Hazardous changes in soil CO_2 emissions at Vulcano, Italy, in 2021

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Key Points

- Diffuse degassing surveys help track transition toward volcanic unrest periods
- Carbon isotope composition allows quantification of the volcanic CO_2 emitted by soils
- Significant changes in volcanic outgassing state caused increases in soil CO_2 emissions and gas hazard at Vulcano - Italy - during 2021

Abstract

The La Fossa volcano on the Island of Vulcano, Italy, showed signs of more energetic fumarolic–solfataric activity during 2021. Several increases in volcanic gas emissions and seismicity, namely “crisis”, punctuated the passive degassing at Vulcano that had ensued after the last 1888–1890 vulcanian eruption. Most of the gases (i.e., up to 90%) were emitted at the crater cone while the diffuse degassing of CO_2 at Vulcano Porto accounted for more than 10% of the volcanic emissions. Two anomalous degassing zones at the base of the volcanic cone (i.e., Palizzi and Faraglione) showed notable changes in the gas output during the volcanic crisis. In these zones, increases of soil CO_2 flux (φCO_2) had several practical implications other than of volcanological interest, owing to the risk related to people’s exposure to volcanic gas emissions. The results of this study reveal variations of the average φCO_2 from 74 g m^{-2} d^{-1} during September 2021 to 370 g m^{-2} d^{-1} in November 2021, which were 27% and 538% higher than the statistical background since 1988 ($\varphi CO_2 \approx 58$ g m^{-2} d^{-1}), respectively. These observations helped in volcanic surveillance at Vulcano. The soil CO_2 partitioning determined using both φCO_2 and carbon isotope measurements, helped track changes in the volcanic CO_2 output from $9.97 \cdot 10^4$ kg d^{-1} to $101.15 \cdot 10^4$ kg d^{-1}. Estimates for volcanic CO_2 suggest that the instability of a magmatic body caused a transition from background fumarolic–solfataric activity toward an unrest event after September 2021.

Keywords: Diffuse degassing; Soil CO_2 flux; Carbon isotopes; Volcanic unrest; Volcanic degassing; Gas Hazard.

Plain Language Summary

A noticeable increase in volcanic outgassing occurred at Vulcano, Italy, in 2021. Although the volcano has not achieved critical conditions to produce an eruption, the soil CO_2 emissions have prevented access into some zones of the island, due to the volcanic risk known as the gas hazard. Specialised instruments such as fluxmeters and spectrophotometers were used to measure the soil CO_2 flux and the carbon isotopes of CO_2 during four soil gas surveys. To understand why the volcanic system evolved towards a period of unrest, we modelled our measurements using mass balance calculations. We find that the CO_2 increase, almost ten times its baseline, was most likely due to the instability of a magmatic body within the mantle to crustal boundary known as the Moho discontinuity. Because of this magmatic instability, the volcanic CO_2 emissions resumed in some zones of the island where volcanic activity had been dormant for decades. The resumption of volcanic degassing in a short period had not been recorded before at Vulcano, and it is important to understand its cause because future changes in magmatic activity might produce larger CO_2 emissions that will have the added risk of gas hazards as well as that of an explosion.

1. Introduction

Soil CO_2 emissions occur in several different geological settings (Annunziatellis et al., 2003; Almagro et al., 2009; Chiodini et al., 2015; Zhang et al., 2017; Capasso et al., 2019; Venturi et al., 2019; Camarda et al., 2020; Di Martino and Capasso, 2019; Di Martino and Capasso, 2021; Ciais et al., 2021), and investigating their changes over time and space has been the subject of many studies in volcanology (Allard et al., 1991; Valenza, 1993; Farrar et al., 1995; Chiodini et al., 1996; Giammanco et al., 1997; Chiodini et al., 1998; Carapezza and Federico, 2000; Chiodini and Frondini, 2001; Federico et al., 2011; Camarda et al., 2012; Burton et al., 2013; Di Martino et al., 2016a; De Gregorio and Camarda, 2016; Cardellini et al., 2017; Boudoire et al., 2017; Capasso et al., 2017; Camarda et al., 2019) and earth degassing in seismically active zones (Raich and Schlesinger, 1992; Raich and Potter, 1995; Raich and Tufekcioglu, 2000; Camarda et al., 2016; Tamburello et al., 2018; Capasso et al., 2021).

Diffuse degassing has been attracting considerable interest in volcanology over the past century since it was discovered that CO_2 is the main component of magmatic gases behind H_2O. After its formation in the mantle, magma rising at shallower levels releases CO_2 through decompression, which flows into the atmosphere through summit crater vents, fumaroles, and mofetes in peripheral zones. Diffuse degassing has received attention from volcanologists because the amounts of CO_2 emitted by soils are considerably higher during eruptive periods (Valenza, 1994; Giammanco et al., 1998; Chiodini et al., 2001; Hernández et al., 2001; Shinohara et al., 2002; Granieri et al., 2006; Hernández et al., 2012; Di Martino et al., 2013; De Gregorio et al., 2014; Fisher et al., 2019). Notable changes in CO_2 emissions have been observed before the onset of eruptions at several volcanoes (Pérez et al., 2006; Melián et al., 2014), and during transitions toward different activity levels (Badalamenti et al., 1991; Barberi et al., 1991; Inguaggiato et al., 2019; Di Martino et al., 2021a). Therefore, several volcanic observatories have attempted to monitor diffuse degassing at volcanoes through CO_2 flux monitoring networks (Carapezza et al., 2003; Pérez et al., 2006; Viveiros et al., 2008; Liuzzo et al., 2013; Laiolo et al., 2016; Camarda et al., 2019; Inguaggiato et al., 2020).

One of the most significant current discussions in diffuse degassing studies is concerned with the origin of the CO_2. Investigations of either the isotope compositions or isotopic fractionation represent a growing field (Camarda et al., 2007; Chiodini et al., 2008; Di Martino et al., 2016b; Viveiros et al., 2020) because unique carbon isotope signatures can typically be established for different gas sources. Some recent developments in carbon isotope determinations have allowed the identification of the origin of CO_2 in both soil and atmospheric gases (Clark and Fritz, 1997; Capasso et al., 1997; Clark-Thorne and Yapp, 2003; Cox et al., 2013; Capasso et al., 2017; Camarda et al., 2019; Di Martino and Capasso, 2019; Di Martino and Gurrieri 2022). When the carbon isotopic signature of a gas source is reasonably well established, isotopic changes can help in i) revealing the fractionation processes that different gases have been subjected to during their transport from the reservoir to the Earth's surface and ii) better quantifying volcanic degassing (Parks et al., 2013; Di Martino et al., 2016b). Over the past years, there has been an increase in the application of soil CO_2 flux surveys for investigating changes in the Earth's crustal permeability to CO_2-rich fluids that often prevail in seismically active zones. In recent years, several attempts have been made at linking diffuse degassing transients with changing crustal stress caused by seismic activity (Werner et al., 2014; Fisher et al., 2014; Camarda et al., 2016; Tamburello et al., 2018; Camarda et al., 2019; Chen et al., 2020).

In recent years, the availability of stable isotope measurements has increased, enabling extensive surveys of the carbon isotopes of soil CO_2 emissions. Indeed, $^{13}C/^{12}C$ ratios are a key parameter for identifying the gas source, and measurements of $\delta^{13}C\text{-}CO_2$ in the field can play an important role in quantifying the amounts of volcanic CO_2 emissions. Therefore, the systematic surveying of $\delta^{13}C\text{-}CO_2$ in combination with soil CO_2 flux (φCO_2) measurements can provide a key strategy for improving volcano surveillance programs. Research in the area of volcanic surveillance has yielded more precise estimates of volcanic CO_2 outputs and allowed a highly sensitive tracking of changes in volcanic degassing (Di Martino et al., 2020a and reference therein).

This study aims to investigate a recent change in the volcanic CO_2 emissions at Vulcano on the Aeolian Island (Italy). Since the end of September 2021, the visible volcanic emissions from the crater rim have quickly risen, thus prompting the Italian civil defence authorities to switch the alert code from "green" to "yellow" at Vulcano. This paper traces the evolution of both the φCO_2 and $\delta^{13}C\text{-}CO_2$ of the soil CO_2 at Vulcano Porto in response to the increase in volcanic degassing. This investigation uses recent integrated analyses of $\delta^{13}C\text{-}CO_2$ and φCO_2 measurements to evaluate the changes of the volcanic CO_2 output throughout the period of surveying.

This study provides an extensive examination of the changes in soil degassing at Vulcano during 2021 alongside garnering new insights into the gas sources feeding the volcanic emissions during a period of unrest. Moreover, it considers the implications of increased volcanic emissions on the gas hazards at Vulcano. There is great variation in the definitions of the "crisis" (Barberi et al., 1991; Aubert and Alparone, 2000) and sometimes the definition fits the activity of a specific volcano. In this paper, the term "crisis" refers to variations in the state of volcanic activity expressed by changes in the signals of geochemical and geophysical indicators (i.e., changes of the concentration of CO_2, He, and N_2 in the fumarolic gas; increases of the gas output; variations in the temperature of the fumarolic gases; increases in the $^3He/^4He$ ratio; changes in δD and $\delta^{18}O$ of the volcanic vapor; changes in $\delta^{13}C\text{-}CO_2$; changes in the appearance of volcanic-tectonic seismic events) leading to an increase in the volcanic hazard as a whole which can evolve into explosive activity (i.e., prodrome to phreatic explosion-phreatic-magmatic explosion-magmatic explosion).

2. Study area

The Aeolian islands (Figure 1) form a volcanic arc resulting from the subduction of the Jonian slab beneath the Calabrian margin (Barberi et al., 1974; Forni et al., 2013 and references therein). The western part of the archipelago exhibits extinct volcanism (i.e., Alicudi, Filicudi, and Salina islands), while active geothermal systems have developed at Lipari and at Panarea, which shows submerged active degassing (Heinicke et al., 2009; Peccerillo et al., 2013).). The subaerial active volcanism occurs at Stromboli and Vulcano, in the south-eastern sector of the Tyrrhenian Sea. The island of Stromboli has developed along a NE–SW trending structure, in an extensional tectonic regimen that control the dynamics of magma rise in the mantle wedge above the subduction zone. The volcanic evolution at Vulcano depends on the Tindari–Letojanni which is an NNW-SSE trending strike-slip fault running from the Lipari-Salina alignment to the island of Sicily (Ventura, 1994; De Astis et al., 2003; De Astis et al., 2013; Forni et al., 2013; Barreca et al., 2014). The rather different geological settings have established significant differences between the typical eruptive activities of these volcanoes. Stromboli is a basaltic volcano which has been characterised by persistent low to middle explosive subplinian-type eruptions since the seventh century A.D. (Rosi et al., 2000), whereas Vulcano has shown subplinan and plinian explosive eruptions of magmas having rhyolitic compositions over the last 12 ka. The most recent eruption occurred at Vulcano between August 3, 1888 and May 17, 1890, and was described in the nineteenth century through direct observation of the explosive activity. In distinguishing various types of eruptions in

1907, Mercalli used the term vulcanian type for classifying this eruption. Vulcanian eruptions consist of multiple explosions of moderate size (i.e., VEI 2-3) and ejecting tephra (volume 0.01-0.1 km^3) through sustained eruptive columns which can rise a few kilometres above the crater (heights of the eruptive column h = 2-15 km). The repose period between vulcanian explosions is of a few minutes to hours or more. The 1888-1890 eruption was preceded by an increase in the temperature and output rate of the fumarolic gas discharge (Delmelle and Stix, 2000). After the end of the eruption, the La Fossa volcano has exhibited quiescent fumarolic-solfataric degassing from the rim of the crater cone, at Faraglione and Levante beach. Thermal groundwater, mud pools, sulphur deposition, gas emissions from the seafloor, and CO_2 emissions from the soils are examples of surface manifestations of the active volcanism at Vulcano Porto at present.

The study area includes the inhabited zones of Vulcano Porto and Palizzi, that are located at the base of the La Fossa cone (Figure 1). Strong emissions of soil CO_2 are present in these areas and the CO_2 emissions represent almost 30% of the CO_2 emissions from the crater (Allard et al.,1991; Aiuppa et al., 2007). Both the spatial distribution of soil CO_2 and the amount of the emissions change over time due to changes in volcanic activity. These changes have not been an outcome of an eruption, but instead were produced by variations in the hydrothermal system which consisted of increasing gas outputs, the convective heat flux, and seismo-tectonic activity. The variations in the relative contributions from shallow groundwater, deeper hydrothermal brines, and magmatic gases have caused several fluctuations in volcanic activity in the past decades. Therefore, with the aim of monitoring volcanic activity, periodic measurements of soil CO_2 flux since 1988 have been carried out in a fixed network of 53 measurement points distributed in this area (Camarda et al., 2006a; Diliberto et al., 2002; Di Martino et al., 2016b; Di Martino et al., 2020a). The employment of a fixed sampling grid is particularly useful for comparing estimates of CO_2 output made over different times (i.e., from September to November, 2021).

3. Materials and Methods

3.1 Soil CO_2 flux measurements

Classifying φCO_2 measurements and measuring $\delta^{13}C\text{-}CO_2$ that are representative for each φCO_2 class are currently the most popular method for determining CO_2 partitioning in soil gases (Chiodini et al., 2001; Carapezza et al., 2011; Inguaggiato et al., 2012; Viveiros et al., 2020). A limitation is that this approach uses a reduced isotopic dataset for representing a large number of φCO_2 measurements. A suggested alternative to this method involves the carbon isotope determination at each φCO_2 measurement point. This method is particularly useful for volcanic surveillance because it allows the point-by-point partitioning of the φCO_2 to be established between shallow and deep-origin gases ((Di Martino et al., 2016b; Capasso et al., 2017; Camarda et al., 2019; Capasso et al., 2019; Di Martino et al., 2020a; Di Martino and Capasso, 2021).

The data reported in this study were collected using two infrared (IR) spectrophotometers, enabling whole CO_2 concentration measurements and $\delta^{13}C$-CO_2 determinations. An IRGA Riken spectrophotometer (Model RI – 550 A) allowed us to measure the φCO_2 in agreement with the dynamic concentration method (Gurrieri and Valenza, 1988). To perform the φCO_2 measurements with this method, a void sampling probe was encased at a 50 cm depth in the soil. The probe was open to the soil gases from the bottom and to the atmosphere at the top. After zeroing the spectrophotometer, the inner pumping unit started collecting the mixture of soil gases and air at a constant flux rate (0.8 l min^{-1}) through the sampling probe. Upon collecting both soil gases and air, this gas sampling system achieved a dynamic equilibrium. Once a hydraulic steady state had been achieved, the CO_2 concentration in the gas mixture (i.e., the so–called “dynamic concentration”) was proportional to the soil CO_2 flux. The empirical relationship between φCO_2 and the dynamic concentration was established in the laboratory, and the φCO_2 (g m^{-2} d^{-1}) was calculated with the following equation (Camarda et al., 2006a):

$$\varphi CO_2 = (32 - 5.8\ k^{0.24}) \cdot Cd + 6.3 \cdot k^{0.6} \cdot Cd^3 \qquad (1)$$

where Cd (ppm vol) is the dynamic concentration of CO_2, and k (μm^2) is the soil gas permeability measured in the field (Camarda et al., 2006b; Camarda et al., 2017).

3.2 Carbon isotope determination

Following the CO_2 flux measurement, a rubber plug was used for closing the air inlet of the probe and a vial container was connected to the IR spectrometer gas output to collect soil gas samples. The vial consisted of a borosilicate glass container (Labco Exetainer® 12 mL Vial) closed at one end with a removable plastic cap with a rubber septum.

The modified soil gas collection system achieved hydraulic stability in less than one minute. While the system was achieving stability, the vials were carefully flushed with the soil gas and a high pumping rate avoided any possible atmospheric CO_2 contamination of the sample. The soil gases were then stored for carbon isotope analysis at Centro Carapezza, which is an operative centre of INGV, where a temporary stable isotopic laboratory was equipped for measuring the isotope composition of the soil CO_2 during the surveys. The measurements of $\delta^{13}C$ in the soil CO_2 were performed using a DeltaRay^{TM} Isotope Ratio Infrared Spectrometer (Thermo Fisher Scientific). This instrument allowed the concentrations of ^{13}COO, ^{12}COO, and $CO^{18}O$ molecules to be measured selectively, owing to their different absorption wavelengths in the mid-IR range. Lambert-Beer's law provided the correlation between the absorption strength and carbon dioxide concentrations, while the Qtegra software was used to calculate $\delta^{13}C$-CO_2 when the CO_2 concentration was in the range of 200-3500 ppm vol. The Qtegra software included all instrumental controls (i.e., gas manager window, equipment, programs, scheduler pane) and provided access to the calibration setting and referencing. A template enclosed all information about the samples, the recording features, the referencing actions, and data export settings. Throughout the text, the carbon isotope composition is expressed in a delta notation ($\delta^{13}C$-CO_2) as calculated by equation:

$$\delta^{13}C - CO_2 = \left[\left(\left({}^{13}C/{}^{12}C\right)_{sample} \Big/ \left({}^{13}C/{}^{12}C\right)_{standard}\right) - 1\right] \cdot 1000$$

The results were referenced against the Vienna Pee Dee Belemnite (VPDB), which is the internationally recognised reference scale (i.e., $\delta^{13}C$-CO_2 in ‰ vs VPDB) having $(^{13}C/^{12}C)_{standard} = 0.0111802$.

Prior to starting the measurement, a calibrated tube was installed in the expander box of the analyser and used to dilute the gas sample and reduce the CO_2 concentrations to within the analyser range (i.e., 200-3500 ppm vol.). The gas was obtained from the vial through an introduction system equipped with two needles. The first needle pierced the rubber septum for sampling the gas, while the second was inserted into the vial to maintain the sample at atmospheric pressure (Di Martino and Capasso, 2021). On analysing the soil gas samples, the spectrophotometer recorded signal variations from the air to an unreferenced $\delta^{13}C$-CO_2 measurement of the gas sample. Once the signal achieved stability for a few seconds (i.e., >30 seconds), the values of $\delta^{13}C$-CO_2 and CO_2 concentrations were averaged and referenced by the analyser using the same procedure on a working standard (i.e., reference $\delta^{13}C$-CO_2 = -0.78 ‰). When measuring the $\delta^{13}C$-CO_2 signature on the working standard, the CO_2 concentration in the analyser was the same as that of the analytical sample. The precision and accuracy achieved with this procedure were deemed suitable for the purpose of this study ($\Delta\delta^{13}C$-CO_2 = ± 0.25‰).

3.3 Data collection and processing method

The CO_2 flux measurements and the soil gas collection for $\delta^{13}C$-CO_2 determinations were performed at each point of the measurement grid (Table 1). Each gas survey required one day of field work for the completion of the measurements and a few hours of work in the laboratory for isotopic analyses. The processing of the datasets collected in the field and in the laboratory provided the lateral changes of both the soil CO_2 flux and the carbon isotope compositions of the soil CO_2. Different methods have been proposed to determine the spatial changes of the soil variables measured in scattered sets of points. In this study, the kriging algorithm with a spherical model of spatial autocorrelation provided the continuous prediction surfaces for both the soil CO_2 flux and the carbon isotope compositions of the soil CO_2. The spherical model had the advantage of providing spatial autocorrelations which changed linearly with distances between neighbouring measurements and which reached the distance at which the locations were statistically uncorrelated asymptotically. The decision to use this model was based on the physical properties of the soils at Vulcano Porto, that are rather homogenous at the spatial scale of the surveys. Spatial distribution simulations of the soil gas variables were carried out using the Quantum GIS software package.

The isotopic dataset helped establish the multiplication factors for φCO_2 for partitioning the soil CO_2 flux between biologic and volcanic components in agreement with a previously discussed three-component mixing model (see Di Martino et al., 2016b). According to Di Martino et al. (2016b), three sources of CO_2, mixed in various proportions, can be recognised in soil gases based on their carbon isotopic signatures: (i) air, (ii) soil respiration, and (III) volcanic sources. Volcanic CO_2 is calculated by multiplying φCO_2 by the coefficient of the mixing proportion derived from modelling the $\delta^{13}C$-CO_2 measurements. Recently, Viveiros et al. (2020) integrated the isotopic signature of carbon in soil CO_2 emission with soil CO_2 flux measurements for estimating the CO_2 released from Furnas do Enxofre degassing area (Terceira Island, Azores archipelago). These authors estimated the emission of CO_2 from deep-origin in agreement with a comparable approach proposed by Chiodini et al. (2008) for discriminating different sources feeding soil CO_2 degassing in volcanic-hydrothermal areas. The sensitivity of the soil CO_2 flux measurement in combination with $\delta^{13}C$-CO_2 determinations for identifying the deep origin gas input events has recently been demonstrated in a report by Di Martino et al., (2020a).

3. Results

3.1. CO_2 flux in the peripheral zone La Fossa cone during 2021.

This section reports on the results of four soil gas surveys carried out at Vulcano for monitoring the volcanic degassing activity in 2021. During each survey, the soil CO_2 flux was measured over a sampling grid of 53 fixed points. Moreover, the soil gases were collected in vials to analyse the carbon isotope compositions of the CO_2 samples.

Figure 2 shows the results of the soil CO_2 flux measurements before and after the shift in the alert code at Vulcano (i.e., from green to yellow), which occurred on September 30, 2021. The threshold of the anomaly for soil degassing was established based on a statistical analysis of φCO_2 measurements at a value higher than 117 g m^{-2} d^{-1} (Di Martino et al., 2020a). A comparison with some data reported in previous studies (Di Martino et al., 2016b) shows that this threshold value represented the highest φCO_2 values sustained by soil respired CO_2. Figure 2a shows the presence of two anomalous degassing zones in the surveyed area: one at Palizzi and the other at Faraglione. Furthermore, this pattern is in good agreement with results reported by other studies in the literature that investigated the spatial distribution of the anomalous degassing zones at Vulcano (Badalamenti et al., 1991; Valenza, 1994; Chiodini et al., 1998; Granieri et al., 2006; Camarda et al., 2006a; Carapezza et al., 2011; Di Martino et al., 2020a). Albeit Palizzi was reported to have a 0.16 km^2 wide anomalous degassing surface (Di Martino et al., 2016b) in the southern side of the volcanic cone, Faraglione had 0.04 km^2 wide anomalous degassing surface at Vulcano Porto with the highest risk from gas hazards owing to the highest people exposure. In fact, the widest village of the island lies at Faraglione, while the Palizzi area is uninhabited and without infrastructure.

Figure 2b shows more vigorous soil CO_2 emissions having occurred during October 2021 relative to September 2021 (Figure 2a). The most interesting result of this comparison is the appearance of new anomalous zones in the western side of the La Fossa cone in October 2021: one at Camping Sicilia and the other at Piano delle Baracche (Figure 2). This situation caused a significant increase in diffuse CO_2 degassing at Vulcano Porto from September to October 2021.

A comprehensive analysis of Figure 2 shows that the greatest changes in soil CO_2 emissions occurred at Palizzi. The threshold isoline shows that a wide increase of anomalous CO_2 emissions occurred through the investigated area and that φCO_2 values lower than 117 g m^{-2} d^{-1} were recorded in the areas of Lentia and the south of Palizzi only. It could be argued that the increases in φCO_2 at Piano delle Baracche, Camping Sicilia, and Faraglione caused a significant increase of CO_2 emissions in the air. In fact, the emissions of large amounts of CO_2 from soils may have created hazardous conditions for human exposure to volcanic gas emissions. The present study has only examined the diffuse degassing at Vulcano Porto and did not evaluate the air CO_2 concentrations resulting from it. This limitation makes an overall conclusion about the gas hazard difficult. However, several studies have noted concurrent increases in the CO_2 concentrations both in the open air and indoor during crisis at Vulcano (Badalamenti et al., 1988; Diliberto et al., 2002; Carapezza et al., 2003). Carapezza et al. (2011) argued that the gas hazard in the inhabited sector of Vulcano Porto dramatically increased during the crisis period. Indeed, they suggested that the threshold value for indoor air CO_2 concentrations should be significantly lower than at the time of the time weighted average (TWA) and short-term exposure limit (STEL) values for domestic environments. In fact, these values refer to a selected population (i.e., workers in good health conditions) exposed to CO_2 for a time span of a maximum of 8h, which is lower than time persons staying at home (e.g., mainly at nighttime). Soil CO_2 emissions and weather variables strongly affect the air CO_2 concentrations. Increase of CO_2 concentrations in air have been observed in either depressed areas or areas with poor ventilation and are known in the literature as representing gas hazards (Diliberto et al., 2002; Carapezza et al., 2003, 2011; Di Martino et al., 2021b; Camarda et al., 2022a, 2022b). During the survey performed in October 2021 in the areas affected by anomalous diffuse degassing of CO_2, small dead reptiles and some dead birds were found showing that the risk from gas hazard increased owing to the exposure of inhabitants to these volcanic emissions. Further research is required in order to better understand the relationship between the diffuse degassing and the gas hazard at Vulcano Porto. Since June 2021, a specific monitoring network has been installed in the inhabited zone of Faraglione for gas hazard mitigation (Gurrieri et al., 2022). Despite the fact that preliminary data analysis provides encouraging results (Di Martino et al., 2021c), the available dataset does not provide conclusive indications on the evolution of the gas hazard at Vulcano for 2021. However, future studies should include synchronous measurements of φCO_2 and air CO_2 concentrations to establish a warning system for gas hazards.

3.2. Carbon isotope composition of the soil CO_2 in the peripheral zone of La Fossa cone during 2021

The determination of the $\delta^{13}C$-CO_2 in the laboratory enabled an accurate spatial analysis of the volcanic origin of the soil CO_2 emissions at Vulcano Porto in 2021 (Figure 3). The analysis of the isotopic dataset shows that $\delta^{13}C$-CO_2 in the ground gases ranged from ~-24‰ to +0.5‰. The more ^{13}C-depleted CO_2 has a biological origin, whereas the volcanic CO_2 has the less ^{13}C-depleted CO_2 (Capasso et al., 1997; Paonita et al., 2013). In September 2021 (Figure 3a), the soil CO_2 exhibited the less ^{13}C-depleted values (i.e., $\delta^{13}C$-CO_2 ranges from-3 ‰ up to +0.5 ‰) at the anomalous degassing zones. On the contrary, soil gases had the most ^{13}C -depleted CO_2 (i.e., $\delta^{13}C$-CO_2 ~-24‰) near Monte Lentia, in the western side of the surveyed area. These results are in good agreement with previously reported data on the evolution of the diffuse degassing at Vulcano (Di Martino et al., 2016b; Di Martino et al., 2020a).

The $\delta^{13}C$-CO_2 depends on the mixing proportion among biologic CO_2 (e.g., CO_2 from organic matter decomposition, root respiration, and soil respiration), air CO_2, and volcanic CO_2. The carbon isotopic signature of the biologic CO_2 is widely ^{13}C–depleted in comparison with the air CO_2, which has $\delta^{13}C$-CO_2 = -8‰ (Yakir, 2003). Thus, diffuse degassing shows that for ^{13}C–depleted CO_2 in soils (Lucic et al., 2015), the specific range of $\delta^{13}C$-CO_2 would depend on which the dominant population in the ecosystem would be. At Vulcano, the soil respired CO_2 has a $\delta^{13}C$-CO_2 roughly analogous with the C3 plants (~ –27‰ on the average) owing to the relevant floristic population which encloses several of these species widely spreading in the Mediterranean area (e.g., *Carpobrotus acinaciformis*, *Cichorium intybus* or *Ampelodesmos mauritanicus*, *Agave*, *Opuntia ficus–indica*, *Spartium junceum*, *Rubus ulmifolius* or *Arundo donax*, *Eucalyptus* and *Pinus*). Therefore, the minimum value of $\delta^{13}C$-CO_2 = –24‰ observed in the field could represent a suitable endmember for the carbon signature of the soil respired CO_2 (biologic).

A comprehensive evaluation of our isotopic dataset shows (Table 2) the average carbon isotope signature of the soil CO_2 shifted toward less ^{13}C-depleted values (i.e., $\Delta\delta^{13}C$-CO_2 = +2‰) in October (Figure 3b) in comparison with September 2021 measurements (Figure 3a). At a closer inspection, the spatial distribution of the dataset collected in October 2021 (Figure 3b) shows the less ^{13}C–depleted soil CO_2 at Piano delle Baracche and Camping Sicilia in comparison with data for September 2021 when the volcanic signature of the carbon was evident in the soil CO_2 of the anomalous degassing zones. Further decreases of the ^{13}C-depletion were measured thereafter. The $\delta^{13}C$-CO_2 = 0‰ was measured in the soil gases collected at Camping Sicilia in November 2021 (Figure 3c, 3d). These values are characteristic of volcanic emissions such as fumarole gases from the crater rim at Vulcano (Paonita et al., 2013), and they were usually observed only in the soil CO_2 from the anomalous zones of Vulcano Porto (i.e., Palizzi and Faraglione).

Further interesting results of the soil gas surveys were the changes toward less ^{13}C-depleted CO_2 in the inhabited zone of Vulcano Porto. The soil CO_2 showing less ^{13}C-depleted values also at Lentia both during October and November 2021 in comparison with the most ^{13}C-depleded CO_2 that the same zones emitted on September. Overall, these results broadly supported the increase of soil CO_2 emissions caused by some transient toward a period of unrest at Vulcano.

4. Discussion

A strong relationship between the changes in the φCO_2 and the transients toward a period of volcanic unrest has been reported in the literature. The island of Vulcano experienced a period of low levels of CO_2 emissions from the soils of Vulcano Porto ($\varphi CO_2 < 57$ g m^{-2} d^{-1} based on the statistics of the dataset collected since 1988 (Camarda et al., 2022b)). Since the episode of volcanic unrest of 1988-1992 and thereafter, the passive degassing has been punctuated by some “crisis” (i.e., increases of temperature of emissions for the fumarole gases; thermal anomalies at the crater area; $\varphi CO_2 > 87$ g m^{-2} d^{-1} based on the statistics of the dataset collected since 1988 (Camarda et al., 2022b); $CO_2 > 10$ %vol in the crater fumaroles; increases of $^3He/^4He$ in the fumarole gases; increases of $\delta^{13}C$-CO_2 in both dry gases and CO_2 dissolved in thermal groundwater; increases of both δD and $\delta^{18}O$ of the vapour, volcano-tectonic seismicity) revealed by the instrumentations (Granieri et al., 2006; Mannini et al., 2019; Di Martino et al., 2020a) and the retrospective analysis of both the gas chemistry and isotopic data (Paonita et al., 2013; Di Martino et al., 2020a). Although these crises had a great relevance and enabled testing sophisticated techniques for volcano surveillance, the consequent increase in the volcanic gas emissions did not give rise to change in the alert code. This study was designed to determine the evidence of the increase in the volcanic emissions in 2021 at Vulcano through the diffuse degassing of CO_2 from the soils and the plausible increase in volcanic risk owing to the gas hazard.

The results of this study show an evident increase of φCO_2 at Vulcano Porto between September and October 2021, and it was preceded by notable variations in both gas chemistry and temperature of the fumarolic emissions at the crater rim of La Fossa (https://cme.ingv.it/bollettini-e-comunicati/bollettini-settimanali-vulcano). Thereafter, the diffuse degassing continued to increase during October and achieved a relative maximum in November 2021. Measurements of δ^{13}C-CO_2 were not collected for soil CO_2 after the November 2021. Therefore, the amount of volcanic CO_2 could not be estimated in agreement with the method proposed in this paper after November 2021. Measurements of φCO_2 collected from December 2021 to June 2022 for routine volcanic surveillance suggest that a slow decrease in soil CO_2 emissions began after November 2021, although the average φCO_2 for the area of Vulcano Porto had not yet returned to values below those measured in October 2021. The results of four surveys (Table 2) showed changes in the average value of the φCO_2 measurements. The average value of φCO_2 in September 2021 was 74 g m^{-2} d^{-1}, somewhat higher than the average values measured in 2015–2016 (i.e., 62 g m^{-2} d^{-1}) and lower than 2018 (i.e., 88 g m^{-2} d^{-1}). However, the data collected in September 2021 were 57%, 71.3%, and 80.4% lower than the average soil CO_2 flux measured in October (172 g m^{-2} d^{-1}) and November 2021 (258 g m^{-2} d^{-1}, and 377 g m^{-2} d^{-1}), respectively. The lateral distribution of the φCO_2 shows widespread increases of the diffuse degassing. These increases mainly occurred at Palizzi and Faraglione but notable changes in the diffuse degassing took place from new anomalous degassing zones at Camping Sicilia and Piano delle Baracche. In these zones, the diffuse degassing almost doubled the amount of CO_2 emitted before, and thereafter it increased again (Figure 2). These anomalous zones extended NW of the volcanic cone with a rate never observed before. These areas were affected by the appearance, during periods of high volcanic activity, by mofetes and low temperature fumarolic emissions (i.e., T <100°C), as reported by Sicardi (1940), describing the relevant increase of exhalative emissions in 1923. The explanation for these results consists in the presence of a hidden geological structures (i.e., the Tindari-Letoianni fault) draining the volcanic fluids when the magmatic gas pressure increases owing to the transition toward more vigorous volcanic activity.

The most interesting finding of this study is the transient of the soil CO_2 toward less ^{13}C-depleted isotope composition, broadly evident across Vulcano Porto. The analysis of the isotopic dataset shows that soil CO_2 was initially much less ^{13}C-depleted at Faraglione and Palizzi. After October 2021, the soil CO_2 at Camping Sicilia, Piano delle Baracche, and the eastern edge of the investigated area was enriched in ^{13}C. Furthermore, the diffuse degassing showed a more evident volcanic isotopic signature in the soil CO_2 emitted by several inhabited zones of Vulcano Porto. This result is explained by the increase of volcanic component in the soil CO_2, which has a carbon isotope signature of ~0‰.

During October 2021, the soil CO_2 showed striking changes in the carbon isotope composition of the zones of Piano delle Baracche ($\Delta\delta^{13}C-CO_2 \approx +8‰$) and Camping Sicilia ($\Delta\delta^{13}C-CO_2 \approx +15‰$) in comparison with those of September 2021. The trend of increase in $\delta^{13}C-CO_2$ continued in the successive months and the carbon isotopes showed a biologic signature ($\delta^{13}C-CO_2 \approx -22‰$) which only occured in a restricted zone near Lentia in November 2021. The results of the isotopic surveys suggested a clearly volcanic origin of the CO_2 which rose through preferential pathways due to either crustal fractures or faults. These results agree with recent studies (Di Martino et al., 2016b; 2020) indicating the relevance of the volcanic degassing through the soils of not anomalous zones where volcanic CO_2 mixes in variable amounts with shallow originated biologic CO_2. As a result of the mixing, the $\delta^{13}C-CO_2$ shows intermediate values ensued between pure biologic CO_2 ($\delta^{13}C-CO_2 \approx -24‰$) and volcanic/hydrothermal CO_2 ($\delta^{13}C-CO_2 \approx -2.5‰$). The spatial analysis of our isotopic dataset revealed that the intermediate $\delta^{13}C-CO_2$ values were measured at the transition between anomalous and not anomalous degassing zones of the Vulcano Porto area (Figure 3).

The primary objective of this study was evaluating the response of the diffuse degassing at Vulcano to the transient toward volcanic unrest. A combination of the soil CO_2 flux measurements and the carbon isotope determinations allowed us to estimate the amount of deep originated CO_2 emitted by soils and help track the transient in volcanic degassing during 2021 at Vulcano. According to Di Martino et al. (2016b) the amount of soil CO_2 included three sources of carbon dioxide (i.e., volcanic/hydrothermal CO_2, biologic CO_2, and air CO_2), with a distinctive carbon isotopic signature. A combination of the φCO_2 measurements and $\delta^{13}C$ allows the partitioning of the diffuse degassing between shallow and deep-origin CO_2 and quantifying the proportion of volcanic CO_2 which is emitted by soils. According to the three components mixing model (Di Martino et al. 2016b), the relationships between CO_2 concentrations and $\delta^{13}C-CO_2$ allowed us to establish the fractions of volcanic/hydrothermal CO_2 by knowing the carbon isotopic signatures of the three endmembers (i.e., volcanic/hydrothermal CO_2, biologic CO_2, and air CO_2). The CO_2 concentrations and the carbon isotopic signatures of the three CO_2 sources in the soils were determined in agreement with the measurements collected at Vulcano. The atmospheric endmember (i.e., air CO_2) was represented by $CO_2 = 380$ ppm vol. and $\delta^{13}C-CO_2 = -8‰$ (Carapezza et a., 2011; Di Martino et al., 2016b; Di Martino et al., 2020a). These values agree with both concentrations and carbon isotope compositions of the CO_2 in the air at a global scale (Keeling et al., 2005; Sturm et al., 2013). Albeit the soil gases could have various proportions of CO_2 and the carbon isotope compositions could be heavily ^{13}C-depleted (Cerling, 1984; Lucic et al., 2015), the biologic endmember at Vulcano were selected as the soil gases having: i) the highest CO_2 contents (i.e., CO_2 concentrations ~ 4.0 vol %) and ii) the most ^{13}C-depleted isotopic signature (i.e., $\delta^{13}C\text{-}CO_2 = -24‰$). The selected biologic endmember values were in line with those observed in earlier studies at Vulcano (Di Martino et al., 2016b; Di Martino et al., 2020a), and were consistent with those of Lucic et al. (2015) who investigated the origin CO_2 in soil gases at Long Valley Caldera - USA. A $\delta^{13}C\text{-}CO_2$ vs. the CO_2 concentrations plot shows graphically several mixing volcanic-biogenic-air mixing curves (Figure 4), and the curve for carbon isotope fractionation by advective-diffusive transport through soils (Capasso et al., 2001; Camarda et al., 2007). This plot allows the partitioning of φCO_2 because of soil CO_2 consisting of three contributions: i) biologic CO_2; ii) volcanic/hydrothermal CO_2, and iii) air CO_2 which contributes to various extents; since CO_2 has a concentration of several orders of magnitude lower than in other two sources, it is arguable that atmospheric CO_2 dilutes for variable degrees the primary mixing between volcanic CO_2 and biological CO_2. The position of the experimental data relative to the mixing lines in the plot provides the respective proportions of volcanic/hydrothermal and biological CO_2. The volcanic/hydrothermal proportion is then used as the multiplier for the full φCO_2 for distinguishing point-by-point the amount of volcanic CO_2 emitted by soils (i.e., the deep-originated soil CO_2 emission). Interpolation of these data and integration over the surface of the study area allows of the estimation of the amount of CO_2 having either volcanic or biogenic origin. Previous studies have evaluated the amount of volcanic/hydrothermal CO_2 emitted by either anomalous or not anomalous degassing zones at Vulcano Porto through the application of this method (Di Martino et al., 2016b; Di Martino et al., 2020a). According to these studies, the CO_2 partitioning has helped track changes in the volcanic degassing system of Vulcano. A comprehensive analysis of the soil CO_2 partitioning in this study has shown an increase of deep-origin CO_2 which began at the end of September 2021, and continued thereafter (Figure 5a). The volcanic emissions in October 2021 were more than double the amount of the volcanic CO_2 estimated for September 2021, while volcanic CO_2 emissions had increased by 64% by November 9th in comparison with October, and by 91% on November 23th compared to the previous survey (i.e., November 9th). The emissions of volcanic CO_2 had increased from $13 \cdot 10^4$ kg d^{-1} to $107 \cdot 10^4$ kg d^{-1} throughout the 63 days at an average rate of ~ 15 t d^{-2}.

The soil CO_2 partitioning also allowed the calculation of the biologic CO_2 contents, whose amount was almost one order of magnitude lower than the volcanic CO_2. Albeit the biologic CO_2 was 40-60% higher in November 2021 than October, a comparison with data for both 2015-2016 and 2018 (Table 3) showed similar patterns during the autumnal period in the shallow originated CO_2 (Di Martino et al., 2020a). These results can be explained by the behaviour of the biologic CO_2 in the soil gases that achieved a maximum at the end of the summer period owing to dominant plants across the island of Vulcano.

The volcanic to biologic mass ratio of CO_2 ranged from 5 to 17 in 2021 (Figure 5b). These results agree with those of Di Martino et al. (2020a) who also found that the deep-originated to biologic CO_2 ratio helped track the transient toward a period of volcanic unrest owing to the remarkable increases were observed when the volcanic gas output strengthened from September to November 2018 (Mannini et al., 2019). During 2021, the increase of the volcanic to biologic mass ratio began after a few decades of very low values of soil CO_2 emissions (i.e., <50 g m^{-2} d^{-1} of soil CO_2 flux measured since 1998 which correspond to $\sim 10 \cdot 10^4$ kg d^{-1} for volcanic CO_2 calculated in agreement with Di Martino et al. (2016b) since 2015) which can be explained as passive degassing from a magma body at depth. According to Mandarano et al. (2016), the degassing of a shallow Latite/Trachyte magma body at 2-5 km (De Astis et al., 2013) sustains the emissions at La Fossa crater rim, while the increase of volcanic degassing that punctuated the fumarolic–sulphataric activity at Vulcano can be explained as the effects of shallow magma bodies moving toward the surface (Nicotra et al., 2018).

Since the past century, several papers in the literature have reported a strong correlation between the CO_2 output and the amount of magma in a volcanic feeding system (Carroll and Holloway, 1994; Wallace and Anderson, 2000). In this study, the carbon isotopic signature has shown that the wider proportion of the soil CO_2 during 2021 at Vulcano had a magmatic origin. This strongly suggests that a link may exist between the diffuse degassing increases and the magma dynamics in the feeding system at Vulcano. The evaluation of the CO_2 output implies the possibility of estimating the amount magma having been involved in the volcanic degassing. Prior studies have shown that soil diffuse degassing accounts for almost 10% of the CO_2 output from the crater rim fumaroles at Vulcano (Chiodini et al., 1998; Carapezza et al., 2011), and the wider proportion of the diffuse degassing occurs from the zone of Vulcano Porto. However, this proportion can change owing to the increase of diffuse degassing during unrest periods (Allard et al., 1991; Badalamenti et al., 1991; Carapezza et al., 2011; Inguaggiato et al., 2012). The soil CO_2 at Vulcano Porto changed from ordinary proportion (~10%) to a proportion characteristic for an event of unrest (~50%), due to a wide increase of the volcanic degassing, as that occurred in a previous crisis recorded in 2005 (Carapezza et al., 2011). Assuming a linear increase from 10% up to 50% for the proportion of diffuse degassing to crater emissions, during the period of observation (i.e., 63 days), the CO_2 emissions from the crater ranged from $546.6 \cdot 10^4$ kg d^{-1} to $744.1 \cdot 10^4$ kg d^{-1}, and the resulting cumulative CO_2 emissions of around $38881.5 \cdot 10^4$ kg (Figure 5c). These estimates allow a useful comparison between CO_2 emissions from the crater with volcanic CO_2 emitted by soils of Vulcano Porto and estimate the whole volcanic CO_2 involved in the degassing crisis of 2021 at Vulcano. Using a 2rd order polynomial function, the best fitting curve of our estimates of the volcanic CO_2 ($R^2 = 0.9977$) allows describing the evolution of the volcanic CO_2 emitted by soils. The integration of the volcanic CO_2 over this function gives $12037.13 \cdot 10^4$ kg for the volcanic CO_2 emitted by soils of Vulcano Porto, which has the same order of magnitude of the amount of volcanic CO_2 emitted from the crater area. Therefore, the comprehensive amount of volcanic CO_2 emitted from September to November 2021 at Vulcano implies a gas reservoir supplying almost $50918.6 \cdot 10^4$ kg. These results conceivably underestimate the role of volcanic degassing from the crater area, albeit they agree with estimates (i.e., average CO_2 flux ~3500 t d^{-1}; range from 640 t d^{-1} to 6400 t d^{-1}) retrieved by using both the SO_2 fluxes reported in the weekly bulletin for volcano surveillance (i.e., https://cme.ingv.it/bollettini-e-comunicati/bollettini-settimanali-vulcano) and the current evaluation of the C/S ratio at Vulcano (Tamburello et al., 2011).

Previous studies have shown that the CO_2 contents have a strong relationship with magma composition. According to these studies (Carroll and Holloway, 1994), the CO_2 dissolved in silicic magmas achieves up to 0.3 wt%, and has an almost inverse relationship with the amount of H_2O dissolved at a given pressure (i.e., depth in the Earth interior). Furthermore, silicic composition affects magma density and its ability to rise toward the surface. A value of ~0.35 km^3 can be estimated for magmas which sustained the volcanic degassing from September to November 2021 at Vulcano. This value corresponds to $\sim 8.48 \cdot 10^8$ tons of magma which have supplied $50918.6 \cdot 10^4$ kg of CO_2. The estimates of both mass and volume for magmas were based on average values for CO_2 solubility in the magma (i.e., 0.06 wt%) and density (~2.5 g cm^{-3}). In this study, estimates of volcanic CO_2 were shown for September to November 2021. Taking into account the range 310-290 MPa for crystallization pressure of the magma feeding the volcanic degassing at Vulcano (Nicotra et al., 2018) and 0.5 wt% water contents, the CO_2 solubility in the magma at Vulcano would be around 1800 ppm

(Carroll and Holloway, 1994). Using the same calculation method with this higher value for the CO_2 solubility, the value ~ 0.11 km^3 provides a lower estimation for the volume of magma residing at depth. Therefore, this calculation provides the lowest size for the volume of magma which is compatible with the amount of CO_2 which Vulcano emitted during the volcanic outgassing crisis from September to November 2021. No measurements of $\delta^{13}C\text{-}CO_2$ were collected after the November 2021 soil gas surveying. Therefore, we were unable to apply the method adopted in this work to further φCO_2 measurements for distinguishing volcanic from biogenic CO_2. Since December 2021, the volcanic gas monitoring (i.e., φCO_2, the fumarole gas compositions, and continuous φCO_2 measurements through the geochemical monitoring network which is deployed at Vulcano) showed signs indicating that the culmination of the degassing crisis occurred during from November to early December 2021. Since January 2022, a gradual decrease in the trend for volcanic gas emission began. The φCO_2 and several other parameters used for volcanic surveillance had not yet returned to the values observed before September 2021, indicating that the volcanic crisis was not yet over (https://cme.ingv.it/bollettini-e-comunicati/bollettini-settimanali-vulcano). As a result, the DPC had not changed the alert code back to “green”. The estimates provided in this paper for magma volume (i.e., ~0.35 km^3) should be a minimum, based on volcanic CO_2 emitted during the most intense degassing period of the 2021 crisis.

These findings suggest that this magma body resided at higher depths within a Latite/Trachyte reservoir, and the CO_2 flushed several smaller magma bodies (Nicotra et al., 2018) during its ascent before its entering the atmosphere. Actually, the CO_2 had low solubility in magmas and achieves saturation at either mantel or deep crustal level. According to Nicotra et al., (2018), who integrated petrological and geochemical data, the plumbing system of Vulcano includes several reservoirs connected at the mantle-crustal level (21 – 17 km depth), where a basaltic-shoshonitic magma resides and is thought to feed the shallow magma reservoirs (i.e., between 17 and 2 km) of both Vulcanello and La Fossa.

These data should be interpreted with caution because an underlying hydrothermal system can supply CO_2 for diffuse degassing, determining an over estimation of the magmatic body. Several studies have invoked the interaction of deep magmatic fluids with shallow hydrothermal fluids (Capasso et al., 1997; Chiodini et al., 1998; Nuccio et al., 1999; Paonita et al., 2002; Granieri et al., 2006; Federico et al., 2010; Paonita et al., 2013; Capasso et al., 2017; Di Martino et al., 2020b), where the hydrothermal component consists mainly of hot steam generated by the evaporation of brines entering the high temperature zone surrounding the conduit of rising fluids. In fact, CO_2 is very soluble in water and, therefore, hydrothermal systems are widely recognised as notable CO_2 reservoirs. To evaluate the role of a hydrothermal system in the increased diffuse degassing at Vulcano during 2021, we considered CO_2 solubility in brine (e.g., aqueous NaCl 1 *m*, where *m* is the molality of the solution) at the temperature range 172 – 325 °C. According to Ellis and Golding (1963), who investigated empirically the CO_2 solubility in both brine and water at temperatures above 100 °C, the CO_2 solubility was deemed to have a wide range (i.e., from $5.51\ 10^{-3}$ to $18.4\ 10^{-3}$ moles/mole of H_2O, respectively) with a minimum value of $3.18\ 10^{-3}$ moles/mole of H_2O at 177 °C (Ellis and Golding, 1963). Moreover, the solubility relationship was nonlinear with the lowering of the brine temperature. Considering this range of CO_2 solubility, an amount of brine ranging from $1.13 \cdot 10^7$ to $6.55 \cdot 10^7$ tons must have degassed in order to supply the CO_2 emissions in 2021. Active volcanoes host hydrothermal systems which achieve a stability between the eruptions. Thus, it is arguable that only a small proportion of the hydrothermal reservoir (i.e., 0.1-1% of its volume) contributed to the CO_2 emissions and the overall system has been unchanged at Vulcano. Assuming 1.058 t m^{-3} as a density of the hydrothermal brine, and 15% for the average permeability of the volcanic rocks, the volume for the hydrothermal reservoir involved in the increase of degassing at Vulcano would have ranged from 7.13 to 413 km^3. The sizes of the effective hydrothermal reservoirs at Vulcano were incompatible with this volume estimation, despite several questions having remained unanswered until present. Research questions that could be asked include why the almost steady hydrothermal system became unstable during 2021, and how the energetic transient in the volcanic system could have triggered such a large CO_2 degassing episode.

The results shown in this paper may underestimate of the role of small magma volume rising toward the surface. These batches can release their gas phase and cause degassing crisis at the surface. Actually, the gas released from small magma batches can sustain degassing increase, owing to the decompression and gas solubility decrease by magma migration upward. The volcanic gas can interact with the shallow hydrothermal fluid and provide further contributions to volcanic degassing. Broad increases in volcanic deformation, seismicity, the inflation of the volcanic edifice, and other geophysical signals were expected during magma upraise, and thus, our geochemical dataset prevented us from ruling out this alternative hypothesis. Further studies are needed to ascertain whether a combination of deep residing magma uprising in the shallow crustal level having caused the increase of volcanic degassing and shed light on the mechanism underlying the transient toward a period of unrest at quiescent volcanoes. However, these results provide further insights into the nature of volcanic degassing in quiescent volcanoes. Albeit the quiescent degassing can be sustained by small magma bodies that resides at shallow levels (e.g., < 15 km) and occur continuously replenished from below, the transition toward a period of unrest can involve instability in large magma bodies residing at greater depth.

5 Conclusions

This study examined the impact of the increase in volcanic degassing from 2021 onto soil CO_2 emissions at Vulcano Porto with the aim of scrutinising the plausible effects on gas hazards. Four surveys allowed us to investigate the soil CO_2 emissions over a 2.2 km^2 wide area at the base of La Fossa cone and assess the amount of volcanic CO_2 emitted from September to November 2021. These investigations were frequently based on the statistical processing of soil CO_2 flux measurements. This study evaluated the volcanic CO_2 emissions according to soil CO_2 flux measurements combined with the carbon isotope compositions of the soil CO_2. The measurement dataset collected in the field and in the laboratory was analysed to obtain the simulation surface for both the lateral distribution of the anomalous degassing zones and the origin of the soil CO_2 emissions, provided by the carbon isotopic signature of the known CO_2 sources.

This study has shown two persistent anomalous degassing zones occurring at Palizzi and Faraglione. These zones are well known in the literature because of several distinguishing features between in the gas output in the occurrence of the crisis that punctuated the solfataric–activity at Vulcano in the past decades. While diffuse degassing at Palizzi is known to occur in an uninhabited zone, Faraglione is an area which is at high risk on the Island of Vulcano. Although the present study has not evaluated the air CO_2 concentrations of either of these areas, previous studies in the same areas and preliminary results from continuous monitoring networks have shown that increases in the soil CO_2 emissions have also increased the volcanic risk of these regions owing to the high gas hazard and population's exposure to volcanic emissions. The second major result of this study was that two anomalous degassing zones have been reactivated at Camping Sicilia and Piano delle Baracche, respectively, during 2021. Albeit in 2018 the diffuse degassing at Camping Sicilia already showed measurable variations, during 2021 the increase in volcanic CO_2 emissions preventing the population from accessing it and displacing the population from any areas that were occurring nearby it.

The present study was conducted to thoroughly examine the transients of the volcanic degassing at Vulcano during 2021. The results of our surveys show a remarkable increase in the gas hazard across the inhabited zones of the Island of Vulcano, owing to the increase in the magma degassing at depths. The monitoring of diffuse degassing from a reference area has several implications for risk management and mitigation in volcanic islands. From this standpoint, this research confirms previous findings and contributes additional evidence that suggest that volcanic emissions may cause a significant risk to populations, especially when degassing increase occurs after prolonged passive degassing periods.

The carbon isotope compositions of soil CO_2 allowed partitioning φCO_2 between shallow-originating CO_2 (i.e., biogenic CO_2) and volcanic CO_2 in the not anomalous zones by using an already published mixing model. The proportion of volcanic CO_2 has been used as a multiplication factor of φCO_2 for evaluating the amount of volcanic CO_2 emitted by soils. These estimations have been repeated at Vulcano Porto throughout the period of surveys and the results showed that the volcanic CO_2 emissions during September 2021 contributed 10% of the volcanic CO_2 output. A notable transition toward volcanic degassing unrest occurred on October, 2021, followed by an unprecedently observed quickly rising rate.

Recent studies of the plumbing system at La Fossa volcano have evidenced the existence of an articulated feeding system consisting of multiple magma reservoirs. The results of the present study suggest that the increase of volcanic CO_2 during 2021 had a deep origin, owing to increased magmatic degassing. In general, it appears that a large enough magma body residing at the Moho boundary may have been involved in the transient toward a period of unrest event at Vulcano, despite the alternative of a hypothesis of a small magma batch having risen toward shallower levels not being entirely ruled out based on our dataset.

Data Availability Statement

The soil CO_2 flux data and the carbon isotope composition of the soil CO_2 are from

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Software that we used for data processing: Quantum GIS (https://www.qgis.org/it/site/)

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Figure Captions

Figure 1 The island of Vulcano – Aeolian Islands (Italy) in the south Tyrrhenian Sea. Sampling grid (orange spots) of the soil gases at Vulcano Porto area. The main regional geologic structures are traced in the inset.

Figure 2. Contour plots of CO_2 flux discharged by soils at Vulcano Porto during the 2021 unrest period. a) September, 20; b) October, 10; c) November, 9; d) November, 23. Kriging simulations were realized with QGis Software. Alert levels: green = quiescence (i.e., absent eruptive activity and possible gas emission from crater fumaroles and areas outside the crater); yellow = minor surface hydrothermal crisis (i.e., protracted anomaly for some monitoring parameters; absent and possible eruptive activity).

Figure 3. Contour plots of δ^{13}C of the soil CO_2 at Vulcano Porto during the 2021 unrest period. a) September, 20; b) October, 10; c) November, 9; d) November, 23. Kriging simulations were realized with QGis Software. Alert levels: green = quiescence (i.e., absent eruptive activity and possible gas emission from crater fumaroles and areas outside the crater); yellow = minor surface hydrothermal crisis (i.e., protracted anomaly for some monitoring parameters; absent and possible eruptive activity).

Figure 4. δ^{13}C-CO_2 value CO_2 concentration plots of soil CO_2 at Vulcano Porto. ^{13}C/^{12}C ratio of the soil CO_2 results from volcanic CO_2 mixed with biogenic CO_2, and air dilution. The carbon isotopic signatures of the three endmembers are: i) volcanic/hydrothermal CO_2 (CO_2 content = 100 vol %; δ^{13}C-CO_2 = -2.5‰); ii) biogenic CO_2 (CO_2 content ≈ 4 vol %; δ^{13}C-CO_2 = -24‰); and iii) air CO_2 (CO_2 content = 0.0380 vol %; δ^{13}C-CO_2 = -8‰). Air – Biogenic mixing is indicated with black line, Air – Volcanic/Hydrothermal mixing is shown by a blue line, finally, Biogenic - Volcanic/Hydrothermal mixing is shown with red line. The grey lines indicate the mixing curves between Volcanic/Hydrothermal CO_2 and different proportions of Air - Biogenic CO_2 or air CO_2 and different proportions of Biogenic - Hydrothermal CO_2. The carbon isotope fractionation process of CO_2 by diffusion through porous media (Capasso et al., 2001) is also shown (green curve). The plot shows carbon isotopic dataset for 2021 September, 20 (green spots), 2021 October, 10 (blue spots), 2021 November, 9 (yellow spots), and 2021 November,23 (red spots).

Figure 5 a) Soil CO_2 output partitioning between volcanic (red bars) and biologic (green bars) components at Vulcano in 2021. The regression cure for the output of volcanic CO_2 was used to show the evolution of the soil CO_2 emissions from volcanic origin at Vulcano Porto (R^2 = 0.9977) and retrieve the full CO_2 outgassing as described in Figure 5c. The inset shows a comparison with soil CO_2 emissions during 2018 (Di Martino et al., 2020a); b) The changes in the volcanic to biologic output mass ratio increased after the passive degassing; c) Integrated evaluation of the soil CO_2 emissions. Soil CO_2 cumulative output was calculated by fitting the experimental results for volcanic CO_2 through a 2nd order fitting curve (see also yellow area in Figure 5a). The CO_2 emissions from the crater zone was retrieved from the soil CO_2 emissions by taking into account a linear change from 10% to 50% for the peripheral to crater proportion of the CO_2 output (Allard et al., 1991; Chiodini et al., 2008; Carapezza et al., 2011; Inguaggiato et al., 2012)

Table 1. Dataset of the soil gas survey performed at Vulcano in 2021. (Di Martino et al., 2022).

Table 2 Descriptive statistics of the soil gas survey dataset in 2021. Already published data (with asterisk) from Di Martino et al., 2020awere included for comparison

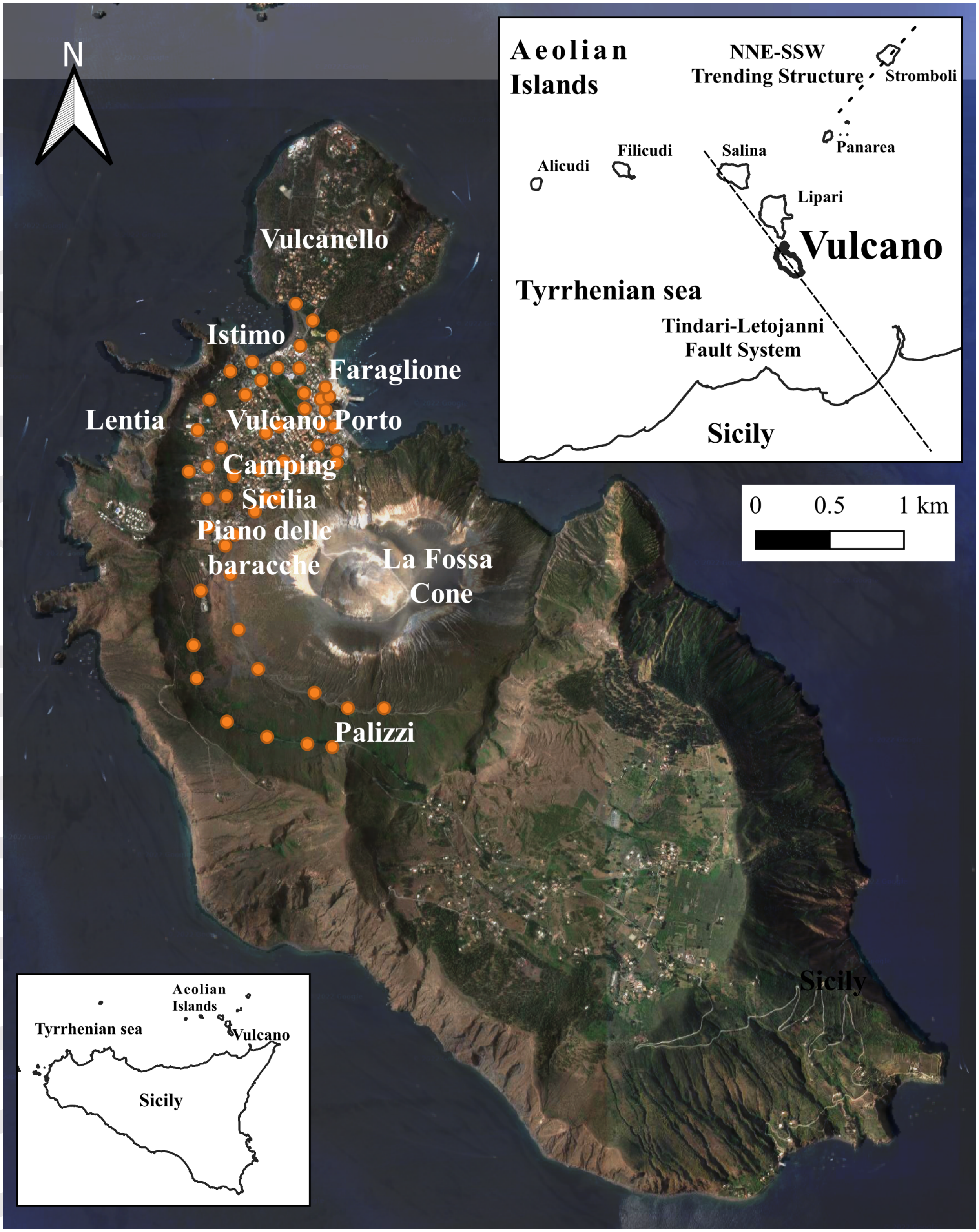
Table 3 Soil CO_2 partitioning at Vulcano from 2015 to 2021. A significant transition between biologic to volcanic output mass ratio was observed during 2021. This change was almost one order of magnitude greater with respect to 2018. Data reported for time window 2015-2018 were retrieved from the literature (Di Martino et al., 2020a) for comparison with the dataset in 2021 (this study).

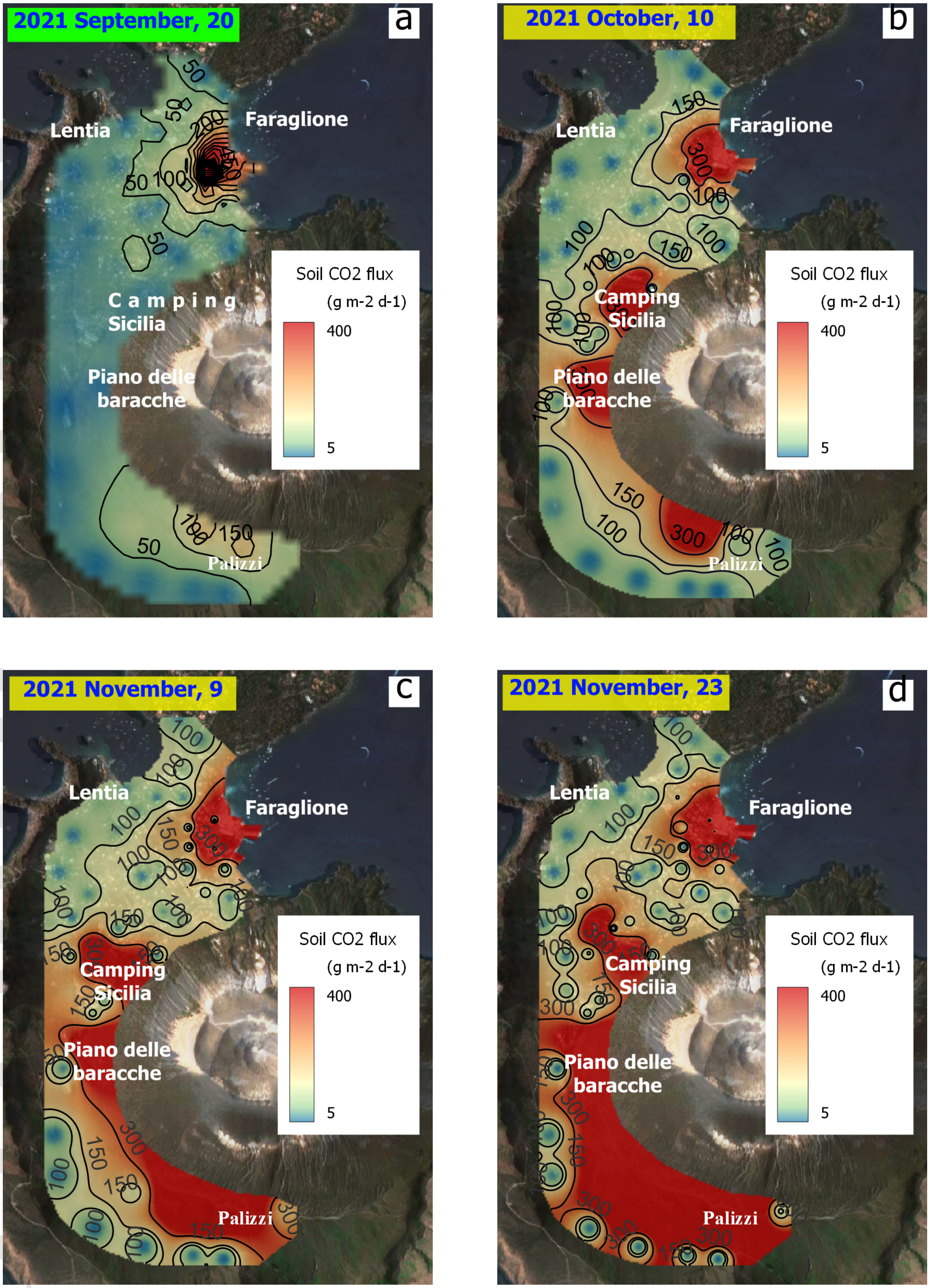
	2021 September, 20		**2021 October, 10**		**2021 November, 09**		**2021 November, 23**	
Grid node	**CO_2 flux ($g\ m^{-2}\ d^{-1}$)**	**$\delta^{13}C$-CO_2 (‰ vs. VPDB)**	**CO_2 flux ($g\ m^{-2}\ d^{-1}$)**	**$\delta^{13}C$-CO_2 (‰ vs. VPDB)**	**CO_2 flux ($g\ m^{-2}\ d^{-1}$)**	**$\delta^{13}C$-CO_2 (‰ vs. VPDB)**	**CO_2 flux ($g\ m^{-2}\ d^{-1}$)**	**$\delta^{13}C$-CO_2 (‰ vs. VPDB)**
2	84	-0.57	25	-4.47	182	0.93	91	0.23
3	173	0.23	69	0.03	456	1.23	695	0.83
4	171	0.13	954	-0.87	2665	-1.47	7112	-0.87
5	100	-1.87	127	-4.47	109	-3.47	1331	0.23
6	5	-14.67	1104	0.03	1297	0.23	2015	1.03
7	24	-22.07	47	-21.37	49	-17.37	73	-12.37
8	18	-20.37	1048	1.73	1161	2.83	383	3.33
9	18	-16.07	29	-16.77	18	-16.37	25	-16.37
10	7	-16.47	18	-13.67	53	-14.97	75	-13.07
11	11	-19.87	46	-20.67	78	-19.57	7	-15.17
12	24	-2.57	13	-4.87	62	-4.27	106	-4.47
13	135	-2.77	182	-3.77	251	-2.67	146	-1.87
14	577	-8.77	787	0.43	82	-5.87	273	1.23
15	35	-14.17	35	-18.87	64	-19.27	25	-19.07
16	9	-22.47	2	-18.00	23	-14.4	20	-19.17
17	4	-19.77	2	-12.77	25	-16.57	27	-19.07
18	38	-21.37	24	-18.97	24	-18.97	18	-20.77
19	27	-9.67	246	-11.07	78	-10.07	173	-6.77
20	16	-24.27	20	-19.47	20	-24.07	38	-25.17
21	11	-14.57	20	-16.37	62	-19.07	16	-17.37
22	9	-14.97	27	-16.77	73	-14.37	9	-14.37
23	13	-19.37	9	-18.47	13	-19.37	7	-7.97
24	13	-19.87	20	-18.77	29	-20.37	76	-14.07
26	13	-15.37	5	-16.97	13	-17.87	11	-18.77
27	13	-21.07	20	-18.57	73	-17.52	25	-17.97
28	22	-22.17	64	-17.47	73	-12.67	18	-22.97
29	20	-20.57	20	-13.77	182	-11.77	53	-20.27
30	4	-19.57	35	-17.87	25	-18.47	9	-17.47
32	15	-17.42	182	-10.7	5467	1.4	1542	1.63

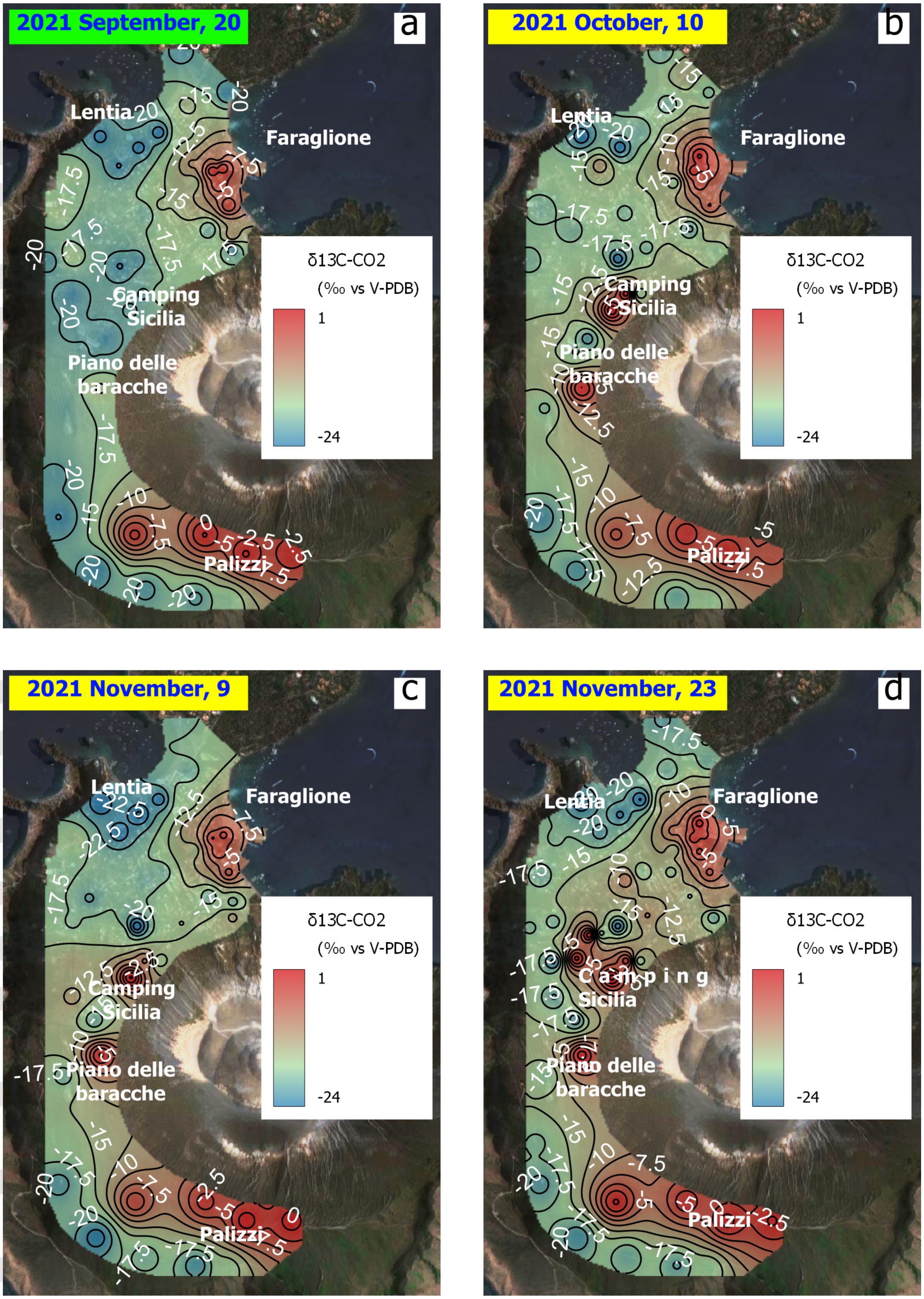
33	7	-15.27	13	-18.67	16	-17.27	11	-19.07
34	7	-15.67	7	-16.57	15	-15.27	15	-17.77
35	36	-23.27	53	-24.07	51	-24.67	46	-24.27
36	11	-22.67	7	-10.97	36	-24.37	33	-21.07
38	47	-23.67	46	-23.97	36	-25.57	27	-23.07
39	7	-19.97	22	-20.96	27	-21.77	7	-19.47
40	9	-15.07	55	-18.57	36	-16.37	29	-9.77
41	91	-21.27	82	-24.07	73	-26.57	113	-23.57
42	16	-20.67	1388	1.13	419	-7.07	787	-1.37
43	26	-16.3	33	-16.87	15	-12.21.	33	-16.07
44	27	-15.37	96	-16.22	29	-16.27	146	-10.67
45	11	-22.47	13	-16.67	11	-16.67	18	-17.97
46	9	-17.47	10	-21.17	9	-23.67	13	-21.77
47	9	-0.37	4	-16.77	5	-16.27	4	-17.07
48	1554	-0.57	1484	-0.87	1796	-2.27	3644	-0.97
49	164	-2.07	310	-1.67	2424	-1.47	273	-1.97
80	32	-18.64	82	-14.27	936	-5.23	91	0.63
81	36	-22.57	49	-17.67	80	-19.47	73	-21.57
82	20	-20.97	25	-22.07	13	-20.97	22	-20.87
83	15	-20.67	9	-11.97	9	-18.47	13	-19.37
84	13	-21.27	11	-19.57	15	-21.77	18	-20.27
85	5	-10.87	5	-17.37	69	-11.97	27	-19.27
86	15	-22.77	55	-13.67	24	-18.57	100	-10.27
41bis	24	-15.37	7	-16.67	24	-15.87	44	-18.37

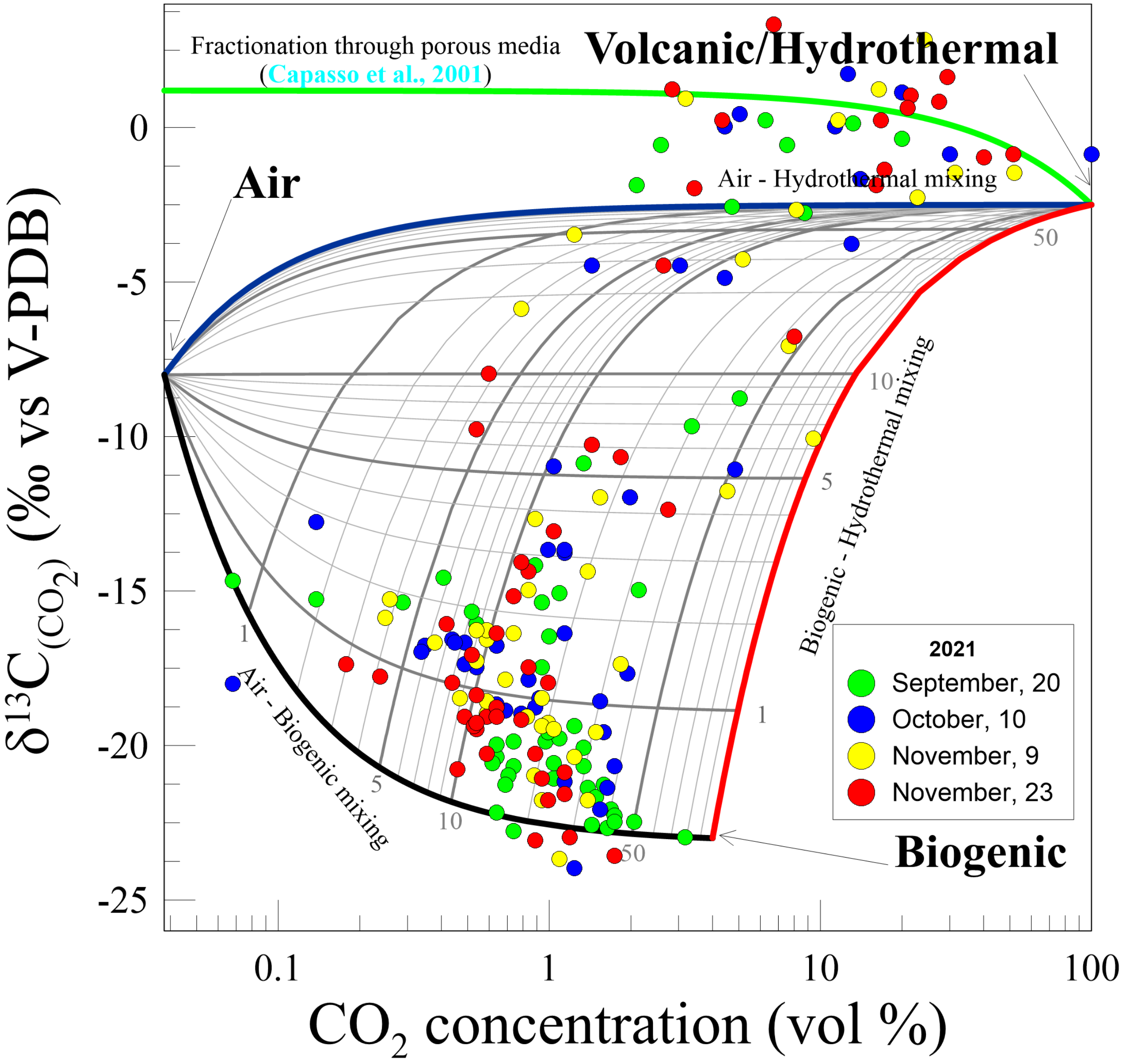
Date	**Average**		**Variance**		**Skewness**		**Kurtosis**		**Mode**	
	CO$_2$ flux (g m^2 d^{-1})	**δ^{13}C-CO$_2$ (‰ vs. VPDB)**	**CO$_2$ flux (g m^2 d^{-1})**	**δ^{13}C-CO$_2$ (‰ vs. VPDB)**	**CO$_2$ flux**	**δ^{13}C-CO$_2$**	**CO$_2$ flux**	**δ^{13}C-CO$_2$**	**CO$_2$ flux (g m^2 d^{-1})**	**δ^{13}C-CO$_2$ (‰ vs. VPDB)**
2015, May*	77	–15	41294	49	4	1	14	0	2	–13
2015, June*	55	–13	17401	29	4	1	13	0	4	–14
2015 November*	65	–15	32666	30	5	1	22	0	2	–18
2016, March*	54	–13	14646	25	3	1	10	1	5	–15
2018 September*	90	–15	48514	52	4	1	20	0	18	–17
2018, November*	86	–15	53501	49	5	1	27	0	9	–18
2021, September 20	74	–16	50388	58	6	1	37	0	9	–20
2021, October 10	172	–14	127472	61	3	1	6	–1	20	–17
2021, November 9	258	–14	326851	66	3	1	9	–1	73	–16
2021, November 23	377	–13	1226587	76	5	1	26	–1	18	–19

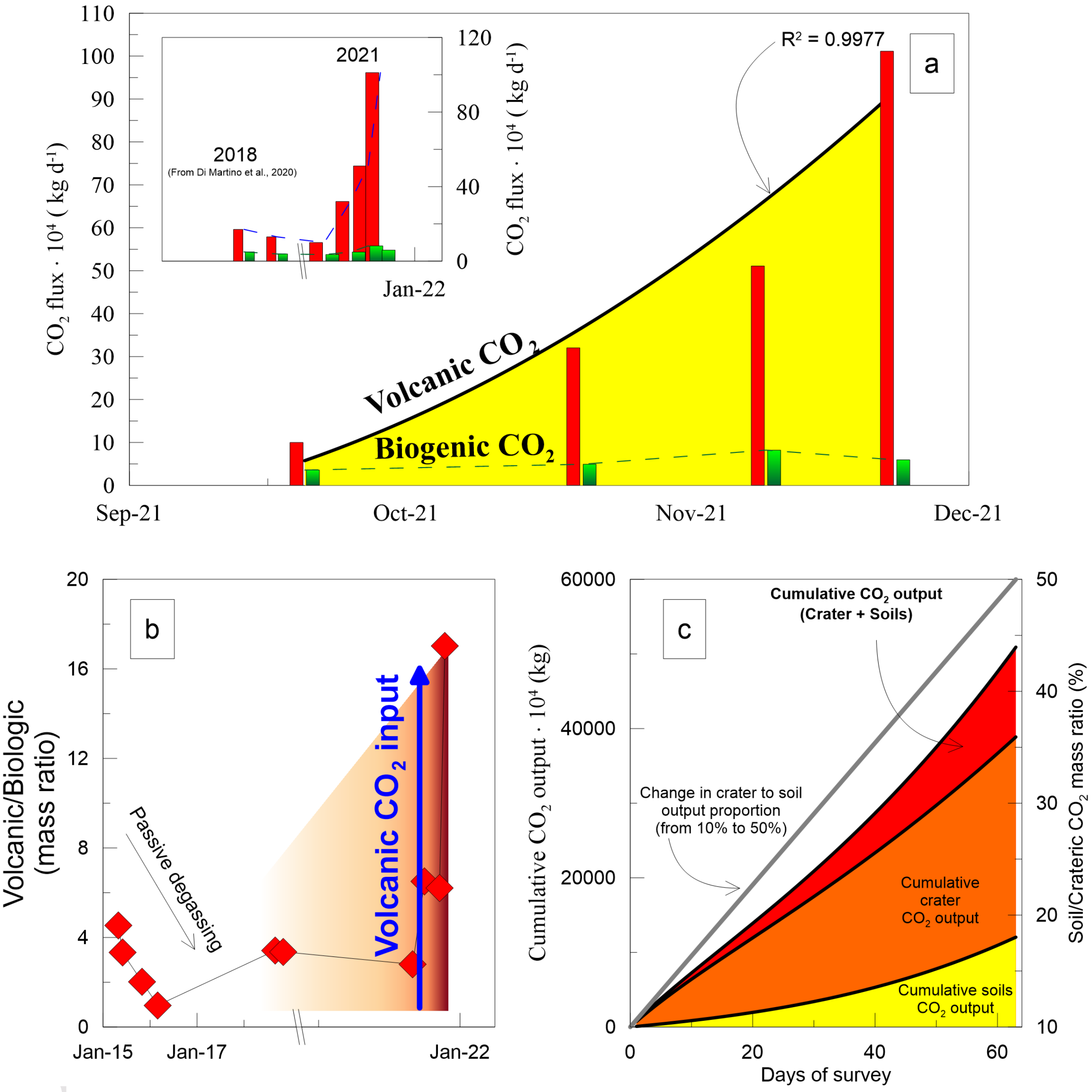
Survey		Soil CO_2 output (volcanic + Biologic) ($\cdot 10^4$ kg d^{-1})	Volcanic CO_2 output ($\cdot 10^4$ kg d^{-1})	Biologic CO_2 output ($\cdot 10^4$ kg d^{-1})	Volcanic/Biologic mass ratio	References
2015	May	14.30	11.72	2.58	4.54	Di Martino et al., 2020
	June	9.24	7.1	2.14	3.32	Di Martino et al., 2016 Di Martino et al., 2020
	November	12.84	8.58	4.26	2.01	Di Martino et al., 2020
2016	March	10.54	5.19	5.35	0.97	Di Martino et al., 2020
2018	September	22.05	17.06	4.99	3.42	Di Martino et al., 2020
	November	16.93	13.05	3.88	3.36	Di Martino et al., 2020
2021	September, 20	13.53	9.97	3.56	2.80	This study
	October, 10	36.93	32.03	4.90	6.54	This study
	November, 9	59.30	51.10	8.20	6.23	This study
	November, 23	107.08	101.15	5.94	17.03	This study


N
Vulcanello
Istimo
Faraglione
Lentia
Vulcano Porto
Camping
Sicilia
Piano delle
baracche
La Fossa
Cone
Palizzi
Sicily
Aeolian
Islands
NNE-SSW
Trending Structure
Stromboli
Panarea
Alicudi
Filicudi
Salina
Lipari
Vulcano
Tyrrhenian sea
Tindari-Letojanni
Fault System
Sicily
0
0.5
1 km
Aeolian
Islands
Tyrrhenian sea
Vulcano
Sicily


2021 September, 20
a
Lentia
Faraglione
Camping Sicilia
Piano delle baracche
Palizzi
Soil CO2 flux
(g m-2 d-1)
400
5
50
100
150
200
2021 October, 10
b
Lentia
Faraglione
Camping Sicilia
Piano delle baracche
Palizzi
Soil CO2 flux
(g m-2 d-1)
400
5
100
150
300
2021 November, 9
c
Lentia
Faraglione
Camping Sicilia
Piano delle baracche
Palizzi
Soil CO2 flux
(g m-2 d-1)
400
5
100
150
300
2021 November, 23
d
Lentia
Faraglione
Camping Sicilia
Piano delle baracche
Palizzi
Soil CO2 flux
(g m-2 d-1)
400
5
100
150
300


2021 September, 20
a
Lentia
Faraglione
Camping
Sicilia
Piano delle
baracche
Palizzi
δ13C-CO2
(‰ vs V-PDB)
1
-24
2021 October, 10
b
Lentia
Faraglione
Camping
Sicilia
Piano delle
baracche
Palizzi
δ13C-CO2
(‰ vs V-PDB)
1
-24
2021 November, 9
c
Lentia
Faraglione
Camping
Sicilia
Piano delle
baracche
Palizzi
δ13C-CO2
(‰ vs V-PDB)
1
-24
2021 November, 23
d
Lentia
Faraglione
Camping
Sicilia
Piano delle
baracche
Palizzi
δ13C-CO2
(‰ vs V-PDB)
1
-24


Fractionation through porous media
(Capasso et al., 2001)
Volcanic/Hydrothermal
Air
Air - Hydrothermal mixing
50
10
5
1
Biogenic - Hydrothermal mixing
1
5
10
50
Air - Biogenic mixing
Biogenic
2021
🟢 September, 20
🔵 October, 10
🟡 November, 9
🔴 November, 23
$\delta^{13}C_{(CO_2)}$ (‰ vs V-PDB)
0
-5
-10
-15
-20
-25
0.1
1
10
100
CO_2 concentration (vol %)


a
R² = 0.9977
Volcanic CO₂
Biogenic CO₂
CO₂ flux · 10⁴ (kg d⁻¹)
0
10
20
30
40
50
60
70
80
90
100
110
Sep-21
Oct-21
Nov-21
Dec-21
2018
(From Di Martino et al., 2020)
2021
Jan-22
CO₂ flux · 10⁴ (kg d⁻¹)
0
40
80
120
b
Volcanic/Biologic (mass ratio)
Passive degassing
Volcanic CO₂ input
0
4
8
12
16
20
Jan-15
Jan-17
Jan-22
c
Cumulative CO₂ output (Crater + Soils)
Change in crater to soil output proportion (from 10% to 50%)
Cumulative crater CO₂ output
Cumulative soils CO₂ output
Cumulative CO₂ output · 10⁴ (kg)
Soil/Crateric CO₂ mass ratio (%)
0
20000
40000
60000
10
20
30
40
50
0
20
40
60
Days of survey