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Mercury isotope fractionation during transfer from post-desulfurized seawater to air

Shuyuan Huang^a, Kunning Lin^a, Dongxing Yuan^{a,*}, Yaqin Gao^a, Lumin Sun^b^a State Key Laboratory of Marine Environmental Science, College of the Environment and Ecology, Xiamen University, Xiamen 361102, China^b Tan Kah Kee College, Xiamen University, Zhangzhou 363105, China

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ABSTRACT

Samples of dissolved gaseous mercury (DGM) in the post-desulfurized seawater discharged from a coal-fired power plant together with samples of gaseous elemental mercury (GEM) over the post-desulfurized seawater surface were collected and analyzed to study the mercury isotope fractionation during transfer from post-desulfurized seawater to air. Experimental results showed that when DGM in the seawater was converted to GEM in the air, the $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values were changed, ranging from -2.98 to -0.04% and from -0.31 to 0.64% , respectively. Aeration played a key role in accelerating the transformation of DGM to GEM, and resulted in light mercury isotopes being more likely to be enriched in the GEM. The ratio $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ was 1.626 in all samples, suggesting that mercury mass independent fractionation occurred owing to the nuclear volume effect during the transformation. In addition, mass independent fractionation of mercury even isotopes was found in the GEM above the post-desulfurized seawater surface in the aeration pool.

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1. Introduction

Mercury (Hg) is one of the most toxic trace metals, and is globally distributed in the environment with the features of persistence, mobility and high bioaccumulation through natural and anthropogenic pathways (Selin et al., 2008; Selin, 2009). Mercury can enter the human body and pose adverse effects on human health through respiratory and digestive tracts and skin (Clarkson, 1997; Sallsten et al., 1996). In order to understand the biogeochemical cycle of mercury, researchers have paid great attention to many aspects, including source (David et al., 2005), interface flux (Carrie et al., 2012), transformation (Ci et al., 2011), bioaccumulation in the food chain (Zhang et al., 2010) and mercury isotope fractionation (Foucher et al., 2013; Jiskra et al., 2015; Yin et al., 2015). It was discovered that a series of processes involved in the mercury biogeochemical cycle could lead to a significant mass dependent fractionation (MDF) of mercury isotopes. As for some special geochemical processes, such as photoreduction (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009) and volatilization (Estrade et al., 2009; Ghosh et al., 2013), mass independent fractionation (MIF) of mercury isotopes occurs. Nowadays, mercury isotopes has been a useful tracer in understanding the sources (Gehrke et al., 2010; Laffont et al., 2011; Ma et al., 2013) and biogeochemical processes (Chen et al., 2012; Kwon et al., 2012; Rolison et al., 2013) of mercury in the environment.

Oceans contain 50 times more mercury than the atmosphere (Mason et al., 1994). Air-sea exchange is an important source of mercury for the atmosphere. Mercury is transferred from water to air mainly in the elemental mercury form (Lamborg et al., 1999), due to its low solubility and high volatilization capability (Sarkar et al., 2004). Elemental mercury is the main species at the water-air interface (Laurier et al., 2004).

The seawater desulfurization technique, which is used in some coal-fired power plants in coastal areas, reduces the SO_2 emissions by utilizing the natural alkalinity of fresh seawater to neutralize SO_2 present in the flue gas (resulting from coal combustion) in the desulfurization tower (Katsuo et al., 2003). Before being discharged into the sea, the post-desulfurized seawater should go through an aeration process to increase its pH and dissolved oxygen levels to meet the discharge standards. However, the strong aeration effect would contribute to a high transfer flux of elemental mercury from post-desulfurized seawater into the air (Sun et al., 2013a). There is a significant difference between the transfer of this type and of that in natural water, where mercury transfer is a natural diffusion process, occurring due to the concentration difference existing between the water and air (Bouchet et al., 2011; Muresan et al., 2007).

The aeration pool and discharge outlet of a coal-fired power plant in Xiamen, China were chosen for analysis in the current study. Using the stable isotopic technique, dissolved gaseous mercury (DGM) in the post-desulfurized seawater and gaseous elemental mercury (GEM) above the seawater were determined for their mercury isotope compositions. Additionally, during the transfer of mercury from water to air,

* Corresponding author.
E-mail address: yuandx@xmu.edu.cn (D. Yuan).

the isotope fractionation of elemental mercury has also been discussed in this work.

2. Materials and methods

2.1. Sampling site and sample collection

The DGM and GEM samples were collected from a typical coal-fired power plant, which was equipped with a seawater flue gas desulfurization unit in Xiamen, China (latitude: 24°26'47.74"N, longitude: 118°01'40.33"E). Sampling sites were set in the aeration pool inside the power plant and in the discharge outlet outside the plant. The study area and sampling sites are shown in Fig. 1.

Samples were collected seven times between December 2014 and January 2016. Out of these seven occasions, three were for collecting samples from the aeration pool, while four were for collecting samples from the discharge outlet. The sampling dates and sample IDs (given in brackets) for the aeration pool were December 2014 (1412), June 2015 (1506) and December 2015 (1512), while for the discharge outlet, these were March 2015 (1504), July 2015 (1507), October 2015 (1510) and January 2016 (1601). Unfortunately, the GEM samples of 1504 and 1506 were not available and therefore, have not been shown in the results. All the sampling operations and cleaning processes were carefully carried out following the USEPA method 1631 (USEPA, 2001).

For DGM sampling, unfiltered surface seawater samples (obtained from 0.2 m depth) were collected into four 2 L borosilicate glass bottles, which were covered with aluminum foil to avoid any effect caused by UV radiation (Sun et al., 2013a, 2013b). DGM was purged for 90 min with mercury-free argon gas having a flow rate of 400 mL/min. The purged DGM was de-moistened with a drying column filled with soda lime and was adsorbed onto the gold traps (Lin et al., 2015).

For GEM sampling, the GEM in air (0.5 m above the sea surface) was trapped onto a series of gold traps using a vacuum pump, which was running at a flow rate of 3 L/min. In order to protect the gold traps from moisture and salt, a drying column was installed at the sampler inlet. The storage time of gold traps with GEM was kept below 10 h in order to avoid GEM loss due to the deactivation of gold traps. Therefore, the sampling times of 1.5 h for the aeration pool and 8 h for the discharge outlet were chosen.

2.2. Reagents and solutions

The solutions were prepared in a fume hood, and ultrapure deionized water (resistivity ≥ 18.2 M Ω cm) was used throughout the

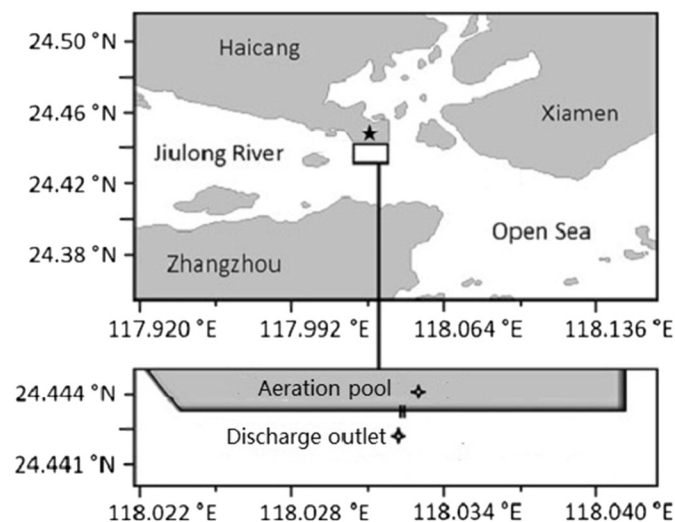


Fig. 1. Location of study area and sampling sites (revised from Sun et al., 2013b).

experiment. The reductant and oxidant reagents, such as stannous chloride, hydroxylamine hydrochloride and bromine monochloride, were prepared following USEPA method 1631E (2002). Potassium permanganate (KMnO₄) solution was made by dissolving 0.06 g KMnO₄ (low in mercury, 99.0%, Alfa Aesar, USA) in 100 mL 10% (v/v) sulfuric acid (guaranteed reagent, Merck, Germany). Mercury gas generator was purchased from the Beijing Rayleigh Analytical Instrument Corp., China. A fresh mercury isotopes stock solution was prepared by diluting mercury standard solution (NIST SRM 3133, National Institute of Standards & Technology, USA) in 3% (v/v) ultrapure nitric acid (guaranteed reagent, Merck, Germany) before each set of experiments to avoid MDF. A thallium isotopes stock solution was prepared using thallium standard solution (NIST SRM 997, National Institute of Standards & Technology, USA) and stored in a refrigerator for no more than one month. The UM-Almadén mercury isotopes in-house standard was kindly provided by Dr. Blum of the University of Michigan, USA.

2.3. Sample preparation

In the laboratory, a thermal desorption device was employed to release Hg⁰ from the gold traps containing DGM. The released Hg⁰ was delivered to 10 mL 0.06% (m/v) KMnO₄ solution using mercury-free argon gas for preconcentration. The bottle of KMnO₄ solution was sealed in double polyethylene bags and stored at 4 °C prior to the analyses of total Hg concentration and Hg isotopes. The GEM samples in the gold traps were processed following the same procedure. For data quality control, blanks, standards and references were periodically analyzed with samples.

2.4. Sample analysis

Mercury concentrations in the KMnO₄ solutions were analyzed with an atomic fluorescence spectrometer AF-610B (Beijing Rayleigh Analytical Instrument Corp., China), which used USEPA method 1631E (USEPA, 2002) as its working principle. About 100 μ L KMnO₄ solution was pre-reduced with hydroxylamine hydrochloride and then, was reduced with stannous chloride. The solution was purged with mercury free argon in a glass bubbler, and then trapped in gold traps. The mercury, adsorbed on the traps, was thermally released into an atomic fluorescence spectrometer for determination. Mercury concentrations in mercury gas generator (C, ng/mL) were calculated using Eq. (1) (Ukita, 1979).

$$C = \frac{3216522.61}{273.15 + T} \times 10 - \left(\frac{3240.871534}{273.15 + T} - 8.134459741 \right) \quad (1)$$

where T is the sampling temperature (°C).

Mercury isotopic ratios were determined with a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, Nu-Plasma Instruments, UK). The NIST SRM 997 T1 standard with exponential law and NIST SRM 3133 mercury standard-sample bracketing method were used to correct the mass bias of MC-ICP-MS. The detailed description of the operational steps and analytical parameters used throughout this study has already been reported in Lin et al. (2015). The mercury concentrations of KMnO₄ solutions were all higher than 1 ng/mL and were pre-reduced with hydroxylamine hydrochloride prior to mercury isotope analysis. δ -values and Δ -values were used to represent the mercury isotopic composition and MIF of mercury isotopes respectively. These parameters are given by Eqs. (2) and (3) (Blum and Bergquist, 2007).

$$\delta^{xxx}\text{Hg}(\text{‰}) = \left[\left(\frac{^{xxx}\text{Hg}/^{198}\text{Hg}}{\text{sample}} \right) / \left(\frac{^{xxx}\text{Hg}/^{198}\text{Hg}}{\text{standard}} - 1 \right) \right] \times 1000 \quad (2)$$

$$\Delta^{xxx}\text{Hg} = \delta^{xxx}\text{Hg} - \left(\delta^{202}\text{Hg} \times \beta \right) \quad (3)$$

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