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A new approach for the measurement of gaseous elemental mercury (GEM) and H_2S in air from anthropogenic and natural sources: Examples from Mt. Amiata (Siena, Central Italy) and Solfatara Crater (Campi Flegrei, Southern Italy)

Jacopo Cabassi [a,b,*], Franco Tassi [a,b], Stefania Venturi [a,b], Sergio Calabrese [c], Francesco Capecchiacci [a,b], Walter D'Alessandro [d], Orlando Vaselli [a,b]

[a] *Dipartimento di Scienze della Terra, University of Florence, Via G. La Pira 4, 50121 Florence, Italy*
[b] *CNR – Istituto di Geoscienze e Georisorse, Via G. La Pira 4, 50121 Florence, Italy*
[c] *Dipartimento di Scienze della Terra e del Mare, University of Palermo, Via Archirafi 36, 90123 Palermo, Italy*
[d] *Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via Ugo La Malfa 153, 90123 Palermo, Italy*

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ABSTRACT

Real-time measurements of GEM and H_2S 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 H_2S 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 H_2S 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 H_2S concentrations at Piancastagnaio were up to 194 and 77 ng/m^3, respectively, whilst at Solfatara Crater were up to 690 and 3392 μg/m^3, respectively. Although the GEM concentrations at Piancastagnaio were lower than the limit value recommended by local regulations for outdoor environment (300 ng/m^3), they were almost one order of magnitude higher than the GEM background both in Tuscany (~3.5 ng/m^3) and Mt. Amiata (3–5 ng/m^3), 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 H_2S concentrations are concerned, the guideline value of 150 μg/m^3, 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 H_2S 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 H_2S 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 H_2S/GEM ratio, calculated by normalizing the measured GEM and H_2S concentrations to their highest values (nH_2S/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, H_2S resulted to be more affected by secondary processes than GEM, possibly related to photochemical oxidation reactions.

1. Introduction

Gaseous elemental mercury (hereafter GEM or Hg^0) and H_2S emitted from a number of different anthropogenic and natural sources

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[*] Corresponding author at: CNR-IGG and Dipartimento di Scienze della Terra, University of Florence, Via G. La Pira 4, 50121 Florence, Italy.
E-mail addresses: jacopo.cabassi@unifi.it, jacopo.cabassi@gmail.com (J. Cabassi).

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(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 Hg^0 (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. Higueras et al., 2013; Higueras 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 (Voltaggio and Spadoni, 2009). According to these methods, GEM and H_2S 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 H_2S 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 H_2S 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 H_2S 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 H_2S 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/m^3 (USEPA, 1997; Ebinghaus et al., 2002), although locally higher values were recorded worldwide, e.g. ~3.5 ng/m^3 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 Hg^{2+} 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/m^3 (WHO, 2000), whereas EPA (2001) suggests three action levels: 1) ≥10,000 ng/m^3 (real-time measurements), residents must immediately be relocated; 2) from 1000 ng/m^3 to 10,000 ng/m^3 (real-time measurements), relocation must be scheduled as soon as possible; and 3) ≤1000 ng/m^3 (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/m^3 (Thorsteinsson et al., 2013 and references therein). H_2S 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 H_2S in ambient air range from 0.14 to 0.40 μg/m^3 and its guideline value (24-h TWA) is 150 μg/m^3 (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 H_2O and CO_2 is the most abundant gas species released from hydro/geothermal gases (D'Alessandro et al., 2013). Owing to the relatively high GEM and H_2S 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 SO_2, 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 H_2S 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 km^2) 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 CO_2-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 CO_2, H_2S and GEM (Bravi and Basosi, 2014); however, most GEM and H_2S 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 H_2S 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/m^3, much higher than the limit imposed by the Tuscany Regional Decree 1447 (1998) (300 ng/m^3 at 20 °C and 100 cm above the ground; Vaselli et al., 2013). To the best of our knowledge, no H_2S measurements in air were carried out in this area.