



## Article

# Environmental and Volcanic Implications of Volatile Output in the Atmosphere of Vulcano Island Detected Using SO<sub>2</sub> Plume (2021–23)

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**Abstract:** The volatiles released by the volcanic structures of the world contribute to natural environmental pollution both during the passive and active degassing stages. The Island of Vulcano is characterized by solfataric degassing mainly localized in the summit part (Fossa crater) and in the peripheral part in the Levante Bay. The normal solfataric degassing (high-temperature fumarolic area of the summit and boiling fluids emitted in the Levante Bay area), established after the last explosive eruption of 1888–90, is periodically interrupted by geochemical crises characterized by anomalous degassing that are attributable to increased volcanic inputs, which determine a sharp increase in the degassing rate. In this work, we have used the data acquired from the INGV (Istituto Nazionale di Geofisica e Vulcanologia) geochemical monitoring networks to identify, evaluate, and monitor the geochemical variations of the extensive parameters, such as the SO<sub>2</sub> flux from the volcanic plume (solfataric cloud) and the CO<sub>2</sub> flux from the soil in the summit area outside the fumaroles areas. The increase in the flux of volatiles started in June–July 2021 and reached its maximum in November of the same year. In particular, the mean monthly flux of SO<sub>2</sub> plume of 22 tons day<sup>-1</sup> (t d<sup>-1</sup>) and of CO<sub>2</sub> from the soil of 1570 grams per square meter per day (g m<sup>2</sup> d<sup>-1</sup>) increased during this event up to 89 t d<sup>-1</sup> and 11,596 g m<sup>2</sup> d<sup>-1</sup>, respectively, in November 2021. The average annual baseline value of SO<sub>2</sub> output was estimated at 7700 t d<sup>-1</sup> during normal solfataric activity. Instead, this outgassing increased to 18,000 and 24,000 t d<sup>-1</sup> in 2021 and 2022, respectively, indicating that the system is still in an anomalous phase of outgassing and shows no signs of returning to the pre-crisis baseline values. In fact, in the first quarter of 2023, the SO<sub>2</sub> output shows average values comparable to those emitted in 2022. Finally, the dispersion maps of SO<sub>2</sub> on the island of Vulcano have been produced and have indicated that the areas close to the fumarolic source are characterized by concentrations of SO<sub>2</sub> in the atmosphere higher than those permitted by European legislation (40 µg m<sup>-3</sup> for 24 h of exposition) on human health.

**Keywords:** SO<sub>2</sub> output; soil CO<sub>2</sub> fluxes; air pollutant; Vulcano Island; geochemical crisis; summit degassing; SO<sub>2</sub> map dispersion; extensive parameters



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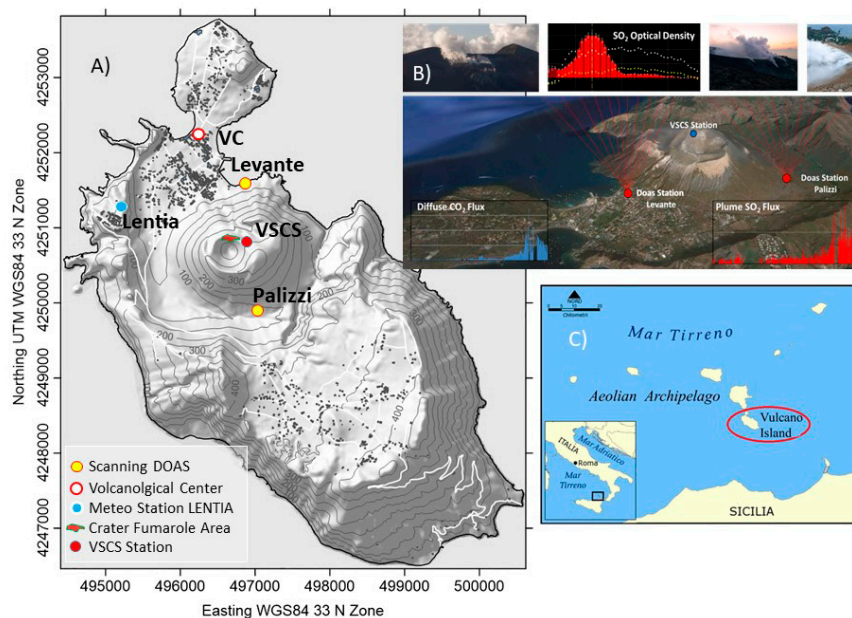
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## 1. Introduction

The volatiles emitted in different ways from the active volcanoes during the active and passive degassing are responsible for the increase in atmospheric natural pollution caused by gases, such as CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S, both during active and quiescent phases of the volcanic activity [1–4]. The volatiles are exsolved from the magma batch located below the

volcano edifice and can interact with surficial fluids during the rising towards the surface acting as aquifers and can be emitted diffusively by soil and fumarole or bubbling gases from surficial water. The high-temperature fumaroles show a chemical composition that varies over time as a function of the level of volcanic activity and the compositional molar ratios of the most abundant gases, i.e.,  $H_2O/CO_2$  and  $CO_2/SO_2$  ranging within 4–11 and 30–67, respectively [5–9]. Among the gases released by active volcanoes, sulfur dioxide ( $SO_2$ ) is generally the most abundant of the dry gases after carbon dioxide ( $CO_2$ ) [10,11], with worldwide emissions of over 27 Tg  $SO_2/y$  [12]. The volcanic emissions in the world represent 10% of the  $SO_2$  in the atmosphere [3,4].

Vulcano Island is located in the Aeolian archipelago on the southern side of Italy (Figure 1). The last volcanic eruption occurred in 1888–1990 (VEI = 3), followed by solfataric activity at the summit of the volcano and hydrothermal activity in the lower part of the island. The island of Vulcano in the last century has been affected by various geochemical crises characterized by increases in the degassing of volcanic fluids both from the fumarolic area of the summit and in diffuse form from the soil in the summit and peripheral area (extensive parameters). Moreover, these crises are characterized by compositional variations of the fumarolic fluids, indicating the arrival of more oxidizing volcanic fluids with higher  $CO/CH_4$  and  $SO_2/H_2S$  and  $CO_2/H_2O$  compositional ratios (intensive parameters). In June 2021, a new geochemical crisis was observed in the island of Vulcano inferred by an increase in degassing activity from June 2021 reaching a maximum during September 2021 [13–16] and by significant variations in the chemical and isotopic composition of high-temperature fumarolic fluids [9]. The intensification of gas emissions during this geochemical crisis also contributes to the contamination increase in natural gases in the atmosphere, especially near the gas-emitting fumaroles fields and in the neighboring areas of the island. The gas contamination in the atmosphere is a function of the emitted fluxes of gases that cause an increase in gas concentrations and the speed and direction of the prevailing winds that define the gas distribution. The degassing activity of Vulcano Island is routinely monitored by the geochemical networks of INGV (Istituto Nazionale di Geofisica e Vulcanologia-Italy).



**Figure 1.** (A) Vulcano island map which includes the location of the following monitoring stations: The  $SO_2$  fluxes network stations (Palizzi and Levante), yellow circles; Soil  $CO_2$  fluxes station (VSCS), red circle; Meteorological station (Lentia), light-blue circle; Volcanological Center, white circle. Red square indicates the Vulcano Island position. ATLFS: Aeolian–Tindari–Letojanni fault systems. (B) Inset of the geochemical network with a few pictures of the solfataric area showing the strong degassing that occurred in 2021 and an  $SO_2$  optical density spectrum of DOAS instruments; (C) Sicily Island map.

The study is mainly focused on: (1) monitoring the SO<sub>2</sub> plume and the soil CO<sub>2</sub> fluxes at La Fossa Cone as well as evaluating and identifying processes that change volcanic activity and (2) evaluating the dispersion of SO<sub>2</sub> and the possible environmental implications during the last crisis that started in June 2021.

## 2. Materials and Methods

### 2.1. SO<sub>2</sub> Output Network

Near-continuous SO<sub>2</sub> plume flux measurements have been carried out with a network system of SO<sub>2</sub> measurements at Vulcano Island, Italy. Two scan-DOAS stations belonging to the NOVAC Project are located at NE and SW of the volcanic cone, respectively (Figure 1). This configuration allowed to track over 80% of plume emissions during the solar year.

NOVAC (Network for Observation of Volcanic and Atmospheric Change) is a permanent network for the measurement of volcanic gas emissions established in 2005 due to a European project to create and install automated prototypes capable of monitoring gases from volcanic plumes around the world [17]. The main objective was to quantify global volcanic gas emissions and increase knowledge on changes in volcanic activity by estimating the gases emitted by each individual volcanic system. The remote sensing technique used is the DOAS (Differential Optical Absorption Spectroscopy) [18,19]. The analysis of solar radiation in the ultraviolet region, collected by spectrometers during the daytime, allows us to quantify the optical density column of different magmatic volatiles emitted by active volcanoes (e.g., SO<sub>2</sub>, NO<sub>2</sub>, and BrO).

The scan-DOAS NOVAC instrument consists of a conical scanning UV telescope with a 60-degree window rotating terminal, an in-focus optical fiber connected to a UV spectrometer, an embedded PC, a GPS, a timer, a WIFI system for transmitting data in near real-time, and a self-powered system with photovoltaic panel and battery. Details of the instrumentation can be found in Galle et al. [20]. Several steps are performed before calculating the SO<sub>2</sub> flux. The first action in a measurement cycle is the “Sky” spectrum measured at the zenith, and it represents the clear background, and all the spectra of this measurement are divided from this spectrum to derive the differential column density.

To reduce dark current and electronic offset errors, a dark offset spectrum is measured in dark conditions with the shielded window in the nadir position, and this spectrum is subtracted from any other spectrum of the same measurement. A complete measurement is made from all scans measured in one cycle from horizon to horizon across a conical surface intercepting the volcanic plume.

Slant column densities of gas are calculated using the DOAS Method [21], and the emission rate is estimated by multiplying the integral of column density with the wind velocity.

The NOVAC project has involved several volcanological observatories over time. Although the project ended in 2010, the NOVAC community continues to grow. It started with 16 volcanoes and about 30 instruments in 2007 and now has more than 160 stations on 47 volcanoes around the world [17].

At Vulcano Island, there are two permanent Novac-scanning DOAS, one in the Palizzi area and the other in the Levante Bay (Figure 1) installed in 2008 and 2015, respectively [13,22]. Moreover, to complete the network plume measurement, a meteorological station was installed on Mount Lentia and a video camera in the volcanological observatory “Centro Carapezza” to observe the emission zone on the crater la fossa. The acquired data are transmitted in real-time to Chalmers servers and to the NOVAC Database through a wireless system [23].

The long-term measurements of SO<sub>2</sub> flux have given excellent information about the degassing activity of active volcanoes [24,25] as in our Vulcano Island cases [13,26]. This information coupled with CO<sub>2</sub> flux measurements contribute in estimating the number of volcanic gases released, during passive and active degassing of active volcanoes, into the atmosphere [14,27].

## 2.2. Soil Summit CO<sub>2</sub> Flux Monitoring

Near-continuous soil CO<sub>2</sub> flux measurements have been carried out utilizing a geochemical station (VSCS) located on the summit crater area of Vulcano Island (Figure 1), [13,14,28]. This geochemical station measures CO<sub>2</sub> fluxes on the ground using the dynamic accumulation chamber principle [24] and it is engineered and distributed by WEST Systems S.r.l. The detector used for CO<sub>2</sub> concentration measurements is the Dräger Polytron IR spectrometer. Furthermore, sensors for monitoring environmental parameters, such as soil and atmosphere temperature, wind speed and direction, and soil and atmosphere humidity, have also been installed. These environmental parameters are useful for controlling any environmental influences on CO<sub>2</sub> degassing from soil [14]. The monitoring frequency is hourly and the data are sent via internet automatically every hour to the data acquisition center at INGV-Palermo using a WLAN/router service. More technical information is available in [29].

## 2.3. Air Dispersion Model

AERMOD (Lakes Environmental™, Waterloo, ON, Canada; <https://www.weblakes.com/> (accessed on 18 April 2023)) is an atmospheric dispersion model designed to simulate the dispersion of air pollutants from stationary anthropogenic and natural emission sources [30–32]. From November 2005, the United State Environmental Protection Agency (USEPA) formally adopted AERMOD as the preferred air quality dispersion model for regulatory applications and included it in their guidelines [33].

The AERMOD is a steady-state Gaussian air dispersion model based on the planetary boundary layer (PBL) aimed at short-range (source–receptor distance less than 50 km) from a specific source [34]. Gaussian dispersion is characterized by a normal distribution with the capacity to simulate the horizontal and vertical spread of a plume. The algorithm parameters in conjunction with meteorological measurements can characterize the wind vertical variation, wind structure, and turbulence profiles. Moreover, the AERMOD algorithm contains terrain treatment, buoyancy, plume rise, and building downwash. On the contrary, AERMOD does not take into account chemical reactions between atmospheric compounds. The dispersion simulation in the PBL (lower part of the atmosphere, 0–3 km deep) is particularly important considering the direct contact with the earth's surface and its influence in the dispersion, emission, transport, and mixing of contaminants [35,36].

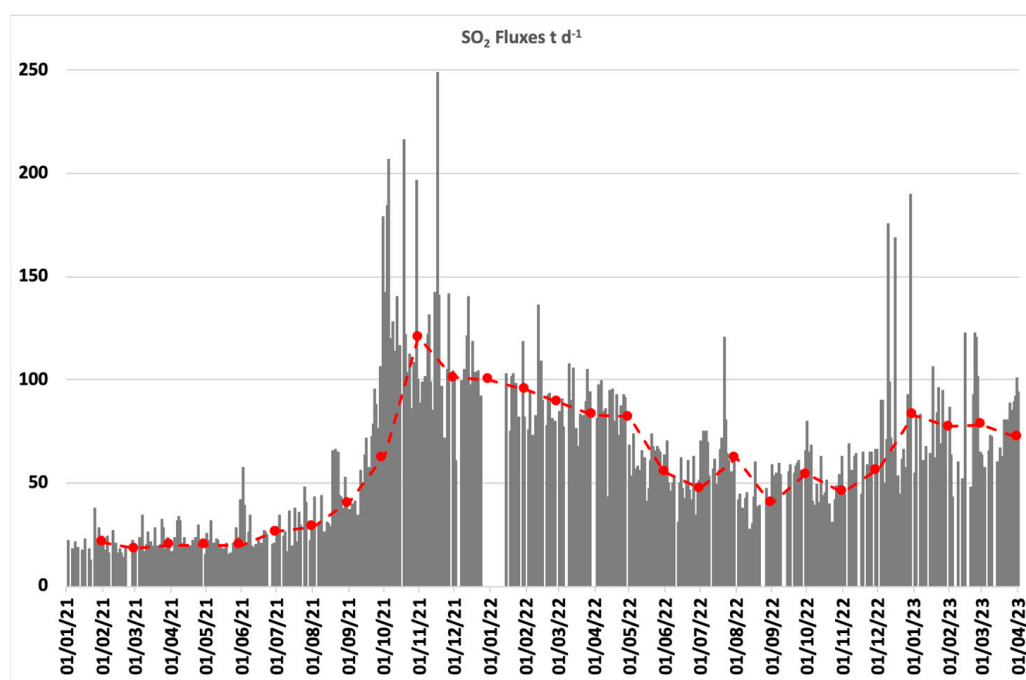
In order to run AERMOD model, a detailed emission inventory is necessary, including pollutant compound and the point source. We used the SO<sub>2</sub> inventory concentration and flux values presented in this work. Furthermore, the model requires some specific information as the location of the source (latitude and longitude), elevation, gas temperature, diameters of the conduct, and flow rate. The value of the radius from the source to develop the model has been set at 3 km, considering the limitations due to the complex terrain as well as the distance from the coastline. By carrying out various tests, we chose 3 km as the best option, which resulted in even fewer errors. The complete AERMOD modeling system includes AERMET and AERMAP. Terrain structure, i.e., landscape formed by specific morphological relief (simple, intermediate, and complex) and meteorological parameters affect the dispersion of contaminants and contribute to building downwash, which influences the air quality modeling. AERMET is a meteorological pre-processor system that provides information about state of surface, mixed layer, and PBL turbulence structure. The meteorological model requires a specific input, such as wind speed and direction, cloud cover, and air temperature, among others, and return friction velocity, mixing height, convective velocity scale, and surface heat flux [37]. The values of wind speed and direction (from January 2021 to February 2023) were obtained from a meteorological station (<http://www.meteosystem.com/dati/vulcano/> (accessed on 10 March 2023)) located near the emission source. On the other hand, AERMAP is a terrain pre-processor that generates receptor grids and the structure of complex terrain using USGS Digital Elevation data (GeoTIFF format and spatial resolution of 30 m) [38] with AERMOD and reports an increase in accuracy in modeling around complex terrain (e.g., mountain areas).

### 3. Results

#### 3.1. Near Real-Time Monitoring of Plume SO<sub>2</sub> Flux and Soil CO<sub>2</sub> Flux

##### 3.1.1. SO<sub>2</sub> Monitoring

The fluxes of SO<sub>2</sub> plume acquired using the UV-scanning DOAS network in the study period (2021–2023) with monthly average values between 20 and 121 t d<sup>-1</sup> (Figure 2). The average background level value of 22 t d<sup>-1</sup> for the period preceding June 2021 is reported in a previous study [14] (Figure 2). Starting from June 2021 onwards, the SO<sub>2</sub> output showed a positive trend with an abrupt increase and reaching the highest monthly value in September 2021 (monthly average value = 121 t d<sup>-1</sup>) and the highest daily measurement on 16 November 2021 (daily average = 238 t d<sup>-1</sup>). Thereafter, the SO<sub>2</sub> output from the plume showed a smoothly decreasing trend but remained at high values (e.g., September 2022, monthly average value = 55 t d<sup>-1</sup>). At the end of 2022, a new small increase in SO<sub>2</sub> flow was recorded with monthly average values of 70 t d<sup>-1</sup> and with daily average peaks over 150 t d<sup>-1</sup>.

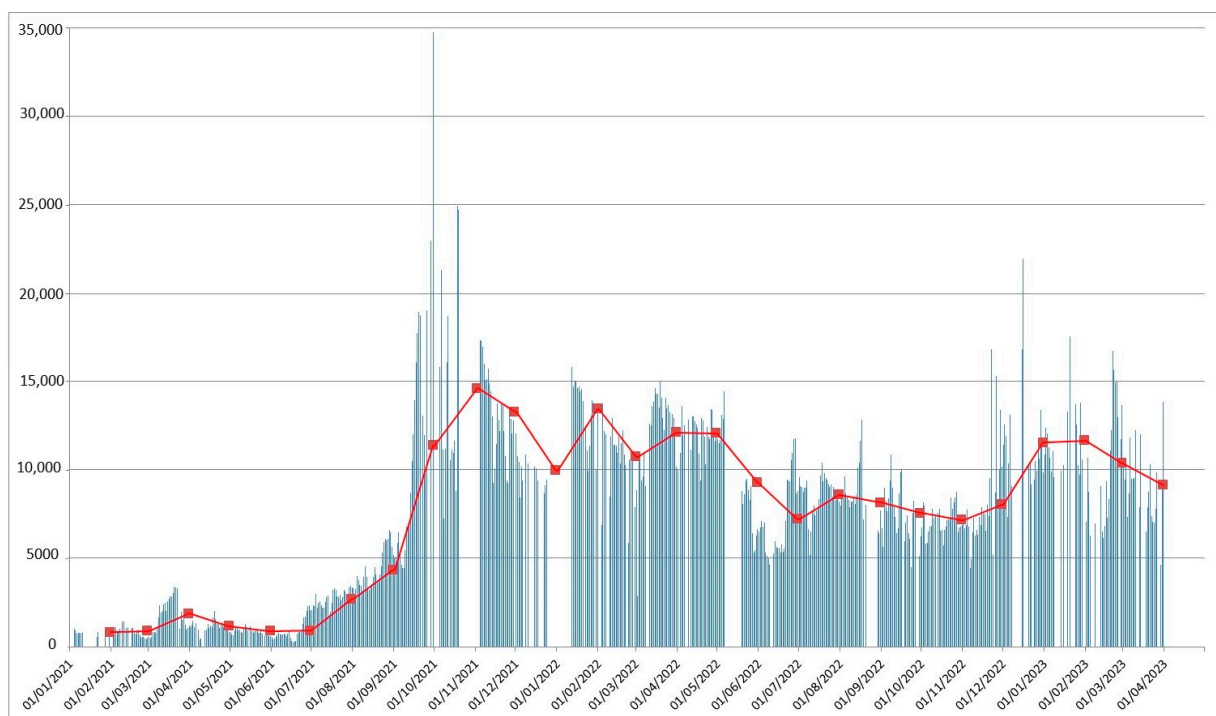


**Figure 2.** Time variation of SO<sub>2</sub> plume monthly output in t d<sup>-1</sup>. The dashed red line indicates the monthly average.

##### 3.1.2. Near Real-Time Soil CO<sub>2</sub> Monitoring

The fluxes of soil CO<sub>2</sub> recorded in the period 2021–2023, by the VSCS station, highlighted the changes of the CO<sub>2</sub> degassing output in the La Fossa crater area of Vulcano Island (Figure 3).

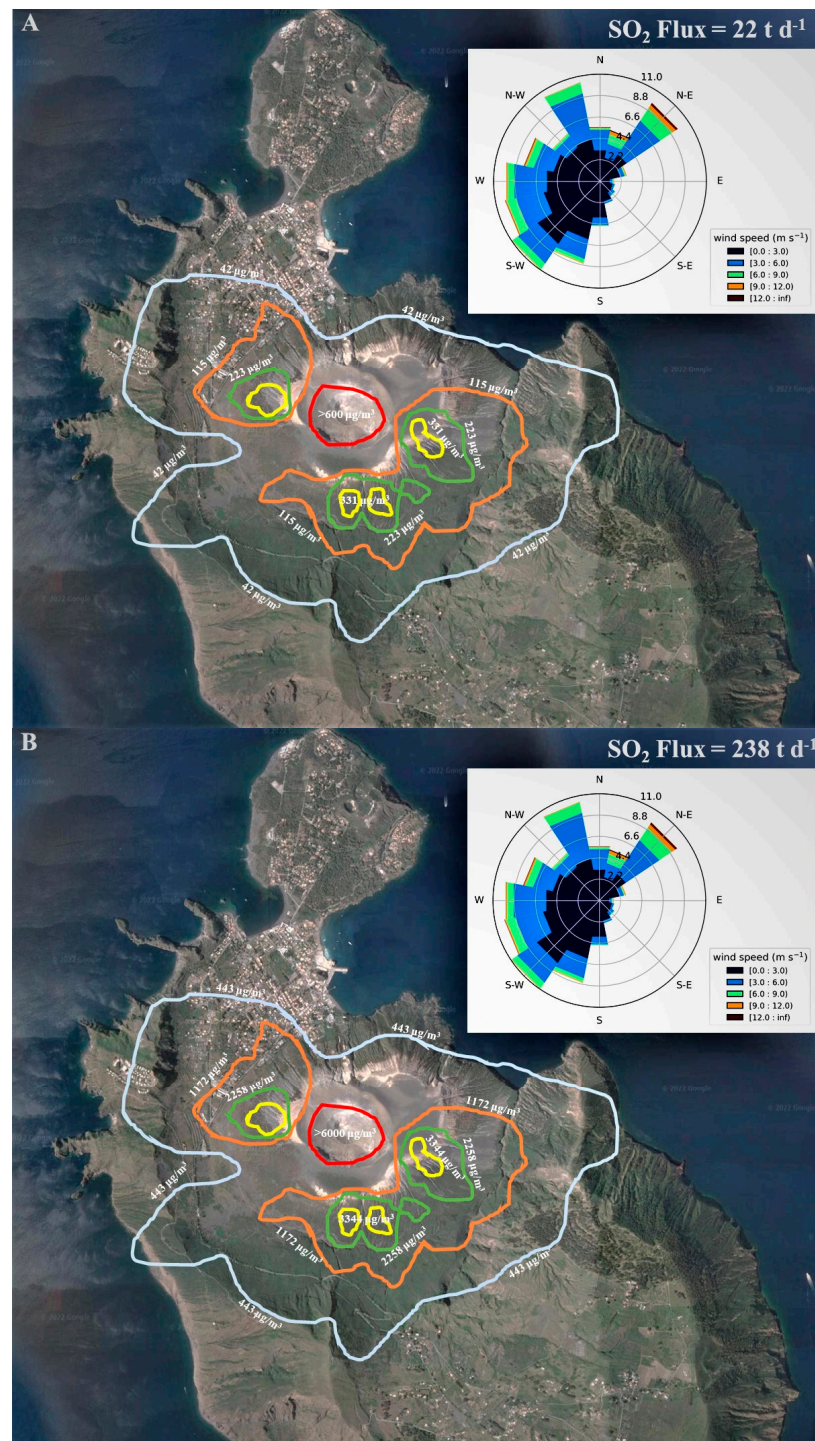
The summit monitoring station (VSCS) showed monthly average values ranging from 800 to 14,000 g m<sup>-2</sup> d<sup>-1</sup>, and the background degassing value of 1720 g m<sup>-2</sup> d<sup>-1</sup> [9] have been calculated using the data from 2018 to June 2021 (before the last crisis) (Figure 3). From June 2021 onwards, the CO<sub>2</sub> output from the VSCS station showed an abrupt increase up to September 2021. In September 2021, the monthly average of the soil CO<sub>2</sub> fluxes sharply increased and reached the maximum value of 14,000 g m<sup>-2</sup> d<sup>-1</sup> in October. Thereafter, the soil CO<sub>2</sub> fluxes in the summit area (VSCS) decrease slowly but remained above 8000–9000 g m<sup>-2</sup> d<sup>-1</sup> until November 2022. Finally, in December 2022, a new input of CO<sub>2</sub> has been recorded reaching in January 2023 monthly average values of up to 12,000 g m<sup>-2</sup> d<sup>-1</sup>.



**Figure 3.** Time variation of soil CO<sub>2</sub> fluxes from the summit and stations (VSCS). We report the monthly average of recorded flux values (continuous red line) to filter out the minor short-term effects registered at the local scale.

#### 4. SO<sub>2</sub> Map Dispersions

AERMOD air quality forecasting model was used for SO<sub>2</sub> pollutant dispersion in the period January 2021 to February 2023. The dispersion models were developed using the average wind speed ( $2.9 \text{ m s}^{-1}$ ) recorded over the considered period. In the wind rose plot (Figure 4), we can recognize 10 preferential directions with the dominant wind coming from NE and NNW, followed by WNW, W, and WSW. As shown in Figure 4A, the contour plot of the average concentration of SO<sub>2</sub> map dispersion in the study site is modeled as 24 h with a flux of  $22 \text{ t d}^{-1}$ . The maximum concentration of SO<sub>2</sub> (red line) were registered in the proximity of the crater and fumarole field, with values  $>600 \mu\text{g m}^{-3}$ . Instead, lower SO<sub>2</sub> concentration (blue line) values of  $42 \mu\text{g m}^{-3}$  was detected close to the village located in the northern area at 1.2 km from the main source. Intermediate concentrations of SO<sub>2</sub> between 115 and  $331 \mu\text{g m}^{-3}$  was recorded in the uninhabited area on the slopes of the volcano. Apparently, due to the dilution effect, the concentrations of SO<sub>2</sub> reaching the southern part of the island are negligible. The SO<sub>2</sub> concentrations registered close to the village are similar to the air quality limit ( $40 \mu\text{g m}^{-3}$ ) established by World Health Organization (WHO). On the other hand, following the current 24 h limit value of the Italian air quality norms ( $125 \mu\text{g m}^{-3}$ ), the concentration of SO<sub>2</sub> is 2.9 times lower. Figure 4B shows the SO<sub>2</sub> concentration contour plot for 24 h with an anomalous flux event of  $238 \text{ t d}^{-1}$ . The highest SO<sub>2</sub> concentration (red line) of  $>6000 \mu\text{g m}^{-3}$  was reported at the bottom of the volcano crater. In this case, distribution maps predicted an SO<sub>2</sub> concentration of about  $443 \mu\text{g m}^{-3}$  that could affect the village (blue line). Under these conditions, the concentration of SO<sub>2</sub> which affects the resident population in the northern area is 11 and 3.5 times higher than the air quality limit established by WHO and Italian norms, respectively. In addition, across the edge and at the foot of the crater, intermediate SO<sub>2</sub> concentrations between 1172 and  $3344 \mu\text{g m}^{-3}$  were recorded. According to the model simulation and considering both scenarios ( $22$  and  $238 \text{ t d}^{-1}$ ), the harbor area (Vulcano Porto) is less affected by SO<sub>2</sub> emissions and the southern area of the Vulcano Island is also less affected.



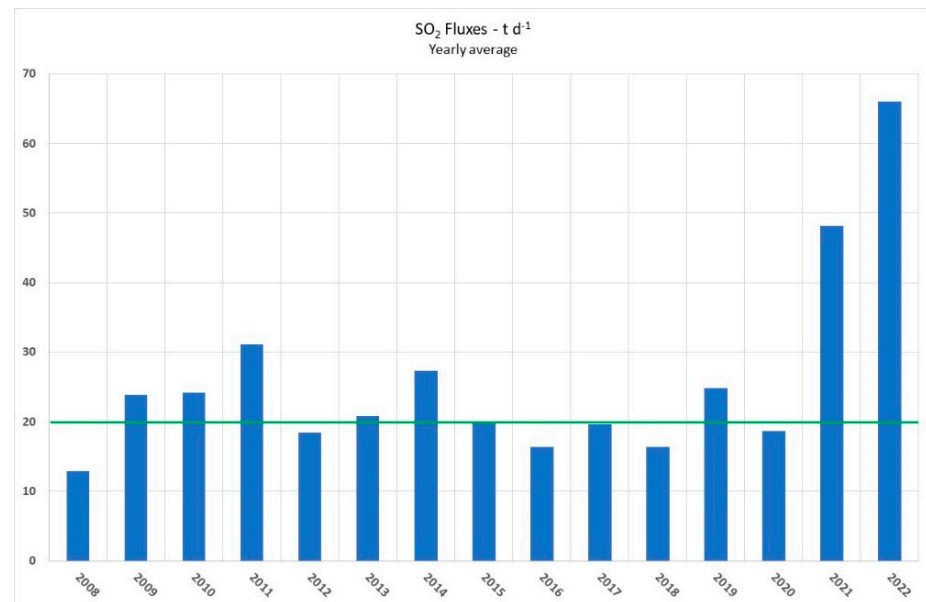
**Figure 4.** The SO<sub>2</sub> contour plot generated from AERMOD simulated model for 2 years (January 2021 to February 2023) in the case of the flux of (A) 22 t d<sup>-1</sup> and (B) 238 t d<sup>-1</sup>. The colored lines identify the different SO<sub>2</sub> concentrations. Isolines of SO<sub>2</sub> concentrations are expressed in µg m<sup>-3</sup>.

## 5. Discussion

The CO<sub>2</sub> and SO<sub>2</sub> fluxes monitoring at Vulcano Island showed a great and sharp increase in the degassing rate, allowing the hypothesis of the arrival of a new magma input [9,14,16] and as a consequence a new higher level of degassing activity.

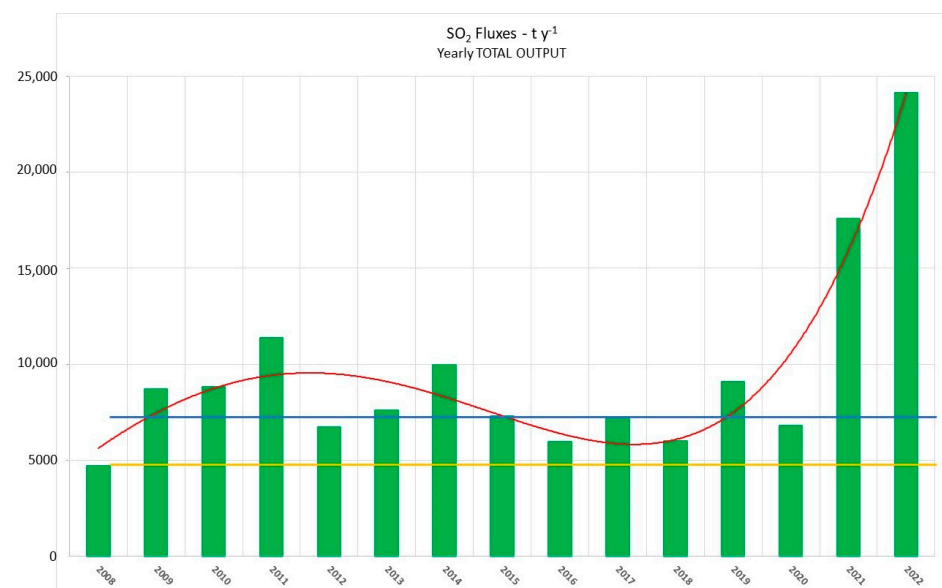
To better frame this increase in the normal outgassing observed over the years in the Vulcano island system, the yearly average of SO<sub>2</sub> plume flux from 2008 to 2022 has been plotted in Figure 5. This graphic showed values around 20 t d<sup>-1</sup> in the observation

period from 2008 to 2020, while a strong increase in SO<sub>2</sub> plume degassing reaching around 50 t d<sup>-1</sup> has been observed in 2021. Finally, in 2022, the yearly average value of SO<sub>2</sub> degassing increased up to around 65 t d<sup>-1</sup> due to a geochemical crisis started in June 2021 and characterized by strong degassing processes.



**Figure 5.** Yearly SO<sub>2</sub> plume degassing from 2008 to 2022. The green line represents the background value (around 20 t d<sup>-1</sup>) of SO<sub>2</sub> degassing in the last decade.

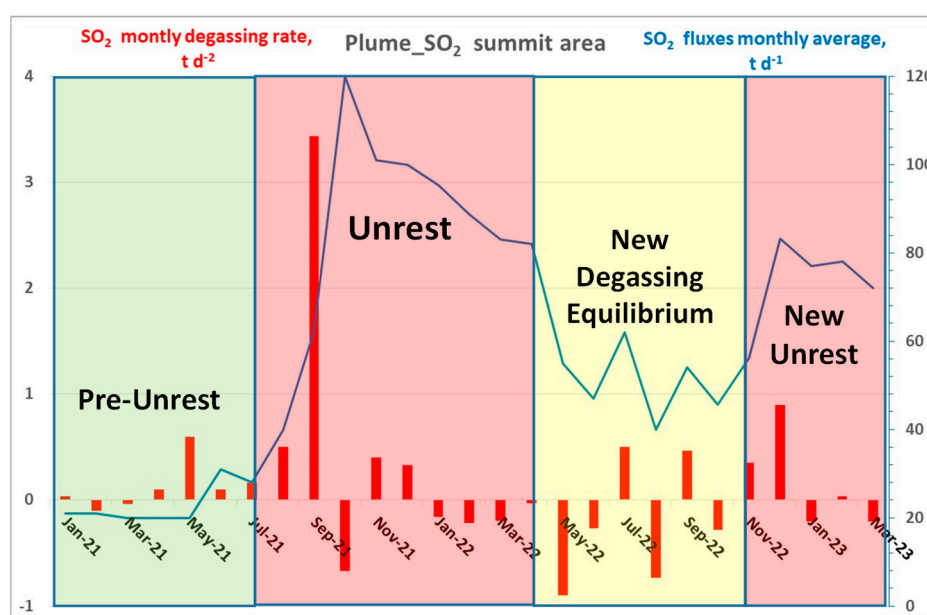
On the basis of the yearly average values, we estimated the yearly output of SO<sub>2</sub> from Vulcano island (Figure 6) that showed a background value of 7700 t calculated for the period 2008–2020, and high values of SO<sub>2</sub> output degassing of 18,000 and 24,000, respectively, for 2021 and 2022.



**Figure 6.** Yearly output of SO<sub>2</sub> emitted from crater solfataric area. The yellow line represents the minimum value of 5000 t SO<sub>2</sub> in 2008. The blue line represents the average SO<sub>2</sub> output value of 7700 t. The red line represents the polynomial curve highlighting the strong increase in SO<sub>2</sub> output in the 2021–2022 period reaching 24,000 t of SO<sub>2</sub>.



Figure 7 shows the values of SO<sub>2</sub> monthly average fluxes and their degassing rate from January 2021 to April 2023. We shared this peculiar degassing period in four phases (Table 1): Pre-Unrest, Unrest, New degassing equilibrium, and New Unrest with mean degassing fluxes of 22 t d<sup>-1</sup>, 89 t d<sup>-1</sup>, 51 t d<sup>-1</sup>, and 78 t d<sup>-1</sup>, respectively (Table 1). It is clear that the big increase in SO<sub>2</sub> degassing rate during the event occurred from June–September 2021, exhibiting an increase from 0.1 to 3.5 t d<sup>-2</sup>. This great and abrupt change in the SO<sub>2</sub> degassing rate resulted in a monthly average SO<sub>2</sub> degassing value of up to 120 t d<sup>-1</sup> in October 2021, causing a strong increase in SO<sub>2</sub> discharged in the atmosphere. Then, we observed decreased SO<sub>2</sub> fluxes from April–November 2022 that indicate a new degassing equilibrium with values around 50 t d<sup>-1</sup>, remaining one order of magnitude higher with respect to the Pre-Unrest phase. Finally, in November 2022 to April 2023, we recorded a new SO<sub>2</sub> input event, with a new increased degassing rate around 1 t d<sup>-2</sup>, and an average SO<sub>2</sub> fluxes that reached 78 t d<sup>-1</sup>.



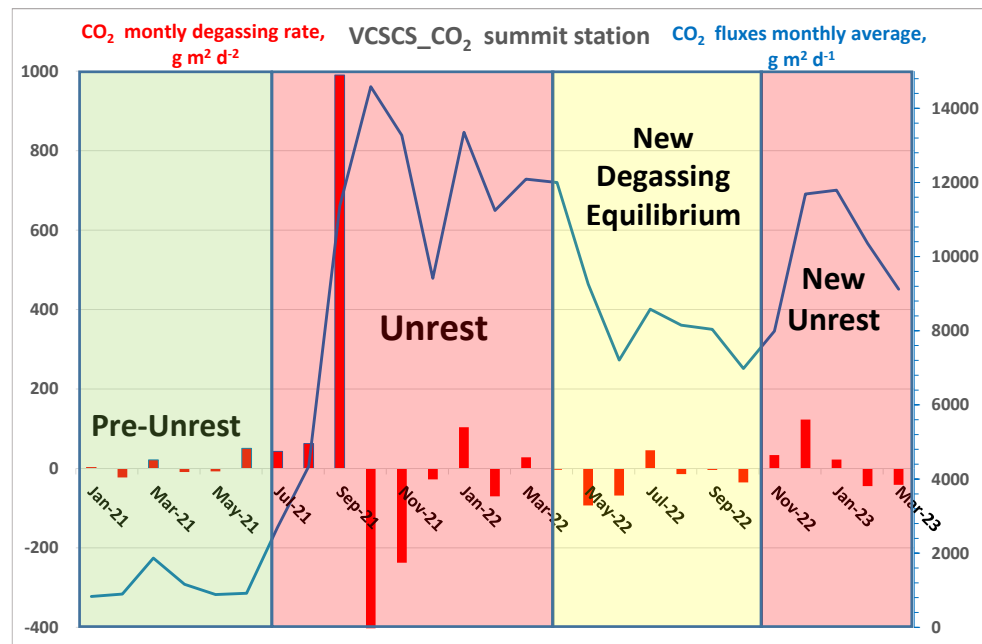
**Figure 7.** SO<sub>2</sub> fluxes monthly average (t d<sup>-1</sup>) blue line and SO<sub>2</sub> degassing rate (t d<sup>-2</sup>) red bars from January 2021 to March 2023.

**Table 1.** Statistical data of SO<sub>2</sub> fluxes from January 2021 to March 2023. The entire period has been shared in four phases.

SO <sub>2</sub> Fluxes	Pre-Unrest	Unrest	New Degassing Equilibrium	New-Unrest
<i>tons day<sup>-1</sup></i>	<i>January–August 2021</i>	<i>August 2021–April 2022</i>	<i>April 2022–November 2022</i>	<i>November 2022–March 2023</i>
<b>min</b>	4.5	14	24	27
<b>max</b>	57.7	239	121	190
<b>mean</b>	22.2	89	51	78
<b>median</b>	20.4	88	51	68
<b>sd</b>	7.9	35	14	32

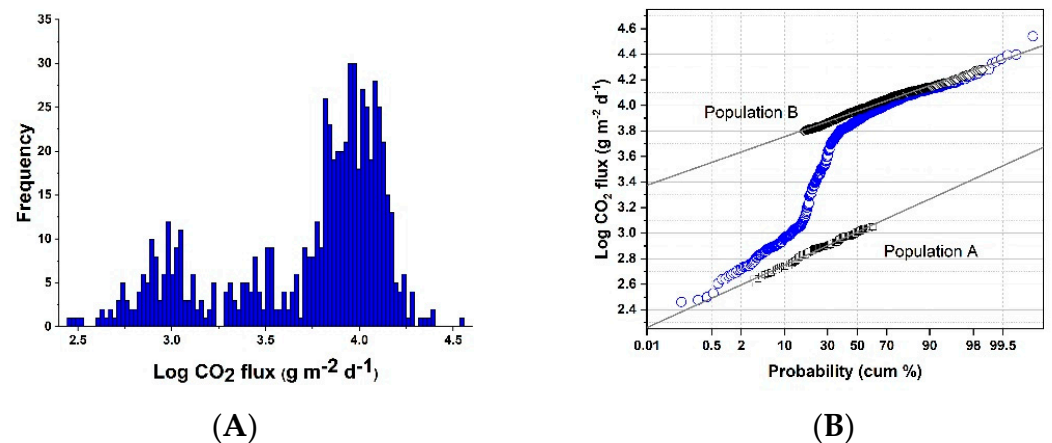
Similar behavior to the SO<sub>2</sub> outgassing style was exhibited by the soil CO<sub>2</sub> summit degassing monitored by the VSCS station (Figure 8).

In fact, a near-synchronous strong degassing of CO<sub>2</sub> has been recorded from June–September 2021 with a high degassing rate of up to 1000 g m<sup>-2</sup> d<sup>-2</sup> that resulted in a monthly CO<sub>2</sub> degassing of 14,000 g m<sup>-2</sup> d<sup>-1</sup> in October 2021. Then, in the last months of 2022, a new input of volatiles was observed in the shallow plumbing system and reaching a monthly CO<sub>2</sub> degassing of about 12,000 g m<sup>-2</sup> d<sup>-1</sup> at the surface.



**Figure 8.** CO<sub>2</sub> fluxes monthly average (g m<sup>-2</sup> d<sup>-1</sup>) blue line and CO<sub>2</sub> degassing rate (g m<sup>-2</sup> d<sup>-2</sup>) red bars from January 2021 to March 2023.

The probability plot resulting from the flux measured at VSCS station (Figure 9) shows two log-normal distributions with one corresponding to background CO<sub>2</sub> flux emissions (Population A) and the second one corresponding to higher CO<sub>2</sub> fluxes (Population B). Table 2 shows the summary of the statistics of the two populations.



**Figure 9.** (A) Histogram of Log CO<sub>2</sub> fluxes for the 2021–2023 period. (B) Log CO<sub>2</sub> fluxes vs cumulated probability for the 2021–2023 period.

**Table 2.** Proportions of each population with the mean CO<sub>2</sub> flux (in g m<sup>-2</sup> d<sup>-1</sup>) and the corresponding 90% confidence intervals obtained using the statistical graphical approach of log-normal distribution for VSCS station.

Population of CO <sub>2</sub> Flux	Mean Flux of CO <sub>2</sub> (g m <sup>-2</sup> d <sup>-1</sup> )	90 % Confidence Interval (g m <sup>-2</sup> d <sup>-1</sup> )	Proportion (%)
A	1144	1064–1246	25
B	9498	8331–9941	75

The statistics of the CO<sub>2</sub> flux from the VSCS station show similar results for the SO<sub>2</sub> flux (Table 3). The pre-event CO<sub>2</sub> flux values were lower in the period before August 2021, and the flux values stayed elevated after the event from August 2021–April 2022, suggesting a new degassing equilibrium after the event.

**Table 3.** Statistical data of CO<sub>2</sub> fluxes from January 2021 to March 2023. The entire period has been shared in four phases.

	Pre-Event January–August 2021	Event August 2021–April 2022	New Degassing Equilibrium April 2022–November 2022	New-Event November 2022–March 2023
min	289	2830	4435	4635
max	4526	34,741	16,859	21,956
mean	1572	11,596	8006	10,556
median	1106	11,871	7785	10,306
sd	1014	4154	1996	2893

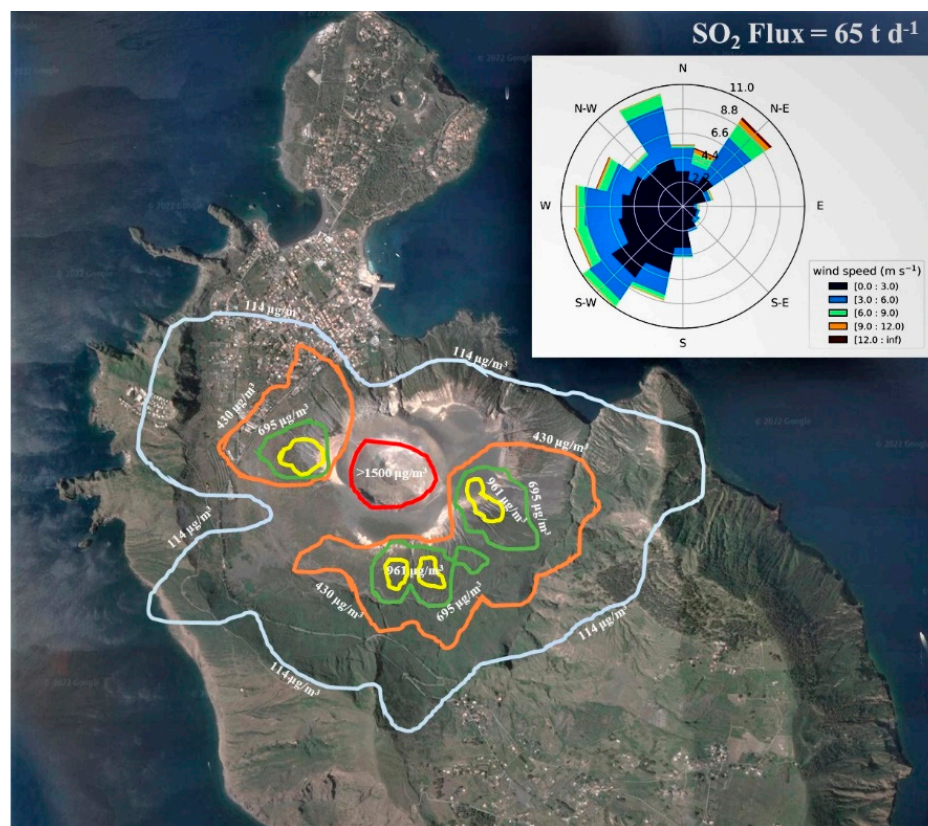
The environmental risk caused by the strong and sudden increase in SO<sub>2</sub> fluxes recorded in 2021 and 2022 affected the SO<sub>2</sub> concentration in the atmosphere of Vulcano Island, leaving 2022 to 2023 average values of degassing fluxes always one order of magnitude higher with respect to the background values recorded in the last two decades [13,14,23,28].

The simulation model of SO<sub>2</sub> pollution described in both scenarios (Figure 4A,B) show that meteorological parameters and local topographic conditions play an important role in atmospheric dispersion. In the vicinity of the village and Vulcano harbor (northern sector), a low health risk has been detected for the resident population considering the average SO<sub>2</sub> flux condition (22 t d<sup>-1</sup>) in short-term exposure. During the peak emission event (238 t d<sup>-1</sup>), high concentrations of SO<sub>2</sub> reached the southern part of the village, with possible health concerns for the population. People walking near the source and the fumarolic field as well as the researchers and technicians that frequently carry out volcanic monitoring campaigns are exposed to high concentrations of SO<sub>2</sub> that could have an adverse effect on health in a short time. Finally, Figure 10 represents the dispersion of SO<sub>2</sub> in the equilibrium condition of the system, with an average wind speed of 2.9 m s<sup>-1</sup> and an average measured flux of 65 t d<sup>-1</sup> (yearly average values of 2022). As seen previously, an important dilution effect affects the area surrounding the Vulcano fumarolic field. The lowest concentrations of SO<sub>2</sub> were recorded in the outermost isoline (white line), with values of 114 µg m<sup>-3</sup>, which is 2.8 times higher than the 24 h exposure limit (40 µg m<sup>-3</sup>) proposed by the WHO (World Health Organization). While considering the 24 h exposure limit proposed by Italian norms (125 µg m<sup>-3</sup>), no adverse health effects were detected. Exposure to low concentrations of SO<sub>2</sub> by the inhabitants of the island does not seem to produce adverse health effects in the short term. The long-term effects have yet to be studied in detail (monthly and yearly exposure), especially considering periods of anomalous activity and the direction of the prevailing winds.

In addition to SO<sub>2</sub>, other pollutants are normally emitted from the volcanic fumaroles system, such as H<sub>2</sub>S and CO<sub>2</sub> [39]. A recent study was carried out on the island of Vulcano by Diliberto et al. 2021 [40] that highlighted the volcanic hazard in the Levante Bay area due to the passive fluid degassing of H<sub>2</sub>S gas and the subsequent anomalous concentrations in the atmosphere and the harmful effects on human health in relation to the concentration and exposure time.

Furthermore, another study on the dispersion of volcanic gases in the atmosphere of the island of Vulcano was carried out by Granieri et al. 2014 [41] that studied the dispersion of the CO<sub>2</sub> emitted by the solfataric area of the summit and produced the iso-concentration maps involving the summit and peripherals area with particular attention to the village of Vulcano Porto. The results of this investigation showed that the CO<sub>2</sub> concentrations in the air at human breathing height, estimated from the dispersion models, are negligible in the Vulcano Village and that the anomalous direct-measured CO<sub>2</sub> concentrations in the atmosphere are due to local outgassing from the surrounding soil. While in the crater area,

the air CO<sub>2</sub> content due to both the soil degassing and crater fumaroles, on the basis of the speed and direction of the wind, may reach CO<sub>2</sub> levels harmful for visitors in some areas of the crater's rim or bottom.



**Figure 10.** The SO<sub>2</sub> contour plot generated from AERMOD simulated model for 2 years (January 2021 to February 2023) in the case of flux value of 65 t d<sup>-1</sup>. The colored lines identify the different SO<sub>2</sub> concentrations. Isolines of SO<sub>2</sub> concentrations are expressed in µg m<sup>-3</sup>.

## 6. Conclusions

The sharp increase in the degassing of volatiles observed in 2021, never recorded in the last two decades, showed two clear fundamental implications: environmental and volcanic. In particular, the anomalous increase in outgassing has worried the scientific community regarding the possibility of the occurrence of a paroxysmal event [9,13–16]. In fact, the near-continuous monitoring data of extensive parameters, such as the SO<sub>2</sub> plume and soil CO<sub>2</sub> degassing in the summit area, showed similar behaviors, highlighting a strong deep volcanic fluids input released from the new and rich magma batch in 2021 and subsequently in 2023 that affected the concentration of these species in the shallow plumbing system. The deep input of volatile degassing that started in 2021 keeps showing up in the 2023 anomalous average values of SO<sub>2</sub> and CO<sub>2</sub> degassing, which have remained well above the normal baseline levels recorded in recent decades. Therefore, the surface fluid system of the volcano is now at a higher energy level both in terms of mass and energy, and a possible new input could act as a trigger for a paroxysmal event, which would find the energy in the large quantity of volatiles stored in the surface system.

Furthermore, the increase in the concentration of volcanic gases in the atmosphere has also caused an environmental alert for public health. Consequently, the Italian Civil Protection declared an environmental state of emergency and ordered the evacuation of the population from the inhabited center of Vulcano Porto in November 2021. In addition, the authorities have also ordered a ban on tourist access to Vulcano Island for a month. Finally, in May 2023, considering the persistence of high fluxes of volatiles (CO<sub>2</sub> and SO<sub>2</sub>) emitted from the summit system into the atmosphere, the Mayor of Lipari regulated the

access of tourists to the crater area of Vulcano, through the weather conditions (wind speed and direction), to avoid access when the wind blows in the direction of the path that leads to the summit of the volcano.

In conclusion, the new geochemical crisis that began in June 2021 has not yet shown irrefutable signs of a return to the background values recorded in the last 20 years of observation. It would seem at the moment that the surface system of the island of Vulcano has settled on a new and higher level of background both in mass and in energy. For this reason, the volcanic system of the island of Vulcano deserves a high level of attention for volcanic monitoring by the scientific community and by the Civil Protection.

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