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Release flux of mercury from different environmental surfaces in Chongqing, China

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Abstract

An investigation was conducted to estimate mercury emission to the atmosphere from different environmental surfaces and to assess its contribution to the local mercury budget in Chongqing, China. Mercury flux was measured using dynamic flux chamber (DFC) at six soil sites of three different areas (mercury polluted area, farmland and woodland) and four water surfaces from August 2003 to April 2004. The mercury emission fluxes were 3.5 ± 1.2–8.4 ± 2.5 ng m^{-2} h^{-1} for three shaded forest sites, 85.8 ± 32.4 ng m^{-2} h^{-1} for farming field, 12.3 ± 9.8–733.8 ± 255 ng m^{-2} h^{-1} for grassland sites, and 5.9 ± 12.6–618.6 ± 339 ng m^{-2} h^{-1} for water surfaces. Mercury exchange fluxes were generally higher from air/water surfaces than from air/soil surfaces. The mercury negative fluxes were found in tow soil sites at overcast days (mean $= -6.4 \pm 1.5$ ng m^{-2} h^{-1}). The diurnal and seasonal variations of mercury flux were observed in all sites. The mercury emission responded positively to the solar radiation, but negatively to the relative humidity. The mercury flux from air/soil surfaces was significantly correlated with soil temperature, which was well described by an Arrhenius-type expression with activation energy of 31.1 kcal mol^{-1}. The annual mercury emission to the atmosphere from land surface is about 1.787 t of mercury in Chongqing.

Keywords: Atmosphere; Dynamic flux chamber; Flux; Mercury; Natural emission

1. Introduction

As a global pollutant, mercury may be methylated in environment and accumulate in organisms, causing serious impacts on ecosystem. Atmospheric mercury plays an important role of global mercury pollution. It mainly comes from anthropogenic and natural mercury emission and it may enter the ocean and terrestrial ecosystems via wet and dry deposition again. So, it is important to understand the emission and cycling of mercury. Research on biogeochemical cycle of mercury in recent years has been mostly concentrated on assessment of mercury release fluxes from environmental surfaces (Schroeder, 1992; Kim and Lindberg, 1995; Kim et al., 1995; Gustin et al., 1999). According to available literatures, natural mercury release from the land contributed about 10% of the total emitted mercury amount, while that from the ocean accounted for about 30% of all (Nriagu, 1989; Lindqvist et al., 1991). The main form of mercury released from natural sources is elemental mercury, which could stay for a relatively long period in the atmosphere. Therefore, the mercury emission from land surfaces is considered to be the major contributors of global atmospheric mercury (Nriagu, 1989; Lindqvist et al., 1991). However, amount of mercury released to the atmosphere from land surfaces is still under debate (Lindqvist et al., 1991). The global biogeochemical cycle of mercury could be fully understood only when the amount of mercury released from the natural sources is clarified. Mercury exchange flux over

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environmental surfaces is a key parameter to estimate global or regional mercury release, to understand and simulate mercury recycling in different area, and to evaluate mercury impacts on the environment as well (Rasmussen, 1994; Fitzgerald et al., 1998; Gustin et al., 1999).

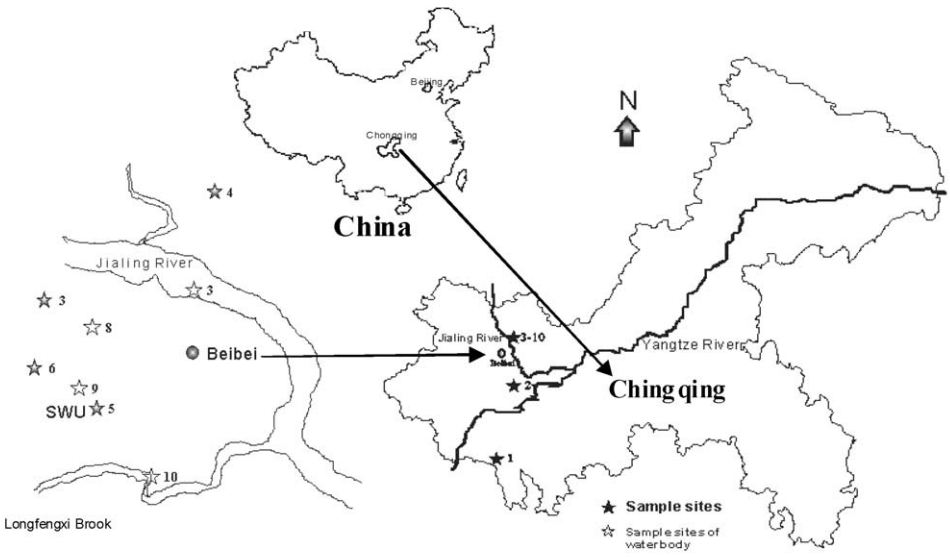
In China, many studies on mercury pollution have been carried out previously. However, the mercury fluxes over environmental surfaces were poorly understood. Here, we measured mercury fluxes from different environmental surfaces in Chongqing, China. Environmental factors affecting the exchange such as soil temperature, solar radiation, relative humidity and air temperature were also investigated. The contribution of mercury emission to the regional mercury budget was estimated as well.

2. Materials and methods

2.1. Site description

Six soil sites (three forests, two grasslands and one farmland) were selected for this study. Three forest sites are located at the Simianshan Mountain (SMSM) of Jiangjin County (28°35′ N, 106°26′ E), the Geleshan Mountain (GLSM) of Shapingba District (29°34′ N, 106°25′ E), and the Jinyunshan Mountain (JYSM) of Beibei District (29°56′ N, 106°22′ E) (Fig. 1). The SMSM site is a hardwood forest with a well-closed canopy (>95%), dominated by broadleaf. The soil at this site is Alliti-Perudic Ferrosols, covered by a 2–4 cm thick of undecomposed hardwood leaf litter. The GLSM site is dominated by privet and phoenix tree (accounting for more than 60%) with a moderately-closed canopy (>85%). There are also a few shrubs. The soil at this site was Typic Purpli-Udic Cambosols, without any deadwood on the surface. The JYSM site with a well-closed canopy (>90%), dominated by broadleaf, is arbor in this area. The soil at this site is also Alliti-Perudic Ferrosols, with a 1–2.5 cm thick of undecomposed hardwood leaf litter. Two grassland sites are situated on the campus of Southwest University (SWU) (29°48′ N, 106°24′ E), and at Weather Observation of Beibei (WOBB) (29°48′ N, 106°24′ E). The soil at the SWU site is Typic Purpli-Udic Cambosols completely covered by 5–8 cm tall grasses. The soil at the WOBB site is also Typic Purpli-Udic Cambosols, which is surrounded by many factories (including clinical thermometer factory, glass factory, and pharmacy factory). The grass is about 2–5 cm tall. The farmland for the study is located at the experimental site of Southwest University (29°48′ N, 106°24′ E), which is 250 m away from a highway. The soil is Typic Purpli-Udic Cambosols with no crops planted.

Four water sites are all in Beibei, Chongqing. They are located at the Jialing River (JLR) (29°50′ N, 106°26′ E), the Longtanzi Reservoir (LTZR) (29°49′ N, 106°24′ E), the Longfengxi Brook (LFXB) (29°49′ N, 106°25′ E), and the pond of SWU (29°48′ N, 106°24′ E). The JLR site is 300 m upriver from a dock, and the water was clear



(1. Simianshan Mountain (SMSM, 28°35' N, 106°26'E) forest soil site; 2. Geleshan Mountain (GLSM, 29°34' N, 106°25' E) forest soil site; 3. Jinyunshan Mountain (JYSM, 29°56' N, 106°22' E) forest soil site; 4. Weather Observatory of Beibei (WOBB, 29°48' N, 106°24' E) soil site; 5. Southwest University (SWU, 29°48' N, 106°24' E) soil site, 6: the open field site in SWU; 7. the site at the Jialing River (JLR, 29°50' N, 106°26' E); 8. the site at the Longtanzi Reservoir (LTZR, 29°49' N, 106°24' E); 9. the site at pond in SWU; and 10. the site at Longfengxi Slot (LFXB, 29°49' N, 106°25' E).

Fig. 1. Schematic diagram of sampling sites.

without any particles. The LTZR site is near the dam, which is surrounded by farmland and house, and there are a factory and residential area in its upriver area. Because industry wastewater and sewage were released to the reservoir, the water was not clear and had obvious particles. The Longfengxi Brook is a branch of the Jialing River, the LFXB site is about 1000 m far away the debouchment. The water in the SWU pond was muddy and dark.

2.2. Measurement methods

2.2.1. Technique for mercury flux measurement

A schematic diagram of a dynamic flux chamber (DFC) with the Lumex® Multifunctional mercury analyzer RA-915+ (operated by CVAAS plus Zeeman Correction, 1-Hz data stream) is given in Fig. 2. The flux chamber dimension of $20 \times 20 \times 60$ cm (Xiao et al., 1991) with a removable bottom plate was constructed with 5 mm thick Plexiglas, and its volume was 0.024 m^3. The Plexiglas was chosen because of its low achievable chamber blank and transparency to light. Its transparency allows good penetration of solar radiation, which is responsible for the formation of photo-induced gaseous mercury in water or soil. When placed on a surface for flux measurements, the bottom plate of the chamber is removed to allow mercury to emit into the chamber from the surface. The chamber was linked through the outlet with Multifunctional mercury analyzer RA-915+ by semi-transparent Teflon™ tube (internal diameter of 0.635 cm). A known volume of ambient air was drawn into the chamber through the inlet ports.

2.2.2. Field measurement of mercury flux

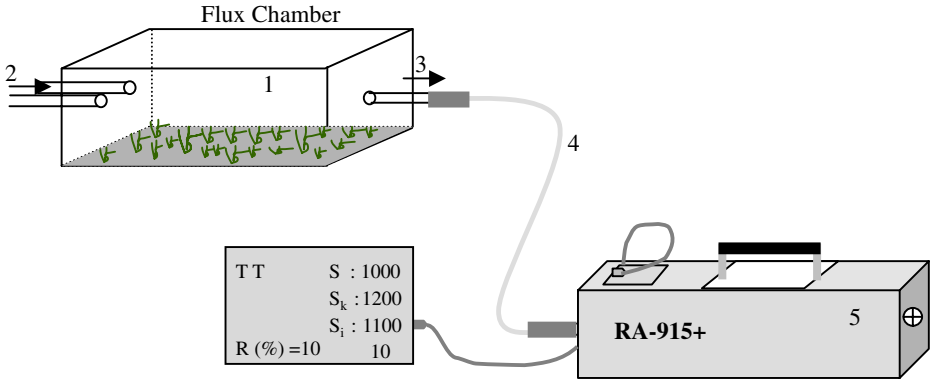
Mercury flux to and from the soil was measured using a flux chamber. The chamber was placed on soil surface with the edges of the chamber pushed 1 cm into the soil. A seal around the edges of the chamber box was made by lightly packing some soil around the outer edges (Gillis and Miller, 2000). Ambient air was pulled through the flux chamber to Lumex® Multifunctional mercury analyzer RA-915+ (sampling flow rate = 20 l min^{-1}, each air sampling time = 5 min). Both inlet (C_i) and outlet (C_o) mercury concentrations were continuously monitored alternatively by the RA-915+ automated mercury analyzer. A 10 min average of C_o (two 5 min samples) and a 10 min-average of C_i (two 5-min samples) were used to obtain a 20 min averaged Hg flux (F) from Eq. (1) (Lindberg and Price, 1999; Zhang et al., 2001):

$$F = \frac{(C_o - C_i)Q}{A} \quad (1)$$

where F is the flux (ng m^{-2} h^{-1}), C_i and C_o are total gas mercury (TGM) concentrations of the DFC inlet and outlet in ng m^{-3}, respectively. Q is flushing flow rate through the chamber in m^3 h^{-1} (1.2 m^3 h^{-1} for these measurements), A is area of the open bottom surface of the chamber.

The chamber blanks were measured in laboratory and field, before and after the flux measurements. The laboratory blanks ($n = 10$), obtained by measuring the mercury flux over a clean Plexiglas sheet, were in the range of 1.2–2.1 ng m^{-2} h^{-1}. The field blanks ($n = 32$), obtained before and after the flux measurements at each sampling site, ranged from 1.1 to 2.3 ng m^{-2} h^{-1}, with an average of 1.33 ± 0.31 ng m^{-3}. The soil temperatures in surface layer (2–3 cm) were measured with a soil temperature meter (Carpi and Lindberg, 1998). Total global solar radiation was measured with a TES®-II *Digital Luminometer* (Taiwan, China). Other environmental parameters (including air temperature, air humidity, air pressure, wind speed) were also measured with Kestrel® 4000 *Pocket Weather*™ Tracker™ (Nielsen-Kellerman, USA).

For measurement of mercury release flux from water, a styrofoam block was used to provide buoyancy (Ferrara and Mazzolai, 1998; Sun et al., 2001). The floating chamber system was immersed 1 cm in the water to ensure a tight seal with the water. The same environmental parameters as those for soil sites were also measured.



(1, flux chamber; 2, inlet port; 3, out port; 4, Teflon tube; 5, RA-915+ automated mercury analyzer)

Fig. 2. Schematic diagram of the dynamic flux chamber operation system.

2.3. Estimate of mercury emission from natural sources in Chongqing

An annual emission of mercury to the atmosphere from natural sources in Chongqing was estimated. Briefly, mercury was considered to release during the warm season (March–October) while deposit during the cold season (November–February). According to the climatical characteristics of Chongqing, mean values of mercury release flux at the end of summer were chosen to represent the release flux for the whole year (Gustin et al., 2000), and a daily emission period was 12 h. Total release was calculated by the differences between emission and deposition.

3. Results and discussion

3.1. Mercury flux from water surface

Table 1 summarized mercury fluxes and TGM concentrations during daytime periods at ten different sites. Air/water surface exchange fluxes of mercury changed obviously during sampling periods for four sites, being higher in midday and lower in the morning and early night. However, TGM concentrations were just opposite (Fig. 3a–d). Mercury fluxes from the water responded rapidly to solar radiation and relative humidity (Table 2), especially at both LFXB and Pond site (Fig. 3c and d). Mercury flux was significantly positively correlated with solar radiation ($r = 0.5525^{**}$, $n = 48$), negatively with relative humidity ($r = -0.4730^{**}$, $n = 48$). To further determine the solar effect on mercury emission, another test was conducted at the LTZR site by alternately shading the flux chamber (FC) for a short period of time (40 min) under umbrage and sunlight. It was demonstrated that solar radiation was responsible for mercury flux from the water (Fig. 3a), where an immediate, large decrease in mercury flux was observed in the FC under umbrage with other factors remaining unchanged. These observations are in good agreement with results of Zhang et al. (2001) who observed that mercury flux immediately decreased after the FC was covered with aluminum foil or by a plastic UV filter. The negative correlation of mercury flux with relative humidity may be due to reduced solar radiation because there are negative correlation between relative humidity and solar radiation.

Higher mercury fluxes from the pond than from the LTZR (Fig. 3) may further show the significance of temperature and solar radiation in mercury flux. Mercury fluxes from the pond were measured in spring, in which temperature and solar radiation were higher, while those from LTZR ware measured in winter, in which temperature and solar radiation were lower. Therefore, air/water exchange flux of mercury is higher in warm season than cold season (Xiao et al., 1991).

The gaseous mercury flux is dependent not only on physical factors (temperature, sunlight and humidity for example) in water and air, but also on initial mercury concentrations in the water (Mason and Fitzgerald, 1993; Mason et al., 1993; Vandal et al., 1995). Difference in mercury fluxes between LFXB (618.6 ± 339 ng m^{-2} h^{-1}) and pond (509.8 ± 296 ng m^{-2} h^{-1}) site indicated the effect of the initial mercury concentrations in the water on the flux (Table 3), as other factors (temperature, sunlight, humidity) were similar between these two sites.

3.2. Mercury flux from soil surface

Mercury flux from different soil sites varied significantly (Figs. 4 and 5). The lowest value was found at the LYSM site with an average mercury flux of 3.4 ± 1.2 ng m^{-2} h^{-1}, while the highest value at the WOBB site with an average mercury flux of 733.8 ± 255 ng m^{-2} h^{-1} (spring). Mercury fluxes from three forest sites were lower than those from three other soil sites, likely due to thick canopy, which

Table 1
Mercury fluxes from waters and soils

Date	Sampling time	Site	TGM (ng m^{-3})		S.D. (n)	Flux (ng m^{-2} h^{-1})		S.D. (n)
			Range	Mean		Range	Mean	
2003/08/19	1130–2100	SMSM	9.6–32.9	19.9	8.6 (8)	5.2–16.3	7.7	3.9 (8)
2003/09/15	1025–1625	JYSM	7.3–13.0	9.9	1.8 (12)	1.2–6.1	3.4	1.5 (12)
2003/01/6	1030–1430	GLSM	6.5–18.0	14.1	3.0 (9)	5.1–13.2	8.4	2.5 (9)
2003/10/28	0830–1750	WOBB	8.8–109.8	29.6	29.7 (10)	9.0–205	101.8	14.3 (10)
2004/04/01	0900–1800	WOBB	5.0–139.3	24.8	38.9 (10)	498–955	733.8	255 (10)
2003/10/18	0900–1700	Open field	21.0–30.4	25.8	2.7 (9)	−107 to −33	−59	20.8 (9)
2003/10/27	0930–1730	Open field	9.5–12.5	10.5	0.9 (9)	−8 to 8	−0.9	5.6 (9)
2004/04/02	0830–1730	Open field	5.0–31.3	19.1	6.9 (8)	1.0–793	317.3	291 (8)
2003/08/26/27	0830–0430	SWU	14.5–51.3	27.8	10.6 (11)	−21 to 98	33.2	36.1 (11)
2003/10/07	0800–1730	LTZR	9.5–32.6	15.0	7.7 (7)	20–132	74	38.1 (7)
2003/10/08	0830–1730	LTZR	6.3–10.5	9.1	1.9 (6)	−12 to 62	13.5	26.1 (6)
2003/10/25	0830–1500	JLR	11.5–26.5	18.8	6.7 (6)	−23 to 38	7.5	20.5 (6)
2003/11/01	0830–1700	JLR	5.0–11.7	7.4	2.2 (7)	−6 to 27	5.9	12.6 (7)
2003/04/04	0800–1800	LFXB	9.7–30.3	21.6	7.5 (11)	69–1196	618.6	339 (11)
2004/04/06	0800–1800	Pond	4.3–54.8	29.4	14 (11)	106–1006	509.8	296 (11)

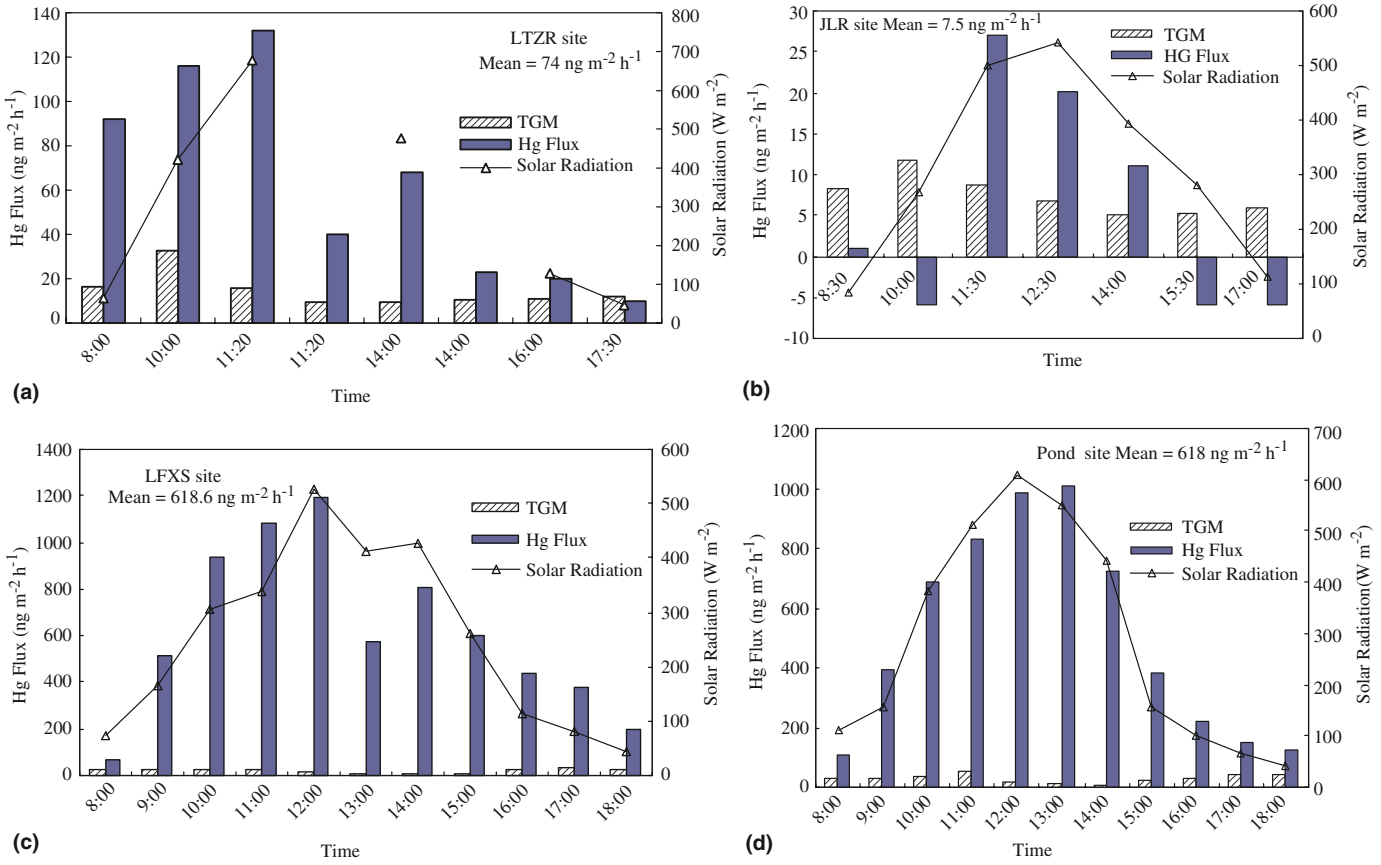


Fig. 3. Mercury fluxes from water surface as influenced by solar radiation.

Table 2
Statistics of environmental parameters during the measurement of mercury flux

Date	Sampling time	Site	Solar radiation (10^2 lux)		Temperature (°C)		Relative humidity (%)	
			Range	Mean	Range	Mean	Range	Mean
2003/08/19	1130–2100	SMSM	7.6–12.1	9.46	21.3–26.5	24.7	69.2–91.2	81.9
2003/09/15	1025–1625	JYSM	9.2–19.2	12.5	22–24.6	23.4	75–93.4	84.7
2003/01/6	1030–1430	GLSM	4.8–7.8 (18–20.5)	6.89 (19.6)	27–30.8	28.7	78–86	82.5
2003/10/28	0830–1750	BBMO	2.5–22.3	10.5	19.2–34	23.1	55–84.2	70.8
2004/04/01	0900–1800	BBMO	234–870	566.9	19.5–29.8	25.3	34–76	45.8
2003/10/18	0900–1700	Open field	21.9–66.5	45.7	18.6–20.3	19.3	83.9–90.2	96.3
2003/10/27	0930–1730	Open field	102.8–363	256.7	18.3–26.6	24.2	44.3–86.1	61.5
2004/04/02	0830–1730	Open field	155.2–711.3	435.3	20.3–28.8	25.8	32.5–70.4	47.6
2003/08/26/27	0830–0430	SWU	123–621.4 (23–25.5)	362.9 (24.8)	25.5–33.4	29.3	47.5–82	64
2003/09/16	0730–1930	SWU	1.4–102.6	70.6	23.5–25.4	24.5	78.2–87.6	82.3
2003/10/07	0800–1730	LTZR	62–813.5	413.4	17.1–27.2	23.5	54–85	65
2003/10/08	0830–1730	LTZR	26.3–232.7	136.4	20.2–26.5	24.6	55–80	65.8
2003/10/25	0830–1500	JLR	24.7–67.5	51.7	18.7–21	20	7.35–84	79.3
2003/11/01	0830–1700	JLR	100.5–650	374.3	16.6–25.8	21.8	46.4–88.8	67
2003/04/04	0800–1800	LFXB	54.5–629.5	299.9	19.2–30.2	25.3	39.6–83.8	57.7
2004/04/06	0800–1800	Pond	51–730.2	341.3	20.6–31.5	27.7	42–79.2	55.2

Note: Soil temperature was in brackets.

greatly reduced sunlight and soil temperature, and in turn decreased volatilization speed of mercury from the forest soils (Boudala et al., 2000).

On the contrary, higher emissions of mercury were observed from WOBB and SWU sites than from the forest sites. These two sites are situated in open field. Their solar radiations were higher than those of three forests by 1–2 magnitude (Table 1) even though they were covered by grass. For WOBB site, results from different seasons differed (Fig. 5), but the mercury fluxes were positively

Table 3
Mercury contents in soils or waters from the sites studied (mg kg^{-1} or μg l^{-1})

Sites	Soils sites						Water body sites			
	SMSM	JYSM	GLSM	BBMO	Open field	SWU	LFXB	JLR	Pond	LTZR
Soil/water type	Alliti-Perudic Ferrosols	Alliti-Perudic Ferrosols	Typic Purpli-Udic Cambosols	Typic Purpli-Udic Cambosols	Typic Purpli-Udic Cambosols	Typic Purpli-Udic Cambosols	IV[a]	II	III	III
Hg content	0.1737	0.1367	0.1964	0.526	0.206	0.185	0.0852	0.0162	0.0474	0.0683

[a] Classing according to the Chinese Surface Water Quality Standard.

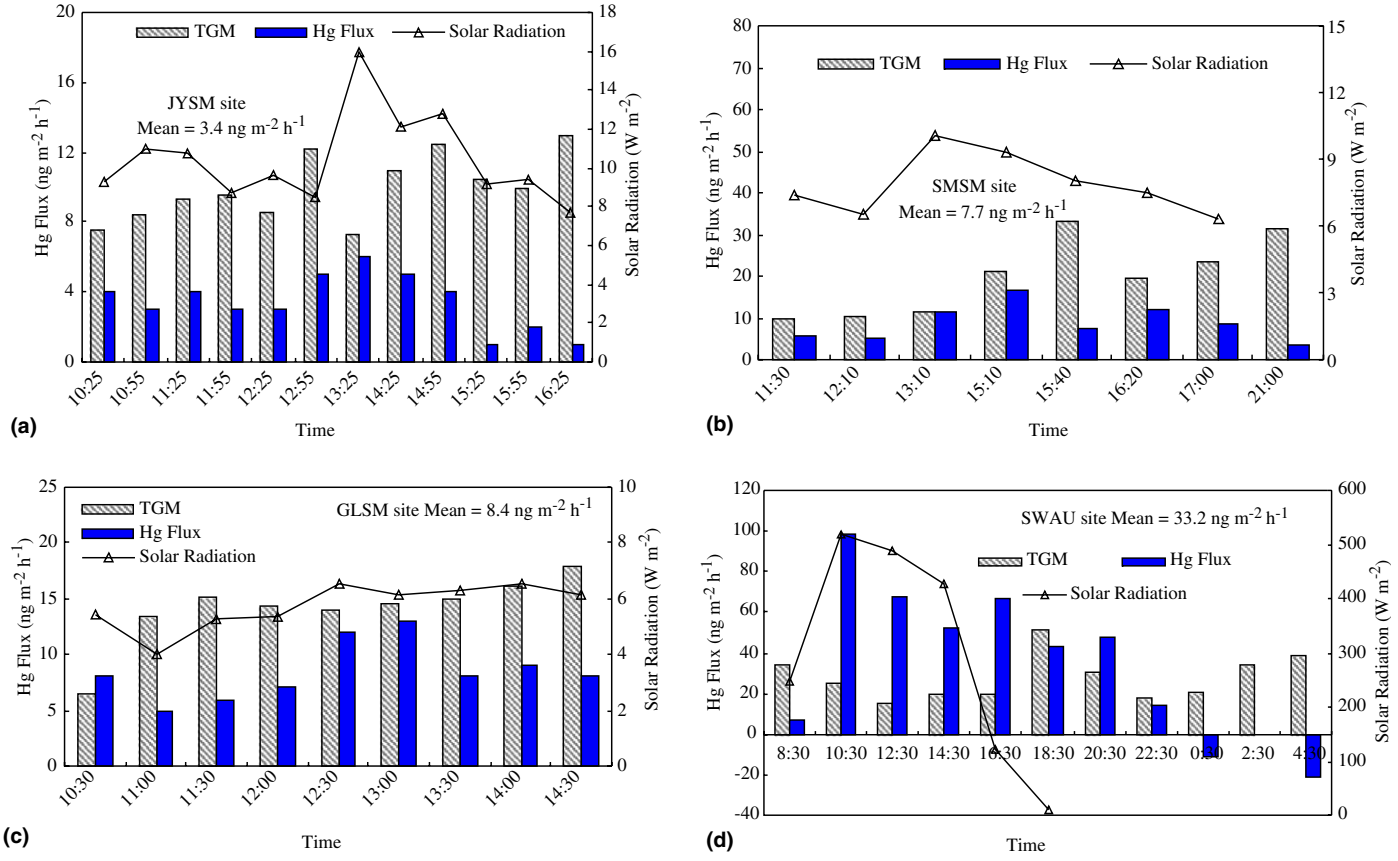


Fig. 4. Mercury fluxes from three forest soil sites and SWU site as influenced by solar radiation.

correlated with solar radiation. The correlation coefficients were 0.5845 and 0.8904 for cold and warm season ($n = 10$), respectively. Mercury flux was also negatively correlated with relative humidity ($r = 0.6429$) (plot not shown). In addition, mercury fluxes were monitored over 24 h at the SWU site. The mean mercury flux was 54 ± 27.4 ng m^{-2} h^{-1} in the daytime and -4.5 ± 6.5 ng m^{-2} h^{-1} in the night time. Therefore, mercury releases to the atmosphere from soil surface during the day, and deposits to earth surface from atmosphere at night.

The variation in mercury fluxes between SWU and WOBB sites was possibly due to the difference in mercury concentrations in soils (Table 3), because these soils were covered by grass and the weather was quite similar at these two sites.

3.3. Change in mercury exchange flux over seasons

Seasonal variation of mercury flux existed at both WOBB (contaminated area) and farming field (farmland) sites. Mercury flux was higher in spring and lower in winter (Fig. 5). At the farming field site, the mean mercury flux was below zero in winter, whereas 317.3 ± 291 ng m^{-2} h^{-1} in spring. At the WOBB site, the average mercury flux in winter was only 14.7% of that in spring, due to the difference in solar radiation and soil temperature between winter and spring. Therefore, variations in climate and weather factors should be taken into consideration when estimating contribution of mercury released from natural source to regional mercury budget.

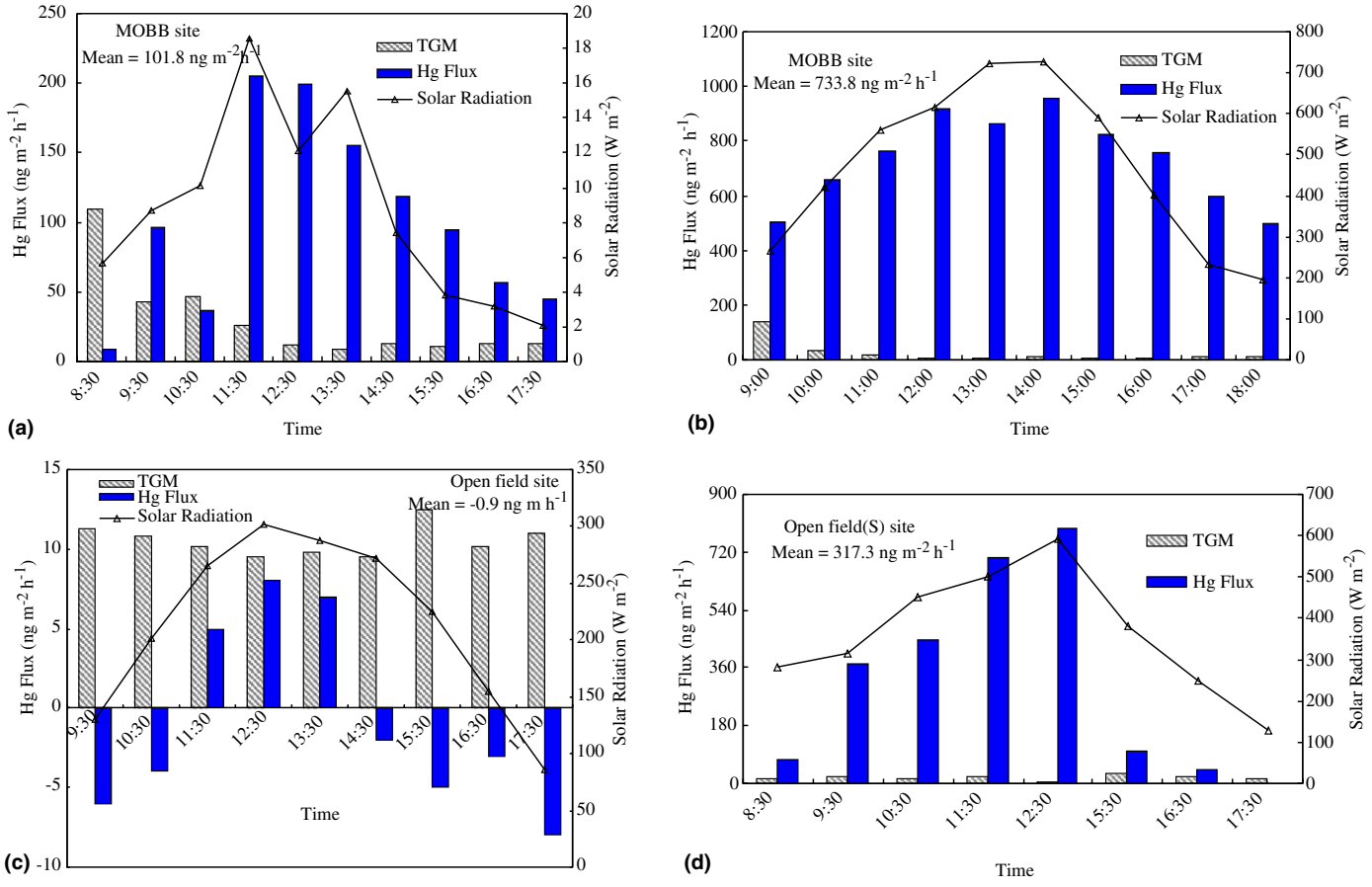


Fig. 5. Mercury fluxes from contaminated soil and open field sites as influenced by solar.

3.4. Factors influencing mercury air/surface exchange

3.4.1. Solar radiation

Positive correlation of mercury air/surface exchange fluxes with solar radiation has been previously observed in both contaminated soils and background soils (Carpi and Lindberg, 1997; Gustin et al., 1998), landfill and water column (Carpi and Lindberg, 1998; Poissant and Casimir, 1998). Our results from different sites also showed that the mercury fluxes mimicked the solar radiation, showing strong linear correlation ($r = 0.7287^{**}$, $n = 135$) (Fig. 6). Solar radiation not only directly enhances mercury emission from soils through the transfer of photo energy to mercury atoms, but also indirectly increases mercury fluxes by increasing soil temperature through conversion of solar energy to thermal energy (Zhang et al., 2001).

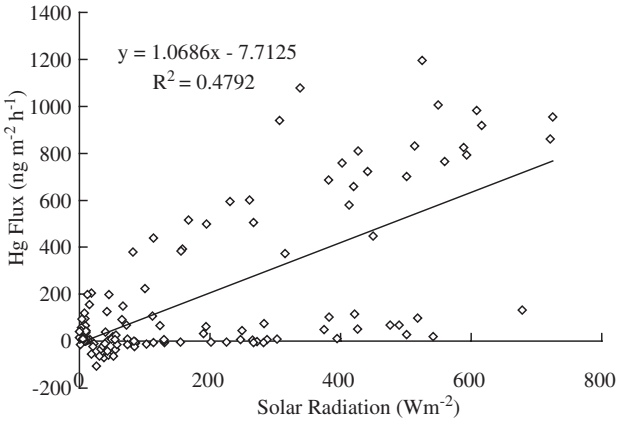


Fig. 6. Correlation of mercury fluxes with solar radiation for all sites.

3.4.2. Relative humidity

Effect of soil moisture on mercury emission flux has been demonstrated in simulated experiment (Scholtz et al., 2003), micrometeorological study (Kim et al., 1995) and field investigation (Kim and Lindberg, 1995; Siegel and Siegel, 1988; Carpi and Lindberg, 1998). However, no consistent conclusion on the effects of humidity on mercury volatilization flux has yet been drawn. Poissant and Casimir (1998) and Boudala et al. (2000)) observed negatively correlation between mercury flux and relative humidity over water surface. In our current study, significantly negative correlation between mercury flux and relative humidity was found over different sites ($r = 0.6117^{**}$, $n = 135$; Fig. 7). The relative humidity may indirectly affect mercury fluxes through modifying solar radiation.

3.4.3. Soil temperature

Soil temperature is an important factor affecting the mercury flux (Gustin et al., 1997; Scholtz et al., 2003).

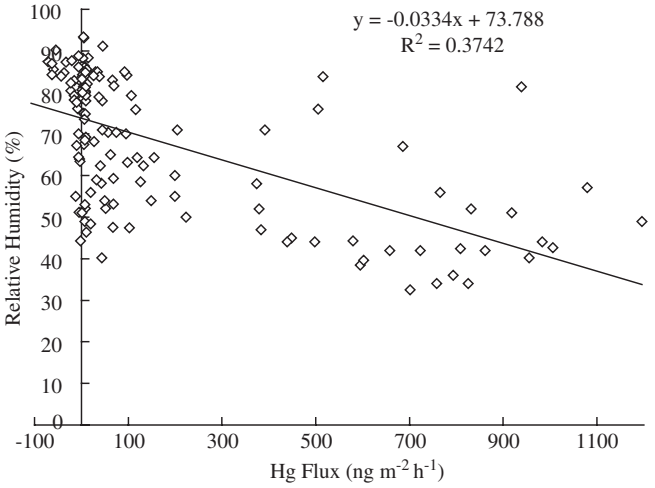


Fig. 7. Correlation between mercury flux and relative humidity for all sites.

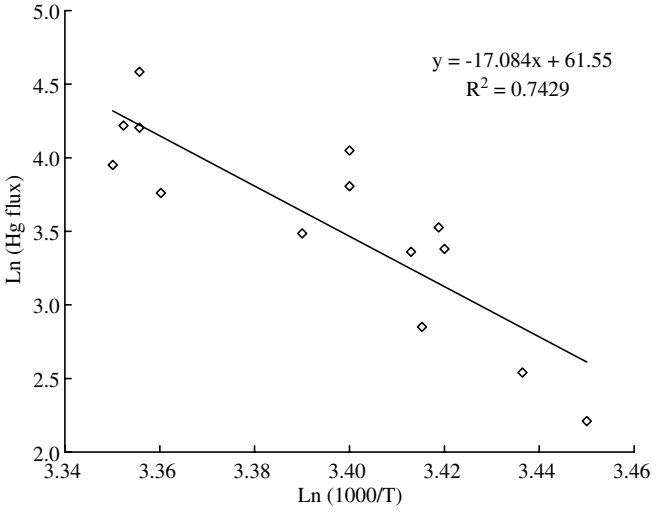


Fig. 9. Mercury flux and soil-surface temperature.

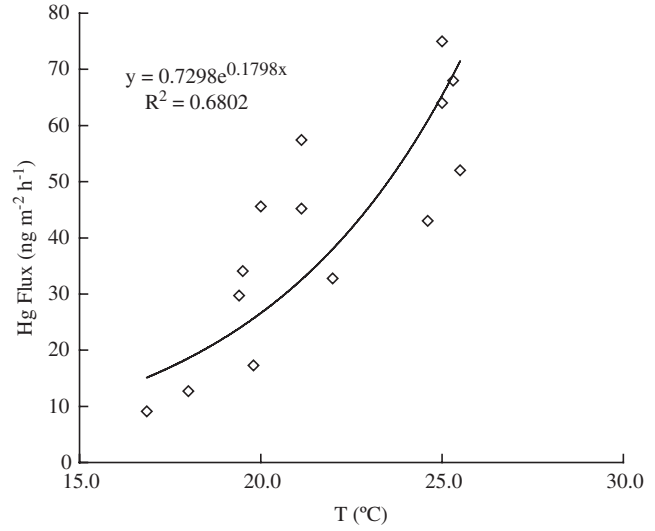


Fig. 8. Correlation between mercury flux and soil temperature at two soil sites.

Table 4
Comparison of observed and modeled Arrhenius activation energy

Reference	Surface	Technique	Activation energy (kcal mol^{-1})
Theoretical value			14.5
Poissant and Casimir (1998)	Pasture	DFC	20.5
Lindberg et al. (1995)	Contaminated soil	MBR	29.6
Kim and Lindberg (1995)	Forest soil	MBR	17.7
Xiao et al. (1991)	Boreal forest lakes	DFC	29.6
Carpi and Lindberg (1998)	Forest soil	DFC	18.0–24.9
Siegel and Siegel (1988)	Dry volcanic soil	Laboratory	13
Scholtz et al. (2003)	Forest soil	Modeled	29.5, 14.0
Zhang et al. (2001)	Forest soil	DFC	29.4
This study	Forest soil	DFC	31.1

Our results showed an exponential correlation of mercury flux with soil temperature ($r = 0.8247^{*}$, $n = 14$; Fig. 8). Such correlation between emission fluxes and soil temperatures has also been reported in other studies (Xiao et al., 1991; Carpi and Lindberg, 1998; Siegel and Siegel, 1988; Zhang et al., 2001). Arrhenius equation has been used to explain the link between the kinetic rate constant of mercury flux and soil temperature:

$$F = A\mathrm{e}^{-\frac{E_a}{RT_S}}$$

where F is the mercury flux, T_S is the soil temperature in K, E_a is the apparent activation energy, R is the gas constant (1.9872 cal K^{-1} mol^{-1}), and A is a constant. The natural logarithm of the mercury flux is plotted against inverse temperature in Fig. 9. The activation energy (E_a) was then calculated to be 31.1 kcal mol^{-1} from the slope of the best-fit line, which was compared to the results previously obtained from other soils (Table 4). This value was higher than the mercury vaporization heat of 14.5 kcal mol^{-1}, implying that the mercury emission from soil surface is not the vaporization process of elemental mercury alone.

3.5. Estimate of mercury emission from land surface in Chongqing

An annual emission of mercury to the atmosphere from natural sources in Chongqing was estimated. Briefly, mercury was considered to release during the warm season (March to October) while deposit during the cold season (November to February). According to the climatical characteristics of Chongqing, mean values of mercury release flux in the end of summer were chosen to represent the release flux for the whole year (Gustin et al., 2000), and a

daily emission period was 12 h (from 7:00 to 19:00). Total release was calculated by the differences between emission and deposition. Total mercury emission to the atmosphere from natural sources was estimated to be 1784.2 kg yr^{-1}, or 21.7 g km^{-2} yr^{-1} in Chongqing. Gustin et al. (2000) estimated the natural release of mercury in mineralization belt of North America and showed that the value was 135 g km^{-2} yr^{-1} according to the flux method while 83 g km^{-2} yr^{-1} by mercury concentration in soils. By using thin-film gas-exchange model, the mercury release from natural sources in equator-pacific region was estimated at 29 ± 19 g km^{-2} yr^{-1} (Kim and Fitzgerald, 1986). Because of limited data, estimation of natural mercury release flux in Chongqing area needs further investigation.

4. Conclusions

Air/surface exchange flux of mercury was investigated at six soil sites and four water surfaces across Chongqing. Air–water surface exchange fluxes of mercury were higher than those of air/soil surface. Average value of mercury flux was 204 ng m^{-2} h^{-1} and 115 ng m^{-2} h^{-1} for air–water and air–soil surface, respectively. The mercury fluxes varied greatly among different sites. Lowest mercury flux occurred at the forest site of Jinyunshan Mountain, with mercury flux of 3.4 ± 1.5 ng m^{-2} h^{-1}, while highest at the water surface in Longfengxi Slot with the value of 618.6 ± 339 ng m^{-2} h^{-1}.

The diurnal and seasonal variations of mercury flux over air/surfaces were observed. The peak values of mercury release occurred around the noon. Mercury fluxes over air/surfaces had bi-directional exchange in the morning and early evening in cold season, but not during the daytime in the warm season. There were higher mercury fluxes in warm than in cold season.

Mercury fluxes over air/surfaces were influenced by many factors such as air temperature, relative humidity, solar radiation and soil temperature. The solar radiation may play an important role in mercury exchange flux. There was significantly positive correlation between solar radiation and mercury flux ($r = 0.7287^{**}$, $n = 135$). The relative humidity was significantly negative correlated with mercury flux ($r = 0.6117^{**}$, $n = 135$). The mercury flux was exponentially correlated with soils temperature, which could be explained by Arrhenius equation. The activation energy (E_a) was calculated to be 31.1 kcal mol^{-1}, higher than the heat of mercury vaporization of 14.5 kcal mol^{-1}. A preliminary estimate of regional mercury emission from land surface was annually 1787 kg in Chongqing.

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