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Notes

Mercury fluxes from volcanic and geothermal sources: an update

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Abstract: We review the state of knowledge on global volcanogenic Hg emissions to the atmosphere and present new data from seven active volcanoes (Poás, Rincón de la Vieja, Turrialba, Aso, Mutnovsky, Gorely and Etna) and two geothermal fields (Las Pailas and Las Hornillas). The variability of Hg contents (*c.* 4–125 ng m^{-3}) measured in gaseous emissions reflects the dynamic nature of volcanic plumes, where the abundances of volatiles are determined by the physical nature of degassing and variable air dilution. Based on our dataset and previous work, we propose that an average Hg/SO_2 plume mass ratio of *c.* 7.8×10^{-6} ($\pm 1.5 \times 10^{-6}$; 1 SE, $n = 13$) is best representative of open-conduit quiescent degassing. Taking into account the uncertainty in global SO_2 emissions, we infer a global volcanic Hg flux from persistent degassing of *c.* 76 ± 30 t a^{-1}. Our data are derived from active volcanoes during non-eruptive periods and we do not have any direct constraint on the Hg flux during periods of elevated SO_2 flux associated with large-scale effusive or explosive eruptions. This suggests that the time-averaged Hg flux from these volcanoes is even larger if the eruptive contribution is considered. Conversely, closed-conduit degassing and geothermal emissions contribute modest amounts of Hg.

A significant amount of heavy metals is emitted into the atmosphere from natural (volcanoes, soil, seawater, etc.) and anthropogenic (industrial and mining activities, fossil fuel combustion, etc.) sources. Volatile emissions in passively or eruptive magmatic degassing volcanoes, fumaroles and geothermal fields influence the composition of the atmosphere and global climate, and impact the biogeochemical cycles of a number of trace elements (e.g. Robock & Oppenheimer 2003; Wallace 2005). Knowledge of the contribution of volcanic degassing systems and geothermal fields to the global budgets of heavy metals in the Earth's atmosphere is essential to evaluate the role that the volcanoes play on the reservoir cycling of these elements and the potential fates they could represent once they reach the ecosystems. Volcanic emissions are the major natural source of several trace metals (e.g. As, Cd, Cu, Pb, Zn, Tl, Sb and Sn) to the atmosphere by contributing 20–40% of volatile elements such as Bi, Pb, As or Sb and up to 40–50% of Cd annually (Hinkley *et al.* 1999; Martínez 2008; Mather *et al.* 2012; Henley & Berger 2013). However, current research on trace element emissions from active volcanism shows that the magnitude of some element fluxes is still highly uncertain. This is the case for atmospheric mercury (Hg) which is a key contaminant in biochemical processes as well as in air, water and soils, for which volcanism may be an important natural contributor (Varekamp & Buseck 1986; Nriagu & Becker 2003; Pyle & Mather 2003; Bagnato *et al.* 2007, 2011; Martin *et al.* 2012). In volcanic plume gaseous elemental mercury (Hg^0 or GEM) is the dominant species (≥90%; Slemr *et al.* 1985; Schroeder & Munthe 1998; Bagnato *et al.* 2007; von Glasgow 2010; Martin *et al.* 2011) with an atmospheric lifetime of *c.* 0.5–1 a (Lindqvist and Rodhe 1985; Slemr *et al.* 1985; Lindberg *et al.* 2007; Aryia *et al.* 2008), allowing it to be transported to great distances from the source. The relative proportions of gaseous $Hg^0_{(g)}$ and Hg(II) species in volcanic gas plumes, and the ratio of gaseous to particulate Hg forms, have rarely been determined in a systematic way (Bagnato *et al.* 2007; Witt *et al.* 2008*a*, *b*). Once deposited in surface waters, Hg is assimilated and processed by the biosphere that converts the relatively inert inorganic Hg into toxic methylated forms which can bioaccumulate in the food chain (Morel *et al.* 1998).

The current estimate of Hg emissions from natural processes (primary mercury emissions + re-emissions), is estimated to be 5207 t a^{-1} which represents nearly 70% of the global mercury

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emission budget (Pirrone *et al.* 2010). Overall, the relative contribution of terrestrial surfaces is 2429 t a^{-1} (47% of the total natural emissions) and that from surface waters is 2778 t a^{-1} (53% of the total natural emissions) (Pirrone *et al.* 2010). Significant research has been published over the last 10 years quantifying and demonstrating the importance of emissions from volcanoes and Hg-enriched substrates (>100 ppb Hg) (Friedli *et al.* 2003; Gustin 2003; Pyle & Mather 2003; Bagnato *et al.* 2007, 2011; Gustin *et al.* 2008). Earlier and more recent studies proposed that cataclysmic volcanic eruptions would have the potential to inject volatile Hg into the stratosphere (Delmas *et al.* 1992; Langway *et al.* 1995; Robock & Free 1995; Schuster *et al.* 2002) to change its global and regional cycle for a few years. In contrast, quiescent degassing and moderate eruptions exhale directly into the troposphere and can have long-term effects on local environments.

Regionally, a single persistently active volcano may act as the most important local point source (e.g. SO_2 emissions from Etna volcano, Sicily, to the Mediterranean and Western Europe; Simpson *et al.* 1999; Bagnato *et al.* 2007). However important, there are currently many difficulties in quantifying the Hg flux from volcanic emissions due to the spatial and temporal variability in the activity from one volcano to another (Ferrara *et al.* 2000; Bagnato *et al.* 2011), or from different emission points on the volcano being studied (Dedeurwaerder *et al.* 1982; Bagnato *et al.* 2007). Due to the logistical restrictions of acquiring measurements at volcanoes (difficulty of access, limited power supply, etc.), Hg measurements often only comprise few data points. Two recent reviews narrow down previous estimates of volcanic Hg emission fluxes of 0.6–830 t a^{-1} (Varekamp & Buseck 1986; Nriagu & Pacyna 1988; Ferrara *et al.* 2000) to 90 t a^{-1} and 700 t a^{-1} (Pyle & Mather 2003; Pirrone *et al.* 2010). Volcanic Hg emissions may therefore represent *c.* 4–28% of natural primary emissions (Pirrone *et al.* 2010).

The large variability of these estimates partly reflects the complexity of the chemical and physical processes that Hg undergoes while interacting with the atmosphere. Most of the Hg observations used in previous inventories are derived from spot measurements taken from a few volcanoes, and there is much concern over the different methods in which different authors have attempted to assess Hg fluxes. All of these limitations may explain the large uncertainties in extrapolating data to global Hg emissions. Finally, the knowledge of Hg emissions from geothermal sources is still poorly investigated; they are therefore often considered as a negligible contributor to the atmosphere.

The objective of this work is to extend and refine the currently limited volcanic Hg dataset. We present here new Hg data for seven active volcanoes (Aso, Turrialba, Poás, Rincón de la Vieja, Etna, Gorely and Mutnovsky) and two important geothermal systems (Las Paillas and Las Hornillas, Costa Rica). We evaluate previous work on volcanic Hg fluxes, and combine the new data with the few relevant estimates of Hg fluxes from previous direct measurements on volcanic plumes to develop a realistic assessment of time-averaged volcanic Hg fluxes. Conventional gold-trap sampling and Lumex®/MultiGAS GPS-synchronized surveys were carried out to obtain real-time measurements of Hg and major volatiles in the fumes of the investigated volcanoes. These measurements, the first carried out at such locations, extend previous combined Lumex®/MultiGAS surveys reported elsewhere (Aiuppa *et al.* 2007; Witt *et al.* 2008*a*, *b*; Bagnato *et al.* 2013), and aim at improving our understanding of the magmatic systems and its degassing budget.

Materials and methods

Study areas

Measurements were carried out on the crater rim of seven quiescently degassing volcanoes and in two active geothermal areas with various surface manifestations. The study sites that are reported on here are located together with other locations discussed in the text in Figure 1. Aso volcano, in the central part of Kyushu Island (32° 53′6.36″N, 131° 5′ 7.44″), Japan is an active volcano with a *c.* 20 km diameter caldera that has some post-caldera central cones, including Mt Nakadake, where the current activity is mainly concentrated. The crater contains one of the hottest and most acidic volcanic lakes, with water temperature in the range 40–80 °C and acidity levels of pH −1 to +1 during calm periods (Ohsawa *et al.* 2003, 2010; Terada & Sudo 2012). Low-temperature gases are emitted from the lake surface, and intense active high-temperature gas emissions (approximately 800 °C) are produced by fumaroles on the southern crater wall (Shinohara *et al.* 2010, 2013).

Gorely, Russia (52° 33′28.8″N, 158° 1′48″E) is a Holocene caldera volcano, located at the northern end of the southern segment of the eastern volcanic belt of Kamchatka, *c.* 75 km SW of Petropavlovsk–Kamchatsky. It is one of the most active volcanoes in southern Kamchatka and currently contains an acidic crater lake which often displays persistent fumarolic activity with a steam plume up to several kilometres high on occasion (Kamchatka Volcanic Eruption Response Team, or KVERT). At the time of our campaign (September 2011),

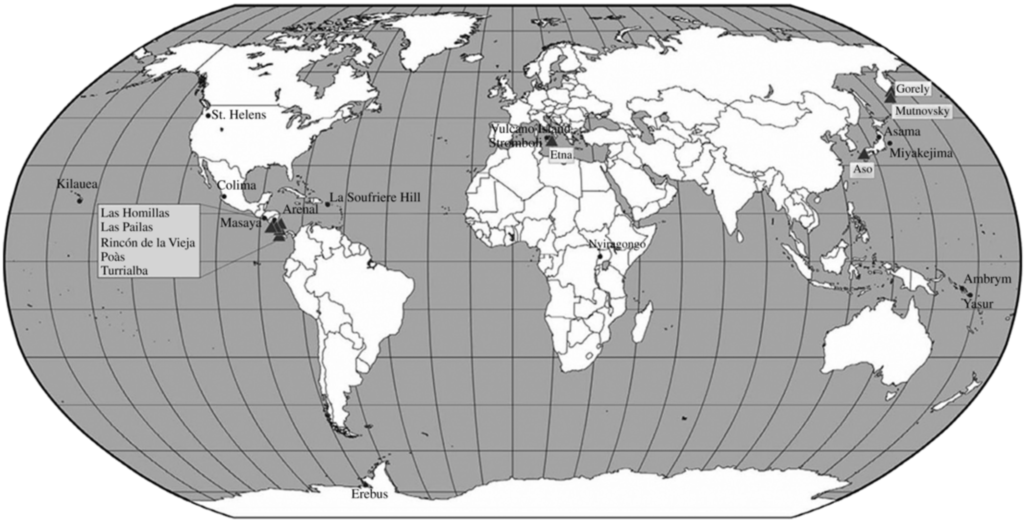

Fig. 1. Locations of the studied volcanoes and geothermal systems for which we reported data on Hg emission rate (black filled triangles), and for which literature data are summarized in Table 2 (black filled circles).

vigorous jet-like degassing was taking place from a hot open vent and hot fractures in the northern wall of the crater.

Mutnovsky volcano (52° 27′20.88″N, 158° 11′ 32.32″) is located in the southern part of the Eastern Volcanic Front of the Kamchatka Peninsula, and has an associated hydrothermal system with magmatic activity (Shishkina *et al.* 2010). There are three individual groups of fumaroles in the Mutnovsky crater which show stable activity for a long period of time: the ‘Active Funnel’ (temperatures exceed 600 °C); the ‘Bottom Field’ (from 100 to 150 °C); and the ‘Upper Field’ (up to 320 °C) (Taran *et al.* 1992). Our investigation focused on the degassing from the first two fumarolic groups.

Mt Etna is the largest volcano in Europe (NE coast of Sicily, south of Italy; 37° 45′18″N, 14° 59′42″E) and one of the most active volcanoes in the world. Its present-day activity consists of persistent passive degassing of magmatic volatiles mostly from the four open vents on the volcano’s summit (North East, Voragine, Bocca Nuova and South East) and diffuse soil emanations (Allard *et al.* 1991), occasionally interrupted by lava emissions associated with paroxysmal terminal to lateral eruptions (Madonia *et al.* 2013; Allard *et al.* 2006).

Poás (10° 12′0″N, 84° 12′0″W) and Turrialba (10° 1′12.23″N, 83° 45′46.92″W) volcanoes, Costa Rica, lie on the Central America Volcanic Front (Carr 1984; Carr *et al.* 2003). Turrialba is a stratovolcano that has seen increased fumarolic activity since 2002, with new fumarolic vents and fractures opening in and outside of the West Crater area in January 2010 and 2012, respectively. From 2007 onwards, after the hydrothermal stage which characterized the fumarolic discharge since at least the 1980s until fall 2001 (e.g. Cheminée *et al.* 1983; Vaselli *et al.* 2010), both the composition and high temperature (up to 800 °C) of the fumaroles indicate that the gases are directly supplied from the magma chamber with only limited interaction with the hydrothermal system.

Poás is an andesitic-basaltic composite volcano about 50 km from the capital San José. Its upper part consists of three distinct eruptive centres roughly aligned NW–SE, including the Main Crater in the middle that hosts a hyper-acidic lake (Laguna Caliente, pH between 1.8 and *c.* 0) (Martínez *et al.* 2000; Melián *et al.* 2007; Martínez 2008). The activity of the lake (Laguna Caliente) is characterized by persistent fumarolic emissions and a long history of sporadic phreatic eruptions, especially since 2006 (Lopes 2005; Martínez 2008).

The Rincón de la Vieja volcanic complex (10° 49′48″N, 85° 19′26″W) is a composite andesitic stratovolcano located in NW Costa Rica, *c.* 25 km from Liberia in the province of Guanacaste and 25 km NW of the Miravalles volcano. It shows a wide range of fluid manifestations (a hyper-acidic crater lake, boiling- and mud-pools, thermal springs and associated gas discharges) (Tassi *et al.* 2005). The fluid vents located inside the Active Crater are likely to represent the most appropriate sampling sites for geochemical surveillance purposes; however, access is fairly difficult due to the steepness of the crater walls.

Las Hornillas and Las Pailas are two important geothermal systems which are part of the Miravalles and Rincón de la Vieja volcanic complexes, respectively (Guanacaste Geothermal Province, Costa Rica). Both show surface manifestations such as vapour discharges from fumaroles and steam-heated pools. Las Hornillas geothermal field is a high-temperature reservoir, located in the NW part of Costa Rica in the Guanacaste Volcanic Range, *c.* 150 km from the capital, San José. Temperatures generally range between 230 and 240 °C and gas discharges are dominated by CO_2 with minor amounts of H_2S and N_2 (Gherardi *et al.* 2002). The Las Pailas is a liquid-dominated two-phase reservoir with temperatures of 220–255 °C (at a depth of about 600–700 m) (Castro 2002), located at the southern flank of the volcano Rincón de la Vieja, Guanacaste Volcanic Cordillera. The heat source is located in the west part of the area and fluid flows are from west to northeast. Fracture permeability enables fluid and heat transport in this reservoir.

Major species in the plume

Major volcanogenic species (H_2O, CO_2 and SO_2) in volcanic plumes and fumaroles in tandem with Hg quantities have been measured at some locations (where logistics and weather conditions allowed) by using the MultiGAS analyser, a portable instrument previously described in Aiuppa *et al.* (2010, 2011). The plume gases are actively pumped into the sampler (using an air pump) at 1.2 L min^{-1} through a 1 μm Teflon membrane particle filter and pumped through a CO_2 gas detector (Licor LI-840 NDIR closed-path spectrometer; measurement range 0–3000 ppm; accuracy ±1.5%) (see Shinohara *et al.* 2008 for details) and a suite of electrochemical sensors for SO_2 (model 3ST/F City Tech. Ltd., calibration range 0–200 ppm), H_2S (model EZ3H City Tech. Ltd., calibration range 0–50 ppm) and H_2 (model EZT3HYT City Tech., calibration range 0–50 ppm) detection. A sensor for relative humidity and *T* (model Galltec; 0–100%, −30 to 70 °C) was used in order to measure water content in the gaseous emissions. The sensors were housed in a weatherproof 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. Signals from sensors are simultaneously captured every 3 s by a datalogger board, which also enables data storage. The raw data are then processed by dedicated software (RatioCalc, by Tamburello, pers. comm. 2013) that allows a derivation of plume mass ratios of various compounds (e.g. CO_2/SO_2, H_2O/CO_2, H_2O/SO_2). Simultaneously, relative concentrations of S and Cl were measured using the alkali-filter technique (Aiuppa *et al.* 2005; Shinohara & Witter 2005), where air was pumped at a known flow rate (from 4 to 6 L min^{-1}) through filter packs containing three cellulose impregnated filters stacked in series for *c.* 60–100 min. After exposure to the plume, $NaHCO_3^-$ impregnated filters were leached with bi-distilled water and H_2O_2 for 2 hours in order to extract SO_4^{2-} and Cl^- (Aiuppa *et al.* 2005). The leaching solution was then analysed for SO_4^{2-} and Cl^- by ion chromatography (IC) at DiSTeM, University of Palermo and INGV sez. Palermo (Italy). Blank filters and field blanks (i.e. filters from filter packs transported into the field and back in an identical manner to samples but not attached to a pump) were also analysed and found to be negligible compared to the measured values.

Hg detection in volcanic emissions

Gaseous mercury concentrations in volcanic plume have been measured mostly by using the conventional gold-trap technique (Ferrara *et al.* 2000; Aiuppa *et al.* 2007; Bagnato *et al.* 2007, 2009*a*, *b*; Witt *et al.* 2008*a*; Mather *et al.* 2012) and, more recently, by a portable mercury analyser LUMEX-RA 915+® (Sholupov *et al.* 2004; Aiuppa *et al.* 2007; Witt *et al.* 2008*b*; Bagnato *et al.* 2013). The Lumex-RA 915+® analyser monitors gaseous elemental mercury (GEM) concentrations using differential atomic absorption spectrometry with correction for background absorption via the Zeeman Effect (Zeeman atomic absorption spectrometry using high-frequency modulation of light polarization or ZAAS-HFM; Sholupov *et al.* 2004). The Hg analysing system operates by pumping the air at 20 L min^{-1} through a *c.* 3 cm diameter inlet to the multi-path detection cell which has an effective path length of 10 m. A zero correction resets the baseline every 5 min during sampling. The detection limit is *c.* 2 ng m^{-3}, and the instrument has an accuracy of 20%. Lumex® allows for measurements at the presence of high levels of humidity (not more than 95%) and H_2S (not more than 100 mg m^{-3}), unlike the conventional gold-trap technique which is instead strongly affected by inhibition of Hg adsorption at high H_2S levels (Schroeder *et al.* 1995). During the surveys, we measured an averaged relative humidity of *c.* 56% and 46% at Poàs and Turrialba volcanoes, respectively. The accuracy and precision of Lumex® has also been assessed through comparison with the traditional gold-trap/cold vapour atomic fluorescence spectrometry (CVAFS) system used in this work and at remote sites elsewhere (Kim *et al.* 2006; Aiuppa *et al.* 2007; Witt *et al.* 2008*b*).

In this study, Lumex® has been employed in a stationary mode to collect gaseous elemental mercury (GEM) in the plumes of Turrialba (near-vent plume aging of a few seconds to a few minutes) and Poás volcanoes and by walking across the fumarolic areas of Las Pailas and Las Hornillas geothermal systems (at about 60 cm from the emitting vents). Gold-coated quartz sand traps (Au-traps; Brooks Rand Labs®) were simultaneously used to collect total gaseous mercury (TGM) in the plumes (and/or fumaroles) of the studied volcanoes, where gas was pumped into the trap at a rate of *c.* 0.5 L min^{-1} for sampling periods of *c.* 30 min. An inline filter pack containing a filter impregnated with 1 M $NaHCO_3$ was used in series with the gold traps to measure the corresponding SO_2 concentration in the gas sampled (Aiuppa *et al.* 2007; Bagnato *et al.* 2007, 2011), and a 45 µm Teflon pre-filter has been located on the head of the gold-trap assembly to filter atmospheric air. On a few occasions a second gold trap was connected in series in order to monitor potential GEM breakthrough on the first trap, but this proved negligible. After sampling, the traps were sealed and analysed at the Midi-Pyrenees Observatory (Toulouse, France) by using dual-stage gold-trap amalgamation with atomic fluorescence detection (AFS, Brook Rand Model III) which employs high-purity argon as a carrier gas. The sampling train consists of the sampling gold trap followed by a new soda lime trap (Tekran Inc.), an analytical gold-coated sand trap (Brooks Rand) and the AFS detector. The soda lime trap was used to neutralize water vapour, residual acid gases and other impurities that may be co-collected on sampling traps under volcanic conditions. The AFS was calibrated using 40–200 uL Hg vapour injections from a thermostated liquid/vapour Hg reservoir. Calibration was repeated every three samples and showed a drift of the signal of <10%. More details on the operating conditions are given in Sonke *et al.* (2008).

Some studies address the question of whether the collection of gaseous Hg using a gold trap quantifies TGM (i.e. GEM plus RGM) or GEM; see Gustin *et al.* (1999) as an example. For the sake of simplicity, GEM and Hg are used without distinction in this article unless otherwise specified since in volcanic emissions GEM is the dominant form (≥90%; Bagnato *et al.* 2007; Zambardi *et al.* 2009; von Glasgow 2010; Martin *et al.* 2011).

Volcanic Hg flux estimate

Estimating the emission flux of Hg from volcanoes (plume and fumaroles) has generally taken the approach of scaling relationships between averaged Hg/SO_2 ratios in gas emissions and SO_2 fluxes (Varekamp & Buseck 1986; Pyle & Mather 2003; Aiuppa *et al.* 2007; Bagnato *et al.* 2007; Witt *et al.* 2008*a*, *b*; Bagnato *et al.* 2011) since volcanic SO_2 is well monitored and there is a degree of consensus over the global volcanic SO_2 flux (Graf *et al.* 1997; Andres & Kasgnoc 1998; Halmer *et al.* 2002; Schmidt *et al.* 2012). If the ratio Hg/SO_2 in volcanic plumes can be reliably constrained, the emission flux of Hg can be estimated. The former ratio is usually determined by connecting alkali-impregnated filters (to trap plume SO_2; accuracy ±10% at 1 s; Aiuppa *et al.* 2004, 2005) in series or in parallel with the gold trap. An additional effective method we used to assess the averaged Hg/SO_2 ratio in volcanic emissions is to combine the Lumex analyser in parallel with the MultiGAS to obtain real-time measurements of Hg and major volatiles in the volcanic fumes (Aiuppa *et al.* 2007; Witt *et al.* 2008*a*, *b*; Bagnato *et al.* 2013). In this study, data on sulphur dioxide flux in the volcanic plumes have been measured directly and acquired from literature reports. At Mt Etna, Gorely and Mutnovsky volcanoes a dual-UV camera set-up was used to obtain time series of the SO_2 flux at a resolution of 0.33 Hz (Kantzas *et al.* 2010; Tamburello *et al.* 2011; Aiuppa *et al.* 2012). This technique allows the whole plume to be captured in a single image, allowing the possibility of exploring spatial variations in SO_2 emissions over a timescale of *c.* 1 s (Mori & Burton 2006; Bluth *et al.* 2007). For the other reported volcanoes, SO_2 flux estimates have been obtained by traversing beneath the plume with an ultraviolet Ocean Optics USB2000 spectrometer coupled to a vertically pointing telescope, or by downloading data from an installed permanent station close to the volcano. Evaluation methods of the acquired spectra are described in McGonigle *et al.* (2002) and Galle *et al.* (2003). All the SO_2 fluxes used in our calculations correspond to the period of our fieldwork. In these calculations, we assume that GEM and SO_2 are the main forms of Hg (Bagnato *et al.* 2007, 2011) and S in the plumes, respectively. Under certain circumstances however, such as those encountered in the geothermal fields (i.e. the S fluxes are very low), the Hg/SO_2 approach for estimating Hg flux is not readily applicable since there is no reliable method for measuring the flux of the dominant form of sulphur in these systems. In those areas, we used an alternative method to estimate Hg flux by combining the kriging contouring technique with the plume speed information (Bagnato *et al.* 2013).

Results

Mercury and major species in volcanic emissions

The simultaneous acquisition of CO_2, H_2S, SO_2 and H_2O by the MultiGAS (Aiuppa *et al.* 2005, 2007,

2011) combined with Lumex Hg analyser allowed us to characterize the abundance of major species in air-diluted volcanic emissions, and therefore examine the relationship between atmospheric Hg concentrations and volcanogenic volatiles (see Tables 1 & 2). More specifically, data from the permanent MultiGAS station installed on the western rim of Turrialba volcano's West Crater showed CO_2/SO_2 molar ratio time series almost constant over a period of two days, ranging from 1.15 to 2.55 and averaging 2.2. Instead, the H_2O/CO_2 molar ratio varies over a wide range from 32 to 230 (mean 109) due to water condensation that removes water from the gas of the low-temperature sources (see Table 1). Here, simultaneous collection of gases by Lumex and gold-trap technique yielded Hg concentrations of 99 and 81 ng m^{-3}, respectively (Table 2), which are comparable to those obtained during previous fieldwork performed in 2010 (averaged GEM *c.* 115 ng m^{-3}, Table 2; Bagnato *et al.* unpublished data). Higher averaged GEM values were measured in the volcanic plumes of Mt Etna's craters (Bocca Nuova and North East craters; 125 and 100 ng Hg m^{-3}, respectively), where the continuous measurements by MultiGAS gave H_2O/CO_2 and H_2O/SO_2 values of *c.* 93 and 46.5, respectively (Tables 1 and 2). We found that Hg data from the North East crater (99 ng Hg m^{-3}; this work) is comparable to the lower value reported by Bagnato *et al.* (2007) (range 114–328 ng Hg m^{-3}; Table 2). A very recent MultiGAS survey on Gorely's volcanic plume (Aiuppa *et al.* 2012) reports $H_2O/SO_2 = 43 \pm 13$, $CO_2/SO_2 = 1.2 \pm 0.1$ and $H_2/SO_2 = 0.11 \pm 0.02$ as a representative mean end-member for arc magmatism in the NW Pacific region (Table 1). These data have been acquired simultaneously to our Hg measurements inside the dilute plume of Gorely (at *c.* 300 m downwind from the source), where we found the lowest GEM concentrations (*c.* 4 ng m^{-3}; Table 2) of those reported in this study.

The four transects performed with the portable MultiGAS on the rim of the dome close to the acidic lake at Poás volcano did not show relevant variability of the chemical composition; the CO_2/SO_2 molar ratio ranged between 0.23 and 0.45 (mean 0.4; Table 1), suggesting a strong homogeneity of the fumarolic field. The H_2O/CO_2 ratio is affected by condensation of water and is therefore more variable (170–215; mean 183; Table 1). The SO_2/H_2S ratio fell within the range 2–6.8, supporting a more extensive re-equilibration of the volcanic gas within the more reducing and colder hydrothermal system. A further short survey was carried out around the edge of the acid lake of Poás volcano, aimed at detecting the chemistry of the steam released by the lake. The results show higher values of both CO_2/SO_2 and H_2O/CO_2, 1.2 and 344 respectively, reflecting the contribution of water evaporation and SO_2 scrubbing processes (Symonds *et al.* 2001). Simultaneous Hg measurements by both gold traps and Lumex system in the fumarolic emissions collected on the top of the dome (hundreds of metres from the emissions) gave very low concentrations (6–7.4 ng m^{-3}; Table 2). In general, given the uncertainties associated with gold-trap techniques, our data exhibit a good agreement by comparing Lumex® and gold-trap results (see Table 2), as also reported elsewhere by other authors (Kim *et al.* 2006; Aiuppa *et al.* 2007).

A first assessment of the chemical composition of gases released by the fumarolic field inside and near the bottom of Rincón de la Vieja's main crater has also been accomplished. Despite the great distance from which the gas was detected by the MultiGAS (hundreds of metres from the fumaroles), the concentrations of volcanic SO_2 and CO_2 were high enough (*c.* 1 and 10 ppm, respectively) to calculate molar ratios. In fact, the 0.8 km^2 wide hyper-acid lake at the bottom of the crater exerts a strong gas scrubbing on the volcanic gas emissions, as demonstrated by the high CO_2/SO_2 molar ratios in the range 15–69, averaging 27 (see Table 1). The measured H_2O/CO_2 ratios are variable (range 84–354) but still comparable to the other volcanoes. As at Poàs, we detected very small Hg concentrations in the emissions from Rincón de la Vieja volcano (in the range 4–5 ng m^{-3}; Table 2). The quite low Hg concentrations found in the fumes of these latter two volcanoes mainly reflect the long distance from which the gas was detected (hundreds of metres from the fumarolic emissions), and probably the gas scrubbing on gaseous emissions exerted by the acid volcanic lakes hosted inside (Symonds *et al.* 2001). However, more research is needed to improve knowledge of the implications of magmatic gas scrubbing on Hg distribution in volcanic emanations.

The fumarolic gas of Aso volcano is a mixture of the original magmatic gas and hydrothermal fluids (Shinohara *et al.* 2010, 2013). The authors suggest that gases deriving from the lake and fumarolic emissions have distinct compositions, with higher CO_2/SO_2 and HCl/SO_2 (3.1 and 0.1, respectively) and lower SO_2/H_2S (19.2) ratios in fumaroles than the lake gases (1.6, 420 and 0.01, respectively), but they have similar H_2/CO_2 ratios (0.06 and 0.03, respectively) (Table 1). Here we attempted separate quantification of Hg in the gases emitted from the Yudamari crater lake (lake gas) and the fumarolic area at the southern wall (fumarolic gas) by using the gold-trap method at two distinct sampling sites. Since the gas source is not a single vent for both the lake gases and the fumarolic gases,

Table 1. *Molar ratios measured in the plume of the investigated volcanoes and in atmospheric emissions of geothermal systems*

Volcano	H_2O/ CO_2	H_2O/ SO_2	CO_2/ SO_2
Turrialba	109	240	2.2
Poás	183	73	0.4
Rincón de la Vieja	201	5424	27
Aso fumarole*	17	52	0.0012
Aso lake gas†	58	94	0.0002
Gorely‡	32	43	1.3
Mutnovsky AF	23	46	0.001
Mutnovsky BF	83	288	0.00004
Etna NEC	93	46	0.5
Etna BN	21	126	6
Geothermal fields			
Las Pailas	378	15 031	41
Las Hornillas	29	3220	113

*Shinohara *et al.* (2010)
†Shinohara *et al.* (2013)
‡Aiuppa *et al.* (2012)

there can be some heterogeneity in composition as well as composition fluctuation. It is therefore quite difficult to estimate the real error in composition determination. Mercury measurements at Aso volcano gave values of *c.* 119 and 8 ng Hg m^{-3} in the fumaroles and fumes generated by the crater lake evasion, respectively (Table 2). The mismatch exhibited by these data mainly reflects the weak gaseous emission from the surface of Yudamari crater lake during the survey compared to the strong degassing exhibited by the fumaroles sampled along the wall of the crater.

Finally, MultiGAS survey performed at the Bottom Field and the Active Crater of the Mutnovsky volcano yielded H_2O/S_{tot} molar ratios in the range *c.* 46.4–288.3, while the measured H_2O/CO_2 and CO_2/S_{tot} ratios were 23.4 and 2 for the former and 83 and 3.4 for the fumaroles of the Bottom Field (Table 1). Simultaneously, we also measured *c.* 40 and 8 ng Hg m^{-3} in the atmospheric emissions from the Active Crater and the Bottom Field, respectively (Table 2).

In general, our results are higher than the background atmospheric Hg values generally found in the unpolluted areas of the Northern Hemisphere (range 1.5–1.7 ng m^{-3}; Lindberg *et al.* 2007; Sprovieri *et al.* 2010), as well in the urban sites (range 2.5–9.8 ng m^{-3}; Liu *et al.* 2002; Rutter *et al.* 2008, 2009; Kim *et al.* 2011). The large variability of GEM concentrations (4–125 ng m^{-3}) we measured in the gaseous emissions of the investigated volcanoes strongly reflects the dynamic nature of the plume, where the abundances of volatiles are determined by variations in Hg emission fluxes from magma and dilution with background air. Overall, our data support the relevance of persistent volcanic activity from open-conduit degassing as a significant source of Hg for the atmosphere (see Table 2), and fall within the range proposed by many authors worldwide (Witt *et al.* 2008*a*, *b*; Bagnato *et al.* 2011; Mather *et al.* 2012; Table 2).

Hg emissions from geothermal fields

There are relatively few published datasets of Hg concentrations measured at or near geothermal features even if many areas characterized by geothermal activity have long been associated with elevated levels of Hg in soils and air (Varekamp & Buseck 1981, 1986; Cox 1983; Siegel & Siegel 1984). Previous studies by Robertson *et al.* (1977) and Christenson and Mroczek (2003) showed that essentially all the Hg in geothermal steam and gases is in the gaseous elemental form (GEM). A Lumex®/MultiGAS GPS-synchronized survey was carried out at Las Hornillas and Las Pailas geothermal fields (Costa Rica) with the aim of quantifying volatile species in the fumarolic emissions distributed in these areas. At each fumarole, measurements were performed by placing the inlet of the instruments close (within a few centimetres) to the emitting vent to reduce mixing with air. The combined Lumex®/MultiGAS technique allowed a large number of simultaneous GEM and SO_2 measurements to be made over short (half an hour) observation periods, and the time variability of the GEM/SO_2 ratio to be evaluated real-time. The MultiGAS survey revealed a spatial variability in terms of gas compositions and emission rate for both investigated geothermal areas (Table 1; Figs 2 & 3). We estimated an averaged CO_2/H_2S ratio ranging between 53 and 179 (with the higher values measured at the northern part of the field) and between 16.3 and 73 at Las Hornillas and Las Pailas, respectively. At Las Hornillas we also estimated an averaged H_2O/CO_2 ratio ranging from 23 to 53, while at Las Pailas H_2O/H_2S and H_2O/CO_2 ratios were estimated to vary from 8835 to 29 994 and from *c.* 230 to 542, respectively (Table 1). By walking around the fumarolic emissions, we estimated GEM concentrations of 140–530 ng m^{-3} (averaged 260 ng m^{-3}) and *c.* 145–1329 ng m^{-3} (averaged 822 ng m^{-3}) for Las Pailas and Las Hornillas emissions, respectively (Table 2; Figs 2 & 3). Measurements showed that both systems are releasing Hg at elevated levels well above those measured in the atmosphere outside the geothermal areas (*c.* 3.6 and 3.2 ng m^{-3} for Las Pailas and Las Hornillas, respectively). Measurements performed by a FLIR SC660 infrared camera (located near the main vents) showed a very homogeneous distribution of

Table 2. *Volcanic mean GEM concentrations (range; SD and number of measurements), mean GEM/SO_2 mass ratios and Hg fluxes for the volcanic systems used in this study*

Volcano	Location	Date	Volcanism	Emission type	GEM (ng m^{-3} (range; SD; n))	Method	GEM/SO_2	ΦSO_2 (t a^{-1})	ΦHg (t a^{-1})	References
Gorely	Kamchatka	06/09/2011	Arc	Plume	4 (*1*)	Au-trap/AFS	3.3×10^{-6}	802[1]	0.95	This study
Mutnovsly AF	Kamchatka	05/09/2011	Arc	Fumaroles	8 (*1*)	Au-trap/AFS	1.9×10^{-7}	150[2]	0.01	This study
Mutnovsly BF(both plumes)	Kamchatka	05/09/2011	Arc	Fumaroles	40 (*1*)	Au-trap/AFS	1.4×10^{-5}	150[2]	0.7 (0.71)	This study
Aso fumarole	Japan	2010	Arc	Fumaroles	119 (*1*)	Au-trap/AFS	5.2×10^{-7}	500[3]	0.09	This study
Aso crater lake (both plumes)	Japan	2010	Arc	Lake fumes	8 (*1*)	Au-trap/AFS	1.3×10^{-6}	500[3]	0.24 (0.33)	This study
Etna BN	Italy	24/06/2011	Non-arc	Plume	125 (*1*)	Au-trap/AFS	7.1×10^{-6}	1130[4]	2.92	This study
Etna NEC (both plumes)	Italy	24/06/2011	Non-arc	Plume	99 (*1*)	Au-trap/AFS	3.4×10^{-6}	1000[4]	1.24 (4.16)	This study
Poás	Costa Rica	16–18/04/2013	Arc	Fumaroles	7.4 (5–10)	Lumex	4.9×10^{-8} $(2.5–3.6 \times 10^{-8})$	120[5]	0.002	This study
Poás	Costa Rica	16–18/04/2013	Arc	Fumaroles	6 (4–7; 1.2; *5*)	Au-trap/AFS	3.7×10^{-8} $(2.1–5.4 \times 10^{-8})$	120[5]	0.0016	This study
Turrialba	Costa Rica	07/03/2011	Arc	Plume	115 (*1*)	Au-trap/AFS	3.9×10^{-6}	1000[6]	1.45	This study
Turrialba	Costa Rica	02–04/04/2013	Arc	Plume	100 (68–174)	Lumex	5.6×10^{-6} $(3–9.8 \times 10^{-6})$	671[7]	1.4	This study
Turrialba	Costa Rica	02–04/04/2013	Arc	Plume	81 (76–85; 4; *3*)	Au-trap/AFS	8.1×10^{-6} $(7.6–8.2 \times 10^{-6})$	671[7]	1.9	This study
Rincón de la Vieja	Costa Rica	07/04/2013	Arc	Fumaroles	5 (4–5; 0.6; 2)	Au-trap/AFS	3.5×10^{-6} $(4.3–2.7 \times 10^{-6})$	n.d.	n.d.	This study
Las Pailas	Costa Rica	08/04/2013	Arc	Geothermal	260 (140–530)	Lumex	1.68×10^{-5}	n.d.	0.0008–0.002	This study
Las Hornillas	Costa Rica	09/04/2013	Arc	Geothermal	822 (145–1329)	Lumex	4.01×10^{-6}	n.d.	0.004–0.01	This study
Nyiragongo	Africa	19–23/06/2010	Non-arc	Plume	373	Au-trap/CVAFS	5.5×10^{-6}	2180	4.4	Bagnato *et al.* (2011)
Yasur	Vanuatu	21/10/2010	Arc	Plume	84	Au-trap/CVAFS	1.7×10^{-5}	940	6	Bagnato *et al.* (2011)
Ambrym	Vanuatu	21/10/2010	Arc	Plume	68	Au-trap/CVAFS	6.4×10^{-6}	7600	18	Bagnato *et al.* (2011)
Stromboli	Italy	24/07/2008	Arc	Plume	28	Au-trap/CVAFS	4.7×10^{-6}	120	0.2	Bagnato *et al.* (2011)
Miyakejima	Japan	02–12/09/2006	Arc	Plume	95	Au-trap/CVAFS	9×10^{-6}	2000	6.6	Bagnato *et al.* (2011)
Asama	Japan	25–29/09/2008	Arc	Plume	41	Au-trap/CVAFS	5.5×10^{-6}	1850	3.7	Bagnato *et al.* (2011)
La Soufriere Hill	Less Antilles	01/07/2008	Arc	Plume	18	Au-trap/CVAFS	1.2×10^{-5}	400	1.8	Bagnato *et al.* (2011)
Kilauea	Hawaii	2008	Arc	Plume	35	Au-trap/CVAFS	1.6×10^{-6}	700	0.2	Mather *et al.* (2012)
Masaya	Nicaragua	24/02–04/03/2006	Arc	Plume	163.5	Au-trap/CVAFS	2×10^{-5}	800	7.2	Witt *et al.* (2008*a*, *b*)
Cumulative flux from open-conduit volcanoes								16 590	*56*	This study
Global volcanism emissions								18 630–38 904[8]	*76 ± 30*	This study

Literature Hg flux with relevant data sources and sampling/analythical methods are also reported: [1]Aiuppa *et al.* (2012), [2]G. Tamburello pers. comm., 2011; [3]Shinohara *et al.* (2010); [4]G. Tamburello pers. comm., 2013; [5]M. DeMoor pers. comm., 2013; [6]Campion *et al.* (2012); [7]G. Avard pers. comm., 2013; [8]Graf *et al.* (1997).

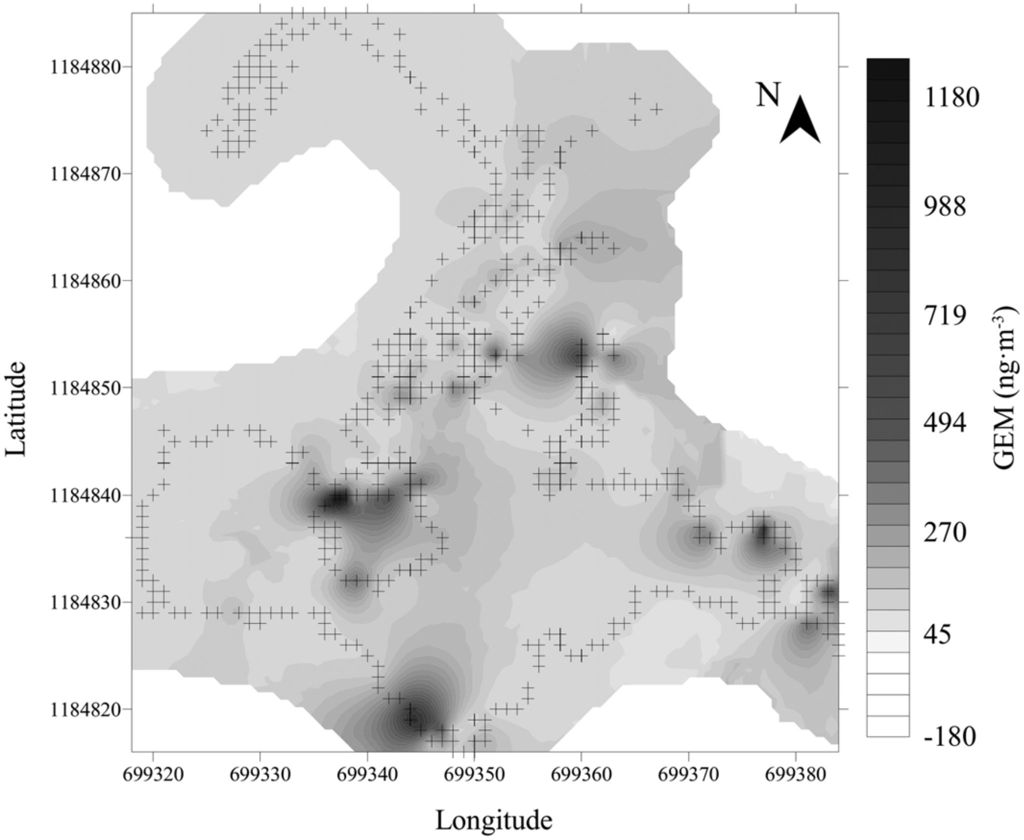

Fig. 2. Mercury distribution (ng m^{-3}) in gaseous emissions at Las Hornillas geothermal field, Miravalles volcano, Costa Rica. The black crosses indicate the walking track across the fumarolic emission sites with the Lumex/MultiGAS synchronized survey. Coordinates are reported in UTM (Zone 16P).

gas temperatures at the emitting vents, generally close to the boiling point of water and ranging from 95 to 98 °C in both geothermal areas. Acquisition by the Lumex® system allowed us to detect pulsed sequences of GEM increases in the atmospheric plumes of the fumaroles of both geothermal systems (Fig. 4a, b). These GEM pulses were closely matched by parallel increases in CO_2 as illustrated in Figure 4a, b, supporting both a volcanic origin for the measured GEM concentrations and the role of early CO_2 escape from magmas as a carrier gas for Hg (Varekamp & Buseck 1981, 1986; Bagnato *et al.* 2013). At Las Pailas we estimated mean GEM/CO_2 mass ratios ranging from 1.4×10^{-9} to 1.7×10^{-8}, comparable with those measured in the gaseous manifestations at Las Hornillas field (from 3.5×10^{-9} to 1×10^{-7}). In general, our estimated GEM/CO_2 values are similar to those obtained in other low-temperature volcanic-hydrothermal systems such as Tatun volcanic field (GEM/CO_2 from 4×10^{-8} to 40×10^{-8}; Witt *et al.* 2008*a*) and the low-*T* (85°–150 °C) CO_2-rich fumaroles of Masaya volcano (GEM/CO_2 from 0.1×10^{-8} to 1.9×10^{-8}; Witt *et al.* 2008*b*). Measurements at the higher-temperature (250 °C) fumaroles of La Fossa Crater, Vulcano island indicated GEM/CO_2 mass ratio of 6.0×10^{-8} (Aiuppa *et al.* 2007). Our data are also close to the values 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 H_2S (1.6×10^{-9} to 2.6×10^{-9}; Engle *et al.* 2006). The GEM concentrations derived from the real-time measurements at Las Pailas geothermal field also correlate well with the real-time H_2O concentrations at all the active vents (Fig. 4b) with estimated mean GEM/H_2O mass ratios ranging from 4.3×10^{-11} to 3.6×10^{-10}. These results provide new important information, improving the

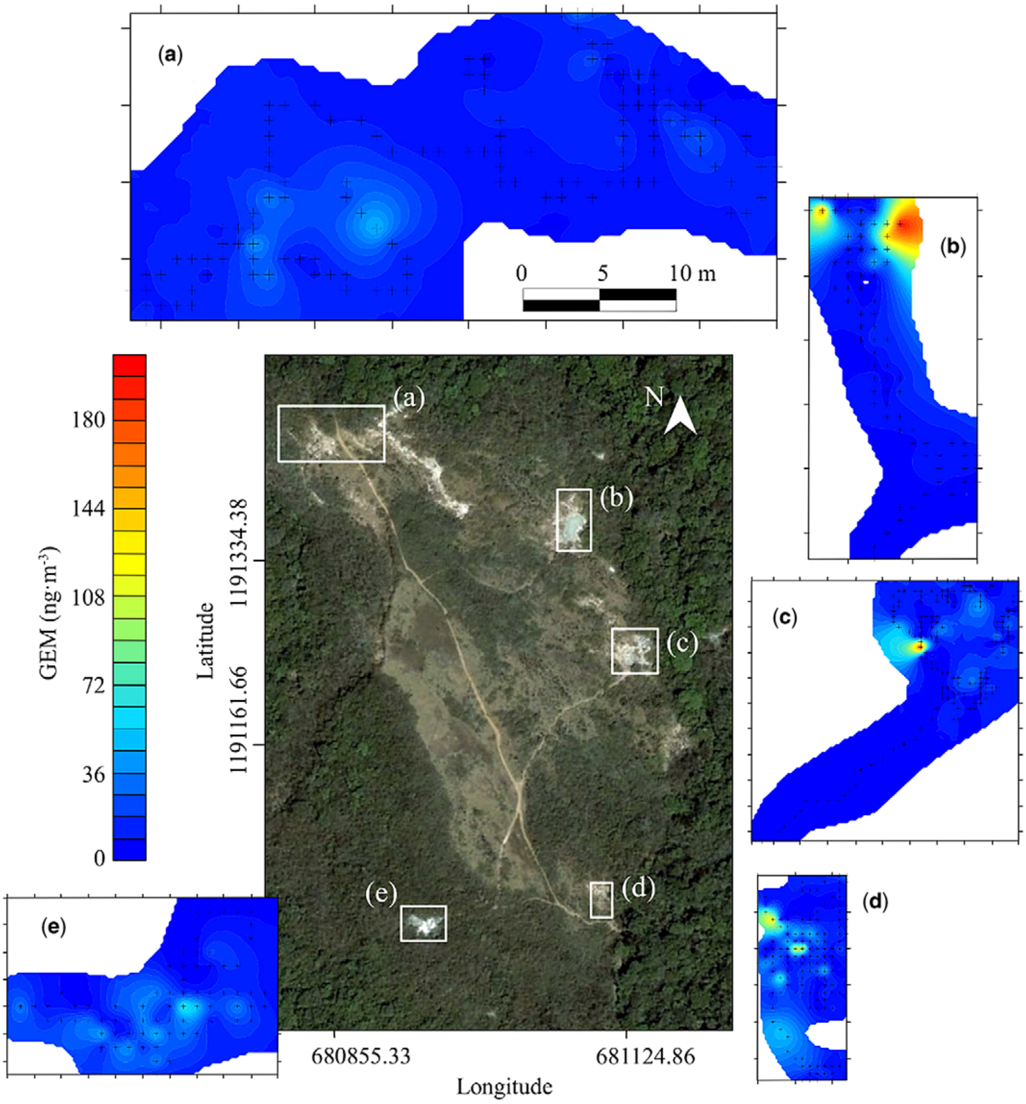

Fig. 3. Mercury distribution (ng m^{-3}) in gaseous emissions at Las Pailas geothermal field, Rincón de la Vieja volcano, Costa Rica by the Lumex/MultiGAS acquisition technique. Here the surveyed areas are reported in five separated sectors (**a–e**) due to the extended surface area of the geothermal field. Coordinates are reported in UTM (Zone 16P).

currently sparse Hg database for gases from volcanogenic origin worldwide (Weissberg & Rohde 1978; Cox 1983; Siegel & Siegel 1984; Varekamp & Buseck 1986; Nakagawa 1999; Engle *et al.* 2006). Previous research suggested that steam condensation can affect GEM to other chemicals ratios (Varekamp & Buseck 1981, 1986). In this study, we did not attempt to measure Hg concentration in fumarolic steam condensates, so we cannot rule out the possibility that our derived Hg emissions are underestimating the real emissions to some extent (Nakagawa 1999; Aiuppa *et al.* 2007). The release of Hg from previously enriched substrates as a result of geothermal processes has not been determined at Las Pailas and Las Hornillas, but it might contribute significantly in estimating the cumulative Hg flux from geothermal systems as recently demonstrated elsewhere (e.g. Nea Kameni fumarolic fields, Greece; Sulphur Banks, Hawaii, Varekamp & Buseck 1986; Miravalles volcano, Melián *et al.* 2004; United States, Engle *et al.* 2006; la Solfatara, Pozzuoli, Bagnato *et al.* 2009*a*, 2013).

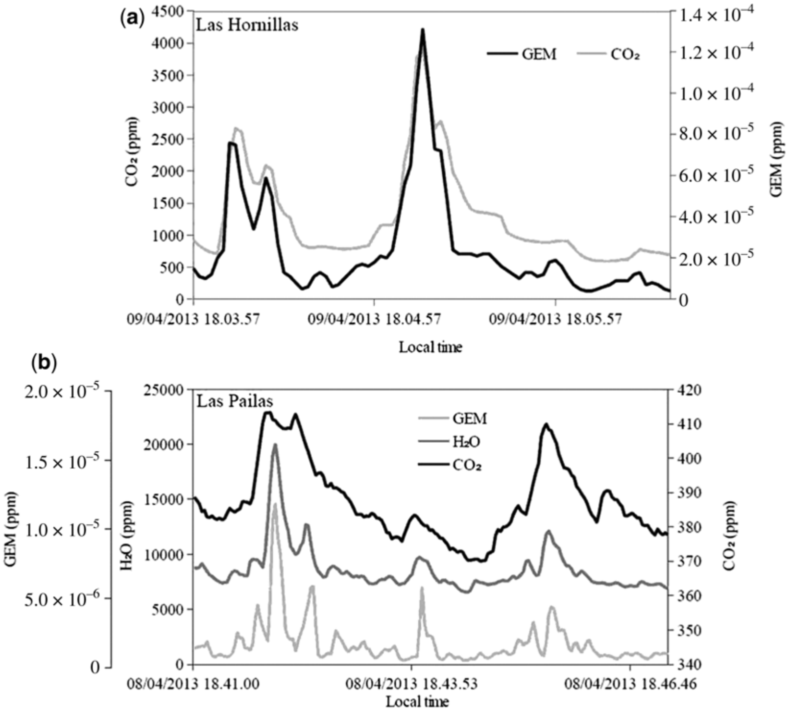

Fig. 4. Temporal variations in CO_2 (grey line), GEM (black line) and H_2O (light grey line) measured with MultiGAS and Lumex, respectively at (**a**) Las Hornillas and (**b**) Las Pailas geothermal systems. The positive temporal correlation exhibited by the two species may support CO_2 as potential carrier gas in transporting GEM in magmatic systems.

The importance of Hg/S ratio

Concentrations of gaseous plume species at crater rims depend on both volcanic (gas flux) and non-volcanic factors (extent of mixing and dilution in the vent, wind speed and direction); comparing the concentrations of species between different volcanoes is therefore not necessarily meaningful and it is more useful to compare ratios of various species. A large variety of chemical methods have been used in the past to quantify Hg/SO_2 proportions in volcanic emissions (e.g. Varekamp & Buseck 1981; Nakagawa 1999; Ferrara *et al.* 2000; Bagnato *et al.* 2007), the majority of which require complex and time-consuming post-sampling analytical determinations in a laboratory, precluding real-time measurement and limiting the acquisition of robust datasets. The literature reported Hg/SO_2 mass ratios in volcanic emissions span four orders of magnitude (Pyle & Mather 2003), including fumarolic condensates and vapours which dominate the available data. Fumarolic emissions may differ in composition from the high-temperature gases released directly from magma (Symonds *et al.* 1992). The uncritical use of fumarolic Hg/SO_2 as a proxy for magmatic Hg/SO_2 will underestimate volcanic Hg emission rates because SO_2 is mostly from high-temperature sources (magmatic), while low-temperature fumarolic environments are to some extent enriched in H_2S (Pyle & Mather 2003; Aiuppa *et al.* 2007). This means that in estimating the Hg emission flux, it is more appropriate to consider the Hg/S_{tot} ratio (where $S_{tot} = SO_2 + H_2S$) rather than the single S-species. Some recent assessments of global volcanic emissions of Hg have not properly accounted for this (Unni *et al.* 1978; Nriagu 1989; Ferrara *et al.* 2000). These considerations are especially important as the most significant factor that influences volcanic Hg flux estimates is the value of Hg/SO_2 that is adopted in the calculation. The variability we found in the averaged GEM concentrations (see Table 2) measured in gaseous emissions of the investigated volcanoes strongly highlights the importance of using Hg/S ratios to compare volcanic emissions. Given the uncertainties associated with the gold-trap technique, we found a good agreement by comparing atmospheric Lumex®/MultiGAS measurements and those made with gold-traps/filterpacks in determining Hg/SO_2 mass ratios (see Table 2, especially for Poás and Turrialba volcanoes). Most of the measured GEM/SO_2 range from 10^{-6} to 10^{-5}, except for Aso fumaroles, Mutnovsky Active Funnel plume and Poás volcano which displays the lowest mass ratios ranging from 10^{-8} to 10^{-7} (see Table 2). At Rincón de la Vieja volcano, we measured a mean fumarolic GEM/SO_2 ratio of *c.* 3.5×10^{-6} (range $4.3–2.7 \times 10^{-6}$; Table 2). The GEM/SO_2 mass ratios estimated in the plumes of the North East Crater and Bocca Nuova at Mt Etna ($3.4–7.1 \times 10^{-6}$ respectively; Table 2) are comparable to the mean value reported by Bagnato *et al.* (2007) (*c.* 8.8×10^{-6}). Finally, at Las Pailas and Las Hornillas we measured GEM/SO_2 of 1.68×10^{-5} and 4.1×10^{-6}, respectively.

A broad correlation was found by plotting GEM versus $SO_{2(g)}$ concentrations (Hg/SO_2 *c.* 10^{-7} to 10^{-5}) in the plume of active degassing volcanoes from arc and non-arc setting (taken from both literature and this study; Fig. 5). The most likely reason for the differences observed in GEM/SO_2 mass ratios among the reported volcanoes from similar settings may simply be compositional variability (i.e. Hg and S contents; Fig. 5). Further, since Hg

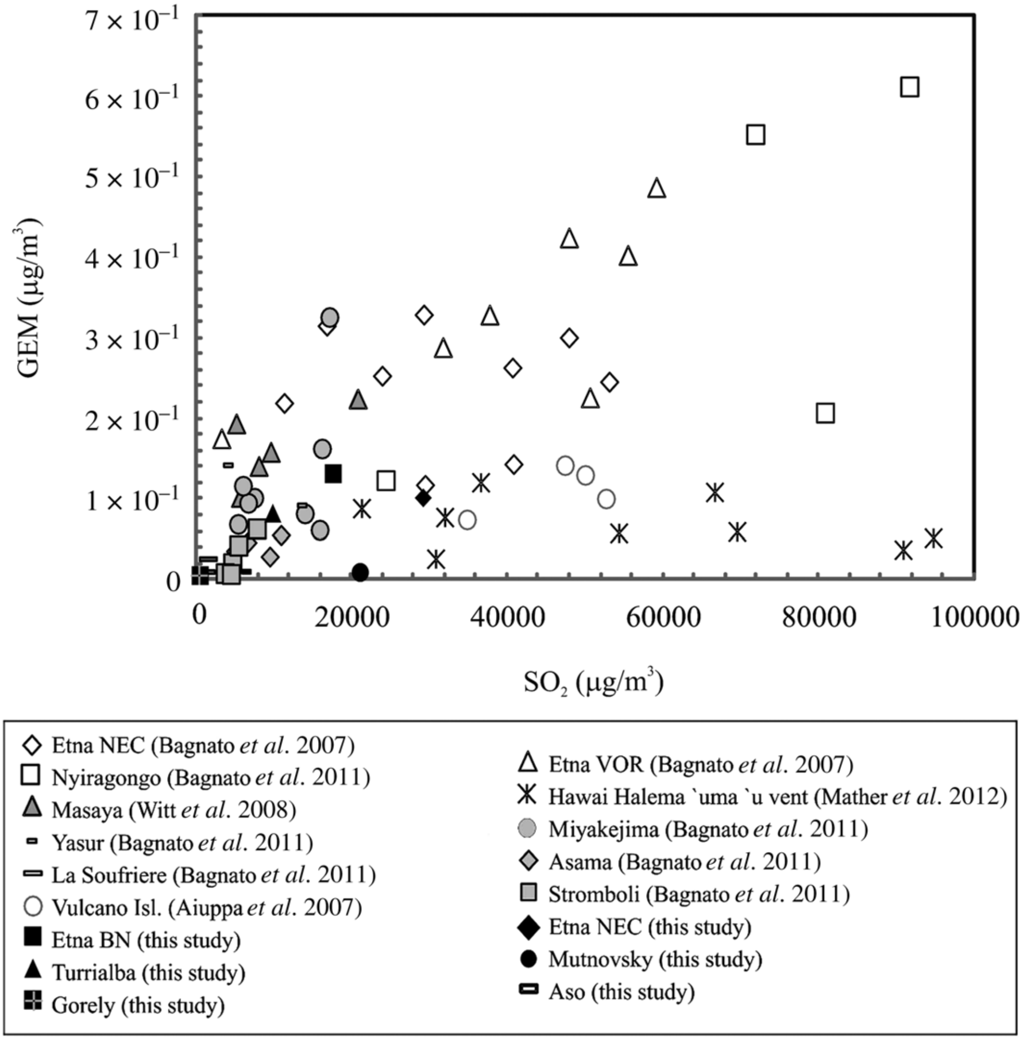

Fig. 5. Scatter plot of gaseous elemental mercury (GEM) v. $SO_{2(g)}$ concentrations in the vent plumes of active volcanoes from arc and non-arc volcanism (grey filled symbols and black open symbols, respectively) (GEM/SO_2 ranging from 10^{-7} to 10^{-5}; see Table 2). Our original data (black filled symbols) are set in the context of published volcanic gas compositions. Arc-volcanism setting: Masaya (Witt *et al.* 2008*a*), Miyakejima, Yasur, Stromboli, Asama, La Soufriere (Bagnato *et al.* 2011), Vulcano island (Aiuppa *et al.* 2007); non arc-volcanism setting: Etna NEC and Etna VOR (Bagnato *et al.* 2007), Nyiragongo (Bagnato *et al.* 2011), Hawai Halema'uma'u vent (Mather *et al.* 2012).

and SO_2 have different solubility in silicate melts, they will be fractionated during magmatic degassing, implying that Hg/SO_2 will be significantly changing in both time and space. Volcanoes with acidic lakes, such as Poàs and Rincón de la Vieja, can also fractionate the Hg/SO_2 through scrubbing in the lakes of both SO_2 and Hg as H_2SO_4 and $HgCl_2$, respectively (Symonds *et al.* 2001; Shinohara *et al.* 2010). In such a case, the gaseous emanations from the lake will be fractionated in Hg/SO_2 as a result of SO_2 or Hg dissolution, or both. There is of course a need for continuing work to characterize both volcanic lake evasion fumes and low- and high-temperature volcanic emissions and to establish the factors which control the Hg/S ratios at different degassing volcanoes. Previous estimates of the global non-explosive volcanic Hg flux have used Hg/SO_2 ratios between 10^{-7} and 10^{-5} (Varekamp & Buseck 1986; Nriagu 1989; Ferrara *et al.* 2000; Nriagu & Becker 2003) with 10^{-6} as the best representative of gas emissions from quiescent open-conduit degassing volcanoes (Fig. 6). In general, most of our GEM/SO_2 data from continuous degassing are in agreement with this ratio (Figs 6 & 7), and are similar to the value reported in Varekamp & Buseck's (1986) global estimate for passive emissions from non-erupting volcanoes (3.7×10^{-6}). Our data also fall within the range of best estimates (10^{-4} to 10^{-6}) proposed by Pyle & Mather (2003) for non-explosive volcanic degassing and are also in agreement with the ratios found at other passive degassing volcanoes (see Tables 2 & 3; Fig. 7). However, our data together with most of the reported GEM/SO_2 in the literature should probably be considered as the lower bounds because they mainly refer to passive emissions from non-erupting volcanoes; these are lower than the ratios measured during explosive eruptions which are also often accompanied by considerable SO_2 emission (such as those documented for Kilauea, Arenal and Mt St Helens volcanoes; GEM/SO_2 from 10^{-4} to 10^{-3}; Varekamp & Buseck 1981; Ballantine *et al.* 1982; Fig. 7). Previous estimates of Hg/SO_2 ratios from explosive volcanic eruptions gave values varying much more, between 10^{-2} and 10^{-5} (Buat-Menard & Arnold 1978; Varekamp & Buseck 1981; Ballantine *et al.* 1982; Shuster *et al.* 2002), suggesting that emissions from large explosive eruptions are rich in Hg.

By comparing plume GEM/SO_2 mass ratios to the corresponding plume H_2O/SO_2 ratios (Fig. 8; see Tables 1 & 2 for data sources), most of the open conduit 'arc' volcanoes (grey filled triangles in Fig. 8) show an overall positive correlation between H_2O/SO_2 and GEM/SO_2 ratios ($r^2 = 0.8$). This may suggest that gas emissions in subduction zones contain more Hg (relative to SO_2) than those from divergent (or within-plate) plate volcanism, as also previously suggested by some authors (Kim *et al.* 2000; Bagnato *et al.* 2011). Data from Rincón de la Vieja volcano as well as the two geothermal fields (Las Pailas and Las Hornillas) fall outside the main trend exhibited

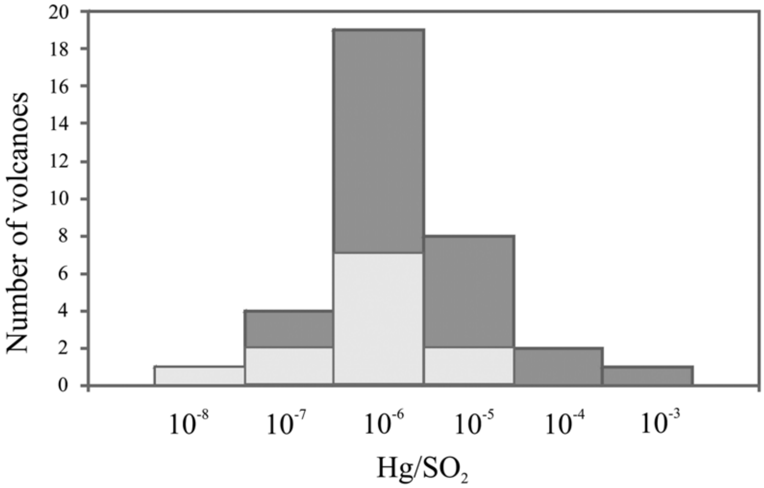

Fig. 6. Summary of measured GEM/SO_2 mass ratios in the volcanic bulk plume, compiled from this work (light grey bars) and published data (as reported in Fig. 5). The compilation strongly supports 10^{-6} to 10^{-5} for the Hg/SO_2 plume ratio from quiescent degassing volcanoes as representative of gas emissions from the open-conduit degassing volcanoes.

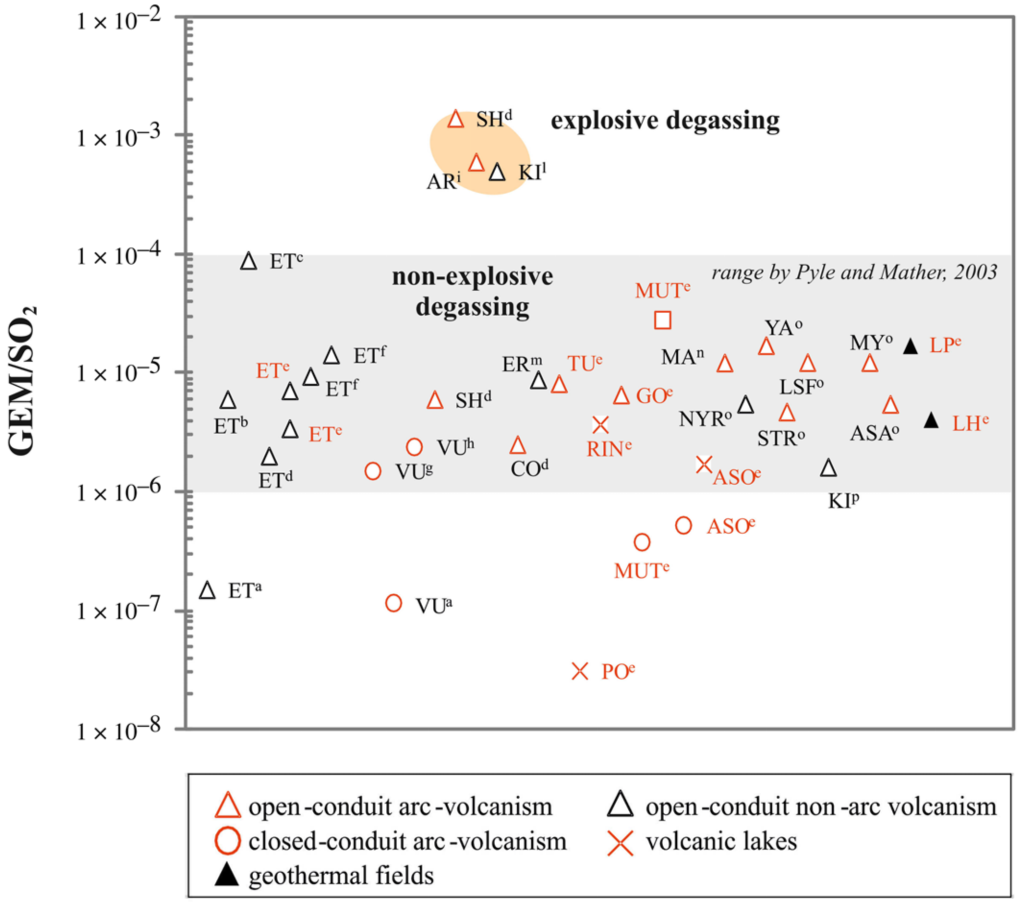

Fig. 7. Summary of measured GEM/SO_2 mass ratios in worldwide volcanic emanations. The graph was constructed from results obtained in this study (red text), and previously published data (black text). A distinction was made between the emission type plotted in the graph to show open/closed conduit, arc/non-arc volcanism, volcanic lake evasion and geothermal fields. Most of the reported GEM/SO_2 values are lower than those measured for Kilauea, Arenal (10^{-4}) and Mt St Helens volcanoes, during explosive eruptions (pink-coloured area). Reported data are taken from: [a]Ferrara *et al.* (2000); [b]Dedeurwaerder *et al.* (1982); [c]Buat-Menard & Arnold (1978); [d]Varekamp & Buseck (1986); [e]this work; [f]Bagnato *et al.* (2007); [g]Bichler *et al.* (1995); [h]Aiuppa *et al.* (2007); [i]Ballantine *et al.* (1982); [l]Siegel & Siegel (1984); [m]Kyle *et al.* (1990); [n]Witt *et al.* (2008*a*, *b*); [o]Bagnato *et al.* (2011); [p]Mather *et al.* (2012). ET, Etna; ER, Erebus; PO, Poás; ASO, Aso; MUT, Mutnovsky; GO, Gorely; MA, Masaya; KI, Kilauea; NY, Nyiragongo; YA, Yasur; TU, Turrialba; ASA, Asama; CO, Colima; VU, Vulcano Island; STR, Stromboli; RIN, Rincón de la Vieja; LSF, La Soufriere Hill; MY, Miyakejima; SH, St Helens; AR, Arenal; LP, Las Pailas; LH, Las Hornillas. The grey-coloured area shows the typical range of GEM/SO_2 ratios for continuous degassing volcanoes, as suggested by Pyle & Mather (2003).

by the other volcanoes (Fig. 8). We note that for the former, it is likely that either the sulphur scrubbing action in the acid lakes or the distance from which we sampled gases may have influenced the H_2O/SO_2 and GEM/SO_2 values. To date however, we are not able to say which of the two factors dominates. The excess of water detected in the gaseous emissions at Las Hornillas and Las Pailas geothermal fields may explain the low estimated GEM/H_2O mass ratios at these locations (black filled triangles in Fig. 8). More data are required to explore this relationship further, however. A stronger correlation between GEM and SO_2 is evident for samples collected within plate/rift volcanism (Figs 5 & 8), in agreement with their similar degassing behaviour.

In arc-volcanism the origin of Hg can be manifold and fairly hard to understand. Metals released by gaseous discharges in volcanic arcs are ultimately sourced in the heterogeneous mantle wedge

Table 3. *Literature Hg/SO_2 mass ratios for active volcanoes worldwide*

Volcano	Hg/SO_2	References
Etna's bulk degassing	8.9×10^{-5} to 1.5×10^{-7}	Dedeurwaerder *et al.* (1982), Varekamp & Buseck (1986), Ferrara *et al.* (2000)
Etna North East's fumaroles	2×10^{-6}	Varekamp & Buseck (1986)
Colima	2.5×10^{-6}	Varekamp & Buseck (1986)
Vulcano Island	1.16×10^{-7} to 2.4×10^{-6}	Ferrara *et al.* (2000), Aiuppa *et al.* (2007), Zambardi *et al.* (2009)
Mt Erebus	8.8×10^{-6}	Kyle *et al.* (1990)
White Island	2.9×10^{-6}	Wardell *et al.* (2008)
Mt Shasta	39×10^{-6}	Varekamp & Buseck (1986)
Mt Hood	7.1×10^{-6}	Varekamp & Buseck (1986)
Mt St Helens	6.0×10^{-6}	Varekamp & Buseck (1986)

beneath volcanoes (Jenner *et al.* 2010; Stracke 2012) by processes involving volatile release from the underlying hydrated subducting slab and entrained oceanic sediment (Mungall 2002; Labanieh *et al.* 2012; Henley & Berger 2013). More data are required to better explore Hg behaviour from volcanoes where a subduction component is involved in magmagenesis; recent studies (Pyle & Mather 2009) suggested that a significant component of Hg in volcanic emissions may originate from the subducting slab, as observed for other elements such as Br, Cl and I in volcanic emissions.

By putting our new data into the context of published volcanic gas compositions from various geodynamic settings (arc volcanism and within plate/rift volcanism; Fig. 9, data source in Tables 1 & 2), we find an extremely variable composition ranging from Hg to H_2O-rich, respectively. The Hg-rich end-member of the triangular plot shown in Figure 9 corresponds to the 1980 Mt St Helens explosive eruption (SH), characterized by fairly high Hg to sulphur mass ratio (3.3×10^{-3}; Varekamp & Buseck 1986) which differs significantly from the ratio which usually characterizes the phase of passive degassing of the volcano (6×10^{-6}; Varekamp & Buseck 1986). Gaseous emissions from Rincón de la Vieja volcano (RIN) are H_2O-rich and poor in sulphur and Hg, probably due to the strong gas scrubbing by the lake and/or the high air dilution of the collected fumes. Intermediate compositions identify no clear trend and emphasize the presence of a compositional gap for sulphur-poor, Hg- and H_2O-rich volcanic gases. Water in volcanic gas represents an intrinsically highly variable parameter affected by condensation at numerous sites (fractures, hydrothermal systems, lakes and atmosphere), and its variability in this dataset is not surprising (as confirmed by the highly variable H_2O/S_{tot} ratios). Gases from closed-conduit volcanoes in a fumarolic stage of activity and from volcanic lakes of arc-volcanism (i.e. Poás, Rincón de la Vieja, Mutnovsky and Aso) show very low Hg contents, probably due either to (1) the role played by the omnipresent wall-rock–gas and water–gas interactions which potentially favour Hg deposition in the hydrothermal envelope, or (2) the lake's gas scrubbing, respectively. Although limited, our data however suggest that there is no clear Hg/S_{tot} and Hg/H_2O dependence on volcanic setting, but further detailed investigations are required.

Hg emission fluxes from volcanic degassing

Mercury emission rates from volcanoes are usually assessed by scaling the determined GEM/SO_2 to the simultaneously determined SO_2 emission rates. The volcanic Hg emissions inventory is summarized in Table 2, where Hg fluxes from the literature with relevant data sources are also reported. The lowest Hg flux ($0.002\ t\ a^{-1}$) in our dataset is derived for Poás volcano, followed by Aso (*c.* $0.33\ t\ a^{-1}$), Mutnovsky ($0.71\ t\ a^{-1}$), Gorely ($0.9\ t\ a^{-1}$), Turrialba ($2.4\ t\ a^{-1}$) and Etna ($4.2\ t\ a^{-1}$). While our estimates of Hg flux in the plumes of Aso and Etna volcanoes are comparable to those reported in the literature by previous authors (*c.* 0.3 and $5.4\ t\ a^{-1}$, respectively; Andres & Kasgnoc 1998; Bagnato *et al.* 2007), our bulk Hg emission flux measured at Mutnovsky volcano ($0.71\ t\ a^{-1}$) is about one order of magnitude higher than the value proposed by Taran *et al.* (1992) of $0.05\ t\ a^{-1}$. The difficult meteorological conditions encountered on the top of Rincón de la Vieja volcano in April 2013 did not allow us to estimate SO_2 emissions needed for calculating the Hg flux. No data on SO_2 flux related to Rincon's recent degassing activity are available; Hg emission rate from this volcano has not been included in our calculation of the cumulative flux from active volcanism.

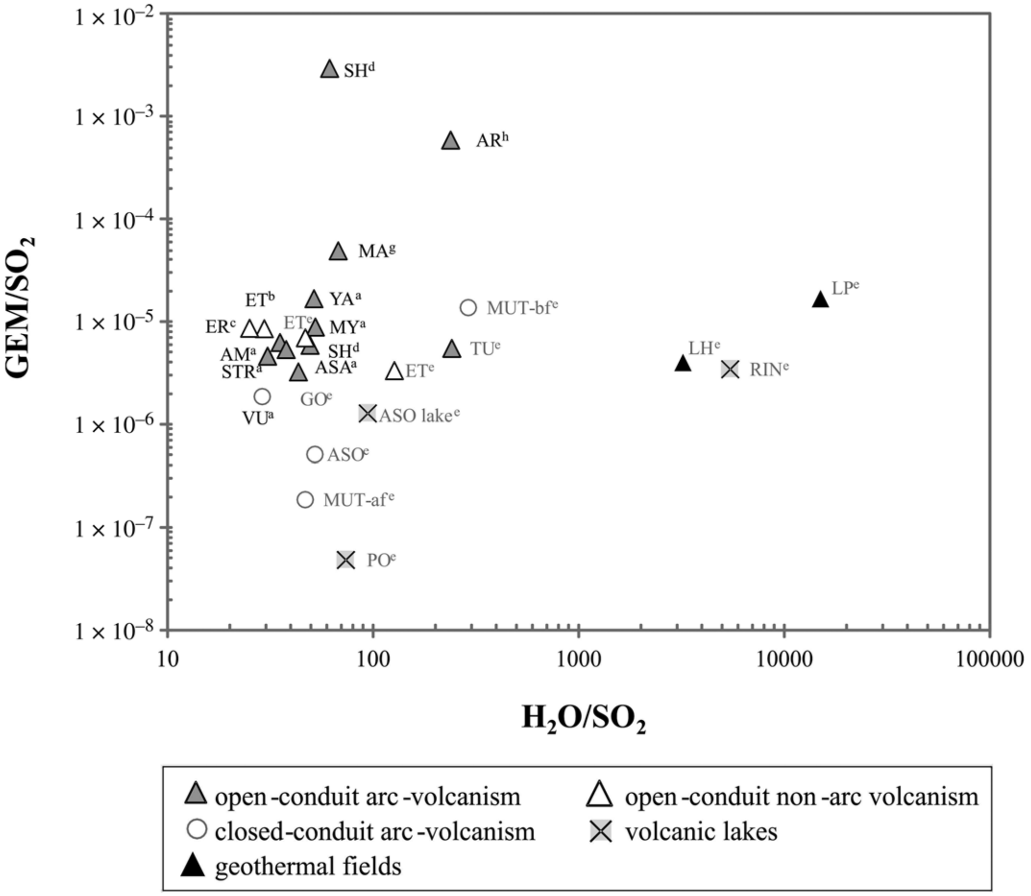

Fig. 8. Scatter plots of GEM/SO_2 (mass) ratio v. H_2O/SO_2 (molar) ratio of arc (grey symbols) and non-arc (black open triangles) volcanoes. The graph was constructed from results obtained in this study (grey text) and previously published data (black text). A distinction was made between the emission type plotted in the graph to show open/closed vent, arc/non-arc volcanism, volcanic lake evasion and geothermal fields. The diagram suggests that there is some difference between the GEM/SO_2 in arc and non-arc setting (see Table 2). 'Arc' volcanoes show an overall positive correlation between H_2O content and GEM/SO_2 ratios, which might suggest that gas emissions in subduction zones may contain more Hg (relative to SO_2) than those from divergent (or within-plate) plate volcanism. Literature H_2O/SO_2 data and GEM/SO_2 mass ratios are from [a]Bagnato *et al.* (2011) (NY, Nyiragongo; YA, Yasur; AM, Ambrym; STR, Strombolim; ASA, Asama; MY, Miyakejima; VU, Vulcano); [b]Bagnato *et al.* (2007) (ET, Etna); [c]Kyle *et al.* (1990) (ER, Erebus); [d]Varekamp & Buseck (1986) (SH, St Helens); [e]this study (ET, Etna; PO, Poás; TU, Turrialba; RIN, Rincón de la Vieja; LH, Las Hornillas; LP, Las Pailas; ASO, Aso; MUT, Mutnovsky; GO, Gorely). Hg and H_2O concentrations have been multiplied and divided, respectively, for a certain factor in order to improve the representation of data inside the graph.

The large spread of our estimated Hg fluxes reflects the variable GEM/SO_2 ratios (10^{-5} to 10^{-8}) exhibited by the investigated volcanoes and reveals variability in the SO_2 mass flux and hence in the underlying mode of degassing. We stress that data presented here refer to volcanoes in a state of passive degassing activity, and that the above-cited values have to be considered as a lower bound (Table 2). Our calculations confirm that the continuous year-on-year emission from passively degassing volcanoes is relatively small if compared to explosive eruptions, which are usually accompanied by considerable SO_2 emission (e.g. 1991 Pinatubo eruption, Ansmann *et al.* 1997; 1980 Mt St Helens eruption, Varekamp & Buseck 1981). The most significant single-event emissions are those associated with rare, large explosive eruptions occurring once or twice per century

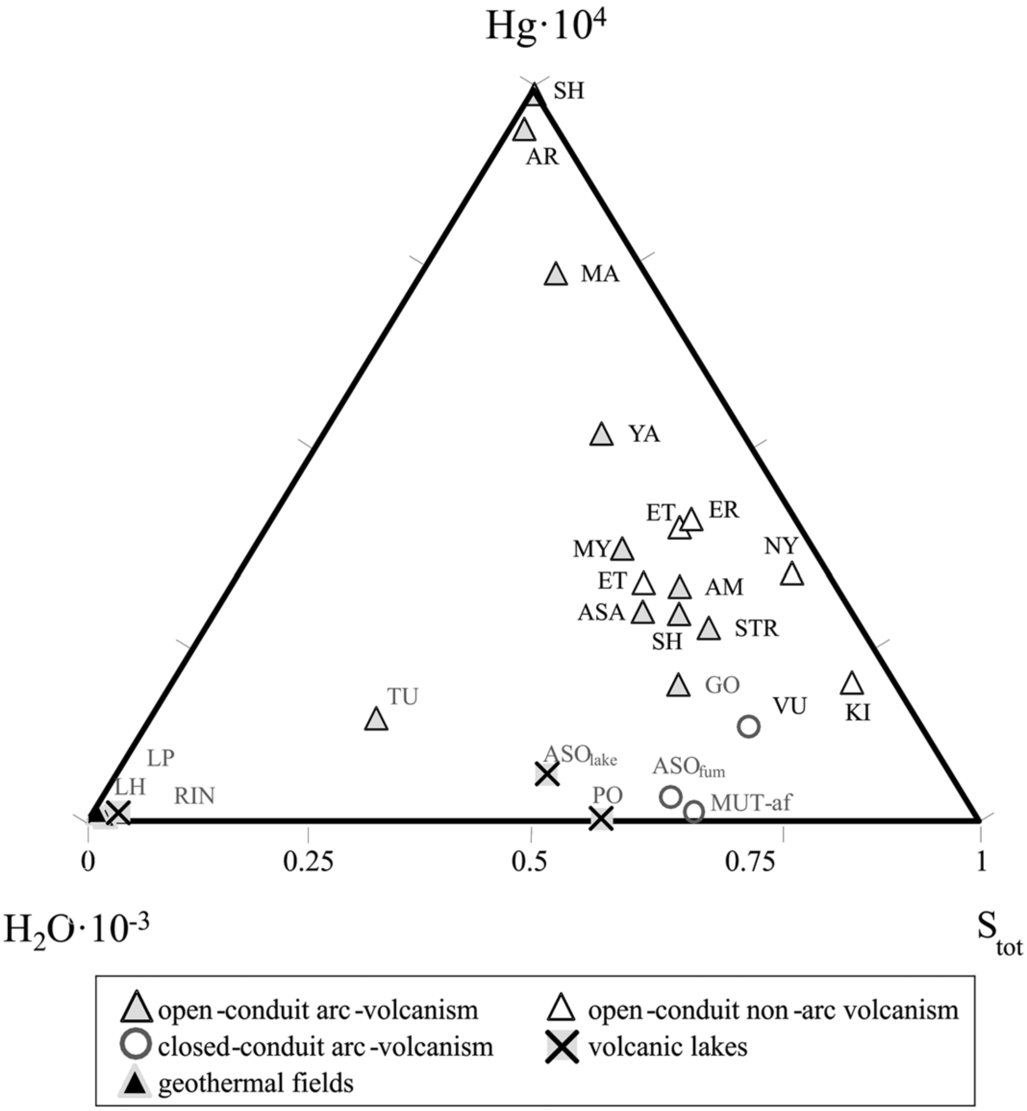

Fig. 9. SO_2–H_2O–Hg triangular plot of relative concentrations in the plumes of the investigated volcanoes. Our original data (grey text) are set in the context of published volcanic gas compositions from various geodynamic settings (black text). A distinction was made between the emission type plotted in the graph to show open/closed vent, arc/non-arc volcanism, volcanic lake surface and geothermal fields. Our dataset exhibits a very variable composition ranging from Hg to H_2O-rich, respectively. The most H_2O-poor composition is observed at Nyiragongo and Kilauea (NY and KI). Stromboli (ST) gases are S-enriched (and depleted in H_2O) relative to 'typical' arc volcanic gases. The most H_2O-rich composition is observed at Rincón de la Vieja volcano while the most Hg-rich composition is observed for Mt St Helens explosive eruption in 1980 (SH) and Arenal (AR). Data source are taken from Tables 1 and 2 (this study) and from the literature: NY, Nyiragongo; YA, Yasur; AM, Ambrym; STR, Stromboli; ASA, Asama; VU, Vulcano, Bagnato *et al.* (2011); MA, Masaya, Witt *et al.* (2008*a*, *b*); ET$_{bulk}$, Etna bulk, Bagnato *et al.* (2007); SH, St Helens, Varekamp & Buseck (1986); AR, Arenal, Zimmer *et al.* (2004); Ballantine *et al.* (1982); ER, Erebus, Kyle *et al.* (1990).

which may instantaneously release 10 to 10^3 Tg SO_2 to the atmosphere (Pyle & Mather 2003). Such large eruptions, which may release $>10^3$ to 10^4 Mg Hg per event, are thought to significantly perturb the atmospheric Hg reservoir for *c.* 1 yr (Pyle & Mather 2003).

Hg emission fluxes from geothermal areas

Mercury fluxes from geothermal areas are still poorly investigated and highly uncertain due to the complexity of making appropriate measurements of Hg emissions (e.g. Gustin 2003), but probably total $\leq$60 t Hg a^{-1} (Varekamp & Buseck 1986; Nriagu & Becker 2003; Pyle & Mather 2003). The Hg/SO$_2$ approach for estimating Hg flux from volcanoes is not readily applicable to geothermal sources since the hydrothermal fluids are efficient sulphur scrubbers and there is no reliable method for measuring the flux of the dominant form of sulphur in these systems. In order to define Hg emission rates from Las Pailas and Las Hornillas geothermal fields, we interpolated (using the kriging contouring technique) the site-specific emission data to obtain contour maps of the Hg deposition flux which, by integration over the entire area covered by the survey (Fig. 3), allowed calculation of the integrated amount of Hg on a horizontal surface above the fumarolic areas (ng m^{-1}). In order to calculate the Hg fluxes through these contoured area, the gas rising speed was extrapolated from *in situ* observations, displaying similar values to other not over-pressurized fumarolic emissions (Vulcano island, Tamburello *et al.* 2011; Campi Flegrei, Aiuppa *et al.* 2013; Nea Kameni, Bagnato *et al.* 2013). By considering a highly variable gas speed of 0.5–1.5 m s^{-1}, we estimated a time-averaged total Hg flux ranging from 0.0008 to 0.0024 t a^{-1} for Las Pailas and from 0.004 to 0.012 t a^{-1} for Las Hornillas emissions (Table 2). The cumulative Hg flux released from both geothermal fields therefore ranges from 0.005 to 0.014 t a^{-1}, appearing less important than the volcanic flux from continuous passive degassing and accounting for a very small proportion of the global Hg flux for geothermal emissions (*c.* 60 t a^{-1}; Varekamp & Buseck 1986).

Discussion

Our measurements provide new information to the debate on Hg emission from active volcanism (Table 4). Worldwide volcanic Hg fluxes vary widely since volcanoes display a wide range of activity from continuous to short-lived events, matched perhaps by their diversity and geographic distribution. While it has long been known that volcanoes are important atmospheric sources of Hg (Varekamp & Buseck 1981, 1986; Bagnato *et al.* 2007, 2009*a*, *b*, 2011), considerable uncertainty remains about the global volcanic Hg flux as the available data on volcanogenic Hg emissions is still sparse and incomplete (Pyle & Mather 2003). Using the database on active and passively degassing volcanoes of the island arc type, Anderson (1975) came up with a value of 100 t a^{-1}. This estimate contrasts with a much lower flux of 3–9 t a^{-1} reported by Unni *et al.* (1978). From measurements of non-eruptive emissions at Kilauea (Hawaii), Colima (Mexico), Cascades volcanoes (Mt Shasta, Mt Hood and Mt St Helens) and Etna (Italy), Varekamp & Buseck (1986) estimated the global Hg emission to be 830 t a^{-1}. Based on measurements of Hg/S ratios at three volcanoes (Kilauea, Etna and White Island), Fitzgerald (1986) was able to derive a global Hg flux of 20–90 t a^{-1}. More recently, Ferrara *et al.* (2000) used the Hg/S data for three volcanoes in Italy and Sicily (Etna, Stromboli and Volcano) to derive a global annual flux of only 0.6–1.3 t a^{-1}. Nriagu & Becker (2003) derived a global Hg fluxes ranging from 37.6 (from degassing plume) to 57 t a^{-1} (from explosive activity). More recently, Pyle & Mather (2003) suggested that Hg contributed annually by passively degassing volcanoes globally is of the order 75 t a^{-1} (range 6–900 t a^{-1}), or 700 t a^{-1} (range 80–4000 t a^{-1}) if considering the total time-averaged annual emission from degassing and erupting volcanoes. It is clear from Table 4 that there is a considerable range in estimates of the total Hg flux from volcanoes. The differences between previous Hg fluxes principally reflect the paucity of appropriate data on Hg in volcanic emissions and the ways that previous authors interpreted published data on volcanic Hg.

Table 4. *Previous estimates of global volcanic emission rates of mercury*

Source	Emission rate, ton Hg a^{-1}
Pyle & Mather (2003)	75 (passive degassing) – 700 (explosive activity)
Nriagu & Becker (2003)	37.6 (passive degassing) – 57 (explosive activity)
Varekamp & Buseck (1986)	30 (passive degassing) – 830 (explosive activity)
Ferrara *et al.* (2000)	0.6–1.3
Fitzgerald (1986)	20–90
Nriagu (1989)	500 (range 30–1000)
Unni *et al.* (1978)	3–9.0
Anderson (1975)	100

Table 2 summarizes our new observations on passive volcanic degassing, as well as previously published work. If considering the 12 volcanoes reported in Table 2 and referring to plume emission type, they account for a cumulative SO$_2$ flux of *c.* 6 Mt a^{-1} or 62% of the global SO$_2$ volcanic emissions from continuously passive degassing volcanoes (9.7 Mt a^{-1}; Andres & Kasgnoc 1998). We can therefore estimate Hg emissions in two ways: (1) a cumulative Hg emission flux based on Hg/SO$_2$ ratios and SO$_2$ fluxes at these 12 individual volcanoes, which amounts to 56 t a^{-1}; and (2) a global Hg emission flux based on the globally averaged Hg/SO_2 ratio of 7.8×10^{-6} ($\pm 1.5 \times 10^{-6}$; 1 SE, $n = 13$) and the global volcanic SO_2 flux of 9.7 Mt a^{-1} (Andres & Kasgnoc 1998). While Andres & Kasgnoc (1998) did not present an uncertainty budget associated with their 9.7 Mt a^{-1} SO_2 flux estimate, a second study on volcanic SO_2 fluxes proposed an uncertainty of 35% relative standard deviation (Graf *et al.* 1997) and is widely considered as appropriate (Schmidt *et al.* 2012). By combining our updated average Hg/SO_2 plume mass ratio for quiescent volcanic activity of 7.8×10^{-6} ($\pm 1.5 \times 10^{-6}$; 1 SE, $n = 13$) (Table 2) and the uncertainties on SO_2 flux we therefore obtain a global volcanic Hg flux from continuous passive degassing of 76 ± 30 t a^{-1} (Table 2). Our estimate is similar to that of Pyle & Mather (2003), but for the first time includes an estimate of uncertainty.

Since the global SO_2 emission rate used in this calculation (9.7 Mt a^{-1}; Andres & Kasgnoc 1998) represents open-conduit passive degassing, the total Hg flux from volcanoes during strong eruptive events may be even larger than that provided by the reported data in this study (Roos-Barraclough *et al.* 2002; Schuster *et al.* 2002).

The measurements of gas emissions from closed-conduit volcanoes in a fumarolic-stage of activity and geothermal emissions suggest a much smaller flux of Hg released from these activities. We estimated a cumulative Hg flux from three closed-conduit volcanoes (Aso, Mutnovsky and Poás; this study) and both geothermal fields (Las Pailas and Las Hornillas; this study) of *c.* 1 t a^{-1} (Table 2). If we also consider Hg fluxes from various quiescent degassing closed-conduit volcanoes in a fumarolic stage of activity recently reported in literature (0.55–0.65 t a^{-1}; Bagnato *et al.* 2011), our estimated cumulative Hg flux from closed-conduit volcanoes would increase to *c.* 1.6 t a^{-1} (*c.* 2% of our estimate of the yearly global Hg emission from passive degassing volcanoes). Although comprising a marginal contribution to the global volcanic non-eruptive Hg emissions from closed-conduit degassing volcanoes, these new data represent the first available assessment of Hg emissions directly sampled at these locations. The minor Hg input from closed-conduit volcanoes in fumarolic-stage of activity compared to open-conduit volcanoes mainly reflects different SO_2 degassing rates and the role played by the omnipresent wall-rock–gas and water–gas interactions, which potentially favour Hg deposition in the hydrothermal envelope (Figs 5 & 6).

Concluding remarks

This study provides new information to expand the limited database of volcanic Hg emissions and allows some inferences to be made regarding the quality of previous estimates of global volcanic Hg inventories. A critical assessment of the published literature suggests that some global Hg emission estimates are likely to be significantly underestimated. We demonstrate that volcanic degassing is an important component of the global atmospheric Hg budget, even when only considering quiescent phases of volcanic activity. Using our dataset in tandem with literature information, we propose a mean Hg/SO_2 mass ratio of *c.* 7.8×10^{-6} ($\pm 1.5 \times 10^{-6}$; 1 SE, $n = 13$) from quiescent degassing volcanoes as representative of gas emissions from the open-conduit degassing volcanoes used in this study. Taking into account the uncertainty in global SO2 emissions, we derive a global volcanic Hg flux from quiescent volcanoes of *c.* 76 ($\pm$30) t a^{-1}, which is comparable to previous literature estimates. Our analysis suggests that volcanoes in a state of passive degassing represent an important contribution to global volcanic mercury emissions into the atmosphere. It is therefore likely that volcanic contributions to the global atmospheric Hg budget will be even more important during large eruptive events. For this reason, the measurement of Hg in eruptive gases is a priority for future research.

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