Fumarole compositions and mercury emissions from the Tatun Volcanic Field, Taiwan: Results from multi-component gas analyser, portable mercury spectrometer and direct sampling techniques

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ABSTRACT

Gas emissions from Tatun volcanic group, northern Taiwan, were studied for the first time using a multi-component gas analyser system (Multi-GAS) in combination with Giggenbach flask methods at fumaroles and mud pools at Da-you-keng (DYK) and Geng-tze-ping (GZP). CO_2/S molar ratios observed at DYK ranged from 3–17, similar ratios were observed using a Multi-GAS sensor box of 8–16. SO_2 at GZP was low, higher concentrations were observed at DYK where SO_2/H_2S ratios were close to 1 for both methods. A lower CO_2/H_2S ratio was measured via Giggenbach flask sampling (7.2) than was found in the plume using the gas sensor at GZP (9.2). This may reflect rapid oxidation of H_2S as it mixes with background air. Gaseous elemental mercury (GEM) levels were observed in the fumarole gases using a portable mercury spectrometer. These are the first such measurements of mercury at Tatun. Mean GEM concentrations in the fumarole plumes were ~20 ng m^{-3}, with much higher concentrations observed close to the ground (mean [GEM] 130 and 290 ng m^{-3} at DYK and GZP, respectively). The GEM in the fumarole plume was elevated above concentrations in industrial/urban air in northern Taiwan and the increase in GEM observed when the instrument was lowered suggests high levels of mercury are present in the surrounding ground surface. The GEM/CO_2 (10^{-8}) and GEM/S (10^{-6}) ratios observed in the fumarole gases were comparable to those observed at other low-temperature fumaroles. Combining the Hg/CO_2 ratio with a previous CO_2 flux value for the area, the annual GEM flux from the Tatun field is estimated as 5–50 kg/year.

1. Introduction

The Tatun volcanic group lies in northern Taiwan just north of the Taipei basin, and includes more than 20 Quaternary volcanic centres, predominantly of calc-alkaline andesites (e.g. Chen and Wu, 1971). The Tatun volcanoes are generally considered to be dormant, with no evidence of eruptions within the past 20 ka, although recent seismic and geochemical data (e.g. ^{3}He/^{4}He ratios of up to 6.8 R/R_A) suggest that there may still be an active magmatic source beneath the Tatun field (Song et al., 2000; Chen and Lin, 2002). At the present day, hot springs and gas fumaroles are found throughout the volcanic field (Fig. 1).

The chemistry of fumarole gases is related to the activity of the underlying volcanic system, and studies of fumarole chemistry have proved helpful in understanding both the sources of volcanic fluids, and for volcano surveillance (e.g. Giggenbach, 1992; Chiodini et al., 1995; Fischer et al., 1997). Study of the gases emitted may also be of interest in terms of their impact as atmospheric pollutants (e.g. Mao et al., 2005;

Fulignati et al., 2006). Mercury is a metal of particular interest due to its high toxicity, its volatility and long atmospheric lifetime (Mason et al., 1994; Fitzgerald et al., 1998). In the atmosphere, mercury is mainly found as the relatively inert form of gaseous elemental mercury (GEM). While anthropogenic sources of atmospheric mercury remain significant (Hylander and Meili, 2003), it is also clear that volcanic and geothermal areas may be important natural sources of mercury, since Hg concentrations in volcanic gases are significantly enhanced above background levels (e.g. Varekamp and Buseck, 1981; Ferrara et al., 2000; Bagnato et al., 2007). However, global volcanic Hg fluxes remain poorly constrained, and there is a need for continuing work to characterise both low-temperature (fumarolic) and high-temperature volcanic emissions (e.g. Pyle and Mather, 2003).

Fumarolic fluids of the Tatun field have been well characterised by Lee et al. (2005), using the methods developed by Giggenbach (1975) in which gases are collected for subsequent analysis. The Giggenbach flask technique is well established and enables determination of a large number of chemicals within fumarole gases over a specific time period; however the time-consuming laboratory based measurements prevent real-time observations. More recently, Lan et al. (2007)

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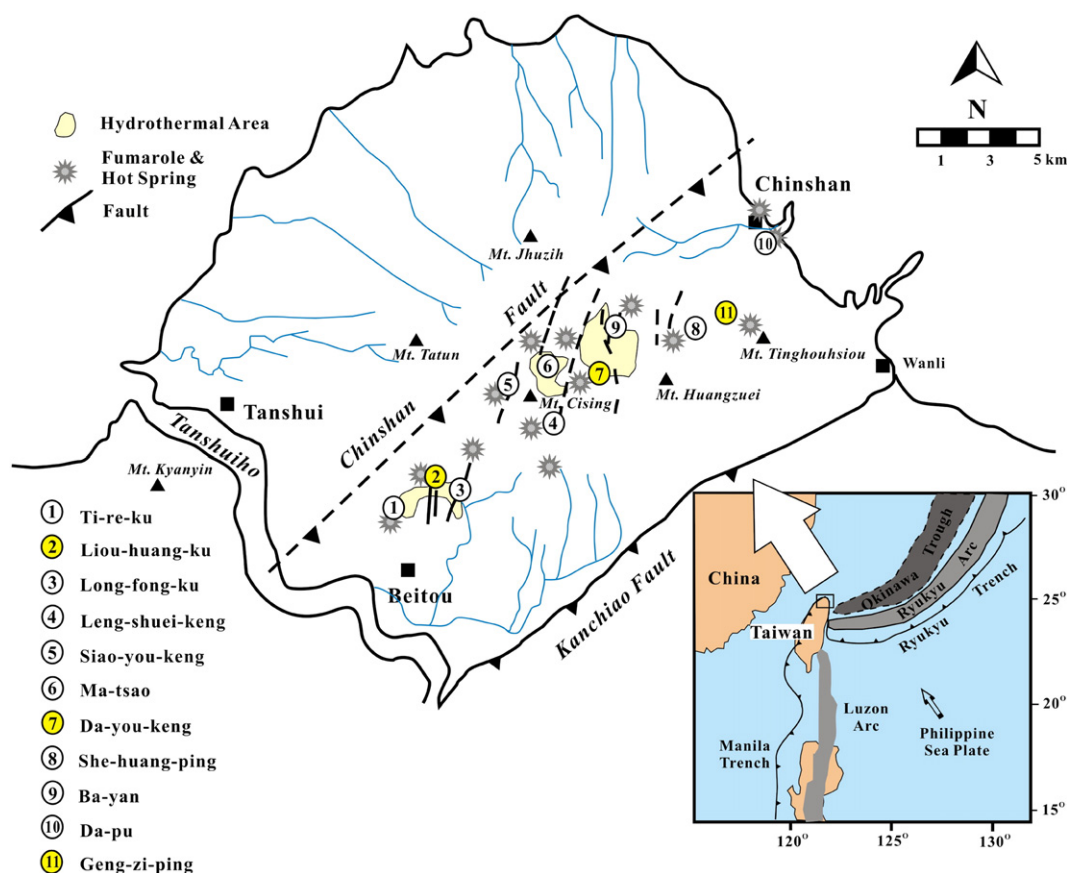 E-mail address: melanie.witt@earth.ox.ac.uk (M.L.I. Witt).

Fig. 1. Location of the Tatun Volcanic Field and the active fumarole sites within the field (adapted from Lee et al., 2005).

determined the soil CO_2 flux from the area, using closed-chamber methods (Chiodini et al., 1998). Here, we report real-time measurements of fumarole gas compositions using a portable multi-sensor gas analyser (Aiuppa et al., 2005; Shinohara, 2005), which was deployed at active fumaroles around Tatun in parallel with a portable mercury analyser, and direct gas sampling. These complementary approaches allow us to investigate changes in gas compositions on short timescales (s); to monitor the effects of mixing of fumarole gases with background air, and to compare directly real-time and time-integrated techniques for the analysis of volcanic fluid compositions.

2. Methods

Fumarole gases were sampled over several days during April 2007 at a number of sites within the Tatun Volcanic Field (Fig. 1). In particular, we focussed on measurements at the largest fumaroles of the Tatun group, at Da-you-keng (DYK). Measurements were also made at fumaroles and bubbling mud pools at Geng-tze-ping (GZP), a site close to DYK with similar chemistry. The fumaroles investigated all had similar temperatures of around 100 °C. Helium isotope measurements suggest a magmatic source may be present below DYK. It is here that the highest $^3He/^4He$ ratios are observed (6.8 R/R_A; Yang et al., 1999; Lan et al., 2007); while at locations on either side of DYK the gases become progressively less magmatic as distance increases. GZP is located close to DKY and has the second highest $^3He/^4He$ ratio of the sites studied (Yang et al., 2003). The soil CO_2 flux from this site is also lower than at DYK.

2.1. Gaseous elemental mercury (GEM)

Continuous mercury measurements were made using a Lumex 915+ portable mercury vapour analyser. The analyser sampled air at

20 l min^{-1} through a dust filter to remove particles from the air flow. The analyser uses differential atomic absorption spectrometry with correction for background via the Zeeman Effect (Zeeman Atomic Absorption Spectrometry with High Frequency Modulation of Light Polarisation) (Sholupov et al., 2004). During sampling a zero correction was carried out to reset the baseline every 5 min by switching the airflow through a mercury absorption filter. The instrument software then corrects for baseline drift. Only gaseous elemental mercury is detected by the Lumex instrument. The detection limit was 2 ng m^{-3} and the instrument has an accuracy of 20%. We have reported elsewhere similar measurements from volcanic fumaroles in Italy and Nicaragua made using a Lumex, and detailed comparisons with side-by-side gold trap measurements (Aiuppa et al., 2007a; Witt et al., 2008).

Mercury concentrations were monitored in the fumarole gases at DYK and GZP using the Lumex mercury analyser. These are the first such measurements carried out at this location. The advantage of this technique is that it can be carried out at low-temperature fumaroles in the presence of high levels of humidity and H_2S. Gold-coated sand traps have been used in a number of studies at similar volcanic sites by passing air over the trap so that gaseous mercury is collected as a gold amalgam for later analysis (e.g. Engle et al., 2006; Aiuppa et al., 2007a; Bagnato et al., 2007). Use of gold traps is difficult in such conditions as high levels of H_2S can lead to passivation (Schroeder et al., 1995).

2.2. Multi Multi-component gas analyser system (Multi-GAS)

Concentrations of SO_2, CO_2, and H_2S were monitored using a Multi multi-component gas analyser system (Multi-GAS) (Aiuppa et al., 2005; Shinohara, 2005). Gas was drawn into the sampler using an airchek 500 pump at 0.8 l min^{-1} through a 0.2 µm Teflon membrane particle filter, passed through a CO_2 infrared detector (Gascard II

Edinburgh instruments; 0–5000 ppm) followed by a series of electrochemical sensors which detected SO_2 (0–100 ppm) and H_2S (0–50 ppm) (Membrapor). The SO_2 sensor had an inbuilt filter to prevent interference from H_2S. Temperature and relative humidity were measured with an external probe (Rotronics hydroclip combined RH/temp probe), and the whole system was housed in a weather-proof box mounted on a backpack frame. Sensors were calibrated, before and after fieldwork, with calibration gases (100 ppm SO_2, 50 ppm H_2S and 4000 ppm CO_2 supplied to 2% accuracy) mixed with ultrapure nitrogen to provide a range of concentrations. The CO_2 and electrochemical sensors have an accuracy of 2% quoted by Membrapor. The calibration gases also enabled cross-sensitivity of the H_2S sensor to SO_2 to be evaluated. The response of the H_2S sensor to SO_2 gas was established during calibration (0.08–0.18 ppm H_2S/ppm SO_2 depending on individual sensor). The SO_2 concentration detected in the field was used at each time point to subtract the contribution to the H_2S signal. The other cross-sensitivities of the sensors were found to be negligible during calibration.

2.3. Direct gas sampling using Giggenbach flasks

Samples were collected using the standard Giggenbach sample method (Giggenbach and Gougel, 1989) where a titanium tube is inserted into the fumarole and connected to an evacuated glass bottle via Tygon tubing. The evacuated sample bottle contains approximately 50 ml 5 N NaOH. Acid gases absorb in the caustic solution and are analyzed by standard wet chemical techniques. Non-reactive gases are concentrated in the headspace of the bottle and analyzed by gas chromatography. The samples were analyzed in the volcanic and hydrothermal fluids analyses laboratory at the University of New Mexico using a gas chromatography system and standard wet chemical techniques (Zimmer et al., 2004).

3. Results and discussion

The Multi-GAS system has been previously employed at volcanoes in Japan, Italy and Chile where the variations in H_2O, CO_2 and SO_2 have been successfully investigated (Shinohara et al., 2003; Aiuppa et al., 2005, 2006, 2007b; Shinohara and Witter, 2005). In order to use the Multi-GAS data to determine the ratios of the various species in the fumarole gases, plots were constructed to look for correlations between species after they had been corrected for interferences. If necessary, the data was time shifted to best align peaks in concentrations to correct for differences in sensor response times. Examples of these plots are shown in Fig. 2. Only where a correlation significant at the 95% level was seen are ratios quoted. The values in Table 1 represent measurements at 100–1000 time points; uncertainties quoted for the ratios are based on minimum and maximum slopes through the data points. Measurements were . made around a number of fumaroles at Tatun, and downwind from

Table 1
Molar ratios measured in gases using Multi-GAS and Giggenbach bottles at hydrothermal sites GZP and DYK in the Tatun volcanic group

	$H_2O/$ (S_{total})	$CO_2/$ (S_{total})	$CO_2/$ H_2S	$SO_2/$ H_2S	$HCl/$ (S_{total})	$CO_2/$ HCl
GZP A (Giggenbach)	346.6	7.15	7.15	*	0.01	1073
GZP fumarole A (Multi-GAS via tube)	127±25	7.8±1.3	7.8±1.3	–		
GZP fumarole A (Multi-GAS in plume)	82.8±45	8.4±1.8	8.5±1.8	–		
GZP fumarole B (Multi-GAS)	–	8.7±3	8.7±3	–		
GZP bubbling mud (Multi-GAS)	176±41	11.6±1.4	11.8±1.5	–		
DYK C (Giggenbach)	328.8	3.30	8.57	1.60	0.20	16.6
DYK upwind of fumarole C (Multi-GAS)	–	13.1±1.5	24.6±7.1	0.89±0.2		
DYK D (Giggenbach)	633	16.6	37.8	1.27	0.73	22.8
DYK fumarole D (Multi-GAS)	–	16.4±4.4	37.7±19	1.44±0.3		

Where there was no clear correlation observed between species a dash is shown. *SO_2 was below detection in the GZP Giggenbach sample.

their emission points. Spikes in real-time measurements of H_2S, CO_2, humidity and temperature were detected in these plumes. Measurements of mercury in the gases of the fumaroles revealed concentrations elevated above background levels. During the measurements, Giggenbach samples were collected at DYK C and D as well as GZP A.

3.1. Multi-GAS measurements at Geng-tze-ping (GZP)

Measurements were made at a fumarole (A) at GZP by passing gas from the titanium and Tygon sampling tube used for Giggenbach sampling straight into the inlet of the Multi-GAS sensor (Fig. 3) to try to minimize the dilution of the gas with background air before sampling. Measurements were also made with the inlet of the instrument in the plume of the fumarole gases. The concentrations of species measured in the gas plume and via the sampling tube at this fumarole are similar, despite the probable changes in the proportion of background air sampled (Fig. 4a). During this sampling period SO_2 was at or below the detection limit of the sensor (0.4 ppm) in the GZP gases. H_2S, H_2O and CO_2 concentrations all correlate well during sampling at this fumarole.

With the exception of H_2O, the ratios of the species to total S in the gases were similar when sampling with or without the titanium/Tygon sampling tube (Table 1) and peak humidity values and peak concentrations of H_2S and CO_2 were of a similar magnitude in the plume and when measured via the titanium/Tygon tube.

Other sites within the GZP area were also studied with the Multi-GAS. Fumarole B (Fig. 3), is a small fumarole which was gently releasing gases. Higher concentrations of gases were recorded during sampling at this fumarole than were recorded at fumarole GZP A (Fig. 4, Table 3), however, ratios observed in the gases of the GZP fumaroles were similar (Section 3.4). Measurements at a bubbling mud pool at GZP were also made (Fig. 3). At this location elevated concentrations of H_2S (9 ppm)
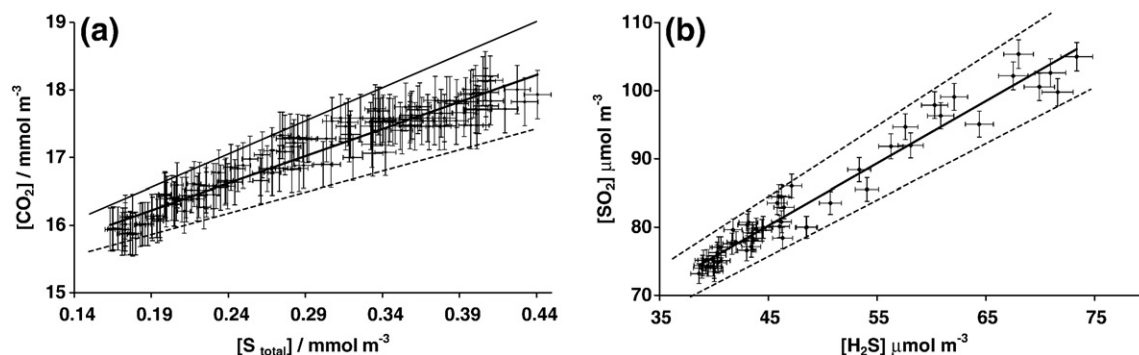
Fig. 2. Examples of data plots used to calculate ratios of species in fumarole gases. (a) Measurements made of CO_2 vs. SO_{total} in the plume of fumarole GZP A, 157 data points, r^2 0.923. (b) Measurements made of H_2S vs. SO_2 in the plume of fumarole DYK C, 55 data points, r^2 0.952.
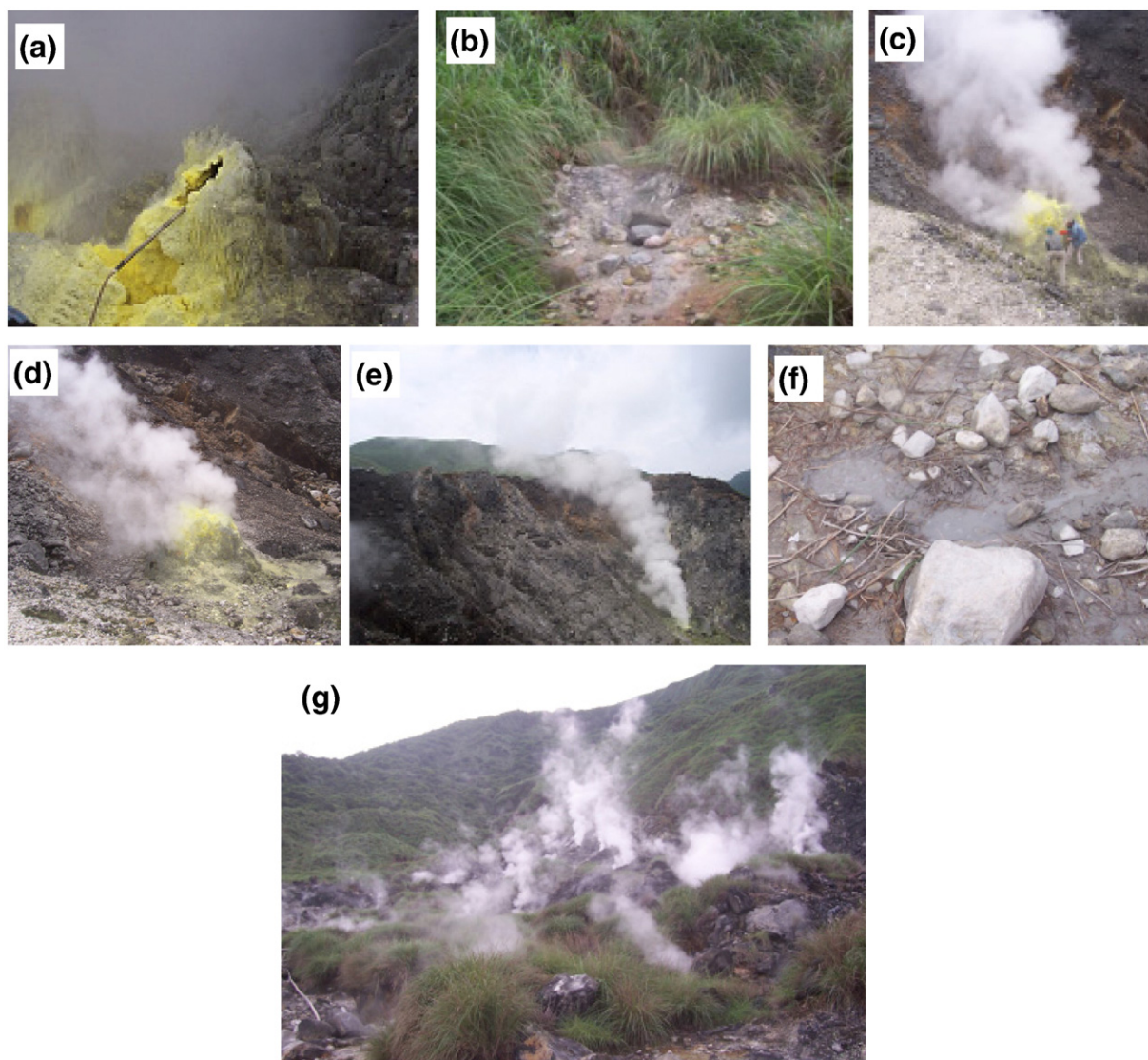
Fig. 3. (a) Fumarole A at GZP, GERTI used in conjunction with sampling tube shown, (b) Small fumarole B at GZP, (c) Fumarole C at DYK, (d) Fumarole D at DYK. (e) GERTI and Lumex measurements made at top of crater rim (elevation 585 m, 25.172° N, 121.580° E). Fumarole C on right of photo, plume of fumarole D just visible on left (f) bubbling mud at GZP (g) fumaroles at GZP.

and CO_2 (540 ppm) were also observed. The CO_2/S_{total} ratios were slightly higher than those recorded at the fumaroles in the area.

3.2. Multi-GAS measurements at Da-you-keng (DYK)

The temperatures measured at the fumaroles at DYK were around 116 °C. This is higher than measurements made here 2 years ago which were around 100 °C (Lee et al., 2005). A similar range in concentrations was observed at fumaroles C and D with the Multi-GAS at DYK. This is perhaps an unexpected result as the measurements were made at a distance of 10–20 m from fumarole C whereas measurements were made adjacent to fumarole D. The fumarole C did appear to have a smaller plume than fumarole D and measurements at both locations may have been influenced by variations in the amount of dilution with background air as wind patterns changed on a short timescale.

3.3. Giggenbach flask sampling at Tatun

Giggenbach samples were collected at fumarole A at GZP and at fumaroles C and D at DYK. A number of species were determined in

these samples and their concentrations are reported in Table 2. As for the Multi-GAS, SO_2 was not detected in the fumarole gases at GZP while a signal was observed at DYK. In previous work, Lee et al. (2005) found that DYK had the highest concentration of SO_2 of all of the sites studied around Tatun and recorded a SO_2/H_2S ratio of 0.18 in 2003 in Giggenbach samples collected here. The SO_2/H_2S ratios reported for DYK in Table 2 are higher than this ratio. Subsequent work by Lee et al. (2008-this issue) investigating temporal variations over 3 years at Tatun suggested an increasing SO_2/H_2S ratio in the sampling period.

3.4. CO_2/S ratios recorded with Multi-GAS and Giggenbach sampling

The Multi-GAS CO_2/S ratio measured via the titanium/Tygon sampling tube at GZP A was about 10% higher than observed with the Giggenbach techniques. Shinohara (2005) also found CO_2/SO_2 ratios in Giggenbach samples at a fumarole at Tokachi volcano agreed with Multi-GAS results to within 10%. The Multi-GAS CO_2/S ratios in the plume of GZP A and GZP B were higher than when sampling via the tube. The highest CO_2/S ratio was recorded at the bubbling mud pool at GZP. All of the CO_2/S ratios at GZP were of a similar magnitude with a variation of less than 10% between all of the CO_2/S ratios at GZP A and GZP B measured by the techniques.
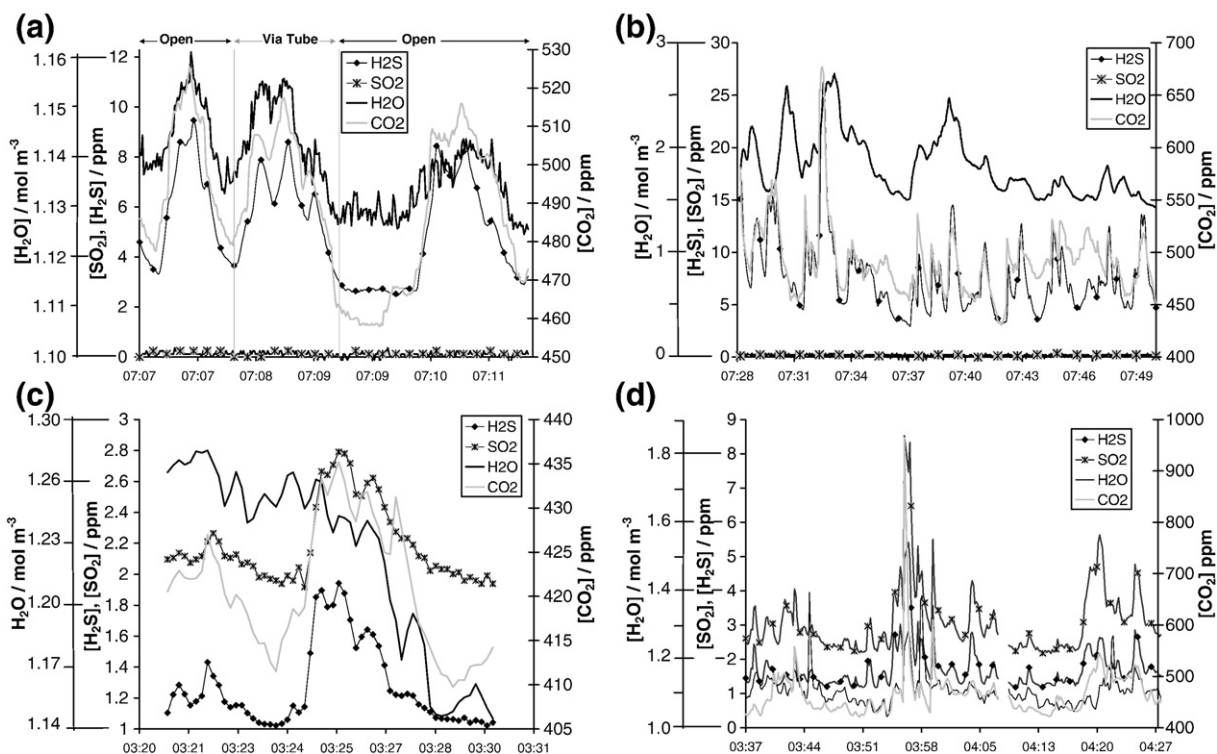
Fig. 4. Variations in H_2S, CO_2, H_2O and SO_2 measured with Multi-GAS at Tatun volcanic group. (a) Fumarole A at GZP, areas marked "open" in the graph were measured in the gas plume, area marked "Via Tube" measured via titanium/Tygon sampling tube. (b) Fumarole B at GZP. (c) Upwind of fumarole C at DYK. (d) Fumarole D at DYK. Sampling time shown along *x*-axis in UTC, local time is UTC+8.

A similar result was found at the fumaroles at DYK, where sampling was made closest to the fumarole at DYK D, the CO_2/S ratios recorded by the Giggenbach method and with the Multi-GAS showed around 1% difference. At DYK C, where the Multi-GAS was 10–20 m from the fumarole the Multi-GAS CO_2/S ratio was approximately 4 times higher than the Giggenbach value.

3.5. H_2O/S and H_2S/SO_2 ratios recorded with Multi-GAS and Giggenbach sampling

Other molar ratios investigated with the Multi-GAS and Giggenbach sampling methods showed a greater variation than the CO_2/S ratios. The SO_2/H_2S ratios at DYK were all of the same order of magnitude (geometric mean based on all measurements of SO_2/H_2S 1.4). At DYK D Multi-GAS measurements were made closer to the fumarole and the S ratios of the techniques showed less than 10% variation. At DYK C, where the Multi-GAS measurements were made at a distance from the fumarole, a greater difference between the Giggenbach and Multi-GAS SO_2/H_2S ratios were observed (43%).

The $H_2O/(H_2S+SO_2)$ ratios measured by the two techniques showed a most variability between techniques. The humidity data from DYK did not show a significant correlation with the other species simultaneously monitored and so this data could not be compared to the Giggenbach results. The Multi-GAS values for the water content of the plume are based on the relative humidity and temperatures recorded, as the fumarolic gas is probably supersaturated with H_2O, water vapour is visible at the vent, and the humidity sensor will not detect water

droplets. This could lead to a poor correlation between humidity data and variation in other species. A correlation was observed between the humidity data and the S species on only two occasions, at GZP A and at the bubbling mud at GZP. The Multi-GAS H_2O/S ratio at GZP A was around 3 to 4 times lower than seen in the Giggenbach samples. The poor agreement in the H_2O/S ratio between these techniques and the lack of correlation between the humidity and other species at other sites suggests further work is required before the humidity data can be used to obtain reliable estimates for water content in the gases.

3.6. Mercury at Tatun

The mercury analyser monitored the concentration of gaseous elemental mercury (GEM) and reports values as 10 second averages. The mean and range of concentrations measured in the fumaroles are listed in Table 3. A similar mean Hg concentration was observed in the fumarole plumes of A, C and D of around 20 ng m^{-3}. This is an order of magnitude greater than concentrations found in background air at clean air locations (~2 ng m^{-3}, e.g. Ebinghaus et al., 2002) and significantly higher than reported from both rural (6 ng m^{-3}) and urban/industrial sites (8–9 ng m^{-3}) elsewhere in northern Taiwan (Kuo et al., 2006).

At GZP, measurements were made with the sample inlet several centimeters above the ground and at about 1–1.5 m above the ground. Gustin et al. (1996) found that mercury concentrations above mercury enriched ground decreased exponentially with height and that the mercury flux rose by 1–2 orders of magnitude on exposure to incident light. When the sample inlets were placed close to the ground, mercury

Table 2
Measurements made with Giggenbach bottles 29th and 30th April 2007

	T (°C)	H_2O	CO_2	S_{Total}	SO_2	H_2S	HCl	Ar	O_2	N_2	CH_4	H_2	HF	He	CO
GZP A	110	96,779	1996	279	0	278	1.86	0.097	0.030	33.3	2.188	0.022	0.124	0.040	0.00289
DYK C	116	98,247	986	299	184	115	59.3	0.155	0.228	21.5	0.416	0.584	0.065	0.024	0.00067
DYK D	112	96,849	2531	153	85.3	67.2	111.2	1.278	24.13	105.0	0.351	0.016	0.258	0.028	0.00125

Units (1000×) mol% of total gas. Column T shows fumarole temperature in °C.

Table 3
Concentrations measured in fumarole gases at GZP and DYK, Tatun, using Multi-GAS and a portable mercury analyser

	Mean (range) Hg ng m^{-3}	Mean (range) S$_{tot}$ mmol m^{-3}	Mean (range) CO$_2$ mmol m^{-3}	Hg/CO$_2$ molar (mass)	Hg/S$_{tot}$ molar (mass)
GZP A plume	23.2 (3.9–104)	0.270 (0.199–0.388)	19.6 (17.3–24.3)	–	–
GZP A close to ground	291.5 (12.7–696)	0.141 (0.067–0.307)	18.0 (14.7–39.0)	–	–
GZP B plume	5.45 (2.2–16.9)	0.132 (0.112–0.179)	13.9 (13.5–14.5)	$9.8 \pm 5.5 \times 10^{-9}$ ($4.5 \pm 2.8 \times 10^{-8}$)	–
DYK C plume	18.9 (9.0–28.3)	0.127 (0.082–0.316)	15.4 (13.9–21.3)	$8.5 \pm 0.3 \times 10^{-8}$ ($3.9 \pm 0.1 \times 10^{-7}$)	$1.2 \pm 0.3 \times 10^{-6}$ ($5.0 \pm 0.9 \times 10^{-6}$)
DYK D plume	19.7 (3.9–66.3)	0.117 (0.095–0.163)	16.0 (15.5–16.9)	$3.5 \pm 0.2 \times 10^{-8}$ ($1.6 \pm 0.7 \times 10^{-7}$)	$9.7 \pm 1.8 \times 10^{-7}$ ($2.4 \pm 0.9 \times 10^{-6}$)
DYK D close to ground	129.8 (22.9–219)	0.337 (0.243–0.546)	17.8 (16.3–20.0)	–	–

Hg/CO$_2$ and Hg/S$_{tot}$ ratios are molar ratios (mass ratio in brackets below) based on the best line fit of Multi-GAS and Lumex measurements. Where there was no clear correlation observed between species a dash is shown.

concentrations rose sharply, concentrations up to ∼700 ng m^{-3} were recorded close to the ground. A similar observation was made at DYK where GEM concentrations rose sharply when the instrument inlet was placed close to the ground from 19.7±9.3 ng m^{-3} to 130±42 ng m^{-3}. The peaks in GEM recorded close to the ground at GZP coincided with periods when the sun broke through the clouds at the site, and did not always correspond to the occurrence of CO$_2$ or H$_2$S peaks; this dependence of mercury evasion on solar radiation flux is well known (e.g. Poissant and Casimir, 1998; García-Sánchez et al., 2006). Re-volatilization of Hg from soils and surfaces is an established source of Hg to the atmosphere (Poissant and Casimir, 1998). In addition to volatilization from soil surfaces, mercury may be released through the soil flux in a similar manner to the release of CO$_2$. Although gases released through the soil in volcanic regions may have a similar origin to those released at fumaroles, the composition may vary due to differences in the interactions prior to release. In studies at the Tatun site Liu-Huang-Ku the composition of the soil gas was found to be similar to that of the fumaroles gases for a number of species (Lan et al., 2007). The scatter in the Hg to CO$_2$ and S data plots at some locations suggests gases sampled originated from a mixture of these three gas release mechanisms.

The high GEM concentrations observed in the vicinity of the fumaroles which did not correlate with other volcanic gases, suggest there are high levels of mercury on the ground surface in the area. This mercury is presumably deposited from the continuous Hg emissions of the fumaroles and remobilised by a variety of processes in the presence of water, heat and sunlight (e.g. Landa, 1978; Lindberg et al., 1999; Gustin et al., 2000). Similar features have been reported from hydrothermal systems elsewhere (Engle et al., 2006), but much further work is needed to understand and quantify the controls on the rates of mercury deposition and evasion around active fumaroles.

3.7. Molar ratios in Tatun gases

Measurements made at fumarole A, may show the changing chemistry of the fumarolic gases as they mix with background air. The measurements based on analysis of the Giggenbach flask should show the smallest influence of background air (1), the Multi-GAS measurements made via the titanium/Tygon tube may be considered intermediate (2), while the most mixing was expected when measuring the fumarole plume (3). The CO$_2$/H$_2$S ratios measured increased with greater mixing and were (1) 7.18, (2) 7.81 and (3) 8.42. A similar result was observed at DYK; measurements made at fumarole C with a Giggenbach flask yielded a CO$_2$/H$_2$S ratio of 8.6, whereas measurements made with the Multi-GAS at the crater rim, several meters downwind of the fumarole, resulted in a CO$_2$/H$_2$S ratio of 24.6. This rise in CO$_2$/H$_2$S

ratio may suggest a rapid oxidation of the H$_2$S on mixing with background air. However this rise in CO$_2$/H$_2$S is not accompanied by a corresponding rise in SO$_2$ in the samples. Another possibility could be an additional source of CO$_2$ from soil degassing. If the CO$_2$/H$_2$S ratio from soil is higher than in the fumarole gas this could also lead to such a rise. Also contributing to a higher CO$_2$/H$_2$S ratio could be the increased dilution of volcanic gases with background air.

The ratios measured at the fumaroles with the Multi-GAS show some variations over time. Some of this variability may have been due to instrumental effects as the various sensors have differing response times to the analytes. This makes it difficult to establish if the changes in molar ratios observed over short time periods are artefacts or genuine changes in chemistry. The ratios reported in Table 1 are based on the correlation between the various species over the entire sampling period, and as such offer a ratio based on a large number of data points, increasing the confidence in the values.

Plots of GEM concentrations against CO$_2$ and S$_{total}$ were used to determine molar ratios at the fumaroles (Fig. 5, Table 3). Hg/CO$_2$ ratios
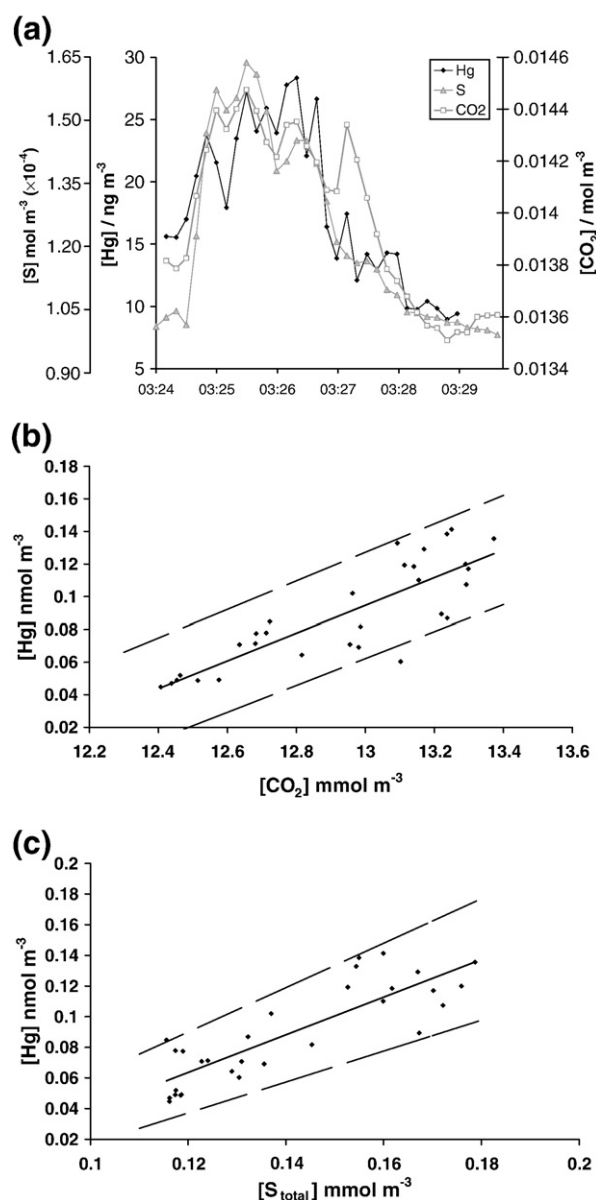
Fig. 5. GEM, S and CO$_2$ concentrations measured at fumarole DYK C, Tatun. (a) Variations in GEM, CO$_2$ and S over time, (b) GEM vs. CO$_2$ (c) GEM vs. S. Data points represent 10 second averages based on measurements made every second.

from the plumes measured at the DYK fumaroles suggest a molar ratio of ~ 4–9×10^{-8}. This is similar to results using these same instruments from low-temperature steam-dominated fumaroles near Masaya volcano (molar $Hg/CO_2 \sim 0.4 \times 10^{-8}$;(; Witt et al., in press), and in fumaroles at Vulcano, Italy (molar $Hg/CO_2 \sim 10^{-8}$; Aiuppa et al., 2007a). These values are significantly higher than the clean, background atmosphere ($\sim 5 \times 10^{-10}$), and emphasise the potential significance of fumarole emissions for regional atmospheric mercury budgets.

Prior estimates of the global flux of Hg from fumarole systems have used the scaling relationships between heat flux and gas emissions (e.g. Varekamp and Buseck, 1986; Engle et al., 2006). For the Tatun field, there are not yet sufficient data on CO_2 and thermal fluxes for us to make a rigorous assessment of the total net Hg flux using geostatistical techniques (c.f. Engle et al., 2006). However, Lan et al. (2007) recently measured the soil CO_2 emission rate from the nearby Liu-Huang Ku (LHK) hydrothermal area as ~ 20 Mg/day (580–660 Mg km^{-2} day^{-1}). While the emissions measured in the fumaroles gases may differ to some extent to the composition of the soil gas, they represent the best estimate available to obtain the Hg emission flux at present. Assuming a molar $Hg/CO_2 \sim 5 \times 10^{-8}$, and assuming, conservatively, that the soil CO_2 fluxes from other two main hydrothermally-altered areas of the Tatun field (Fig. 1) are of the same order of magnitude as LHK, this gives a daily CO_2 flux of 60–600 Mg, and a total annual Hg flux of ~ 5–50 kg/year. This value approaches the order of magnitude of total annual Hg emissions from Vulcano (4–7 kg Hg/yr; Aiuppa et al., 2007a) or Yellowstone (15–50 kg Hg/yr; Engle et al., 2006).

The Hg/S ratios were also investigated in the fumarole gases. At GZP, where S is predominantly present as H_2S, no good correlation was observed between total S and gaseous elemental mercury concentrations. This may reflect variable scrubbing of S species in the hydrothermal system. At DYK, gaseous elemental mercury and S_{total} signal were correlated, with a molar Hg/S ratio of 0.7–1.2×10^{-6}.

Measurements at Tatun show that the system is releasing mercury at levels elevated well above those of the background. While much of the GEM emitted at Tatun is likely to be transported to great distances prior to deposition, the elevated levels of mercury measured close to the ground near the fumaroles suggest that deposition from the high concentration plume to the ground is locally important. Studies of the speciation of mercury in volcanic and fumarolic gases have found significant levels of particulate and reactive gaseous mercury to be present (e.g. 1–2% Hg as RGM in Yellowstone; 1% Hg as Hg_p in high-temperature emissions from Etna; Bagnato et al., 2007; Engle et al., 2006). These forms of mercury will be readily removed from the atmosphere, particularly in a steam-saturated, condensing plume, potentially enhancing local Hg deposition fluxes.

4. Conclusions

We performed the first measurements of gas species at Tatun volcano with a Multi-GAS analyser and portable mercury spectrometer. The data obtained allowed for the comparison of abundance ratios measured by sensors to the results obtained simultaneously from direct fumarole sampling using Giggenbach flasks. The comparison of the results obtained by both techniques shows that a) there is good agreement of some abundance ratios ($CO_2/(H_2S+SO_2)$); b) water contents measured in situ are consistently lower than in the gas samples this is likely due to supersaturation of the air with steam and the formation of water droplets which are not detected by the sensors; and c) increased mixing with air and resulting oxidation of H_2S to SO_2 is a likely explanation for the observed variations of $CO_2/(H_2S-SO_2)$ ratios at some localities. Further and systematic comparison of sensors and direct sampling techniques is critical for better understanding volcanic degassing and the evolution of gases as they mix with air.

Mercury concentrations in the fumarole gases were elevated above levels observed in urban/industrial areas of northern Taiwan. High GEM concentrations observed when the sample inlet was lowered suggest that the ground surface surrounding the fumaroles is enriched in mercury. Hg/CO_2 ratios measured in the fumarole gases at DYK and GZP were comparable to those of similar low-temperature systems at other locations, and combined with a local soil flux estimate suggest an annual Hg flux of 5–50 kg/year from the Tatun field.

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