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Chemical and olfactometric inventory of gaseous spot vents in Mt. Amiata volcanic-geothermal area (Italy)

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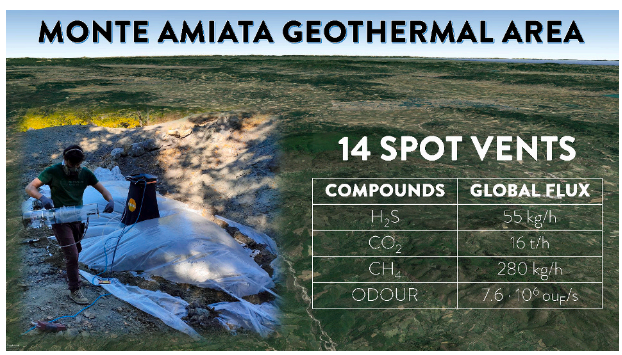
HIGHLIGHTS

- Mt. Amiata district is an important geothermal area, rich in gas spot vents.
- The main components of vent emissions were CO_2, CH_4 and H_2S.
- Odour concentrations measured at these emissions were very high (10^6 ou_E/m^3).
- Different hood strategies have been used for the measurement of gaseous flowrate.
- Total measured spot vent fluxes were 55 kg/h of H_2S, 16 t/h of CO_2, 280 kg/h of CH_4.

GRAPHICAL ABSTRACT



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ABSTRACT

Geothermal areas are typically characterised by the presence of gases and odours in the background atmosphere, stemming from natural emissions and possible mining exploitation of the area. This study presents the first olfactometric investigation of endogenous gas emissions from natural and archaeo-industrial vents in a geothermal area. Mt. Amiata is known for its complex geology and historical cinnabar mining. This study offers an inventory of spot gas emissions, not only in terms of odour and chemical concentration but also including flux data, a ground-breaking achievement in this field. The primary challenge of this investigation was estimating the emitted flow from ground holes or mine entrances, posing the risk of hazardous anoxic conditions. To address this challenge, an innovative and adaptive approach was adopted. The main breakthrough method involved the adaptation of a balometer, typically employed for indoor ventilation systems, to measure the flow of endogenous gases. Field surveys revealed odour concentrations that can exceed 10^6 of ou_E/m^3, surpassing industrial emission level considerably. Chemical concentrations, primarily consisted of CO_2 (80/90 $\%_{v/v}$) and CH_4 ($\sim 10\%_{v/v}$), providing critical insights into the global warming potential (GWP) associated with natural emissions. Moreover, these spots, often located at ground level and lacking a substantial atmospheric dilution, pose potential risks to nearby individuals, with concentrations of gases such as H_2S surpassing safety thresholds. Total emissive flux of the investigated spot vents in the Mt. Amiata area, showed that the emission rate of H_2S is notably substantial (55 kg/h), roughly equivalent to emissions from approximately four 20 MW geothermal plants, as along with

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odour emission rates in the order of 10^7 ouE/s. Considering the GWP derived from emitted gases, the total inventory assessment of the spot vents resulted in 36 t/h or 23 t/h CO_2eq, depending on the time horizon considered (GWP_{20} or GWP_{100} respectively).

1. Introduction

Geothermal areas are sites where natural heat transfer processes occur because of excess heat in the subsurface. These areas often exhibit elevated surface temperatures, hydrothermal activity, and the presence of fumaroles emitting hot volcanic gases (Sæmundsson and Sigurgeirsson, 2022). Emissions from these geothermal sites can contribute to background environmental odours, which are typical of such areas. Despite their importance in terms of global warming potential (GWP) and local hazards, the characterisation of these natural endogenous gas emissions is often neglected due to difficulties in obtaining of reliable inventory data. Although various methods are available for chemical characterisation, few research activities have focused on directly measuring of the *amount* of gas emitted, possibly because of the diverse nature of emission spots, and their complex fluid dynamics. Moreover, the measurement of the odour potential of these emissions has not been addressed before. This study aims to address these issues by providing useful methodological information and describing the implementation of such methods and measurements directly through field experience. The field campaigns did not concentrate on a single emission source, but focused on an entire area, specifically Mt. Amiata in Tuscany, Italy. This approach allowed us to encounter various types of spot vents, typical of natural geothermal. Developing new and flexible measurement approaches, was necessary to navigate difficult-to-reach and highly dangerous areas, characterised by presence of toxic and asphyxiating gases. Mt. Amiata, located in central-southern Tuscany, is an isolated relief, with a maximum altitude of 1738 m a.s.l. This area primarily consists of volcanic rocks, covering an area of approximately 81 km^2. Mt. Amiata is an integral part of the complex geological-structural landscape of the northern Apennines and southern Tuscany, with the average height of the outcrop area is approximately 1050 m a.s.l.

The geological structure of the area has been the subject of numerous studies (Bigazzi et al., 1981; Brogi, 2004; Brogi et al., 2023; Vezzoli and Principe, 2023) and is characterised by the superposition of pre-Neogene tectonic units, which outcrop along a North-South oriented tectonic structure called Montalcino — Mt. Amiata–Mt. Razzano.

This structure is surrounded by continental and marine deposits of the Cinigiano—Baccinello, Velona and Siena—Radicofani basins. The area is home to two relatively small and temporally separate volcanic edifices: the Pleistocene monogenetic volcano of Radicofani (1.3–1.1 My) and the Middle Pleistocene (304–263 ky) volcano of Mt. Amiata itself (Laurenzi et al., 2015).

In addition, Mt. Amiata is a substantial reserve of cinnabar, HgS, forming part of a mercury belt that extends to the Tyrrhenian Sea (Bargagli et al., 1986; Rimondi et al., 2012). Although, mining activities on the Amiata have ancient origins, modern cinnabar exploitation began in 1846 (Marroni et al., 2015). However, all mines in the area have since closed following the discovery of the toxicity of mercury.

The spontaneous emission of deep gases in the Mt. Amiata area is well-known and has been investigated from several points of view. Studies have focused on elemental mercury present in groundwater and vapour form (Bagnato et al., 2007; Ferrara et al., 1998; Pierotti et al., 2017; Tamasi and Cini, 2004; Vaselli et al., 2013, 2015). In addition, several researchers concentrated their efforts on the measurement of gas molecules alone (Chiodini et al., 1999; Collettini et al., 2008; Frondini et al., 2009; Minissale et al., 1997; Sbrana et al., 2020): CO_2 is the most investigated gas, followed by CH_4, H_2S, O_2, H_2 and N_2. This study aligns with these investigations and provides information on the odour potential of these emissions.

Other studies investigated the presence of H_2S and Hg in ambient air, linking their presence only to geothermal power plants (Cabassi et al., 2017; Somma et al., 2017) or measuring the nearby fallout of spot vents (Venturi et al., 2016). Furthermore, an epidemiological study was recently conducted, but it only considered the emissions from electric generation facilities (Nuvolone et al., 2019).

In this study, a series of field survey campaigns were conducted in the Mt. Amiata region, to identify, sample and characterise natural and archaeo-industrial spot vents present in the area, from a chemical and an olfactometric point of view. This study aims to present the findings of the surveys conducted, reported not only in terms of chemical and odour concentrations, but also in terms of mass and odour emission rates estimated from airflow field measurements. The results were obtained by using innovative techniques, never used in the field of geological investigations, allowing a quantitative characterisation of the fluxes and not just the concentrations emitted. Moreover, a prior novelty of this study lies in the investigation of the odour potential of endogenous gases—the first study exploring dynamic olfactometry of this kind of emissions contributing to the efforts of the Olfactometric Laboratory of *Politecnico di Milano* in the field of characterising complex odour sources (Invernizzi et al., 2020; Invernizzi and Sironi, 2021; Lotesoriere et al., 2022; Tagliaferri et al., 2021, 2023a, 2023b). The measurements presented for this study represent important progress in the measurement of endogenous gas fluxes; despite the sampling for composition analysis being well-known and widespread in different geothermal areas, the aerodynamic gas flow measurement is rarely conducted and may provide useful information for the understanding and the quantification of background odour in geothermal areas. As a final note, to the best knowledge of the authors, the study represents the most recent and complete quantitative emission inventory of endogenous gases emitted by spot vents in the Mt. Amiata area.

2. Materials and methods

2.1. Sources localisation

Different exploration and measurement campaigns were conducted based on the available literature, technical reports and direct dialogue with the local population, which lasted for >2 years (January 2020–October 2022).

After the field campaigns, approximately 50 emissions were discovered: many of them, anyway, were quite small and marginal in terms of mass flows emitted. In this study, the most important, in terms of emission, were considered.

Fig. 1 reports the investigation area, with the localisation of the considered spot vents, and Table 1 summarises the localisation and the emission kind and the origin of each source. In SM (Figs. SM1 to SM15) a photograph of every source has been provided.

2.2. Gaseous flowrate measurements

As shown in Table 1 and Figs. SM1–SM15, the typed of spot vents may vary greatly, in terms of shape and emitted gas flow. A few of them (Acquapassante 1 ex SMI and Ermeta 1 ex SMI) were old mine ventilation spots, which were essentially constituted by chimneys. Mine exhaust ducts, connected to mines gates, often have horizontal tubes, reflecting similar examples. In these cases, the quantitative measurement of flue-gas flow rate was nearly trivial, because of the presence of a well-defined emission duct. The emitted gas velocity was measured via Pitot tube coupled with a differential pressure sensor (Testo 420 or MRU Optima 7 Biogas, depending on the measurement range). The exit velocity of the gas, v, was calculated, via the Bernoulli principle, as presented in Eq. (1).

$$v = K\sqrt{\frac{2 \bullet \Delta P}{\rho_{gas}}} \tag{1}$$

where K is the empirical factor specific to the Pitot tube (in this case equal to 1), ΔP [Pa] is the differential pressure measured with the Pitot tube, ρ_{gas} [kg/m^3] is the emitted gas density, obtained by the measured gas composition (see Section 2.3).

In some cases (i.e. The Hole and Anteie 1), in order to funnel the gaseous flow, and have a more precise diameter to be associated with the exit velocity, a tube was installed and sealed between the proper emission point and the measurement point. In the case, of the Zancona boiling pond (Fig. SM15), a floating capping was used to channel the entire bubble stream (Rogie et al., 2000).

In the cases described thus far, the molar emitted gas flow, $\dot{n}$ [mol/s], was calculated via Eq. (2):

$$\dot{n} = \frac{v \bullet \left(\frac{\pi D^2}{4}\right) \bullet P}{R \bullet T} \tag{2}$$

where D [m] is the measurement duct diameter, P [Pa] is the atmospheric pressure, R [J/mol•K] is the gas constant, and T [K] is the emitted gas temperature.

The most challenging aspect of this study was estimating the emitted flow from ground holes or the mine entrances. These sources often spread over several metres of uneven surfaces, posing the risk of falling

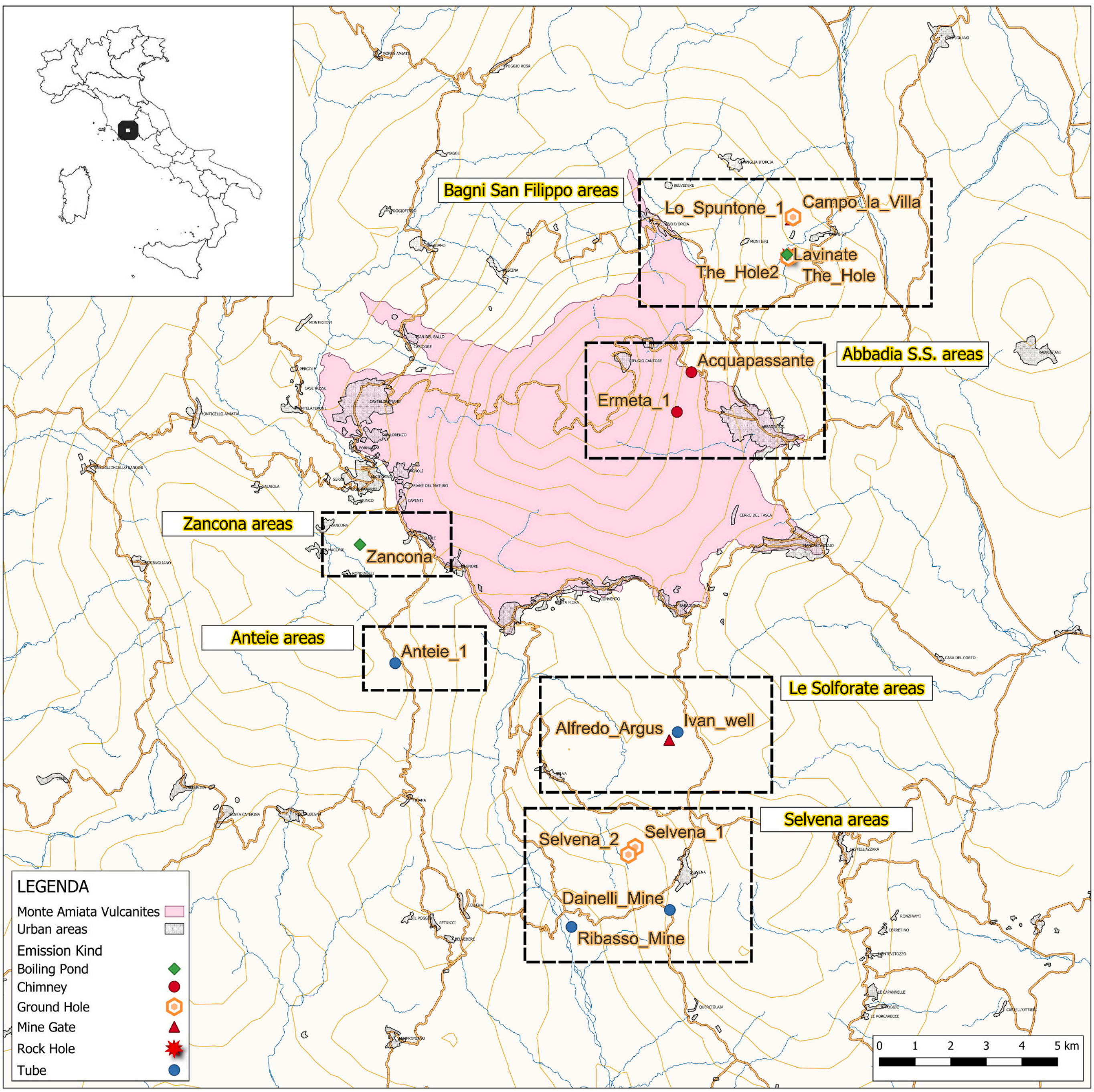

Fig. 1. Investigated area and localisation of spot vents.

Table 1
Localisation and kind of the most important identified spot gaseous emissions in Mt. Amiata.

Emission name	Emission kind	Origin	Lat [°]	Long [°]
Acquapassante 1 ex SMI	Chimney	Human	42.89420	11.65199
Ribasso Mine	Tube	Human	42.75520	11.60491
Dainelli Mine	Tube	Human	42.75870	11.63881
The Hole	Rock hole	Natural	42.92270	11.68660
The Hole 2	Ground hole	Natural	42.92240	11.68660
Ivan well	Tube	Human	42.80350	11.64340
Ermeta 1 ex SMI	Chimney	Human	42.88430	11.64660
Alfredo Argus well (former GM1)	Mine gate	Human	42.80160	11.64040
Anteie 1 (Anteie tunnel)	Tube	Human	42.82310	11.54720
Boiling pond Lavinate	Boiling pond	Natural	42.92310	11.68610
Lo Spuntone 1	Ground hole/ mine gate	Human	42.93190	11.68780
Campo la Villa	Ground hole	Natural	42.93250	11.68860
Selvena 1	Ground hole	Natural	42.77480	11.62760
Selvena 2	Ground hole	Natural	42.77300	11.62520
Zancona	Boiling pond	Natural	42.85327	11.53633

into hazardous dangerous anoxic conditions, and no established and standardised methodology was available. The innovative solution devised for measuring the gas flow in such situations involved the use of a balometer, usually used for indoor ventilation systems, which was revamped to measure endogenous gas flow. The Testo 420 balometer consisted of a flexible hood, with an integrated volume flow straightener, coupled with a multi-point cross Pitot. The hood conveyed gas to the straightener and the flow was sent to a known-area gas flow velocity matrix where velocity was measured via Eq. (1) (with a $K = 0.82$). To accommodate the large emission area of some sources, the balometer, grafted onto a mobile support framework, was often equipped with an additional plastic towel, up to 100 m^2, to maximise the capture of secondary flows.

Fig. 2 gives application examples of flow measurement systems developed and used in the field. The kind of flow measurement is summarised as follows:

- Balometer (The Hole 2, Alfredo Argus well (former GM1), Boiling Pond Lavinate, Lo Spuntone 1, Campo la Villa, Selvena 1 and Selvena 2);
- Floating capping (Zancona);
- Pitot tube without additional tube (Acquapassante 1 ex SMI, Ribasso Mine, Dainelli mine, Ivan well and Ermeta 1 ex SMI);
- Pitot tube with additional tube (The Hole and Anteie 1 [Anteie tunnel]).

2.3. Chemical analysis

Gaseous samples were collected using glass gas sampling pipettes, sealed with PTFE valves and hydraulic guards. Gas composition was

Fig. 2. Examples of measurements conducted in different sites: A: via balometer (The Hole 2, Alfredo Argus well (former GM1), Boiling Pond Lavinate, Lo Spuntone 1, Campo la Villa, Selvena 1, Selvena 2); B: via floating capping (Zancona); C: Pitot tube without additional tube (Acquapassante 1 ex SMI, Ribasso Mine, Dainelli mine, Ivan well, Ermeta 1 ex SMI); D: Pitot tube with additional tube (The Hole, Anteie 1 [Anteie tunnel]).

measured using gas chromatographic methods at Enel Green Power Laboratory of Larderello. An AGILENT model 7890B gas chromatograph customised for gas sampling and injection and equipped with 2 channels was employed for the analysis. The first channel used a HayeSep R packed column (1.8 m) connected to a Molsieve 13× packed column (3 m) with Helium as a carrier gas, connected to a TCD (Thermal Conductivity Detector) allowing the determination of carbon dioxide (CO_2), methane (CH_4), hydrogen sulphide (H_2S), nitrogen (N_2), and oxygen (O_2). The second channel employed a Packed Molsieve 13× column (3 m) with nitrogen as a carrier gas, connected to another TCD detector, for hydrogen (H_2) analysis. The separation of various components was obtained using a customised thermal cycle in the oven. For H_2S concentrations below 1000 ppm_v, a second AGILENT model 7890B gas chromatograph, equipped with a CP-SilicaPLOT capillary column (30 m) and helium as a carrier gas, connected to a TCD detector, was used. Based on the chemical concentrations, expressed in volume percentage, $\%_{v/v}$, x_i, the molar gaseous flow rate, $\dot{n}$ [mol/s], and the molar mass for each chemical compound PM_i [g/mol], it was possible to estimate the mass emission rate, ER_i [g/s], for each chemical investigated for each source considered using the following equation:

$$ER_i = \dot{n} \bullet x_i \bullet PM_i \tag{3}$$

2.4. Dynamic olfactometry

Dynamic olfactometry, standardised by method EN13725:2022 (CEN, 2022), is the preferred method to measure odour concentration, C_{od}, expressed in European ou_E/m^3. This method utilises a dilution scheme and relays on human noses as detectors. Sampling involved withdrawing a portion of the emitted gaseous flow inside a plastic bag (i.e. Nalophan®) by lung-method pumps, followed by analysis with an olfactometer and at least 4 human panels, within 30 hs of sampling. The panels are selected based on their sensitivity to the standardised reference material, n-butanol and are positioned around the olfactometer, functioning as a controlled dilutor. Initially, the analysis, the sample is highly diluted with neutral air, to render the odour imperceptible at the panels' ports. The machine then gradually decreases the sample dilution ratio, until each panel detects an odour different from neutral air. Following several repetitions, and statistical elaboration of the detection threshold data, the odour concentration, in ou_E/m^3, can be assessed. Simply put, it represents the dilution ratio needed to render the odour imperceptible to 50 % of the panel members; if 1000 ou_E/m^3 are measured, it means that a dilution with a ratio of at least 1:1000 with neutral air is needed to eliminate the odour for the majority of the panels.

Dynamic olfactometry analyses presented in this study were held in Olfactometric Laboratory, at the Chemical, Materials and Chemical Engineering Department 'Giulio Natta' of Politecnico di Milano University, using a 4-port TO8 Olfasense olfactometer.

After measuring C_{od} [ou_E/m^3], it was possible to estimate the odour emission rate, *OER*, which is essentially the equivalent of the mass emission rate, but representative of odour potential. According to the standard EN13725:2022, due to the environmental condition of the analysis in the olfactometric chamber, the flowrate, Q_{olf} should be expressed in m^3/h, normalized at 20 °C and 101,325 Pa. By this, OER [ou_E/s] can be calculated with Eq. 4:

$$OER = C_{od} \bullet Q_{olf} \tag{4}$$

3. Results

For all the spot vents listed in Table 1, a chemical and olfactometric analysis was conducted. The list of detected concentrations are listed in Table 2.

As observed, carbon dioxide was the most prevalent gas. The second most prevalent gases varied depending on the site, with methane or nitrogen, usually detected in the order of a few $\%_{v/v}$. Following the descending order, oxygen had an average concentration of 0.5$\%_{v/v}$, while hydrogen, often below the sensitivity of the analytical technique, showed a mean value approximately 0.1$\%_{v/v}$.

An exception was found with 'Acquapassante 1 ex SMI' where, higher concentrations of nitrogen and oxygen were present compared with other sources. Owing to the nature of this source, as a ventilation channel, it could not be ruled out that false air was introduced into the aeraulic system from the network of channels in the old mine (Abbadia San Salvatore). This hypothesis was strengthened by a N_2/O_2 ratio near 4.

In terms of odour concentration and odorous gas (H_2S) the orders of magnitude of the different spot vents were comparable, where the odour concentration 1,000,000–10,000,000 ou_E/m^3, and the hydrogen sulphide concentration was 1,000–10,000 ppm_v. The exception was the 'Dainelli mine' source, which showed a limited odorous load.

The obtained chemical data were comparable with previous studies available in the literature (Collettini et al., 2008; Frondini et al., 2009), CO_2 was always the most highly concentrated compound (>80$\%_{v/v}$), and H_2S was generally at 10^3 ppm_v. However, Tassi et al. (2009) detected lower concentration values (generally <10^3 ppm_v). As observed in the literature (Duchi et al., 1987; Rogie et al., 2000), Selvena spots showed the highest hydrogen sulphide concentrations, with of 10^4 ppm_v. Table 3 presents the measured molar fluxes, $\dot{n}$, and the emission rates of H_2S, CO_2 and CH_4 and the OER for every source mentioned here.

From Table 3, it is easy to understand that different sources had different potential impacts. Indeed, despite an overall similarity in chemicals and odour concentrations, the emitted gaseous flow varied among different sites. The main spot vents identified were the 'Alfredo Argus well (former GM1)', 'Ribasso mine' and 'Ivan well' sites,

Table 2
Gaseous concentrations, ±standard deviations, detected in Mt. Amiata spot vents.

Emission name	H_2 [$\%_{v/v}$]	O_2 [$\%_{v/v}$]	N_2 [$\%_{v/v}$]	CH_4 [$\%_{v/v}$]	CO_2 [$\%_{v/v}$]	H_2S [ppm_v]	C_{od} [ou_E/m^3]
Acquapassante 1 ex SMI	0.02 ± 0.01	8.6 ± 2.6	31.5 ± 6.1	0.8 ± 0.1	58.9 ± 2.1	1847 ± 200	8,000,000 ± 1,600,000
Ribasso Mine	<0.01	0.2 ± 0.1	1.8 ± 0.4	5.5 ± 0.5	92 ± 5	4443 ± 645	4,100,000 ± 820,000
Dainelli Mine	<0.01	0.8 ± 0.3	7.6 ± 1.5	5.4 ± 0.4	86.3 ± 3.6	93 ± 12	1,400,00 ± 280,00
The Hole	<0.01	0.2 ± 0.1	2.9 ± 0.7	1.6 ± 0.1	95.3 ± 3.3	1039 ± 102	620,000 ± 124,000
The Hole 2	<0.01	0.8 ± 0.2	5.4 ± 1.2	1.3 ± 0.1	92.4 ± 5.3	743 ± 89	1,200,000 ± 240,000
Ivan well	0.92 ± 0.06	0.1 ± 0.1	1.5 ± 0.3	4.4 ± 0.4	92.5 ± 5.5	4772 ± 657	2,600,000 ± 520,000
Ermeta 1 ex SMI	0.03 ± 0.01	0.3 ± 0.1	2.1 ± 0.5	4.2 ± 0.2	93.2 ± 4.1	1788 ± 205	2,200,000 ± 440,000
Alfredo Argus well (former GM1)	0.14 ± 0.01	0.1 ± 0.1	1.3 ± 0.3	4.4 ± 0.4	93.6 ± 3.2	4549 ± 494	2,400,000 ± 480,000
Anteie 1 (Anteie tunnel)	<0.01	0.1 ± 0.1	4.7 ± 1.1	7.5 ± 0.5	87.2 ± 4.4	4173 ± 554	1,400,000 ± 280,000
Boiling pond Lavinate	<0.01	<0.01	2 ± 0.5	1.8 ± 0.1	96.1 ± 2.8	1130 ± 150	1,300,000 ± 260,000
Lo Spuntone 1	<0.01	0.6 ± 0.2	4.6 ± 1	1.7 ± 0.1	92.9 ± 5	1434 ± 169	3,000,000 ± 600,000
Campo la Villa	<0.01	2 ± 0.6	10.2 ± 3.1	1.7 ± 0.1	85.9 ± 2.6	1204 ± 129	1,500,000 ± 300,000
Selvena 1	0.24 ± 0.01	1.4 ± 0.4	6.8 ± 2	5 ± 0.3	85.7 ± 4.9	8242 ± 864	4,400,000 ± 880,000
Selvena 2	0.13 ± 0.01	0.3 ± 0.1	2.4 ± 0.7	5.7 ± 0.5	90.7 ± 6	8074 ± 935	5,300,000 ± 1,000,000
Zancona	<0.01	0.3 ± 0.1	2.7 ± 0.8	12.9 ± 0.7	84.1 ± 5.2	907 ± 132	1,800,000 ± 360,000

Table 3
Gaseous emission rates, ±standard deviations, estimated in Mt. Amiata spot vents.

Emission name	ṅ [mol/h]	ER H_2S [kg/h]	ER CO_2 [kg/h]	ER CH_4 [kg/h]	OER [ou_E/s]
Acquapassante 1 ex SMI	4700 ± 700	0.3 ± 0.1	122 ± 18	0.6 ± 0.1	250,000 ± 62,500
Ribasso Mine	100,000 ± 15,000	15 ± 2.7	4051 ± 613	87.4 ± 14.1	2,700,000 ± 675,000
Dainelli Mine	4900 ± 1000	0.02 ± 0.003	186 ± 28	4.2 ± 0.7	4600 ± 1150
The Hole	1100 ± 200	0.04 ± 0.007	46 ± 7	0.3 ± 0.04	4700 ± 1175
The Hole 2	16,000 ± 2400	0.4 ± 0.07	650 ± 98	3.4 ± 0.5	120,000 ± 30,000
Ivan well	58,000 ± 9000	9.4 ± 1.7	2360 ± 357	41.2 ± 6.7	1000,000 ± 250,000
Ermeta 1 ex SMI	32,000 ± 5000	1.9 ± 0.4	1312 ± 199	21.5 ± 3.5	460,000 ± 115,000
Alfredo Argus well (former GM1)	120,000 ± 18,000	18.6 ± 3.3	4944 ± 748	85 ± 13.7	1,900,000 ± 475,000
Anteie 1 (Anteie tunnel)	4000 ± 600	0.6 ± 0.1	154 ± 23	4.8 ± 0.8	38,000 ± 9500
Boiling pond Lavinate	12,000 ± 1800	0.5 ± 0.1	507 ± 77	3.4 ± 0.5	100,000 ± 25,000
Lo Spuntone 1	3800 ± 1000	0.2 ± 0.03	155 ± 24	1.1 ± 0.2	76,000 ± 19,000
Campo la Villa	6900 ± 1000	0.3 ± 0.1	261 ± 39	1.8 ± 0.3	69,000 ± 17,250
Selvena 1	17,000 ± 2600	4.8 ± 0.9	641 ± 97	13.6 ± 2.2	500,000 ± 125,000
Selvena 2	9500 ± 1000	2.6 ± 0.5	379 ± 57	8.7 ± 1.4	340,000 ± 85,000
Zancona	500 ± 100	0.02 ± 0.003	18 ± 3	1 ± 0.2	6000 ± 1500

appearing to contribute to >70 % of the overall emission rate of Amiata spot vents. Fig. 3 shows pie charts of the contributions of each emission. Notably, to the best of our knowledge, these emission sites were never reported in the scientific literature in terms of gaseous emission.

Compared with sources quantified in previous literature, the 'Selvena' site showed a higher CO_2 emission in this study than previously estimated 0.7 t/h (Rogie et al., 2000), likely due to considering two nearby spot vents instead of just one.

For 'Acquapassante 1 ex SMI' and 'Ermeta 1 ex SMI', our results in terms of CO_2 aligned well with a previous study (Nisi et al., 2014). However, estimates for other gases, were approximately double. In general, for CH_4 and H_2S, concentrations were higher in our study compared with the cited one.

4. Discussion

The odour concentration values found in this study which are unusually high compared with typical olfactometric studies: with levels exceeding some regulatory standards, for industrial emission sources: 200–1000 ou_E/m^3 (Bokowa et al., 2021). These emissions are usually located on the ground, or at a very low height above ground, without a particular momentum or buoyant plume rise, leading to a very scarce atmospheric dilution. Therefore, this emission scenario may be one of the causes of the presence of the typical background odour of geothermal areas.

In terms of chemical composition, these emissions showed a large presence of carbon dioxide, with smaller amounts of methane and hydrogen sulphide. On a global scale, the investigation of gaseous geothermal spot vents could provide important information about the resulting GWP gaseous emission inventory and the sulphur budget. Moreover, on a local scale, this may have a huge impact in terms of risk in approaching these gas sources. In the field campaigns, an ABEK mask was always needed and, in two cases, namely 'Alfredo Argus well (former GM1)' and 'Selvena 1', it was not enough; due to the scarce presence of oxygen in the nearby, self-contained breathing apparatus was used. The danger of the investigated places was very clear even in the huge presence of dead wild animals, as shown in Figs. SM17–SM18.

The approach to these emissions without particular personal protective equipment may be very dangerous. Note that the industrial hygiene short term limit value, TLV-STEL, of H_2S is 5 ppm (ACGIH, n.d) and, Immediately Dangerous to Life and Health level, ILDH is 100 ppm_v (CDC, 2019), several orders of magnitude below the concentrations detected at the investigated sources.

Table 4 presents the total inventory of the investigated spot vent sources. GWP was added, according to various time horizons (Forster et al., 2007).

Regarding the H_2S emission scenario, the total amount is very substantial, considering that a 20 MW geothermal plant may emit, on average, 14 kg/h of hydrogen sulphide (ARPAT, 2022), the estimated emission rate from natural and archaeo-industrial spot vents can be considered equal to approximately 4 power plants. This behaviour can be linked to the presence of the abatement system for mercury and hydrogen sulphide, AMIS, in geothermal power plants; this system allows an overall reduction of plant emission in the range of 95 %–99 % for mercury and 75 %–85 % for H_2S (Baldacci et al., 2005).

In terms of carbon dioxide, a recent study focused on deep gases diffused through the soil in Mt. Amiata region estimated the deep CO_2 emission scenario of Amiata at 572 t/h (Sbrana et al., 2021). For this datum, it appears that spot vents are an important contribution to endogenous CO_2 inventory, although they represent a minority compared with diffuse emissions from the soil (~3 %).

Notably, the overall scenario presented here may show an *underestimation*; as mentioned above in Section 2.1, only the most important sources are considered, and the presence of further unknown spot vents could not be excluded. In addition, the capping used in the field campaigns, was always settled to the best of the possibility and subject to the safety criteria to be adopted for working in these areas. A photograph of the sampling phase at 'Alfredo Argus well (former GM1)' is reported in Fig. SM16. The capping of the entire emissive area, and the channelling to the balometer, was, in this case, made with a 100 m^2 plastic towel, closed by an edging using filler sand. The operation was carried out trying to seal the entire emission in the best possible way, but never being able to achieve perfection. Fig. 4 reports the measured flow rate over the time, while sealing operations were conducted; the continuously rising value vividly depicts that these measurements lead to flux values that can asymptotically approach the true value but can never reach it due to technical difficulties.

5. Conclusions

This study aimed to quantitatively measure the spot gaseous emissions present in an area of geothermal significance. To obtain quantitative data, an adaptive approach was necessary to obtain concentration data and emitted flux data. In particular, the innovative use of the balometer here was a turning point in the measurement of the fluxes of these sources. This case-study application could be an example for further research activity in the field. This adaptive approach, to the measurement of gas fluxes, made the development of this study possible, facing the case-study of Mt. Amiata gaseous spots. To the best of our knowledge, this is the most recent and complete collection of gaseous endogenous spot fluxes in this geothermal area.

Moreover, this first olfactometric campaign on natural gaseous geothermal spot vents showed that they may reach millions of ou_E/m^3 of odour concentration. These levels are rarely reached even in industrial

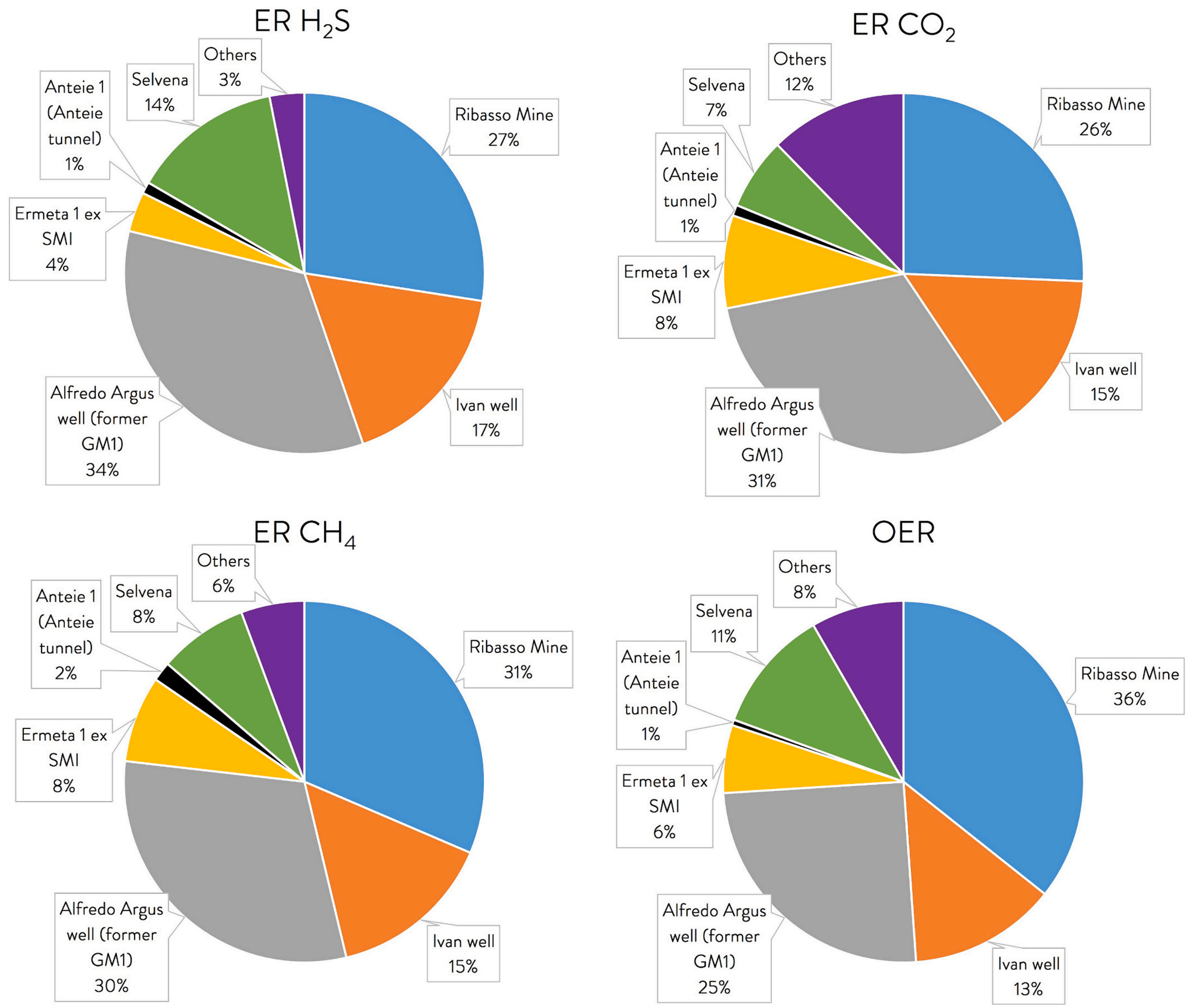

Fig. 3. Emission rate specific contributions.

Table 4
Overall emission inventory from spot vent investigated in Mt. Amiata region.

Flux	Mt. Amiata inventory
H_2S [kg/h]	55
CO_2 [t/h]	16
CH_4 [kg/h]	280
OER [ou_E/s]	$7.6 \cdot 10^6$
CO_2 eq – GWP_{20} [t/h]	36
CO_2 eq – GWP_{100} [t/h]	23

sites, leading to their potential responsibility in the presence of typical background odours of geothermal areas.

A call for dissemination goes out to all the researchers in the field and to local institutions, to foster widespread knowledge of their own territory and its risks, particularly given the concentrations of H_2S observed, which are almost always higher than ILDH levels.

Future developments of this study might focus on the extension of this study to other geothermal areas (i.e. Larderello and Campi Flegrei) and continuous monitoring, to assess the evolution of these spot vent emissions. Alternatively, a trial of diffuse emission estimation for H_2S, like the one conducted for CO_2 (Sbrana et al., 2021) can be considered. This study can be further improved by exploring the input of these emission data in an atmospheric dispersion model, to estimate the fallout at areas of human settlement or even passage (i.e. roads), and to estimate the specific ambient air contributions deriving from geothermal plants and natural spot vents.

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CRediT authorship contribution statement

Marzio Invernizzi: Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Giacomo Domenico Scolieri:** Methodology, Investigation, Data curation. **Francesca Tagliaferri:** Writing – review & editing, Methodology, Investigation, Data curation. **Marcello Cinci:** Writing – original draft, Validation, Investigation, Conceptualization. **Alessandro Lenzi:**

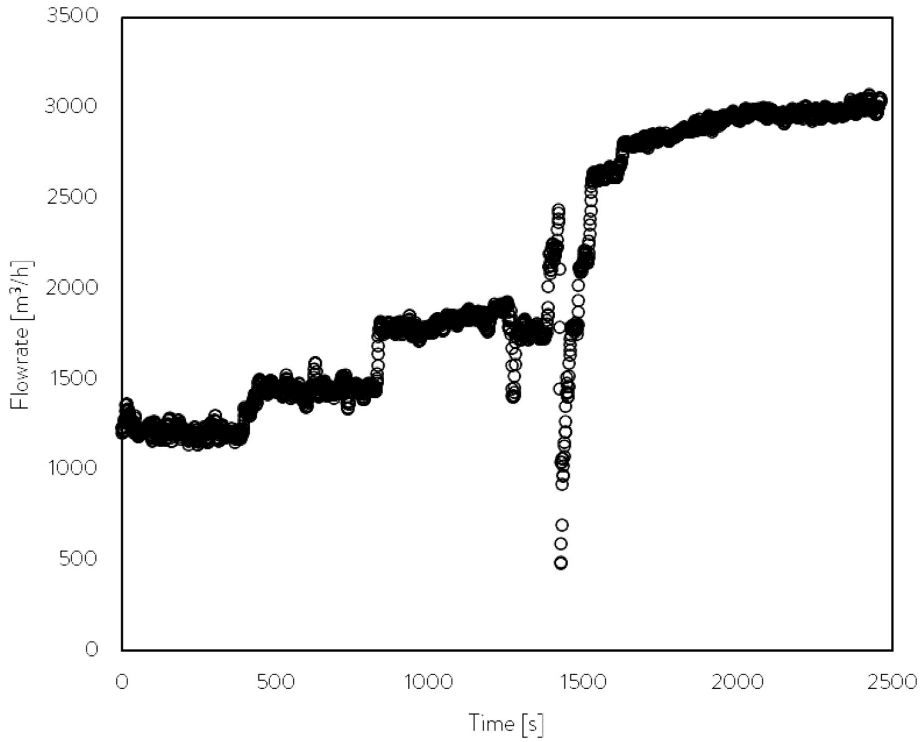

Fig. 4. 'Alfredo Argus well (former GM1)' gas flowrate measurement with the proceeding of the sealing operations.

Investigation. **Selena Sironi:** Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare no competing interest.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.172607.

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