

Gaseous mercury exchange rate between air and water over Baihua reservoir, Guizhou, China during cold season

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Abstract. Field measurement campaigns over lake water surface at Baihua reservoir in Guiyang, Southwestern China were conducted to measure mercury flux using a dynamic flux chamber technique coupled with automatic mercury vapor-phase analyzer from October 30 to November 4, 2001. The dynamic flux chamber is made of quartz glass, and has low blanks. Water samples were collected, and dissolved gaseous mercury (DGM), reactive and total mercury concentrations in water were measured using gold trap pre-concentration and AFS detection method. Meanwhile meteorological parameters, such as wind speed, wind direction, intensity of solar radiation, air and water temperature, and relative humidity were monitored using a portable weather station. Water surface is a net atmospheric mercury emission source even at cold season (autumn), and the average mercury emission rate is $3.0 \text{ ng m}^{-2} \text{ h}^{-1}$. We observed a strong correlation between wind speed and mercury emission rate, suggesting that strong wind facilitate mercury evaporation process from the water system during cold season. No significant correlations between Hg emission rate and solar radiation, water and air temperature were obtained.

1. INTRODUCTION

Mercury exchange between air and water surfaces (including fresh water and sea water) is recognized to be of significance in the global biogeochemical cycling of mercury [1,2]. Mercury emission from water surfaces is considered as one of atmospheric sources [2]. On the other hand, the process of mercury emission reduces the burden of mercury in the water and may limit the methylmercury production and accumulation in fish [3]. This de-toxification process can thus serve to ameliorate the risks associated with mercury contamination especially in fresh water systems. With recent development of high time resolved atmospheric mercury analyzers, such as Tekran 2537A, continuous measurement of gaseous mercury (GM) exchange rate between air and water surfaces becomes feasible [4-6]. As a part of Hg mass balance study of Baihua Reservoir, we measured mercury exchange fluxes between air and water surface at cold season by using a quartz flux chamber method coupled with high time resolved atmospheric Hg analysis technique.

2. Experimental Section

2.1 Sampling Site

Baihua reservoir (106°27'-106°34'N, 26°35'-26°42'E) dammed in 1966 is situated 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 mercury as a catalyst to produce acetic acid, is located at upper reaches of Baihua Reservoir. GOCP went into operation in 1980, and so far around 160 ton mercury has been consumed. From 1980 to 1985, the wastewater from GOCP was directly discharged into Dongmen river without any treatment, which seriously contaminated the surrounding environments including Baihua Reservoir. After 1985, a mercury removal device that designed by the factory went into operation to prevent mercury discharging into Dongmen river. Since the technology implemented is out of date, mercury concentration in treated waste-water is still as high as up to $212.4 \mu\text{g l}^{-1}$. In addition, 7 small coal mines, one iron mine and Guizhou Aluminum Plant are situated upper reach of the reservoir, and these may also be mercury emission sources to the reservoir. Even though Baihua Reservoir might be seriously contaminated in terms of mercury, so far no serious research related to mercury biogeochemical cycling in Baihua Reservoir has been conducted yet. The total water surface area of Baihua Reservoir is 14.5 km^2 , and one sampling site was chosen for GM exchange fluxes measurement between air and water surface. The measurement campaign was carried out from October 31 to November 4, 2001.

2.2 Sampling techniques

The mercury flux measurement was conducted with a dynamic flux chamber of Quartz. It is portable and relatively inexpensive. Xiao et al. [7] and Schroeder et al. [8] firstly introduced chamber method to measure mercury exchange flux between air and water and soil surfaces. The semi-cylinder, open-bottom chamber ($\text{Ø}20 \times 60 \text{ cm}$) is placed on a partial bottom -open boat made of Plexi glass and wrapped with polystyrene blocks, which keeps the chamber to float on the water surface. Mercury flux from the water surface exposed in the chamber was calculated using equation from literatures [4,9]. The inlet and outlet mercury concentrations were monitored alternately by Tekran 2537A mercury analyzer in a time interval of 5 min. A magnetic valve was used to switch the sampling port of mercury analyzer between inlet and outlet. The mercury analyzers were calibrated by injecting a volume of mercury 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 usually negligible blanks were detected.

300 ml sampled surface water was immediately after collection transferred into an extensively cleaned borosilicate glass impinger, and purged with mercury free argon with a flow rate of 300 ml min^{-1} for 30 minutes and dissolved gaseous mercury (DGM) was collected on a pre-blanked gold trap in the field. Mercury collected on the gold traps was analyzed using dual-stage amalgamation coupled with AFS detection [6]. 50 ml water samples were stored in pre-cleaned Teflon bottles with addition of 0.5% HNO_3 and preserved at low temperature for reactive mercury and total mercury. Reactive mercury was analyzed by direct reduction of SnCl_2 and dual-stage amalgamation coupled with AFS detection, and total mercury was done by BrCl oxidation followed with reduction of SnCl_2 and dual-stage amalgamation coupled with AFS detection [6,10]. The meteorological parameters, such as air temperature, water temperature, wind speed, solar irradiation and relative humidity were monitored using a portable weather station (Global Logger IIIB).

3. RESULTS AND DISCUSSION

Total Hg and reactive Hg concentrations in surface water at the sampling site was 33.2 and 4.6 ng l^{-1} respectively. Obviously total mercury concentrations in surface water of the sampling site are much higher than those of pristine water from Sweden and North American [1, 4-6], which definitely results from mercury discharge from GOCP and other potential sources. TGM concentrations measured were 7.5 ng m^{-3} , which was elevated comparing to the global background value that is believed to be around 1.5 ng m^{-3} .

m⁻³ [2]. Except for a few occasions (10 out of 297) during the sampling period that mercury deposition occurs, mercury evasion from water surface is the predominant process. According to Henry's law coefficient of Hg⁰ (0.29@20°C) and the average TGM concentration, the saturated DGM concentrations are computed to be 25.9 pg l⁻¹. The measured DGM concentration was however 3 pg l⁻¹, which imply that the surface water was under saturated in terms of DGM.

High temporal resolved Hg flux measurement results as well as solar irradiation are illustrated in Figure 1. No significant correlation between mercury flux and solar irradiation was observed in cold season. The correlations between Hg flux and other meteorological parameters, such as wind speed, air temperature, relative humidity, and water temperature were also studied as shown in Figure 2. Significant correlation (p<0.001) between Hg flux and wind speed was observed, while no correlations between Hg flux and air temperature, relative humidity, and water temperature were obtained.

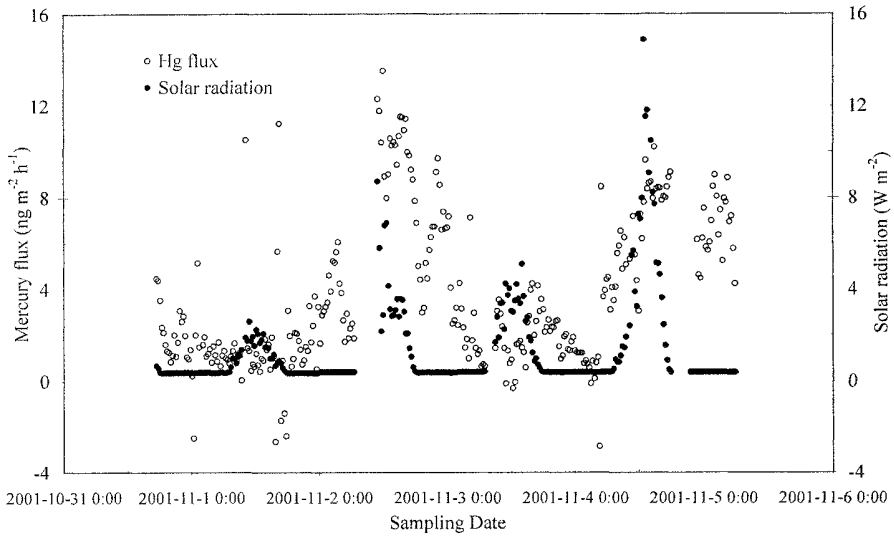


Figure 1. Relationships between Hg flux and solar irradiation.

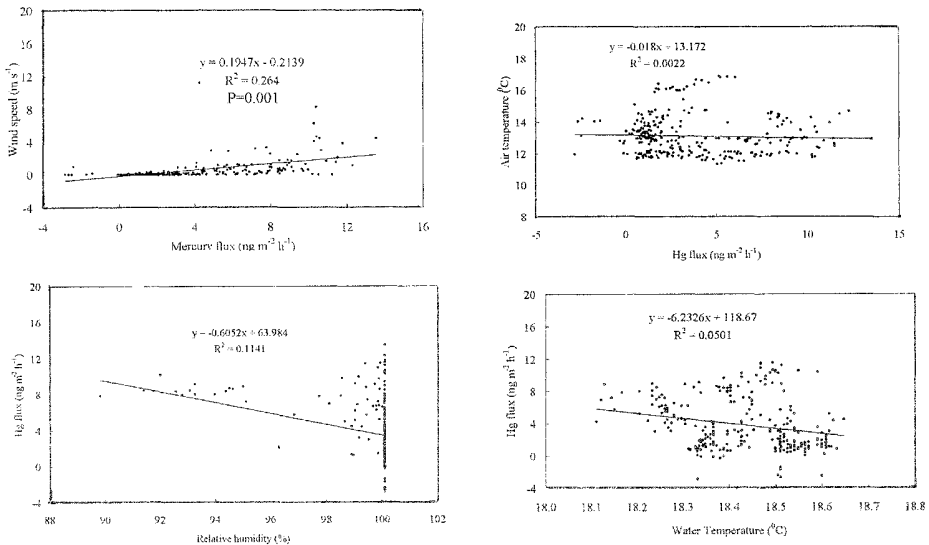


Figure 2. Correlation between Hg flux and other meteorological parameters such as wind speed, air temperature, relative humidity, and water temperature.

DGM was under saturated in surface water in cold season, Hg emission from water to air was, however, still the predominant process. Investigation of the DGM formation mechanisms in water system in cold season is still on the way in our laboratory. Our observation that Hg emission flux strongly correlated with wind speed suggested that the turbulence of surface water caused by strong wind was the driving force of Hg emission from water to air because DGM is not stable at this condition.

Acknowledgments

This work was financially supported by Chinese Academy of Sciences through “Hundred Talent Plan” and CAS innovation project (KZCX2-105), and by Chinese Natural Science Foundation (40173037).

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