

Mercury emissions from soils and fumaroles of Nea Kameni volcanic centre, Santorini (Greece)

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EMANUELA BAGNATO,¹ GIANCARLO TAMBORRELLI,² ALESSANDRO TRUFFA,³ MARIO STROVIERI,⁴
GEORGE E. VOUGIOUKALAKIS⁴ and MICHELLE PARKS⁵

¹DiSTeM, University of Palermo, Via Archirafi 36, Palermo, Italy

²Istituto di Geofisica e Vulcanologia, Via U. La Malfa 153, Palermo, Italy

³IAMC-CNR, Via del Mare 3, Torretta Granitola, Fraz. Campobello di Mazzara (TP), Italy

⁴Institute for Geology and Mineral Exploration, 3rd exit Olympic village, 13677, Acharne, Athene, Greece

⁵Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, U.K.

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There have been limited studies to date targeting mercury emissions from volcanic fumarolic systems, and no mercury flux data exist for soil or fumarolic emissions at Santorini volcanic complex, Greece. We present results from the first geochemical survey of Hg and major volatile (CO₂, H₂S, H₂O and H₂) concentrations and fluxes in the fumarolic gases released by the volcanic/hydrothermal system of Nea Kameni islet; the active volcanic center of Santorini. These data were obtained using a portable mercury spectrometer (Lumex 915+) for gaseous elemental mercury (GEM) determination, and a Multi-component Gas Analyzer System (Multi-GAS) for major volatiles. Gaseous Elemental Mercury (GEM) concentrations in the fumarole atmospheric plumes were systematically above background levels (~4 ng GEM m⁻³), ranging from ~4.5 to 121 ng GEM m⁻³. Variability in the measured mercury concentrations may result from changes in atmospheric conditions and/or unsteady gas release from the fumaroles. We estimate an average GEM/CO₂ mass ratio in the fumarolic gases of Nea Kameni of approximately 10⁻⁹, which falls in the range of values obtained at other low-T (100°C) volcanic/hydrothermal systems (~10⁻⁸); our measured GEM/H₂S mass ratio (10⁻⁵) also lies within the accepted representative range (10⁻⁴ to 10⁻⁶) of non-explosive volcanic degassing. Our estimated mercury flux from Nea Kameni's fumarolic field (2.56 × 10⁻⁷ t yr⁻¹), while making up a marginal contribution to the global volcanic non-eruptive GEM emissions from closed-conduit degassing volcanoes, represents the first available assessment of mercury emissions at Santorini volcano, and will contribute to the evaluation of future episodes of unrest at this renowned volcanic complex.

Keywords: volcanogenic mercury, volcanic degassing, Santorini, mercury flux inventory, trace metals

INTRODUCTION

The fate of metals in the natural environment is of great concern, particularly near urban and industrial areas. Natural sources, like active volcanoes, have long been recognized as key trace metals contributors to the atmosphere and aquatic environments (Pyle and Mather, 2003; Bagnato *et al.*, 2011). Among these metals, mercury (Hg) is of special concern, in light of its high toxicity (Barringer *et al.*, 2005) and its tendency to bio-accumulate in aquatic ecosystems in methylation processes (Winfrey and Rudd, 1990). There is therefore an urgent need to monitor Hg concentrations in the Earth's ecological systems. The present-day average atmospheric Hg concentrations range between 1.5 and 5 ng m⁻³ in the Northern Hemisphere

(NH), and between 1.1 and 1.3 ng m⁻³ in the Southern Hemisphere (SH), being therefore much lower than the critical load considered to exert harmful effects on human life (Kim *et al.*, 2005; Lindberg, 2007). Hg is stable in the earth's atmosphere as its vapor-phase elemental form (GEM: Gaseous Elemental Mercury ~98% of the total atmospheric mercury; Schroeder and Munthe, 1998), which has low solubility and high volatility. These properties determine a relatively long atmospheric lifetime for GEM (~0.5–2 yr; Lindqvist and Rodhe, 1985; Slemr *et al.*, 1985), and allow its long-range transport away from source. Mercury released to the atmosphere is eventually removed through wet and dry deposition (Schroeder and Munthe, 1998), and some of the deposited Hg may be re-emitted back to the atmosphere, depending on the surface and environmental conditions (Ericksen *et al.*, 2005 found that about 6–8% of deposited Hg volatilizes back to the atmosphere).

Likewise other toxic compounds in the environment, Hg is sourced by both natural and anthropogenic reser-

*Corresponding author (e-mail: emanuelabagnato@virgilio.it)

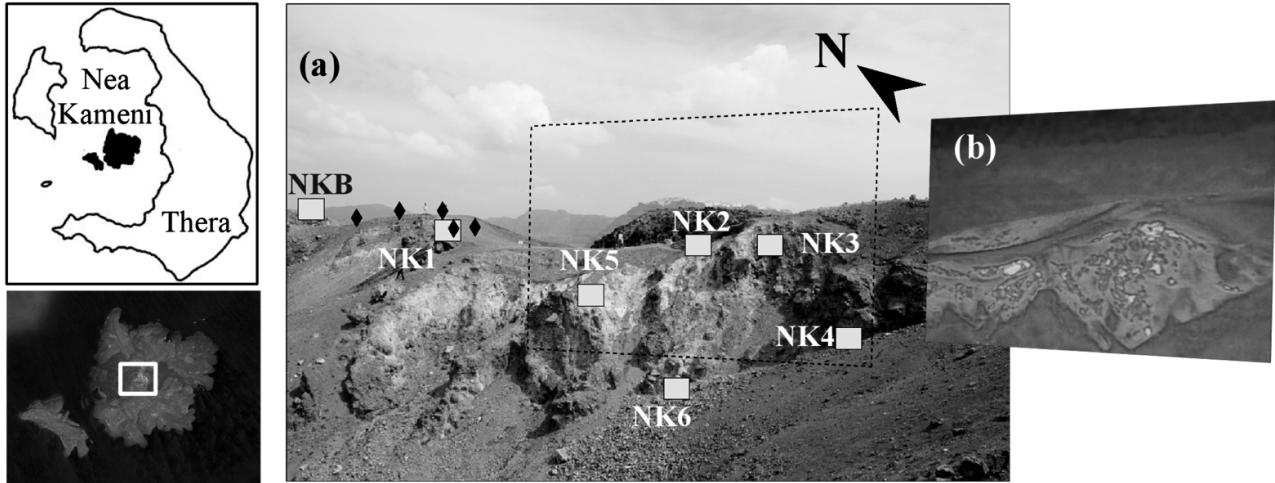


Fig. 1. (a) Location of the Nea Kameni Volcanic Field and the active fumarole sites within the field (NK1 to 6; white squares). Background location outside the fumarolic field is also illustrated (NKB). Soil degassing detection points (black diamonds) have been chosen closer to the fumarolic vent of NK1. (b) Thermal image taken by the Multiparametric network of the University of Florence (a courtesy of Dr. Delle Donne) showing how the ground temperature changes in the fumarolic field.

voirs. Significant work has been done in the last years to quantify emissions from volcanoes, Hg-enriched soils and large-scale Hg mineral belts (Pyle and Mather, 2003; Friedli *et al.*, 2003; Gustin, 2003; Varekamp and Buseck, 1981; Bagnato *et al.*, 2011). Volcanic and geothermal areas have been suggested as important natural sources of mercury, accounting for ~60% of total natural Hg emissions into the atmosphere, as also testified by particularly high Hg concentrations in volcanic gases relative to background air (Varekamp and Buseck, 1981, 1986; Pyle and Mather, 2003; Nriagu, 1989; Bagnato *et al.*, 2007, 2009a, 2009b). For this reason, it remains highly important to identify the factors governing the rate of Hg transport from magma to the atmosphere, and to refine current estimates of volcanic Hg fluxes.

In this paper, we focus on quantifying GEM emissions from soils and gas vents of Nea Kameni volcano, a small islet belonging to the Santorini volcanic complex, the site of one of the largest volcanic events in human history. Santorini is heavily populated (14,000 inhabitants on about 90 km², Vougioukalakis, 2002), imposing an accurate evaluation of volcanic hazard and risk, both in term of potential eruptions and possible environmental impact (“pollution”) of gas discharges. We used a portable mercury analyzer (Lumex-RA915+) in parallel with a Multi-component Gas Analyzer (MultiGAS; Aiuppa *et al.*, 2005, 2011; Shinohara and Witter, 2005; Shinohara, 2008) to obtain real-time measurements of mercury and major volatiles in the fumes of Nea Kameni. These measurements, the first carried out at such location, extend previous combined MultiGAS-Lumex surveys reported elsewhere (Aiuppa *et al.*, 2007; Witt *et al.*, 2008a, b; Mather

et al., 2012), and aim at improving our understanding of the magmatic systems and its degassing budget.

STUDY AREA

The Aegean volcanic arc (Fig. 1) is a 450 km long chain of late Pliocene–Quaternary volcanoes formed by northward subduction of the African plate underneath the continental Aegean micro-plate (Francalanci *et al.*, 2005; Zellmer *et al.*, 2000). Santorini is situated in the central part of the arc on a 23–26 km thick continental crust, approximately 120 km north of Crete, and hosts two of the three active volcanic Aegean centers, Kameni and Kolumbo (Vougioukalakis and Fytikas, 2005). Volcanism on Santorini started at least 650 ka ago, and produced one of the largest volcanic events in human history, the Minoan eruption of the late Bronze Age (~3600 BP) (Bond and Sparks, 1976; Pyle, 1990; Cioni *et al.*, 2000); this eruption discharged about 60 km³ of rhyodacitic magma and ash, which dispersed over a large area of the eastern Mediterranean and Turkey (Sigurdsson *et al.*, 2006). After the Minoan eruption, submarine volcanic activity continued, in the intra-caldera region. Lava flows initially emerged above sea level in 197 BC (Fytikas *et al.*, 1990) and since this time have gradually built up the volcanic islands of Palea and Nea Kameni (between 197 BC and 1950 AD; Vougioukalakis and Fytikas, 2005; Zellmer *et al.*, 2000), the subaerial expressions of a ~2 km³ intra-caldera shield volcano which rises to ~500 m above the caldera floor. This dome-forming phase has comprised effusive and moderately explosive activity, producing lava domes, blocky lava flows and pyroclastic cones. Although

the volcano is currently in a dome-forming phase the Kameni islands are still part of a larger caldera system and precursory signals of unrest at large caldera systems are often difficult to interpret. Recently Druitt *et al.* (2012) investigated pre-eruptive magmatic processes using chemically zoned crystals from the “Minoan” caldera-forming eruption of Santorini, providing insights into how rapidly large silicic systems may pass from quiescence to eruption. They showed that the reactivation, growth and assembly of large silicic magma bodies before eruption can occur on very short geological timescales (Druitt *et al.*, 2012). This idea is consistent with evidence for late-stage recharge on similar timescales before caldera eruptions elsewhere (Morgan *et al.*, 2006; de Silva *et al.*, 2008).

At present, the current volcanic activity at Santorini consists of weak, diffuse fumarolic degassing in the vicinity of the craters on the summit of Nea Kameni volcanic field (covering an area of about 0.02 km²), and several hot springs which are located on the eastern and western coasts of Nea Kameni and the eastern side of Palea Kameni. In addition, in early 2011 an anomalous sequence of earthquakes began inside the caldera. Although these recent events represent the most significant activity observed since the last eruptive sequence ending in 1950, it is not certain that an eruption is imminent (Newman *et al.*, 2012; Parks *et al.*, 2012).

MATERIALS AND METHODS

Techniques

A measurement survey was performed in late March 2012, targeting six main fumaroles located within the Nea Kameni volcanic/hydrothermal system (Fig. 1). Previous studies have demonstrated that Nea Kameni fumaroles are made up to a large extent of heated atmospheric air and CO₂, with minor constituents (CH₄, H₂, CO) present in variable proportions (Vougioukalakis and Fytikas, 2005). During our field expedition, we measured gas temperatures of 60–70°C, somewhat lower than reported in previous studies (60–97°C, Vougioukalakis and Fytikas, 2005). A significant drop in surface gas discharge has been observed since 2002, probably caused by a self-sealing process operated by circulating hot fluids (Vougioukalakis and Fytikas, 2005). By the time of our campaign, most fumaroles discharges occurred mainly through loose pyroclastic deposits and were readily dispersed in the atmosphere in the form of weak plumes.

Gaseous elemental mercury (GEM)

During our survey, we measured GEM concentrations in the weak atmospheric plumes of six fumaroles distributed within the Nea Kameni volcanic field (Fig. 1). GEM concentrations in such plumes were made, at short dis-

tances (40–50 cm) from individual degassing vent(s), using a Lumex-RA 915+ (Lumex St Petersburg, Russia) portable mercury vapor analyzer. This instrument allows for measurement at low-temperature fumaroles in the presence of high levels of humidity and H₂S, unlike the conventional gold trap technique (which is instead strongly affected by inhibition of Hg adsorption at high H₂S levels; Schroeder *et al.*, 1995). The Hg analyzing system is designed to only monitor GEM concentrations (for the sake of simplicity, GEM and Hg are used without distinction in this article, unless otherwise specified). The RA-915+ operates by sampling air at 10 l min⁻¹ through a dust filter to remove particles from the air, followed by GEM detection via differential Zeeman atomic absorption spectrometry using a high-frequency modulation of light polarization (ZAAS-HFM = Zeeman Atomic Absorption Spectrometry with High Frequency Modulation of Light Polarization) (Sholupov *et al.*, 2004). During the measurements (taken at 0.5 Hz rate), a zero correction was applied (every 5 min) to reset the baseline by switching the airflow through a mercury absorption filter. The detection limit was ~2 ng m⁻³ and the instrument accuracy about 10%. There are a number of advantages in using the RA-915+, at least compared with gold trap techniques. The analyzer is portable, low power consumption, does not require special carrier gas and has low limits of detection and high frequency of data acquisition (minimum time between sampling of 1 s). It also has the advantage of performing automatic pre-concentration and detection in the same apparatus, with appropriate limits of detection and frequency of sampling. In addition, the potential interference by other species absorbing in the ultraviolet region (such as some organic compounds and SO₂) are solved by coupling a Zeeman Effect corrector.

Diffusive GEM measurements

Mercury degassing from Nea Kameni was also monitored using passive dosimeters, in the attempt to highlight the potential of this alternative method in volcano studies, to evaluate the local-scale atmospheric dispersion of volcanic mercury, and to compare with/integrate data obtained by Lumex active sampling. Diffusive samplers are commonly used in environmental monitoring for evaluating time-averaged air concentrations of gaseous pollutants. They take advantage of molecular diffusion and of the use of a specific adsorbent support? to accumulate volatiles from the air parcels they are exposed to. The dosimeters we used in this work (Inorganic Mercury Passive Samplers by SKC, Inc.) have an equivalent air uptake rate of 0.02 l min⁻¹ (at $T = 20^{\circ}\text{C}$ and $P = 101\text{ kPa}$), and employ a solid sorbent (Hydrar®), which has an irreversible Hg-specific affinity. In this application, 5 diffusive samplers were installed along the crater’s rim, and about 50–70 cm from NK1–2 fumaroles (Fig. 1). A pas-

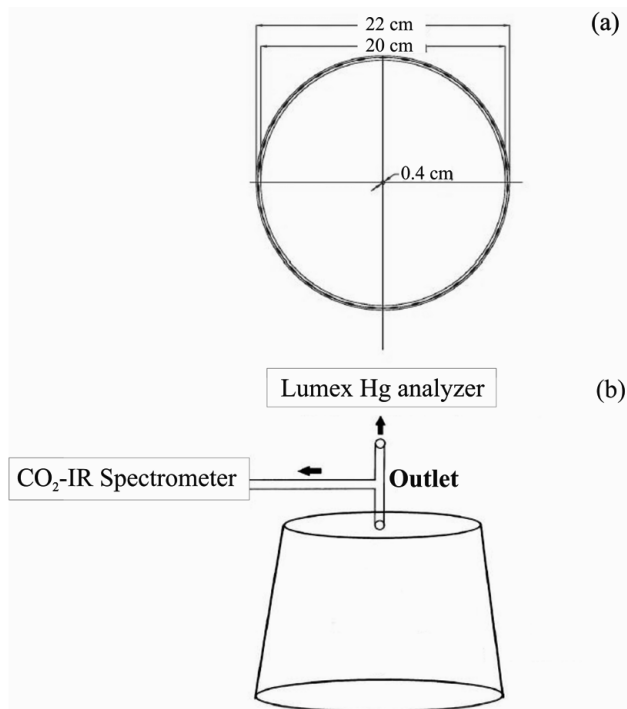


Fig. 2. Schematic representations of the DFC (Diffusive Flux Chamber) used in this study according to the scheme proposed by Eckley *et al.* (2010).

sive sampler was also located outside the degassing area to estimate background levels. After an exposition period of about 3 days (which corresponds to a total sampled air volume of $\sim 0.08 \text{ m}^3$), samplers were carefully re-collected and stored in sealed plastic bags until measurement; adsorbed mercury was estimated by a direct analyzer (Milestone DMA-80), which uses the principle of thermal decomposition, amalgamation and atomic absorption, in operation at IAMC-CNR (Capo Granitola).

Multi-GAS measurements

The concentrations of major volcanogenic constituents in the fumarolic plumes of Nea Kameni were monitored by using the custom INGV-type Multi-component Gas Analyzer System (MultiGAS) previously described in Aiuppa *et al.* (2010, 2011). Gas was drawn into the sampler (using an air pump) at 1.2 lpm through a $1 \mu\text{m}$ Teflon membrane particle filter, and pumped through a $\text{CO}_2/\text{H}_2\text{O}$ gas detector (Licor LI-840 NDIR closed-path spectrometer) and a series of electrochemical sensors for SO_2 (0–200 ppm; 3ST/F electrochemical sensor by City Technology Ltd.), H_2S (0–50 ppm; EZ3H electrochemical sensor by City Technology Ltd.) and H_2 (0–200 ppm; EZT3HYT electrochemical sensor “Easy Cal” City Technology Ltd.) detection. The sensors were housed in a weather-proof box mounted on a backpack frame, and

were calibrated, before and after fieldwork, with standard calibration gases (200 ppm SO_2 , 50 ppm H_2S , 20 ppm H_2 and 3014 ppm CO_2) mixed with ultrapure nitrogen to provide a range of desired concentrations (Aiuppa *et al.*, 2011). The calibration gases also enabled cross-sensitivity of the H_2S sensor to SO_2 to be evaluated.

The 0.5 Hz acquisition frequency of the MultiGAS allowed us to monitor short-lived changes in gas compositions, and to study the effects of mixing fumarolic gases with background air.

Soil GEM flux measurements

Mercury soil fluxes were determined using a custom-made field chamber built according to the scheme proposed by Eckley *et al.* (2010) (Fig. 2). The field chamber was used in conjunction with a RA-915+ Lumex Hg vapor analyzer and an IR-Spectrometer (Crowcon Triple Plus+) for co-determining Hg and CO_2 concentrations. Measurements were performed at five sites located at variable distances from one of the most representative CO_2 -rich fumaroles of the studied system (NK1 fumarole; see black diamonds in Fig. 1). The 3 liter chamber consisted of a polycarbonate body with a major radius of $\sim 10 \text{ cm}$. The Lumex unit and the CO_2 -IR spectrometer attached to the chamber were used to sample air inside the chamber, and then to acquire GEM and CO_2 concentration data every 30 sec.

RESULTS

Composition of Nea Kameni's fumaroles

The simultaneous acquisition of CO_2 , H_2S , SO_2 , H_2O and H_2 by the MultiGAS (Aiuppa *et al.*, 2005, 2007, 2011; Shinohara *et al.*, 2003) allowed us to characterize the abundance of major species in the fumarolic plumes, and therefore examine the relationship between atmospheric GEM concentrations and volcanogenic volatiles (Fig. 3). Our results confirm (Suárez Arriaga *et al.*, 2008; Vougioukalakis and Fytikas, 2005) a distinct hydrothermal nature for Nea Kameni fumaroles, which compositions are dominated by H_2O , CO_2 and H_2 , with minor H_2S (and SO_2 typically absent). The fumaroles measured during this survey are characterized by low fluxes and temperatures ($< 70^\circ\text{C}$), suggesting water condensation processes are occurring within the fumaroles' conduits (D'Alessandro *et al.*, 2010): these would justify the prevailing low $\text{H}_2\text{O}/\text{CO}_2$ ratios (1–4, Table 1). Alternatively, a magmatic source particularly rich in carbon could be invoked (a possible, but less likely, case). All the fumaroles exhibit very low sulphur contents (mean atmospheric H_2S concentration of $\sim 10^2 \text{ ppb}$) with $\text{CO}_2/\text{H}_2\text{S}$ molar ratios ranging from 194 to 9268, suggesting extensive scrubbing of sulphur by reaction/condensation in the conduit system. Hydrogen is a significant component of

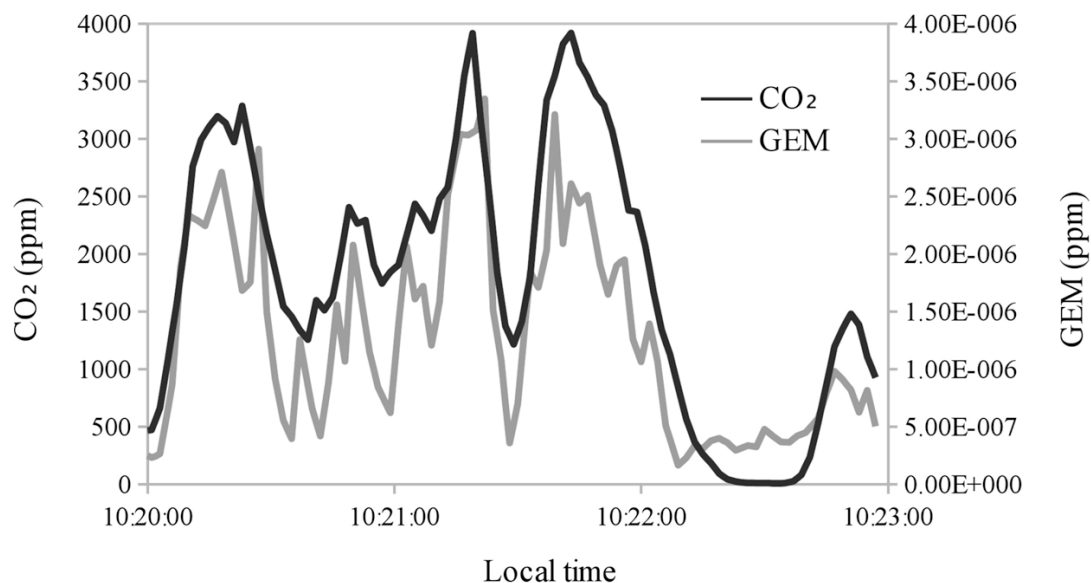


Fig. 3. Example of temporal variations in CO_2 (black line) and GEM (grey line) measured with Multi-GAS and Lumex, respectively, at Nea Kameni fumarolic field. The positive temporal correlation exhibited by the two species may support CO_2 as potential gas carrier in transporting GEM in magmatic systems.

Table 1. Molar ratios (mass ratio in brackets below) of the major chemical species measured in the Nea Kameni's fumaroles

Fumaroles	Temperature ($^{\circ}\text{C}$)	$\text{CO}_2/\text{H}_2\text{S}$ molar (mass)	$\text{H}_2\text{O}/\text{CO}_2$ molar (mass)	$\text{H}_2/\text{H}_2\text{O}$ molar (mass)
NK1	70	8853 (11457)	2.2 (0.9)	1.85×10^{-3} (2.06×10^{-4})
NK2	63	194 (251)	2.8 (1.1)	1.61×10^{-2} (1.79×10^{-3})
NK3	60	5430 (7028)	3.4 (1.4)	2.04×10^{-3} (2.27×10^{-4})
NK4	61	5927 (7670)	1.8 (0.7)	3.08×10^{-3} (3.42×10^{-4})
NK5	57	8553 (11068)	1.2 (0.5)	4.11×10^{-3} (4.57×10^{-4})
NK6	77	9268 (11994)	1 (0.4)	4.11×10^{-3} (4.57×10^{-4})

the fumarolic gases, resulting in very high atmospheric concentrations (up to ~ 70 ppm) and $\text{H}_2/\text{H}_2\text{O}$ molar ratio ranging from 2.1×10^{-3} to 1.7×10^{-2} . These ratios are higher (up to two orders of magnitude) than those previously estimated at other closed-conduit volcanoes worldwide (White Island, 8.9×10^{-4} , Giggenbach, 1987; Mutnovsky, 2.1×10^{-4} , Zelenski and Taran, 2011; Vulcano Island, 8.9×10^{-4} , Chiodini *et al.*, 1991).

Among the fumaroles, those located along the rim (NK1 and NK2) are the most representative of the fumarolic system in terms of chemical composition, since

they are characterized by somewhat higher and more stable emissions. During our survey, NK1 and NK2 fumaroles displayed strong variations in their CO_2 and H_2 compositions, exhibiting $\text{CO}_2/\text{H}_2\text{S}$ ratios of 8853 and 194 and $\text{H}_2/\text{H}_2\text{O}$ ratios of 1.9×10^{-3} and 1.7×10^{-2} , respectively (Table 1).

Active sampling of GEM in Nea Kameni's fumaroles

Gaseous elemental mercury (GEM) concentrations in fumarolic plumes of Nea Kameni were detected at 2s intervals using the Lumex RA-915+. At each fumarole,

Table 2. Concentrations of GEM and molar ratios (mass ratio in brackets below) measured in the fumarolic gases at Nea Kameni using Multi-GAS and a portable mercury analyzer. GEM concentrations are reported as ng m^{-3}

Fumaroles	GEM mean (range)	GEM/CO ₂ molar (mass)	GEM/H ₂ S molar (mass)	GEM/H ₂ molar (mass)	GEM/H ₂ O molar (mass)
NK1	27.4 (9–121)	4.3×10^{-10} (1.96×10^{-9})	8.5×10^{-6} (5.0×10^{-5})	7.06×10^{-8} (7.08×10^{-6})	2.7×10^{-10} (3.01×10^{-9})
NK2	24 (8.9–66)	7.34×10^{-10} (3.35×10^{-9})	6.27×10^{-6} (3.70×10^{-5})	1.21×10^{-7} (1.21×10^{-5})	2.45×10^{-10} (2.73×10^{-9})
NK3	4.8 (4.5–13.5)	2.23×10^{-10} (1.02×10^{-9})	1.76×10^{-6} (1.04×10^{-5})	1.2×10^{-7} (1.20×10^{-5})	5.58×10^{-11} (6.21×10^{-10})
NK4	32.7 (8.3–64.8)	4.32×10^{-10} (1.97×10^{-9})	3.14×10^{-6} (1.85×10^{-5})	4.86×10^{-8} (4.87×10^{-6})	8.3×10^{-11} (9.25×10^{-10})
NK5	19 (9.6–43)	3.16×10^{-10} (1.44×10^{-9})	2.72×10^{-6} (1.60×10^{-5})	4.81×10^{-8} (4.82×10^{-6})	6.44×10^{-11} (7.17×10^{-10})
NK6	35.5 (9.3–79)	4.2×10^{-10} (1.91×10^{-9})	2.0×10^{-6} (1.18×10^{-5})	4.96×10^{-9} (4.21×10^{-8})	6.8×10^{-11} (7.57×10^{-10})

measurements were performed placing the instrument’s inlet close to (a few centimeters from) the emitting vent, to reduce mixing with air. During the survey, we recorded an averaged wind speed of about 10 km/h and an air temperature of about 20°C. Background GEM concentrations were measured several times during the field survey with the Lumex at site NKB, located upwind from the fumarolic gases (Fig. 1).

Our Lumex measurements were able to detect pulsed sequences of GEM increase in the fumaroles’ atmospheric plumes (Fig. 3). These GEM pulses were closely matched by parallel increases in CO₂, as illustrated in Fig. 3, supporting a volcanic origin for our measured GEM.

The highest GEM concentrations were detected in the plume of NK1 fumarole, with peaks of up to ~121 ng GEM m⁻³ (Table 2). Exposure to fumarolic gases was not continuous at each sample location. Occasionally, gases moved away from the instrument inlet due to changing wind directions, leading to variability in GEM concentration ranges (Table 1). In addition, all the investigated fumaroles displayed weak plumes, such that measurements were influenced by variations in the extent of dilution with background air as wind patterns changed randomly and rapidly. This notwithstanding, the measured GEM concentrations remained typically above background GEM levels measured at Santorini (~4 ng GEM m⁻³, see Table 1) and in other remote areas (~1.5–2 ng GEM m⁻³; Ebinghaus *et al.*, 1999).

The GEM concentrations derived from the real-time measurements at Nea Kameni correlate well with the real-time sensed H₂S, CO₂ and H₂ concentrations at all the active vents, as illustrated in Fig. 4. The plots shown in Fig. 4 were produced after applying a lag correction to the initial data to account for differences between the

Lumex and MultiGAS measurements: the Lumex signal typically lags behind CO₂ and H₂O signals by 4 s; while the hydrogen signal lags behind GEM by 8 s. The obtained scatter plots were then used to derive characteristic GEM/gas ratios in fumarolic plumes (from the gradient of the best-fit regression lines).

In detail, the scatter plot of Fig. 4a demonstrates a high correlation between CO₂ and GEM measurements acquired during the survey ($r^2 = 0.7–0.8$). The estimated mean GEM/CO₂ molar ratios range from 2.23×10^{-10} (mass ratio: 1.02×10^{-9}) for NK3 fumarole, to 7.34×10^{-10} (mass ratio: 3.35×10^{-9}) for NK2 fumarole (Table 2). Our measured GEM/CO₂ mass ratios are comparable to those obtained in other low-temperature volcanic-hydrothermal systems, such as Tatun volcanic field (GEM/CO₂ from 4 to 40×10^{-8} ; Witt *et al.*, 2008a), and the low-T (85°–150°C) CO₂-rich fumaroles of Masaya volcano (GEM/CO₂ from 0.1 to 1.9×10^{-8} ; Witt *et al.*, 2008b). Measurements at the far higher-temperature (250°C) fumaroles of La Fossa Crater, Vulcano island, indicated GEM/CO₂ mass ratio of 6.0×10^{-8} (Aiuppa *et al.*, 2007). Our data are also close to those reported by Engle *et al.* (2006) for the fumaroles at Yellowstone Caldera, a hydrothermal system with temperatures ranging from 85° to 95°C and in the presence of H₂S (1.6 to 2.6×10^{-9} ; Engle *et al.*, 2006).

We also find positive correlation between H₂S and GEM ($r^2 \sim 0.6$; Fig. 4d) for each of the investigated fumaroles, and estimate an averaged GEM/H₂S molar ratio for the fumarolic field of 4.06×10^{-6} (mass ratio: 2.4×10^{-5} ; Table 2). Our GEM/S data are consistent with compositions quoted by Varekamp and Buseck (1986) in their global inventory of passive emissions from non-erupting volcanoes (3.7×10^{-6}), and fall within the best-

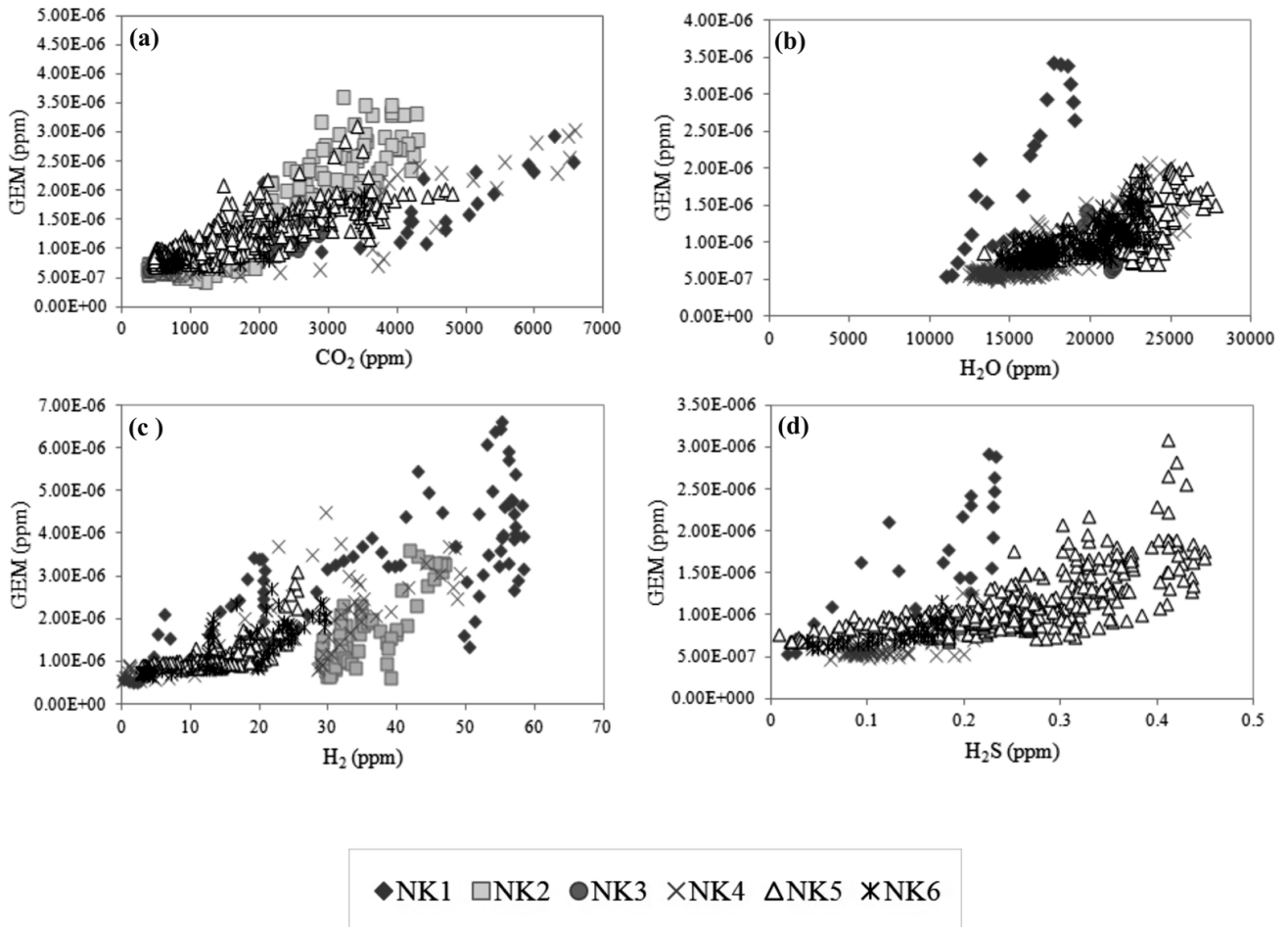


Fig. 4. Gaseous Elemental Mercury (GEM) concentrations recorded at Nea Kameni's fumaroles plotted against simultaneously measured concentrations of (a) CO_2 ($r^2 = 0.7\text{--}0.8$), (b) H_2O ($r^2 = 0.6\text{--}0.8$), (c) H_2 ($r^2 = 0.7$), and (d) H_2S ($r^2 = 0.6$). Data have been corrected for differential signal lag times existing between Lumex and MultiGAS acquisition: GEM signal lags behind the CO_2 and H_2O signals 4 s; while the hydrogen signal lags behind the GEM 8 s.

estimated range (10^{-4} to 10^{-6}) of compositions of non-explosive volcanic gas emissions (Pyle and Mather, 2003). The range of literature GEM/S ratios in volcanic exhalations is in fact much broader, between 10^{-2} and 10^{-5} (Bagnato *et al.*, 2011; Ballantine *et al.*, 1982; Varekamp and Buseck, 1981; Buat-Menard and Arnold, 1978). Part of this GEM/S variability may reflect differences in the composition of degassing magmas, or the temperature dependence of volcanic gas chemistry (Bagnato *et al.*, 2007; Martin *et al.*, 2006). Previous research has shown that gaseous elemental mercury (GEM) may leave the magma in the early stages of degassing, and that early CO_2 escape from magmas may serve as a carrier gas for mercury, leading to high GEM/S ratios before eruptions (Varekamp and Buseck, 1981, 1986). Gas reactions with wall-rocks and steam condensation can also affect GEM/S ratios: previous works has demonstrated a large GEM affinity for steam condensate in the fumarolic

environment, which implies that formation of even small amounts of liquid prior to sampling can deplete the mercury content of residual gases significantly (Bagnato *et al.*, 2009a, b; Aiuppa *et al.*, 2007). In this occasion, we did not attempt measurement of GEM concentration in fumarolic steam condensates, so we cannot exclude that our derived mercury emissions are under-estimating the real emissions to some extent.

Temporal and spatial variations of GEM/ H_2 molar ratios in volcanic emissions may represent potentially excellent tracers of processes which operate in deep magmatic systems, due to low solubility in groundwaters and hydrothermal fluids of both species (Giggenbach, 1987; Aiuppa *et al.*, 2011). GEM and H_2 also have relatively inert atmospheric behavior over typical timescales of volcanic gas release and atmospheric transport. For Santorini, we estimate average a GEM/ H_2 molar ratio of 6.81×10^{-8} (mass ratio: 6.83×10^{-6} , Table 2). It is our

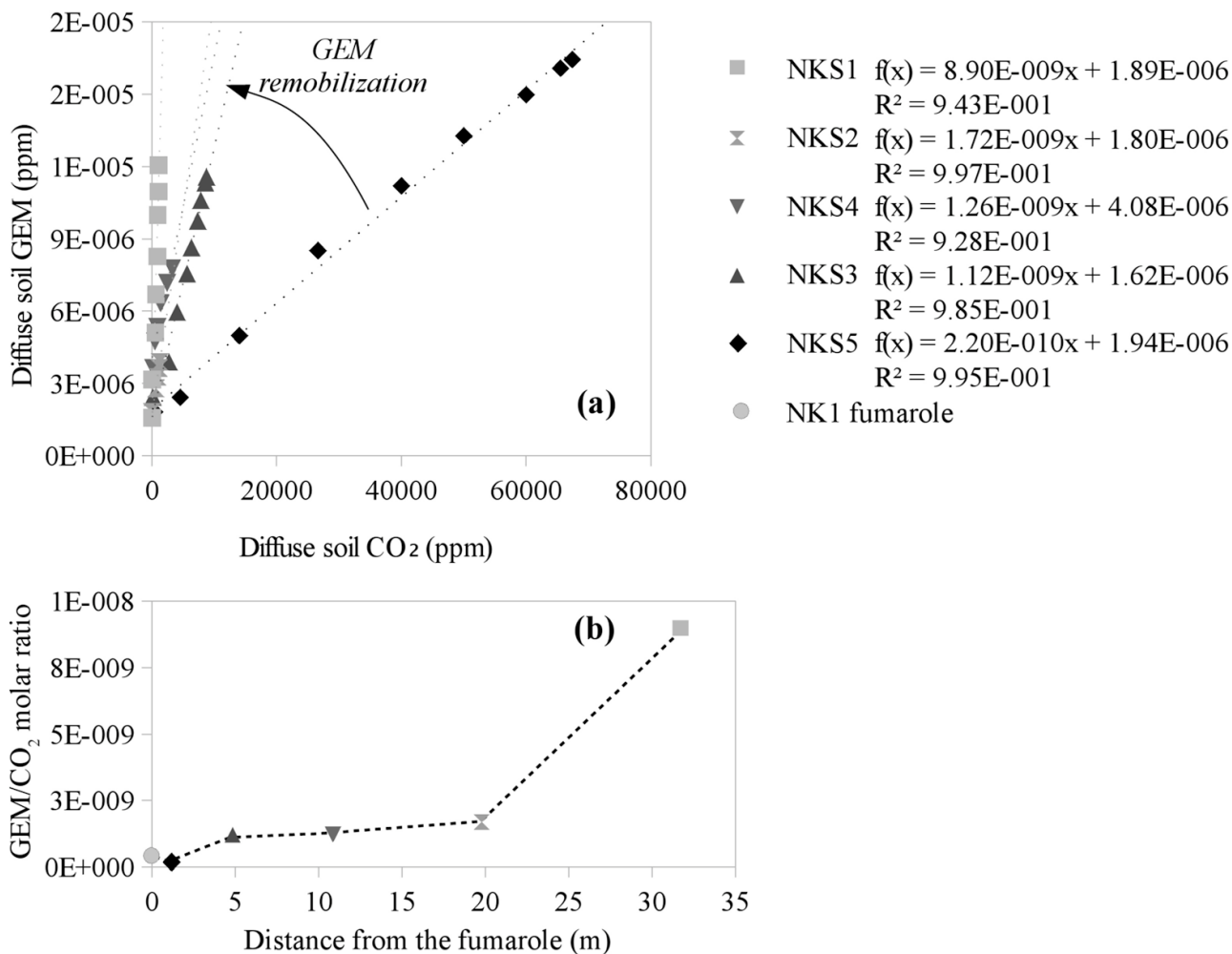


Fig. 5. Scatter plots showing (a) the positive correlation found at each sites ($r^2 = 0.9$) between CO_2 and GEM degassed from soil: the higher correlation found at the NKS5 site suggests CO_2 as the potential carrier gas of GEM at this site. The higher slopes (that is GEM/ CO_2 ratios) exhibited by the regression lines referring to the other sites (NKS1–4) probably reflect the contribution to our soil diffuse degassing measurements of further Hg, derived from remobilization of previously deposited GEM to the ground enhanced by solar irradiation; (b) the variation of the slope of the regression line with distance from the NK1 fumarole (gray circle).

understanding that these results represent the first measured GEM/ H_2 ratios in a volcanic fumarole's plume.

Passive sampling of GEM in Nea Kameni's fumaroles

Analysis of the solid sorbent of the exposed diffusive samplers revealed GEM concentrations ranging from ~ 14 to 30 ng m^{-3} . These values are in the same range as those measured by Lumex-RA 915+ (active sampling) at comparable distances from fumaroles (Table 2), offering mutual validation for the two independent techniques. The passive sampler sited outside the fumarolic area yielded a GEM concentration of $\sim 5 \text{ ng m}^{-3}$, which agrees well with background mercury levels detected by Lumex active measurements at same site ($\sim 4 \text{ ng m}^{-3}$; Table 2).

Soil GEM flux

Published Hg emission estimates from volcanic areas are based on measurement of either hydrothermal/magmatic gas emissions or Hg fluxes from substrate, while combined observations of both are lacking (Varekamp and Buseck, 1986; Nakagawa, 1999; Gustin, 2003). From our accumulation chamber measurements, we find, at each soil measurement site, a strong positive ($r^2 > 0.9$) correlation between GEM and CO_2 (Fig. 5a). Our derived soil GEM/ CO_2 molar ratios range from 3.3×10^{-9} to 3.9×10^{-8} (average: 2.2×10^{-8}), and are therefore up to 1–2 orders of magnitude higher than in the fumaroles (characteristic GEM/ CO_2 molar ratio of $\sim 10^{-10}$; Fig. 5b and Table 2): this suggests an additional Hg contribution from

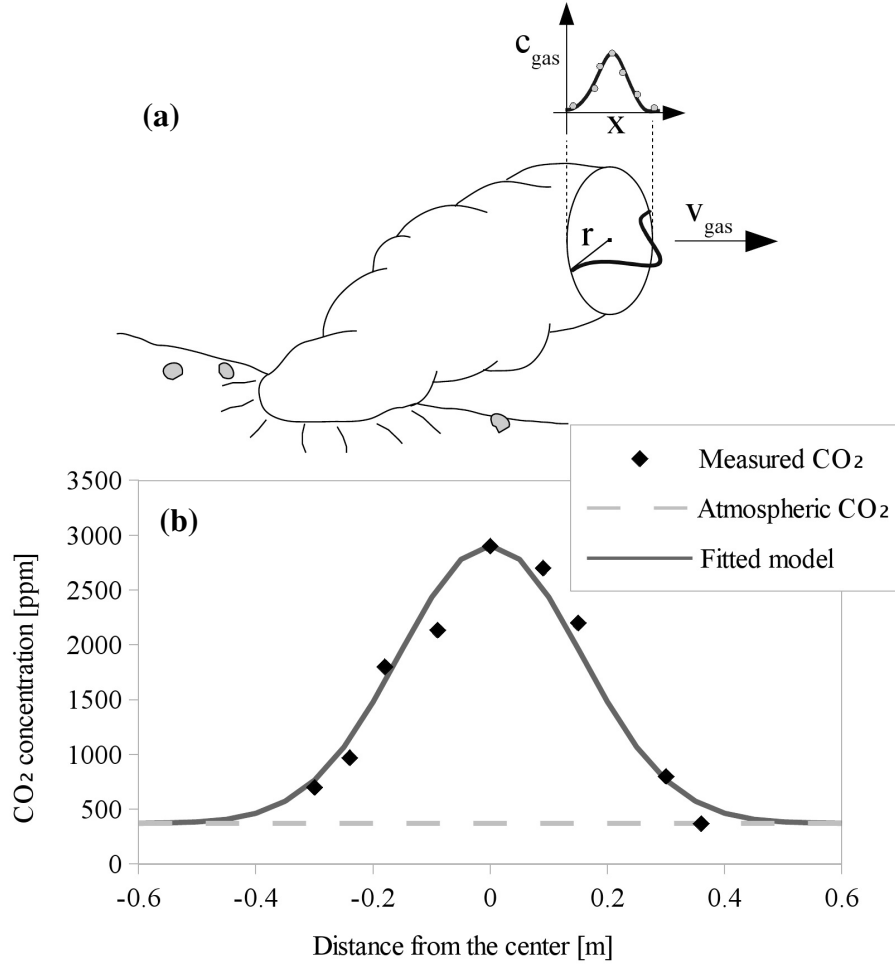


Fig. 6. (a) Schematic illustration of the fumarole section used for the model; (b) CO_2 concentrations (black squares) measured at different distances from the central part of the NK1 fumarolic plume. Dark line indicates the best fit models for CO_2 concentrations profile related to plume radius of 0.22 m.

a secondary (non-fumarolic) source. This is further supported by that the fact that GEM/ CO_2 ratios increase with distance from fumarolic vents (the case of NK1 fumaroles is illustrated in Fig. 5b). The temperature of gas will increase drastically moving from soil (ambient temperature) to fumaroles (up to 70°C , Fig. 1b), and we argue that these different temperature environments may have a role in controlling the patterns of Hg release. In the soil system, remobilization of previously deposited Hg will take place during the daylight hours, when solar irradiation promotes photochemical reduction reactions (Zhang *et al.*, 2001; Witt *et al.*, 2008b; Fu *et al.*, 2008; Engle *et al.*, 2006; Gustin, 2003), a process that could well justify the increased soil GEM/ CO_2 ratios (relative to fumaroles). Emission of this secondary (re-mobilized) GEM from soil will likely be suppressed upon approaching the fumaroles, because the higher thermal flux prevailing there will act

against development of Hg deposition/re-volatilization cycles: at site NKS5, the closest to NK1 fumarole, we obtain a low GEM/ CO_2 ratio, in all similar to the fumarolic ratio (Fig. 5b).

From data shown in Figs. 5a and b, mercury soil flux emissions were calculated from relation (1):

$$F_{\text{GEM}} = Q(C_o - C_i)/A \quad (1)$$

where F_{GEM} is the GEM total emission rate per and unit area and time ($\text{ng m}^{-2} \text{sec}^{-1}$); $(C_o - C_i)$ is the difference in GEM concentrations in air exiting (C_o) and entering (C_i) the chamber (ΔC) (in ng m^{-3}); A is the area of the chamber in m^2 ; and Q is the flow rate of ambient air flowing through the chamber (in $\text{m}^3 \text{sec}^{-1}$). In order to calculate a flux, the concentration differential used in the flux calculation must be greater than the system blank, which we

Table 3. List of published total mercury flux estimates ($t\ yr^{-1}$) from various quiescent closed-conduit volcanoes in Solfatara stage of activity. Mercury flux from Nea Kameni's fumaroles (this study) is also reported

Volcano	ΦHg ($t\ yr^{-1}$)	Reference
La Soufriere (Guadeloupe)	8×10^{-4}	Bagnato <i>et al.</i> , 2009a
Vulcano Island (Aeolian Arc)	4×10^{-4} – 7×10^{-3}	Aiuppa <i>et al.</i> , 2007
La Solfatara (Pozzuoli Bay)	7×10^{-3}	Bagnato <i>et al.</i> , 2009b
Tatun Field (Taiwan)	5×10^{-3} – 5×10^{-2}	Witt <i>et al.</i> , 2008b
Masaya's low T fumaroles (Nicaragua)	1.57×10^{-4}	Witt <i>et al.</i> , 2008a
Yellowstone Caldera (Wester United States)	2×10^{-4} – 1.6×10^{-3}	Engle <i>et al.</i> , 2006
Lassen Volcanic Center (Wester United States)	9×10^{-2} – 1.4×10^{-1}	Engle <i>et al.</i> , 2006
Kilauea's fumaroles (Hawaii)	1.5×10^{-3}	Varekamp and Buseck, 1986
Colima's fumaroles (Mexico)	4.4×10^{-1}	Varekamp and Buseck, 1986
Nea Kameni's fumaroles (Greece)	2.56×10^{-7}	This work
Cumulative Hg flux	0.54–0.65	

determined based on the ΔC difference measured while the chamber was situated on a clean surface (a clear polycarbonate plate in our case). We find a system blank value ($GEM_{\text{blank}} \sim 0.13\ \text{ng}\ \text{m}^{-3}$) in agreement with those reported in literature ($\sim 0.2\ \text{ng}\ \text{GEM}\ \text{m}^{-3}$; Gustin *et al.*, 1999; Eckley *et al.*, 2010; Engle *et al.*, 2006). These measurements, thought limited to only five investigated sites, allow us to make a first order assessment of diffuse GEM emissions from soils, which we infer are in the range of 1.3 – $4.8 \times 10^{-2}\ \text{ng}\ \text{m}^{-2}\ \text{s}^{-1}$ (~ 47 – $173\ \text{ng}\ \text{m}^{-2}\ \text{h}^{-1}$). These values are similar to those proposed by Engle *et al.* (2006) for the substrates of the Lassen Volcanic Center hydrothermal system (range: 12 – $271\ \text{ng}\ \text{m}^{-2}\ \text{h}^{-1}$) and the Yellowstone Caldera (range: 83 – $140\ \text{ng}\ \text{m}^{-2}\ \text{h}^{-1}$).

DISCUSSION

Our measurements add a new piece of information to the growing puzzle of mercury emission inventories from active volcanism. While it has long been known that volcanoes are important atmospheric sources of mercury (Varekamp and Buseck, 1981, 1986; Bagnato *et al.*, 2007, 2009a, 2009b, 2011), considerable uncertainty still remains over the magnitude of such global volcanic mercury flux, the available data on volcanogenic Hg emissions still remaining sparse and incomplete (Pyle and Mather, 2003).

Past estimates of gaseous mercury fluxes from fumarolic systems have generally taken the approach of scaling relationships between averaged GEM/sulfur ratios in gas emissions and sulfur fluxes (Aiuppa *et al.*, 2007; Bagnato *et al.*, 2007, 2011; Witt *et al.*, 2008a, b; Varekamp and Buseck, 1986; Engle *et al.*, 2006). However, the very low S fluxes (virtually immeasurable by UV-based remote sensing techniques) make this method-

ology useless at Nea Kameni, requiring the use of alternative techniques.

An attempt is made here to quantify gas fluxes from the MultiGAS-derived gas concentrations in the fumarolic plumes' cross-sections. The principle of the technique is illustrated in Fig. 6, which shows the results of the in-plume CO_2 measurements done about 50 cm downwind the active NK1 fumarolic vent. Measurements were operated by sequentially rotating the instrument inlet to capture plumes at a range of orthogonal distances from the central core of the fumarole's plume. Under such conditions, we measured a peak CO_2 concentration of ~ 2900 ppm in the plume's center, and close to background concentrations at the plume's margin; background CO_2 concentrations in the ambient atmosphere (~ 370 ppm) were obtained by taking out of plume measurements upwind of the vents prior to and after each acquisition, and were subtracted from each data set to obtain background corrected (excess) CO_2 concentrations. By assuming a Gaussian distribution for the vertical and crosswind dispersion of a plume (Sutton, 1947a, b; Beychok and Milton, 2005; Lewicki *et al.*, 2005), it was possible to fit the measured CO_2 concentration profiles with a model line (Fig. 6), obtained from the following equation:

$$\text{CO}_{2,\text{calc}} = (\text{CO}_{2,\text{max}} - \text{CO}_{2,\text{atm}})\exp(-(x/r^2)) + \text{CO}_{2,\text{atm}} \quad (2)$$

where, x is the distance from the center of the fumarolic plume, r is the radius of the fumarole section at the sampling point (Fig. 6), $\text{CO}_{2,\text{max}}$ is the highest concentration measured (2904 ppm) and $\text{CO}_{2,\text{atm}}$ is the atmospheric background value (~ 370 ppm). The model curve shown in Fig. 6 was obtained from relation (2) by fixing the radius of fumarolic plume's section at 0.22 m (for which we obtain the best fit between model and observations).

CO₂ vs. x functions were integrated over the total plume section (0.5–0.8 m) to get the total volcanogenic CO₂ amount in a cross-section of the fumarole (6.95×10^{-4} kg m⁻¹), which we then multiplied by the gas transport speed (~ 1 m s⁻¹) to derive a CO₂ flux (~ 0.06 t d⁻¹).

In order to calculate the total gas flux from Nea Kameni, we extended the same procedure to all the fumaroles present, and estimated a total volcanogenic CO₂ flux of ~ 0.24 t d⁻¹ (or 86 t yr⁻¹). This, used in tandem with the above estimated GEM/CO₂ mass ratio for each fumarole (range 1.02×10^{-9} to 3.35×10^{-9} ; Table 2), corresponds to a total fumarolic mercury flux of 7×10^{-10} t d⁻¹ (or $\sim 2.56 \times 10^{-7}$ t yr⁻¹; Table 3).

With the numbers above, our calculations here suggest that the Nea Kameni's contribution to the global volcanic non-eruptive mercury flux is small. The global volcanic budget is dominated, in fact, by persistently degassing open-vent volcanoes such as Etna (5.4 t yr⁻¹; Bagnato *et al.*, 2007), Masaya (7.2 t yr⁻¹; Witt *et al.*, 2008a), Myakejima island (9 t yr⁻¹; Bagnato *et al.*, 2007) and others (see Pyle and Mather, 2003; Bagnato *et al.*, 2011).

Our above-estimated fumarolic CO₂ flux is orders (from 2 to 3) of magnitude lower than the soil CO₂ diffuse flux from Nea Kameni degassing, evaluated in the 90 s by Chiodini *et al.* (1998) (range: 2983–21498 t yr⁻¹), and, more recently, by Parks *et al.* (2013) in 2012 (range: 11680–16060 t yr⁻¹). This suggests that soil degassing can represent a substantial fraction of emitted GEM, too. An initial estimate of this soil GEM flux can be obtained in the crude assumption that our measured soil GEM fluxes ($1.3\text{--}4.8 \times 10^{-2}$ ng m⁻² s⁻¹; cfr. 3.3) can be extrapolated to the whole fumarolic area of Nea Kameni islet (~ 0.02 km²), to calculate a total soil diffusive GEM flux of 0.008 to 0.03 t yr⁻¹. This estimated flux, while supporting the idea of a soil mercury contribution likely overwhelming the fumarolic flux, is admittedly incomplete and inaccurate in light of the small number ($n = 5$) of measurements available: these would hardly account for the extreme heterogeneity of degassing regimes normally encountered in volcanic soil environments (Chiodini *et al.*, 1998).

In light of the above, we find more realistic to build our soil mercury flux budget estimate upon the combination of our measured GEM/CO₂ mass ratios in soil air (10^{-8} – 10^{-7}) with the Parks's *et al.* (2013) CO₂ flux estimate of 11680–16060 t yr⁻¹, the more recent measurements (January 2012) performed at Nea Kameni to date. This procedure leads to a more conservative soil mercury flux estimate in the range of 0.0002 and 0.002 t yr⁻¹, where both the volcanogenic Hg and the combined volcanogenic + re-mobilized Hg emission have been considered, respectively. Of course, it is difficult to estimate a net total Hg flux from soil diffuse degassing at Nea Kameni vol-

cano with the field chamber due to the combination of diffuse Hg-bearing magmatic gas flow through the soil and re-mobilization of Hg previously deposited to the substrates.

We conclude from the calculations above that, even when the GEM flux sustained by soil diffuse degassing is considered, the contribution of Nea Kameni to the global volcanic GEM budget remains trivial. Our above-estimated fumarolic GEM flux (2.56×10^{-7} t yr⁻¹) is about two orders of magnitude lower than the GEM flux usually reported for closed-conduit volcanoes in fumarolic-stage of activity (GEM flux range: 0.0008–0.4 t yr⁻¹; Table 3). Fumarolic degassing from Nea Kameni would therefore account for a very few % of the yearly global volcanic GEM emissions into the atmosphere (~ 700 t yr⁻¹ Varekamp and Buseck, 1986), and of mercury being annually contributed by passively degassing volcanoes globally (~ 75 t yr⁻¹; Pyle and Mather, 2003). While marginal at global scale, our derived GEM budget for Nea Kameni remains the first available estimate of background emissions from this dormant volcano, to date; also in light of the recent (started in 2011) seismic and geodetic evidences of unrest at Santorini Caldera, our measurements here will contribute to identifying and understanding any future evolution of the volcanic-hydrothermal system.

CONCLUSIONS

Passively degassing volcanoes are fascinating natural laboratories in which to investigate a large variety of interesting atmospheric processes. We present the first real-time simultaneous measurements of GEM, H₂S and CO₂ concentrations in fumarolic emissions at Nea Kameni volcano, and have evaluated the characteristic GEM/CO₂ and GEM/H₂S (mass) ratios for this volcanic system at $\sim 10^{-9}$ and $\sim 10^{-5}$, respectively. By using the above GEM/CO₂ mass ratio in tandem with our derived fumarolic CO₂ flux, we have obtained a total fumarolic mercury flux of $\sim 2.56 \times 10^{-7}$ t yr⁻¹, representing only a small fraction of the global volcanic mercury emissions into the atmosphere. These flux estimates will aid the identification/interpretation of any change in the degassing dynamics of this quiescent, but potentially hazardous, volcano.

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