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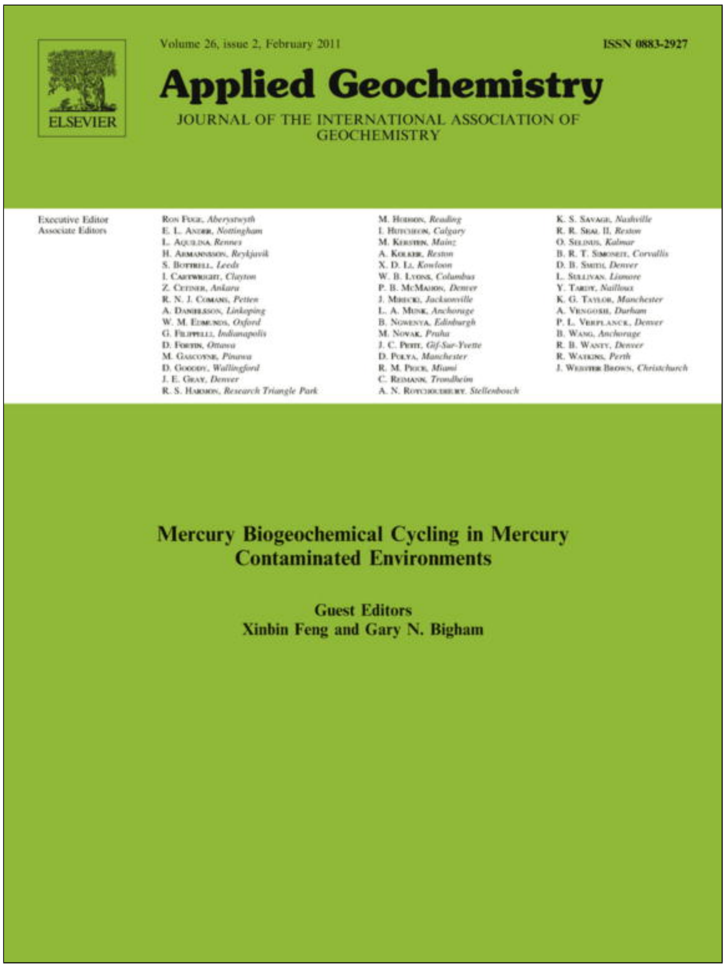

Volume 26, issue 2, February 2011
ISSN 0883-2927

Applied Geochemistry

JOURNAL OF THE INTERNATIONAL ASSOCIATION OF GEOCHEMISTRY

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Mercury Biogeochemical Cycling in Mercury Contaminated Environments

Guest Editors
Xinbin Feng and Gary N. Bigham

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Applied Geochemistry 26 (2011) 242–248

Contents lists available at ScienceDirect

Applied Geochemistry

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Seasonal and diel patterns of total gaseous mercury concentration in the atmosphere of the Central Valley of Costa Rica

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ARTICLE INFO

Article history:
Available online 30 November 2010

ABSTRACT

Monitoring of Hg in the atmosphere near volcanoes is limited with no previous data for Costa Rica. Seasonal and daily patterns of total gaseous mercury (TGM) were observed at the main sampling location at the Universidad Nacional, Heredia, Costa Rica. The area (lat. 10.000230 long. −84.109499) is located in the Central Valley of Costa Rica and is 27 km SE of the Poas volcano (lat. 10.199486 long. −84.231388). Measurements were made from May 2008 to May 2009 at this location with some additional values obtained at other sites near the Poas volcano including San Luis and Grecia as well as near, Turrialba and Irazu volcanoes. Total gaseous Hg was determined in samples collected at a height of 2 m using the Tekran 2537A (Tekran Inc.) gas-phase Hg vapor analyzer. Meteorological data (temperature, relative humidity, wind speed, wind direction, radiation and precipitation) were obtained from the airport weather station located at Alajuela. Monthly precipitation is typically 85 mm during the dry season (December to April) with winds from the west. The wet season begins in late April and continues to December with monthly rainfall of 328 mm and winds from the NE. The annual mean temperature is 20 °C. With the onset of the wet season TGM increased from typical values near 10 to 905 ng m^{-3}. Measurements made within 5 km of the Poas volcano were higher than at Heredia at that time. Diel values measured at the university site increased until midday along with temperature and radiation. Relative humidity showed a reciprocal pattern. It was found that high values of TGM were not related to wind velocity or direction. The strong diel pattern increased with sunrise, peaked at midday and was lowest during the night time. It would seem that Hg^0 from the volcano is oxidized and is deposited to the soils during the dry season when winds are blowing from the volcano. With the onset of heavy rains in April, Hg in the soil is reduced and re-volatilized resulting in the high levels in the atmosphere. Values at other volcano sites were provided. The role of atmospheric pollutants such as H_2O_2 and O_3 should be included in future studies as they may result in oxidation of reduced Hg. The instability in the air masses may also be a factor and local pollution sources may result in high levels that is emitted from the volcanoes of Hg being circulated to ground level as radiation intensity increases.

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1. Introduction

Elemental Hg (Hg^0) is a volatile metal and represents the predominant form in the atmosphere and is the form involved in long range transport (Schroeder and Munthe, 1998; Steffen et al., 2008; Sunderland and Mason, 2007; Li et al., 2008). It is also the principal form of Hg released from volcanoes (Pirrone et al., 1996; Nriagu and Becker, 2003). Since elemental Hg is not very soluble in water, wet deposition occurs following an oxidation step or directly as particulate Hg (O'Driscoll et al., 2005). Mercury in wet deposition is principally in the form of oxidized (Hg^{2+}) Hg (Boszke et al., 2003; Lin and Pehkonen, 1997; Han et al., 2004; Lindqvist et al., 1991; Schroeder, 1996; O'Driscoll et al., 2005, and references therein). Both wet and dry deposition processes contribute to removal of Hg from the atmosphere (Krug and Winstanley, 2004). In addition, particulate Hg is also scavenged or washed out during rain events. Since chemical speciation of the atmospheric Hg remains incomplete, the operational term used to describe Hg in the atmosphere is total gaseous mercury (TGM).

Upon deposition to soils and water, oxidized Hg can be reduced and re-emitted to the atmosphere as Hg^0 (O'Driscoll et al., 2003; Poisant et al., 2004). This can be either a photochemical reaction or a chemical reaction. Perhaps the most complete overview of the topic is presented by Schroeder et al. (2005). They compared both micrometeorological techniques and dynamic flux chambers

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0883-2927/$ - see front matter © 2011 Published by Elsevier Ltd.
doi:10.1016/j.apgeochem.2010.11.024

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or both and related flux values to meteorological data. Flux rates from soil and water are known to be related to temperature, wind velocity, humidity and Hg substrate level.

Researchers who calculate global emissions for Hg (Pacyna et al., 2006) are unable to distinguish re-emitted Hg from that coming from human activities (UNEP, 2008). Nevertheless, volcanoes have been thought to be a major "natural" source of Hg. Pirrone et al. (1996) have estimated that 5220 tonnes of Hg are emitted from all sources and less than half is considered to be "natural". The total global volcanic emission of Hg is between 20% and 40% of total natural emissions where 75% of these emissions are sporadic eruptions rather than the large quantities of explosive eruptions (Pyle and Matter, 2003). This amount should however be put into perspective as about 40% of the anthropogenic emissions are from burning coal and only 2% of the total is from volcanoes (Nriagu and Becker, 2003).

At the study location, there are other sources of Hg due to industrial activity and urban pollution of the Central Valley. In addition, it is known that there is volatilization from the oceans but these concentrations tend to be low (Sunderland and Mason, 2007). Other emissions occur from mineral deposits of Hg (Ferrara et al., 2000; Pyle and Matter, 2003; Nriagu, 1989; Pirrone et al., 1996) but such sites have not been identified.

In Costa Rica, there are more than 120 volcanic centres, most of them old and extinct. This unique geological feature makes Costa Rica, especially the Central Valley an ideal study site. This location is called the Central Volcanic Range and is surrounded by some of the largest volcanoes in the country with the most prominent being Poas, Irazu and Turrialba (Martínez et al., 2000; Barquero and Fernandez, 1990; Nriagu and Becker, 2003).

The tropical climate in Costa Rica is defined by the wet season from April to November and the dry season from December to April. The overall climate of Costa Rica is influenced by two types of winds. The trade winds from the NE present during the dry season and the equator winds from the west during the rainy season. The annual mean temperature is 20 °C and monthly precipitation is typically 85 mm during the dry months and 328 mm from April to November.

The focus of the present paper is to document the diel and seasonal patterns of TGM at UNA in Heredia, Costa Rica 27 km from the Poas Volcano (Martínez et al., 2000) in the Central Valley of Costa Rica and relate these values to temperature, solar radiation, wind speed and direction and compare these values to other sites.

2. Materials and methods

2.1. Sampling sites

The longest and most detailed observations were made at the urban sampling point in Heredia at the facilities of the Laboratory for Atmospheric Chemistry (LAQAT) (10°00′00, 93″N and 84°06′34, 15″W). Samples were taken from May 2008 to early May 2009. Another sampling site was located on Pyroclasts Hill at Irazu Volcano (9°58′47, 87″N and 83°50′14, 43″W). This is located in the province of Cartago. Samples were taken from 3 to 9 March 2009. In the province of Alajuela, two sampling points were monitored. One was located in Poas Volcano National Park (10°11′45, 41″N and 84°13′50, 05″W). Another was located in the town of San Luis, Grecia (10°09′04, 8″N and 84°17′47, 3″W). It was monitored from October 31 to November 8, 2008. The above sampling points are located in rural areas. Sampling sites are shown in Fig. 1.

2.2. Method of sampling and analysis

Atmospheric air was sampled from a height of 2 m and fed to a total Hg vapor analyzer (Tekran 2537A). The flow rate of sampled air was 1.5 L min^{-1} and samples were collected over 5 min on the Au traps. Teflon filters (47 mm diameter, 0.2 μm pore size) were used at the inlet of the sample lines (unheated) to remove particulates. The two cartridges were packed with ultra high purity Au which has the ability to amalgamate Hg from the air sample. Once the amalgam is formed, it is thermally desorbed and detected using spectrophotometry by Cold Vapour Atomic Fluorescence (CVAFS). The detection limit is less than 0.1 ng m^{-3} and replication is within 5%. The instrument was equipped with an internal permeation source which allows automatic unattended recalibrations.

2.3. Meteorological data

Temperature, wind speed, wind direction, radiation, and precipitation were obtained from the National Meteorological Institute

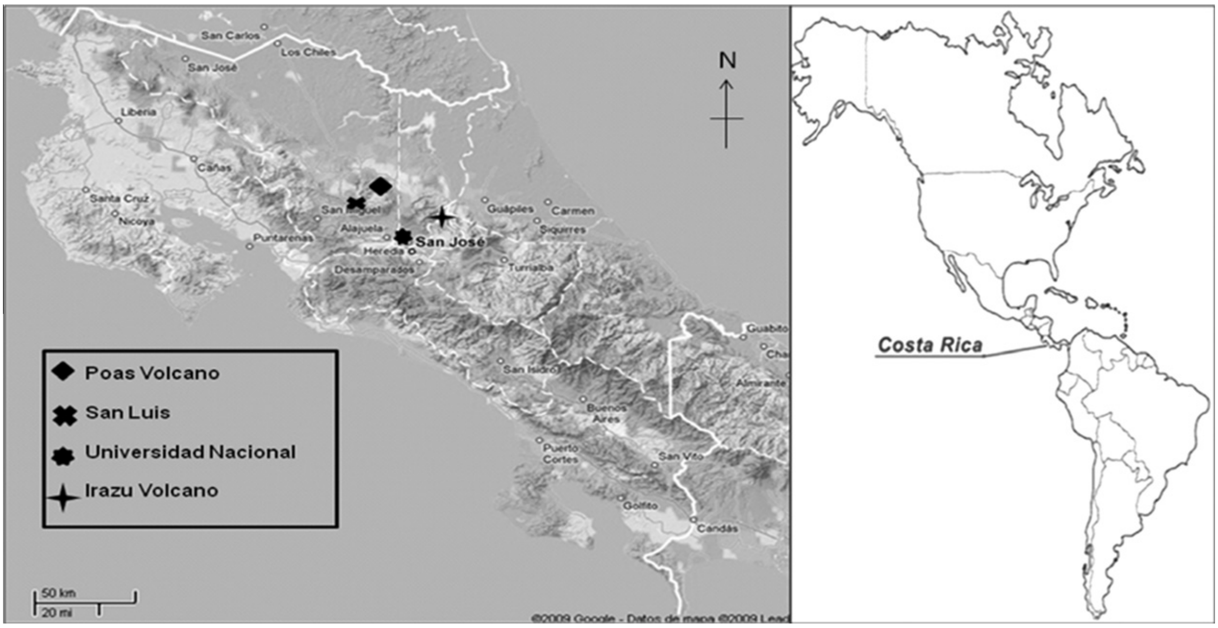

Fig. 1. Total gaseous mercury (TGM) sampling locations in Costa Rica.

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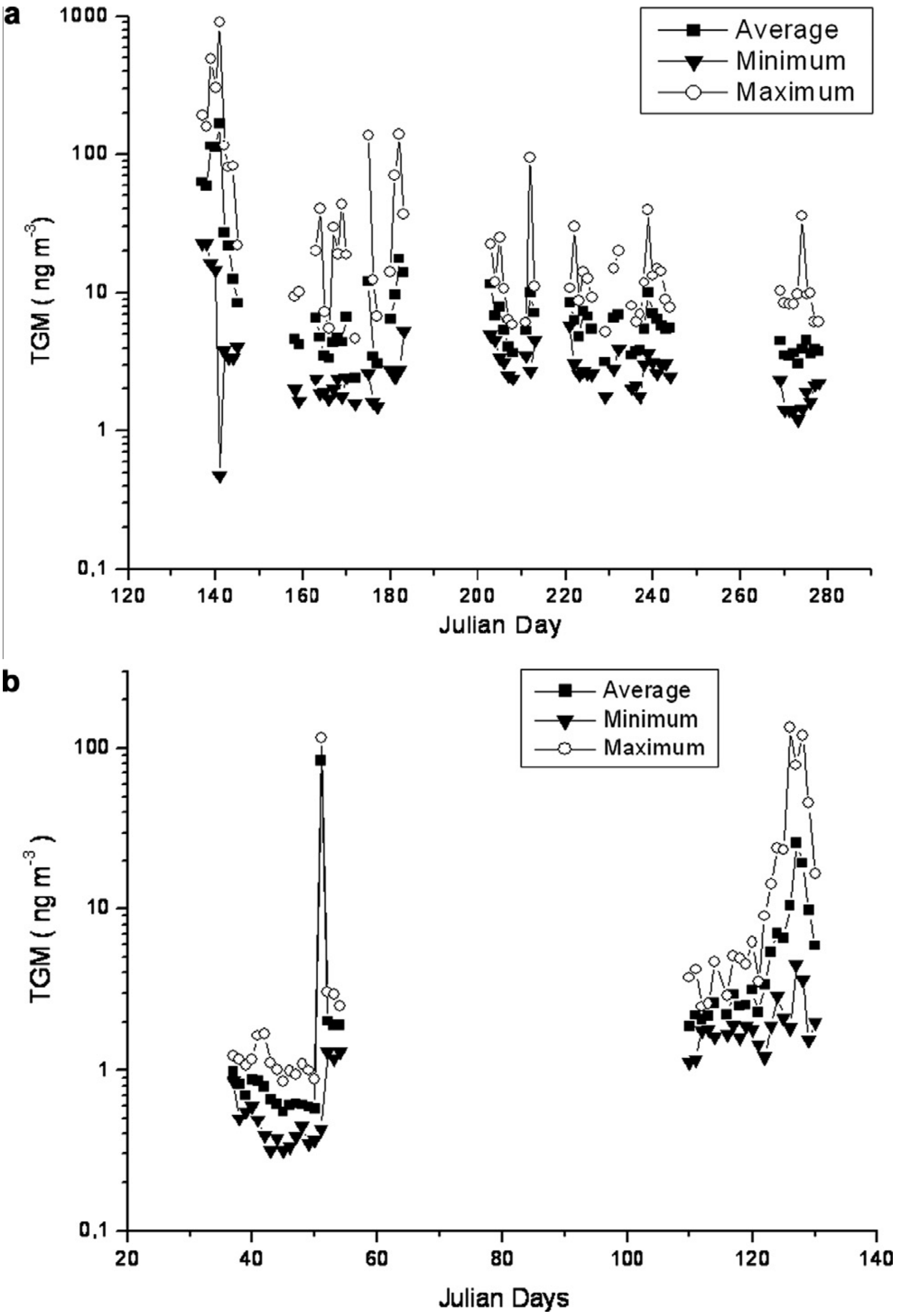

Fig. 2. (a) Daily averaged TGM values measured at Universidad Nacional, Costa Rica (May to December 2008). (b) Daily averaged TGM values measured at Universidad Nacional, Costa Rica (January to May 2009).

Table 1
Summary of maximum, minimum and average values for TGM (ng m^{-3}) measured at the study sites.

Study site	Sampling time	Maximum	Minimum	Average
Poas volcano	21 May 2008	807	403	583
San Luis	31 October–8 November 2008	628	1.03	69.8
Grecia	11–18 November 2008	442	1.48	29.7
Alajuela	17 December 2008–25 January 2009	15.3	0.40	2.92
UNA, Heredia	May–October 2008	903	0.48	14.1
UNA, Heredia	February–May 2009	135	0.32	5.80
Turrialba Volcano	10–15 October 2008	3.87	0.54	1.31
Turrialba Volcano	21 October 2008	113	27.5	57.4
Irazu Volcano	3–8 March 2009	6.45	0.24	0.98

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(IMN) located on the Irazu Volcano and Juan Santamaría International Airport in Alajuela, about 11.3 km west from Heredia 09°59′North 84°10′West, altitude 913 m above sea level. Meteorological data collection in the volcanic areas was done by using a portable Campbell CR10 weather station equipped with an HMP155 air temperature and humidity probe, and a CNR4 Net Radiometer.

3. Results and discussion

Soon after the instrument was installed the authors were surprised to observe values in excess of 50 ng m^3 but even more surprised when they reached a maximum of 905 ng m^3 (Fig. 2a). By chance, the work began soon after the onset of the rainy season. Suspecting that something was wrong the calibration was rechecked and local contamination sources were looked for without success. To ensure that there was no contamination deriving from the sample line it was replaced. The intake was extended so that samples would be collected far from the building. The first value was relatively low (15), as most of the sample came from the content of the line itself. With subsequent sampling, however, high values were again found and it was concluded that the values were reliable.

Throughout the rest of the year and to May 2009 (Fig. 2a and b), values would occasionally reach 100 but were as low as 0.48 ng m^3. The average was still quite high at 14.1 ng m^3. Measurements made in February 2009 (Fig. 2b) were generally low but in May 2009 reached levels of over 100 ng m^3. The onset of the rains was late that year and the extremely high values of the previous year were not observed.

On a day when it was raining heavily in May 2009, a plastic sample collector was set out with a zip lock bag inserted inside. This was a make shift apparatus which illustrated that future work must be conducted with reliable estimates of wet deposition. Zip lock bags are known to be low in Hg so it was likely that the sample container was not contaminated. A wet deposition rate of 2 μg m^{-2}

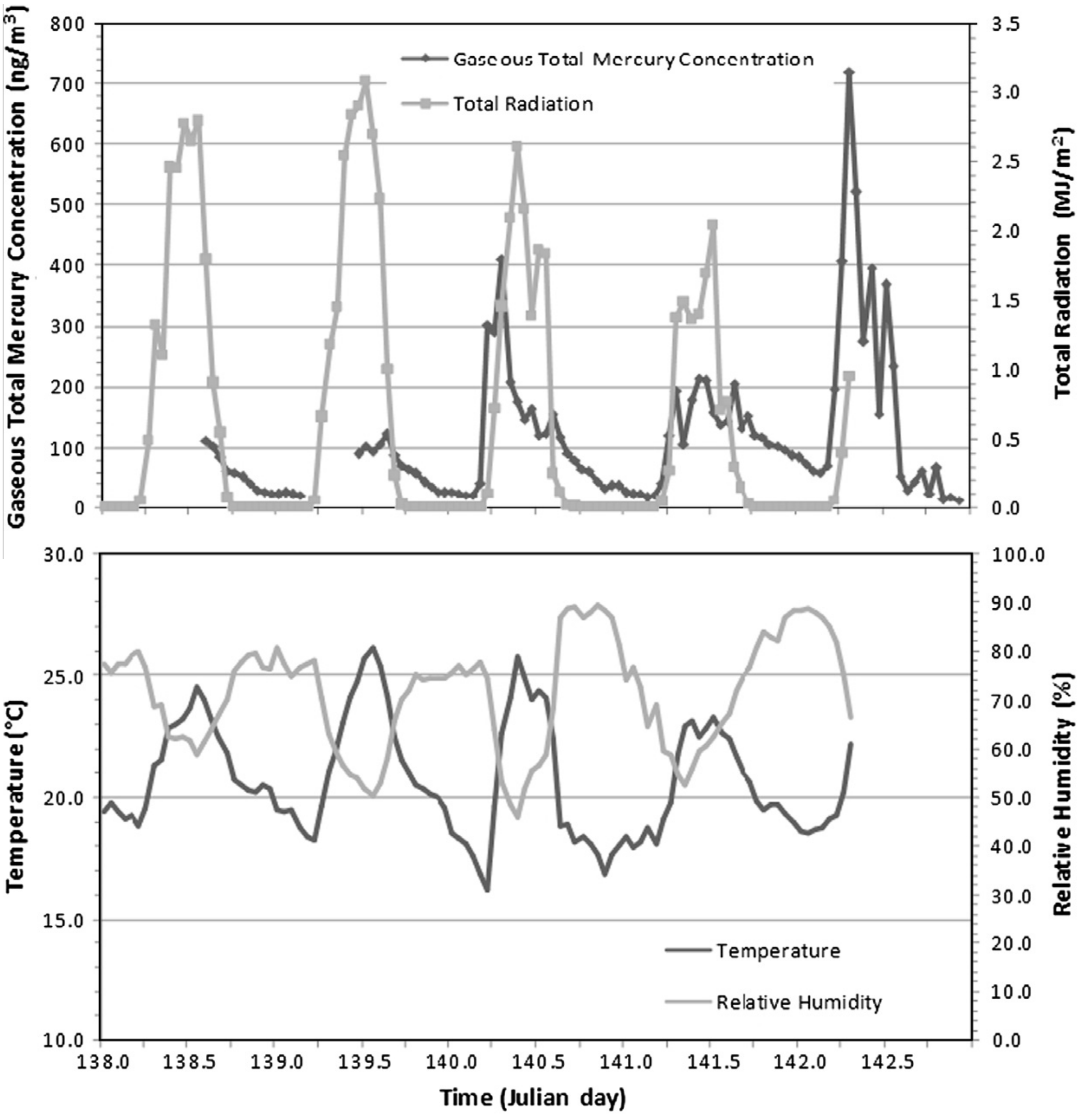

Fig. 3. Hourly averaged patterns of TGM concentration during days 138–143 (May 16–21, 2008) related to total radiation, temperature and relative humidity.

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was obtained in one 24 h period. This should be placed in context with typical values for wet deposition in north temperate regions of about 10 or less μg Hg m^{-2} a^{-1}. Clearly, future work must include thorough measurements of wet and dry deposition rates.

By the end of May 2008, values had declined to about 10–15 ng Hg m^{-3} and the equipment was taken to within 5 km of the volcano in Poas Volcano National Park. The average concentration obtained on 27 May was 583 ng Hg m^{-3} (Table 1). The highest concentration measured was 807 ng Hg m^{-3} at 2:30 pm but by 3:45 the concentration was 403 ng Hg m^{-3}. No measurements were made at night in the park.

Data were examined more closely and the patterns observed from days 138 to 143 were related to other environmental information. Strong diel patterns (Fig. 3) were observed that were related to temperature, relative humidity, radiation and inversely with relative humidity.

When the wind direction and velocity for this period were examined (Fig. 4a) it could be seen that the predominant air mass was from the NE direction. The highest values were recorded on day 141 on which there was almost no wind at all. Since the Poas volcano is located at about 300° but wind does come from that direction during the dry season.

Additional data are provided in Table 1. Values for San Luis and Grecia 10 km away from the Poas volcano are indeed elevated and much higher than at Heredia (Fig. 2a). The average daily concentration was 70 ng m^{-3} TGM (Table 1). At the Irazu volcano, low values were recorded, with an average concentration of only 0.98 ng m^{-3} TGM. These values indicate that either not all volcanoes have the same capacity for emitting Hg, the plume may have been missed or measurements were made at the wrong time of the year. The remote sites would also not have the same level of oxidants in the atmosphere as at Heredia.

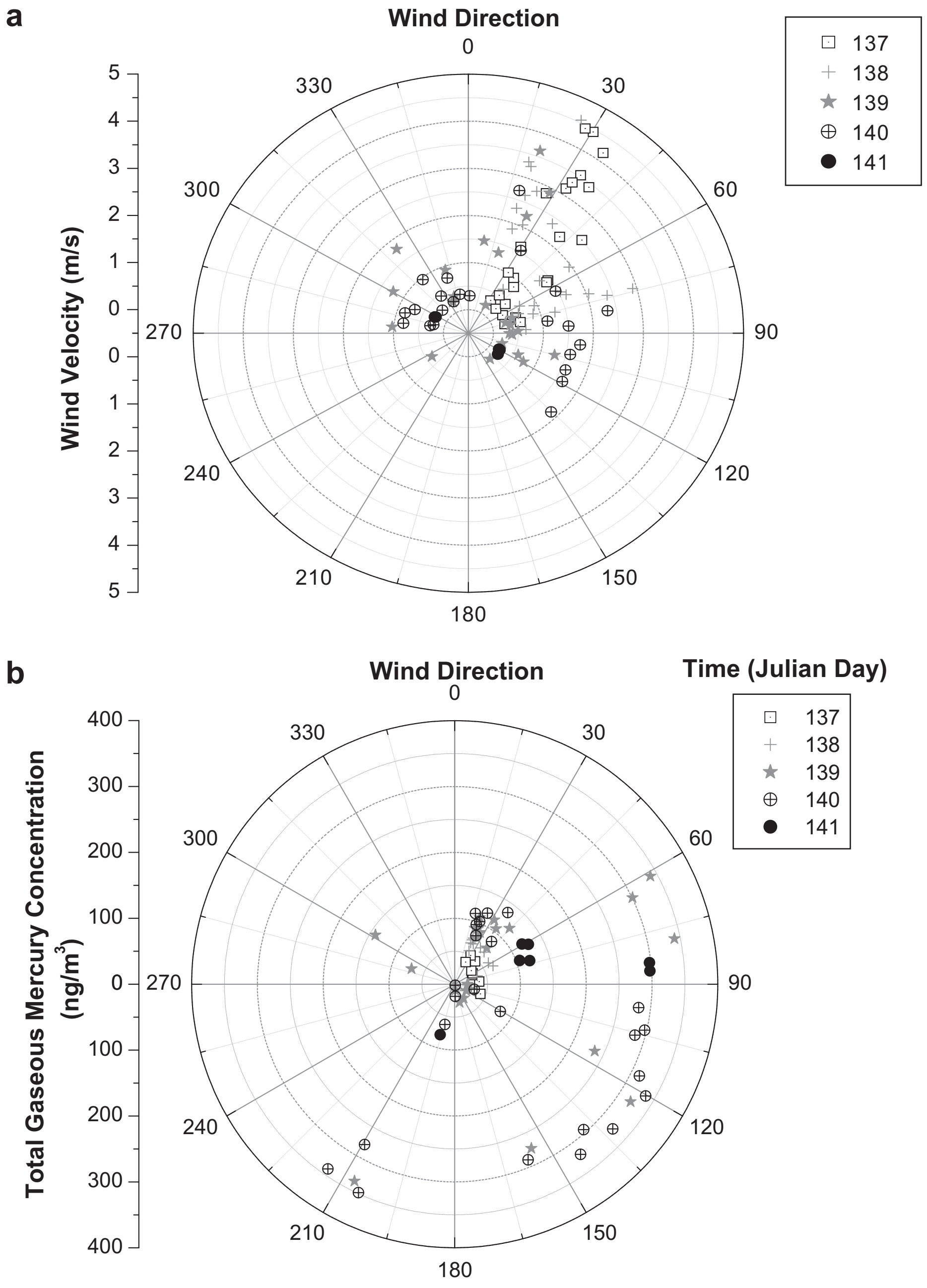

Fig. 4. (a) Wind direction and velocity during days 137–141 (May 16–21, 2008). (b) TGM concentration in relation to the wind direction during days 137–141 (May 16–21, 2008). Scale has a maximum of 400 ng/m^3.

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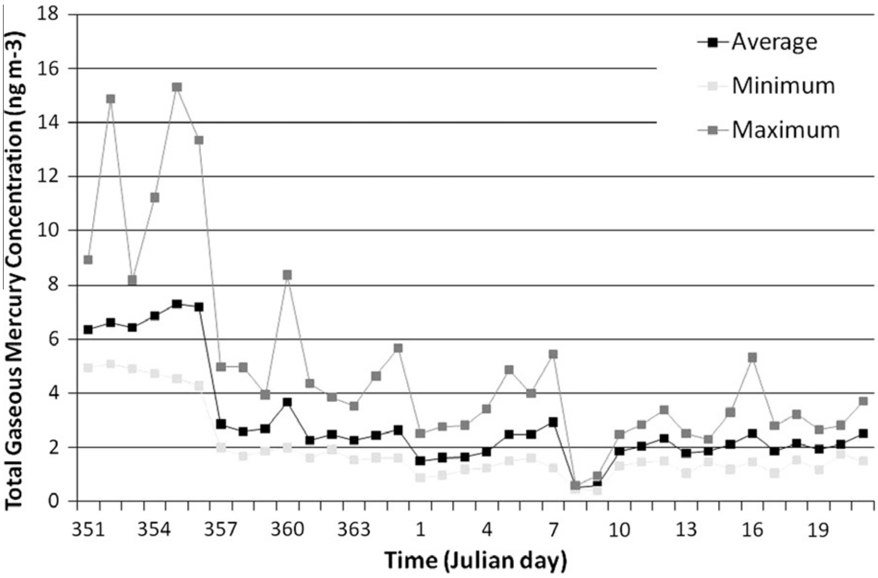

Fig. 5. Maximum, minimum and average concentrations of TGM in Alajuela from 17 December 2008 (day 351) to 21 January 2009. The major earthquake at Cinchona occurred on 8 January at 13:21 h. It had a magnitude of 6.2 on the Richter scale.

A series of measurements were made at Alajuela (Table 1) which is near the airport. The data were collected from 17 December 2008 to 25 January 2009 (days 351–25) (Fig. 5). On 8 and 9 January, data were not recorded due to multiple power outages that occurred following a major earthquake at Cinchona on 8 January at 13:21 h. It had a magnitude of 6.2 on the Richter scale with an epicenter just 30 km from the sampling point. Following the earthquake, the concentrations were low (Fig. 5). Earlier, on 21 Dec TGM concentrations ranged from 4.3 to 15.3 ng m^{-3} Hg with peak concentrations at midday. The average was 7.2 ng m^{-3} Hg. By 26 December values ranged from 1.7 to 8.4 but declined further to an average of 2.6 just before the earthquake. After the earthquake, values increased again so that by 12 January the concentrations were 2–3 ng m^{-3} Hg. On subsequent days TGM values were 0.44, 1.3, 1.6, 1.6, 1.3, 1.0 and 1.47 ng m^{-3} Hg. Clearly, the relationships between Hg emissions and tectonic activity are not yet obvious.

This work comprises the first measurements of TGM in Costa Rica and those related to meteorological data relationships. There are many logistical problems in sampling volcanoes. The plume coming directly from the volcano is harmful to both instruments and people. Consequently, investigators are always faced with doing work at downstream locations where uncertainty of plume dispersion and direction is problematic. In addition, due to instabilities in the air mass, changes in temperature can result in mixing of tropospheric plumes resulting in a diel pattern that is not a true measure of emission patterns from the volcano itself. Nevertheless, this information provides new insights that may be useful for future investigations. It illustrates that very high values of TGM can be observed in air near volcanoes and suggests linkages to oxidants such as O_3 and H_2O_2. Measurements made by researchers at UNA have confirmed that levels are elevated in this region. As such, deposition rates of Hg from the atmosphere to soil and water may be elevated in areas where air pollution is elevated compared with non urban areas where levels are lower. This should be carefully investigated in further studies.

Diel measurements of elemental Hg were also made by Tomiyasu et al. (2006) near the Sakurajima Volcano in Japan. They observed higher atmospheric Hg concentration during the daytime than nighttime and showed a temperature dependency but their values were much lower (1.65–29.4 ng m^{-3}) than were observed at UNA (up to 905 ng m^{-3}). As in the present study, there was no relationship with wind direction. The day to night difference was greater at 3 m than at 12 m suggesting that these changes were driven by soil conditions.

Elevated levels of Hg could potentially be influenced by both photochemical (uv radiation) and chemical reduction which gives rise to high levels of re-emission back to the atmosphere during the onset of the rainy season. The role of moisture due to the onset of the rainy season has only been discussed in a few papers previously. One paper (Song and Van Heyst, 2005) showed that volatilization of Hg from soils increased when water was added to simulate a rain even. The experiments were conducted in controlled laboratory conditions. The soil was initially dry (5–6 vol.%) but volatilization of Hg was enhanced by 12–16 times after the soil moisture content was increased to >15 vol.%. If the soil was initially wet, no enhancement was observed. In other work, Poisant et al. (2004) used flux chambers to evaluate the emission of Hg^0 from bare and flooded wetland soils. They found that the principal mechanism controlling emission of H^0 from dry soil was diffusion and from wet soil it was due to photoreduction. Together, these studies support the influence soil moisture content has on volatilization rates.

4. Conclusions

One hypothesis consistent with the observed concentrations is that Hg emitted from the volcanoes would become oxidized and then deposited to the soil during the dry season. This deposition may be influenced by atmospheric pollutants such as H_2O_2 and O_3. With the onset of the wet season, oxidized Hg (Hg^{2+}) may become reduced to Hg^0 in the presence of UV radiation and re-emitted into the atmosphere as Hg^0 resulting in high concentrations in ambient air. The highest concentrations of Hg were recorded during midday when radiation levels were highest. Measurements made at the Poas Volcano and San Luis confirmed that values were much higher near the volcano that at distance.

It is unlikely that the elevated concentrations came directly from the volcano since one would not expect diel and seasonal patterns for volcanic emissions. In addition, the highest values were not observed when the winds were from the direction of the volcano. The exact mechanism(s) for the elevated concentrations cannot be confirmed at this time but future work should include

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estimates of flux rates from soils measured before, during and after the onset the rainy season. Techniques required have been outlined in Schroeder et al. (2005). Either or both micrometeorological techniques and dynamic flux chambers could be used to determine flux rates with meteorological data as flux rates from soil and water are known to be related to temperature, wind velocity, humidity and Hg substrate level.

While the contribution of volcanoes to the global budget is significant, the concentration of Hg in the air near the volcano may contribute to elevated levels of Hg in the food chain. The deposited oxidized Hg is potentially available for methylation. It is methyl Hg that is biomagnified in food chains leading to man and it is the form that crosses the blood brain and placental membranes. Methyl Hg is likely to be the most important form leading to toxicity in humans (Clarkson, 2002).

Acknowledgements

We are grateful to M.Sc. Eliecer Duarte, Lic. Eric Fernadez, Lic. Sebastian Miranda from Observatorio Vulcanológico y Sismológico de Costa Rica (OVSICORI-UNA) for the support provided during sampling campaigns. We also thank M.Sc. Alfonso Liao for his help with meteorological data analysis. Organization of American States International Graduate Fellowship to Paleah Black, support from UNA and research grants to DL are acknowledged.

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