Mercury gas emissions from La Soufrière Volcano, Guadeloupe Island (Lesser Antilles)

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ABSTRACT

Quantifying mercury (Hg) emissions from active volcanoes is of particular interest for better constraining the global cycle and environmental impact of this highly toxic element. Here we report on the abundance of total gaseous (TGM = $Hg^0_{(g)}$ + $Hg^{II}_{(g)}$) and particulate ($Hg_{(p)}$) mercury in the summit gas emissions of La Soufrière andesitic volcano (Guadeloupe island, Lesser Antilles), where enhanced degassing of mixed hydrothermal-magmatic volatiles has been occurring since 1992 from the Southern summit crater. We demonstrate that Hg in volcanic plume occurs predominantly as gaseous mercury, with a mean $TGM/Hg_{(p)}$ mass ratio of ~63. Combining the mean TGM/H_2S mass ratio of the volcanic plume (~3.2×10^{-6}), measured close to the source vent, with the H_2S plume flux (~0.7 t d^{-1}), determined simultaneously, allows us to estimate a gaseous mercury emission rate of 0.8 kg yr^{-1} from La Soufrière summit dome. Somewhat lower TGM/S_{tot} mass ratio in fumarolic gases from the source vent (4.4×10^{-7}) suggests that plume chemical composition is not well represented by the emission source (fumaroles) due to chemical processes prior to (or upon) discharge. Current mercury emission from La Soufrière volcano represents a very small contribution to the estimated global volcanic budget for this element.

1. Introduction

Among the several trace volatile elements identified in volcanic emissions (Oppenheimer et al., 2003; Pyle and Mather, 2003; Barghgiani and Ristori, 1991), mercury (Hg) is one of the most environmentally-significant (Mason et al., 1994), but also one of the most problematic to investigate. Particular attention is devoted to the study of its distribution in the environment due to both its extreme mobility and toxicity (Lamborg et al., 2003). In the last years, the outcome of experimental and theoretical studies has been dedicated to improve our understanding of processes involved in the dynamics of atmospheric Hg and to redistribute global Hg budget in terms of natural and human activity contributions. On a global basis, at present total anthropogenic Hg emissions into the atmosphere (mostly from combustion and waste incineration) account for about 2200 t yr^{-1} (Pacyna et al., 2006; Wilson et al., 2006) against 4000 t yr^{-1} estimated some years ago (Porcella et al., 1997). While the anthropogenic input to the atmospheric mercury budget is well documented (Hylander and Meili, 2003; Pirrone et al., 1996; Mason et al., 1994; Khalil and Rasmussen, 1994; Porcella et al., 1997; Pacyna et al., 2006; Wilson et al., 2006), mercury emissions from natural sources are still a

matter of great debate (accounting for a cumulative Hg flux ranging between 500 and 2000 t yr^{-1}; Selin et al., 2007; Mason et al., 1994). Particular importance has been devoted to the study of Hg contribution from active volcanoes, these last considered to account for a significant fraction of the natural mercury emissions into the atmosphere (12–78% of natural emissions; Zambardi et al., 2009; Varekamp and Buseck, 1981, 1986; Pyle and Mather, 2003).

In spite of this, volcanic and geothermal sources are still poorly investigated and often considered as negligible Hg contributors to the atmosphere even if significant Hg concentrations in volcanic gases have been systematically determined in many occasions (Varekamp and Buseck, 1981, 1986; Kyle et al, 1990; Ferrara et al., 2000; Bagnato et al., 2007; Aiuppa et al., 2007a; Witt et al., 2008a,b; Pyle and Mather, 2003). 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 mercury in soils and air (Varekamp and Buseck, 1981, 1986; Siegel and Siegel, 1984; Cox, 1983; Weissberg and Rohde, 1978).

Owing to its complex chemical behaviour, mercury is one of the most problematic trace elements to investigate. The large uncertainties on Hg transport mechanisms, reaction paths and residence times in the volcanic plume (Pyle and Mather, 2003) reflect the complex chemical and physical atmospheric processing of this element. Mercury can exist in the atmosphere in at least two different oxidation states (Hg^0 and $Hg(II)$) and in both gaseous and particulate

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forms (Mason et al., 1994; Lin and Pehkonen, 1999; Fitzgerald and Lamborg, 2003). Elemental mercury (Hg^0) is relatively chemically inert and represents the most abundant phase among the gaseous forms in the atmosphere (~98% of mercury in the atmosphere; Lindqvist et al., 1991). 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 systemic way (Bagnato, 2007; Bagnato et al., 2007; Witt et al., 2008a,b).

Divalent and particulate Hg are at least 10^5 times more soluble than Hg^0 (Lindberg and Stratton, 1998) and are readily removed from the atmosphere after emission by wet and dry deposition processes (Lindqvist et al., 1991; Slemr et al., 1985; Schroeder and Munthe, 1998). Due to its substantial vapour pressure Hg^0 exists predominantly in the gaseous phase, and its lower solubility prevents its efficient removal through wet deposition while it is mainly transported back to the surface through dry deposition at very low rate (Lin and Pehkonen, 1999). The chemical speciation and physical forms of mercury are therefore critical to determine the fate and environmental (and health) impacts of this metal once emitted from the emission sources. Near source, contamination is mostly related to the emission of divalent and particulate forms of Hg. Wide-scale dispersion of volcanic Hg can be expected if this element prevalently occurs in the form of elemental mercury ($Hg^0_{(g)}$) at emission and during transport, owing to its relatively-long atmospheric lifetime (~0.5–2 yr; Lindqvist and Rodhe, 1985; Slemr et al., 1985). On the other hand, fast oxidative reactions in the atmosphere and low chemical reactivity (Lindqvist and Rodhe, 1985), giving rise to the formation of more reactive (and often condensed) Hg(II) species, may potentially lead to rapid deposition of volcanic Hg. The chemistry of mercury in the atmospheric environment may take place in the gas or in the aqueous phase as well as in the heterogeneous phase in aerosol, through complex physical–chemical transformations governed by oxidation of elemental Hg and reduction of divalent Hg. Important oxidants in the aqueous phase are represented by ozone, hydroxyl radical and chlorine; while in the atmospheric gaseous phase ozone, hydroxyl radical, nitrate radical and hydrogen peroxide tend to oxidise $Hg^0_{(g)}$ to more soluble forms (Lin and Pehkonen, 1999). In the atmosphere, divalent mercury can react with numerous ligands such as OH^-, Cl^-, Br^-, I^-, etc., to form relative stable inorganic complexes such as $HgCl_2$, $Hg(OH)_2$ (Seigneur et al., 1994). Particulate Hg is formed when divalent Hg complexes are adsorbed onto particles particularly within atmospheric water droplets (Plejiel and Munthe, 1995a,b). It was suggested that up to 35% of the dissolved divalent mercury species can be adsorbed onto particulate matter consisting mainly of sparingly soluble compounds such as HgO and HgS (Seigneur et al., 1994), primarily removed via dry deposition. Hence, the fate of mercury upon plume dispersion will depend on which form (elemental or divalent) prevails in volcanic emissions and on the extent to which $Hg^0_{(g)}$ is oxidised to Hg(II) forms depending on plume humidity, aerosol content and of the concentrations of the most important oxidative agents.

Available determinations of mercury fluxes from active volcanoes (see Pyle and Mather, 2003, for a review) were obtained by measuring the total (gaseous + particulate) Hg concentrations in volcanic plumes, and then scaling the Hg(tot)/SO_2 concentration ratio to the SO_2 plume flux, measured by UV remote sensing (e.g. McGonigle et al., 2002). However, while such an approach works for high-temperature SO_2-dominated magmatic gas emissions, it cannot be applied on the many quiescent volcanoes with hydrothermal activity, whose low temperature emissions contain only or prevalently H_2S as S-bearing gas species (e.g. Giggenbach, 1996). Now, most of the active subaerial volcanoes on Earth display low temperature hydrothermal activities, frequently for very long periods, between their magmatic eruptions. The lack of informations about their mercury emissions thus contributes a significant uncertainty to the estimated global Hg volcanic inventory (Nriagu and Becker, 2003; Pyle and Mather, 2003; Varekamp and Buseck, 1986). Determining mercury flux on these volcanoes then requires alternative approaches, such as measure-

ments of both Hg(tot)/H_2S concentration ratio and H_2S emission rates. Since H_2S cannot be retrieved with available remote sensing techniques (O'Dwyer et al., 2003), direct measurements of its concentration and output in volcanic plumes are necessary using either specific multi-gas sensors (Aiuppa et al., 2005a,b; Bernard et al., 2006) or even filter-packs (Aiuppa et al., 2005a,b).

Here, we report on the first measurements of total gaseous mercury (TGM) and particulate mercury and H_2S concentrations in both summit fumaroles and volcanic plume of La Soufrière volcano, in Guadeloupe island (Lesser Antilles arc).Persistent emission of H_2S-rich fumarolic gases from the South Crater (SC) summit vent of this andesitic volcano generates a small volcanic plume whose production rate in H_2S and other major gas components was determined simultaneously to our measurements (Allard et al., 2006, pers. comm. and Allard et al., submitted for publication). This allows us to quantify the emission rate of mercury from this Caribbean volcano. Moreover, the comparison between TGM/H_2S ratios in the concentrated fumarolic gases and the diluted volcanic plume provides insight into the chemical processing that can affect both Hg and H_2S upon emission of volcanic gases in the cold and oxidizing atmosphere. Such a comparison offers new data relevant to the interpretation of the atmospheric behaviour of these environmentally significant two species.

2. Study area and methods

La Soufrière volcano makes part of a large andesitic volcanic complex (La Grande Decouverte) built in the southern part of the volcanic Basse Terre island of Guadeloupe. It is topped by a lava dome (1400 m a.s.l.) that was extruded during the last magmatic eruption in 1530 A.D. (Boudon et al., 1988; Komorowski et al., 2008). Since then, intense hydrothermal activity, sustained by continuous input of magma-derived gases into the hydrothermal system (Allard et al., 1998), has persisted at La Soufrière. Manifestations include fumaroles along fractures cutting the lava dome, solfataras, and hot springs around the base of the dome, and occasional series of phreatic eruptions. The last phreatic eruption, in 1976–1977, consisted in 26 outbursts associated with dense steam-and-ash columns rising above the volcano summit (Le Guern et al., 1980; Boudon et al., 1988). After May 1977, fumarolic activity on and around the dome gradually declined and became essentially concentrated at the South Crater (SC) fracture vent on top of the dome (Fig. 1). However, in coincidence with anomalous seismicity, fumarolic degassing at the crater markedly increased since 1992, producing very acid (pH ≤ 1) HCl–H_2S-rich emissions and sustaining a true volcanic plume (Zlotnicki et al., 1992; Komorowski et al., 2001). The origin of this enhanced acid gas discharge remains poorly understood; it may reflect either an increased influx of HCl-rich magmatic fluid into the hydrothermal system (Villemant et al., 2005; Bernard et al., 2006); or/and an increasingly concentrated gas flow through the central conduits of the volcano due to gradual sealing of the lateral degassing areas since 1977 (Zlotnicki et al., 1992; Allard et al., 2006 and Allard pers. comm. and in submitting).

Our measurements were carried out in March 2006 during a period of sustained degassing from the SC fracture vent. They benefited from very favourable (rare) weather conditions, with ambient temperature ranging from 19–16.0 °C and an average relative humidity as low as 48% (rather than commonly close to 100%).The wind speed averaged ~3.5 m s^{-1}. This allowed easy sampling of the issuing fumarolic gases (108 °C) and accurate analysis of the small volcanic plume whose dimensions could be clearly defined (Allard et al., 2006, and in submission).

Mercury concentrations and speciation were determined in the concentrated fumarolic gas feeding the plume. Gas sampling from the NW–SE trending SC steaming fracture (Fig. 1) was performed with the routine procedure operated by the local volcano Observatory, using a 3-m long insulated tubing of the vent and pre-evacuated glass bottles with stopcocks. The fumarolic gas, soon analysed after sampling at the
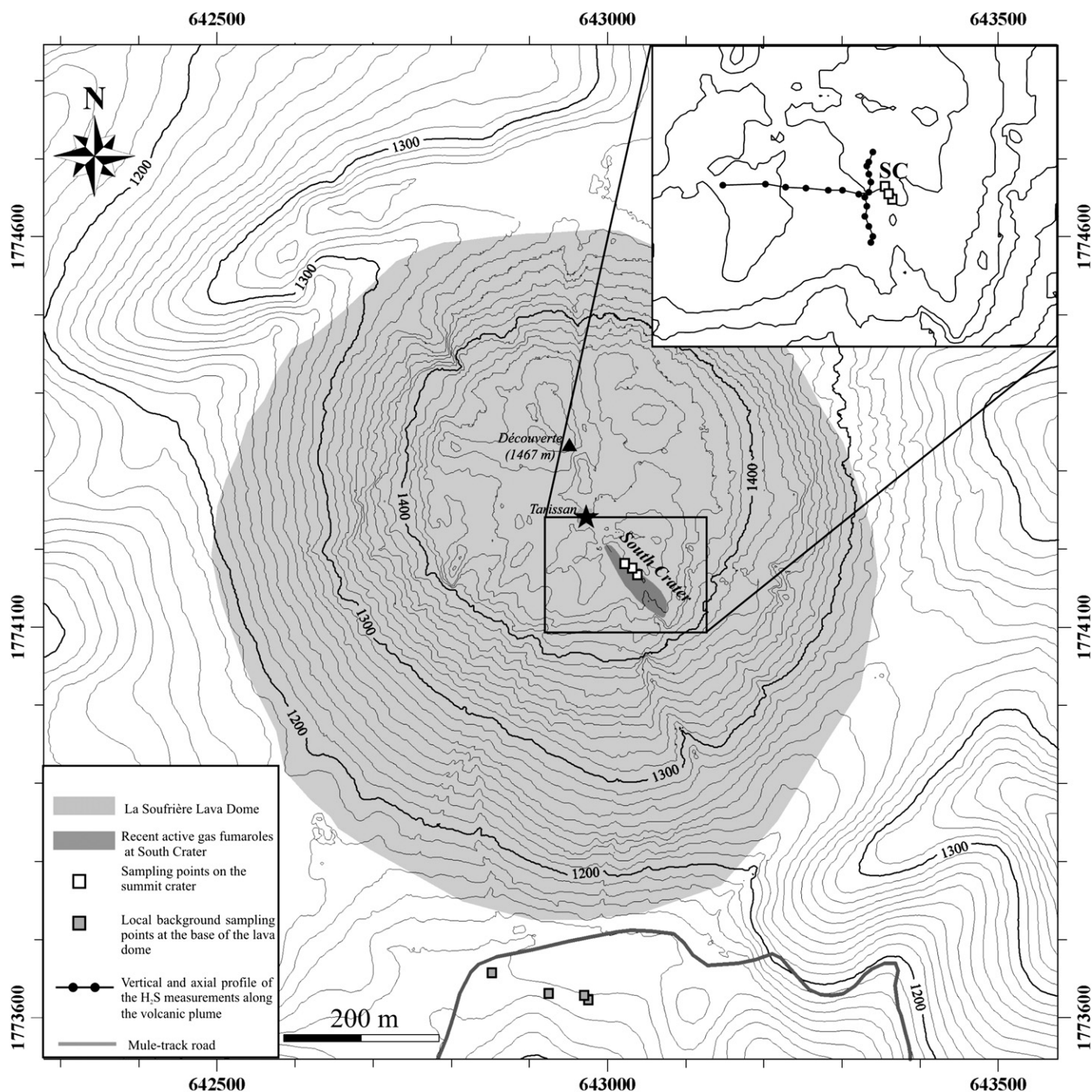
Fig. 1. Sampling locations on the Crater South, La Soufrière, Guadeloupe (white squares). For each point, two TGM collections were carried out by gold traps (in total six collected sampling sites). Local background sampling points at the base of the volcano are also reported (grey squares). The crossed lines in the insert correspond to the two transects (axial and vertical profiles) used to measure H_2S concentrations and flux in the Crater South plume emissions (Allard pers. comm. and in submission).

Soufrière volcano Observatory, was dominated by steam (97.8 mol% of H_2O); and contained, in the water-free gases, 66.4% of CO_2, 30.9% of H_2S and 0.62% of SO_2 (Table 1). TGM concentration was determined in both the condensed steam fraction and in the 'dry' gas phase simultaneously collected using a home-made portable system similar to that developed by Nakagawa (1999) and already used at La Fossa Crater, Vulcano Island (Bagnato, 2007; Aiuppa et al., 2007b). This device consists of two condensate traps connected in series with a gold-trap. The steam coming from the fumarole was first condensed using a condenser–separator in which the fluid was cooled rapidly from 108 °C to about 30 °C using acetone as a coolant. The condensate formed was collected in two glass vessels. The uncondensed gas

fraction was then pumped to the Au-trap. After collection, total dissolved mercury in the condensed phase was measured by CVAFS after reduction with tin chloride, according to the EPA Method 1631 procedure (1999a). The Au-trap was analysed with the conventional US-EPA Method IO-5 (US EPA, 1999b).

Plume sampling for mercury analysis was carried out only about 2 m downwind of the South Crater fracture vent. We collected both the total gaseous mercury ($TGM = Hg^0_{(g)} + Hg^{II}_{(g)}$) and particulate mercury ($Hg_{(p)}$). Background measurements outside the plume were also performed for comparison (all measurement locations are indicated in Fig. 1). TGM in the volcanic plume was collected on gold-coated bead traps, through which the diluted plume was pumped at a nominal flow

Table 1
Crater South's fumarole composition in March 2006.

Temperature	108
H_2O	97.8
Dry gas	2.2
CO_2	66.4
SO_2	0.62
H_2S	30.9
H_2	0.79
O_2	0.26
N_2	1.01
CH_4	0.081
Condensed Hg fraction	0.45×10^{-7}
Un-condensed Hg fraction	0.0046×10^{-7}
TGM content in fumarole	0.46×10^{-7}
TGM/S_{tot} mass ratio	4.4×10^{-7}

Data are a courtesy of IPGP – Guadeloupe, except for Hg species.
All concentrations are in mol% and temperature in °C.

rate of $0.5 \, l \, min^{-1}$ (Ebinghaus et al., 1999) for periods ranging from 20 to 60 min. The collected Hg was measured in lab by cold vapour atomic fluorescence spectrometry (CVAFS) with a Tekran 2600, based on the conventional thermal-desorption amalgamation technique (EPA Method IO-5; US EPA, 1997, 1999a,b; Ebinghaus et al., 1999). Uncertainty on TGM concentrations is ~10%. Particulate mercury ($Hg_{(p)}$) was collected using AES Minitraps (Lu et al., 1998), which consisted of a quartz fibre filter of 7-mm diameter, housed in a quartz glass tube of 140-mm length and supported by a pure Ni-screen grid (Wängberg et al., 2001, 2003). Pumping through the quartz tubes was at a flow rate of $3–5 \, l \, min^{-1}$. For its analysis, particulate mercury trapped on the filters was first thermally desorbed by heating to 800–900 °C in a stream of pure argon, then converted to $Hg^0_{(g)}$ and detected by CVAFS (Bloom and Fitzgerald, 1988). The presence of sulphur on the filters reduced the efficiency of the method, providing a detection limit of about $0.2 \, ng \, m^{-3}$ and a precision of $\pm 30\%$, rather than potential respective values of $0.003 \, ng \, m^{-3}$ and $\pm 10\%$ (Wängberg et al., 2003).

H_2S concentrations in the volcanic plume were measured simultaneously by using a specific portable electrochemical sensor (Membrapor H_2S/S-50, $\pm 2\%$ accuracy; see Aiuppa et al., 2005b). Concentrations were measured, both vertically and horizontally, within the plume cross-section at 5 m downwind of SC fracture vent, during a 40 m-long walking traverse orthogonal to the blowing plume direction. Detailed vertical and horizontal profiling of H_2S concentrations in the plume cross-section (Allard et al., submitted for publication) showed that the geometry of the plume was well defined at 5 m distance from the SC vent. The sharp increase of both H_2S and relative humidity with respect to ambient air at both edges of the transect (Fig. 2) constrains a plume cross-section width of ~35 m. Their vertical distribution, measured at several points, shows that the volcanic plume was comprised between ~0.2 m and 2 m height above the ground: no H_2S and typical air background temperature and RH% values were detected below and above these heights. We thus infer a maximum average plume thickness of ~1.8 m, in agreement with visual estimates (Fig. 2). The volcanic flux of H_2S was then determined by scaling the H_2S distribution in the volcanic plume to the plume dimensions and the time-averaged wind speed. Finally, the flux of mercury was calculated combining together the TGM/H_2S ratio and the volcanic H_2S output (Allard et al., 2006, and Allard et al., submitted for publication).

3. Results

3.1. Mercury content of the fumarolic fluid

The chemistry of fumarolic gases is related to the activity of the underlying volcanic system, providing helpful in understanding both the sources of volcanic fluids and for volcano surveillance (Giggenbach, 1992; Chiodini et al., 1995; Fisher et al., 1997). At present, there is a need of further work to characterize Hg distribution among volcanic plume
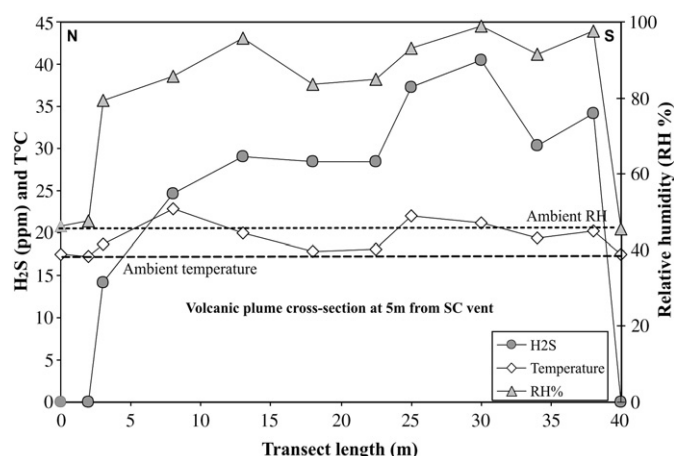

Fig. 2. Variation of H_2S, T(°C) and relative humidity in the plume of Crater South along the covered walking transects (error $\pm 10\%$, is also reported).

and fumarolic fluid, and actually Hg transformation during plume evolution as a function of temperature and physicochemical variations is quite poor documented. As previously focused by many authors (Aiuppa et al., 2007b; Zambardi et al., 2009; Sakamoto et al., 1989; Noda, 1983; Fukuzaki et al., 1983; Nakagawa, 1984, 1985, 1999), it is equally important to study the speciation of volcanic Hg in the fumarolic gases and during the evolution of volcanic plumes.

The total mercury content of the fumarolic fluid issuing from Southern crater vent (Table 1) is given by the TGM concentrations measured in the steam condensates ($5 \, \mu g \, l^{-1}$) and in the un-condensed gas-fraction given by the in-line Au-trap ($0.005 \, \mu g$ of $Hg \, l^{-1}$). Data suggest that, even if a part of Hg is released to the atmosphere from fumaroles, an important amount of Hg dissolved in the condensed steam exists, being probably strongly associated as mercury sulphide complexes ($Hg(H_2S)_2$ and $Hg(HS)_2$) or Cl-complexes ($HgCl_2$).; Christenson and Mroczek, 2003).We thus find that 99% of mercury was recovered in the condensate. Combining the above numbers with the volume of condensate and the measured steam/gas volumetric ratio (45), we derive a total mercury concentration of 0.46×10^{-7} mol% in the fumarolic fluid. The measured H_2S concentration of 0.66 mol% in the same fluid (Table 1) yields a TGM/H_2S molar ratio of 7×10^{-8} (or 4.4×10^{-7} by weight).

3.2. Mercury concentrations in the volcanic plume

The evaluation of Hg contribution from degassing volcanoes has been limited by the lack of simultaneous determinations of all the relevant Hg species in volcanic plume (Bagnato et al., 2007; Pyle and Mather, 2003). Previous studies evidenced that Hg is enriched in volcanic and hydrothermal gases (Varekamp and Buseck, 1981, 1986) and tends to leave the magma in the early stage of degassing, suggesting that early escape of CO_2 from magma might distil Hg too, leading to high Hg/SO_2 ratios before eruptions; quietly emplaced magmas (e.g., domes) probably emit Hg-depleted vapors.

Table 2
Concentrations and ratios observed in the plume of Crater South Guadeloupe island on March 2006.

Mean (n = 6) TGM ng m^{-3}	Mean (n = 4) Hg$_{(P)}$ ng m^{-3}	Mean (n = 4) background TGM level ng m^{-3}	Mean (n = 12) H_2S at 2 m from the SC mg m^{-3}	Mean H_2S emission rate t d^{-1}	Mean TGM/ H_2S Plume mass ratio	Mean Hg emission rate kg yr^{-1}
157 (108-189)	2.5 (2.3-3.1)	19 (15-20)	49 (46-52)	0.7	3.2×10^{-6}	0.8

Average mercury emission rate is also reported (kg yr^{-1}).

Table 2 shows the concentrations of the different Hg species in the near-vent volcanic plumes. TGM concentrations range from 108 to 189 ng m^{-3}, with a mean value ($n = 6$) of 157 ng m^{-3}, and are about one order of magnitude higher than those measured in air samples at the base of the volcano (range: 15–20 ng m^{-3}, near Col de l'Echelle, Fig. 1). The plume concentration of particulate Hg (Hg(p)) averages only 2.5 ng m^{-3} ($n = 4$, range: 2.3–3.1 ng m^{-3}). Therefore, ~98% of the mercury present in La Soufrière volcanic plume was gaseous, the particulate fraction accounting for about 2% under the examined conditions (poor ash content and a volcanic plume with average relative humidity of 92%, just under water vapour saturation). This 2% could be associated with the H_2SO_4 droplets that are present in volcanic plumes (Rose et al., 1982), because Hg is quite soluble in H_2SO_4 (Varekamp and Buseck, 1986).

At the site where TGM was determined, we measured an average H_2S molar concentrations of 49 ppm (and ranging from the mean value of 49 ppm at 2 m to 4 ppm at 55 m from the South Crater); as well as an average SO_2 concentration of 2.7 ppm (range: 1.7 to 4.2), by using filter packs connected in-series with Au-trap (Bagnato et al., 2007). This gives a H_2S/SO_2 molar ratio of 18, that is 2.5 lower than that measured in the fumarolic fluid (Table 1) and probably reflect partial air oxidation of H_2S into SO_2 as the fluid is strongly air diluted while emitted into the atmosphere (Allard pers. comm. and Allard et al., submitted for publication). It remains, however, that H_2S is the prevalent S-bearing gas species in La Soufrière volcano emissions (Bernard et al., 2006; G. Hammouya, pers. comm.). Fig. 2 shows the variation of H_2S concentration in the plume of Crater South along the covered walking transects. Our results thus imply a TGM/S_{tot} mass ratio of 3.0×10^{-6} in the expanding volcanic plume and a TGM/H_2S weight ratio of 3.2×10^{-6}. This latter value is about one order of magnitude higher than the ratio determined in the fumarolic fluid (4.4×10^{-7}). The factor 10 difference between plume and fumarole compositions provides evidence for that low-T and low-flux fumarolic gas emissions are not good proxies for Hg gas emissions from a fuming volcano. In particular, we propose that Hg depletion in the fumarole (relative to S and the plume) might be due to Hg aqueous phase processing, likely due to steam condensation prior to (or upon) surface discharge, or even upon sampling.

3.3. Volcanic flux of mercury

From the distribution mapping of H_2S in the volcanic plume cross-section and the measured wind speed (3 m s^{-1} on average), the average plume emission rate volcanic H_2S was found to be ~0.7 t d^{-1} in March 2006 (Allard et al, 2006, and in submission). The average plume TGM/H_2S weight ratio then allows us to estimate the emission of 0.8 kg yr^{-1} (or ~2.2×10^{-6} t d^{-1}) of mercury from La Soufriere summit fumarolic activity in March 2006 (Table 2).

4. Discussion

The results obtained in this study provide new constrains on the abundance and the chemical speciation of mercury in hydrothermal volcanic fluids. The following four main observations were made:

(i) We confirm recent experimental observations (Bagnato, 2007; Bagnato et al., 2007) that mercury is predominantly emitted as a gaseous species (compared to other condensed liquid or particulate forms) in passive (ash-poor) volcanic plumes fed by both hydrothermal and magmatic degassing. For instance, the small fraction of Hg in the particulate phase (Hg$_{(p)}$), in La Soufriere hydrothermal volcanic plume (~2%) is comparable to that found in Mount Etna's magmatic-type volcanic plume (~1%; Bagnato et al., 2007). Previous determinations of Hg speciation in volcanic plumes had not yet provided such a clear consensus. For example, DeDuerwarder et al. (1982) had

reported much higher (up to ~60%) and more variable proportions of Hg(p) in volcanic plumes.

(ii) The average TGM/S_{tot} weight ratio of 3.0×10^{-6} measured in La Soufrière volcanic plume falls in the range of the ratios found at other volcanoes in passive degassing, such as Kilauea in Hawaii (5.0×10^{-4}, Siegel and Siegel, 1984), Etna (8.9×10^{-5} to 1.5×10^{-7}; Buat-Menard and Arnold, 1978; DeDuerwarder et al., 1982; Ferrara et al., 2000; Varekamp and Buseck, 1986; Bagnato et al., 2007), Colima (2.5×10^{-6}; Varekamp and Buseck, 1986), Arenal (6.0×10^{-4}; Ballantine et al., 1982), Vulcano (1.16×10^{-7} to 2.4×10^{-6}; Ferrara et al., 2000; Bichler et al., 1995; Aiuppa et al., 2007b), Mt. Erebus (8.8×10^{-6}; Kyle et al, 1990), Masaya (2.0×10^{-5}; Witt et al., 2008a), Mount St. Helens (6.0×10^{-6}; Varekamp and Buseck, 1986), and Tatun volcanic filed (0.7–1.2×10^{-6}, Witt et al., 2008b). The TGM/S_{tot} ratio at La Soufriere falls however at the lower end of the range (10^{-4}–10^{-6}; see Fig. 3) considered typical for non-explosive volcanic volcanism (Pyle and Mather, 2003).

(iii) Our determination of the Hg emission rate from La Soufriere (0.8 kg yr^{-1}) adds new information to the limited data base about the volcanic mercury source strength. We find that La Soufrière volcano presently contributes a very trivial fraction (~0.001%) of Pyle and Mather (2003)'s estimate for global Hg emissions from continuously degassing volcanoes (7.5×10^4 kg yr^{-1}).

(iv) Data from both volcanic plumes and fumarolic condensates have recently been integrated in order to assess the volcanic Hg source strength on a global scale (e.g., Nriagu and Becker, 2003). However, the extent to which both types of data provide consistent Hg concentrations at a given volcanic system has not previously been demonstrated. Indeed, both Hg and S (as either SO_2 or H_2S) can be chemically processed prior to or upon emission of volcanic fluids into the cold and oxidizing atmosphere, potentially leading to a mismatch between plume and source compositions. Our results for the TGM/S_{tot} mass ratio in the plume and the fumarolic condensates of La Soufrière volcano differ for a factor ~10, suggesting contrasting behaviour of Hg and H_2S in the fumarolic system, or during atmospheric transport. In particular, the higher Hg/H_2S proportion in the plume, relative to the fumarole, would require faster H_2S processing (than Hg) upon atmospheric dispersal, which is however unlikely in light of
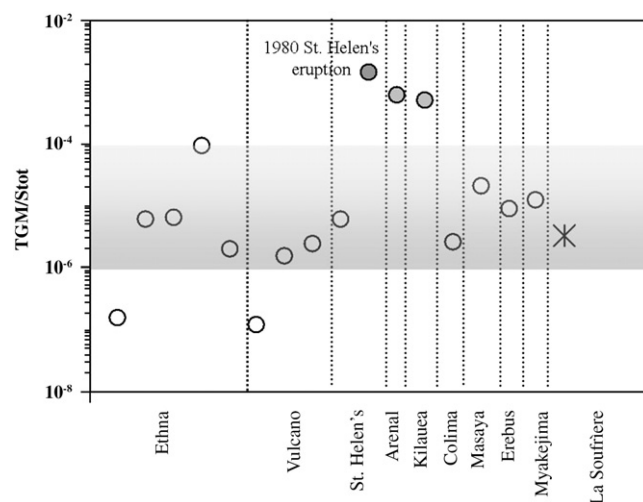

Fig. 3. Summary of measured TGM/SO_2 mass ratios in worldwide volcanic emanations. The picture was compiled from results obtained by this work (referring to La Soufrière lava dome, represented in figure by asterisk point), and published data (blank fill circles). It is manifest that TGM/SO_2 ratio varies as a function of the state of the activity of a volcano: most of the reported data results lower than the measured one at Kilauea, Arenal volcanoes (10^{-4}) (Siegel and Siegel, 1984; Ballantine et al., 1982) and Mt. St. Helen's (Varekamp and Buseck, 1981, 1986), during eruptive periods (grey fill circles). For other published data see text discussions.

the relatively high H$_2$S stability in a short-lived (non-condensing) volcanic plume (Aiuppa et al., 2007b). We suggest instead that mismatch of Hg/H$_2$S compositions might be due to some extent of Hg removal in the fumaroles, due to pre- or syn-collection condensation processes. The large Hg affinity for the aqueous-phase in La Soufrière fumaroles (Table 1) implies that formation of even small amounts of condensate prior to sampling might deplete the residual gas in a substantial way. If this interpretation is correct, it once more emphasizes that low-T fumaroles are not good proxies for Hg compositions of the main gas discharges from a volcano, and should thus not be used to estimate Hg budgets.

5. Conclusions

We performed the first measurements of the abundance and speciation of mercury in both the plume and the fumarolic fluids emitted from the summit lava dome (Southern crater) of La Soufrière volcano. We demonstrate that mercury is overwhelmingly emitted as gaseous metal, few of it (~2%) being transported as particulate Hg$_{(p)}$. The mass ratio of total mercury to total sulphur in the volcanic plume is not consistent with the same ratio measured in the issuing fumarolic fluids. This mismatch suggests that plume chemical composition is not well represented by the emission source (fumaroles) due to chemical processes prior to (or upon) discharge. The mean plume Hg/H$_2$S mass ratio of 3.2×10^{-6}, combined with the H$_2$S emission rate (0.075 kg s^{-1}), allow us to estimate that La Soufriere currently releases 0.02×10^{-3} kg d^{-1} (or 7 kg y^{-1}) of total mercury from its summit lava dome. This production represents a trivial contribution to the global non-eruptive Hg emissions from continuously degassing volcanoes, in agreement with the current stage of volcanic rest of La Soufrière since its last eruption in 1976–1977.

Acknowledgements

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