

Seasonal variation of gaseous mercury exchange rate between air and water surface over Baihua reservoir, Guizhou, China

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Abstract

Mercury (Hg) exchange between air and water surface is recognized to be one of the most important processes governing the biogeochemical cycling of Hg in aquatic system. Baihua reservoir is seriously contaminated with Hg due to anthropogenic activities. As a part of Hg mass balance study of Baihua reservoir, we measured Hg exchange fluxes between air and water surface at different seasons by using a quartz flux chamber method coupled with high time resolved atmospheric Hg analysis technique. Hg evasion from water surface is the predominant process at all seasons, and the overall total gaseous Hg emission flux in warm season is significantly larger than that in cold season. Hg flux significantly correlated with the intensity of solar radiation at all sampling campaigns, but it only correlated with wind speed at cold season when the solar radiation was weak. Sunlight induced reduction of divalent Hg to Hg⁰ is the predominant process of dissolved gaseous Hg formation in surface water of Baihua reservoir, and the process is very fast. The annual Hg emission from Baihua reservoir to the air is 752 g, constituting of 3% of total Hg in water body of the reservoir. Our study implies that Hg emission process plays an important role in Hg cycling in Baihua reservoir. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Water/air exchange; Dissolved gaseous mercury; Emissions; Biogeochemistry; Contamination; Reservoir

1. Introduction

Due to relatively high volatility of mercury (Hg) and most of its compounds, it cycles in the environment with atmosphere as the transportation medium as a result of natural and anthropogenic activities (Lindqvist et al., 1991). The amount of Hg mobilized and released into the atmosphere has increased since the beginning of the industrial age (Mason et al., 1994; Schroeder and Munthe, 1998). Hg exchange between air and water surfaces (including fresh water and sea water) is

recognized to be of significance in the global biogeochemical cycling of Hg (Lindqvist et al., 1991; Mason et al., 1994). Hg emission from water surfaces is considered as one of the atmospheric sources (Mason et al., 1994). On the other hand, the process of Hg emission reduces the burden of Hg in the water and may limit the methylmercury production and accumulation in fish (Fitzgerald et al., 1991). This de-toxification process can thus serve to ameliorate the risks associated with Hg contamination especially in fresh water systems. As a part of Hg mass balance study of Baihua reservoir, we measured Hg exchange fluxes between air and water surface at different seasons by using a quartz flux chamber method coupled with high time resolved atmospheric Hg analysis technique.

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2. Experimental section

2.1. Sampling site

Baihua reservoir (26°35'–26°42' N, 106°27'–106°34' E) dammed in 1966 is situated at 16 km Northwest of Guiyang, the capital of Guizhou Province. Guizhou organic chemical plant (GOCP), which is the only one in China that uses metallic Hg as a catalyst to produce acetic acid, is located at the upper reach of Baihua reservoir (see Fig. 1). GOCP went into operation in 1980, and so far around 160 ton Hg has been consumed. From 1980 to 1985, the waste-water from GOCP was directly discharged into Dongmen river without any treatment, which seriously contaminated the surrounding environments including Baihua reservoir. After 1985, a Hg removal device went into operation to prevent Hg discharging into Dongmen river. At present, total Hg concentrations in this river range from 250 to 1000 ng l⁻¹. In addition, 7 small coal mines, one iron mine and Guizhou aluminum plant are situated at the upper reaches of the reservoir, and these may also be Hg emission sources. Even though Baihua reservoir is

seriously contaminated in terms of Hg, so far no research related to Hg biogeochemical cycling in Baihua reservoir has been conducted yet. The total water surface area of Baihua reservoir is 14.5 km², the average water depth is 12 m, and the average salinity and DOC concentrations are 0.2‰ and 0.3 mg l⁻¹, respectively. Three sampling sites were chosen for Hg exchange fluxes measurement between air and water surface as shown in Fig. 1. Three measurement campaigns were conducted. The first one representing the cold season was carried out from 31 October to 4 November, 2001 at Matuo site, the second representing the warm season was performed from 23 to 30 May, 2002, at Matuo site and the third representing the transition from the cold to the warm season was conducted from 31 March to 6 April, 2003 at all 3 sampling sites.

2.2. Sampling techniques

The Hg flux measurement was conducted with a dynamic flux chamber (DFC) of Quartz. It is portable and relatively inexpensive. Xiao et al. (1991) and Schroeder et al. (1989) firstly introduced chamber

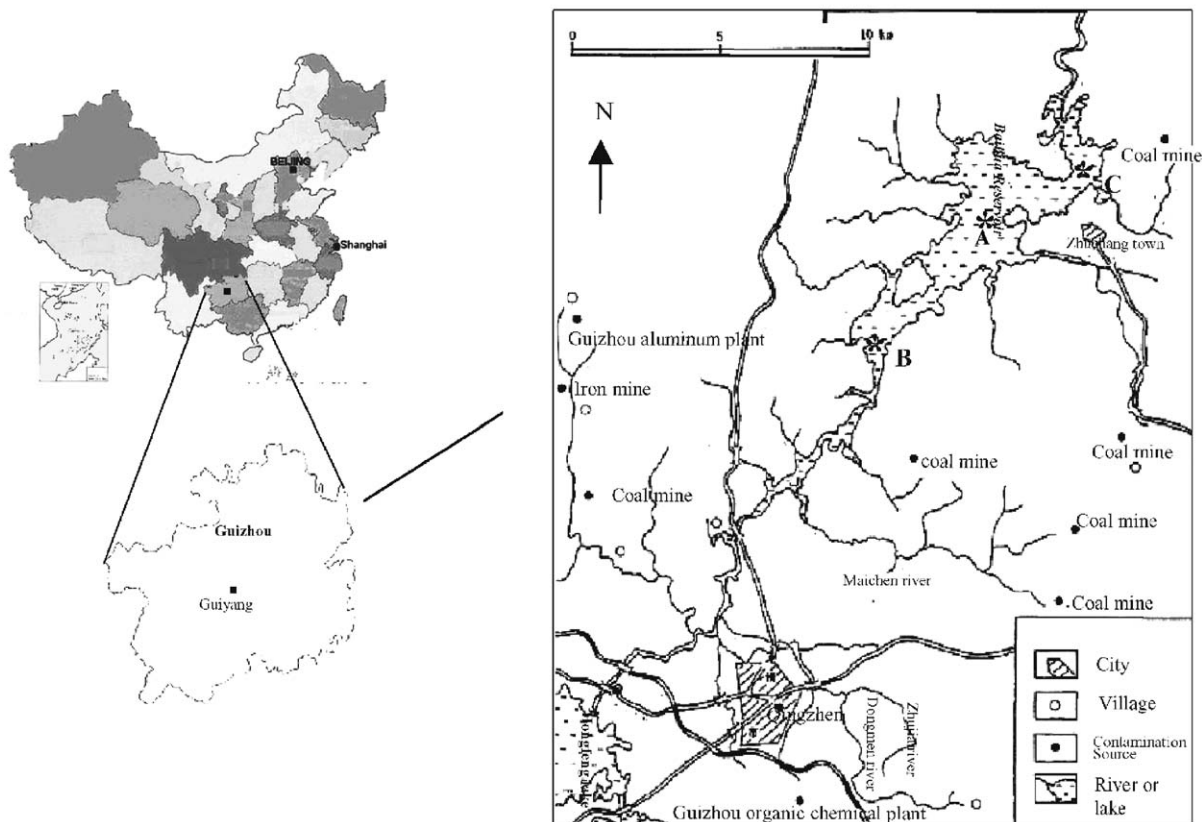


Fig. 1. Sampling locations for gaseous Hg exchange flux measurement over Baihua reservoir (*). (A) Matuo; (B) Huaqiao; (C) Daba.

method to measure Hg exchange flux between air and water/soil surfaces, and afterwards this method was widely used in Hg flux measurement between air and soil/water surface (e.g. Feng et al., 1996; Poissant and Casimir, 1998; Ferrara and Mazzolai, 1998; Gustin et al., 1999; Carpi and Lindberg, 1998; Gårdfeldt et al., 2001, 2003; Feng et al., 2002). The semi-cylinder, open-bottom chamber ($\varnothing 20 \times 60$ cm) is placed on a partial bottom-open boat made of Plexi glass and wrapped with polystyrene blocks, which keeps the chamber floating on the water surface. The chamber is completely exposed to the ambient conditions and the inlet holes of the chamber were exposed to ambient wind. In order to prevent the wind and water movement factors causing rapid pressure fluctuations inside the chamber, 3 large inlet holes with 8 mm diameter are applied to the chamber. Hg flux from the water surface exposed in the chamber was calculated using Eq. (1) (Poissant and Casimir, 1998; 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 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 ng m^{-3} , respectively; A is the bottom surface area of the chamber in m^2 (0.12 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 at a flow rate of 1.5 l min^{-1} . Switching from the inlet and the outlet of the chamber every 10 min was achieved using a magnetic valve provided from Tekran (Tekran 1110) (Fig. 2). To keep flow rate through the chamber constant, another mass flow controller combined with the second magnetic valve that is synchronous with the first one was employed to compensate flow rate decrease when Tekran is sampling air from the inlet of the chamber. Studies (Zhang et al., 2002; Lindberg et al., 2002) demonstrated that soil Hg emission fluxes measured by DFC operations strongly depend on the flushing air flow rates used, and high flushing flow rates (e.g. $\sim 15\text{--}40 \text{ l min}^{-1}$ for DFCs of common design) are adopted. We used a high flushing flow rate of 15 l min^{-1} ($0.9 \text{ m}^3 \text{h}^{-1}$) to prevent the possibility of underestimating Hg flux at low flushing flow rates, though no reports showed that flushing flow rates affect Hg flux measured over water surface. The Hg analyzers were calibrated by injecting a volume of Hg saturated air with known concentration. The blank of the chamber after being cleaned with diluted HNO_3 following with Milli-Q water was measured by sealing the chamber bottom with a Quartz glass plate and the results showed that negligible blanks were detected ($0.1\text{--}0.2 \text{ ng m}^{-2} \text{h}^{-1}$).

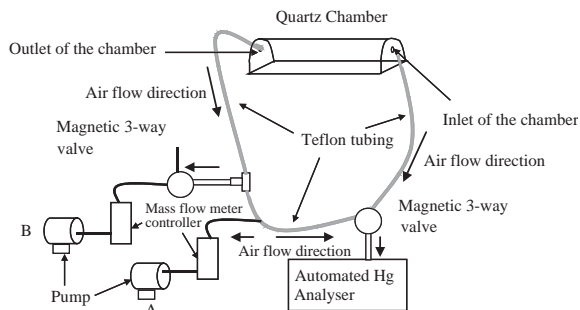


Fig. 2. The set-up of the dynamic flux chamber for measuring Hg flux over water surface. The automated Hg analyzer used in this study is Tekran 2537 A, and its sampling flow rate is 1.5 l min^{-1} . The sampling flow rate of pump A and B that controlled by a mass flow controller is 13.5 and 1.5 l min^{-1} respectively.

Three hundred milli liter sampled surface water was immediately after collection transferred into an extensively cleaned borosilicate glass impinger, and purged with Hg free argon with a flow rate of 300 ml min^{-1} for 30 min and dissolved gaseous mercury (DGM) was collected on a pre-blanked gold trap in the field. Hg collected on the gold traps was analyzed using dual-stage amalgamation coupled with AFS detection (Feng et al., 2002). Fifty milli liter unfiltered water samples were stored in pre-cleaned Teflon bottles with addition of 0.5% HNO_3 and preserved at low temperature for reactive and total Hg analysis. Reactive Hg was analyzed by direct reduction of SnCl_2 and dual-stage amalgamation coupled with AFS detection, and total Hg was done by BrCl oxidation followed with reduction of SnCl_2 and dual-stage amalgamation coupled with AFS detection (Feng et al., 2002; Bloom and Crecelius, 1983). The meteorological parameters, such as air temperature, water temperature, wind speed, solar irradiation and relative humidity 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 is given by Feng et al. (2003, 2004). The weather station was located on the roof of the boat, which was about 4 m above water surface.

3. Results and discussion

3.1. Hg in surface water

Hg concentrations in surface water at the sampling sites from different sampling periods are list in Table 1. Obviously total Hg concentrations in surface water of

the sampling site are much higher than those of pristine water from Sweden and North American which are generally less than 2 ng l^{-1} (e.g. Lindqvist et al., 1991; Poissant and Casimir, 1998; Gårdfeldt et al., 2001; Fitzgerald et al., 1991; Watras et al., 2000), demonstrating that the surface water of Baihua reservoir is contaminated with Hg. It is noted that total Hg concentrations in surface water at Matuo site during warm season (May campaign) are significantly lower than those in other two campaign. Since the rainy season covers from May to August in the research area and the rainfall during this season accounts for 55% of the total annual rainfall that is 1200 mm, it is, therefore, reasonable to believe that the lower total Hg concentrations in

surface water during warm season sampling period results from the dilution due to the recharge from sufficient precipitations and consequently from the runoffs in the catchment basin. In March 2003 campaign, there were no significant difference in terms of total Hg in surface water among the three sampling site which indicating that total Hg was evenly distributed in the surface water of Baihua reservoir.

3.2. Total gaseous Hg (TGM) in the air over water surface

The gaseous Hg exchange fluxes measured over the water surface using the dynamic chamber as well as the TGM concentrations which were measured at the chamber inlet holes are given in Table 2. TGM concentrations measured at all sampling periods were elevated comparing to the global background value that is believed to be around 1.5 ng m^{-3} (Mason et al., 1994). This might result from local/regional HgHg emissions from domestic and industrial coal combustion (Feng et al., 2003), and from Hg emissions from the reservoir itself because Hg evasion from water to the atmosphere is the predominant process during all campaigns (as see in Table 2). TGM concentrations over water surface measured with high time resolution (5 min) during all sampling periods are depicted in Fig. 3. A consistent diurnal TGM distribution pattern that two TGM peaks (one appeared during daytime around noon and the other occurred during night) was observed during the sampling periods. The daytime TGM peak is obviously related to Hg emission from water surface which will be discussed in the following section. The nighttime TGM peak is generally attributed to the fact that on most

Table 1
Hg concentration in surface water (in ng l^{-1})

Sampling date	Sampling site	DGM	Reactive Hg ^a	Total Hg ^a
2001-11-03	Matuo	n.a.	4.6	33.2
2002-05-27	Matuo	0.093 ^b	3.0	12.1
2003-03-27	Matuo	0.210 ^c	1.8	42.6
2003-03-28	Huaqiao	0.242 ^d	3.1	37.8
2003-03-27	Daba	0.117 ^e	1.6	29.5

^a only one water sample was analyzed for both reactive and total Hg concentration.

^b average concentration of 72 samples collected every hour between 23 and 27 May, 2002.

^c average concentration of 24 samples collected every hour between 31 March–1 April, 2003.

^d average concentration of 22 samples collected every hour between 2 to 3 April, 2003.

^e average concentration of 12 samples collected every hour between 4 to 5 April, 2003.

Table 2
Statistical summary of TGM and Hg flux measurement results over Baihua reservoir

Sampling date	Sampling site	Min	Max	Average	SD	n	
31 Oct–05 Nov, 2001	Matou	TGM (ng m^{-3})	2.9	17.3	7.5	2.5	297
		Evasion ($\text{ng m}^{-2} \text{ h}^{-1}$)	0.05	13.5	4.0	3.1	287
		Deposition ($\text{ng m}^{-2} \text{ h}^{-1}$)	0.05	2.9	1.4	1.2	10
23–30 May, 2002	Matou	TGM (ng m^{-3})	2.9	9.0	4.6	1.1	441
		Evasion ($\text{ng m}^{-2} \text{ h}^{-1}$)	0.1	38.4	8.1	5.4	441
31 Mar–02 Apr, 2003	Matou	TGM (ng m^{-3})	0.90	18.38	4.4	2.3	273
		Evasion ($\text{ng m}^{-2} \text{ h}^{-1}$)	0	43.2	9.7	10.2	105
		Deposition	0.01	2.7	0.7	0.5	32
02–04 Apr, 2003	Huaqiao	TGM (ng m^{-3})	4.62	21.55	8.09	2.41	266
		Evasion ($\text{ng m}^{-2} \text{ h}^{-1}$)	0.06	50.5	7.9	9.6	124
		Deposition ($\text{ng m}^{-2} \text{ h}^{-1}$)	0.5	1.5	0.8	0.4	7
04–06 Apr, 2003 ^a	Daba	TGM (ng m^{-3})	4.2	37.6	9.96	7.5	242
		Evasion ($\text{ng m}^{-2} \text{ h}^{-1}$)	0	40.0	8.4	10.4	88
		Deposition ($\text{ng m}^{-2} \text{ h}^{-1}$)	0.2	13.5	2.1	3.1	18

^a Hg flux data measured between 18:00, 4 April and 9:00, 5 April, 2003 were excluded because during that period of time local pollution sources caused high TGM concentrations and large TGM concentration variation at short term, which makes Hg flux measurement using DFC method impossible.

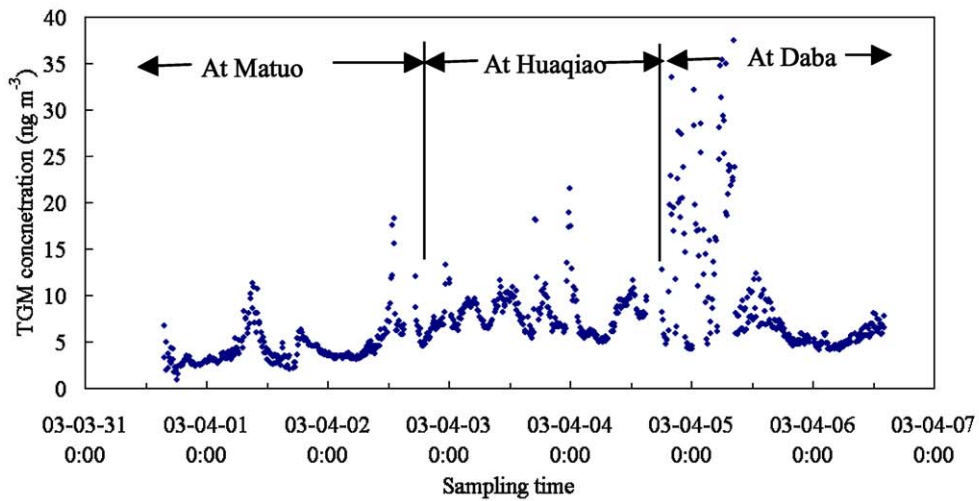
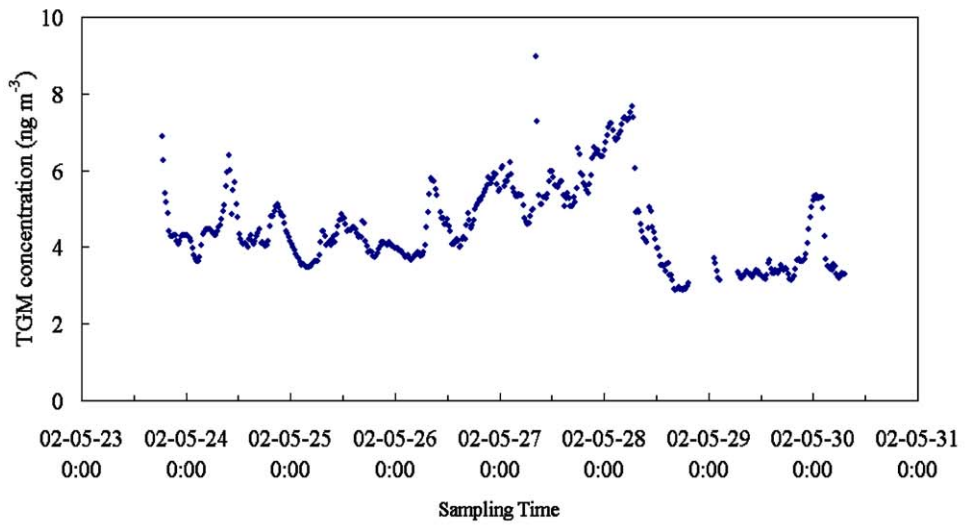
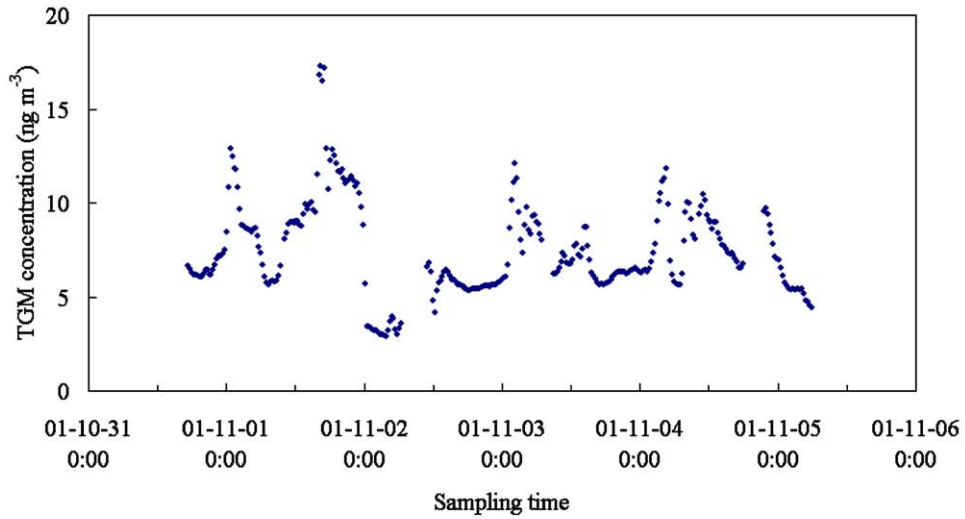


Fig. 3. TGM concentrations in the air 20cm above the water surface during all flux measurement campaigns.

Table 3
Statistical summary of meteorological parameters measured during Hg flux measurement campaigns over Baihua reservoir

Sampling date	Sampling site		Min	Max	Average	SD	<i>n</i>
31 Oct–05 Nov, 2001	Matuo	Wind speed (m s ⁻¹)	0	7.9	1.2	1.6	744
		Solar radiation (W m ⁻²)	0	352.1	18.4	47.0	744
		Air temperature (°C)	11.3	16.9	13.1	1.2	744
		Water temperature (°C)	18.1	18.6	18.4	0.1	744
23–30 May, 2002	Matuo	Wind speed (m s ⁻¹)	0	4.3	0.6	1.1	1872
		Solar radiation (W m ⁻²)	0	811.1	103.4	183.8	1872
		Air temperature (°C)	10.9	22.2	15.4	2.6	1872
		Water temperature (°C)	16.1	23.3	18.7	1.2	1872
31 Mar–02 Apr, 2003	Matuo	Wind speed (m s ⁻¹)	0	9.9	2.8	2.1	576
		Solar radiation	0	894.9	192.5	281.1	576
		Air temperature (°C)	12.4	26.9	21.7	4.2	576
		Water temperature (°C)	14.5	28.5	16.6	16.6	576
02–04 Apr, 2003	Huaqiao	Wind speed (m s ⁻¹)	0	7.2	2.9	1.2	574
		Solar radiation (W m ⁻²)	0	744.0	70.0	118.7	574
		Air temperature (°C)	9.6	21.9	12.2	3.0	574
		Water temperature (°C)	15.3	26.7	16.5	1.6	574
04–06 Apr, 2003	Daba	Wind speed (m s ⁻¹)	0	7.3	2.6	1.6	537
		Solar radiation (W m ⁻²)	0	744.8	60.1	127.1	537
		Air temperature (°C)	6.4	14.6	10.1	2.2	537
		Water temperature (°C)	10.8	17.0	13.6	0.8	537

nights shallow nocturnal boundary layers form to trap TGM near the surface (Feng et al., 2004). From 18:00 pm 4 April to 9:00 am 5 April, an abnormal TGM distribution pattern with high TGM concentrations and large short term variations of TGM was observed, which was definitely caused by local Hg emissions. It is noted from Table 2 that average TGM concentration at Matuo site is higher in cold season with regard to those of summer season, this is mainly because during cold season local domestic coal combustion for house heating occur more frequently and coal combustion is a strong Hg emission source in Guizhou (Feng et al., 2004).

3.3. Meteorological parameters during the sampling periods

The climate of Baihua reservoir area represents a typical subtropical humid monsoon with an average annual temperature of 15°C. No extreme hot weather during summer and no extreme cold weather during winter are the features of its climate. Table 3 summarized the statistical results of meteorological parameters monitored during all measurement campaigns. From Table 3 it can be concluded that the first campaign carried out from 31 October to 4 November, 2001 at Matuo site represented the cold season, the second performed from 23 to 30 May, 2002, at Matuo site represented the warm season and the third conducted from 31 March to 6 April, 2003 at all 3 sampling sites represented the transition from cold to warm season.

3.4. DGM concentrations in surface waters

DGM concentrations in surface water at each sampling site were determined except the first campaign which was carried out from 31 October to 4 November, 2001. According to Henry's law coefficients of Hg⁰ (0.29 at 21.7°C, 0.25 at 15.4°C, 0.23 at 12.2°C, and 0.22 at 10.1°C) determined by Sanemasa (1975) and the average TGM concentrations at all sampling periods, the saturated DGM concentrations are computed and listed in Table 4 together with statistical summary of DGM measurement results. DGM in surface water were over saturated at all samples except one collected at 8:00 am 5 April, 2003 at Daba site. Generally DGM concentrations peaked during daytime and minimized during night time as showed in Fig. 4. DGM concentrations significantly positively correlated with the intensity of solar radiation at all sampling periods except the one performed in Daba. At Daba site DGM concentrations were measured between 23:00 pm 4 April and 10 am 5 April, 2003, and most DGM samples collected during night. Therefore, the correlation coefficient between DGM concentration and intensity of solar radiation obtained at Daba site is not representative (Table 5).

3.5. TGM exchange flux rate between air and water surface

High temporal resolved Hg flux measurement results as well as solar irradiation are illustrated in Fig. 5. At Daba measurement site, short-term large variation of

Table 4
DGM concentrations in surface waters of Baihua reservoir at different sampling sites (in ng l^{-1})

Sampling date	Sampling site	Min	Max	Average	SD	<i>n</i>	Saturated DGM
23–27 May, 2002	Matou	0.073	0.145	0.093	0.019	72	0.019
31 Mar.–01 Apr., 2003	Matou	0.023	0.378	0.151	0.098	24	0.015
02–03 Apr., 2003	Huaqiao	0.071	0.519	0.278	0.130	22	0.036
04–05 Apr., 2003	Daba	0.019	0.190	0.105	0.040	12	0.046

DGM concentrations were measured every hour at each sampling site; saturated DGM concentrations were computed according to average TGM concentrations in the air and Henry's law coefficients of Hg^0 at the average air temperatures at each sampling period.

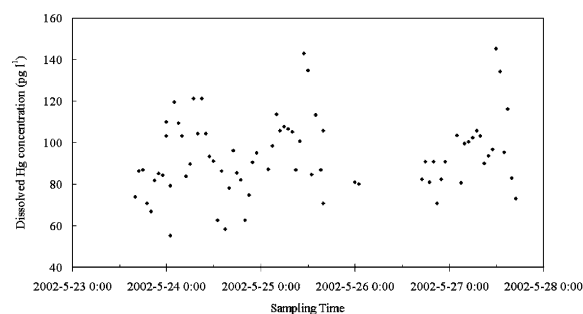


Fig. 4. The temporal change of dissolved gaseous Hg concentrations in surface water at Matou site from 23 to 28 May, 2002 ($n = 72$).

Hg events occurred between 18:00 pm 4 April and 9:00 am 5 April. This is obviously caused by the local Hg emission source that led elevated and rapidly varied TGM concentrations as stated in previous section. Definitely Hg flux measured during that period of time using our method could not represent the true Hg flux values, and these data were therefore excluded in statistical calculations in Tables 2 and 6. It points out that our DFC method is not applicable to measure Hg flux between air and water/soil surface when irregularly large short-term TGM fluctuation occurs due to local Hg emissions. At all sampling campaigns, Hg flux significantly positively correlated with solar irradiation with linear correlation coefficients of 0.38 ($p < 0.01$) at Matou site in cold campaign in 2001, of 0.57 ($p < 0.01$) at Matou site in May 2002 campaign, of 0.82 ($p < 0.01$) at Matou site in March–April 2003 campaign, of 0.91 ($p < 0.01$) at Huaqiao site in April 2003 campaign, and of 0.87 ($p < 0.01$) at Daba in April 2003 campaign, respectively. This observation agrees well with previous studies (Poissant and Casimir, 1998; Gårdfeldt et al., 2001; Feng et al., 2002).

At the campaign carried out in cold season at Matou site, the least significant correlation between Hg flux and solar irradiation was observed ($r = 0.38$, $p < 0.01$). The weather during the campaign was cloudy all the time as

can be seen from Table 3 and Fig. 5 that the intensities of solar radiation were very low and that wind was very strong and varied rapidly. More significant correlation between Hg flux and wind speed ($r = 0.66$, $p < 0.01$) was observed in cold sampling period, but the same correlation was not obtained, however, in other sampling periods (Fig. 6). Even though the chamber affects wind condition, strong wind will result in intensive wave which in turn increases the evasion rate of Hg from water to the air. Thus wind speed controlled the exchange process of Hg between air and water surface at this meteorological conditions. We could therefore conclude that wind effect concealed in some extent the correlation between Hg flux and solar radiation at this meteorological conditions.

The correlations between Hg flux and other meteorological parameters, such as air temperature, relative humidity, and water temperature were also studied as shown in Table 6. Interestingly both positive, negative and no correlation between Hg flux and air and water temperature ($1000/T$), and both negative and no correlation between Hg flux and relative humidity were observed from different sampling periods. This implies that air and water temperatures and relative humidity were not the driving forces of Hg exchange between water and the air. Generally when the intensity of solar radiation are very strong on relatively clear days, air and water temperatures significantly positively correlate with solar irradiation and relative humidity negatively correlates with solar irradiation, and Arrhenius relationships between Hg flux and water and air temperature (Hg flux negatively correlated with air and water temperature in $1000/T$) and negative correlation between Hg flux and relative humidity could be observed. On cloudy days, air and water temperature, and relative humidity vary in a narrow range, and the correlations between solar irradiation and those meteorological parameters observed on clear days will not occur frequently. This observation could be verified from previous studies since both Arrhenius and non-Arrhenius relationship between Hg flux and water and air temperatures were reported from the literature (e.g. Xiao et al., 1991; Poissant and Casimir, 1998; Gårdfeldt

Table 5
Correlation coefficient between DGM concentration and intensity of solar radiation at different sampling periods

Sampling date	Sampling site	Correlation coefficient	<i>n</i>	<i>p</i>
23–27 May, 2002	Matuo	0.50	72	<0.01
31 Mar.–01 Apr., 2003	Matuo	0.45	24	<0.05
02–03 Apr., 2003	Huaqiao	0.55	22	<0.01
04–05 Apr., 2003	Daba	−0.39	12	—

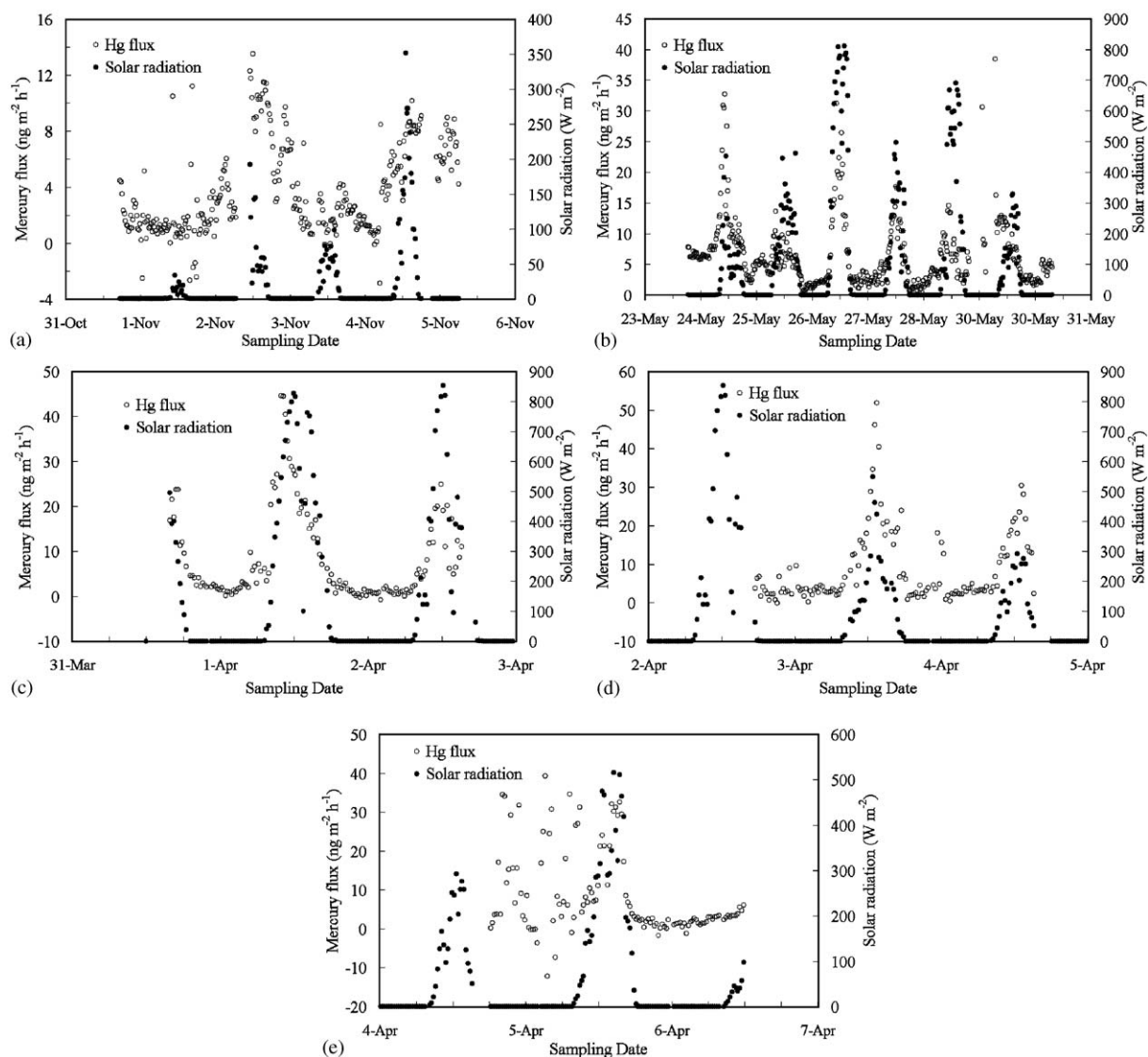


Fig. 5. Relationships between Hg flux and solar irradiation at five sampling campaigns. (a) 31 October–05 November, 2001 at Matuo; (b) 23–30 May, 2002 at Matuo; (c) 31 March–02 April, 2003 at Matuo; (d) 02–04 April, 2003, at Huaqiao; (e) 04–06 April, 2003 at Daba.

et al., 2001). Our study therefore supports the hypothesis that solar radiation plays a major role in the Hg exchange process between air and water surfaces,

though water temperature also affects Hg evasion since the equilibrium between water and air is dependent on temperature.

Table 6

Correlation coefficients between Hg flux and air temperature (1000/*T*), water temperature (1000/*T*) and relative humidity at different sampling period

Sampling date	Sampling site	Hg flux AT ^a			Hg flux and WT ^b			Hg flux and RH ^c		
		<i>r</i>	<i>n</i>	<i>p</i> ^d	<i>r</i>	<i>n</i>	<i>p</i> ^d	<i>r</i>	<i>n</i>	<i>p</i> ^d
31 Oct–05 Nov, 2001	Matuo	0.21	293	<0.01	0.22	293	<0.01	−0.34	293	<0.01
23–27 May, 2002	Matuo	−0.24	441	<0.01	−0.24	441	<0.01	−0.15	441	<0.01
31 Mar. –01 Apr., 2003	Matuo	−0.45	137	<0.01	0.01	137	—	−0.54	137	<0.01
02–03 Apr., 2003	Huaqiao	0.03	131	—	−0.07	131	—	−0.09	131	—
04–05 Apr., 2003	Daba	0.004	77	—	−0.43	77	<0.01	−0.43	77	<0.01

^a AT standards for air temperature in 1000/*T* and *T* in Kelvin.

^b WT stands for water temperature in 1000/*T* and *T* in Kelvin.

^c RH stands for relative humidity in %.

^d *p*: significance level—no significant correlation.

DGM could be formed in many processes in the water system. Demethylation (Fitzgerald et al., 1994), bacterial reduction from water (Fitzgerald et al., 1994) and sediment (Mason et al., 1995), reduction by humic and fulvic acid in water (Allard and Arsenie, 1991), and photo-induced reduction in water (Amyot et al., 1997a, b, c, 1994; Costa and Liss, 1999; Nriagu, 1994) are so far the possible processes suggested to be responsible for the formation of DGM in aquatic system. Although several of these processes are well-known, it was not until quite recently that photo-induced Hg reduction and subsequent volatilization became the subject of theoretical (Nriagu, 1994), laboratory (Munthe and McElroy, 1992; Xiao et al., 1994, 1995; Pehkonen and Lin, 1998) and field (Amyot et al., 1997a, b, c, 1994) investigations. The conclusions obtained from these studies are that certain Hg species could be photo-reduced to Hg⁰ and organic matter such as humic and fulvic acids do enhance the reaction rate. Our data showed that DGM concentration in surface water strongly correlated with solar irradiation and the surface water was over-saturated with DGM during most time of campaigns. All those facts suggested that solar induced Hg reduction is the predominant process producing DGM in surface water though contribution from other processes could not exclude so far, and the super-saturation of DGM in surface water is the driving force of Hg emission from water to the air.

O'Driscoll et al. (2003) observed that DGM concentrations in surface water correlated significantly with solar radiation and by time-shifting the solar radiation data (cross-correlation analysis) peaks and lows in solar radiation were observed to occur 65–90 min before corresponding peaks and lows in DGM. By doing cross-correlation analysis between Hg flux and solar radiation, we noticed that at all campaigns expect the one carried out at Matuo site in cold sampling period the time shifts between Hg flux and solar radiation are very short, varying between 0 and 20 min (Fig. 7). This

implied that the process of Hg emissions from water to the air induced by solar radiation was very fast. At the campaign carried out in cold season at Matuo site, with an increase of shift time of solar radiation data, the correlation increased gradually. This is mainly due to wind effect on Hg flux as stated previously in the section.

Our study showed that both in cold and warm seasons or in the transition season from cold to warm the water surface of Baihua reservoir is a strong atmospheric emission source to the local environment. This is because that the Hg concentrations in water body of the reservoir are elevated due to Hg contamination from anthropogenic activities, which could result in high Hg emission rate definitely. Moreover, since the bedrock of the drainage area of the reservoir is limestone, the pH of the reservoir is generally close to 8. Studies (Fitzgerald et al., 1991; Mattiessen, 1998) already showed that increases in pH results in an increase in Hg⁰ production and consequently Hg emission flux. Therefore the alkaline water of the reservoir is in favor of Hg emission from water surface to the air. Strong Hg emissions from water surface could partly explain the elevated TGM concentrations in the air 20 cm above water surface in all sampling campaigns.

According to the climate in Baihua reservoir area, we could divide one year into cold season (November, December, January, February), warm season (May, June, July, August) and cold–warm transition season (March, April, September, October). Using our Hg flux measurement data we calculated the annual Hg emission from Baihua reservoir to the air to be 752 g. The Hg mass balance study in Baihua reservoir is still on-going in our group, and the relative importance of Hg emission process to the Hg cycling in Baihua reservoir is yet to be determined. However, the Hg reservoir in Baihua reservoir is computed to be 4550 g (Feng and Yan, 2004), and the water resident time is 2.1 months. Thus the annual overall retention of Hg in the reservoir is 25,529 g. We can see that about 3% of Hg in water

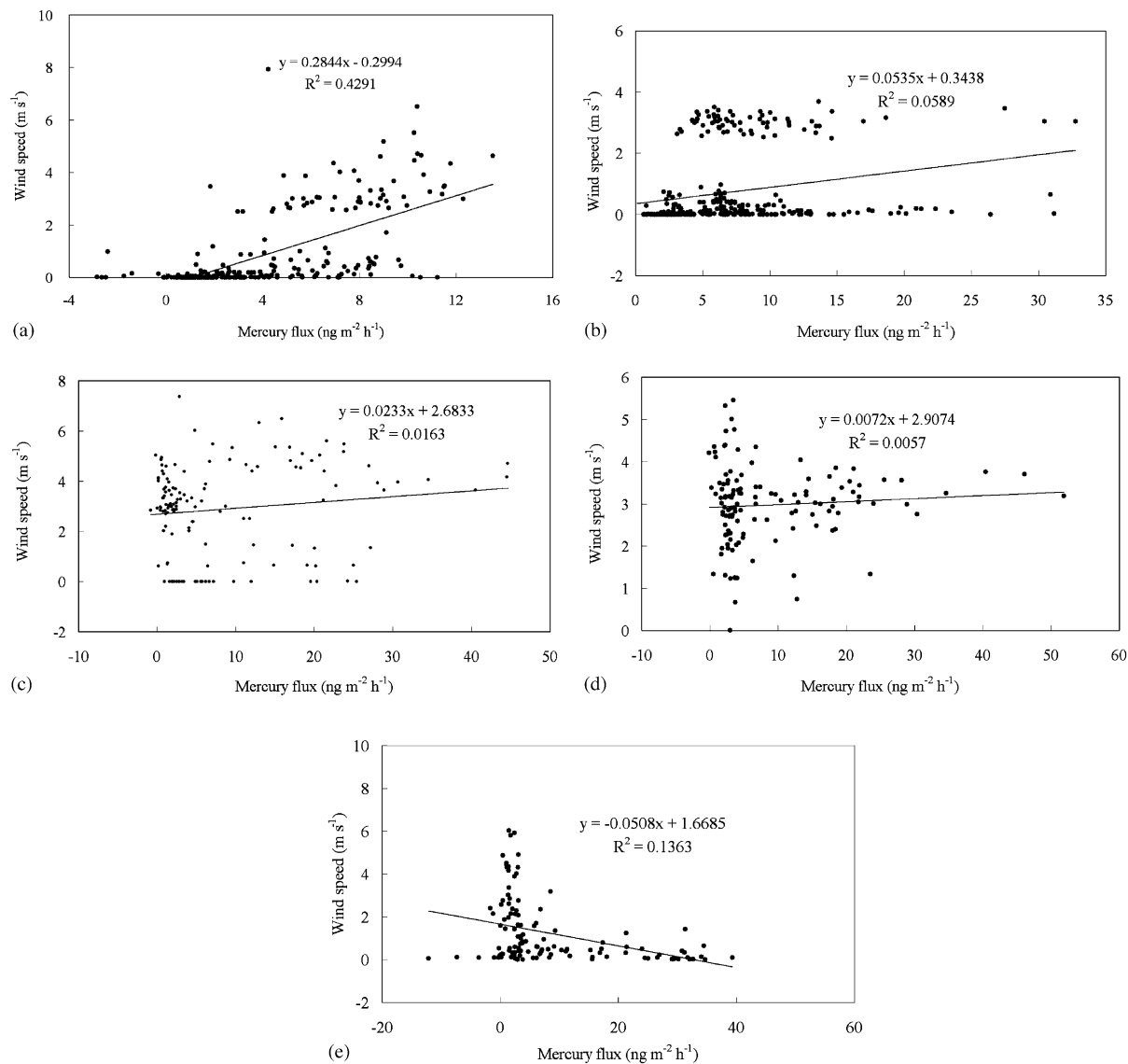


Fig. 6. Correlation between Hg flux and other meteorological parameters such as wind speed, air temperature, relative humidity, and water temperature. (a) 31 October–05 November, 2001 at Matuo; (b) 23–30 May 2002 at Matuo; (c) 31 March–02 April, 2003 at Matuo; (d) 02–04 April, 2003, at Huaqiao; (e) 04–06 April, 2003 at Daba.

body of the reservoir emitted to the ambient air each year, which implies that Hg emission process plays an important role in Hg cycling in Baihua reservoir.

4. Conclusions

Hg concentrations in surface water of Baihua reservoir are elevated due to anthropogenic emissions. TGM concentrations in the ambient air over the surface water of the reservoir are elevated compared to the

global background values, and a consistent diurnal TGM distribution pattern that two TGM peaks (one appeared during daytime around noon and the other occurred during night) was observed during the sampling periods. Generally DGM in surface water are over-saturated and it correlated significantly with the intensity of solar radiation. The surface water of Baihua reservoir is a strong local atmospheric emission source at all seasons. Sunlight induced reduction of divalent Hg to Hg^0 is the predominant process of DGM formation in surface water of Baihua reservoir, and the process is very

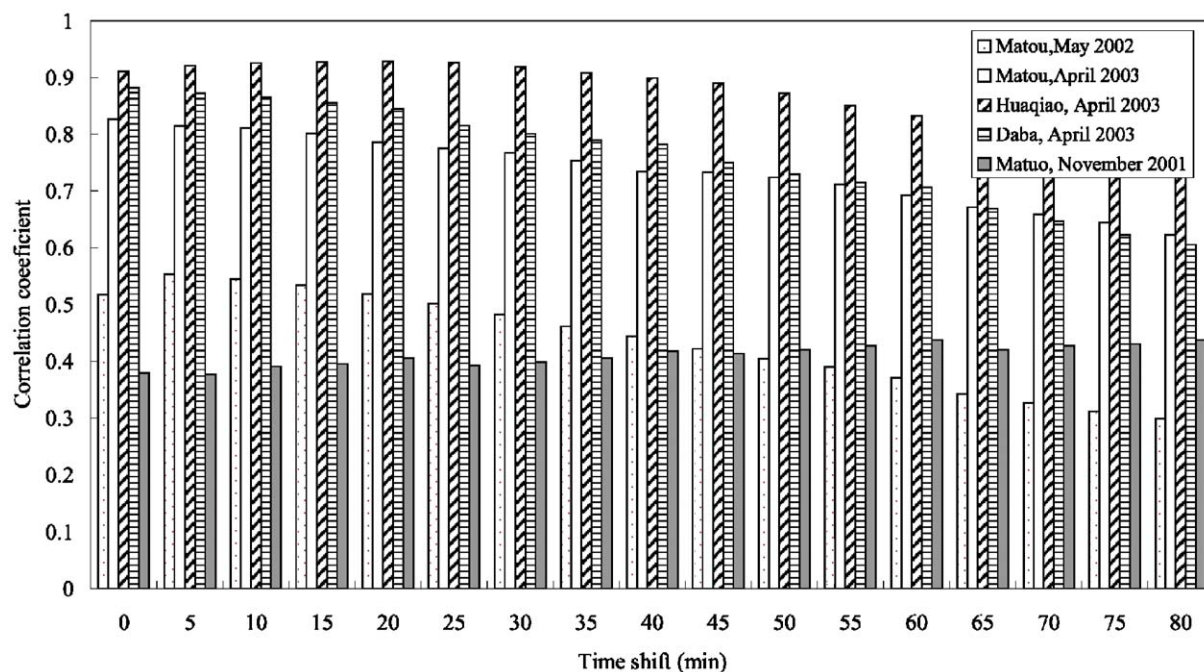


Fig. 7. Cross-correlation analysis for Hg flux and solar radiation.

fast. The annual Hg emission from Baihua reservoir to the air is 752 g, constituting of 3% of total Hg in water body of the reservoir.

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