



A new approach for the measurement of gaseous elemental mercury (GEM) and H₂S in air from anthropogenic and natural sources: Examples from Mt. Amiata (Siena, Central Italy) and Solfatara Crater (Campi Flegrei, Southern Italy)



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ABSTRACT

Real-time measurements of GEM and H₂S discharged from natural and anthropogenic sources are a valuable tool to investigate the dispersion dynamics of these contaminants in air. In this study, a new approach to measure GEM and H₂S concentrations in air, carried out by coupling a portable Zeeman atomic absorption spectrometer with high frequency modulation of light polarization (Lumex RA-915M) and a pulsed fluorescence gas analyzer (Thermo Scientific Model 450i), was applied to two distinct areas: (i) in the surroundings of Piancastagnaio (Siena, Central Italy), located in the eastern flanks of Mt. Amiata (a 200,000 years old volcano), where three geothermal plants are operating and whose exhaust gases are dispersed in the atmosphere after passing through the turbines and an abatement system to mitigate the environmental impact on air, and (ii) at Solfatara Crater (Campi Flegrei, Southern Italy), a volcanic apparatus characterized by intense hydrothermal activity. In 2014, seven GEM and H₂S surveys were carried out in the two areas along pre-defined pathways performed by car at both the study sites. The lowest and highest recorded GEM and H₂S concentrations at Piancastagnaio were up to 194 and 77 ng/m³, respectively, whilst at Solfatara Crater were up to 690 and 3392 µg/m³, respectively. Although the GEM concentrations at Piancastagnaio were lower than the limit value recommended by local regulations for outdoor environment (300 ng/m³), they were almost one order of magnitude higher than the GEM background both in Tuscany (~3.5 ng/m³) and Mt. Amiata (3–5 ng/m³), suggesting that the main source of GEM was likely related to the geothermal plants. At Solfatara Crater, the highest GEM values were recognized in proximity of the main fumarolic gas discharges. As far as the H₂S concentrations are concerned, the guideline value of 150 µg/m³, recommended by WHO (2000), was frequently overcome in the study areas.

Dot (in the surroundings of Piancastagnaio) and contour (at Solfatara Crater) maps for GEM and H₂S concentrations built for each survey highlighted the important effects played by the meteorological parameters, the latter being measured by a Davis® Vantage Vue weather station. In particular, the GEM and H₂S plumes were strongly affected by the wind speed and direction that were able to modify the dispersion of the two parameters in air in a matter of hours, indicating that the proposed analytical approach is able to produce a more realistic picture of the distribution of these air pollutants than that provided by using passive traps.

Finally, the H₂S/GEM ratio, calculated by normalizing the measured GEM and H₂S concentrations to their highest values (nH₂S/GEM), was used as a good proxy for the chemical-physical processes that these two gas species can suffer once emitted in the air. In particular, H₂S resulted to be more affected by secondary processes than GEM, possibly related to photochemical oxidation reactions.

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1. Introduction

Gaseous elemental mercury (hereafter GEM or Hg⁰) and H₂S emitted from a number of different anthropogenic and natural sources

(e.g. Mason et al., 1994; WHO, 2000; D'Alessandro et al., 2013) have a significant impact on air quality due to their negative effects on the environment and human health (WHO, 2007). The development of specific instrumentations and analytical techniques aimed to provide reliable measurements of the concentrations of these gases in air is a necessary prerequisite for establishing their spatial distribution and localizing their emitting sources. GEM measurements in air are commonly analyzed by thermal desorption and quantification via cold vapor atomic fluorescence spectrometry (CVAFS; EPA, 1999) after trapping Hg⁰ (and possibly GOM: gaseous oxidized mercury, e.g. Gustin and Jaffe, 2010) on an Au-coated substrate operating as a passive collector, i.e. no pumping systems are applied (Ferrara et al., 1994; Ebinghaus et al., 1999; Nakagawa, 1999; Bagnato et al., 2007). More recently, passive samplers with better performances have been developed (e.g. Zhang et al., 2012; Peterson et al., 2012; Pirrone et al., 2013 and references therein). Lately, a number of studies (e.g. Higuera et al., 2013; Higuera et al., 2014 and references therein) used GEM data measured with Lumex® instruments to investigate the environmental impact of this air pollutant in different anthropogenic and natural systems.

Hydrogen sulfide in air is collected by passive/diffusive traps, such as the Radiello® samplers (Fondazione Maugeri, 2007; D'Alessandro et al., 2009, 2013). Other sampling methods use (i) molecular diffusion passive samplers (Campos et al., 2010), (ii) treated black and white photographic paper (Horwell et al., 2005), and (iii) copper passive samplers (Votaggio and Spadoni, 2009). According to these methods, GEM and H₂S concentrations are calculated on the basis of empirical or theoretical relationships between the amount of the trapped analyte and environmental parameters, such as air temperature and humidity, wind direction and speed (Brown, 2000; Delgado-Saborit and Esteve-Cano, 2006). The concentrations of GEM and H₂S determined with the passive traps are thus time-averaged (e.g. days or weeks) integrated values, since this methodological approach cannot provide an instantaneous or continuous measurement of the air quality, preventing the recognition of the emitting source.

In this study, GEM and H₂S concentrations in air were measured in situ with portable instruments (Lumex® RA-915M and Thermo® 450i, respectively) operating at high-frequency data acquisition. Measurements were carried out in two areas that are known to be characterized by anomalous GEM and H₂S emissions: (i) Mt. Amiata (Siena, Central Italy), an extinct volcanic system characterized by the occurrence of a world-class, now decommissioned, Hg-mining area and five active geothermal plants, and (ii) Solfatara Crater, a hydrothermally altered tuff-cone located in the densely populated town of Pozzuoli (Southern Italy).

The main aims of this work were those to demonstrate that our approach i) is a valid and reliable alternative to the classical methods used to estimate air quality in contaminated areas, and ii) allows to build thematic iso-concentration maps of the two different pollutants measured contemporaneously in real-time, thus providing new insights into their behavior once released in the air.

2. Background and guideline values of GEM and H₂S in the atmosphere

Mercury is present in air mainly in its elemental form (GEM ~98%; Slemr et al., 1985; Schroeder et al., 1991). The background air concentration in unpolluted areas is ~2 ng/m³ (USEPA, 1997; Ebinghaus et al., 2002), although locally higher values were recorded worldwide, e.g. ~3.5 ng/m³ in Tuscany (Central Italy) (Bargagli, 1990). GEM residence time in air is estimated to be between 1 and 2 years (Lindqvist and Rodhe, 1985) and down to 0.6 years (Weiss-Penzias et al., 2003) due to its relatively low solubility and chemical inertness (Schroeder and Munthe, 1998). It is then likely oxidized to Hg²⁺ by atomic bromine and bromine containing radicals, e.g. Obrist et al. (2011).

Mercury is highly toxic to human health, since exposure to elevated concentrations can affect nervous, digestive and immune systems, lungs

and kidneys, eventually leading to death (WHO, 2007). The guideline value (1-year time-weighted average, TWA) for GEM in ambient air is 1000 ng/m³ (WHO, 2000), whereas EPA (2001) suggests three action levels: 1) ≥10,000 ng/m³ (real-time measurements), residents must immediately be relocated; 2) from 1000 ng/m³ to 10,000 ng/m³ (real-time measurements), relocation must be scheduled as soon as possible; and 3) ≤1000 ng/m³ (8-h TWA), no actions are necessary.

Hydrogen sulfide is an irritating and suffocating weakly acidic gas, whose unpleasant smell can be detected at concentrations as low as 7 µg/m³ (Thorsteinsson et al., 2013 and references therein). H₂S residence time in atmosphere is 1–5 days (Hobbs, 2000), although it can be up to 42 days in wintertime (WHO, 2003). Background concentrations of H₂S in ambient air range from 0.14 to 0.40 µg/m³ and its guideline value (24-h TWA) is 150 µg/m³ (WHO, 2000, 2003).

GEM released from volcanic and hydrothermal systems accounts for ~2% of the total amount discharged from natural sources (Varekamp and Buseck, 1986; Pyle and Mather, 2003; Bagnato et al., 2007; Pirrone et al., 2010). Hydrogen sulfide after H₂O and CO₂ is the most abundant gas species released from hydro/geothermal gases (D'Alessandro et al., 2013). Owing to the relatively high GEM and H₂S concentrations in geothermal fluids (e.g. Bayer et al., 2013; Peralta et al., 2013), since 2002 most geothermal plants in Italy have adopted the AMIS® abatement system to mitigate the environmental impact on air of their exhausted vapors (Baldacci, 2004; Regione Toscana, 2010). This system, patented by ENEL (National Agency for Electricity), allows the GEM removal by using either selenium or active carbon permeated by sulfur. Hydrogen sulfide is removed by catalytic oxidation to form SO₂, which is almost completely scrubbed by the geothermal condensate recovered after the steam has passed through the turbines to produce electricity (Baldacci, 2004).

3. GEM and H₂S sources in the studied areas

3.1. Mt. Amiata Volcano

Volcanic activity at Mt. Amiata, the most recent (~0.3 Ma old; Laurenzi et al., 2015) and largest volcanic apparatus (~90 km²) of the Tuscan Magmatic Province (Conticelli et al., 2004, 2015), is related to the Pliocene emplacement of a magmatic body at 6–7 km depth (Pasquarè et al., 1983; Gianelli et al., 1988; Marroni et al., 2015). This system is part of the circum-Mediterranean Hg belt, it hosts the 4th largest Hg-producing district in the world and is known since the Etruscan times, although the industrial exploitation mostly occurred in the last century (e.g. Rimondi et al., 2012; Vaselli et al., 2013). The hydrothermal system, feeding CO₂-rich cold and thermal emissions mostly located in the eastern and southeastern sectors of the volcanic apparatus (e.g. Frondini et al., 2009; Tassi et al., 2009; Nisi et al., 2014), consists of two bi-phase fluid reservoirs, located at 500–1000 m and >3000 m depth, with a temperature of 200–230 °C and up to 350 °C, respectively (Calamai et al., 1970; Bertini et al., 1995). Close to Piancastagnaio (Fig. 1), three geothermal plants (PC3, PC4 and PC5) (Bacci et al., 2000) emit vapor plumes rich in CO₂, H₂S and GEM (Bravi and Basosi, 2014); however, most GEM and H₂S occurring in the exploited geothermal fluids are scrubbed (up to 95 and 75%, respectively) by AMIS (Baldacci, 2004; Baldacci et al., 2005). According to Bacci et al. (2000), the total GEM emission rates from the Mt. Amiata geothermal plants account for 3–4 g/h per MW electrical installed capacity, whereas those of H₂S are 7–8 kg/h. Preliminary surveys of GEM concentrations in air nearby the former Hg-mining area (Ferrara et al., 1998; Vaselli et al., 2013) reported values up to 1000 ng/m³, much higher than the limit imposed by the Tuscany Regional Decree 1447 (1998) (300 ng/m³ at 20 °C and 100 cm above the ground; Vaselli et al., 2013). To the best of our knowledge, no H₂S measurements in air were carried out in this area.

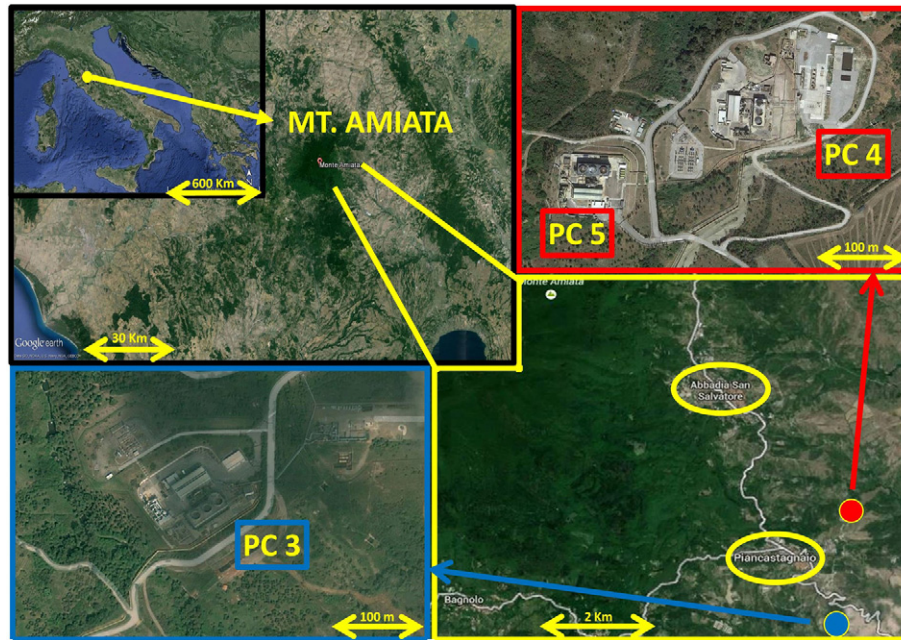


Fig. 1. Geographical location of Mt. Amiata and the PC3, PC4 and PC5 geothermal power plants near Piancastagnaio. The village of Abbadia San Salvatore is also reported.

3.2. Solfatara crater

Solfatara Crater, a ~4 ky old crater in the Campi Flegrei Caldera, is characterized by an intense fumarolic activity, which is mainly related to two fumarolic vents (Bocca Grande, BG, and Bocca Nuova, BN; Fig. 2), and an anomalously high diffuse soil CO₂ degassing from the bottom of the crater, especially in the NE and SE sectors (e.g. Chiodini et al., 2001; Tassi et al., 2013, 2015). The discharged fluids originate at depth from a hydrothermal reservoir receiving significant contributions of magmatic fluids. Their composition is dominated by H₂O and CO₂, followed by H₂S, N₂, H₂, CH₄, He, Ar and CO (Caliro et al., 2007, 2014). The hydrothermal emissions have a strong impact on air at a local scale. For example, H₂S concentrations in air at a close distance from the fumarolic vents typically exceed 210,000 µg/m³ (Aiuppa et al., 2013) and are significantly higher than the background values all

over the crater (Carapezza et al., 1984). GEM concentrations in the vapors discharged from Bocca Grande, the main fumarole of the crater, are up to 295 ng/m³, whereas the background value outside the fumarolic field is 18 ng/m³, ranging from 10 to 24 ng/m³ (Bagnato et al., 2009).

4. Materials and methods

4.1. Instruments for GEM and H₂S analysis

GEM and H₂S measurements were carried out using a Lumex® RA-915M and a Thermo® 450i, respectively. The Lumex® analyzer is a portable atomic absorption spectrometer with Zeeman effect with high frequency modulation of light polarization (ZAAS-HFMLP). The separation of the spectral lines (at λ = 254 nm) is operated by a permanent

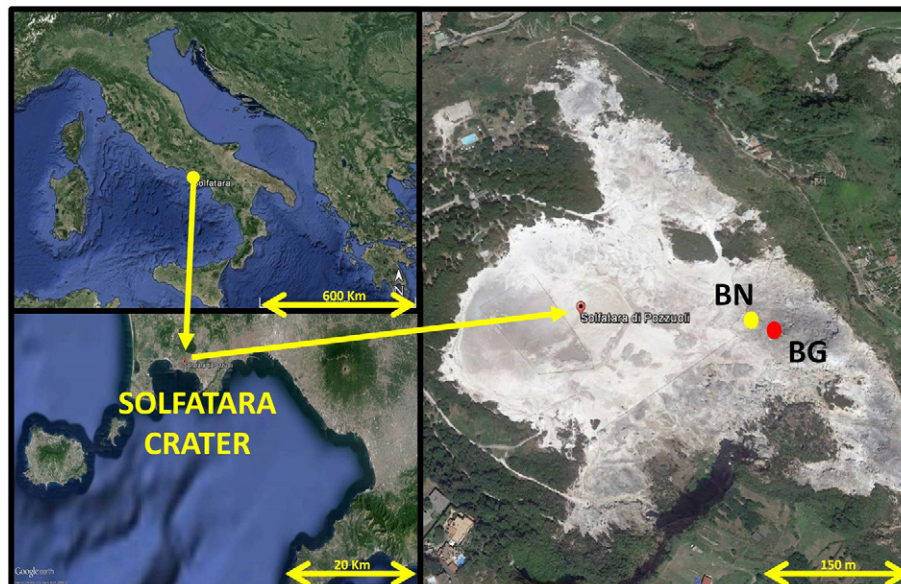


Fig. 2. Geographical location of Solfatara Crater in the Bay of Pozzuoli and of the two main fumarolic discharges: Bocca Grande (BG) and Bocca Nuova (BN).

external magnetic field, into which a source of radiation (Hg lamp) is placed (Sholupov and Ganeyev, 1995; Sholupov et al., 2004). The Zeeman background correction and a multipath analytical cell provide high selectivity and sensitivity (Sholupov et al., 2004; Vaselli et al., 2013). The instrument operates at a flow rate of 10 L/min, whereas its rechargeable battery allows up to 8 h of continuous measurements. The detection limit is 2 ng/m³ while the accuracy of the method is 20% from 2 to 50,000 ng/m³ (Sholupov and Ganeyev, 1995; Sholupov et al., 2004).

The Thermo® analyzer measures SO₂ and H₂S, the latter being detected after oxidation to SO₂ (Thermo Scientific, 2007; Thorsteinsson et al., 2013). The H₂S-SO₂ converter has an efficiency >80% (Thermo Scientific, 2012). The detector (photomultiplier tube, PMT) receives UV emission from SO₂ excited by pulsating UV light generated by a fluorescence chamber. During the H₂S-SO₂ conversion, the instrument measures the combined sulfur (CS) concentrations (SO₂ + H₂S), whereas bypassing the converter the analyzer measures SO₂. The difference between the two measurements (converted and no-converted H₂S) provides the H₂S concentration (Thermo Scientific, 2012). The operative flux of the instrument is set at 1 L/min. The duration of a single measurement is 1 s, although the instrument provides average concentrations calculated using data measured over a defined period (60 s). The detection limit is 1.4 µg/m³; the maximum measurable concentration is 14,000 µg/m³ with a precision of ± 1% (Thermo Scientific, 2012). An external power supply (a high capacity battery) is connected to the instrument through an AC/DC converter.

4.2. Field measurements

GEM and H₂S measurements were carried out along pathways within the study areas, following a strategy recently adopted to evaluate the spatial distribution of air contaminants in areas where natural (Bagnato et al., 2014; Rizzo et al., 2014) and/or anthropogenic (Vaselli et al., 2013; Olafsdottir et al., 2014a; Zazzeri et al., 2015) sources occur. In the present study, the pathways were selected by considering the location of the potential contaminant sources. The instruments were fixed on a car moving at an average speed ~6 km/h, avoiding any interferences with the exhaust gases. Consequently, the distance between two consecutive H₂S measurements was ~100 m, since the frequency of the measurement acquisition of Thermo® was of 1 min. GEM data measured during this time intervals (~58 measurements) were averaged and simultaneously coupled with those of H₂S. The pathways were digitalized using a portable GPS (Garmin® GPSMAP 62), whilst the meteorological parameters (air temperature and humidity, wind speed and direction) were measured by a Davis® Vantage Vue weather station that was deployed in a fixed position within the surveyed area.

4.3. Data processing

The spatial distribution of GEM and H₂S in air of the two contaminated sites was visualized by using two graphical representations: 1) dot-maps, where selected concentrations intervals were recognized and

plotted using circles filled with different colors; and 2) contour maps, which were constructed according to a classical Graphical Statistical Approach (GSA). The interpolation on the contour maps was carried out by using the kriging estimation method (ESRI® ArcGis 9.3), which is based on mandatory preliminary steps: (i) construction of an experimental variogram and (ii) selection of the best fitting mathematical model. Finally, the fitted models were cross-validated with the experimental data in order to check the performance of the kriging model.

5. Results

5.1. Mt. Amiata

In June 2014, 432 measurements were carried out in four days along a pathway running from the neighbourhoods of PC4 and PC5 geothermal plants to Abbadia San Salvatore (822 m a.s.l.), passing through Piancastagnaio (772 m a.s.l.) and the proximity of PC3 geothermal plant (Fig. 1). During the measurements, winds predominantly blew from S with a speed up to 15 m/s, whereas air temperature and humidity ranged from 15 to 21 °C and from 48 to 77%, respectively. The maximum GEM concentrations measured in the four surveys (from 51 to 194 ng/m³) did not exceed the limit value recommended by local regulations for outdoor environment (300 ng/m³) and were significantly lower than those reported by Ferrara et al. (1998) for this area (up to 1000 ng/m³). The minimum GEM concentrations (from 21 to 24 ng/m³) were almost one order of magnitude higher than the GEM background both in Tuscany (~3.5 ng/m³; Bargagli, 1990) and Mt. Amiata (3–5 ng/m³; Ferrara et al., 1998), indicating a widespread anomaly (Table 1), as already highlighted by Vaselli et al. (2013). The maximum H₂S concentrations (up to 690 µg/m³) exceeded the guideline value recommended by WHO (2000), whereas the lowest ones (from 0.06 to 0.61 µg/m³) were consistent with clean air values (WHO, 2003), i.e. more than one order of magnitude lower than the limit of odor nuisance (7 µg/m³). The GEM and H₂S standard deviations during

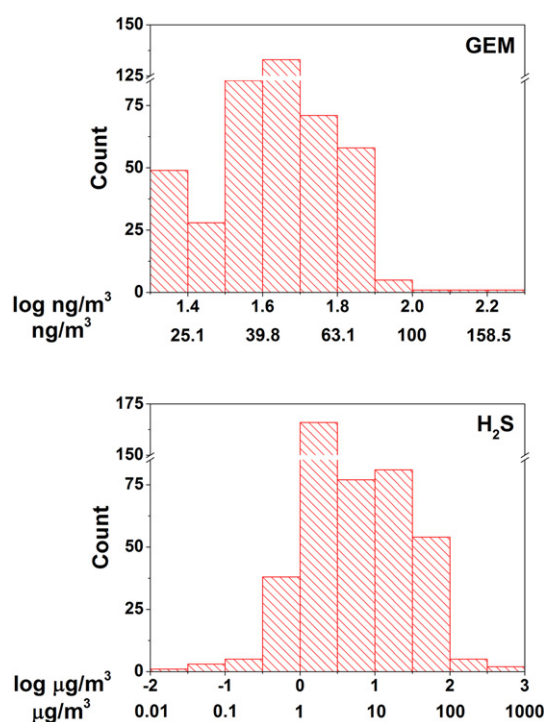


Fig. 3. Histograms of GEM (in log ng/m³ and ng/m³, upper diagram) and H₂S (in log µg/m³ and µg/m³, lower diagram) concentrations in air for the June 2014 survey at Mt. Amiata.

Table 1

GEM (in ng/m³) and H₂S (in µg/m³) measurements in air at Mt. Amiata in June 2014. N = number of measurements; Std. dev. = standard deviation.

AMIATA	Gas	N	Mean	Median	Std. dev.	Max.	Min.
24/06/2014	GEM (ng/m ³)	127	50	45	20	194	24
	H ₂ S (µg/m ³)		17	2.8	75	690	0.14
25/06/2014	GEM (ng/m ³)	53	27	24	16	115	21
	H ₂ S (µg/m ³)		11	1.7	34	185	0.32
26/06/2014	GEM (ng/m ³)	126	40	40	5.1	51	22
	H ₂ S (µg/m ³)		4.8	2.5	7.2	43	0.06
27/06/2014	GEM (ng/m ³)	126	57	59	15	100	22
	H ₂ S (µg/m ³)		26	25	19	101	0.61

the 4 days of measurements ranged from 5.1 to 20 ng/m^3 and from 7.2 and 75 $\mu\text{g}/\text{m}^3$, respectively (Table 1). The GEM and H_2S average values ranged from 27 to 57 ng/m^3 and from 4.8 and 26 $\mu\text{g}/\text{m}^3$, respectively, whilst the medians ranged from 24 to 59 ng/m^3 and from 1.7 and 25 $\mu\text{g}/\text{m}^3$, respectively (Table 1). As shown in the histograms of Fig. 3, the most frequent GEM and H_2S values were between ~ 20 and 80 ng/m^3 and between ~ 0.3 and 100 $\mu\text{g}/\text{m}^3$, respectively.

The spatial distribution of GEM and H_2S concentrations measured at Mt. Amiata is only shown using dot-maps. No contour maps were built since the presence of dense vegetation and the lack of roads prevented a homogeneous distribution of the measurements (Figs. 4 and 5). However, this simple graphical representation allowed to clearly depict a GEM and H_2S dispersion plume that, considering the wind direction, was originated from the two geothermal power plants. Noteworthy, on June 24, 2014, when the wind speed from S ranged from 9 to 13 m/s, a N-oriented plume from PC3 reached the eastern part of Piancastagnaio

town (GEM concentrations >60 ng/m^3 ; Fig. 4a), placed at an altitude significantly higher (772 m) than that of the power plants (446, 558 and 586 m for PC3, PC4 and PC5, respectively). At lower wind speed (from 3 to 8 m/s) and E to W wind direction (on June 26 and 27, 2014), the two air pollutants showed a less regular spatial distribution. For example, on June 27, 2014 the highest concentrations (up to 100 ng/m^3 and 101 $\mu\text{g}/\text{m}^3$ for GEM and H_2S , respectively; Figs. 4d and 5d) were measured a few meters from the PC3 geothermal plant.

5.2. Solfatara Crater

On the 16th (morning and afternoon) and 17th (morning) of April 2014, 378 measurements were carried out along three pathways in an area including both the vegetated zone, in the western sector of the crater, and the main fumarolic discharges (Fig. 2). The speed of the dominant wind (from NE) was up to 11 m/s, whereas air temperature and

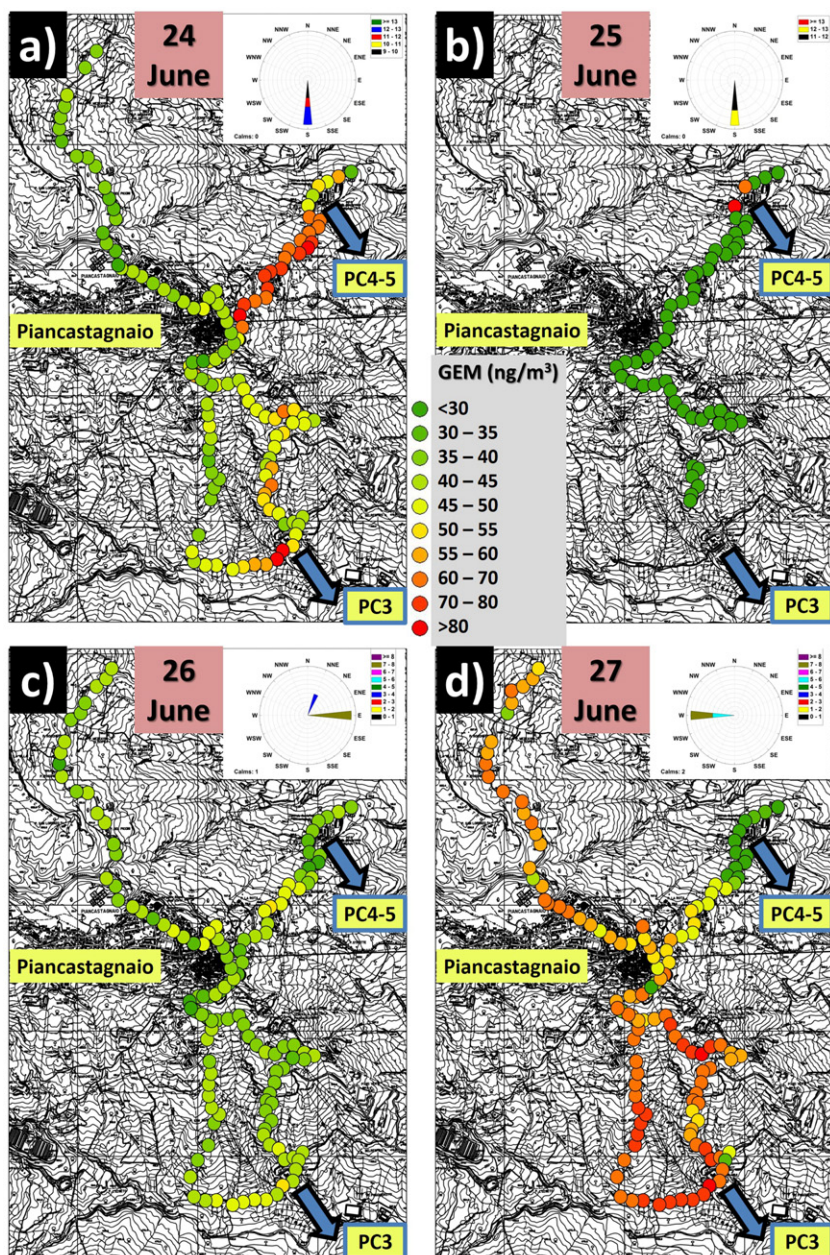


Fig. 4. Dot-maps of the GEM (in ng/m^3) measurements in air performed near Piancastagnaio (Mt. Amiata) by car along pre-defined pathways. The GEM concentrations were divided into 10 classes for the a) 24, b) 25, c) 26 and d) June 27, 2014 surveys. Piancastagnaio and the geothermal power plants (PC3, PC4 and PC5) are evidenced. The prevailing wind direction and intensity for each surveying day are also indicated.

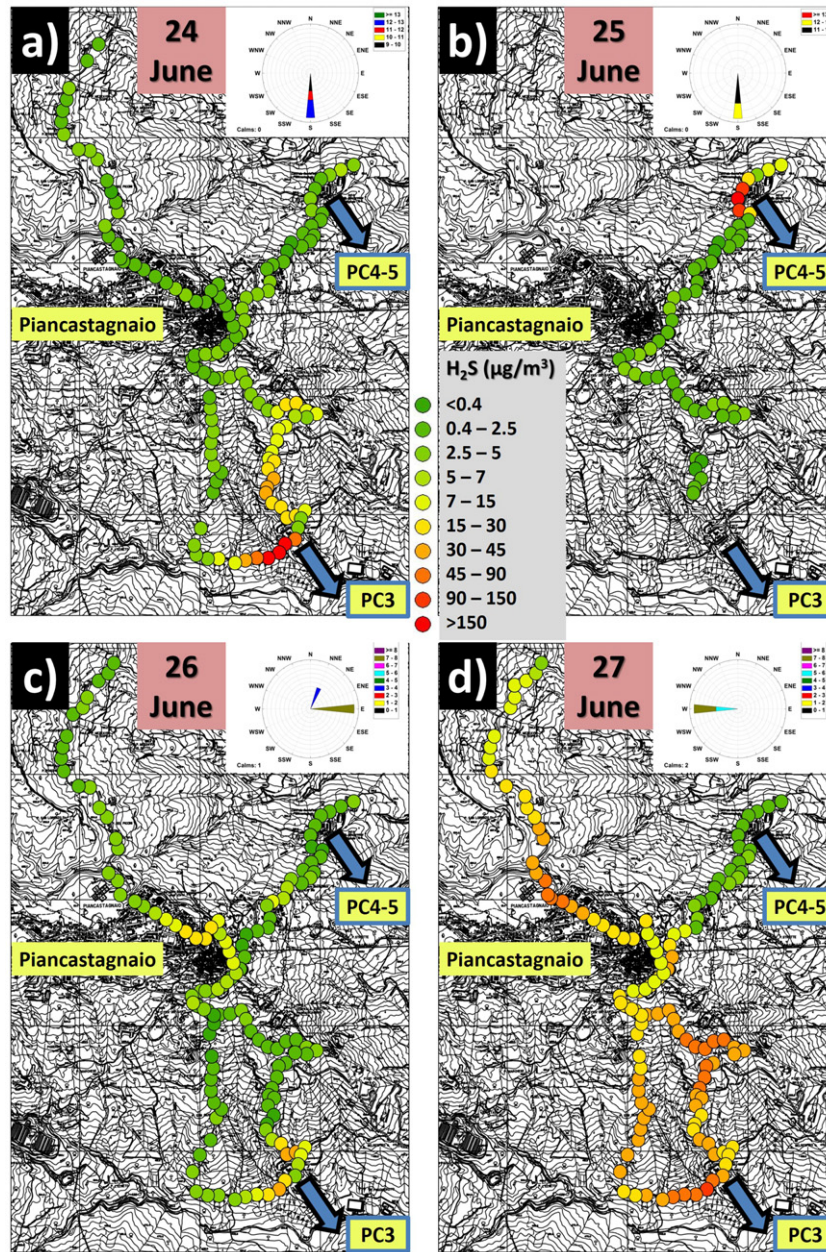


Fig. 5. Dot-maps of the of H_2S (in $\mu\text{g}/\text{m}^3$) measurement in air performed near Piancastagnaio (Mt. Amiata) by car along pre-defined pathways. The H_2S concentrations were divided into 10 classes for the a) 24, b) 25, c) 26 and d) June 27, 2014 surveys. Piancastagnaio and the geothermal power plants (PC3, PC4 and PC5) are evidenced. The prevailing wind direction and intensity for each surveying day are also indicated.

humidity ranged from 12 to 15 °C and from 36 to 52%, respectively. The highest GEM concentrations were from 51 to 77 ng/m^3 , whereas the lowest ones ranged from 12 to 19 ng/m^3 , the latter being recorded in the vegetated areas of the crater, where a camping area, frequented by many tourists, is located. In this peripheral zone, the H_2S concentrations

(down to 0.33 $\mu\text{g}/\text{m}^3$) were mostly below the nuisance odor concentration limit of 7 $\mu\text{g}/\text{m}^3$ (Table 2). The central and SE parts of the crater showed H_2S concentrations up to 3392 $\mu\text{g}/\text{m}^3$, i.e. consistent with those reported by Badalamenti et al. (2001) and largely exceeding the WHO (2000) guideline value (150 $\mu\text{g}/\text{m}^3$). The GEM and H_2S standard

Table 2

GEM (in ng/m^3) and H_2S (in $\mu\text{g}/\text{m}^3$) measurements in air at Solfatara Crater in April 2014. N = number of measurements; Std. dev. = standard deviation.

SOLFATARA	Gas	N	Mean	Median	Std. dev.	Max.	Min.
16/04/2014 (morning)	GEM (ng/m^3)	124	27	25	5.8	51	19
	H_2S ($\mu\text{g}/\text{m}^3$)		442	312	467	2821	2.5
16/04/2014 (afternoon)	GEM (ng/m^3)	124	28	25	10	77	17
	H_2S ($\mu\text{g}/\text{m}^3$)		420	143	698	3392	0.78
17/04/2014	GEM (ng/m^3)	130	25	22	9.5	70	12
	H_2S ($\mu\text{g}/\text{m}^3$)		497	216	599	2187	0.33

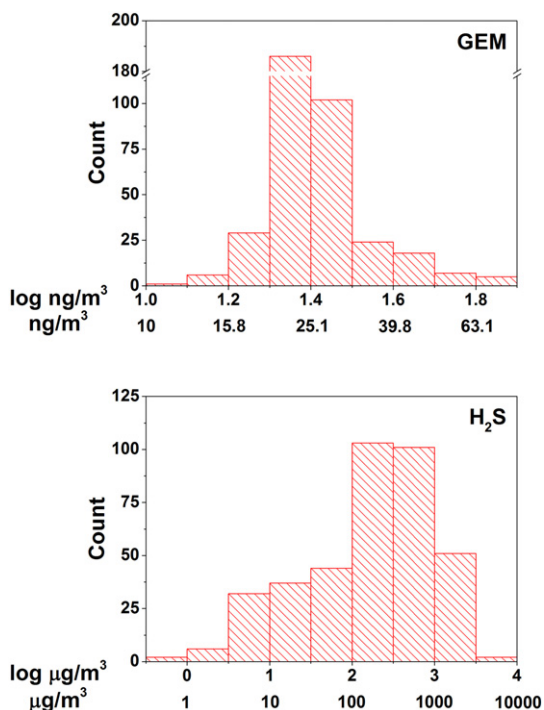


Fig. 6. Histograms of GEM (in $\log \text{ ng/m}^3$ and ng/m^3 , upper diagram) and $\text{ H}_2\text{ S}$ (in $\log \mu\text{ g/m}^3$ and $\mu\text{ g/m}^3$, lower diagram) concentrations in air for the April 2014 survey at Solfatara Crater.

deviations were up to 10 ng/m^3 and $698 \mu\text{ g/m}^3$, respectively (Table 2). The average and median GEM values (Table 2) were similar, ranging from 25 to 28 ng/m^3 and from 22 to 25 ng/m^3 , respectively, whereas those of $\text{ H}_2\text{ S}$ significantly differed since they were ranging from 420 to $497 \mu\text{ g/m}^3$ and from 143 to $312 \mu\text{ g/m}^3$, respectively. When summarizing the whole GEM and $\text{ H}_2\text{ S}$ measurements in the histograms of Fig. 6, the most recurrent concentrations were between ~ 20 and 30 ng/m^3 and between 100 and $1000 \mu\text{ g/m}^3$, respectively.

Since the GEM and $\text{ H}_2\text{ S}$ measurements almost uniformly covered the study area, contour maps for April 16 (morning and afternoon) and April 17 (morning) 2014 and all the data for the Solfatara Crater are reported in Figs. 7 and 8, respectively. When considering the whole GEM and $\text{ H}_2\text{ S}$ concentrations, the highest values were recorded in correspondence of the most intense emissions of gas discharges occur (Figs. 7d and 8d), as follows: (i) the southeastern border of the crater bottom, in correspondence of the BG and BN fumarolic vents; (ii) a relatively

small zone in the northeastern crater sector, i.e. nearby two ancient caves (namely, “Le Stufe”: the Stoves) that were used as *sudatoria* (sweat rooms); and (iii) the central part of the crater, hosting bubbling pools (namely, “La Fangaia”: the mud pit) fed by meteoric water and hydrothermal gases. This spatial distribution is reflected when the single periods of measurements are taken into account (Fig. 7 and Fig. 8), although this is more clearly evidenced for the GEM thematic maps since those of $\text{ H}_2\text{ S}$ show a more homogeneous distribution.

Noteworthy, the occurrence of wind from NE likely caused the relatively high GEM concentrations in the SW part of the crater (e.g. up to 35 ng/m^3 in the afternoon of April 16, 2014; Fig. 7b). At lower wind speed ($<7 \text{ m/s}$; e.g. Figs. 7a and 8a) a large variation in terms of GEM and $\text{ H}_2\text{ S}$ concentrations was recorded.

6. Discussion

Surveys aimed to monitor the presence and determine the concentrations of air pollutants in contaminated areas are mostly based on continuous measurements carried out at a fixed station (e.g. Peralta et al., 2013; Olafsdottir et al., 2014b). However, the selection a priori of a single measurement site strongly affects the capability to discriminate the effective role played by the different parameters (e.g. weather conditions, air pollutant input rate) on air quality, especially in areas (e.g., urban and industrial settlements) characterized by multiple potential sources of contaminants (Kolb et al., 2004; Herndon et al., 2005). The spatial distribution of air pollutants can be investigated by using passive traps that are placed at different sites within a selected study area (e.g. Klánová et al., 2006; Pavilonis et al., 2013; Pirrone et al., 2013 and references therein; Akdemir, 2014; Marć et al., 2015). Notwithstanding, the exposure time (from a few hours to a few days) of these traps is affecting these measurements since short-term or sudden contamination events cannot be recorded, the retrieved concentrations being a weighted average passively registered by such devices.

In this paper, a different approach was applied that allowed to depict both the spatial distributions of the air pollutants and their evolution in time. At Piancastagnaio, the local geothermal plants were likely responsible of the measured GEM and $\text{ H}_2\text{ S}$ concentrations, which were significantly changing in a few hours or daily with no apparent relationship to the wind direction and speed (Figs. 4 and 5). Based on the morphological features, which are characterized by relatively strong differences in terms of altitude, it is likely that these results were related to vertical movements of the air masses. During the field survey carried out on June 24 and 27, 2014 (Figs 4a, d and 5a, d), the cloudy and high humidity weather conditions likely favored air stratification. Hence, the dispersion in air of both GEM and $\text{ H}_2\text{ S}$ was strongly limited, as supported by the anomalously high concentrations measured at relatively large

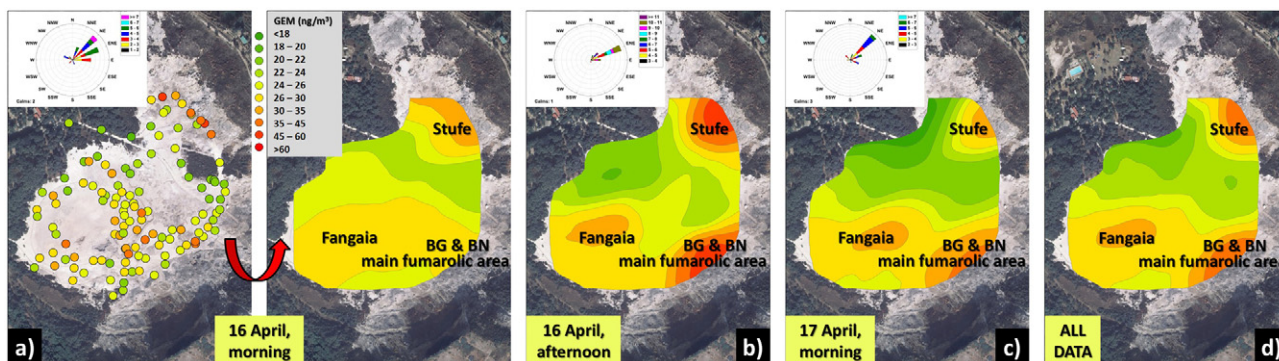


Fig. 7. Contour maps of the GEM (in ng/m^3) measurements in air performed inside Solfatara Crater by car along pre-defined pathways. The recorded concentrations were divided into 10 classes for the April 2014 surveys carried out on the: a) 16th in the morning, b) 16th in the afternoon and c) 17th in the morning, while in d) the contour map for all GEM data recorded during the April 2014 survey is also reported. For comparison, the 16 April, morning dot-map is also shown. The location of Stufe, Fangaia, the main fumarolic area, including the Bocca Grande (BG) and Bocca Nuova (BN), fumaroles is evidenced. The prevailing wind direction and intensity for each surveying day are also indicated.

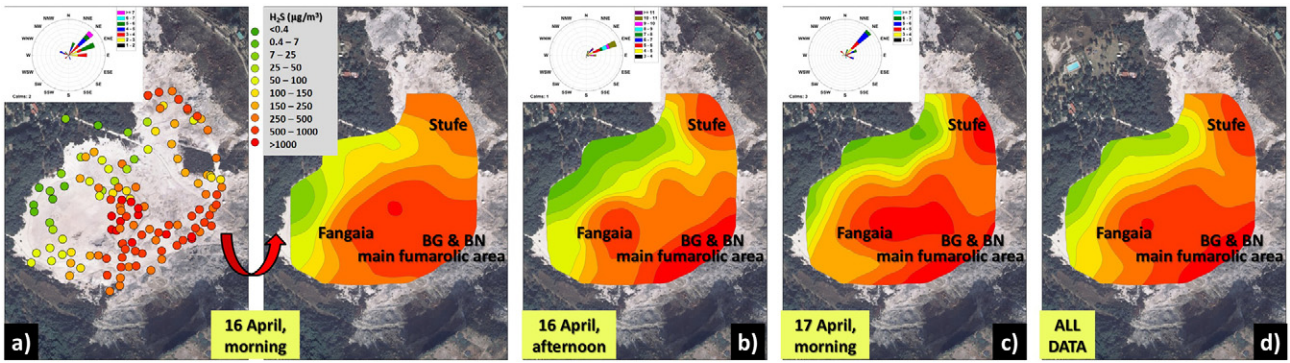


Fig. 8. Contour maps of the H_2S (in $\mu g/m^3$) measurements in air performed inside Solfatara Crater by car along pre-defined pathways. The recorded concentrations were divided into 10 classes for the April 2014 surveys carried out on the: a) 16th in the morning, b) 16th in the afternoon and c) 17th in the morning, while in d) the contour map for all GEM data recorded during the April 2014 survey is also reported. For comparison, the 16 April, morning dot-map is also shown. The location of Stufe, Fangaia and the main fumarolic area, including the fumaroles Bocca Grande (BG) and Bocca Nuova (BN), is also evidenced. The prevailing wind direction and intensity for each surveying day are also indicated.

distances from the contaminant sources and similar to what observed by Esbrí et al. (2016) in the mining polluted site of Almadén town (Spain). On June 25 and 26 (Figs. 4b, c and 5b, c), the GEM and H_2S measurements were carried out under a sunny weather that favored an efficient vertical air mixing and a consequent rapid dispersion of the emitted pollutants.

At Solfatara Crater, which has a flat bottom contoured by relatively steep flanks, the spatial distributions of both GEM and H_2S concentrations measured during the three distinct surveys (Figs. 7a–c and 8a–c, respectively) seem to be mainly depending on the location of the emitting sources (fumarolic areas, Stufe and Fangaia) and wind direction. It is worth noting that the H_2S/GEM ratios, calculated by normalizing the measured GEM and H_2S concentrations to their highest values (nH_2S/GEM), decreased by 3 orders of magnitude in a short distance (up to 300 m), moving away from the main emission sources towards the central and SE portion of the crater and the vegetated area at NW (Fig. 9a–c). A similar strong decrease of GEM concentrations at increasing distance from the contaminating source in the Almadén district (Spain) was also described by Llanos et al. (2010).

The different spatial trends of the GEM and H_2S concentrations, which were measured under pretty similar weather conditions, were likely depending on the chemical-physical processes regulating the different behavior of the two pollutants once they are released in the air. For instance, photochemical oxidation is able to efficiently consume H_2S to form SO_2 (De Kok et al., 1988; Cihacek

and Bremner, 1993; Kristmannsdóttir et al., 2000; Bacci et al., 2000; Chow Pineda, 2007; Vallero, 2014), whereas GEM is relatively stable (Sommar et al., 2001; Fu et al., 2012), unless scavenged by dry deposition on vegetation (Zhang et al., 2005; Fu et al., 2010). According to these considerations, in areas characterized by a relatively simple spatial geometry, such as Solfatara Crater, the proposed approach may provide useful indications for investigating the transport mechanisms and degradation processes affecting air pollutants once emitted in the air. This approach could be improved by including other air pollutants (e.g. NO_x , CO, CH_4 , C_2H_6 , SO_2 , CO_2 , H_2O , O_3) simultaneously measured at high frequency using analytical instruments deployed on mobile platforms (e.g. Bukowiecki et al., 2002; Kolb et al., 2004; Herndon et al., 2005; Adams et al., 2012; Van Poppel et al., 2013; Riley et al., 2014).

At Mt. Amiata, the spatial distribution of the nH_2S/GEM ratios was relatively homogeneous, even at distances >1 km from the geothermal power plants (Fig. 10a–d). In this case, the influence of the morphological/weather parameters, invoked to explain the temporal variations recorded for GEM and H_2S (Figs. 4a–d and 5a–d), seems able to mask the distinct behavior of the two pollutants in response to chemical-physical processes occurring in air. In this case, a reliable evaluation of the temporal and spatial evolution of the impact on air quality of potential contaminating sources cannot overlook the acquisition of a comprehensive meteorological and morphological dataset.

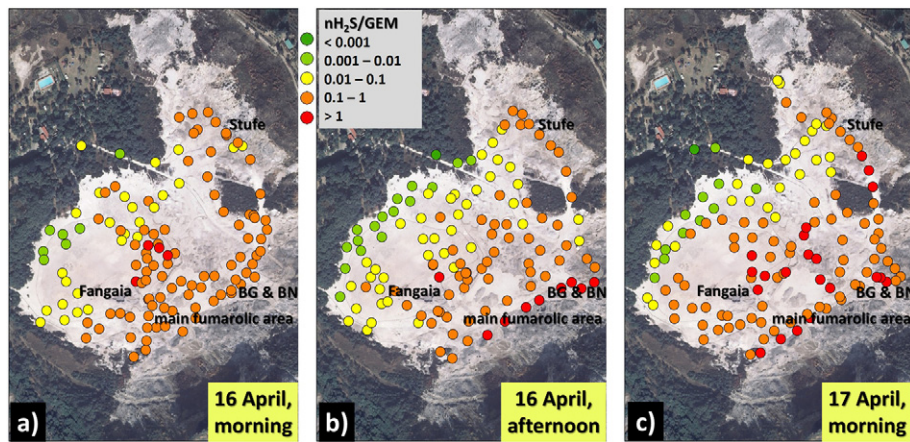


Fig. 9. Dot-maps of the H_2S/GEM ratios in air, calculated by normalizing the measured GEM and H_2S concentrations to their highest values (nH_2S/GEM), performed inside Solfatara Crater. The values of the normalized ratios were divided into 5 classes for the April 2014 surveys carried out on the: a) 16th in the morning, b) 16th in the afternoon and c) 17th in the morning. The location of Stufe, Fangaia and the main fumarolic area, including the fumaroles Bocca Grande (BG) and Bocca Nuova (BN), is also evidenced.

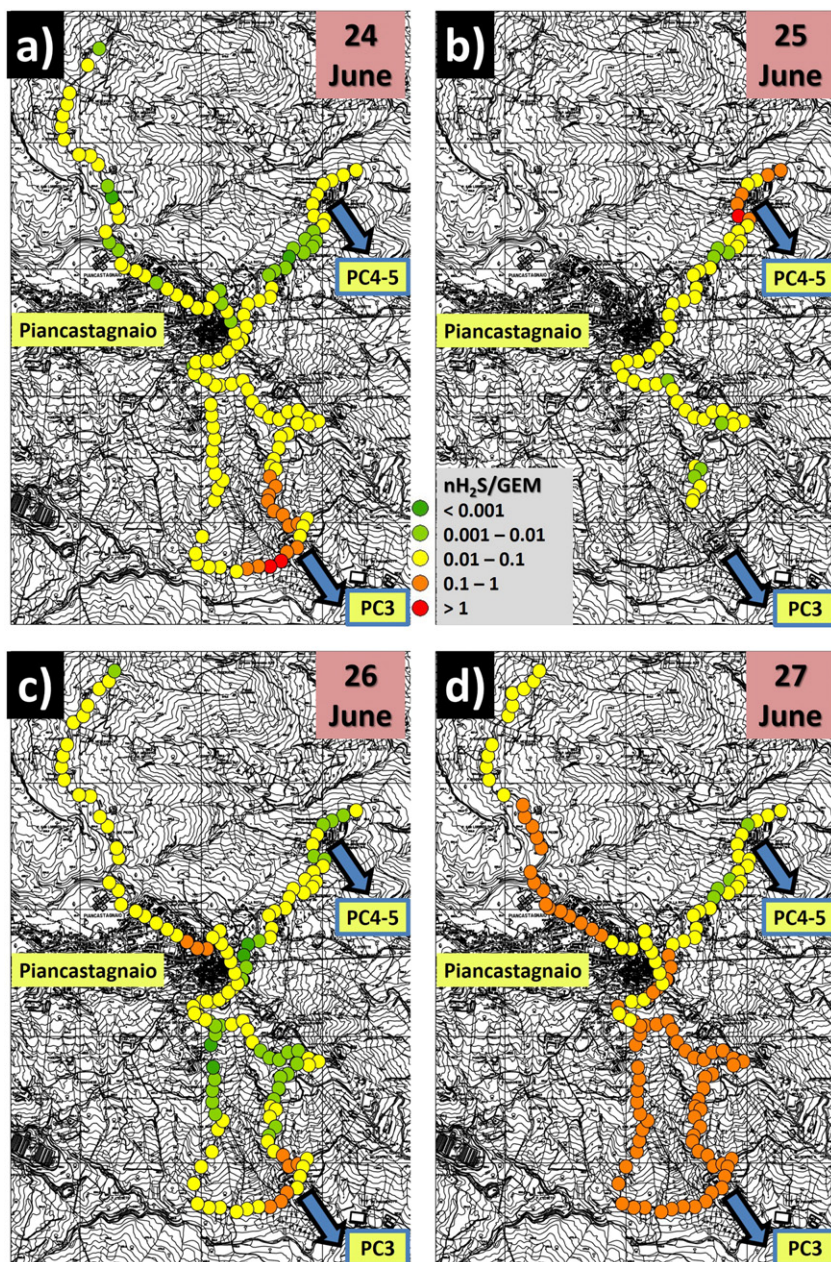


Fig. 10. Dot-maps of the H_2S/GEM ratios in air, calculated by normalizing the measured GEM and H_2S concentrations to their highest values (nH_2S/GEM), performed near Piancastagnaio (Mt. Amiata). The values of the normalized ratios were divided into 5 classes for the June 2014 surveys carried out on the a) 24th, b) 25th, c) 26th and d) 27th. The location of Piancastagnaio and the geothermal power plants (PC3, PC4 and PC5) is also evidenced.

7. Conclusions

The present study demonstrated that continuous GEM and H_2S measurements applied to different environmental situations allow to recognize the air concentration variability that these two pollutants may have over periods of hours or days, providing a more realistic picture than that obtained by using passive traps. Furthermore, the simultaneous recording of GEM and H_2S concentrations is highly suitable for defining both anthropogenic (geothermal power plants at Mt. Amiata area) and natural (Solfatara Crater) pollution sources. This implies that once the emitting source(s) were recognized, appropriate instrumentations can be deployed along with meteorological stations to ascertain the pollutants air dispersion and verify whether the threshold concentrations indicated by WHO and national or local authorities are exceeded. Such measurements are necessary in order to undertake appropriate actions

to mitigate the risk for the local community or tourists as in the case of Mt. Amiata and Solfatara, respectively.

Finally, the nH_2S/GEM ratio is a good indicator of the chemical-physical processes that these two gas species can suffer once emitted in the air. In particular, H_2S results to be more affected by secondary processes than GEM, possibly related to photochemical oxidation reactions.

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