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# Characteristics of mercury exchange flux between soil and air in the heavily air-polluted area, eastern Guizhou, China

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**Abstract**

To investigate the characteristics of mercury exchange between soil and air in the heavily air-polluted area, total gaseous mercury (TGM) concentration in air and Hg exchange flux were measured in Wanshan Hg mining area (WMMA) in November, 2002 and July–August, 2004. The results showed that the average TGM concentrations in the ambient air (17.8–1101.8 $ng\,m^{-3}$), average Hg emission flux (162–27827 $ng\,m^{-2}\,h^{-1}$) and average Hg dry deposition flux (0–9434 $ng\,m^{-2}\,h^{-1}$) in WMMA were 1–4 orders of magnitude higher than those in the background area. It is said that mercury-enriched soil is a significant Hg source of the atmosphere in WMMA. It was also found that widely distributed roasted cinnabar banks are net Hg sources of the atmosphere in WMMA. Relationships between mercury exchange flux and environmental parameters were investigated. The results indicated that the rate of mercury emission from soil could be accelerated by high total soil mercury concentration and solar irradiation. Whereas, highly elevated TGM concentrations in the ambient air can restrain Hg emission from soil and even lead to strongly atmospheric Hg deposition to soil surface. A great amount of gaseous mercury in the heavily polluted atmosphere may cycle between soil and air quickly and locally. Vegetation can inhibit mercury emission from soil and are important sinks of atmospheric mercury in heavily air-polluted area.


*Keywords:* TGM concentration in air; Mercury exchange flux; Factors controlling mercury exchange flux; Wanshan Hg mining area (WMMA)

## 1. Introduction

Geologically Hg-enriched areas are important atmospheric mercury sources (Gustin, 2003; Mason et al., 1994; Rytuba, 2003). In the past decades, considerable progress on understanding mercury emission from Hg-enriched soil has been made (Coolbaugh et al., 2002; Engle and Gustin, 2002; Engle et al., 2001; Ferrara et al., 1998a, b; Gustin, 2003; Gustin et al., 1999a, b, 1996; Poissant et al., 1999; Feng et al., 2005; Wang et al., 2005). Previous field measurements suggest that mercury emission flux from Hg-enriched soil is 1–3 orders of magnitude greater than the forecasted value (1.1 $ng\,m^{-2}\,h^{-1}$; Lindqvist et al., 1991), and the contribution of Hg from natural soil to the atmosphere in

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earlier models may be underestimated. To estimate the annual mercury emission flux accurately, the mechanisms and processes of mercury exchange between soil and air need to be understood well under various conditions. Engle et al. (2001) proved that mercury emission flux would be inhibited when inlet gaseous mercury concentration was elevated in laboratory, Nacht et al. (2004) observed a period of Hg deposition which corresponded with significantly increased air concentrations, and Wang et al. (2005) found the reverse relationship between inlet total gaseous mercury (TGM) concentration and Hg flux at night in a mercury-enriched area without anthropogenically atmospheric Hg sources, respectively. TGM concentrations in the ambient air may have a strong impact on mercury exchange between soil and air. High mercury emission fluxes were measured in some heavily atmospheric Hg-polluted area using Lidar technique (Ferrara et al., 1998a, b; Gronlund et al., 2005). However, due to the limitation of Lidar technique, the characteristics of mercury exchange between soil and air cannot be investigated.

Wanshan Hg mining area (WMMA) has a long history of metallic mercury refining. Until the shutdown of Wanshan metallic Hg refining plant in the summer of 2001, around 37 000 t of metallic mercury had been produced in the past 52 years. According to the emission factor of 1.69% (Tan et al., 1997), about 625.3 t of gaseous elemental mercury was released to the atmosphere in WMMA. However, indigenous Hg smelters are still operating for mercury refining intermittently in WMMA. Due to the disadvantaged technique and instruments, the illegal Hg refining activities have made heavier atmospheric Hg pollution than the large-scale furnaces in WMMA (Qiu, 2005; Qiu et al., 2005). Under this heavily atmospheric Hg pollution, mercury exchange flux between soil and air in WMMA may differ from background areas significantly. To completely understand the impact of heavy atmospheric Hg pollution on mercury exchange between the interface of soil and air, for the first time the characteristics of mercury exchange flux between soil and air were studied using field chamber method in WMMA in this paper.

## 2. Experimental

### 2.1. Field site

Wanshan Hg mine (N: 27°24′–27°38′, E: 109°07′–109°24′), eastern Guizhou province (Fig. 1), is characterized by mountainous, karstic area and a sub-tropical humid weather with an annually average precipitation ranging from 1200 to 1400 mm. Wanshan Hg mine is the biggest one in China. There are around 13 000 000 t of ore that the average Hg grade is 0.3% in Wanshan Hg mine and the total reserve of metallic Hg accounts for 78% of the total reserve in China (Hua and Cui, 1995).

Two separate sampling campaigns were conducted in WMMA in December, 2002 (11-11 to 11-23) and July–August, 2004 (7-31 to 8-11), respectively. For the first trip Hg flux, TGM concentration in air, meteorological parameters, and surface soil Hg concentrations were collected at F1, F2 and F3 sites, respectively. During the second trip data were collected at F1, F4, F5, F6, F7 and F8 sites, respectively. Eight sampling locations are shown in Fig. 1.

To investigate the impact of high TGM concentrations in air on Hg exchange flux between soil and air, we conducted sampling at eight sites systematically. Site F1, located nearby the Wanshan Hg refining plant, was influenced most seriously by the long-term Hg refining activities. Sites F2, F4, F5 and F6 located at downwind direction of site F1 with different distances were selected. Site F6 was located in a rice field. The height of rice and distance between plants were around 80 and 30 cm, respectively. Because site F7 was chosen at upwind direction of site F1, TGM concentration in air was not influenced by anthropogenic activities. Sites F3 and F8 were located on two roasted cinnabar banks for the estimation of mercury emission from roasted cinnabar in WMMA.

### 2.2. Soil Hg concentration

Representative surface soil samples were collected from the area under the field chamber at the eight sampling sites. All soil samples were air-dried, milled and sieved (<80 mesh). The sample 300–500 mg was oxidized with 5 ml concentrated $HNO_3 + HCl$ (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 this was filled with Mill-Q water. The total Hg concentration was determined using BrCl oxidation and $SnCl_2$ reduction coupled with cold-vapor atomic absorption spectrometry (CVAAS) (Feng and Hong, 1999; Feng et al., 2004a, 2005). National soil reference material (GBW0740) was analyzed to ensure the

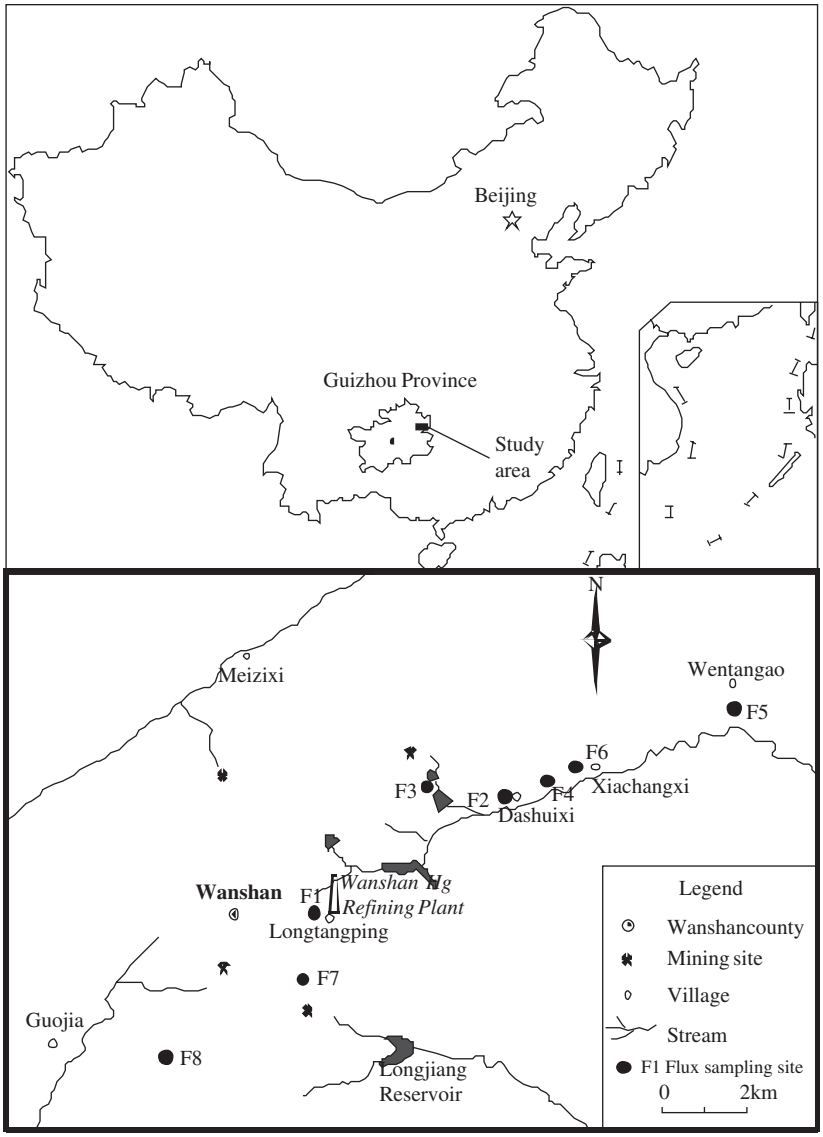


Fig. 1. The hydrography and location of WMMA, Hg flux, meteorological parameters and soil Hg measurement sites.

accuracy of the total Hg concentration analysis. 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.

### 2.3. Hg flux and TGM concentration in air

The dynamic flux chamber (DFC) method was used to measure mercury exchange fluxes between surface and air widely (e.g. Feng et al., 2004b). A semi-cylinder, open-bottom chamber of transparent quartz ($\varnothing 20 \times 30$ cm) was used during our two sampling campaigns. 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 exchange flux between soil and air exposed in the chamber was calculated as (Feng et al., 2005)

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

where $F$ is the flux of the total gaseous Hg, which consists of mostly $Hg^0$ (Schroeder and Munthe, 1998) in ng Hg $m^{-2}$ $h^{-1}$; $C_o$ and $C_i$ represent concentrations of Hg in air at the outlet and inlet of the chamber in ng $m^{-3}$, respectively; $A$ is the

Table 1
The meteorological parameters and soil Hg concentrations at all sampling sites during the sampling periods

| Site | Date | Meteorological parameters | | | | | Soil Hg concentration ($mg\,kg^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | Air temp. (°C) | Relative humidity (%) | Soil temp. (°C) | Solar irradiation ($W\,m^{-2}$) | $n$ | |
| F1 | 2002-11-17 to 19 | 7.6±3.3 | No data | 9.0±2.8 | 58±173 | 636 | 743.5 |
| F1 | 2004-8-8 to 9 | 24.1±2.7 | 80.1 ±14.1 | 26.2±2.8 | 244±330 | 306 | 743.5 |
| F2 | 2002-11-19 to 21 | 5.6±1.7 | No data | 7.0±1.5 | 50±122 | 559 | 215.2 |
| F3 | 2002-11-22 to 23 | 9.6±1.2 | No data | 12.4±4.1 | 187±271 | 186 | 102.0 |
| F4 | 2004-7-31 to 8-1 | No data | No data | No data | No data | | 55.6 |
| F5 | 2004-8-1 to 3 | 26.4±8.4 | 76.9±25.0 | 27.9±4.7 | 99±207 | 299 | 1.0 |
| F6-1 | 2004-8-3 to 4 | 24.1±4.2 | 81.5±19.9 | 25.1±1.6 | 235±325 | 295 | 113.0 |
| F6-2 | 2004-8-4 | 30.1±0.8 | 56.1±4.9 | 27.3±0.2 | 518±309 | 48 | 113.0 |
| F7 | 2004-8-9 to 10 | 24.5±2.7 | 75.1±13.2 | 29.7±8.2 | 251±341 | 298 | 51.2 |
| F8 | 2004-8-10 to 11 | 24.5±4.1 | 74.6±21.3 | 24.6±6.6 | 232±316 | 295 | 78.8 |

Meteorological parameters recorded every 5 min are shown as mean ± standard deviation.

chamber covered soil surface area in $m^2$ ($0.06\,m^2$); and $Q$ is the air flushing flow rate through the chamber in $m^3\ h^{-1}$. The positive and negative results calculated from Eq. (1) represent net Hg emission flux and net Hg dry deposition flux, respectively.

TGM concentrations in air were measured twice in the ambient air entering the inlet of the chamber and twice in the air exiting the outlet of the chamber using the two parallel gold traps (A and B), with a 5 min sampling resolution using an automated Hg analyzer (Tekran 2537A). Switching between sampling air in the inlet and the outlet of the chamber every 10 min was achieved using a magnetic vale (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. To prevent the possibility of underestimating Hg flux at low flushing flow rates, a high flushing flow rate of $15\,l\,min^{-1}$ ($0.9\,m^{-3}\,h^{-1}$) corresponding to a flushing flow rate of 3.2 turnovers per minute was adopted (Gillis and Miller, 2000; Lindberg et al., 2002; Zhang et al., 2002). Because relative flux would be underestimated when the inlet end of the box faced an oncoming wind of a speed $\geqslant 1\,m\,s^{-1}$, the inlet of chamber was placed facing the downwind direction to avoid influences produced by wind (Gillis and Miller, 2000). The Hg analyzer (Tekran 2537A) was calibrated manually before and after the sampling campaign by injecting a volume of Hg saturated air with known concentration. Blanks of DFC were not subtracted from results of fluxes because they are negligible compared to our in situ fluxes.

The meteorological parameters including air temperature, soil temperature, solar irradiation and relative humidity were monitored using a portable weather station (Global Water III, USA) with a time resolution of 5 min which matched to the 5 min sampling times of the Tekran2537A. The results of the micrometeorological parameters, total Hg concentration in soil and descriptions of all sampling sites are shown in Table 1.

## 3. Results and discussion

### 3.1. TGM concentration in air and Hg flux

The average TGM concentrations in air ranged from $17.8 \pm 10.3\,ng\,m^{-3}$ ($n = 155$) to $1101.8 \pm 526.3\,ng\,m^{-3}$ ($n = 154$) throughout the two measurement campaigns (Table 2). The spatial distribution of TGM concentration in air was measured by Qiu et al. (2005) in March, 2005. It was obvious that TGM concentrations in air in WMMA were elevated by 1–3 orders of magnitude compared to the global background value (around $1.5\,ng\,m^{-3}$, e.g. Schroeder et al., 1998).

Elevated TGM concentration in air in WMMA is an important mercury source to local, regional or global atmosphere. Tan et al. (2000) suggested that WMMA was the main contributor of the atmospheric Hg in Fanjing Natural Reserve.

Table 2
The statistical data of Hg flux, and TGM concentrations in air for all sampling sites in WMMA

| Site | Season | Time sampled (duration) | Hg flux[a] ($ng\,m^{-2}\,h^{-1}$) | | | Inlet TGM[b] ($ng\,m^{-3}$) | |
|---|---|---|---|---|---|---|---|
| | | | | Mean | $n$ | Mean | $n$ |
| F1 | Cold | 11:05 to 14:55 (51 h) | Emission | 968 ± 2137 | 54 | 143.6 ± 79.1 | 286 |
| | | | Deposition | 570 ± 550 | 83 | | |
| F1 | Warm | 11:55 to 12:55 (25 h) | Emission | 8385 ± 6770 | 40 | 1101.8 ± 526.3 | 154 |
| | | | Deposition | 3638 ± 2575 | 33 | | |
| F2 | Cold | 18:35 to 17:00 (46 h) | Emission | 519 ± 967 | 60 | 291.8 ± 342.6 | 271 |
| | | | Deposition | 1766 ± 2044 | 76 | | |
| F3 | Cold | 10:00 to 17:55 and 9:35 to 16:55 (15 h) | Emission | 1711 ± 2073 | 44 | 31.2 ± 20.1 | 90 |
| | | | Deposition | 1 | 1 | | |
| F4 | Warm | 10:40 to 12:20 (26 h) | Emission | 393 ± 344 | 63 | 65.1 ± 72.2 | 152 |
| | | | Deposition | 151 ± 182 | 13 | | |
| F5 | Warm | 18:45 to 19:30 (25 h) | Emission | 162 ± 99 | 29 | 48.6 ± 35.5 | 150 |
| | | | Deposition | 118 ± 66 | 40 | | |
| F6-1 | Warm | 11:45 to 12:10 (24 h) | Emission | 338 ± 287 | 45 | 119.3 ± 63.4 | 141 |
| | | | Deposition | 314 ± 291 | 22 | | |
| F6-2 | Warm | 13:20 to 17:00 (3:40) | Emission | 1061 ± 549 | 11 | 67.5 ± 23.6 | 24 |
| | | | Deposition | – | 0 | | |
| F7 | Warm | 14:50 to 15:10 (24 h) | Emission | 880 ± 895 | 73 | 17.8 ± 10.3 | 155 |
| | | | Deposition | – | 0 | | |
| F8 | Warm | 18:35 to 18:50 (24 h) | Emission | 5724 ± 4419 | 70 | 259.3 ± 178.8 | 142 |
| | | | Deposition | 320 | 1 | | |

[a]Hg fluxes were calculated every 20 min.
[b]Inlet TGM concentrations were measured twice every 20 min. Hg flux and inlet TGM concentrations are expressed as mean ± standard deviation.

The results of mercury exchange flux between soil and air measured at eight sampling sites are presented in Table 2 and Fig. 2. The maximum mean of mercury emission flux of $8385 \pm 6770$ (108–27 827, $n = 40$) $ng\,m^{-2}\,h^{-1}$ and the maximum mean of mercury negative flux of $3638 \pm 2575$ (40–9434, $n = 33$) $ng\,m^{-2}\,h^{-1}$ were found at site F1 in the warm season (Table 2). The lowest average mercury emission flux of $33 \pm 36\,ng\,m^{-2}\,h^{-1}$ was measured at site F5 in the warm season. In the cold season, mercury exchange flux between soil and air was almost in equilibrium at site F1, but net mercury deposition was obtained from site F2. In the warm season, overall, despite strong mercury deposition at night, net mercury emissions were found at all sampling sites.

The results indicate that the bi-directional mercury exchange between soil and air in Wanshang Hg mining area is 1–4 orders of magnitude stronger than that in the background area (Ericksen et al., 2006; Kim et al., 1995; Poissant and Casimir, 1998).

Temporal trends of TGM concentrations in air and Hg fluxes at all sampling sites are shown in Fig. 2. In the cold season, ruleless variations of TGM concentrations in air were observed at sites F1 and F2 (Fig. 2). Elevated values of TGM concentration in air found at site F2 represented the strong impact of anthropogenic Hg refining activities (Fig. 2C). In the warm season, because the illegal Hg refining activities were only carried out during night and had to be stopped in the morning to evade punishment, TGM concentration in air ascended overnight and reached the peak at dawn in WMMA. Due to little influence of Hg refining activities, the fluctuation of inlet TGM concentration was relatively small at site F7 (Fig. 2I). No significantly diurnal trend of mercury exchange fluxes was observed in the cold season (Fig. 2A, C and D). In the summer season, it was observed that mercury exchange fluxes changed along with solar irradiation and reached peak at midday and the lowest value at night at most sampling sites, respectively (Fig. 2).

It can be seen that Hg flux varies opposite to TGM concentration in air at all sampling sites except site F7 (Fig. 2). The relationships between Hg flux and TGM concentration in air were investigated (Table 3). Significantly negative

relationships between TGM concentrations in air and mercury exchange fluxes were obtained at all sampling sites during night and at all sites but site F1, F4 and F8 during daytime (Table 3). Using the whole day's data, the relationships between TGM concentrations in air and TGM exchange fluxes almost were negative at all sites but site F7 (Table 3).

### 3.2. Factors controlling mercury exchange flux

A great number of studies proved that many factors can influence mercury exchange flux between soil and air including total mercury concentration in soil (Coolbaugh et al., 2002; Engle et al., 2001; Feng et al., 2005; Gustin et al., 2000; Nacht et al., 2004; Wang et al., 2005; Zehner and Gustin, 2002), solar irradiation (Gillis and Miller, 2000; Gustin et al., 2002; Moore and Carpi, 2005; Wang et al., 2005; Zehner and Gustin, 2002), humidity of soil (Ericksen et al., 2006; Gustin and Stamenkovic, 2005), soil temperature (Gillis and Miller, 2000; Moore and Carpi, 2005), TGM concentration in air (Engle et al., 2001; Nacht et al., 2004; Wang et al., 2005), rainfall (Carpi and Lindberg, 1997; Lindberg et al., 1999), vegetation (Ericksen et al., 2006; Kim et al., 1995) and so on. However, as a result of the total effect of all kinds of factors, under different conditions, the impact of each factor on mercury exchange between soil and air will be different.

The total Hg concentration in soil was considered as the dominant factor (Gustin, 2003). Soil with higher total Hg concentration has higher potential

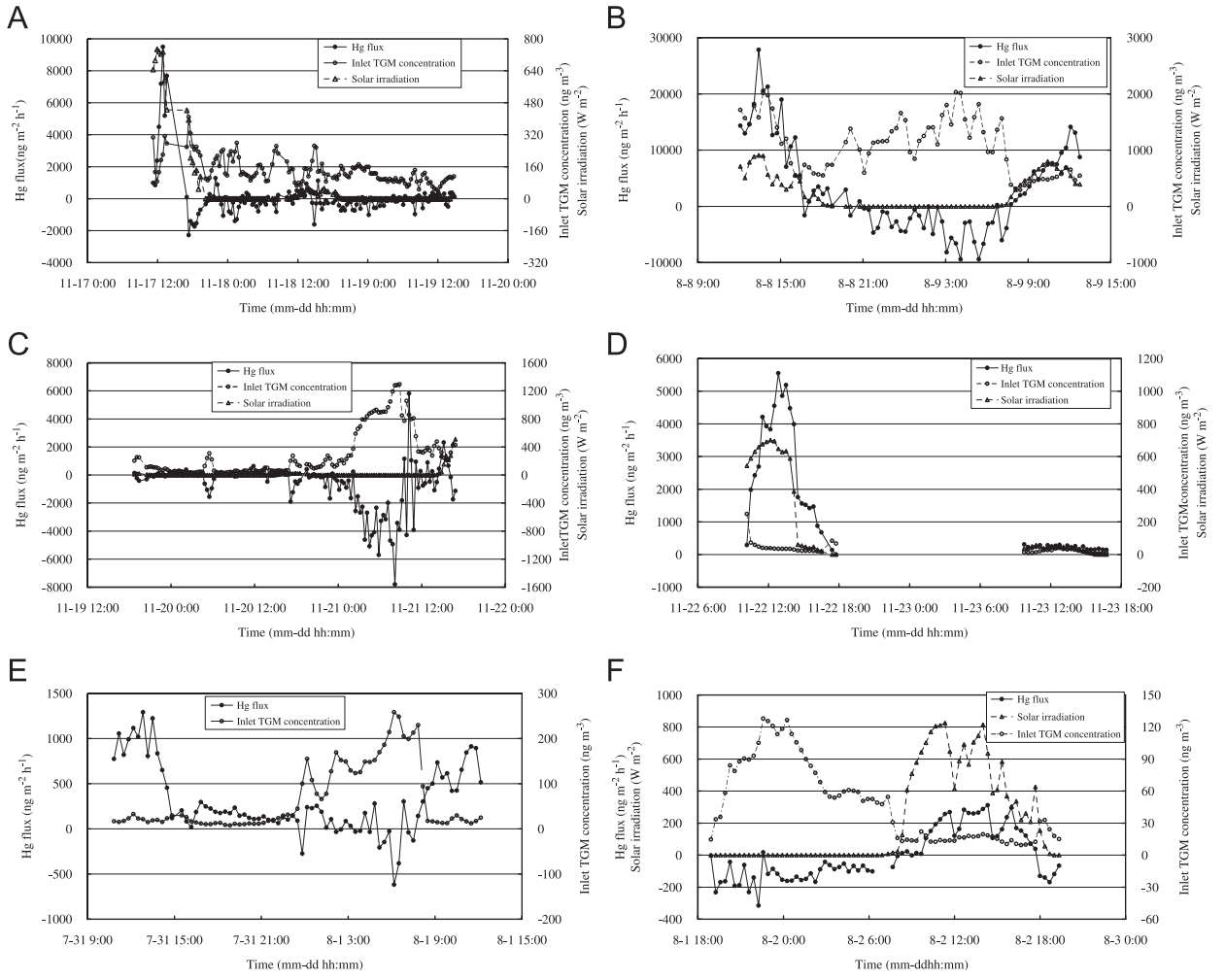


Fig. 2. Temporal trends of Mercury flux, inlet TGM concentration and solar irradiation collected at eight sites in WMMA. (A) At site F1 in cold season, (B) at site F1 in warm season, (C) at site F2, (D) at site F3, (E) at site F4, (F) at site F5, (G) at site F6-1, (H) at site F6-2, (I) at site F7, (J) at site F8. Inlet TGM concentrations and solar irradiations are average values of data for every 20 min.

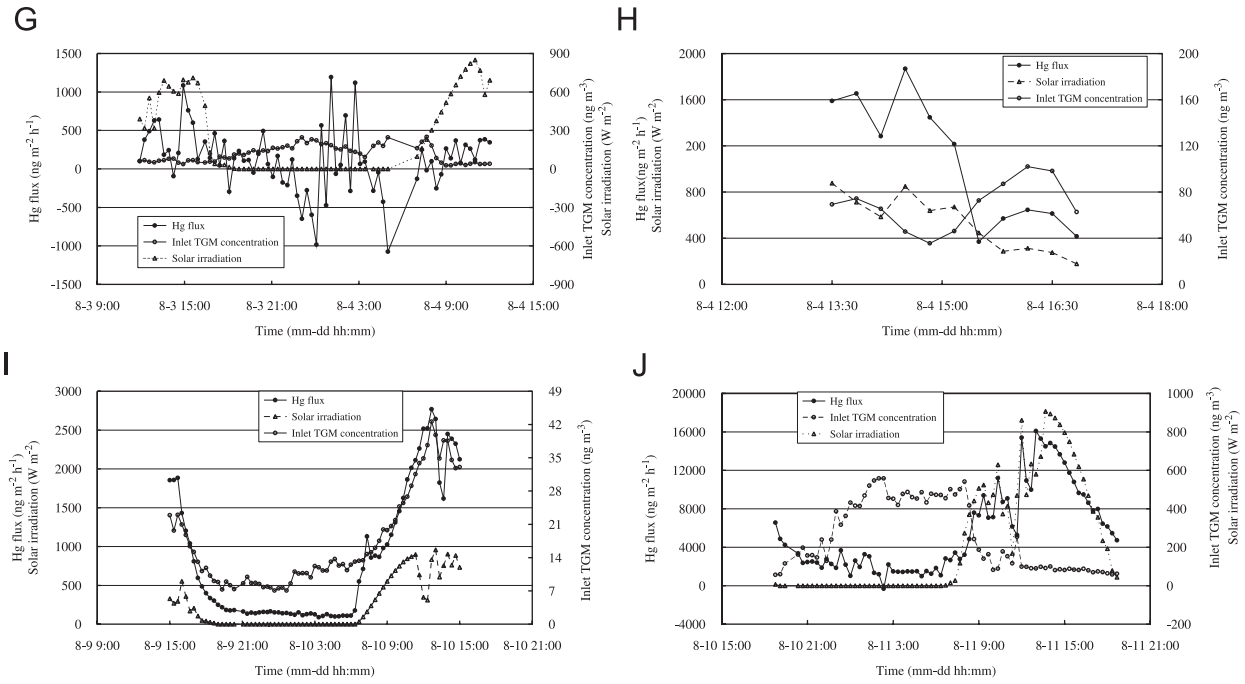


Fig. 2. (*Continued*)

Table 3
The correlation coefficients between Hg exchange flux and TGM concentration in air at all sampling sites in WMMA

| Site | Season | Daytime | Night | Whole |
|---|---|---|---|---|
| F1 | Cold | 0.20, $p<0.05$ | −0.49, $p<0.01$ | 0 |
| F1 | Warm | 0.50, $p<0.01$ | −0.71, $p<0.01$ | −0.08, $p>0.05$ |
| F2 | Cold | −0.60, $p<0.01$ | −0.92, $p<0.01$ | −0.73, $p<0.01$ |
| F3 | Cold | −0.24, $p<0.05$ | – | −0.24, $p<0.05$ |
| F4 | Warm | 0.08, $p>0.05$ | −0.52, $p<0.01$ | −0.56, $p<0.01$ |
| F5 | Warm | −0.27, $p<0.01$ | −0.21, $p<0.01$ | −0.69, $p<0.01$ |
| F6-1 | Warm | −0.31, $p<0.01$ | −0.19, $p<0.05$ | −0.38, $p<0.01$ |
| F6-2 | Warm | −0.57, $p<0.01$ | – | −0.57, $p<0.01$ |
| F7 | Warm | −0.20, $p<0.01$ | −0.31, $p<0.01$ | −0.30, $p<0.01$ |
| F8 | Warm | 0.93, $p<0.01$ | −0.62, $p<0.01$ | 0.95, $p<0.01$ |
| F9 | Warm | −0.60, $p<0.01$ | −0.64, $p<0.01$ | −0.62, $p<0.01$ |

of Hg emission to the atmosphere. It has been found that there was a log–log relationship between total Hg concentration and daily average Hg emission flux (Coolbaugh et al., 2002; Engle et al., 2001; Feng et al., 2005; Gustin et al., 2000; Nacht et al., 2004; Wang et al., 2005; Zehner and Gustin, 2002). This relationship is a good tool for estimating the annual Hg emission flux from a whole district, but the similar relationship cannot be constructed using our data measured in WMMA. However, the site with higher soil Hg concentrations still contributed high Hg emission flux in WMMA (Tables 1 and 2). It indicates that some other factors besides total Hg concentration in soil and solar irradiation can strongly affect the Hg exchange between soil and air.

Photo-induced reduction plays a significant role in the process of mercury emission from soil and water surfaces (Feng et al., 2004b; Gillis and Miller, 2000). Researches demonstrated that Fe(III) and DOC could accelerate the rate of photo-reduction of $Hg^{2+}$ in water under solar condition, but in dark condition, these effects are very weak (Costa and Liss, 1999, 2000; Zhang and Lindberg, 2001). Laboratory experiments proved that Hg emission flux from soil can be enhanced significantly by solar irradiation (Gustin et al., 2002; Moore and Carpi, 2005). Significantly linear relationships between Hg emission fluxes and solar irradiations were obtained at all sampling sites except sites F2 and F7 in our study area (Table 4).

Hg air/soil exchange depends on both interfacial exchange characteristics and mercury diffusion potential across the exchange interface. The mercury diffusion potential is decided by the gradient of TGM concentration between soil air and above air (Zhang et al., 2002). Gaseous mercury will diffuse

from the medium with high concentrations to the medium with low concentrations. When TGM concentration in air increases, the reduction of mercury diffusion potential will decelerate mercury emission from soil. Thus, besides TGM concentration in soil air, the change of TGM concentration in air also can influence the rate and direction of Hg diffusion (Engle et al., 2001; Nacht et al., 2004; Wang et al., 2005). It is obviously seen that the highly elevated TGM concentrations in air restrained Hg emission fluxes and even induced strong atmospheric Hg depositions in WMMA (Fig. 2). Influenced by ruleless variation of TGM concentration in air, Hg exchange flux varied rulessly at site F2 (Fig. 2C). Together with weak solar irradiation, ruleless variations of Hg exchange fluxes concealed the relationship between solar irradiation and Hg flux at sites F2 and F7 (Table 4). Though TGM concentration in air was very high, strong Hg emission flux and positive relationships between Hg exchange flux and TGM concentration in air were still obtained at site F1 during daytime (Table 3). This indicates that significant mercury emission flux can influence TGM concentration in air and mercury-enriched soil is an importantly atmospheric Hg emission source in WMMA during daytime.

Table 4
The correlation coefficients between Hg exchange flux and solar irradiation at all sampling sites in WMMA

| Site | Season | Correlation coefficients ($r$) |
|---|---|---|
| F1 | Cold | 0.74, $p<0.01$ |
| F1 | Warm | 0.83, $p<0.01$ |
| F2 | Cold | 0.16, $p<0.05$ |
| F3 | Cold | 0.83, $p<0.01$ |
| F5 | Warm | 0.38, $p<0.05$ |
| F6-1 | Warm | 0.41, $p<0.01$ |
| F6-2 | Warm | 0.92, $p<0.01$ |
| F7 | Warm | 0.02, $p>0.05$ |
| F8 | Warm | 0.83, $p<0.01$ |
| F9 | Warm | 0.95, $p<0.01$ |

The role of vegetation in the biogeochemical cycle of atmospheric Hg is far from well understood. Field and laboratory experiments demonstrated that vegetation could absorb and/or release Hg (Ericksen and Gustin, 2004; Ericksen et al., 2003; Lindberg and Zhang, 2000; Zhang and Lindberg, 2000). However, recent researches have reported that forest and grassland are important Hg sources of the atmosphere in the background area (Ericksen et al., 2006; Hanson et al., 1995; Kim et al., 1995; Lindberg et al., 1998). The influence of vegetation on mercury exchange flux was investigated at sites F6 and F8 in WMMA. We measured Hg emission fluxes from soil both shaded (F6-1) and unshaded (F6-2) by rice, respectively (Fig. 2G and H). The results of the same time of two days showed that in spite of similar soil temperature, solar irradiation and TGM concentration in air, the mean of Hg emission flux from soil shaded by rice was two times lower than that from unshaded soil under the similar meteorological conditions (Fig. 3). Because the field flux chamber was put on soil surface directly, vegetation could not adsorb/absorb gaseous mercury in the chamber. Therefore, weakened photo-reduction of $Hg^{2+}$ shaded by rice is the main reason that mercury emission flux decreased. Additionally, mercury exchange flux was measured on bare soil and grassland at site F8, respectively. Diurnal mercury emission flux from bare soil was

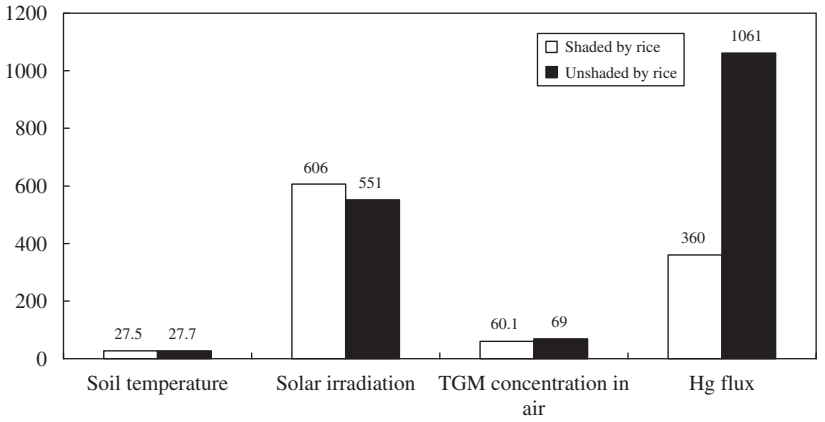


Fig. 3. Average value of soil temperature (°C), solar irradiation ($W\,m^{-2}$), TGM concentration in air ($ng\,m^{-3}$) and Hg flux ($ng\,m^{-2}\,h^{-1}$) at sites F6-1 and F6-2 from 13:30 to 17:00 in 8-3 and 8-4, respectively. Solar irradiation data were observed above the rice plants.

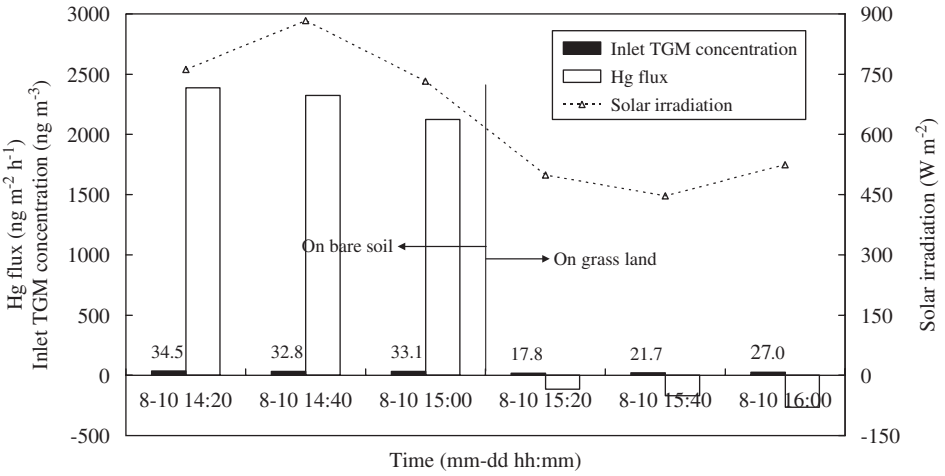


Fig. 4. Hg flux, inlet TGM concentration and solar irradiation measured on bare soil and grassland at site F7.

observed before 15:10, August 10, 2004 (Fig. 2J). After the field flux chamber was moved on grassland, only mercury deposition event was observed and the average mercury dry deposition flux was $183 \pm 76\,ng\,m^{-2}\,h^{-1}$ ($n = 3$) (Fig. 4). It indicates that vegetation can inhibit mercury emission flux and adsorb/absorb atmospheric Hg significantly. Three hypotheses were proposed to explain the impact of vegetation: (i) the construction of new interface of soil–vegetation–air increases the resistance of mercury emission from soil; (ii) vegetation can strongly adsorb/absorb mercury with high concentration in field flux chamber (Lodenius et al., 2003); and (iii) solar irradiation reaching soil surface is weakened by vegetation cover, and the rate of photo-reduction of $Hg^{2+}$ descends. Because TGM concentrations in air in Wanshan were 1–3 orders of magnitude higher than those observed in previous researches (Ericksen et al., 2006; Kim et al., 1995; Lindberg et al., 1998), it is believed that vegetation is an important sink of atmospheric mercury in WMMA. Qiu et al. (2005) have found a significant relationship between TGM concentrations in air and vegetation in Wanshan district.

### 3.3. Hg emission from roasted cinnabar banks

It has been reported that roasted cinnabar banks are an important Hg source of the atmosphere (Coolbaugh et al., 2002; Ferrara et al., 1998a). About $100\,000\,m^2$ roasted cinnabar banks are exposed to the ambient air widely in WMMA. High Hg emission fluxes were measured from both roasted cinnabar banks (Table 2, Fig. 2D and J). The Hg emission fluxes from slagheaps reached $1171 \pm 2073\,ng\,m^{-2}\,h^{-1}$ ($n = 44$) at site F3 in the cold season and $5724 \pm 4419\,ng\,m^{-2}\,h^{-1}$ ($n = 70$) at site F9 in the warm season, respectively. These Hg emission fluxes are 3 orders of magnitude higher than those in the background area and are at same order with Hg fluxes measured from roasted cinnabar banks by Coolbaugh et al. (2002). At the same time, a few Hg deposition events (<3% in both banks, Table 2, Fig. 2D and J) were observed. It is said that the roasted cinnabar banks are net Hg sources of the atmosphere in WMMA. If the roasted cinnabar is homogeneous in WMMA, by considering the area of cinnabar banks, the annual Hg emission flux of 1.0–5.0 kg was roughly estimated in WMMA.

## 4. Conclusions

Bare soil surface and roasted cinnabar banks are importantly atmospheric Hg sources in WMMA. However, high TGM concentration in air inhibits mercury emission from soil strongly. Dry deposition of mercury from the ambient air occupies a great proportion of mercury exchange between soil and air. Net mercury dry deposition investigated at site F2 indicates that under darkness and high TGM concentrations in air, mercury-enriched soil may become the sink of atmospheric Hg rather than source. Mercury diffused from soil and emitted from anthropogenic sources may deposit back to soil surface or water body very quickly, and the local cycle of mercury between soil and air is dynamic in WMMA. The results also showed that

vegetation can inhibit mercury emission from soil and adsorb/absorb a great amount of mercury from the ambient air. It indicates that although the load of atmospheric mercury could be reduced by vegetation, more mercury entering the food chain may threaten the health of local residents.

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