanic edifice. The high flux population (population A) comprises a low percentage of the total samples (2% in October 2006 and 3% in April-May 2000), all clustered within the crater in zones where active faults and/or the permeability contrast between the (impervious) lava filling the conduit and the (more pervious) hosting rocks preferentially convey the volcanic-hydrothermal gas rising from depth. In contrast, the population with extremely low flux data (population C) includes the majority of the samples (95% in October 2006 and 88% in April-May 2000) distributed over the flanks of the cone. Here, the poorly developed organic soils accounts for the low mean flux values (1.7 g m^{-2}d^{-1} in April-May 2000 and 3.2 g m^{-2}d^{-1} in October 2006) that are somewhat

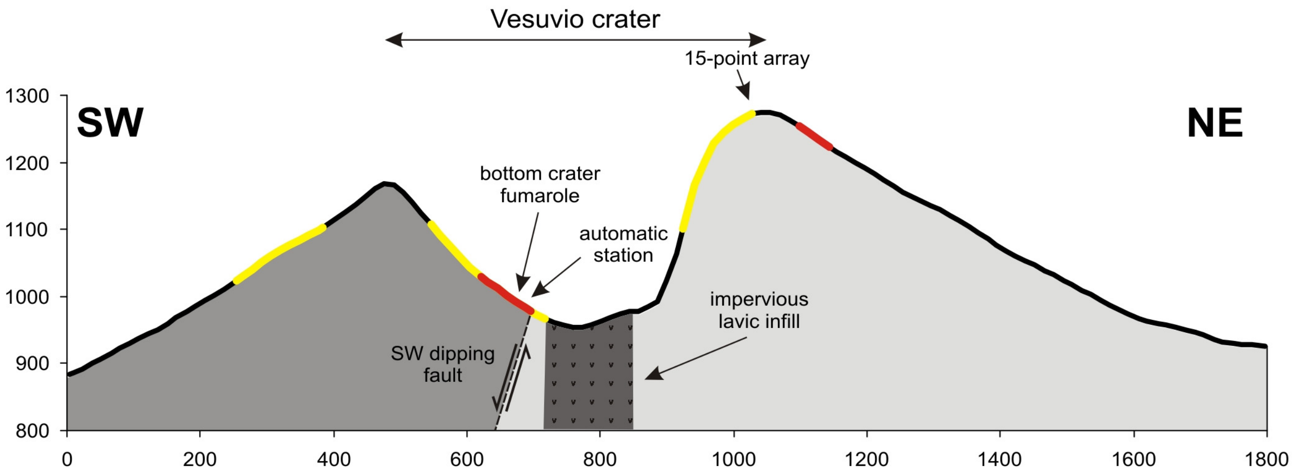

Figure 9. Cross section along the a-a1 trace of Figure 7. Red thick strokes correspond to sectors with high-CO_2 emission in October 2006, yellow in April-May 2000.

lower than those typically reported for other volcanic soils (from 10 to 40 g $m^{-2}d^{-1}$) [Chiodini et al. 2001] but similar to those found in the crater area of Stromboli [Carapezza et al. 2009]. Intermediate population (B population) probably reflects the interaction between the rising deep CO_2 and air, forced into the highly fractured lavas and pyroclastic deposits of the cone by the wind. In support of this interpretation, the evidence that the same process is responsible for the differences of the fumarolic system in the bottom and over the rim of the crater. In the bottom-crater high-temperature fumaroles (FC1, FC2, FC5; Figure 7) air is virtually absent (N_2/Ar > 200) [Caliro et al. 2011] and the typical composition is representative of a deep hydrothermal system [Chiodini et al. 2001, Caliro et al. 2011]. Indeed, the fumaroles of the crater rim (B1 and B2; Figure 7) have lower temperature and a composition characterized by atmospheric air, variably enriched in CO_2 of deep origin (0.2% - 2%) [Caliro et al. 2011].

Results of 2000 and 2006 surveys coherently indicate that the highest CO_2 exhaling area of Vesuvio is the inner crater that massively contributes to the total degassing budget. Granieri et al. [2010] always suggested that the bottom of the crater is the preferential degassing area at Vesuvio, on the basis of comparison of long-term series of CO_2 flux recorded in that area and CO_2 flux series recorded over the northeastern sector of the rim. In the former area the mean value of the flux is about 5 times higher than the flux measured over the rim (Figure 8). Such a preferential degassing could be due to the presence of fractures/faults that reach the hydrothermal reservoir and favour the escape of the gas to the surface. It is likely that the NW-SE trending regional fault is responsible for the enhanced degassing of deep fluids. In fact, this active structural element extends from the carbonate basements to the surface and cuts the volcanic cone [Mostardini and Merlini 1986, Cassano and La Torre 1987, Cella et al. 2007]. Most of the Vesuvio lineaments (faults, fissures, aligned eruptive vents, fault scarps, valley floors, etc.,) as well as the spatial distribution of high-T fumaroles and high CO_2 soil flux zones (Figures 7 and 9) trend in NW-SE direction. A possible variation/integration to this model would be that deep hydrothermal fluids rise preferentially along the feeder conduit of the last eruption of the Vesuvio (in the 1944). As they near the surface, most of these fluids diverts from the conduit to the surrounding more pervious rocks and induce anomalous degassing in the bottom of the crater (Figure 9). In this model, the NW-SE trending fault could act as the terminal preferential pathway for ascending gas. Supporting this interpretation, is the presence of clear CO_2 emissive areas in the bottom of the crater, across the main NW-SE trending fault, both in 2006 and in 2000 (A1 and B1, respectively; Figure 7). These areas are characterized by the highest CO_2 fluxes of the surveys, all belonging to the anomalous A population (Table 2). In spite of their limited extension (2.2% of the total investigated area in 2006 and 7.8% in April-May 2000) the contribution to the total CO_2 emission is massive with 52.2 t/day out of 138.7 t/day (i.e., 37.6% of the total CO_2) in October 2006 and 71.8 t/day out of 122.5 t/day (i.e., 58.6% of the total output) in April-May 2000 (Table 3). Considering the contribution of the other emissive sectors of the cone, lying externally to the crater (A2-A5 in October 2006 and B2-B4 in April-May 2000; Figure 7) the total CO2 emission from all the "anomalous" areas of Vesuvio cone (CO2 flux > 100 g m-2d-1) is comparable over a time span of 6 years (94.7 t/day or 68.3% of the total CO_2 emission in 2006 and 80.9 t/day or 66.0% of the total CO_2 emission in 2000; Table 3). Accordingly, the contribution of the areas characterized by CO_2 rate emission < 100 g $m^{-2}d^{-1}$ is similar for the two campaigns (44 t/day or 31.7% of the

Survey	Area	Position		Amount (t/day)	Proportion (%)
October 2006	A1	Inner crater		52.2	37.6
	A2	External crater		11.6	8.4
	A3	External crater		16.6	12.0
	A4	External crater		5.4	3.9
	A5	External crater		8.9	6.4
			Areas >100 g $m^{-2}d^{-1}$ Subtotal	94.7	68.3
			Areas <100 g $m^{-2}d^{-1}$ Subtotal	44.0	31.7
			Total	138.7	100
April-May 2000	B1	Inner crater		71.8	58.6
	B2	External crater		0.5	0.4
	B3	External crater		5.0	4.1
	B4	External crater		3.6	2.9
			Areas >100 g $m^{-2}d^{-1}$ Subtotal	80.9	66.0
			Areas <100 g $m^{-2}d^{-1}$ Subtotal	41.6	34.0
			Total	122.5	100

Table 3. Contribution of different exhaling areas to the total CO_2 emission of Vesuvio cone.

total CO_2 emission in 2006 and 41.6 t/day or 34% of the total CO_2 emission in 2000; Table 3).

The lack of significant variations in the total CO_2 discharged by the whole cone during the two campaigns, together with the comparable ratios between more and less emissive areas, strongly confirm that both campaigns were carried out during period of "regular" degassing, without drastic changes in the degassing pattern. Conversely, a substantial difference between the two investigations is the extension and the magnitude of the main emissive area located within the crater. In fact, A1 (2006) area is concentrated on a limited side of the bottom crater, whereas B1 (2000) surface is spread over the bottom of the crater and along most of the inner crater walls (Figure 7). During the October 2006 survey, some sample localities inside the crater (Figure 6a, white area) were impossible to reach for safety reason. Although this fact could in part explain the different geometry of the A1 and B1 anomalies inside the crater, we believe that the general degassing pattern of the oriental sector of the cone was changing in the time span between the two campaigns. This conviction is supported mostly by inspecting the CO_2 flux maps over the eastern rim of the crater, where a cluster of measurements was collected during both campaigns; in the October 2006 map there is any evidence for the ring-like anomaly detected at April-May 2000 (Figure 6a,b). We infer that such an expansion of the 2000 CO_2 exhaling area can be associated with the anomalous seismicity observed at Vesuvio in the late 1999 when the area was affected by an intense seismic swarm that culminated with the most energetic Ml = 3.6 earthquake of October 9, 1999 [Del Pezzo et al. 2004]. Caliro et al. [2011] suggested that the seismic crisis of 1999 was accompanied by pressure buildup in the hydrothermal system due to the input of deep magmatic fluids. In addition, they showed that the peak in the pressure was reached at the end of 2001 – early 2002. According to these findings we believe that the bottom of the crater was actually an active site for the diffuse leakage of CO_2 during early 2000 because of the reactivation of the SE prolongation of the NW-SE fault (Figure 7). The peak of degassing likely occurred some time after the 1999 seismic crisis, probably at the end of 2001 when PCO_2 reached the maximum value in the hydrothermal system [Caliro et al. 2011] and CO_2 flux variations up to one order of magnitude have been observed at the station (Figure 8).

In conclusion, our data of October 2006 in addition to the April-May 2000 study of Frondini et al. [2004] from which we have extracted and reinterpreted a subset of data, confirm that the main NW-SE trending tectonic line is actually an active fault leaking deep gas to the bottom of Vesuvio crater. The degassing could be locally enhanced by the "aspiration" effect of the recent (1944) conduit of the volcano. Bottom crater is the preferential site for monitoring the degassing process, as here early gas anomalies related to volcanic unrest should appear. However, also the anomalous degassing areas external to the crater indicated in Figure 7 deserve attention, also because of their easier and lower risk access. In any case the 2000 and 2006 surveys provide a sound background of the rate of degassing of Vesuvio, that will be precious for recognizing early signs of future unrests.

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References

Aiuppa, A., A. Caleca, C. Federico, S. Gurrieri and M. Valenza (2004). Diffuse degassing of carbon dioxide at Somma-Vesuvius volcanic complex (Southern Italy) and its relation with regional tectonics, J. Volcanol. Geoth. Res., 133, 55-79.

Allard, P., J. Carbonnelle, D. Dajlevic, J. Le Bronec, P. Morel, M.C. Robe, J.M. Maurenas, R. Faivre-Pierret, D. Martin, J.C. Sabroux and P. Zettwoog (1991). Eruptive and diffuse emissions of CO_2 from Mount Etna, Nature, 351, 387-391.

Andronico, D., G. Calderoni, R. Cioni, A. Sbrana, R. Sulpizio and R. Santacroce (1995). Geological map of Somma-Vesuvius Volcano, Per. Mineral., 64, 77-78.

Barberi, F., and M.L. Carapezza (1994). Helium and CO_2 soil gas emission from Santorini (Greece), Bull. Volcanol., 56, 335-342.

Baubron, J.C., P. Allard and J.P. Toutain (1990). Diffusive volcanic emission of carbon dioxide from Vulcano Island, Italy, Nature, 344, 51-53.

Bergfeld, D., F. Goff and P. Allard, eds. (2001). High CO_2 flux measurements in volcanic and geothermal areas, methodologies and results, Chem. Geol., 177 (1/2), 1.

Berrino, G., G. Corrado and U. Riccardi (1998). Sea gravity data in the Gulf of Naples; a contribution to delineating the structural pattern of the Vesuvian area, J. Volcanol. Geoth. Res., 82, 139-150.

Bianco, F., M. Castellano, G. Milano, G. Ventura and G. Vilardo (1998). The Somma-Vesuvius stress-field induced by regional tectonics: evidences by seismological and mesostructural data, J. Volcanol. Geoth. Res., 82, 199-218.

Brantley, S.L., and K.W. Koepenick (1995). Measured carbon-dioxide emissions from Oldoinyo-Lengai and the skewed distribution of passive volcanic fluxes, Geology, 23 (10), 933-936.

Brombach, T., J. Hunziker, G. Chiodini, C. Cardellini and L. Marini (2001). Soil diffuse degassing and thermal energy fluxes from the southern Lakki plain, Nysiros (Greece), Geophys. Res. Lett., 28 (1), 69-72.

Caliro, S., G. Chiodini, R. Avino, C. Cardellini and F. Frondini (2005). Volcanic degassing at Somma-Vesuvio (Italy) inferred by chemical and isotopic signatures of groundwater, Appl. Geochem., 20, 1060-1076.

Caliro, S., G. Chiodini, R. Avino, C. Minopoli and B. Bocchino (2011). Long time-series of chemical and isotopic compositions of Vesuvius fumaroles: evidence for deep and shallow processes, Annals of Geophysics, 54 (2), 137-149.

Carapezza, M.L., and D. Granieri (2004). CO_2 soil flux at Vulcano (Italy): comparison of active and passive methods and application to the identification of actively degassing structure, Appl. Geochem., 19, 73-88.

Carapezza, M.L., S. Inguaggiato, L. Brusca and M. Longo (2004). Geochemical precursors of the activity of an open-conduit volcano: The Stromboli 2002-2003 eruptive events, Geophys. Res. Lett., 31, L07620; doi:10.1029/2004GL019614.

Carapezza, M.L., T. Ricci, M. Ranaldi and L. Tarchini (2009). Active degassing structures of Stromboli and variation in diffuse CO_2 output related to the volcanic activity, J. Volcanol. Geoth. Res., 182 (3/4), 231-245; doi:10.1016/j.jvolgeores.2008.08.006.

Carapezza, M.L., F. Barberi, M. Ranaldi, T. Ricci, L. Tarchini, J. Barrancos, C. Fischer, N. Perez, K. Weber, A. Di Piazza and A. Gattuso (2011). Diffuse CO_2 soil degassing and CO_2 and H_2S concentrations in air and related hazards at Vulcano Island (Aeolian arc, Italy), J. Volcanol. Geoth. Res., 207, 130-144.

Cardellini, C., G. Chiodini and F. Frondini (2003). Application of stochastic simulation to CO_2 flux from soil: mapping and quantification of gas release, J. Geophys. Res., 108 (B9), 2425; doi:10.1029/2002JB002165.

Cassano, E., and P. La Torre (1987). Geophysics, In: R. Santacroce (ed.), Somma-Vesuvius, Quaderni de "La Ricerca Scientifica", CNR, 114, 53-103.

Cella, F., M. Fedi, G. Florio, M. Grimaldi and A. Rapolla (2007). Shallow structure of the Somma-Vesuvius volcano from 3D inversion of gravity data, J. Volcanol. Geoth. Res., 161, 303-317.

Chiodini, G., F. Frondini and B. Raco (1996). Diffuse emission of CO_2 from the Fossa crater, Vulcano Island (Italy), Bull. Volcanol., 58 (1), 41-50.

Chiodini, G., R. Cioni, M. Guidi, B. Raco and L. Marini (1998). Soil CO_2 flux measurements in volcanic and geothermal areas, Appl. Geochem., 13, 543-552.

Chiodini, G., L. Marini and M. Russo (2001). Geochemical evidence for the existence of high-temperature hydrothermal brines at Vesuvio volcano, Italy, Geochim. Cosmochim. Acta, 65, 2129-2147.

Cioni, R., R. Santacroce and A. Sbrana (1999). Pyroclastic deposits as a guide for reconstructing the multi-stage evolution of the Somma-Vesuvius Caldera, Bull. Volcanol., 60, 207-222.

David, M. (1977). Geostatistical Ore Reserve Estimation, New York, Elsevier Sci., 364 pp.

Del Pezzo, E., F. Bianco and G. Saccorotti (2004). Seismic source dynamics at Vesuvius volcano, Italy, J. Volcanol. Geoth. Res., 133, 23-39.

Deutsch, C.V., and A.G. Journel (1998). GSLIB: Geostatistical Software Library and Users Guide, New York, Oxford Univ. Press, 369 pp.

Diliberto, I.S., S. Gurrieri and M. Valenza (2002). Relationships between diffuse CO_2 emissions and volcanic activity on the island of Vulcano (Aeolian Islands, Italy) during the period 1984-1994, Bull. Volcanol., 64, 219-228.

Federico, C., A. Aiuppa, P. Allard, S. Bellomo, P. Jean-Baptiste, F. Parello and M. Valenza (2002). Magma-derived gas influx and water-rock interactions in the volcanic aquifer of Mt. Vesuvius, Italy, Geochim. Cosmochim. Acta, 66, 963-981.

Federico, C., A. Aiuppa, R. Favara, S. Gurrieri and M. Valenza (2004). Geochemical monitoring of groundwaters (1998-2001) at Vesuvius volcano (Italy), J. Volcanol. Geoth. Res., 133, 81-104; doi:10.1016/S0377-0273(03)00392-5.

Fiebig, J., G. Chiodini, S. Caliro, A. Rizzo, J. Spangenberg and J.C. Hunziker (2004). Chemical and isotopic equilibrium between CO_2 and CH_4 in fumarolic gas discharges: generation of CH_4 in arc magmatic-hydrothermal systems, Geochim. Cosmochim. Acta, 68, 2321-2334.

Finetti, I., and C. Morelli (1974). Esplorazione di sismica a riflessione dei Golfi di Napoli e Pozzuoli, Boll. Geof. Teor. Appl., 16, 175-222.

Frondini, F., G. Chiodini, S. Caliro, C. Cardellini, D. Granieri and G. Ventura (2004). Diffuse CO_2 degassing at Vesuvio, Italy, Bull. Volcanol., 66, 642-651.

Giammanco, S., S. Gurrieri and M. Valenza (1997). Soil CO_2 degassing along tectonic structures of Mount Etna (Sicily); the Pernicana Fault, Appl. Geochem., 12, 429-436.

Granieri, D., G. Chiodini, W. Marzocchi and R. Avino (2003). Continuous monitoring of CO_2 soil diffuse degassing at Phlegraean Fields (Italy): influence of environmental and volcanic parameters, Earth Planet. Sci. Lett., 212, 167-179.

Granieri, D., M.L. Carapezza, G. Chiodini, R. Avino, S. Caliro, M. Ranaldi, T. Ricci and L. Tarchini (2006). Correlated increase in CO_2 fumarolic content and diffuse emission from La Fossa crater (Vulcano, Italy): evidence of volcanic unrest or increasing gas release from a stationary deep magma body?, Geophys. Res. Lett., 33, L13316; doi:10.1029/2006GL026460.

Granieri, D., R. Avino and G. Chiodini (2010). Carbon dioxide diffuse emission from the soil: ten years of observations at Vesuvio and Campi Flegrei (Pozzuoli), and linkages with volcanic activity, Bull. Volcanol., 72, 103-118; doi:10.1007/s00445-009-0304-8.

Klusman, R.W. (1993). Soil Gas and Related Methods for Natural Resource Exploration, New York, Wiley, 1-483.

Lewicki, J.L., G.E. Hilley, T. Tosha, R. Aoyagi, K. Yamamoto and S.M. Benson (2007). Dynamic coupling of volcanic CO2 flow and wind at the Horseshoe Lake tree kill, Mammoth Mountain, California, Geophys. Res. Lett., 34, L03401; doi:10.1029/2006GL028848.

Madonia, P., C. Federico, P. Cusano, S. Petrosino, A. Aiuppa and S. Gurrieri (2008). Crustal dynamics of Mount Vesuvius from 1998 to 2005: Effects on seismicity and fluid circulation, J. Geophys. Res., 113, B05206; doi:10.1029/2007JB005210.

Mostardini, F., and S. Merlini (1986). Appennino centro meridionale. Sezioni geologiche e Proposta di Modello Strutturale, Mem. Soc. Geol. Ital., 35, 177-202.

Notsu, K., K. Sugiyama, M. Hosoe, A. Uemura, Y. Shimoike, F. Tsunomori and P.A. Hernandez (2005). Diffuse CO2 flux from Iwojima volcano of the Izu-Ogasawara arc, Japan, J. Volcanol. Geoth. Res., 139, 147-161.

Rogie, J.D., D.M. Kerrick, M.L. Sorey, G. Chiodini and D.L. Galloway (2001). Dynamics of carbon dioxide emission at Mammoth Mountain, California, Earth Planet. Sci. Lett., 188, 535-541.

Salazar, J.M.L., N.M. Pérez, P.A. Hernández, T. Soriano, F. Barahona, R. Olmos, R. Cartagena, D.L. López, R.N. Lima, G. Melían, I. Galindo, E. Padrón, H. Sumino and K. Notsu (2002). Precursory diffuse carbon dioxide degassing signature related to a 5.1 magnitude earthquake in El Salvador, Central America, Earth Planet. Sci. Lett., 205, 81-89.

Salazar, J.M.L., P.A. Hernández, N.M. Pérez, R. Olmos, F. Barahona, R. Cartagena, T. Soriano, D.L. López, H. Sumino and K. Notsu (2004). Spatial and temporal variations of diffuse CO_2 degassing at the Santa Ana–Izalco–Coatepeque volcanic complex, El Salvador, Central America, Geol. Soc. America, Special Paper 375,135-146.

Sinclair, A.J (1974). Selection of thresholds in geochemical data using probability graphs, J. Geochem. Explor., 3, 129-149.

Santacroce, R., ed. (1987). Somma-Vesuvius, Quaderni de "La Ricerca Scientifica", CNR, 114 (Progetto finalizzato Geodinamica, Monografie finali, 8), 251 pp.

Santacroce, R., and A. Sbrana, eds. (2003). Geological map of Vesuvius 1:15,000 scale, Firenze, SELCA.

Santacroce, R., R. Cioni, P. Marianelli, A. Sbrana, R. Sulpizio, G. Zanchetta, D.J. Donahue and J.L. Joron

(2008). Age and whole rock–glass compositions of proximal pyroclastics from the major explosive eruptions of Somma-Vesuvius: A review as a tool for distal tephrostratigraphy, J. Volcanol. Geoth. Res., 177, 1-18.

Sugisaki, R., M. Ido, H. Takeda, Y. Isobe, Y. Hayashi, N. Nakamura, H. Satake and Y. Mizutani (1983). Origin of hydrogen and carbon dioxide in fault gases and its relation to fault activity, J. Geol., 91, 239-258.

Tarquini, S., I. Isola, M. Favalli, F. Mazzarini, M. Bisson, M.T. Pareschi and E. Boschi (2007). TINITALY/01: a new Triangular Irregular Network of Italy, Annals of Geophysics, 50 (3), 407-425.

Ventura, G., G. Vilardo and P.P. Bruno (1999). The role of flank failure in modifying the shallow plumbing system of volcanoes: an example from Somma-Vesuvius, Italy, Geophys. Res. Lett., 26, 3681-3684.

Werner, C., S.L. Brantley and K. Boomer (2000). CO_2 emissions related to the Yellowstone volcanic system. Statistical sampling, total degassing, and transport mechanisms, J. Geophys. Res., 10, 10831-10846.

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