

# Mercury emission to atmosphere from Lanmuchang Hg–Tl mining area, Southwestern Guizhou, China

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## Abstract

In situ mercury emission fluxes from soil in Lanmuchang Hg–Tl mining area, southwestern Guizhou, China, were measured using dynamic flux chamber (DFC) method in December 2002 and May 2003, respectively. Huge mercury emission fluxes from soil were obtained in the mining area, ranging from  $-623$  to  $10\,544\text{ ng m}^{-2}\text{ h}^{-1}$  ( $n = 92$ ) with the maximal mean Hg flux of  $2283 \pm 2434\text{ ng m}^{-2}\text{ h}^{-1}$ . Meanwhile, highly elevated total gaseous mercury (TGM) concentrations in the ambient air observed during the sampling periods varied from  $35.2 \pm 26.1\text{ ng m}^{-3}$  ( $7.9\text{--}353.8\text{ ng m}^{-3}$ ,  $n = 532$ ) in cold season to  $111.2 \pm 91.8\text{ ng m}^{-3}$  ( $12.7\text{--}468.0\text{ ng m}^{-3}$ ,  $n = 903$ ) in the warm season, respectively. The correlations between mercury emission fluxes and environmental parameters, such as solar radiation, temperature, TGM concentration in air, relative humidity and soil Hg concentration are studied. The strong Hg emission fluxes resulted in the elevated TGM concentrations in the ambient air in the study area. We acquired a significant Log–Log correlation between the ratio of average Hg flux and average solar radiation and the soil Hg concentrations at all sampling sites in warm and cold seasons. Within the Lanmuchang Hg–Tl mining area with a total area of  $\sim 2.9\text{ km}^2$ , the annual Hg emission rate is calculated to be  $\sim 3.54\text{ kg Hg}$ , which is a strong mercury emission source to the local ambient air.

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## 1. Introduction

Mercury as a toxic heavy metal has a strong ability to enter environment (Schroeder and Munthe, 1998; Ebinghaus et al., 2002). Mercury ( $\text{Hg}^0$ ) can evaporate from both natural sources and anthropogenic sources to

the atmosphere and move to remote area through atmospheric cycle due to its long residence time in the atmosphere (0.5–2 years) (Hall, 1995; Schlüter, 2000; Rasmussen, 1994). It has been estimated that during the last 100 years, the average TGM concentration in the troposphere has increased by a factor of three (Fitzgerald, 1995). Those increased TGM in the air may eventually up-concentrate to toxic levels for biosystem through atmospheric deposition (Schlüter, 2000; Lindqvist et al., 1991). In contrast to point sources

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that emitted both  $\text{Hg}^0$  and reactive gaseous Hg, natural and anthropogenic diffuse terrestrial sources contribute primarily  $\text{Hg}^0$  to the atmosphere (Lindqvist et al., 1991). Simultaneously, natural and anthropogenic Hg-enriched areas are long-lived sources of Hg to the atmosphere ( $10^3$  to  $\sim 10^9$  years), whereas anthropogenic point sources have lifetimes more of the order of 50 years (Gustin, 1999a).

Geological Hg-enriched areas worldwide are, in general, regarded as a huge atmospheric mercury emission source for a long time (Mason et al., 1994; Rytuba, 2003; Gustin, 2003). On the global scale, three mercuriferous belts which associate with plate tectonic boundaries contain many large or super-large Hg mines, such as Almadén, Spain, Mt. Amiata, Italy, Wanshan, China, and California and Nevada, USA (Fig. 1). Considerable progresses of understanding mercury geochemistry have been made in those Hg mining areas recently (Gustin, 2003; Gustin et al., 1996, 1999a, b, 2003; Ferrara et al., 1998a, b; Engle et al., 2001) with the development of interfacial mercury fluxes measurement technology. Total mercury emission rates to the atmosphere from the Almadén mine district varied from 600 to  $1200 \text{ g h}^{-1}$  (Ferrara et al., 1998a). Soil/air Hg exchange fluxes as well as annual Hg emission rates at the California and Nevada mining district were determined and estimated (Coolbaugh et al., 2002; Engle et al., 2001). However, most recent works showed that the mercury emission rates from those Hg-enriched areas were much greater than previously predicted (Coolbaugh et al., 2002; Engle et al., 2001; Feng et al., 1996; Ferrara et al., 1998a, b; Gustin et al., 2000, 2003).

In order to better estimate mercury emission from Hg-enriched areas worldwide, more field studies at different climate zones and different geographical locations are urgently needed.

Guizhou province ( $\text{N}24^{\circ}30' - 29^{\circ}13'$ ,  $\text{E}103^{\circ}1' - 109^{\circ}30'$ ), southwestern China, is one of the most important mercury production centers over the world. It is situated on the Guizhou–Yunnan Plateau with an average elevation of 1100 m above sea level. It has a typical subtropical humid monsoon climate characterized by an average annual temperature of  $15^{\circ}\text{C}$  and an annual precipitation of 1100–1400 mm. Many hydrothermal deposits, such as Hg, Pb, Zn, Au, and Sb mines, occur in the province. The total resources of cinnabar in Guizhou province reach up to 88 100 tons, constituting approximately 70% of the total mercury resources in China. Guizhou has experienced a long history of Hg mining activities for about 600 years, and from 1936 to 1990 the total production of mercury was 37 000 tons.

Mercury emissions from anthropogenic sources in Guizhou were extensively studied (Feng et al., 2002, 2004a, b; Tang, 2004). Annual TGM concentrations in the air in Guiyang city were determined by using automated Hg vapor analyzer (Tekran 2537A), and TGM concentrations ranged from 1.6 to  $550 \text{ ng m}^{-3}$  with an average concentration of  $8.40 \text{ ng m}^{-3}$  (Feng et al., 2004c). TGM concentrations in Guiyang city is much elevated compared to those in Seoul, Korea, Antarctic, and Arctic region (Kim and Kim, 2002; Ebinghaus et al., 2002; Schroeder et al., 1998). The elevated TGM concentrations observed in Guiyang mainly originate from the local coal combustion

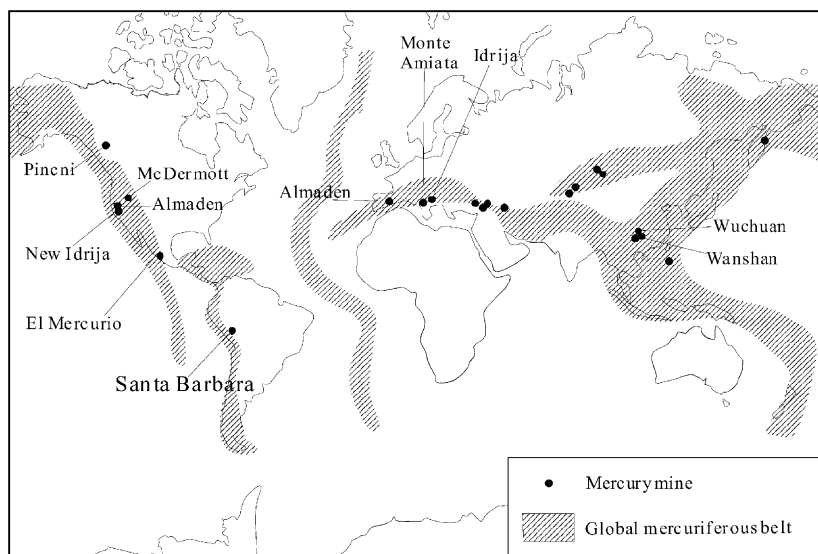


Fig. 1. Sketch map showing the global distribution of natural enrichment of Hg and main mercury mines. Modified from Gustin et al. (1999).

emissions and also mercury emission from Hg enriched soil (Feng and Hong, 1999; Feng et al., 2002, 2004a, 2005). However, only a few studies were conducted on mercury emission measurements from natural sources in Guizhou province (Feng et al., 1996, 2005). It is the first time that we reported the mercury emission fluxes from Hg-enriched soil in the Lanmuchang Hg–Tl mining area.

## 2. Experimental

### 2.1. Study area and sampling sites

The Lanmuchang Hg–Tl mines are controlled by the Lanmuchang normal fault and the Huangnjiang reverse fault (Fig. 2). The regional karstic topography mainly includes peaks, karstic caves, and valleys. The hills are almost bare in Lanmuchang, and only sparsely covered by shrubs and crop. The main mineral containing Hg is cinnabar. There is about 3140 tons of mercury reserve in the Lanmuchang Hg–Tl mines. Mercury concentrations in ores vary between 0.08–0.3 wt% with the maximal grade of 3 wt% (Editorial Board of the Discovery History of Mineral Deposits of China, 1996). According

to the regional recordation, mercury had been refined from Ming Dynasty to 1958 in this area. Although the Hg mining activities have already ceased completely, mercury contaminations to the ecosystem are still a concern. Researches regarding Tl threat to the local inhabitants were conducted recently (Xiao et al., 2003), but mercury contaminations to the local environment have not been investigated yet.

Mercury fluxes between soil and air were measured at three sites (F1–F3) from 4 to 8 December, 2002, and at five sites (F1–F5) from 6 to 18 May, 2003 in Lanmuchang, respectively (Fig. 2). The soil from sampling sites of F1–F3 and F5, where no crops were planted, are mainly composed of clays. The substrate of the sampling site F4 is the black mining tailings. Representative surface soil samples from the 5 sampling sites were collected. All soil samples were air-dried, milled and sieved (<80 mesh). 300–500 mg sample was oxidized with 5 ml concentrated HNO<sub>3</sub> + HCl (1:3 v/v) in a Teflon vial using a Microwave oven (MDS2000, from CEM, USA) for 50 min. The digested solution then was transferred to a 100 ml volumetric flask, and the volume was made up to 100 ml by adding Mill-Q water. Total Hg concentration was determined using BrCl



Fig. 2. Map of sampling sites in Lanmuchang Hg–Tl mine district (Modified from Xiao et al., 2003).

oxidation and  $\text{SnCl}_2$  reduction coupled with cold-vapor atomic absorption spectrometry (CVAAS) (Feng and Hong, 1999; Feng et al., 2004b, 2005). A standard soil sample GBW-07405 (GSS-5) was used to accomplish QA/QC, and the average total Hg concentration of the geological standard of GBW07405 was  $300 \pm 10 \text{ ng g}^{-1}$  ( $n = 8$ ), which is comparable with certified value of  $290 \pm 40 \text{ ng g}^{-1}$ . The precision of our method obtained from replicate analysis is less than 5%. The results demonstrated that the pretreatment procedures can quantitatively recover Hg from the soil samples.

## 2.2. Method of Hg flux measurement

The dynamic flux chamber (DFC) method used to measure mercury fluxes has been described in many documents (e.g. Xiao et al., 1991; Feng et al., 2004c). In the Nevada STORMS Project, this method was inter-compared between different field chambers and was also compared with micrometeorological method by different research groups (Gustin et al., 1999a, b; Wallschläger et al., 1999). A semi-cylinder, open-bottom chamber made of Quartz ( $\text{Ø}20 \times 30 \text{ cm}$ ) was used during our sampling campaign. In order to prevent the wind factors causing rapid pressure fluctuations inside the chamber, six inlets and three outlets holes with 8 mm diameter on the two ends of the chamber are applied. Hg flux from the soil exposed in the chamber was calculated using Eq. (1) (Xiao et al., 1991)

$$F = (C_o - C_i) \times Q/A, \quad (1)$$

where  $F$  is the flux of gaseous Hg, which consists of mostly  $\text{Hg}^0$  (Schroeder and Munthe, 1998) in  $\text{ng Hg m}^{-2} \text{ h}^{-1}$ ;  $C_o$  and  $C_i$  are concentrations of Hg in air of the outlet and inlet of the chamber in  $\text{ng m}^{-3}$ , respectively;  $A$  is the bottom surface area of the chamber in  $\text{m}^2$  ( $0.06 \text{ m}^2$ ); and  $Q$  is the flushing flow rate through the chamber in  $\text{m}^3 \text{ h}^{-1}$  ( $0.9 \text{ m}^3 \text{ h}^{-1}$ ).

Hg concentrations were measured twice in the ambient air entering the inlet of the chamber and twice in the air exiting through outlet of the chamber using the two parallel gold traps (A and B), with a 5 min sampling time. Switching from the inlet to the outlet of the chamber every 10 min was achieved using a magnetic valve (Tekran 1110). Another mass flow controller combined with the second magnetic valve, which is synchronous with the first one, was employed to compensate flow rate decrease when Tekran is sampling air from the inlet of the chamber. A high-flushing flow rate of  $151 \text{ min}^{-1}$  ( $0.9 \text{ m}^{-3} \text{ h}^{-1}$ ) corresponding to a flushing flow rate of 3.2 turnovers  $\text{min}^{-1}$ , was adopted to prevent the possibility of underestimating Hg flux at low-flushing flow rates (Gillis and Miller, 2000; Zhang et al., 2002; Lindberg et al., 2002). Gillis and Miller (2000) found that the relative flux would be near zero when the inlet end of the box faced an oncoming wind of

a speed  $\geq 1 \text{ m s}^{-1}$ . The inlet of chamber was placed facing the down wind direction to avoid influences produced by wind. The Hg analyzers (Tekran 2537A) were calibrated manually before and after the sampling campaign by injecting a volume of Hg saturated air with known concentration. The blank of the chamber after being cleaned with diluted  $\text{HNO}_3$  following with Milli-Q water was measured by sealing the chamber bottom with a Quartz glass plate and the blanks of DFC were detected ( $2.0 \pm 1.6 \text{ ng m}^{-2} \text{ h}^{-1}$ ,  $n = 12$ ). Blanks of DFC were not subtracted from results of fluxes because it is negligible relative to the measured in situ fluxes.

The meteorological parameters, such as air and soil temperature, wind speed, solar irradiation and relative humidity of the air were monitored using a portable weather station (Global Water IIIB, USA) with a time resolution of 5 min which matched to the 5 min sampling times of the Tekran. The detailed description on the weather station was given by Feng et al. (2003, 2004c).

## 2.3. Scaling up area emission of Hg

To scale-up emissions spatially using point source data, a geographic information systems (GIS) framework was used. GIS utilizes geographically referenced data to store, update, query, manipulate, analyze, model, and display the spatial information in vector or raster format. The GIS software used included ArcView (3.3) and Spatial Analyst (2).

## 3. Results and discussion

### 3.1. Mercury concentrations in soil at five sampling sites in Lanmuchang Hg–Tl mining area

Mercury concentrations in soil are 313.0, 247.0, 614.0, 170.0 and  $291 \mu\text{g g}^{-1}$  at sampling sites of F1–F5 in Lanmuchang Hg–Tl mining area, respectively. These concentrations are much higher than the average Hg concentration in soil ( $0.038 \mu\text{g g}^{-1}$ ) in China and are at the same order of magnitude with the Hg concentrations in soil in some mining area in Nevada and California (Engle and Gustin, 2002; Engle et al., 2001; Coolbaugh et al., 2002).

### 3.2. TGM concentrations in the ambient air

The TGM concentrations in the ambient air were measured at the chamber inlet ( $\sim 10 \text{ cm}$  above soil surface) with 20 min intervals at all sampling sites in Lanmuchang Hg–Tl mining area (Table 1, Fig. 3). Overall, the mean TGM concentration in the ambient air in Lanmuchang area was  $35.2 \pm 26.1 \text{ ng}^{-3}$  ( $7.9$ – $353.8 \text{ ng m}^{-3}$ ,  $n = 532$ ) in cold season and  $111.2 \pm 91.8 \text{ ng m}^{-3}$  ( $12.7$ – $468.0 \text{ ng m}^{-3}$ ,  $n = 903$ ) in the warm

Table 1  
Summary of Mercury fluxes, TGM concentrations in air and total Hg concentration in soil in all sampling sites

Sampling site	Sampling date	Average solar irradiation ( $\text{W m}^{-2}$ )	Mercury flux ( $\text{ng m}^{-2} \text{h}^{-1}$ )		TGM ( $\text{ng m}^{-3}$ )			Hg concentration in soil ( $\mu\text{g g}^{-1}$ , dry wt)		<i>n</i>	
			Max	Min	Average $\pm$ SD	Max	Min	Average $\pm$ SD	Emission		Deposition
F1	4–5 Dec, 2002	257	3526	–695	919 $\pm$ 1138	353.8	7.9	48.6 $\pm$ 40.8	313.0	71	10
	17–18 May, 2003	54	1508	–554	242 $\pm$ 377	184.8	12.7	42.0 $\pm$ 28.9		70	9
F2	5–6 Dec, 2002	161	2097	–8	482 $\pm$ 518	72.5	9.5	24.5 $\pm$ 13.0	247.0	64	1
	15–16 May, 2003	217	6922	–1503	783 $\pm$ 1712	227.7	14.0	43.6 $\pm$ 27.4		51	22
F3	6–8 Dec, 2002	30	3864	222	862 $\pm$ 807	47.7	12.6	31.7 $\pm$ 7.8	614.0	113	0
	6–8 May, 2003	145	10544	–623	2283 $\pm$ 2434	468.0	70.6	209.8 $\pm$ 79.1		147	5
F4	9 May, 2003	182	1047	–153	247 $\pm$ 326	63.1	23.7	35.6 $\pm$ 8.5	170.0	27	4
F5	13–15 May, 2003	79	4718	–279	729 $\pm$ 1040	211.9	36.4	117.8 $\pm$ 43.3	291.0	104	4

season, respectively. However, the seasonal difference of TGM concentrations in the ambient air varies between sampling sites. The TGM concentrations in the ambient air in cold season ( $48.6 \pm 40.8 \text{ ng m}^{-3}$  with a range of  $7.9\text{--}353.8 \text{ ng m}^{-3}$ ,  $n = 168$ ) and warm season ( $42.0 \pm 28.9 \text{ ng m}^{-3}$  with a range of  $12.7\text{--}184.8 \text{ ng m}^{-3}$ ,  $n = 160$ ) were in the same range at site F1 (Table 1, Fig. 3), the TGM concentrations in the ambient air in cold season ( $24.5 \pm 13.0 \text{ ng m}^{-3}$  with a range of  $9.5\text{--}72.5 \text{ ng m}^{-3}$ ,  $n = 134$ ) was much lower than that in warm season ( $43.6 \pm 27.4 \text{ ng m}^{-3}$  with a range of  $14.0\text{--}227.7 \text{ ng m}^{-3}$ ,  $n = 220$ ) at sampling site F2 (Table 1, Fig. 3), and a significant increase of TGM concentrations in the ambient air from cold season ( $31.7 \pm 7.8 \text{ ng m}^{-3}$  with a range of  $12.6\text{--}47.7 \text{ ng m}^{-3}$ ,  $n = 230$ ) to warm season ( $209.8 \pm 79.1 \text{ ng m}^{-3}$  with a range of  $70.6\text{--}468.0 \text{ ng m}^{-3}$ ,  $n = 304$ ) (Table 1, Fig. 3) was observed at site F3. The different seasonal variation of TGM concentrations at three sampling sites may be mainly attributed to different Hg emission fluxes induced by meteorological conditions as discussed in Section 3.4. It is clearly observed that TGM concentrations generally peak twice each day, one occurring in the early afternoon and the other at night, respectively (Fig. 3). The peak TGM concentration in the early afternoon may result from the increase of Hg emission flux from soil during the daytime, whereas the peak TGM concentration occurred at night is generally attributed to the fact that shallow nocturnal boundary layers form to accumulate TGM near the surface on most nights (Feng et al., 2004a).

TGM concentrations in the ambient air in Lanmunchang mining area are much elevated by an order of magnitude of 2–3 compared to those obtained in background areas in Northern America and Europe which ranged from  $1.5$  to  $2.0 \text{ ng m}^{-3}$  (e.g. Schroeder et al., 1998; Ebinghaus et al., 2002), but are in the same order of magnitude as reported at the Park and Bowie Mill in central western Nevada (Gustin et al., 1996). There are no anthropogenic mercury emission sources in the vicinity of Lanmunchang area. Therefore, the elevated TGM concentrations in ambient air are mainly attributed to Hg emission from Hg-enriched soil. The diffusion of Hg through atmospheric cycle may lead mercury contamination in the ambient air in neighboring and remote area.

### 3.3. Soil/air Hg exchange fluxes

The mean Hg emission fluxes from soil in Lanmunchang Hg mining area ranged from  $242$  to  $2283 \text{ ng m}^{-2} \text{ h}^{-1}$  (Table 1). The soil showed net Hg emission to the atmosphere. The average Hg emission fluxes were about two-fold and thrice higher in warm season than those in cold season at site F2 and F3, respectively (see Table 1 and Fig. 3). But at site F1, Hg

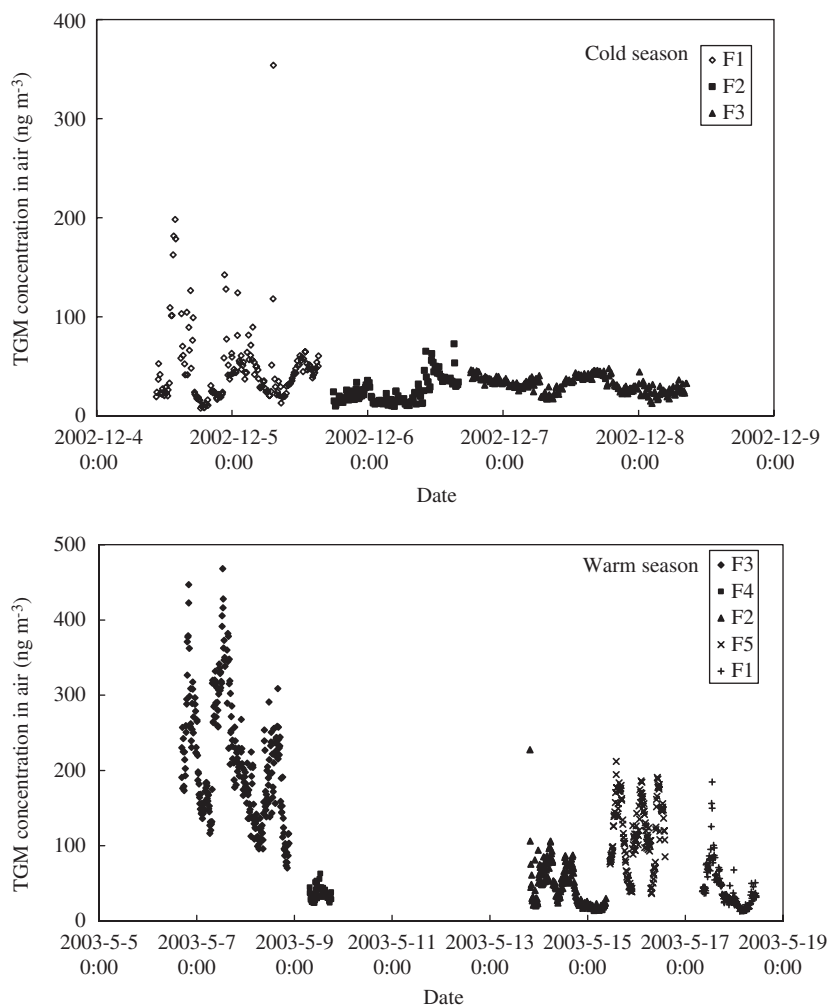


Fig. 3. Variation of TGM concentration in air in Lanmuchang Hg mine in cold season and warm season.

fluxes measured in warm season during a rainy day at the sampling site F1 were much lower than in cold season in a sunny day (Table 1). This can explain the different seasonal variation of TGM concentrations in ambient air at site F1–F3. The seasonal difference of Hg emission fluxes is also attributable to the different meteorological parameters such as solar irradiation (see Section 3.4). Meanwhile, we observed mercury deposition occasionally occurring at all sampling sites. The maximal mercury deposition flux of  $1502 \text{ ng m}^{-2} \text{ h}^{-1}$  was obtained at sampling site F2. Hg fluxes showed a clearly diurnal pattern that Hg emission rate reached maximum at noon and fell to minimum at night (Figs. 4, 5). Overall, Hg exchange fluxes measured in Lanmuchang Hg–Tl mining area are 2–3 order of magnitude higher than those obtained in Hongfeng reservoir region where mercury concentrations in soil

are about  $0.2 \text{ mg kg}^{-1}$  (Wang et al., 2003). All results indicate that soils in Lanmuchang Hg–Tl mining area are huge atmospheric mercury sources.

### 3.4. Factors controlling mercury fluxes

It is widely accepted that mercury evaporated from soil constitutes mainly of elemental mercury (Schlüter, 2000; Carpi and Lindberg, 1998). However, factors controlling emission of volatile  $\text{Hg}^0$  from soil include mercury speciation and concentration in substrate (Gustin et al., 2000; Engle et al., 2001; Coolbaugh et al., 2002; Zehner and Gustin, 2002; Feng et al., 1996, 2005), solar irradiation (Gillis and Miller, 2000; Gustin et al., 2002; Carpi and Lindberg, 1998; Feng et al., 1996), temperature (Lindberg et al., 1995; Carpi and Lindberg, 1998; Gustin et al., 2002); precipitation

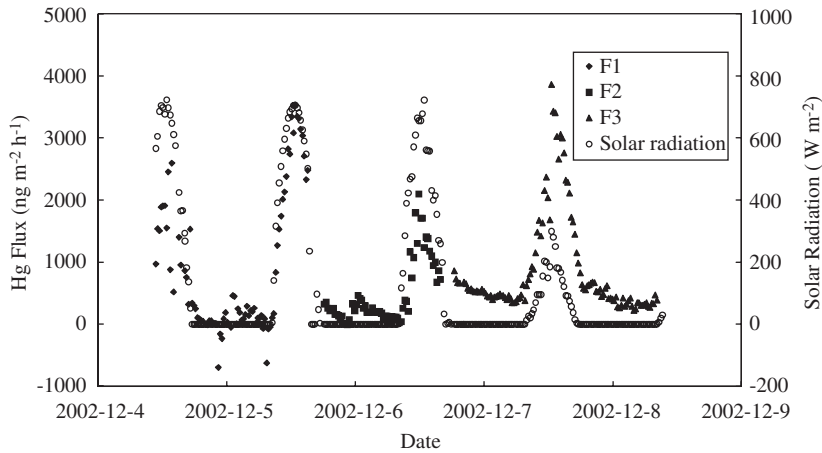


Fig. 4. Variation of Hg flux and solar radiation in Lanmuchang Hg mine in cold season.

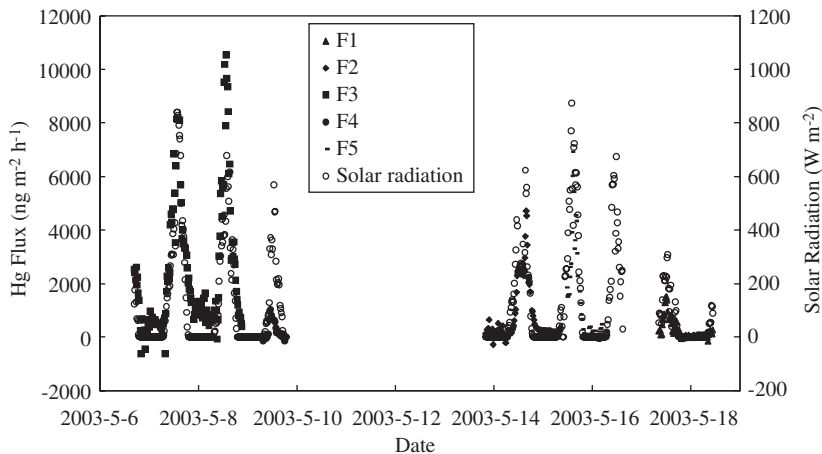


Fig. 5. Variation of Hg flux and solar radiation in Lanmuchang Hg mine in warm season.

(Lindberg et al., 1999; Wallschläger and Kock, 2000), and TGM concentrations in the ambient air (Engle et al., 2001). Recent works have demonstrated that soil mercury concentration is a dominant factor controlling Hg emission flux from the substrate (Gustin et al., 2000; Schlüter, 2000; Feng et al., 1996). There is a significant Log–Log relationship between the total soil Hg concentration and the daily average Hg fluxes measured at desert area where it never rains (Gustin et al., 2000; Engle et al., 2001; Coolbaugh et al., 2002; Zehner and Gustin, 2002).

Zhang et al. (2002) explained the process of soil mercury emission using the gradient between TGM in soil air and that in air above the soil surface.  $\text{Hg}^0$  concentrations in soil not only depend on the soil Hg concentration, but also on the rate of reduction of  $\text{Hg}^{2+}$  by photo-chemistry, thermo-process and biological

activities (Schlüter, 2000). Field and laboratory experiments have demonstrated that solar irradiation plays a significant role in mercury emission from soil and other surfaces (Gillis and Miller, 2000; Costa and Liss, 1999, 2000). Researches on impact factors demonstrated that DOC content and Fe(III) could accelerate formation of dissolved gaseous mercury (DGM) in water under light irradiation, but in dark condition, the process of DOC and Fe(III) for formation of DGM is very slow (Costa and Liss, 1999, 2000; Zhang and Lindberg, 2001). Gustin et al. (2002) demonstrated that solar irradiation could enhance Hg emission from soil significantly and Hg emission flux weakly correlates with soil temperature. It is proposed that  $\text{Hg}^{2+}$  can be photo-reduced to  $\text{Hg}^0$  in soil, the stronger solar irradiation will lead higher  $\text{Hg}^0$  concentration in soil air, which will increase mercury emission rate from soil to the atmosphere.

Significantly linear relationships between mercury fluxes and solar radiations were obtained at all sampling sites in the study area (Figs. 4, 5; Table 2), highlighting that solar radiation contributed significantly to mercury emission process in our study area.

Arrhenius equation (Eq. (2)) characterizes the relationship between substrate temperature and the reaction rate of a chemical process (Lindberg et al., 1995; Carpi and Lindberg, 1998; Gustin et al., 2002)

$$\ln K = \ln A - (\Delta H/RT), \quad (2)$$

where  $A$  is a frequency factor or the number of times the atoms are close enough to react,  $\Delta H$  is the activation energy ( $E_a$ ) or molar heat of vaporization ( $\text{kcal mol}^{-1}$ ),  $T$  is the absolute temperature (K) and  $K$  is a rate constant which may be equated with Hg flux measured at special temperatures.

Mercury emission fluxes and soil temperatures accord well with Arrhenius equation in our results (Table 2), which implies that soil temperature may also control the Hg emission process from soil. The rise of soil temperature may increase activity of  $\text{Hg}^{2+}$  and accelerate the speed of  $\text{Hg}^{2+}$  photo-reduced to  $\text{Hg}^0$ . Meanwhile, the expanding of air volume in soil pore led by elevated soil temperature may drive  $\text{Hg}^0$  diffusing to the atmosphere. However, recent laboratory studies clearly demonstrated that solar radiation is the more dominant process controlling Hg emissions from naturally enriched substrates than soil temperature (Gustin et al., 2002), and that light-induced Hg emission flux is independent of the soil temperature (Bahlmann et al., 2004). As shown in Table 2, the correlation coefficients between Hg fluxes and solar radiation are higher than those between Hg flux and soil temperature. Because soil temperature is mainly controlled by solar radiation in

nature, the good relationship between soil temperature and Hg flux could be the reflection of correlations between solar radiation and Hg flux.

Either in warm season or in cold season, TGM concentrations in air are much higher in Lanmchang area than those measured in Hongfeng reservoir region ( $2.7 \pm 0.7 \text{ ng m}^{-3}$  in warm season, Wang et al., 2003;  $8.9 \pm 6.5 \text{ ng m}^{-3}$  in cold season, unpublished data). This indicates that strong Hg emissions from natural Hg enriched soil resulted in elevated TGM concentrations in the ambient air in Lanmchang Hg–Tl mining area. On the other hand, high TGM concentrations in the ambient air may constrain Hg emission from soil and even result in  $\text{Hg}^0$  deposition to soil (Engle et al., 2001). At night, since the photoreduction process of  $\text{Hg}^{2+}$  ceases, the TGM concentration in soil air will be much lower than that in daytime (Kim et al., 1995). As stated previously in this section, soil/air Hg exchange rates and directions are controlled by the gradient between TGM concentration in soil air and that in air above the surface soil. Thus, even though TGM concentration in air of daytime and night are in the same range generally, the slight increase of TGM concentration can lead the decreasing of Hg emission rates from soil during night period (see Fig. 6). Positive relationships between Hg exchange fluxes and TGM concentrations were obtained during daytime at all sampling sites, whereas, negative relationships were observed at night at all sampling sites except the site F3 in cold season (Fig. 6). From Fig. 6 we observed that even at night, there still were strong Hg emission fluxes from soil at site F3. At the same time, the average TGM concentration in the ambient air at night in cold season at site F3 was an order of magnitude lower than that observed in warm season, which favors mercury emission from soil. The strong Hg emission fluxes from soil still controlled the change of TGM concentration in the ambient air. The negative relationships between soil emission fluxes and TGM concentration in air at night indicate that when photo-reduced production of  $\text{Hg}^{2+}$  ceases, the higher TGM concentrations in air may decrease the rate of mercury diffusion from soil to the air, or/and change the direction of mercury flux.

In our measurement campaigns, a rainfall event with a precipitation of about 5 mm occurred from 2:30 to 3:10 on 8 May 2003 when we were conducting flux measurement at site F3. The rainfall led a significant increase of Hg flux by a factor of 2 (from 758 to  $1458 \text{ ng m}^{-2} \text{ h}^{-1}$  as shown in Fig. 7). Since the soil covered by field chamber was not influenced by the rain, the increase of Hg flux may originate from the entrance of  $\text{Hg}^0$  from soil outside DFC. On the one hand,  $\text{Hg}^0$  in soil outside DFC could be pushed into DFC by rain water through soil pores. On the other hand, the rain water could enter deeper soil covered by DFC, then replace  $\text{Hg}^0$  adsorbed on surface of soil grain, and finally

Table 2  
Correlation coefficients of Hg fluxes and solar radiations at all sampling sites of Lanmchang Hg mine in cold and warm season

Sampling site	Season	Hg flux and solar radiation (Linear equation)	Hg flux and soil temperature (Arrhenius equation)
		$R^2$	$R^2$
F1	Warm	0.70	0.60
	Cold	0.80	0.61
F2	Warm	0.81	0.71
	Cold	0.82	0.43
F3	Warm	0.83	0.69
	Cold	0.89	0.72
F4	Warm	0.67	0.27
F5	Warm	0.91	0.71

Correlations are all significant at the 0.01 level.



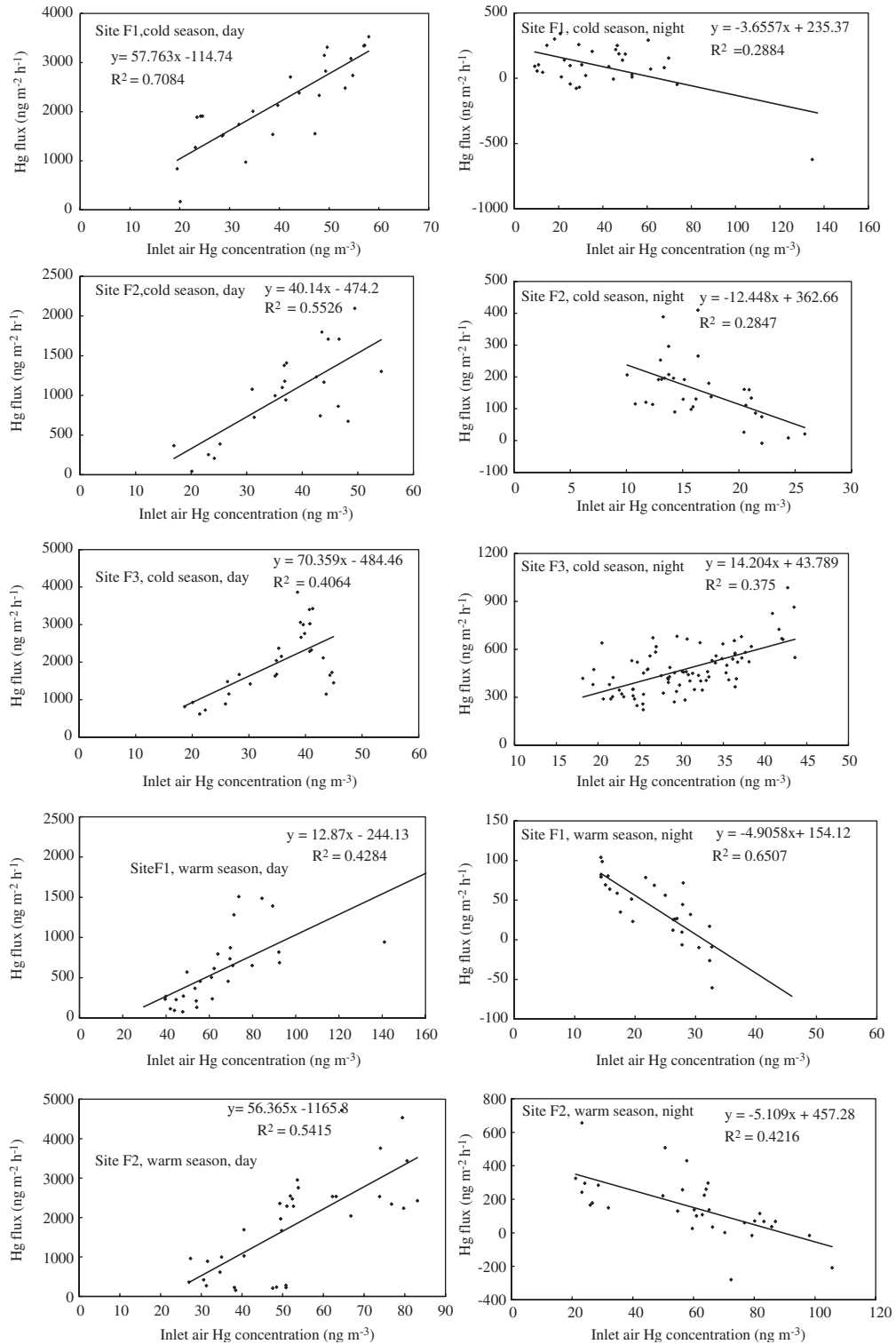


Fig. 6. Figures of different relationship of Hg fluxes vs. inlet air mercury concentration in daytime and night at all sampling sites in Lannuchang Hg–Tl mining area.

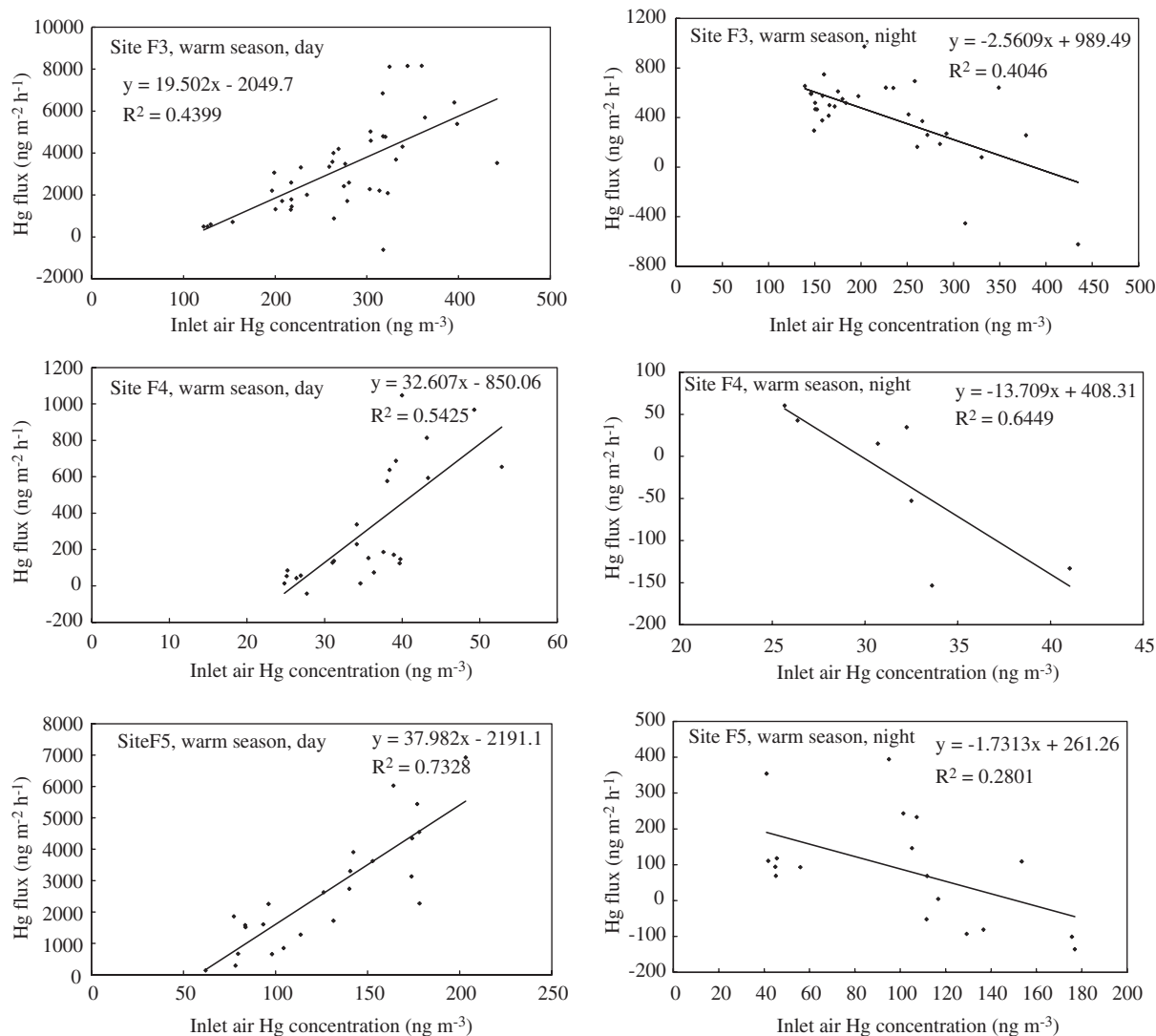


Fig. 6. (Continued)

lead Hg<sup>0</sup> entering DFC, which consequently increases the Hg emission fluxes from soil.

The soil humidity has an important impact to Hg emission flux (Wallschläger and Kock, 2000). We compared Hg fluxes data before and after the rainfall at site F3 as shown in Table 3. On the one hand, an average of 20% increase of Hg fluxes was obtained from the moister soil after the rainfall event compared to those before rainfall during daytime, even though the average solar irradiation and soil temperature were some what lower on the day after the rainfall than those in previous day as shown in Fig. 7 and Table 3. On the other hand, no significant increase of Hg flux was observed before and after rainfall event at night (Fig. 7). These indicate that the moist soil will facilitate mercury

release from soil under solar irradiation. Wallschläger et al. (1999) supposed that abiotic processes were largely responsible for this phenomenon. In soils, Hg<sup>2+</sup> is either present in soil solutions or adsorbed by inorganic or organic components. Adsorption and desorption of Hg<sup>2+</sup> to soil surface may be highly important in indirectly controlling reduction of Hg<sup>2+</sup> to Hg<sup>0</sup> and its subsequent emission (Zhang and Lindberg, 1999). When moisture of soil increases, the distribution of Hg<sup>2+</sup> between soil solution and soil particles will be altered. More Hg<sup>2+</sup> in solid phases will enter soil solution which will be available to the photo-reduction process, eventually resulting in the increase of Hg emission flux. These prove that solar irradiation also plays an important role in mercury emission from soil.

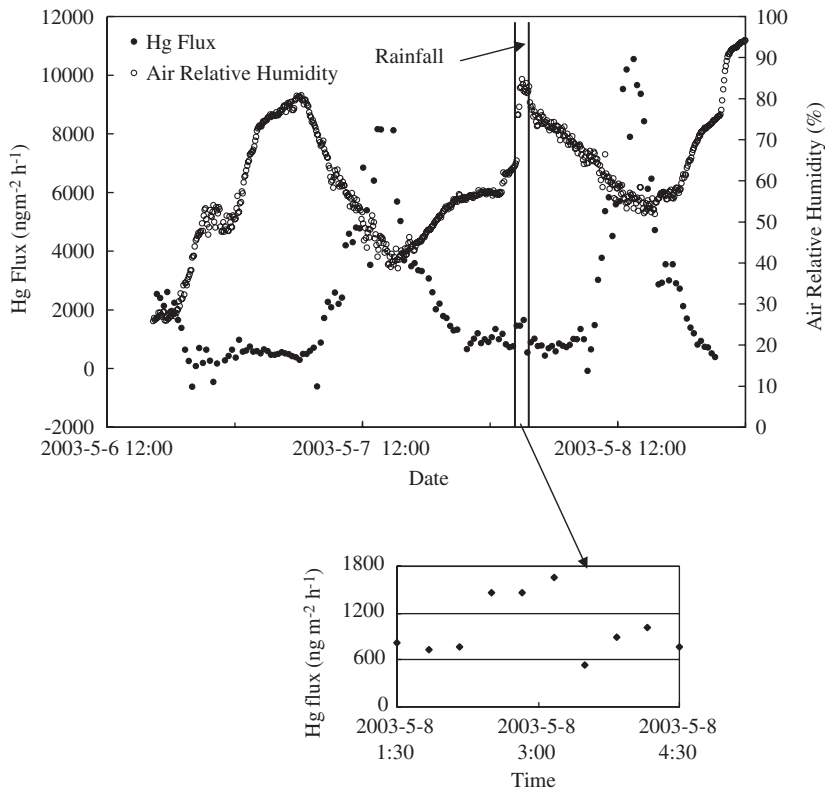


Fig. 7. Relationship between relative humidity and mercury fluxes and impact of rainfall to mercury fluxes at sampling site F3 from 6 to 8 May, 2003.

Table 3

The comparison of Hg fluxes, solar radiation, soil temperature before and after rainfall at the sampling site of F3

Date	Time	Hg flux ( $\text{ng m}^{-2} \text{h}^{-1}$ )			Solar radiation ( $\text{W m}^{-2}$ )		Soil temperature ( $^{\circ}\text{C}$ )	
		Max	Mean	<i>n</i>	Max	Mean	Max	Mean
7–5–2003	8:00–20:00	8157	3907	33	874	343	48	34
8–5–2003	8:00–20:00	10 544	4215	36	850	268	40	28

Generally, the biotic process is very slow in nature (Schlüter, 2000) and thermal-reduction of  $\text{Hg}^{2+}$  is very weaker when temperature is less than  $100^{\circ}\text{C}$  (Raposo et al., 2003), therefore beside soil Hg concentration, solar irradiation is another dominant factor controlling Hg emission from naturally Hg-enriched area from our results.

### 3.5. Estimation of Hg emissions from Lanmuchang Hg–Tl mine area

In recent years, many efforts were diverted to scale up atmospheric Hg emissions from naturally enriched areas

(Gustin, 2003; Zehner and Gustin, 2002; Engle and Gustin, 2002; Engle et al., 2001; Coolbaugh et al., 2002). Gustin (2003) estimated natural Hg emission from Nevada and California based upon the observed Log–Log relationship between daily average Hg fluxes and soil mercury concentrations. Engle et al. (2001) and Engle and Gustin (2002) used in situ Hg emission flux measurements and the diurnal Gaussian Distribution of Hg fluxes to scale up Hg emissions for the naturally enriched soil in Nevada and California. These works were mainly carried out in desert areas.

Guizhou is located in a subtropical altiplano area with moist and rainy weather. Mercury evaporating from soil

in our study area is, obviously, differently day-to-day due to the cloudy weather. Since it never rains in desert, the Gaussian distribution model could be used to present the daily distribution pattern of Hg fluxes

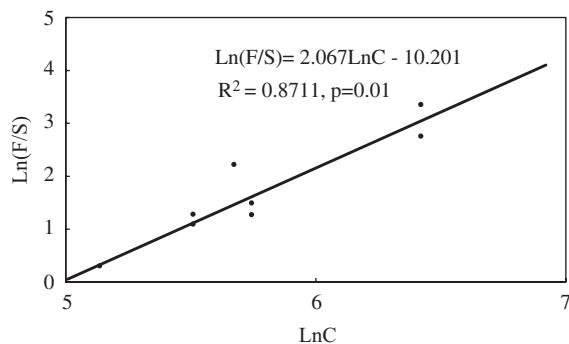


Fig. 8. Graph of the logarithm of ratio of Hg flux and solar radiation vs. the logarithm of substrate Hg concentration for field chamber measurements.

(Engle et al., 2001) and a simple Log–Log model originates from relationship between soil Hg concentrations and Hg flux could be obtained (Gustin, 2003). However, these approaches are not applicable in our study area simply because the daily weather in Lanmuchang Hg–Tl mine district is variable, which is significantly different from the weather in deserts of California and Nevada, USA.

In order to eliminate the effects of solar radiation on mercury emission fluxes from soils, which may conceal the Log–Log relationship between Hg flux and Hg concentration in soil due to the variation of weather condition from day-to-day, we checked the correlation between the ratio of average Hg flux and average solar radiation and the soil Hg concentrations at different sampling sites as shown in Fig. 8. We obtained a significant Log–Log correlation between the ratio of average Hg flux and average solar radiation and the soil Hg concentrations as shown in Eq. (3)

$$\text{Ln}(F/S) = 2.067 \text{Ln} C - 10.201, \quad p = 0.01, \quad (3)$$

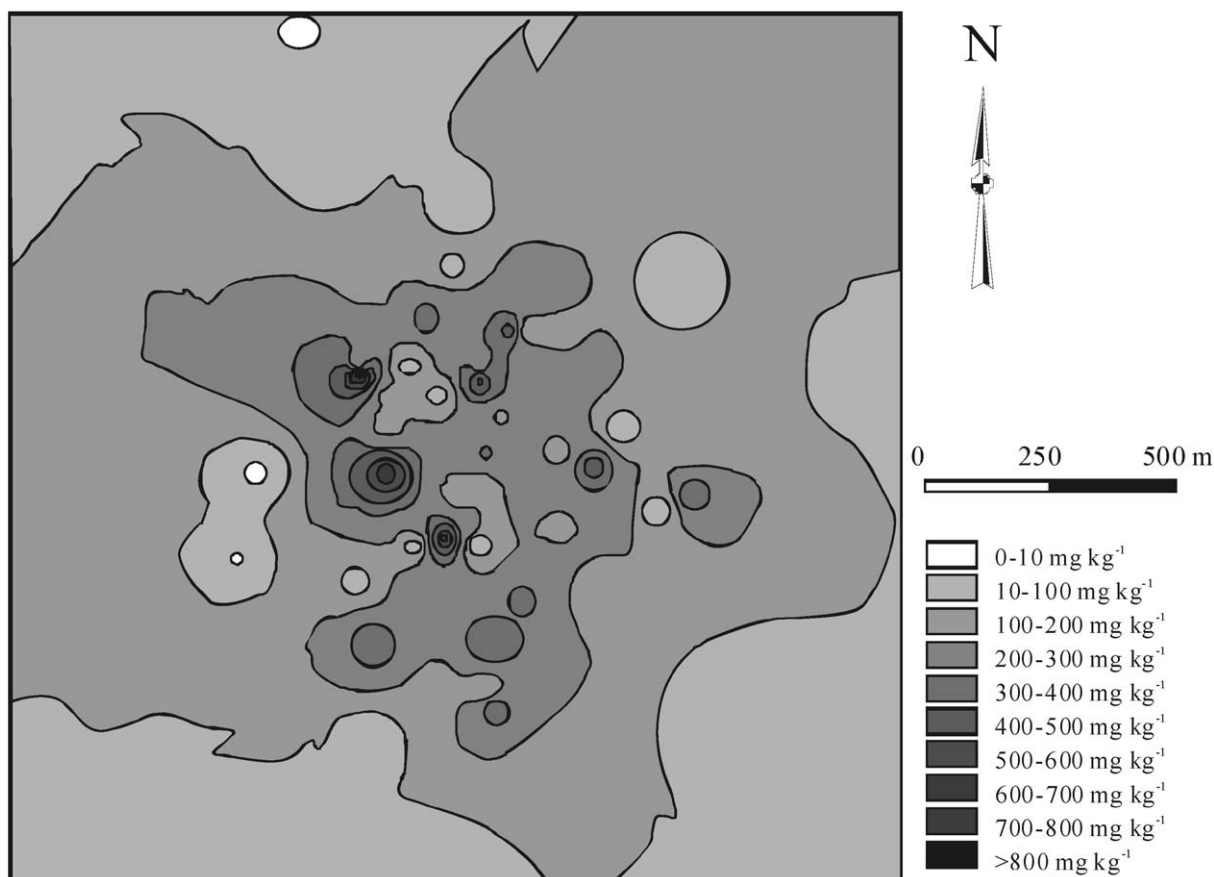


Fig. 9. Map of distribution of Hg in soil in Lanmuchang Hg–Tl mine district.

where  $F$  is Hg flux in  $\text{ng m}^{-2} \text{h}^{-1}$ ,  $S$  is solar radiation in  $\text{W m}^{-2}$ , and  $C$  is Hg concentration in soil in  $\mu\text{g g}^{-1}$ .

To scale-up Hg emissions in the study area, 75 substrate Hg concentrations (Qiu et al., 2005; Xiao et al., 2004) were incorporated into a GIS model to make the map of Hg distribution in surface soil of Lanmuchang Hg–Tl mining area as shown in Fig. 9. In addition, 59482 data of solar irradiation measured from November 2001 to November 2002 were used to calculate the daily solar radiation over the year. The map of the distribution of annual Hg emission fluxes in the study area was obtained by using the Eq. (3) and shown in Fig. 10. A mean Hg emission flux of  $1.22 \text{ mg m}^{-2} \text{ yr}^{-1}$  ( $140 \text{ ng m}^{-2} \text{ h}^{-1}$ ) in Lanmuchang Hg–Tl mining area was obtained, which is at the same order of magnitude with  $114 \text{ ng m}^{-2} \text{ h}^{-1}$  of Hg emission flux obtained from Knoxville Hg mining district (Gustin et al., 2003). Within the Lanmuchang Hg–Tl mining area with a total area of  $\sim 2.9 \text{ km}^2$ , the annual Hg emission rate is calculated to be  $\sim 3.54 \text{ kg Hg}$ , which is a strong mercury emission source to the local ambient air.

#### 4. Conclusions

Geological Hg enriched area in Lanmuchang Hg mining area, southwestern Guizhou is an important atmospheric Hg source. Strong Hg emission from soil results in the elevated TGM concentrations in the ambient air in Lanmuchang Hg–Tl mining area that is 2–3 orders of magnitude higher than TGM concentrations obtained in background areas in Northern Europe and Northern America. The average Hg emission fluxes in the study area range from 241 to  $2283 \text{ ng m}^{-2} \text{ h}^{-1}$ . The maximum emission flux measured in Lanmuchang district reaches  $11544 \text{ ng m}^{-2} \text{ h}^{-1}$  corresponding to the Hg concentration of  $614 \mu\text{g g}^{-1}$  in the substrate. A clear diurnal pattern of Hg flux between air and soil is obtained with Hg evasion during the daytime reaching a maximum at midday followed by reduced fluxes which became deposition during the nighttime period. The diel pattern of Hg flux is mainly driven by solar irradiation.

A Hg flux-solar irradiation-soil Hg concentration model was constructed for scaling up annual Hg emission from Lanmuchang Hg–Tl mining area. Our

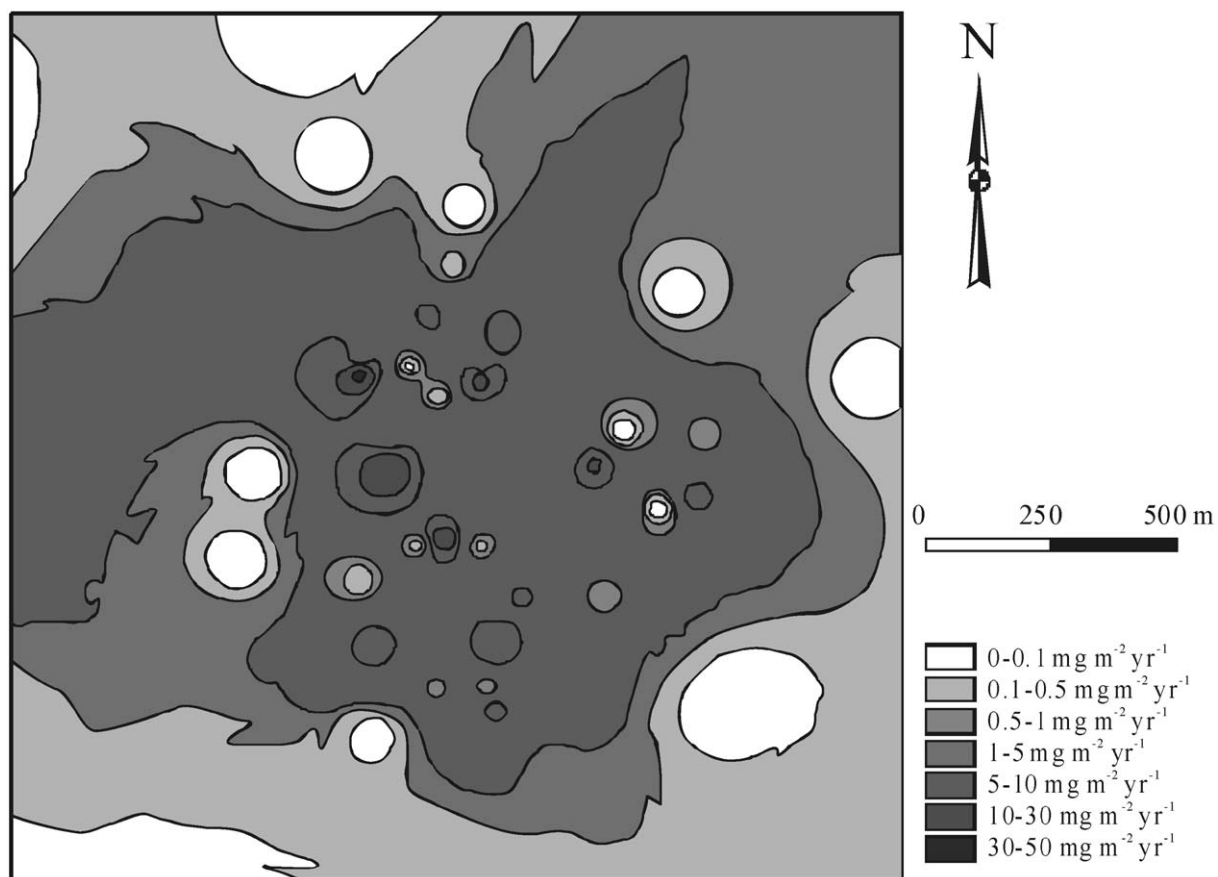


Fig. 10. Map of annual Hg emission flux per square meter from soil in Lanmuchang Hg–Tl mine district.

calculation showed that ~3.54 kg of Hg will diffuse to the atmosphere from Lanmuchang Hg–Tl mining area annually.

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