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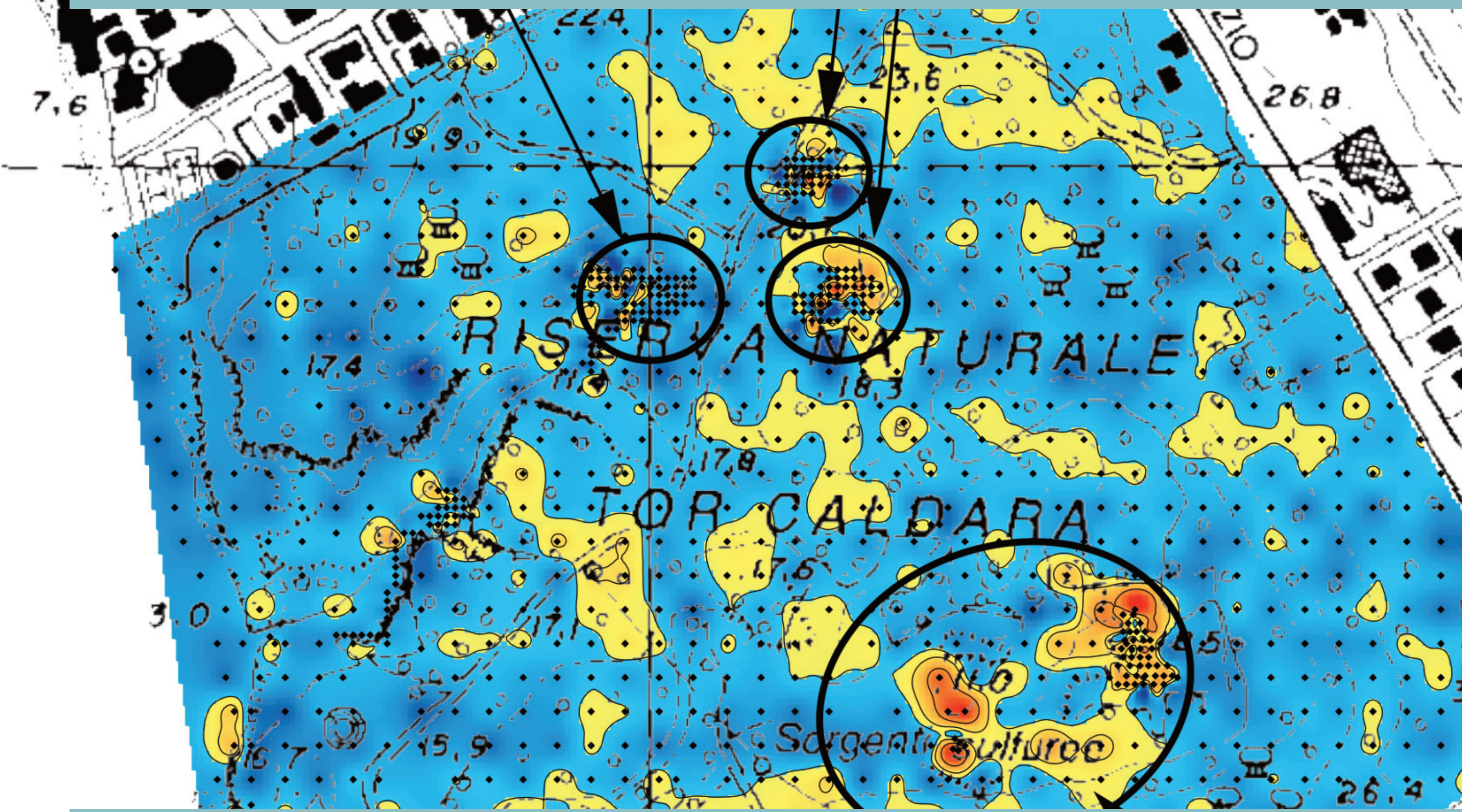

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Continuous monitoring of CO_2 and H_2S air concentration and soil CO_2 flux survey for gas hazard assessment at Tor Caldara nature reserve (Anzio, Italy)

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Abstract

Tor Caldara natural reserve hosts the southernmost discharge of endogenous gas of Colli Albani volcano (mostly CO_2 with a relevant H_2S content up to 6.3 vol.%). Gas discharges in zones where past sulfur mining removed the impervious surficial cover (e.g. Miniera Grande and Miniera Piccola) and along tectonic fissures. A structural study of the reserve has shown the presence of two zones with different characteristics: prevailing directions N-S and N30° in the northern zone; E-W and N60° in the southern one. In March-July 2012 a geochemical study was carried out, including a soil CO_2 flux survey and continuous monitoring (from 2 to 11 days) of air concentration of CO_2 and H_2S in 12 sites of the reserve. Environmental parameters were also monitored. Total diffuse soil flux of endogenous CO_2 was estimated to 17.48 ton*day^{-1} from 1,259 measurements over a 0.47 km^2 surface, with 6.56 ton*day^{-1} only from Miniera Grande. This is the second highest value of soil CO_2 flux at Miniera Grande, after that of 2005 (9.25 ton*day^{-1}) and is significantly higher than in 2009 (1.20 ton*day^{-1}). As both the 2005 and 2012 surveys were made shortly after earthquakes with epicentres near to Tor Caldara (max ML= 4.7 in 2005 and 3.5 in 2012), data confirm that soil CO_2 flux increases during earthquakes because of seismic rock microfracturing and soil shaking. Hazardous air concentrations have been found only for H_2S, up to immediately lethal values (565-1,124 ppm) and with potentially lethal values (≥ 250 ppm) long persisting (up to 12h27') in several no wind nights. Instead, the CO_2 air concentration remained always well below dangerous levels (maximum recorded value = 2.1 vol.%). The most hazardous gas releasing sites were found in Miniera Grande and in a small pond NE of Miniera Piccola, where the carcasses of mammals and other small animals are frequently found. The killer gas is H_2S, and the dangerous sites should be appropriately fenced to prevent access to people and animals.

Keywords Tor Caldara gas hazard assessment; Soil CO_2 flux; CO_2 and H_2S air concentration monitoring | Valutazione della pericolosità da gas a Tor Caldara; Flusso di CO_2 dal suolo; Monitoraggio della concentrazione in aria di CO_2 e H_2S

Introduction

Tor Caldara is a regional natural reserve located near the Tyrrhenian coast at Lavinio (fraction of Anzio municipality, Rome) (Fig. 1a). It lies above a ~N-S oriented structural high (positive gravity anomaly) of the buried carbonate basement, directed toward the Albano crater lake which is at about 24 km distance. Tor Caldara is the southernmost gas discharging site of the quiescent Colli Albani volcano [Carapezza et al., 2019] and it is characterized by the presence of several sites with anomalous discharge of endogenous gas, dominated by CO_2 (> 90 vol.%) but with a significant H_2S content (up to 6.3 vol.%), the highest found in all natural gas discharges of central Italy [Minissale et al., 1997]. The carbon isotopic composition ($\delta^{13}C_{CO2}$ 0.5 ‰ vs. PDB) is similar to that of other endogenous gas discharges of Colli Albani [Carapezza et al., 2019] and falls in the variation range of the hydrothermal CO_2 isotopic composition ($\delta^{13}C_{CO2}$ from -2.0 to +3.0 ‰ vs. PDB) [Minissale et al., 1997]. The relatively low helium isotopic composition (R/Ra 0.27) suggests a contamination in the upper crust of a gas of deep origin [Carapezza et al., 2012].
The main gas discharges occur in sites where the surficial impervious cover has been removed by past mining (sulfur) excavations (Miniera Grande and Miniera Piccola, Fig. 2) or by erosion along a small central river (Fig. 1b). The abundant sulfur deposits represented for centuries, at least since the XVI century up to the first half of the XIX century, an important economic resource.

Figure 1 a) Location of Tor Caldara natural reserve; b) the main gas discharge zones of Tor Caldara (Miniera Grande, Miniera Piccola, ponds and the Caldara-Vignarola ditch). The yellow numbers indicate the sites where air gas concentration has been continuously monitored in 2012. Stars are the sites where weather station was located.

The first soil CO_2 flux survey at Miniera Grande (28 measurements with accumulation chamber over a surface of 15,700 m^2) was carried out by Carapezza et al. [2012] on 23-25 August 2005, just after the M_L= 4.7 Anzio earthquake of 22 August 2005 [Frepoli et al., 2010]. The estimated total soil diffuse flux of endogenous CO_2 (9.25 ±0.07 ton*day^{-1}) is nearly one order of magnitude higher than the value found in July 2009 (1.20 ±0.02 ton*day^{-1}) when a new survey was carried out with 61 measurements over a surface of 11,400 m^2. This was considered evidence that seismic microfracturing of the rock pile above the deep carbonate basement and seismic soil shaking had increased the rock permeability and hence the soil gas flux [Carapezza et al., 2012]. A similar increase of the soil CO_2 flux has been observed also in Torre Alfina geothermal area of central Italy, after the seismic sequence of 30 May-9 June 2016 [Braun et al., 2018]. An experiment at Solfatara crater in Campi Flegrei demonstrated that soil CO_2 flux increased during the passage of artificially generated seismic waves [Gresse et al., 2016].
In July 2009 Carapezza et al. [2012] also measured the air concentration of CO_2 and H_2S at 15 cm height in 67 points located above the most gas emissive sites of Tor Caldara. In 21 of these points, the H_2S air concentration reached the upper detection limit of the used device (portable Drager X-am 7000), i.e. 500 ppm. This represents an immediately lethal value, considering that the potentially lethal threshold of H_2S is 250 ppm [Carapezza et al., 2011 and references therein] and that OSHA [2019] established to 100 ppm the H_2S level that interferes with the ability to escape (IDLH= Immediately Dangerous to Life and Health).
In the points with the highest air concentration of H_2S (≥ 500 ppm), the CO_2 air concentration was extremely variable, from normal air value to lethal values (in five points CO_2 >8 vol.% up to 58 vol.%) [Carapezza et al., 2012]. We remind that a high CO_2 air concentration implies a correspondent reduction of O_2 air concentration and the IDLH level of oxygen is 12.5 vol.% [Mc Manus, 2009] that is reached with a CO_2 air concentration of 8.3 vol.%.
It is clear from these data that some sites of Tor Caldara are exposed to a severe gas hazard. To deepen this problem, in March-July 2012 we carried out *(i)* a new soil flux survey of CO_2 over the whole reserve and *(ii)* continuous monitoring in 12 sites (Fig. 1b) for short periods (from two days to two weeks) of CO_2 and H_2S air concentration, together with some environmental parameters including wind speed.
In this paper we present the results of the 2012 study and discuss the related hazard implications.

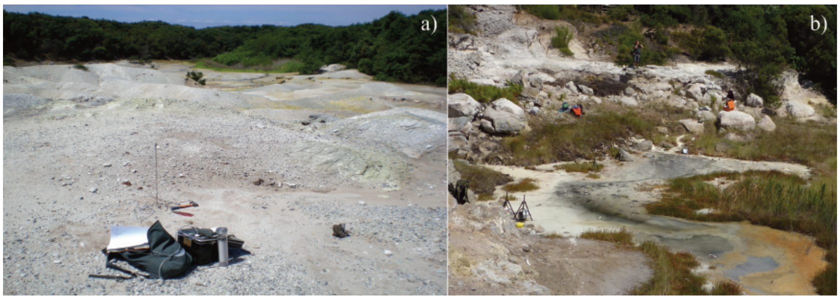


Figure 2 The main gas discharging zones of Tor Caldara. a) Miniera Grande, b) Miniera Piccola.

1. Geological outlines of Tor Caldara

In this sector of the Tyrrhenian coast, the geological substratum is represented by low-middle Pliocene clays; along the cliff from Tor Caldara to Anzio it is represented by clayey and sandy deposits of lower Pleistocene (**Pl**1 in the geological map of Fig. 3a). The outcropping sedimentary deposits indicate a beach environment with some riverine contributions. After a short Pliocene emersion period, the marine ingression of early Pleistocene modified the coastal landscape. The middle-Pleistocene sediments are characterized by the presence of reworked pyroclastic products. Right at the beginning of that period, the eruptive activity of Colli Albani volcano began. Along the entire middle-Pleistocene, glacial-eustatic variations of the sea level occurred, determining an alternation of sedimentation and erosion phases. On the coast, the first volcanic products (**qsm** in Fig. 3a) covered the Plio-Pleistocene sediments when the area was still partly submerged. Later, around 360 ka ago, the Tufo Lionato pyroclastic flow [Giordano and the Carg Team, 2010] deposited here in a subaerial environment. In middle-Tyrrhenian, about 250 ka ago, the sea-level rose to 6-8 m higher than the present level and the final phase of the transgression is represented, in the study area, by the wind deposits of Duna Antica (**qd** in Fig. 3a) that outcrops in a wide belt along the sea-coast. In the post middle-Tyrrhenian regression, a new minor transgressive phase is recorded during upper-Tyrrhenian, when the sea level rose of 2-3 m above the present level. The Duna Antica coastal deposits hindered the inland advancement of the upper-Tyrrhenian sea favouring the formation in the coastal plain of wide lagoons fed also by transversal ditches.

The structural lineaments of Tor Caldara have been studied using field observations and air photograph analyses: a total of 45 features were identified. These data were afterwards organized, represented and managed with ArcGIS software. They are reported in Fig. 3b, together with the related Rosette plot. Two zones with different structural characteristics have been recognized, separated by the Caldara Vignarola ditch crossing the reserve along a prevailing N30° direction. In the northern zone the structural lineaments have prevailing N-S and N30° directions, whereas in the southern one they are prevalently E-W and N60° oriented (Fig. 3b).

More generally, this area represents a transition zone between two sectors with different structural characteristics, as evidenced by the geometry of the coastal margin and the shapes of the waterways of the local hydrographical network:

- North of Lavinio: the river systems have a prevalent direction orthogonal to the coastline, i.e. ~ N60°.
- South of Anzio: the rivers have a prevalent N-S direction.

Lavinio-Tor Caldara area is characterized by the presence of two ditches with different directions: E-W for the Schiavo ditch at Lavinio, whereas the Caldara Vignarola ditch has a N70° direction at Vignarola and a N30° direction in the Tor Caldara reserve. It can be deduced that the N70° and E-W lineaments represent the distinctive structural elements of the described sectors.

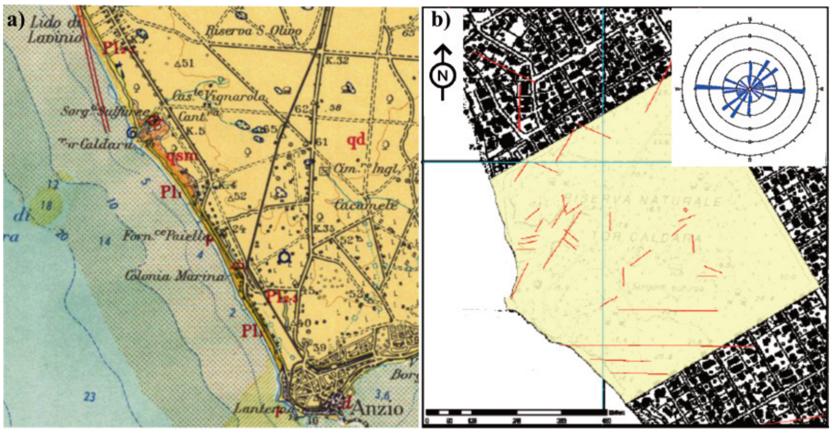


Figure 3 a) Geological map of Tor Caldara-Lavinio area (after Carta Geologica d'Italia 1:100,000 Sheet no. 158 http://193.206.192.231/carta_geologica_italia/tavoletta.php?foglio=158) and b) Structural lineaments of Tor Caldara and relative Rosette plot.

2. Methods

The CO_2 soil flux has been measured with the accumulation chamber method time "0" described by Chiodini et al. [1998], by a portable fluxmeter manufactured by West Systems. The device is equipped with an IR Licor-Li820 detector for CO_2 (single-beam dual-wavelength NDIR; range 0-2 vol.%; accuracy: 3 % of reading). The measurements were always carried out in dry and stable weather conditions to reduce a possible environmental influence on soil gas flux.
Data of CO_2 soil flux has been statistically treated using the Gaussian Mixture Model (GMM; *gmdistribution.fit* function in Matlab R2018a); see Carapezza et al. [2020b] for the description of the method. The Tor Caldara soil CO_2 flux map has been made by Ordinary Kriging in Golden Software, Inc. Surfer 11©, using the sub-population thresholds identified by GMM as contour levels.
Continuous air gas monitoring has been carried out by West Systems instrumentations equipped with Draeger sensors: IR CO_2 detector (0-100 vol.%; accuracy: 3 %) with double beam and temperature compensation, and H_2S sensor WS-H2S-BE with cell working in the range 0-2,000 ppm (accuracy 5 %). The data acquisition frequency was of 1 minute. A Davis Vantage Pro weather station acquired barometric pressure, air temperature (T), wind speed and direction, at 2 m height from the soil, with a frequency of 10 minutes. The technical characteristics are reported in Table 1.

Sensor (*unit*)	Resolution	Range	Accuracy ±
Barometric pressure (*hPa/mb*)	0.1	540-1,100	1.0
Wind speed (*m/s*)	0.5	0-67	1.0
Wind direction (°)	1	0-359	3
Air T at 20 cm height (°C)	0.1	-40/+60	0.5

Table 1 Environmental parameters measured by the weather station *Davis Vantage Pro.*

3. Results

3.1 Soil CO_2 flux survey

In March 2012, a soil CO_2 flux survey was carried out at Tor Caldara, using the portable accumulation chamber described above. A total of 1,259 measurements over a surface of 0.47 km^2 with average 20 m spacing were performed. A more dense survey with spacing of about 5 m was carried out on the main gas-emitting zones, i.e. Miniera Grande, Miniera Piccola and two nearby ponds (measurement points in Fig. 4).
Results have been clustered in four sub-populations using the GMM. Statistical thresholds between clusters are at flux values of: 27.4, 61.7 and 367.3 g*m^{-2}d^{-1} (Table 2).

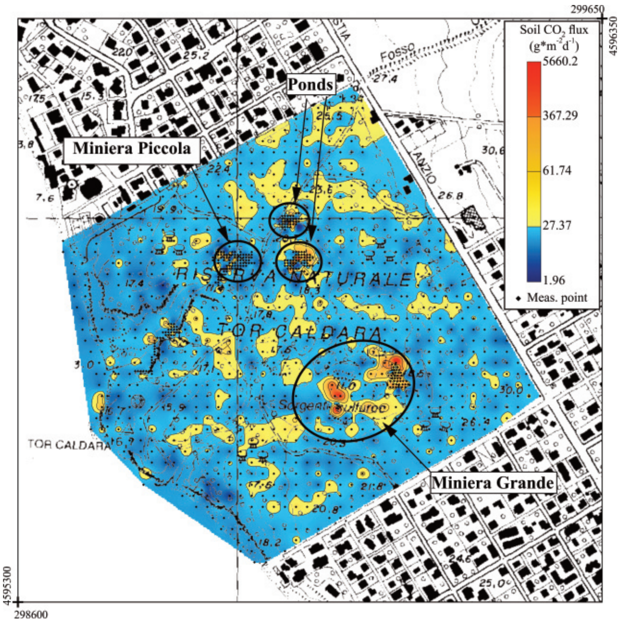
Statistical results				
Gaussian Mixture cluster	*C1*	*C2*	*C3*	*C4*
Proportion %	63.20	28.42	6.89	1.49
Avg. (g*m^{-2}d^{-1})	16.49	32.02	119.13	1,807.87
Std. Dev. (g*m^{-2}d^{-1})	6.38	11.21	70.15	1,663.19
Min-Max (g*m^{-2}d^{-1})	2-27.4	27.4-61.7	61.7-367.3	367.3-5,660

Geostatistical results							
Sub-population	*C1 Soil resp.*	*C2 Low-endog.*	*C3 Mid-endog.*	*C4 High-endog.*	*Total Endog.*	*Total*	*% Endog.*
Area (m^2)	346,200	101,575	16,600	4,850	123,025	469,250	26.22
CO_2 flux (ton*day^{-1})	5.795	3.594	2.139	5.953	11.686	17.48	66.85

Table 2 Soil CO_2 flux partitions of 2012 Tor Caldara survey.

The map of Fig. 4 shows the spatial distribution of the soil CO_2 flux in the studied area. The threshold values identified through the GMM method were used as limits between colours in the map. Most of the area (346,200 m^2 out of 469,250 m^2) is characterized by soil CO_2 flux values ranging from 1.96 to 27 g*m^{-2}d^{-1}, i.e. falling in the variation range of biogenic CO_2 flux (0.2 to 21 g*m^{-2}d^{-1}) [Raich and Schlesinger, 1992; Raich and Tufekcioglu, 2000]. In the second largest area (101,575 m^2) soil CO_2 flux values range from 27 to 62 g*m^{-2}d^{-1} and we designed this population as low-endogenous, as it likely results from a mixing of endogenous with biological CO_2. Mid-endogenous (62-367 g*m^{-2}d^{-1}) and high-endogenous (367-5,660 g*m^{-2}d^{-1}) flux values have been found only in the areas of Miniera Grande, Miniera Piccola, the nearby ponds and in very small spots along the Caldara Vignarola ditch.

Figure 4 Soil CO_2 flux map of Tor Caldara (March 2012 survey). The main gas discharges are encircled.



3.2 Continuous monitoring of CO_2 and H_2S air concentration

The monitoring of CO_2 and H_2S air concentration has been carried out at 20 cm height (sometimes also at 50 cm) above the ground level in 12 sites of Tor Caldara including Miniera Grande, Miniera Piccola, two ponds and the Caldara Vignarola ditch crossing the natural reserve [dataset in Carapezza et al., 2020a]. All the monitored sites were chosen in high soil CO_2 flux zones of Fig. 4. These sites are characterized by the frequent presence of small dead animals (i.e. hedgehogs, voles, reptiles, insects). The specific aim of this monitoring of air gas concentration was to ascertain the cause of the animal death.
In the Appendix we report, for each site, a technical sheet containing the geographic coordinates (in WGS84 UTM33), the description of the site characteristics, the date and duration time of the monitoring of air gas concentration and of environmental parameters. Graphs illustrate the time variation of the recorded parameters. Results having the main gas hazard implications are presented in tables, where statistical data are presented for different concentration of H_2S and CO_2; in the H_2S graphs, the IDHL level of 100 ppm and the potentially lethal threshold of 250 ppm are indicated.
The CO_2 and H_2S air concentration values in almost all monitored sites (Figs. from A2 to A30 in Appendix) show wide diurnal variations; in particular, the gas concentration values are low during the day and are high since sunset and during the night. This behavior depends on environmental parameters particularly on wind speed and air temperature, while a direct correlation with atmospheric pressure is not evident. Sea breeze is the characteristic wind of the site (blowing from the sea to the coast during the day, following local changes in atmospheric pressure). In some sites (e.g. no. 1, 9, 10, 12) the H_2S air concentration remains frequently at dangerous values for many hours and independently from seasons, as at site no. 1, where dangerous values were recorded in winter, spring and summer periods (Figs. A2-A6).
To be noted however, that in sites with usually low air gas concentrations (e.g. sites no. 3, 4, 5, 8), H_2S may episodically increases to dangerous values (Fig. A13).
Gas concentration in air was measured also at 50 cm above the ground, in two of the most discharging sites (sites no. 1 and 12, Figs. A6 and A30 respectively) finding lower values than at 20 cm, but still long lasting dangerous ones. On 3 July, in absence of wind, at site no. 1, H_2S values over the IDLH (100 ppm) lasted for more than 10 hours consecutively at 50 cm height (Table A5 and Fig. A5). The contemporaneous recording at 20 cm height indicates that H_2S values were over the lethal threshold (250 ppm) for 10 hours.

4. Discussion

The graphs mentioned in the previous chapter, indicating the time variation of CO_2 and H_2S air concentration and of environmental parameters, continuously recorded in March-July 2012 in twelve sites of Tor Caldara, allow the following considerations on the gas hazard of the natural reserve.

The environmental parameter most affecting the air gas concentration is wind (sea breeze) that disperses the gas (CO_2 + H_2S) that otherwise, being denser than air, accumulates near the ground particularly in depressed zones. Also air temperature is apparently negatively related to air gas concentration, but this depends on the fact that temperature rises during daytimes when gas is dispersed by the wind.

The highest CO_2 concentrations at 20 cm height have been found at site no. 1, a small pond NE of Miniera Piccola (Fig. 1b), with maxima ranging from 1.5 to 2.1 vol.%. At this site CO_2 air concentration remains frequently for long periods (9 to 17 hours) above 5,000 ppm, both in springtime (8-12 and 21-30 March) and in summer (late June-early July). A relatively high concentration (1.3 vol.%) has been recorded also at site no. 10 in the north-eastern part of Miniera Grande (Fig. 1b), where CO_2 remained frequently and long (3 to 9 hours) above 5,000 ppm in summertime. In sites no. 2, no. 6 and no. 12 (at 50 cm height) the CO_2 air concentration maxima ranged from 5,700 to 7,000 ppm, with duration of periods with concentration constantly above 5,000 ppm, ranging from 2 to 10 hours. These values are significantly lower than the potential lethal threshold of CO_2 (8 vol.%) and they do not reach even the Short-Term Exposure Limit (STEL, 15 minutes) established by NIOSH [2007] to 3 vol. % for people working in closed spaces.

On the contrary the IDLH level of H_2S (100 ppm) has been largely overpassed and for long periods in sites no. 1 (also at 50 cm height), no. 9, no. 10, no. 12 (also at 50 cm height) and it was approached at site no. 2 (94 ppm) and at 50 cm height in site no. 10 (96 ppm).

Immediately lethal H_2S concentrations have been recorded at sites no. 1 (565 to 1,124 ppm) and no. 10 (890 to 1,044 ppm). The hazard of these gas emissions is stressed also by the fact that H_2S air concentration (at 20 cm height) at sites no. 1 and 10 remained long above the potentially lethal threshold of 250 ppm, up to 12h27'and 11h18' respectively, as shown in Table 3.

Site no.	Recording date d/m	No. of periods with H_2S > 250 ppm	Duration range (> 2 hours)	H_2S ppm		CO_2 ppm
				max	avg.	max
1	8-16/3	13	2h07' to 12h27'	794	336	20,631
1	21/3-1/4	13	2h02' to 8h22'	781	345	17,060
1	4-21/4	5	2h47' to 10h55'	565	324	n.r.
1	3-5/7	2	10h08' to 12h20'	1,124	433	15,330
10	7-10/6	6	2h21' to 6h59'	1,044	418	n.r.
10	22/6-1/7	11	2h15' to 11h18'	890	381	12,675
n.r.= not recorded						

Table 3 Number and duration range of the periods during which H_2S air concentration remained continuously >250 ppm; maximum H_2S and CO_2 concentrations, average H_2S concentration in these periods.

During the daytime, the wind blowing with a speed up to 5-8 m/s dispersed the gas released from the soil. It is relevant to note that hazardous gas concentrations have been always recorded since late afternoon, and during night and early morning, when there was no wind and the gas, denser than air, could remain and even accumulate near the ground. At site no. 1 the hourly average H_2S concentration recorded at 20 cm overpassed the IDHL level around 19:00, and the same level was reached at 50 cm height four hours later (Figs. A5 and A6).

5. Conclusions

The removal of the superficial impervious cover and the presence of many tectonic fractures allow at Tor Caldara the free emission to the surface of a deep origin gas (mostly CO_2 and H_2S). The repetition of soil CO_2 flux surveys over nearly the same area confirms that soil flux of endogenous CO_2 significantly increases after local earthquakes, because of seismic fracturing that increases the rock permeability and of seismic soil shaking.
The continuous monitoring from two to eleven days, of the air concentration of CO_2 and H_2S and environmental parameters in 12 different sites of Tor Caldara, permitted to ascertain that only H_2S reaches very high, immediately lethal concentrations at 20 cm height, particularly in sites no. 1 and no. 10 (location in Fig. 1b) where its maximum concentration is > 1,000 ppm. Furthermore, H_2S air concentration during no wind nights (and also in late afternoon and early morning) remained long above the potentially lethal threshold of 250 ppm. On 12 March and 4 July at site no. 1, H_2S concentration remained above 250 ppm for more than half day and at site no. 10 on 30 June for more than 11 hours. Dangerous H_2S concentrations (> 100 ppm for nearly 4 hours) have been recorded also at sites no. 9 and no. 12 (here at 50 cm height on 6 June). The CO_2 air concentration (≤ 2.1 vol.%) was in all sites much lower than its potentially lethal threshold (8 vol.%).
These results indicate that the animals, whose carcasses are frequently found in the above mentioned anomalous gas releasing sites, have been killed by H_2S releasing.
Following our indications, in order to reduce gas hazard, Miniera Grande (sites no. 9, 10, 12, Fig. 1b) and Miniera Piccola are no more accessible to visitors. Other sites have been properly fenced and marked with danger signals.
The area close to the natural reserve is densely inhabited (see Fig. 1b) and it seems logical to assume that some of these houses be prone to gas hazard. Soil gas emission in the house gardens and indoor air gas concentration should be measured in these houses to assess the hazard for the living people. We remind that in 2011 a man lost his life and another one suffered permanent neurological disease, because of the inhalation of a CO_2 and H_2S rich air mixture, while working in a basement water recharging system of a swimming pool of Lavinio, at only 2 km distance from Tor Caldara [Barberi et al., 2019].

Acknowledgments

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APPENDIX

Main characteristics of the monitored sites, temporal variation of CO_2 and H_2S air concentration and of environmental parameters, gas hazard data

Site 1

- Location: 33 T 299090 E 4595982 N
- Area: 1,150 m^2
- Topography: slight depression (2 m below surrounding ground level)
- Vegetation: absent
- Soil alteration: yes
- Water: absent
- Dead animals: frequent invertebrates and mammals
- Gas emission: CO_2 and H_2S both diffuse and advective (presence of small gas vents)
- Recorded parameters: CO_2, H_2S, weather
- Recording periods: 8-16 March; 21 March-1 April; 4-21 April; 3-5 July

The site is located in the NE sector of the reserve within the oak wood (Fig. A1a). The monitoring device (Fig. A1b) was placed in the proximity of a degassing vent in the NW part of the area. Figs. A2 to A6 show the time variations of air CO_2 and H_2S concentrations and of environmental parameters recorded in the different periods. Data related to gas hazard are reported in Tables A1 to A6.

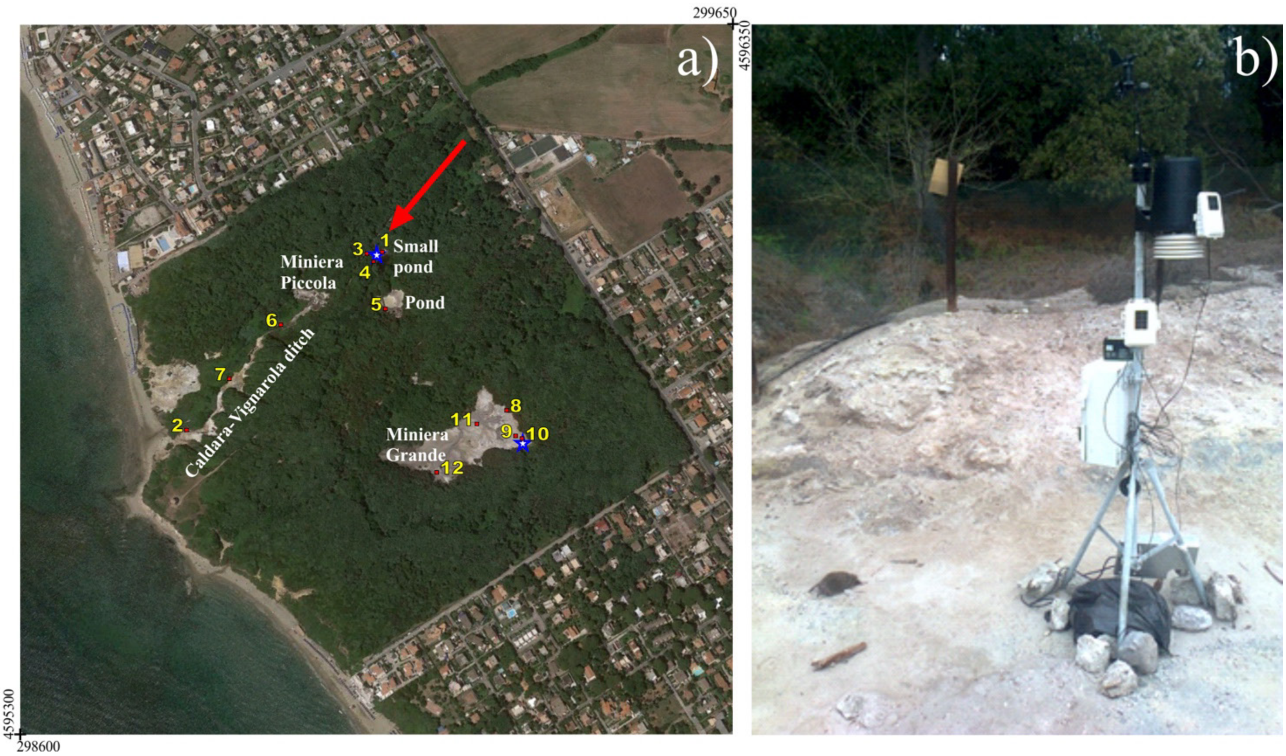

Figure A1. a) Location of site no. 1; b) location of the monitoring station (CO_2 - H_2S - weather); note the dead hedgehog to the left of the station.

Site 1: 8-16 March (20 cm)

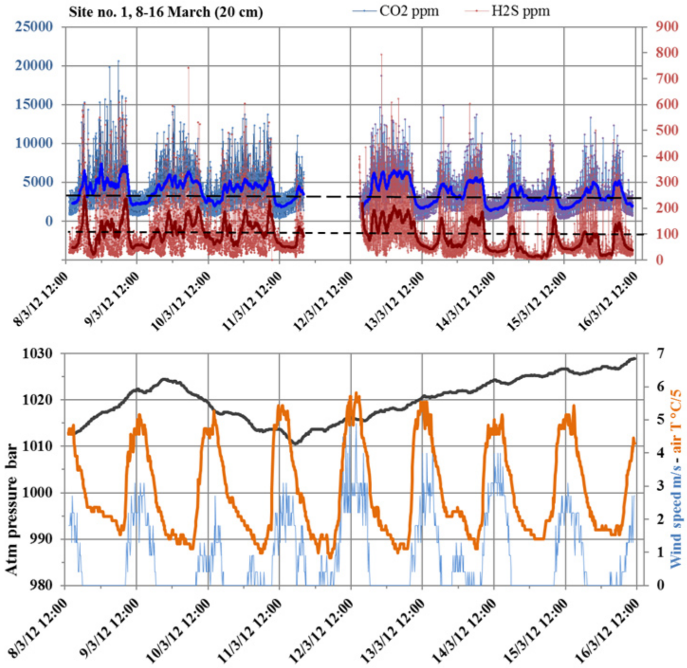

Figure A2. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average) and of environmental parameters (below). Horizontal dotted lines indicate the IDLH level (100 ppm) and the lethal threshold (250 ppm) of H_2S.

Table A1a. Measures and percentages of [H_2S] and [CO_2] at different hazard intervals

	H_2S ppm					**CO_2 ppm**	
	<10	*10-15*	*15-100*	*100-250*	*≥ 250*	*< 5,000*	*≥ 5,000*
Meas. no.	251	335	6,387	2,560	717	7,963	2,285
Meas. %	2.45	3.27	62.31	24.98	7	77.69	22.29
Average	7.2	12.5	51.1	155.9	336	2,844	7,020
Minimum	0	10	15	100	250	214	5,005
Maximum	9.9	14.9	99.9	249.8	794	4,975	20,631

Table A1b. Duration of intervals (>2h) with [H_2S] ≥ 100 ppm, ≥ 250 ppm and [CO_2] ≥ 5,000 ppm

Date	**H_2S ≥ 100 ppm**		**Date**	**H_2S ≥ 250 ppm**		**Date**	**CO_2 ≥ 5,000 ppm**	
	start time	*duration*		*start time*	*duration*		*start time*	*duration*
8 March	14:14 21:22	05h53' 12h01'	8 March	16:22 23:19	02h39' 4h30'	8 March	16:16	16h45'
9 Mar	16:06	43h26'	9 March	05:38 20:34	2h40' 2h22’	9 March	17:06	16h01'
			10 March	00:00 06:29 16:35 22:50	05h36' 02h39’ 02h48’ 02:36’	10 March	16:48	17h23'
11 March	17:01	03h04'	11 March	06:43	02h28'			
12 March	15:00	20h16'	12 March	18:55	12h27'	12 March	18:30	14h37’
13 March	15:50	17h25’				13 March	17:16	04h38'
14 March	17:02	04h16’	14 March	02:34	05h46’	14 March	01:14 16:59	07h11’ 04h19’
15 March	06:08 15:28	02h16’ 07h32’	15 March	06:20	02h07'	15 March	18:06	05h01’
16 March	4:01	05h35’	16 March	4:26	02h21’	16 March	03:52	03h53’

Site 1: 21 March-1 April 2012 (20 cm)

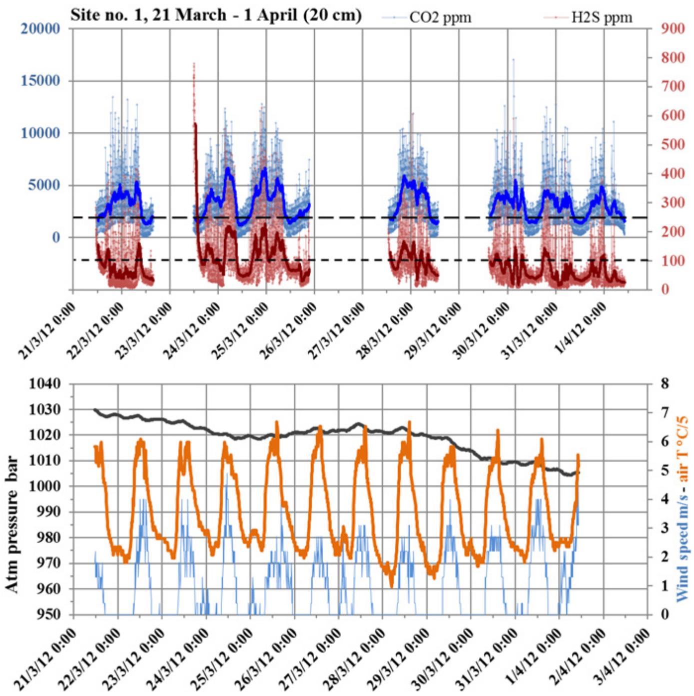

Figure A3. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average) and of environmental parameters (below). Horizontal dotted lines indicate the IDLH level (100 ppm) and the lethal threshold (250 ppm) of H_2S.

Table A2a. Measures and percentages of [H_2S] and [CO_2] at different hazard intervals

	H_2S ppm					**CO_2 ppm**	
	≤ 10	*10-15*	*15-100*	*100-250*	*≥ 250*	*< 5,000*	*≥ 5,000*
Meas. no.	148	429	6,939	2,578	572	8,906	1,758
Meas. %	1.39	4.02	65.06	24.17	5.36	83.51	18.48
Average	8.6	12.5	51.3	151.7	344.6	2,513	6,568
Minimum	0	10	15	100	250	31	5,005
Maximum	9.9	14.9	99.9	249	781	4,975	17,060

Table A2b. Duration of intervals (>2h) with [H_2S] ≥100, ≥250 ppm and [CO_2] ≥5,000 ppm

Date	**H_2S ≥ 100 ppm**		**Date**	**H_2S ≥ 250 ppm**		**Date**	**CO_2 ≥ 5,000 ppm**	
	start time	*duration*		*start time*	*duration*		*start time*	*duration*
21 March	11:20	22h49'	21 March	16:02	03h50'	21 March	16:02	16h59'
			22 March	06:44	02h16'			
23 March	11:50	21h46'	23 March	17:33	03h26'	23 March	17:33	15h07'
24 March	15:15	20h30'	24 March	02:10 16:58	06h30' 07h13'	24 March	16:13	16h13'
25 March	13:46	07h40'	25 March	01:03 03:42	02h02' 04h18'			
27 March	12:51	22h07'	27 March	17:40	08h22'	27 March	17:30	13h45'
			28 March	03:14	03h00'			
29 March	14:50	18h36'	29 March	17:58 22:34	02h34' 02h32'	29 March	16:54	15h03'
30 March	16:58	15h26'	30 March	17:33	03h41'	30 March	17:20	13h54'
31 March	17:05	08h18'	31 March	21:45	02h14'	31 March	17:16	07h12'

Site 1: 4-21 April 2012 (20 cm)

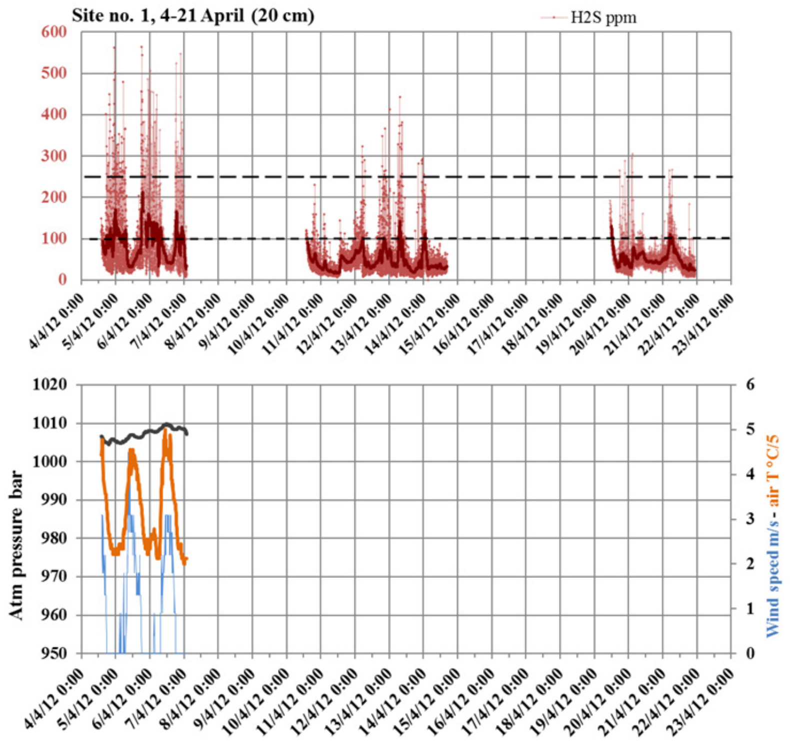

Figure A4. Time variation of H_2S air concentration (continuous red line: hourly H_2S average) and of environmental parameters (below). Horizontal dotted lines indicate the IDLH level (100 ppm) and the lethal threshold (250 ppm) of H_2S.

Table A3a. Measures and percentages of [H_2S] at different hazard intervals

	H_2S ppm				
	≤ 10	*10-15*	*15-100*	*100-250*	*≥ 250*
Meas. no.	77	489	10,856	1,383	215
Meas. %	0.59	3.75	83.37	10.62	1.65
Average	8.6	12.9	45.0	148.1	324.3
Minimum	5.7	10	15	100	251
Maximum	9.9	14.9	99.9	249	565

Table A3b. Duration of intervals (>2h) with [H_2S] ≥100 and ≥250 ppm

Date	**H_2S≥**	**100 ppm**	Date	**H_2S≥**	**250 ppm**
	start time	*duration*		*start time*	*duration*
4 April	14:10	18h01'	4 April	17:21	02h47'
				21:04	09h57'
5 April	14:48	19h38'	5 April	18:09	10h55'
6 April	17:02	08h36'	6 April	18:04	05h14'
10 April	14:12	07h42'			
11 April	13:30	03h10'			
11 April	23:42	08h52'			
12 April	14:54	21h05'			
13 April	18:21	09h15'	13 April	6:10	03h02'
19 April	17:49	17h32'			
20 April	18:57	02h01'			

Site 1: 3-5 July (20 cm)

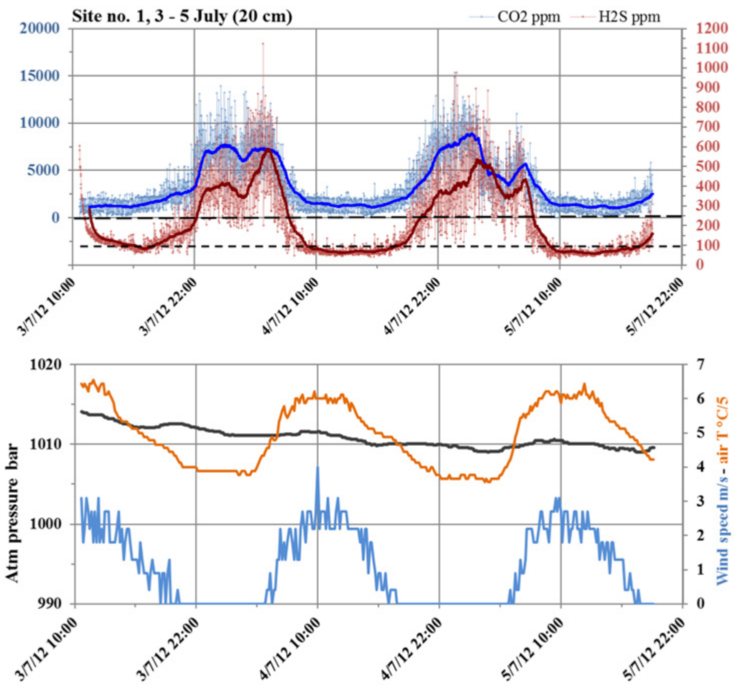

Figure A5. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average) and of environmental parameters (below). Horizontal dotted lines indicate the IDLH level (100 ppm) and the lethal threshold (250 ppm) of H_2S.

Table A4a. Measures and percentages of [H_2S] and [CO_2] at different hazard intervals

	H_2S ppm			**CO_2 ppm**	
	15-100	*100-250*	*≥ 250*	*< 5,000*	*≥ 5,000*
Meas. no.	1,251	1,038	1,102	2,449	840
Meas. %	36.89	30.61	32.49	74.46	25.54
Average	71.6	154.1	433.5	1,960	7,605
Minimum	31	100	250	10	5,015
Maximum	99.9	249.6	1,124	4,984	15,330

Table A4b. Duration of intervals (> 2h) with [H_2S] ≥100, ≥250 ppm and [CO_2] ≥5,000 ppm

Date	**H_2S ≥ 100 ppm**		**Date**	**H_2S ≥ 250 ppm**		**Date**	**CO_2 ≥ 5,000 ppm**	
	start time	*duration*		*start time*	*duration*		*start time*	*duration*
3 July	10:40	48h18'	3 July	20:57	10h08'	3 July	21:41	09h06'
			4 July	18:55	12h20'	4 July	19:31	11h09'
5 July	13:55	05h14'						

Site 1: 3-5 July (50 cm)

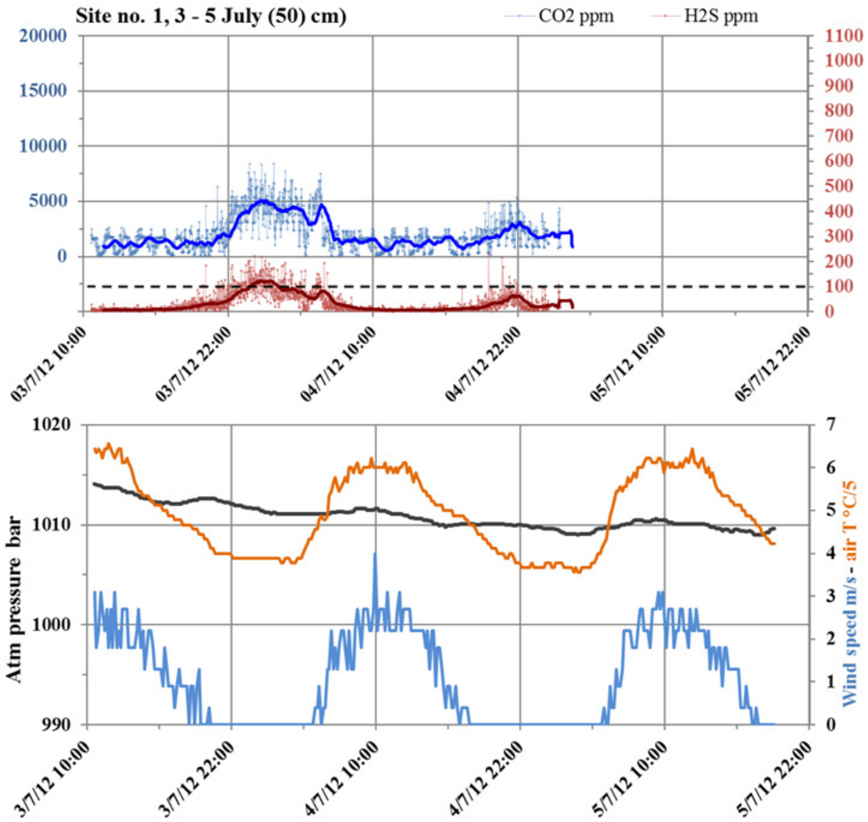

Figure A6. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average). Horizontal dotted line indicates the IDLH level (100 ppm) of H_2S.

Table A5a. Measures and percentages of [H_2S] and [CO_2] at different hazard intervals

	H_2S ppm					**CO_2 ppm**	
	≤ 10	*10-15*	*15-100*	*100-250*	*≥ 250*	*< 5,000*	*≥ 5,000*
Meas. no.	871	297	907	195	-	2,128	142
Meas. %	38.37	13.08	39.95	8.59	-	93.74	6.25
Average	5.8	12.3	45.2	132.7	-	1,764	5,893
Minimum	0.8	10	15	100	-	10	5,015
Maximum	9.9	14.9	99.7	230	-	4,984	8,433

Table A5b. Duration of intervals (> 2h) with [H_2S] ≥100 and [CO_2] ≥5,000 ppm

Date	**H_2S ≥ 100 ppm**		**Date**	**CO_2 ≥ 5,000 ppm**	
	start time	*duration*		*start time*	*duration*
3 July	21:16	10h14'	3 July	23:35	07h30'
4 July	20:56	02h27'			

Site 2

- Location: 33 T 298805 E 4595723 N
- Area: 12,000 m^2
- Topography: slightly depressed, in the bed of the last part of Caldara Vignarola ditch
- Vegetation: reeds
- Soil alteration: yes
- Water: pond within a ditch
- Dead animals: not found
- Gas emission: gas bubbling in the pond
- Recorded parameters: CO_2, H_2S
- Recording period: 10-11 April

Site 2 is located nearby a gas bubbling pond fed by Caldara Vignarola ditch (Fig. A7a). The pond is surrounded by a reed bed where the CO_2 and H_2S devices were set (Fig. A7b). Recorded data are shown in Fig. A8. Data related to gas hazard are reported in Tables A6.

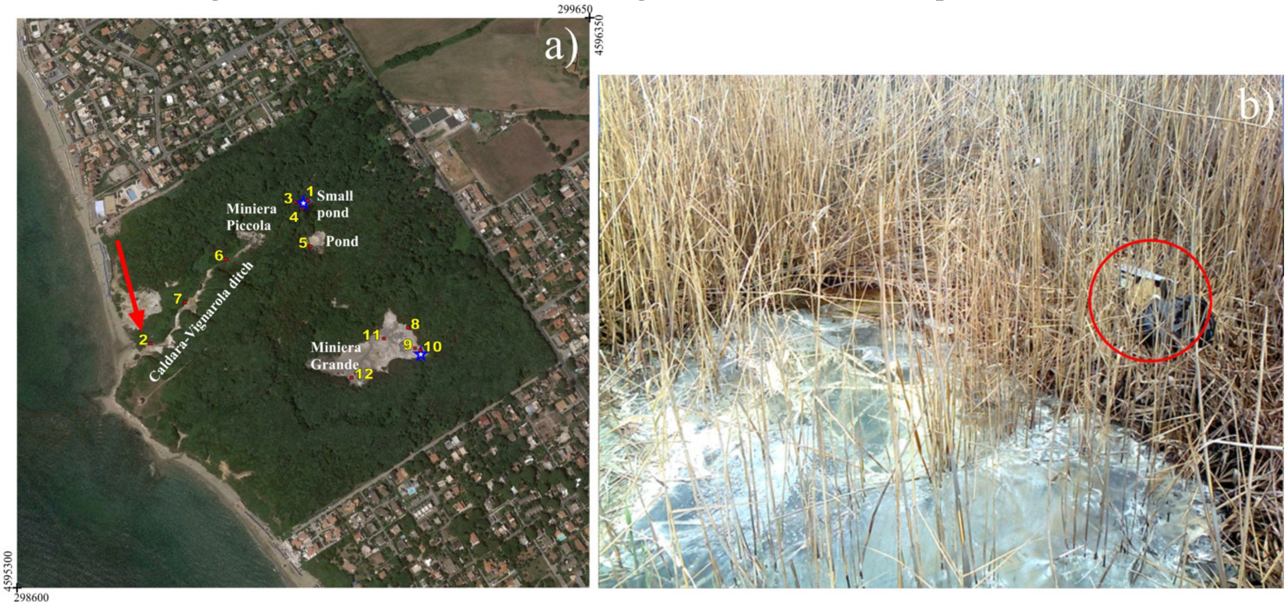

Figure A7. a) Location of site no. 2; b) the monitoring device (red circle) in the reeds near the pond rim.

Site 2: 10-11 April (20 cm)

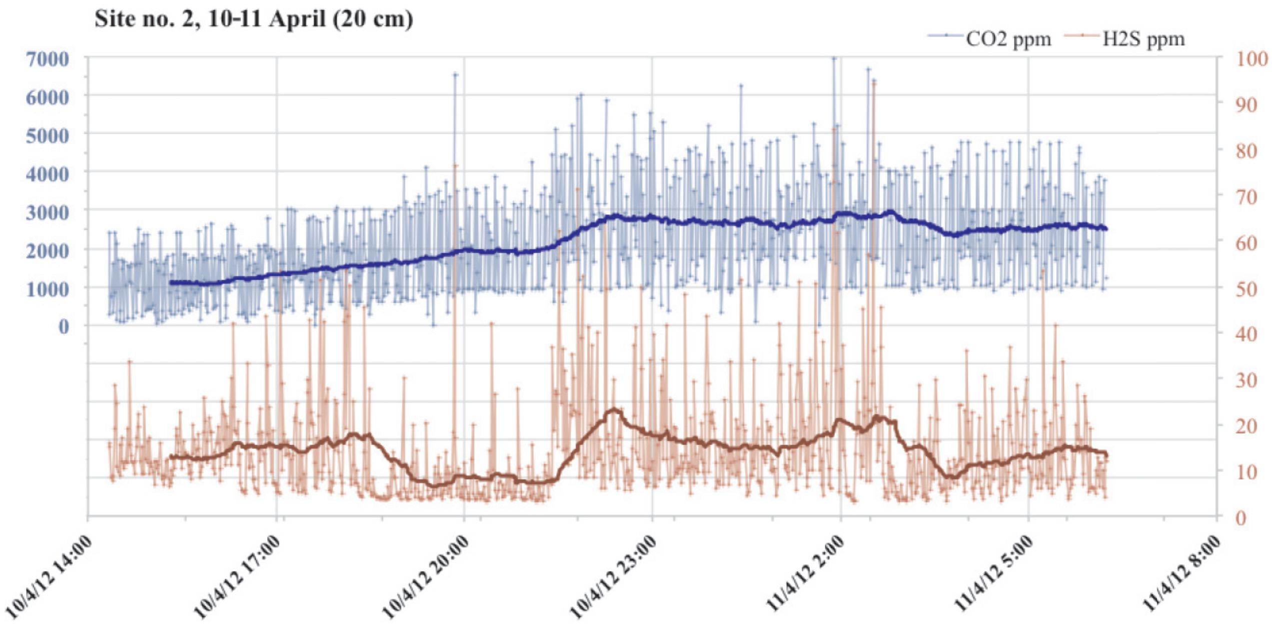

Figure A8. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average).

Table A6. a) Measures and percentages of [H_2S] and [CO_2] at different hazard intervals; b) duration of intervals with [CO_2] ≥5,000 ppm

a)	**H_2S ppm**			**CO_2 ppm**		***b)***	**CO_2 ppm ≥ 5,000**	
	≤ 10	*10-15*	*15-100*	*< 5,000*	*≥ 5,000*	*date*	*start time*	*duration*
Meas. no.	431	216	308	801	17	10-apr	19:51	06h41'
Meas. %	45.13	22.62	32.25	97.92	2.08			
Average	6.3	12.1	26.3	2,032	5,758			
Minimum	3	10	15	5	5,071			
Maximum	9.9	14.8	94	4,919	6,963			

Site 3

- Location: 33 T 299071 E 4595993 N
- Topography: flat
- Vegetation: present
- Soil alteration: no
- Water: absent
- Dead animals: not found
- Gas emission: diffuse from the soil
- Recorded parameters: H_2S, weather
- Recording period: 7-13 May

The site is located 20 m N of site no. 1 (Fig. A9). Time variations of air H_2S concentration and of environmental parameters are reported in Fig. A10. The weather station was located at the near site no. 1. Data related to gas hazard are reported in Table A7.

Figure A9. a) Location of site no. 3; b) Location of the H_2S monitoring station in the ferns underwood.

Site 3: 7-13 May (20 cm)

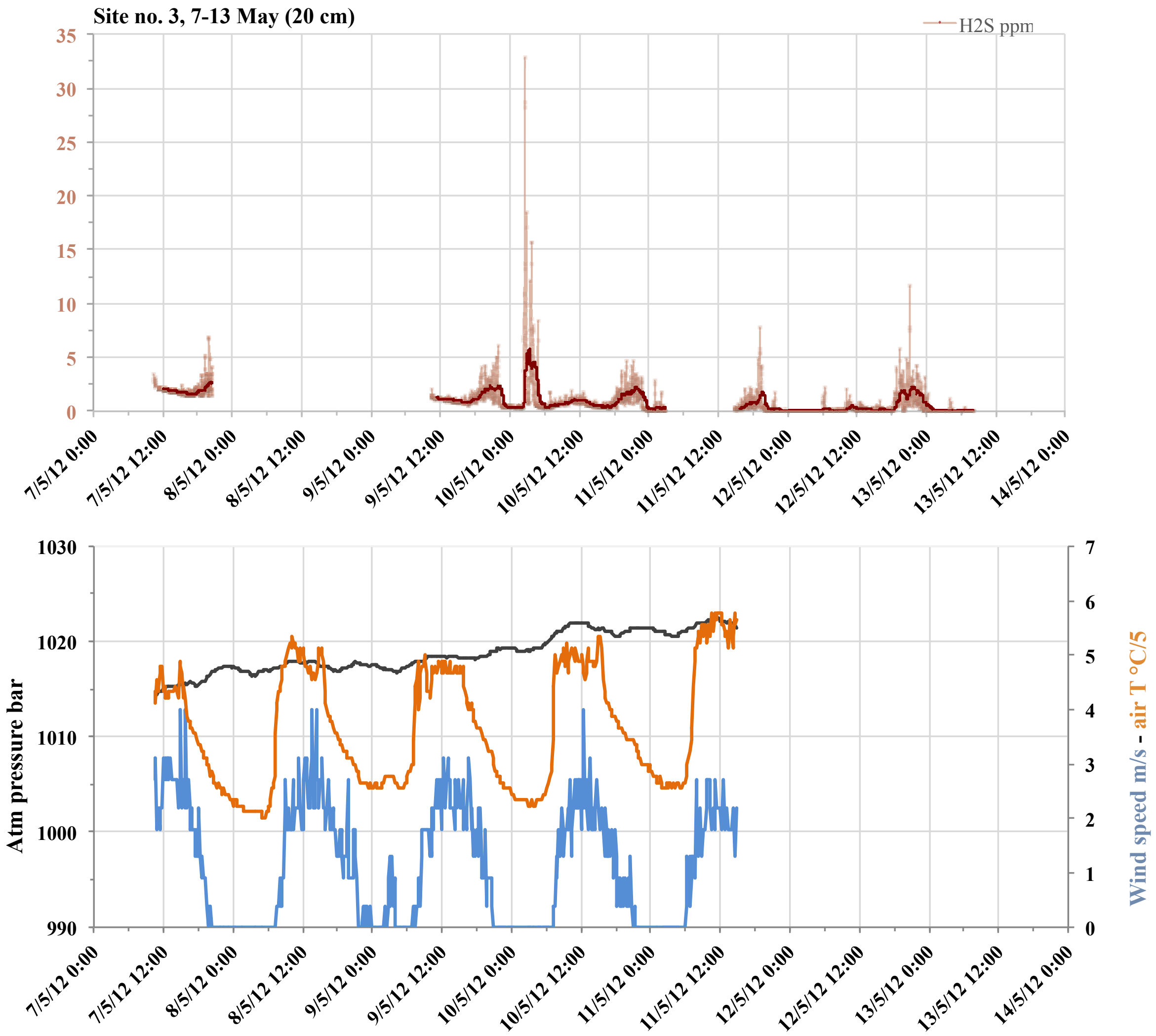

Figure A10. Time variation of H_2S air concentration (continuous line = hourly H_2S average) and of environmental parameters (below).

Table A7. Measures and percentages of [H_2S] at different hazard intervals

	H_2S ppm		
	≤ 10	*10-15*	*15-100*
Meas. no.	5,473	7	7
Meas. %	99.74	0.13	0.13
Average	0.85	12.2	22.4
Minimum	0	10	16
Maximum	9.9	14	33

Site 4

- Location: 33 T 299076 E 4595965 N
- Topography: flat
- Vegetation: present
- Soil alteration: no
- Water: absent
- Dead animals: not found
- Gas emission: diffuse from the soil
- Recorded parameters: H_2S, weather (at the near site no. 1)
- Recording period: 14-16 May

The site is located within the oak wood, along a path to a small bridge SW of site no. 1 (Fig. A11). Time variation of air H_2S concentration is reported in Fig. A12. Data related to gas hazard are reported in Table A8.

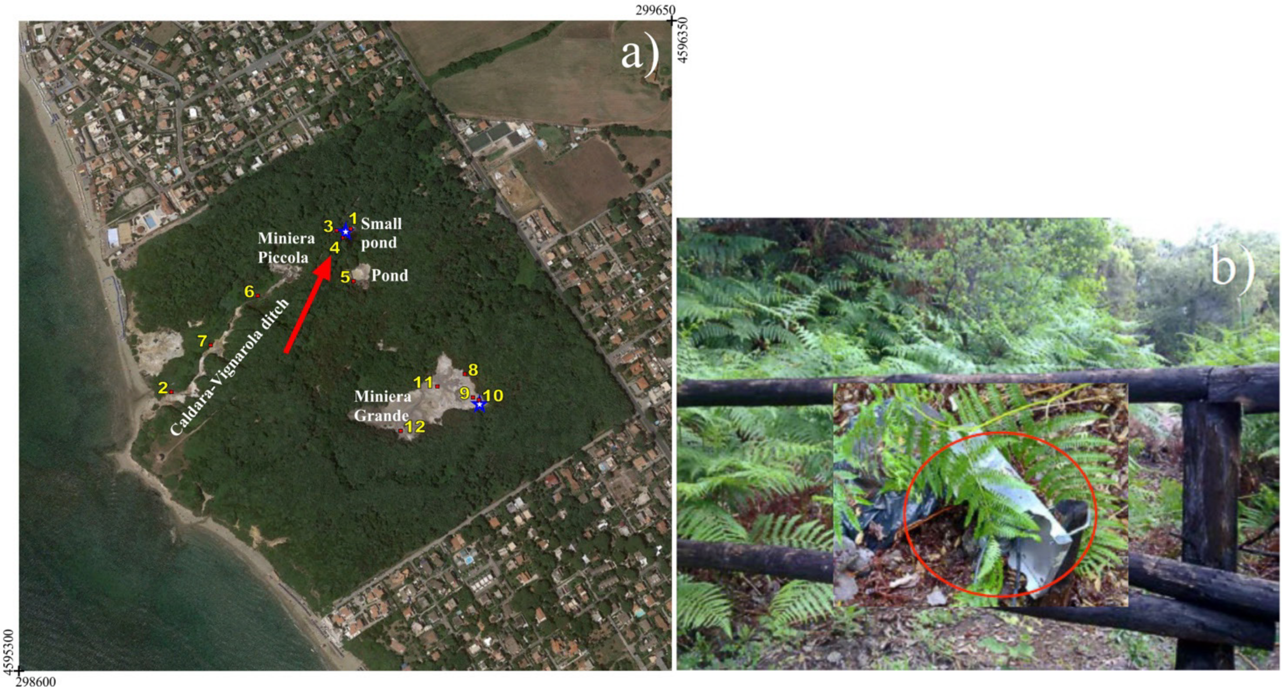

Figure A11. A) Location of site no. 4; b) Location of the monitoring device at site no. 4.

Site 4: 14-16 May (20 cm)

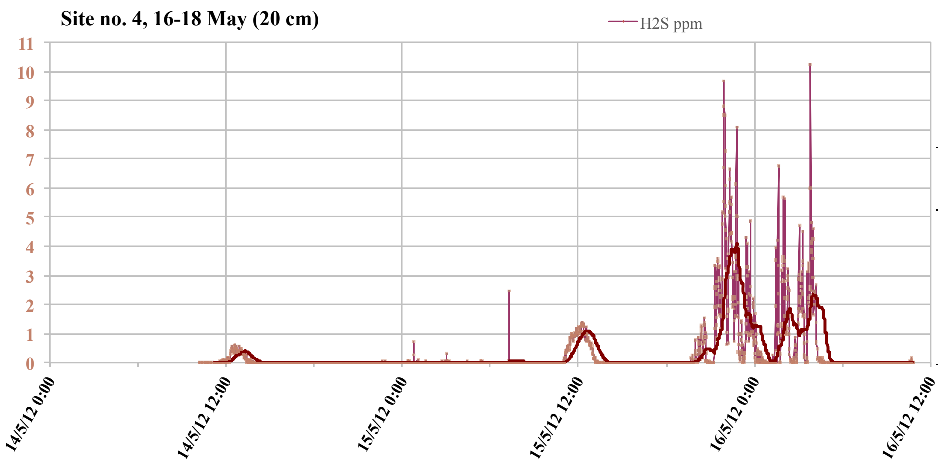

Figure A12. Time variation of H_2S air concentration (continuous line = hourly H_2S average).

Table A8. Measures and percentages of [H_2S] at different hazard intervals

	H_2S ppm	
	≤ 10	*10-15*
Meas. no.	2,919	1
Meas. %	99.96	0.04
Avg.	0.3	-
Min.	0	-
Max.	9.7	10.3

Site 5

- Location: 33 T 299097 E 4595897 N
- Area: 1,000 m^2
- Topography: slight depression (3 m below the surrounding ground level)
- Vegetation: present
- Soil alteration: present
- Water: in the near quagmire pond
- Dead animals: not found
- Gas emission: diffuse from the soil and advective from small vents
- Recorded parameters: H_2S
- Recording period: 16-18 May

Site no. 5 is located within the oak wood, near a wooden bridge above a quagmire (Fig. A13). Time variation of air H_2S concentration is reported in Fig. A14. Data related to gas hazard are reported in Table A9.

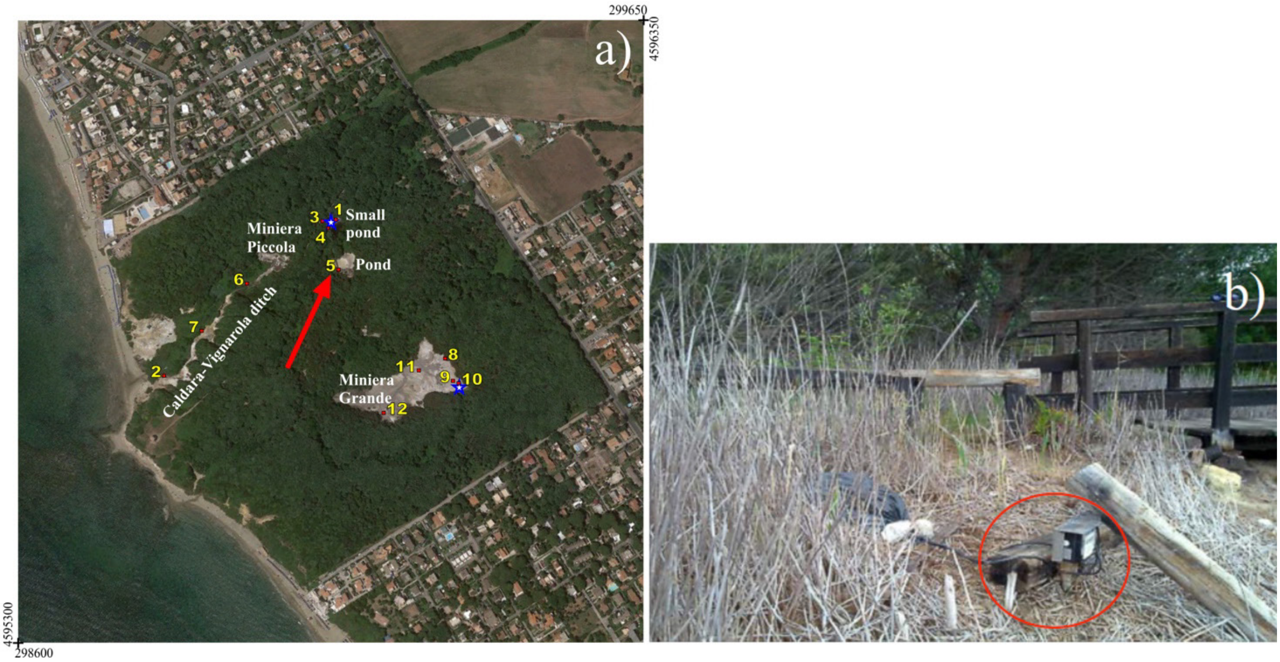

Figure A13. a) Location of site no 5. b) Location of the H_2S device at site no. 5.

Site 5: 16-18 May (20 cm)

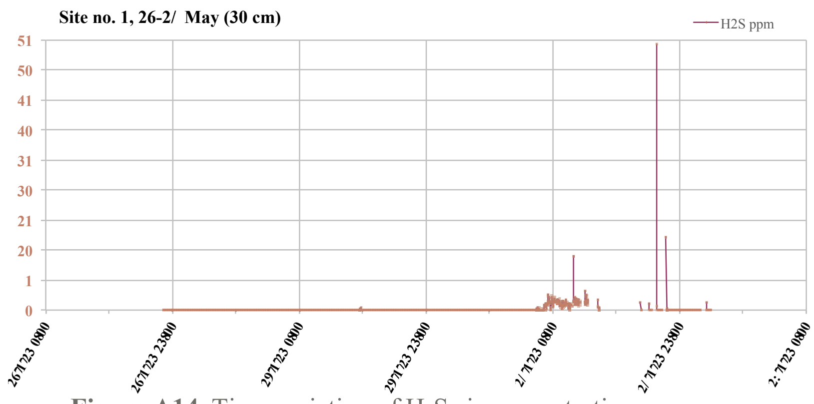

Figure A14. Time variation of H_2S air concentration.

Table A9. Measures and percentages of [H_2S] at different hazard intervals

	H_2S ppm		
	≤ 10	*10-15*	*15-100*
Meas. no.	2,650	1	1
Meas. %	99.92	0.04	0.04
Average	0.1	-	-
Minimum	0	-	-
Maximum	9	12	44

Site 6

- Location: 33 T 298946 E 4595873 N
- Area: 3,300 m^2
- Topography: pond on a gentle slope
- Vegetation: absent, reeds near the pond
- Soil alteration: yes
- Water: in the near pond
- Dead animals: not found
- Gas emission: diffuse from the soil and gas bubbling from the pond
- Recorded parameters: CO_2, H_2S
- Recording period: 14-18 May

Site no. 6 is located in the proximity of a pond near Caldara Vignarola ditch, SW of Miniera Piccola (Fig. A15); here past mining excavations left a depression of 6 m below the surrounding ground level. Time variations of air CO_2 and H_2S concentration are reported in Fig. A16. Data related to gas hazard are reported in Table A10.

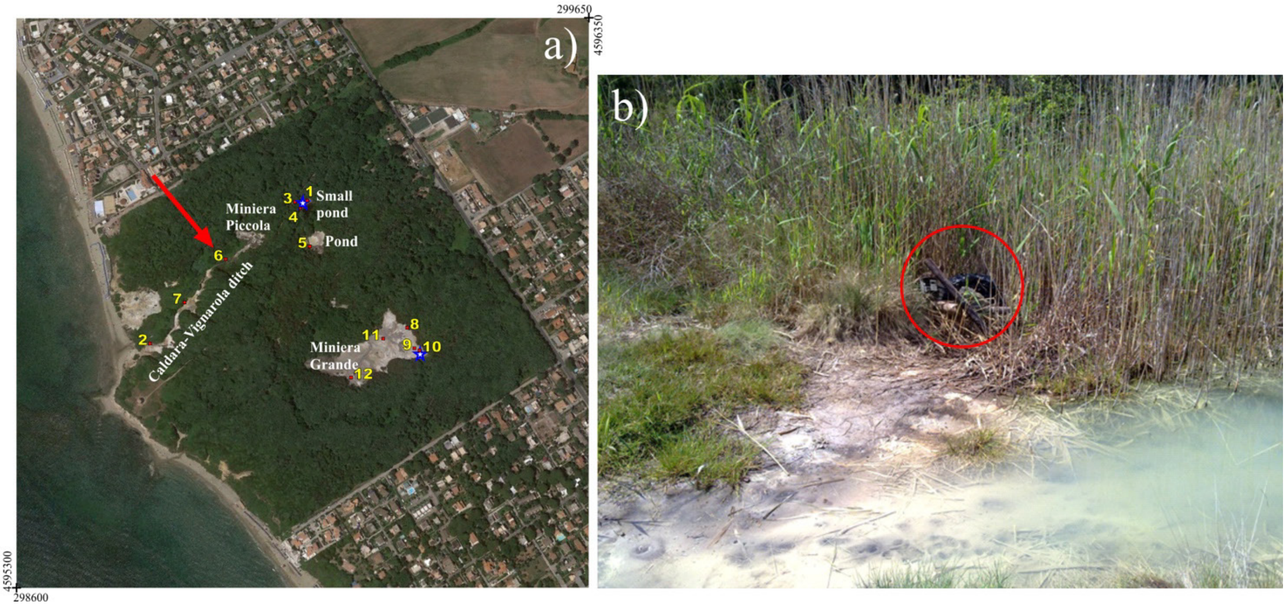

Figure A15. a) Location of site no. 6; b) Location of the gas monitoring device at site no. 6.

Site 6: 14-18 May (20 cm)

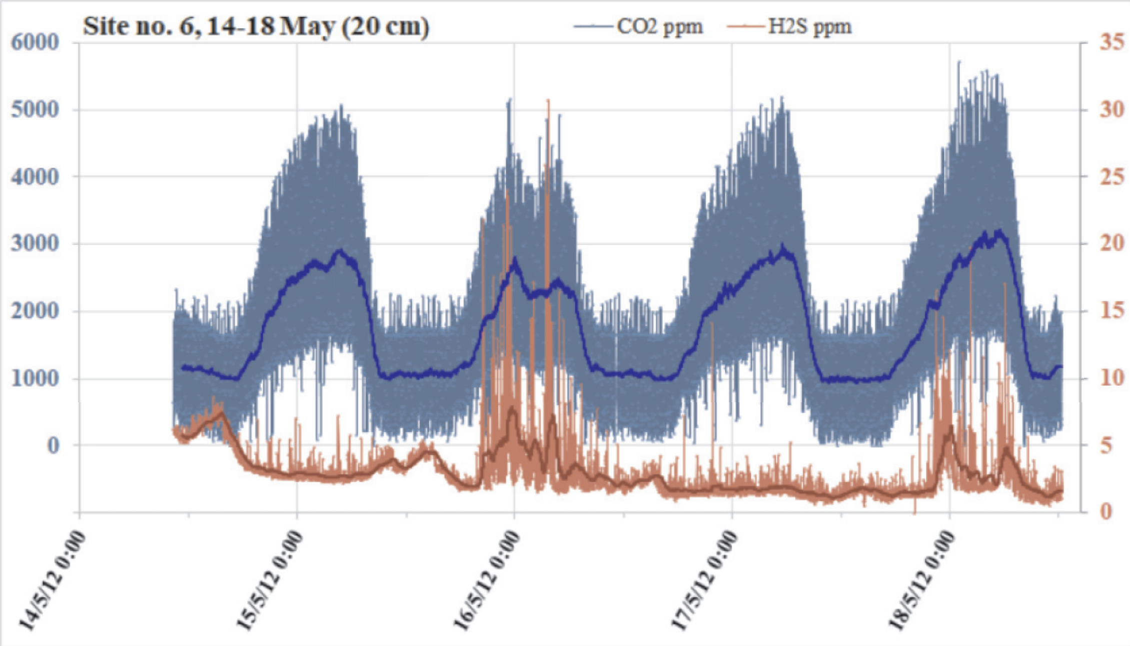

Figure A16. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average).

Table A10. a) Measures and percentages of [H_2S] and [CO_2] at different hazard intervals; b) duration of intervals with[CO_2] ≥5,000 ppm

a)	H_2S ppm			CO_2 ppm		*b)*	$CO_2 \geq 5{,}000$ ppm	
	≤ 10	*10-15*	*15-100*	*< 5,000*	*≥ 5,000*	*date*	*start time*	*duration*
Meas. no.	5,718	53	20	5,208	55	15 May	04:51	spikes
Meas. %	97.39	0.90	0.34	98.95	1.05	16 May	23:14	spikes
Average	2.8	12.0	20.0	1,656	5,198	17 May	03:11	spikes
Minimum	0	10	16	2	5,007	18 May	00:44	05h29'
Maximum	9.9	14.8	31	4,977	5,708			

Site 7

- Location: 33 T 298870 E 4595788 N
- Topography: gentle slope
- Vegetation: reeds
- Soil alteration: yes
- Water: in the near pond and ditch
- Dead animals: not found
- Gas emission: diffuse from the soil and advective from small vents
- Recorded parameters: CO_2, H_2S, weather
- Recording period: 9-14 May

Figure A17. Location of site no. 7.

Site 7 is located along Caldara Vignarola ditch, near a pond at halfway between Miniera Piccola and the sea (Fig. A17). The CO_2 e H_2S device was located near the pond in a site surrounded by reeds. The meteo station was located at site no. 1 and worked only on 9-11 May. The recorded data are shown in Fig. A18. Data related to gas hazard are reported in Table A11.

Site 7: 9-14 May (20 cm)

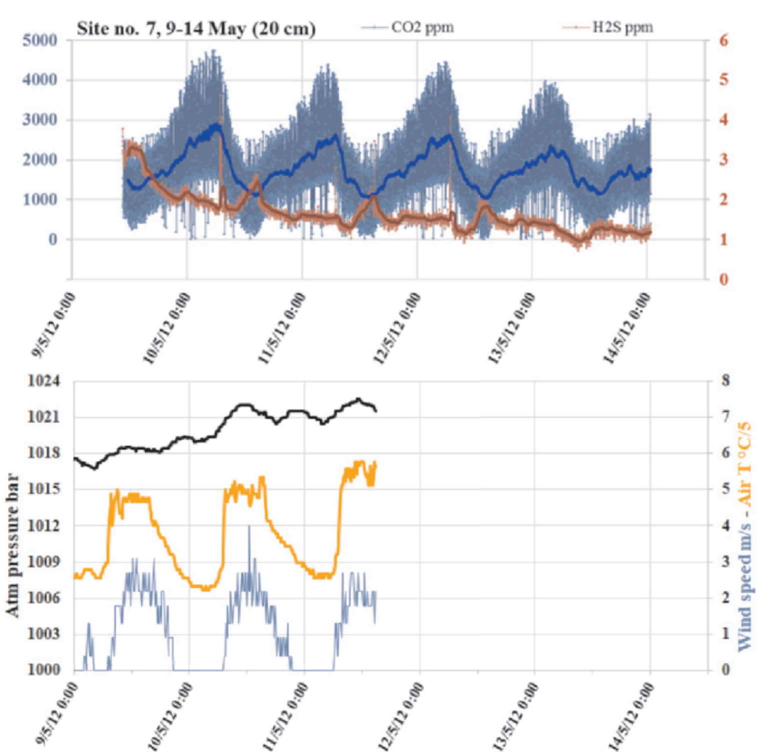

Figure A18. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average) and of environmental parameters.

Table A11. Measures and percentages of air H_2S and CO_2 concentrations

	H_2S ppm	CO_2 ppm
	≤ 10	*< 5,000*
Meas. no.	6,589	6,178
Meas. %	100	100
Average	1.7	1,739
Minimum	0.7	16
Maximum	4.6	4,747

Site 8

- Location: 33 T 299279 E 4595731 N
- Area: 12,000 m^2
- Topography: flat, slightly higher than the surrounding ground level
- Vegetation: absent
- Soil alteration: yes
- Water: absent
- Dead animals: not found
- Gas emission: diffuse from the soil and advective from small vents
- Recorded parameters: H_2S
- Recording period: 21-30 May

The site is at the northeastern limit of Miniera Grande (Fig. A19a), three metres above the excavated depression (Fig. A19b). Time variation of air H_2S concentration is reported in Fig. A20. Data related to gas hazard are reported in Table A12.

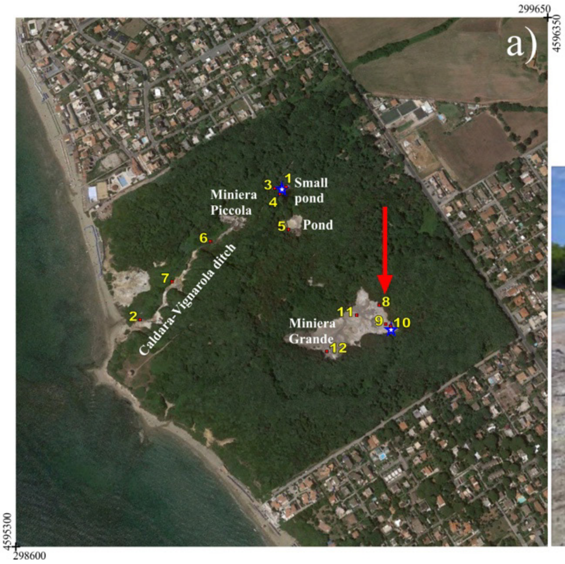

Figure A19. a) Location of site no. 8; b) Location of the gas monitoring device at Miniera Grande.

Site 8: 21-30 May (20 cm)

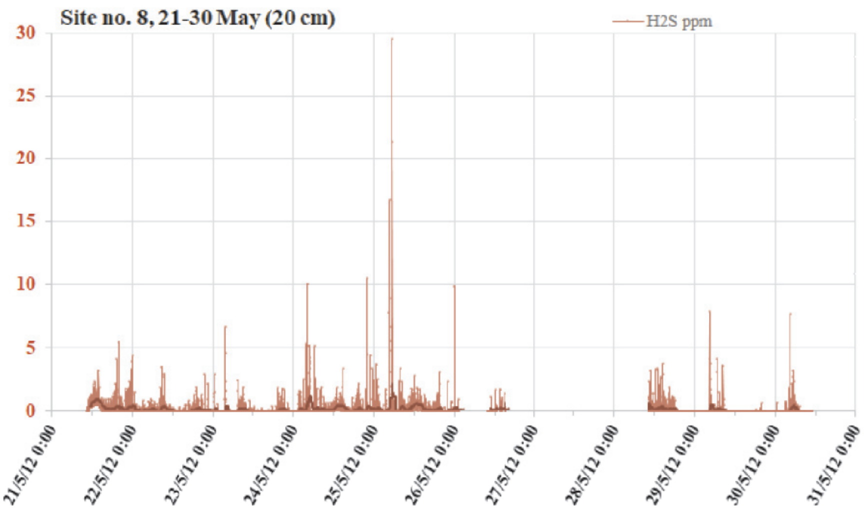

Figure A20. Time variation of H_2S air concentration (continuous red line = hourly H_2S average).

Table A12. Measures and percentages of [H_2S] at different hazard intervals.

	H_2S ppm		
	≤ 10	*10-15*	*15-100*
Meas. %	99.95	0.02	0.03
Avg.	0.13	10.3	22.5
Min.	0	10	17
Max.	9.9	10.5	29.5

Site 9

- Location: 33 T 299289 E 4595694 N
- Area: 12,000 m^2
- Topography: flat surface with small mamilliform knolls having a clayey altered surface with sulfur and sulphate incrustations, formed above and around degassing micro-fractures.
- Vegetation: absent
- Soil alteration: yes
- Water: absent
- Dead animals: frequently found (small mammals, invertebrates)
- Gas emission: advective from mamillons and diffuse from the soil
- Recorded parameters: H_2S and weather (partially)
- Recording period: 30 May-6 June

Site no. 9 is in the upper eastern part of the wide old sulfur mine of Miniera Grande (Fig. A21). The device was placed above one of the many mamillon knolls (Carapezza et al., 2012). Time variations of air H_2S concentration and wind speed are reported in Fig. A22 (meteo station operated only on 4 and 5 June). Data related to gas hazard are reported in Table A13.

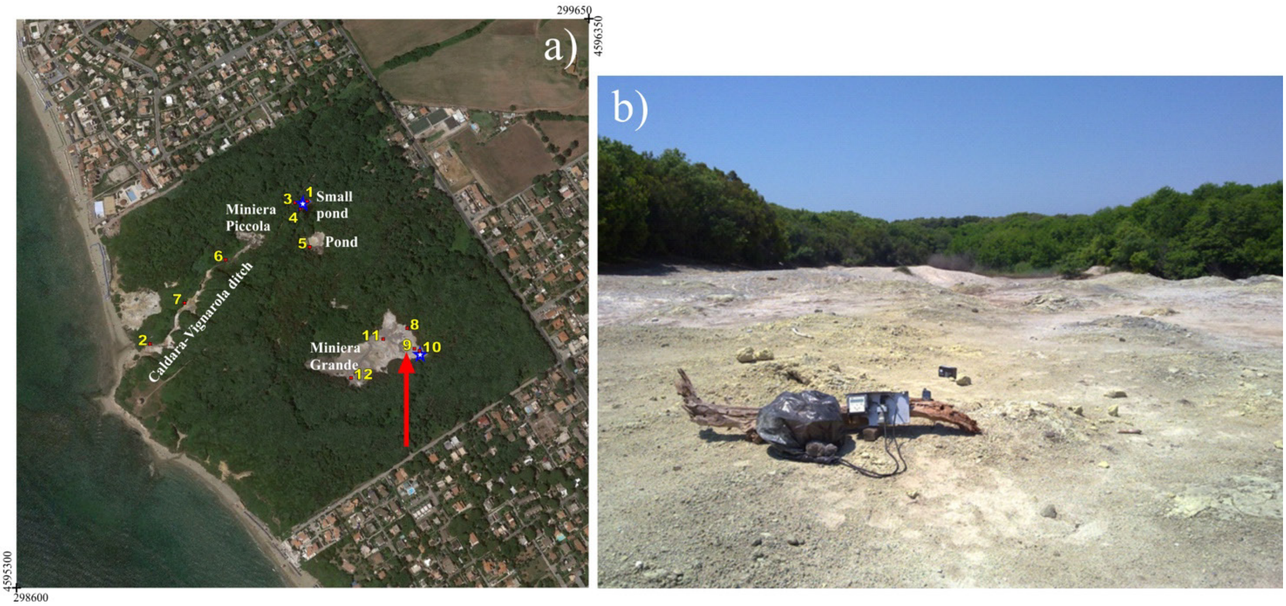

Figure A21. a) Location of site no. 9. b) Location of the gas monitoring device above a mamillon gas vent at Miniera Grande.

Site 9: 30 May – 6 June (20 cm)

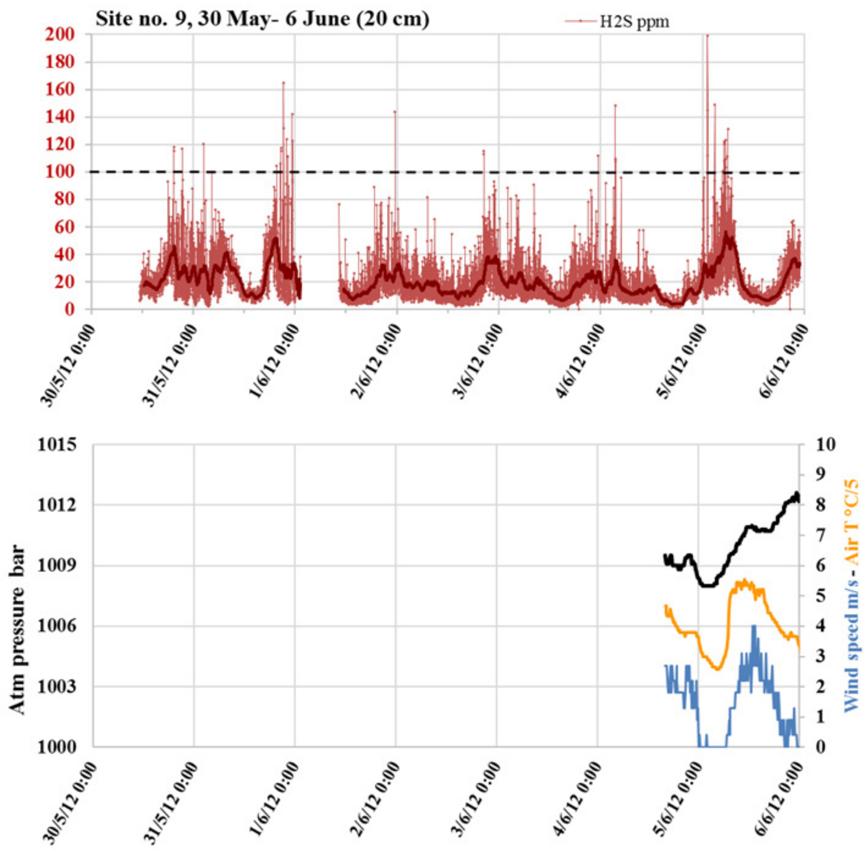

Figure A22. Time variation of H_2S air concentration (continuous red line = hourly H_2S average) and of environmental parameters (below). Horizontal dotted line indicates the IDLH level (100 ppm) of H_2S.

Table A13. a) Measures and percentages of [H_2S] at different hazard intervals; b) duration of intervals with [H_2S] ≥100 ppm

a)	**H_2S ppm**			
	≤ 10	*10-15*	*15-100*	*100-250*
Meas. no.	2,392	1,881	4,450	38
Meas. %	27.3	21.5	50.8	0.4
Average	6.9	12.4	28.83	122
Minimum	1.5	10	15.02	100
Maximum	9.9	14.9	96.4	199

b)	**H_2S ≥100 ppm**	
date	*start time*	*duration*
31 May	19:43	3h53'
2-4 June	~23:00	spikes
5 June	4:44	1h18'

Site 10

- Location: 33 T 299292 E 4595689 N
- Area: 12,000 m^2
- Topography: as for site no. 9
- Vegetation: absent
- Soil alteration: yes
- Water: absent
- Dead animals: invertebrates
- Gas emission: advective from mamillons and diffuse from the soil
- Recorded parameters: CO_2, H_2S and weather
- Recording periods: 7-10 June; 22 June-2 July (at 20 and 50 cm height)

Like site no. 9, also site no. 10 is located in the upper easternmost part of Miniera Grande (Fig. A23). The CO_2, H_2S and weather devices were placed near to a mamillon gas vent (as in Fig. A21). Their time variations are reported in Figs. A24 to A26. Data related to gas hazard are reported in Tables A14 to A16.

Figure A23. Location of site no. 10.

Site 10: 7–10 June (20 cm)

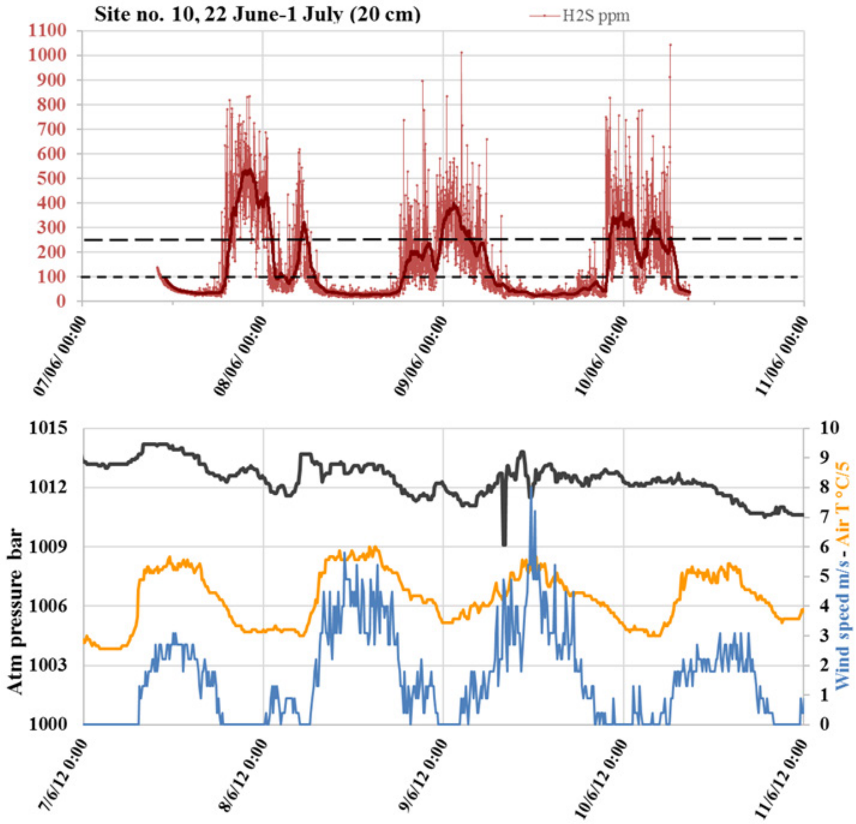

Figure A24. Time variation of H_2S air concentration (continuous red line = hourly H_2S average) and of environmental parameters (below).

Table A14a. Measures and percentages of [H_2S] at different hazard intervals

	H_2S ppm				
	≤ 10	*10-15*	*15-100*	*100-250*	*≥ 250*
Meas. no.	-	10	2,547	772	892
Meas. %	-	0.24	60.34	18.29	21.13
Average	-	13	43	164	418
Minimum	-	11	15	100	250
Maximum	-	14.9	99.9	249.6	1,044

Table A14b. Duration of intervals (>2h) with [H_2S] ≥100 ppm

Date	**H_2S ≥ 100 ppm**		**Date**	**H_2S ≥ 250 ppm**	
	start time	*duration*		*start time*	*duration*
7 June	18:14	13h10'	7 June	18:33	06h18'
8 June	18:22	14h27'	8 June	03:57 18:13 22:46	02h21' 03h48' 06h59'
9 June	19:14 21:44	02h07' 09h41'	9 June	21:38	03h36'
			10 June	01:50	04h21'

Site 10: 22 June – 1 July (20 cm)

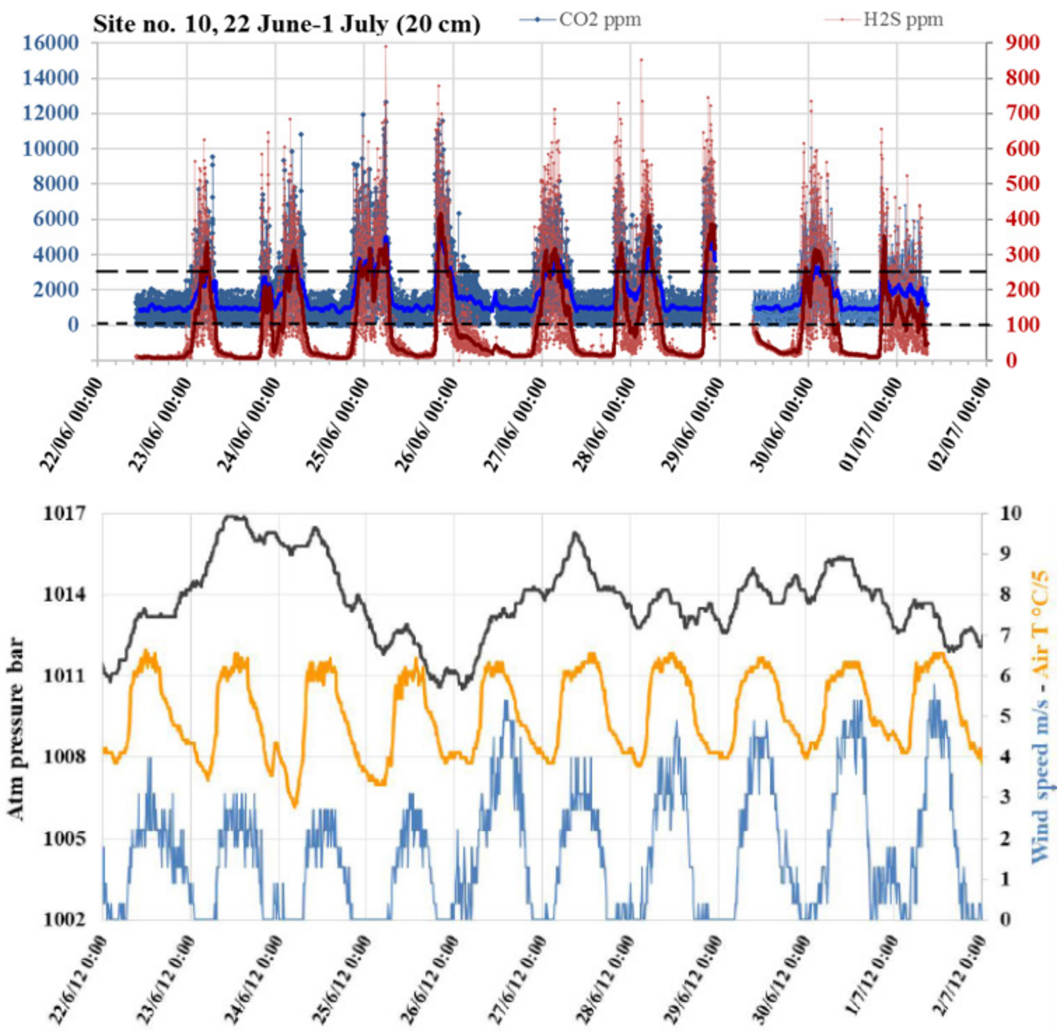

Figure A25. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average) and of environmental parameters (below). Horizontal dotted lines indicate the IDLH level (100 ppm) and the lethal threshold (250 ppm) of H_2S.

Table A15a. Measures and percentages of [H_2S] and [CO_2] at different hazard intervals

	H_2S ppm					**CO_2 ppm**	
	≤ 10	*10-15*	*15-100*	*100-250*	*≥ 250*	*< 5,000*	*≥ 5,000*
Meas. no.	1,430	1,531	5,642	1,879	1,610	9,732	563
Meas. %	11.83	12.66	46.66	15.54	13.31	94.53	5.47
Average	7.9	12.5	38	165	381	1,537	6,431
Minimum	0	10	15	100	250	10	5,015
Maximum	9.9	14.9	99.9	249.9	890	4,984	12,675

Table A15b. Duration of intervals (>2h) with $[H_2S] \geq 100$, ≥ 250 ppm and of $[CO_2] \geq 5{,}000$ ppm

Date	$H_2S\geq$	100 ppm	Date	$H_2S\geq$	250 ppm	Date	$CO_2\geq$	5000 ppm
	start time	*duration*		*start time*	*duration*		*start time*	*duration*
23 June	01:12	06h05'	23 June	01:39	05h20'	23 June	04:50	02h13'
	20:00	02h24'		20:08	02h15'			
	23:37	08h45'						
24 June	20:31	10h21'	24 June	01:55	05h17'	24 June	21:06	8h47'
				21:06	09h09'			
25 June	19:06	08h26'	25 June	19:06	04h55'	25 June	19:11	03h59'
26 June	21:34	10h19'	26 June	22:30	06h57'	26 June	23:24	06h03'
27 June	19:30	12h16'	27 June	19:30	03h28'	27 June	19:34	02h22'
28 June	19:26	04h11'	28 June	01:27	04h43'	28 June	02:41	03h15'
				19:28	03h19'		19:29	03h12'
29 June	21:55	09h53'	29 June	21:38	08h33'			
30 June	19:16	11h25'	30 June	19:12	11h18'	30 June	04:26	03h00'

Site 10: 26 June – 2 July (50 cm)

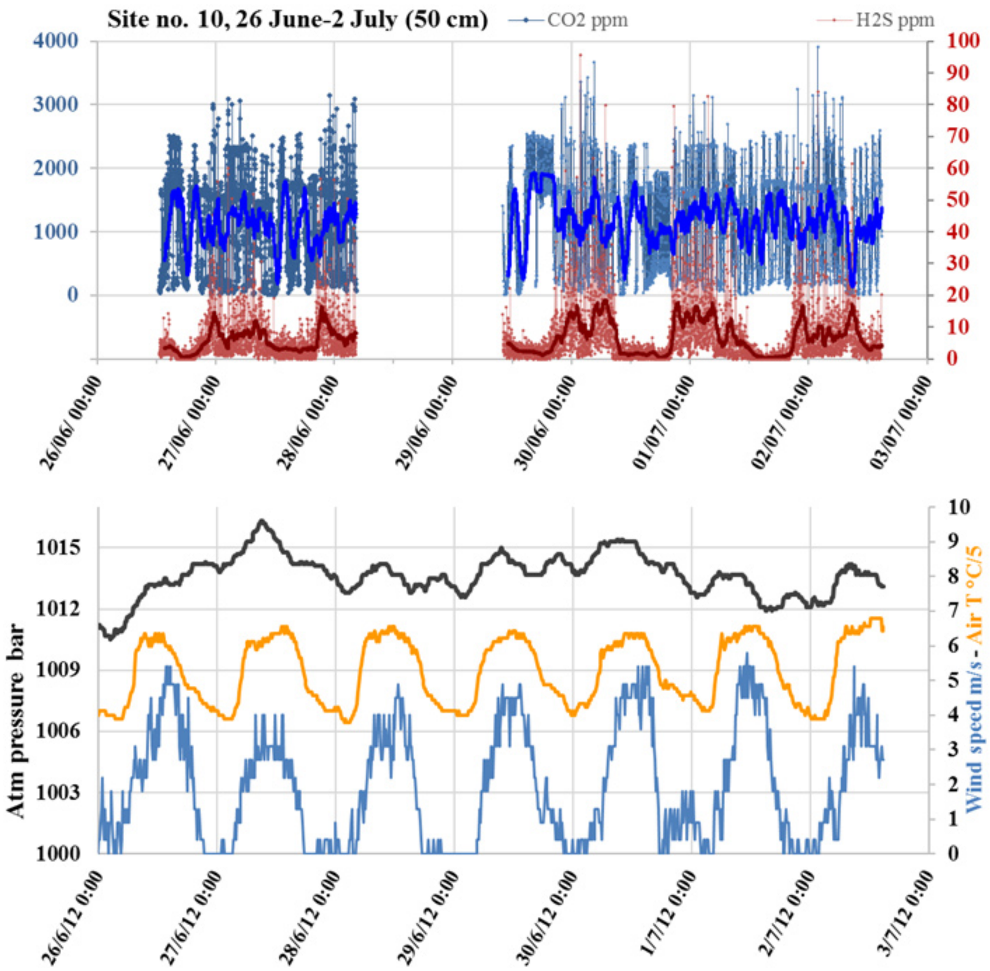

Figure A26. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average) and of environmental parameters.

Table A16. Measures and percentages of [H_2S] and [CO_2] at different hazard intervals

	H_2S ppm			CO_2 ppm
	≤ 10	*10-15*	*15-100*	*< 5,000*
Measure no.	5,552	603	753	6,888
Measure %	80.60	8.75	10.93	100
Average	3.2	12	25	1,163
Minimum	0	10	15	10
Maximum	9.9	14.9	96	3,916

Site 11

- Location: 33 T 299231 E 4595711 N
- Area: 12,000 m^2
- Topography: northern lowered flat part of Miniera Grande
- Vegetation: absent
- Soil alteration: yes
- Water: absent
- Dead animals: not found
- Gas emission: diffuse from the soil
- Recorded parameters: CO_2, H_2S
- Recording period: 21-30 May

Figure A27. Location of site no. 11.

Site no. 11 is located in the northern part of Miniera Grande (Fig. A27) where past mining activity left a lowered level, 3 m below the surrounding ground. Time variations of CO_2 and H_2S air concentration are reported in Fig. A28. Data related to gas hazard are reported in Table A17.

Site 11: 21-30 May (20 cm)

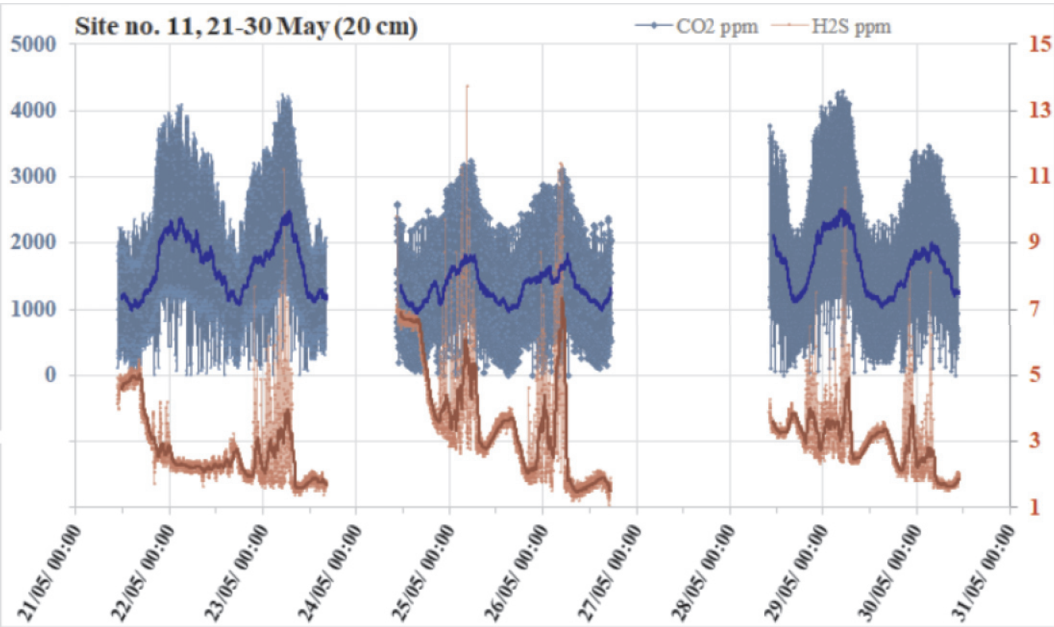

Figure A28. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average).

Table A17. Measures and percentages of [H_2S] and [CO_2] at different hazard intervals

	H_2S ppm		**CO_2 ppm**
	≤ 10	*10-15*	*< 5,000*
Measure no.	9,420	15	8,719
Measure %	99.84	0.16	100
Average	3	11	1,512
Minimum	1	10	2
Maximum	9.9	14	4,305

Site 12

- Location: 33 T 299174 E 4595645 N
- Area: 12,000 m^2
- Topography: southwestern lower part of Miniera Grande
- Vegetation: absent
- Soil alteration: yes
- Water: small streams and springs
- Dead animals: not found
- Gas emission: diffuse from the soil and advective from small fractures
- Recorded parameters: CO_2, H_2S and weather (partially)
- Recording periods: 30 May -6 June; 7-9 June

Site no. 12 is located in the low part of Miniera Grande near the south-westernmost limit of the mine (Fig. A29). Time variations of CO_2, H_2S air concentration and environmental parameters (from 4 to 6 June) are reported in Figs. A30 and A31. The weather station was located at the near site no. 10. Data related to gas hazard are reported in Tables A18 and A19.

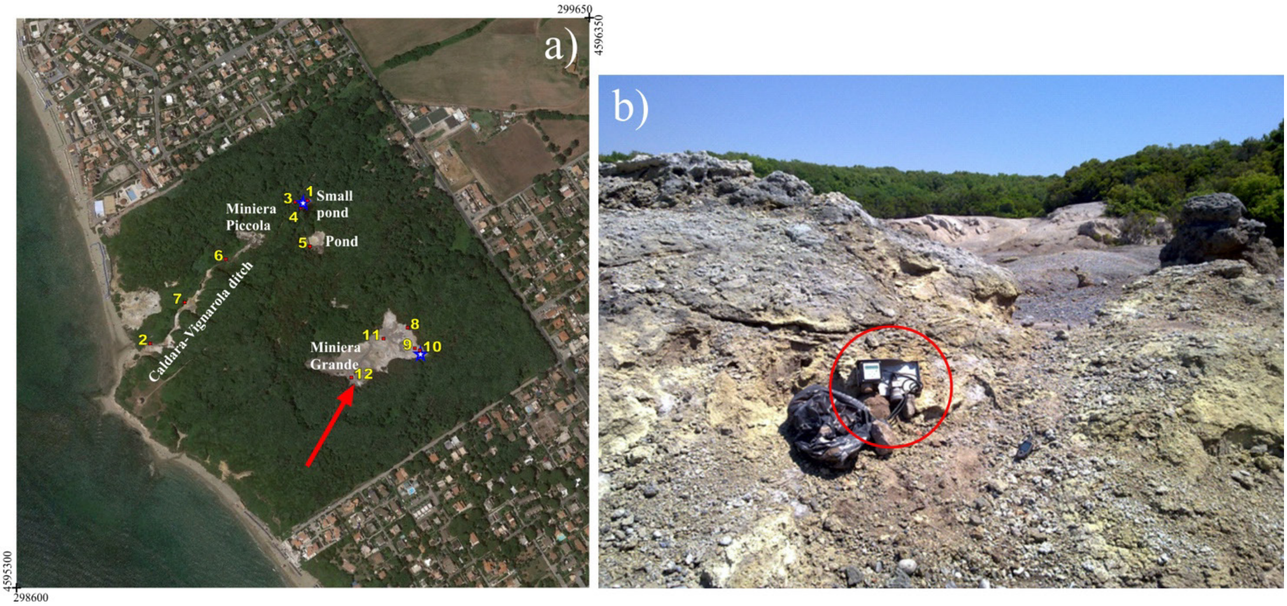

Figure A29. a) Location of site no. 12. b) Location of the gas monitoring device at Miniera Grande.

Site 12: 30 May – 6 June (50 cm)

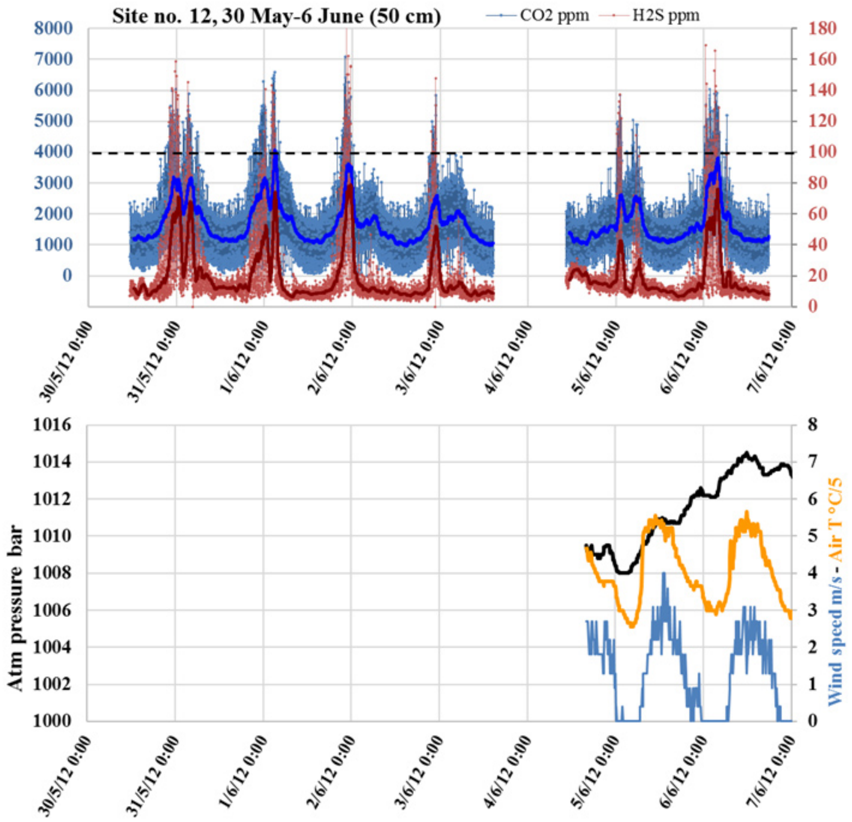

Figure A30. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average) and of environmental parameters (below).

Table A18a. Measures and percentages of [H_2S] and [CO_2] at different hazard intervals

	H_2S ppm				**CO_2 ppm**	
	≤ 10	*10-15*	*15-100*	*100-250*	*<5,000*	*≥ 5,000*
Meas. no.	3,682	2,814	2,919	160	8,905	101
Meas. %	38.45	29.39	30.48	1.67	98.88	1.12
Average	7.3	12	31	120	1,607	5,505
Minimum	3	10	15	100	0	5,004
Maximum	9.9	14.9	99.8	181	4,974	7,080

Table A18b. Duration of intervals with [H_2S] ≥100 ppm and [CO_2] ≥5,000 ppm

Date	**H_2S ≥ 100 ppm**		**Date**	**CO_2 ≥ 5,000 ppm**	
	start time	*duration*		*start time*	*duration*
30 May	22:00	02h33'	30 May	22:18	02h03'
31 May	02:52	01h05'	31 May	02:50	00h46'
				23:02	00h30'
1 June	21:22	02h10'	1 June	02:02	01h50'
				21:50	01h24'
2 June	21:40	01h11'	2 June	21:53	spikes
5 June	00:20	01h12'	5 June	00:26	00h57'
6 June	00:23	03h43'	6 June	00:30	03h00'

Site 12: 7 – 9 June (20 cm)

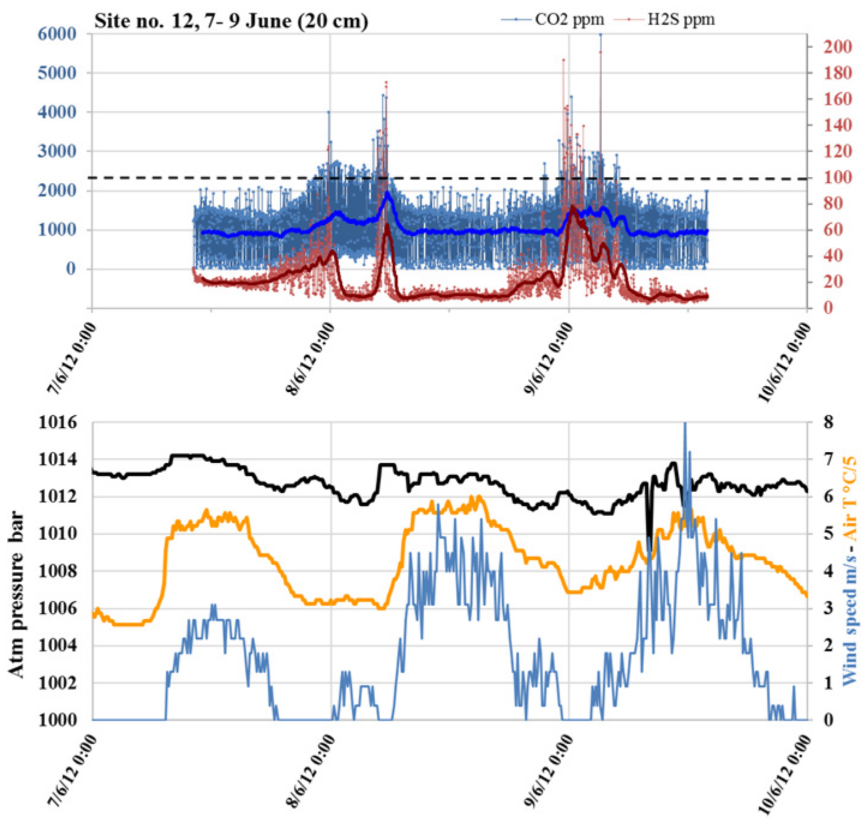

Figure A31. Time variation of CO_2 and H_2S air concentration (continuous lines: blue = hourly CO_2 average, red= hourly H_2S average) and of environmental parameters (below). Horizontal dotted line indicates the IDLH level (100 ppm) of H_2S.

Table A19a. Measures and percentages of [H_2S] and [CO_2] at different hazard intervals

	H_2S ppm				CO_2 ppm	
	≤ 10	*10-15*	*15-100*	*100-250*	*< 5,000*	*≥ 5,000*
Meas. no.	987	602	1,479	42	2,738	1
Meas. %	31.74	19.36	47.56	1.35	99.96	0.04
Average	7.9	12	30	128	1,057	-
Minimum	4	10	15	101	10	-
Maximum	9.9	14.9	99	196	4,435	5,991

Table A19b. Duration of intervals with [H_2S] ≥100 ppm

Date	H_2S≥ 100 ppm	
	start time	duration
8 June	04:26	01h13'
	23:29	01h29'
9 June	00:16	spike

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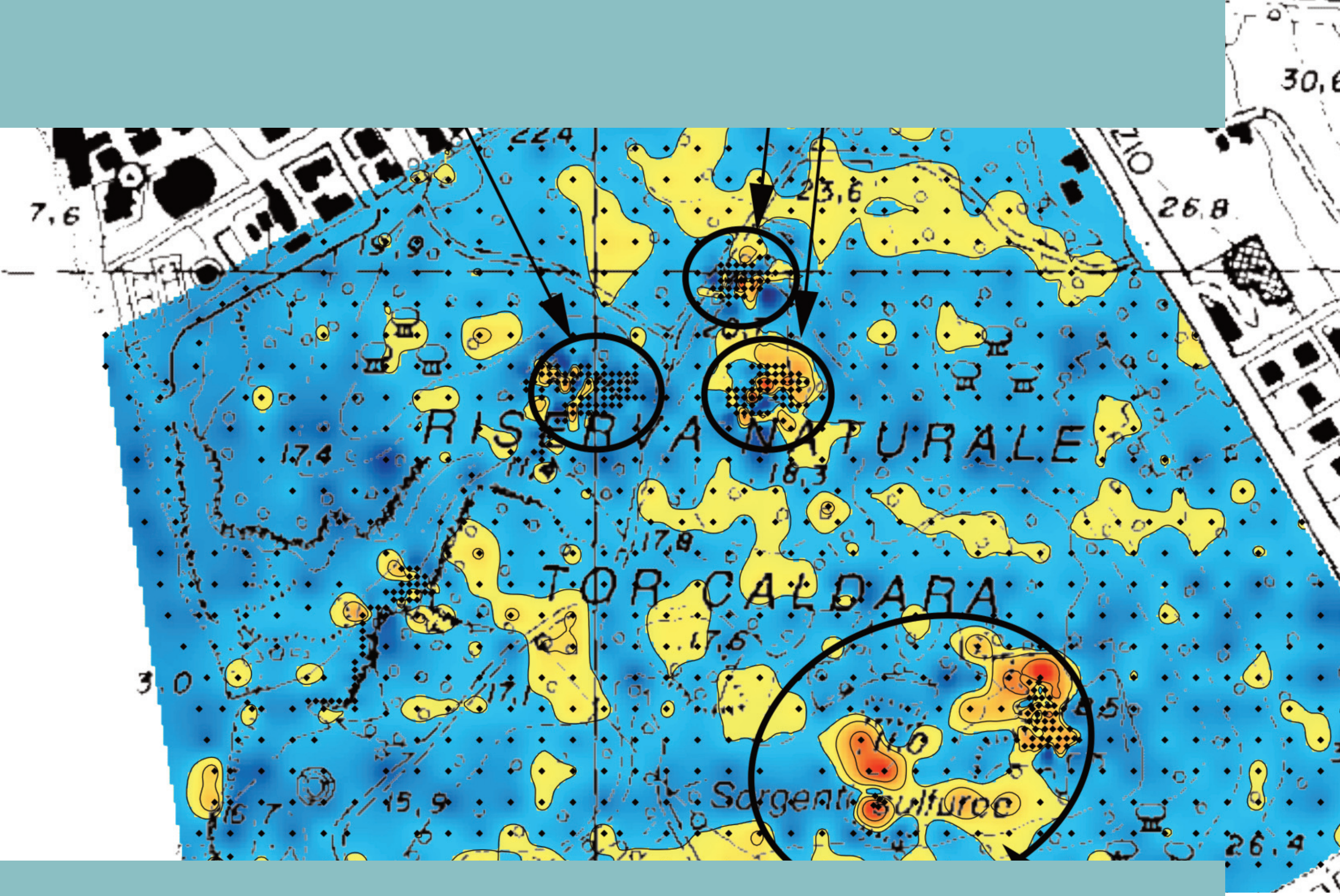

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