



Fractionation of mercury stable isotopes during coal combustion and seawater flue gas desulfurization



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ABSTRACT

In the current study, fractionation of mercury isotopes during coal combustion and seawater flue gas desulfurization (SFGD) in a coal-fired power plant using a SFGD system was investigated. Fourteen samples were collected from the power plant. The samples were pretreated with a combustion-trapping method and were analyzed with a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Compared with the raw coal, the bottom ash was enriched with lighter mercury isotopes with $\delta^{202}\text{Hg}$ values ranging from -0.45 to -0.03% . The fly ash was enriched with lighter mercury isotopes with $\delta^{202}\text{Hg}$ values ranging from -1.49 to -0.73% for Chinese coal and from -1.47 to -0.62% for Indonesian coal. The $\delta^{202}\text{Hg}$ of fresh seawater and desulfurized seawater was found to be -1.32 and -0.32% respectively. These $\delta^{202}\text{Hg}$ values indicated that the desulfurized seawater was enriched with heavier mercury isotopes. Based upon the calculated results obtained from the mass balance equation, it was suggested that the stack emissions were enriched with lighter mercury isotopes. Mass independent fractionation was observed in most of the samples with a $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of approximately 0.96. The results help in improving the understanding of mercury isotope fractionation during coal combustion and SFGD, and are also useful in tracing the mercury emissions from coal fired power plants.

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1. Introduction

Mercury is a toxic heavy metal and due to its various species, it has a complicated biogeochemical cycle (Fitzgerald et al., 2007; Mason et al., 1994). Atmospheric mercury emissions originate mainly from the anthropogenic activities. One of such anthropogenic activities is the coal combustion, which is considered to be a dominant contributor to overall atmospheric mercury emissions (Pirrone et al., 2010). Three different forms of mercury are emitted into the atmosphere through the exhaust stacks of coal-fired power plants. These three forms include gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particulate bound mercury (PBM). GEM is relatively stable in the atmosphere and has a residence time of up to two years, while both RGM and PBM have residence times usually ranging from a few hours to a few weeks (Fitzgerald, 1995; Sheu and Mason, 2001). Both RGM and PBM have

higher water solubility and can be scavenged by both dry and wet deposition processes. Thus, RGM and PBM do not participate in the large-scale mercury transportation (Fitzgerald, 1995; Lamborg et al., 2002).

In order to undertake the isotopic and elemental analysis of mercury, the stable isotope analysis can be used for various samples originating from a wide domain, such as the atmospheric, aquatic and terrestrial environmental samples (Bergquist and Blum, 2009; Cooke et al., 2013; Point et al., 2011; Sherman et al., 2010). Previous reports have suggested that mass dependent fractionation (MDF) (Estrade et al., 2009; Foucher et al., 2009; Gratz et al., 2010) and mass independent fractionation (MIF) (Chen et al., 2012; Demers et al., 2013; Feng et al., 2010) of mercury isotopes can induce significant variations in isotopic composition of natural mercury in natural samples. The MDF and MIF of Hg provide information regarding the behavior of mercury isotopes and can be utilized to understand the sources and fate of mercury in the studied samples.

Previous studies (Biswas et al., 2008; Lefticariu et al., 2011; Sherman et al., 2012) have reported the isotope composition of mercury in coal, and the current data suggest that coal samples,

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originating from different geographical locations and in different coal-forming periods, display significant variations in isotope composition. Such coal samples can isotopically be distinguished from each other using the same specific methods as described in various studies (Biswas et al., 2008; Lefticariu et al., 2011; Sun et al., 2014). These studies (Biswas et al., 2008; Lefticariu et al., 2011; Sherman et al., 2012; Sun et al., 2014) also demonstrate that the stable isotopic analysis technique is not only a powerful tool to discriminate atmospheric mercury emitted from various coal-fired power plants (Lefticariu et al., 2011; Sherman et al., 2012), but can also help to assess the influence of mercury pollution on the surrounding environments.

During the coal combustion process in a coal-fired utility boiler, mercury (present in the coal) is transformed to Hg^0 in the flue gas. Subsequently during the flue gas purification, Hg^0 is oxidized to Hg^{2+} , which forms a complex with fly ash to produce PBM (Hower et al., 2010). The rest of Hg^{2+} remains in the flue gas together with other gases, mainly the sulfur dioxide and nitrogen oxides during the flue gas purification process. Due to its convenience and low cost operation, desulfurization is carried out using seawater in some coastal coal-fired power plants. In such power plants, with the removal of sulfur dioxide from the flue gas, most of the Hg^{2+} is also “washed” into the seawater. The physical transformations (condensation, evaporation and diffusion) and chemical reactions (oxidation, reduction and adsorption) lead to a certain extent of mercury stable isotope fractionation (Sun et al., 2013b).

The current work is aimed at tracing and assessing the transportation and transformation of mercury in coal during the process of coal combustion and flue gas purification using seawater in coal-fired power plants. Various samples of raw coal, bottom ash and fly ash, which were produced in air preheaters and electrostatic precipitators of a coal-fired power plant equipped with a seawater flue gas desulfurization (SFGD) system, were collected and analyzed for mercury isotope composition and fractionation. The results are expected to aid in enhancing the understanding of mercury transformations and hence, to help control the mercury pollution to some extent.

2. Experimental

2.1. Reagents and solutions

All the glassware was cleaned following the USEPA Method 1631 (USEPA, 2001). Ultrapure deionized water (resistivity > 18.2 M Ω cm) was used throughout the experiments. To prepare the bromine monochloride (BrCl) solution, 5.4 g of potassium bromide (reagent grade; Xilong Chemical Corp., China) was dissolved in 0.5 L of hydrochloric acid (technical super pure; Kunshan Jincheng Chemical Reagent Co., China) with solution stirred for approximately an hour. Then, 7.6 g of potassium bromate (reagent grade; Xilong Chemical Corp., China) was slowly added to the mixture while still stirring the mixture for another hour. The aqua regia was prepared by mixing 300 mL hydrochloric acid with 100 mL nitric acid (guaranteed reagent, Merck, Germany). Potassium permanganate (KMnO_4) solution was prepared by dissolving 0.06 g KMnO_4 (low in mercury; 99.0%; Alfa Aesar, USA) in 100 mL of 10% (v/v) sulfuric acid (guaranteed reagent; Merck, Germany). Bituminous coal (NIST 2692c), mercury standard solution (NIST SRM 3133), and thallium standard solution (NIST SRM 997) were purchased from the National Institute of Standards & Technology, USA. The UM-Almadén mercury isotope in-house standard was kindly provided by Dr. Blum of the University of Michigan, USA.

2.2. Sampling site and sample collection

Samples were collected from a coal-fired power plant, which was equipped with an SFGD and was located in Xiamen, China. Since 2013, the power plant has been using two types of coal, namely the Chinese coal (CC) and Indonesian coal (IC) for its 400 MW subcritical boilers. The flue gas purification system consists of a sequence of selective catalytic reduction (SCR) unit, air preheater (AP), electrostatic precipitators (ESPs) and SFGD (as shown in Fig. 1). It has been shown that in the SCR unit, Hg^0 could be oxidized to Hg^{2+} and the oxidation efficiency highly depended on halide oxidant composition of flue gas, which has been well studied by Zhao et al. (2015), even though the SCR unit is designed only for NO_x removal. AP is the device for exchanging heat between the boiler fuel gas and air. Both types of raw coal (CC-RC representing the Chinese coal raw coal and IC-RC representing the Indonesian coal raw coal), their corresponding bottom ashes (CC-BA representing the Chinese coal bottom ash and IC-BA representing the Indonesian coal bottom ash), and fly ashes in the AP (CC-FA-1 and IC-FA-1) and ESPs (CC-FA-2, CC-FA-3 and IC-FA-2, IC-FA-3) were collected from the bottom of each piece of equipment one week after the combustion of one type of coal. The raw coal samples were collected from the coal stacks in the storage. Several sub-samples (about 1 kg each) from different locations were collected, crushed and mixed. Then, a part of the mixed sample was ground and dried to make the final sample. The samples of bottom ash and fly ash were collected from the ash hopper. These were collected in a similar way as the raw coal samples. The samples were manually crushed, sieved and stored under dark, cold and dry conditions.

Fresh seawater was used to desulfurize the flue gas. The desulfurized (De- SO_2) seawater was aerated before being discharged into the adjacent sea area. Seawater samples (2 L each) were collected from the inlet and outlet of desulfurization tower and two aeration pools. These samples were filtered *in situ* with 0.45 μm filter membranes, and the filtered samples were preserved with 0.5% (v/v) BrCl solution (USEPA, 2002). The samples were brought to the laboratory and pretreated the same day samples were collected. The pretreated samples were stored in a refrigerator before analysis.

2.3. Sample pretreatment and analysis

For isotopic analysis, there are two methods by which mercury in solid samples can be extracted and preconcentrated into liquid samples. These methods are called the acid digestion method and the combustion-trapping method. Both methods were adopted and the corresponding results were compared in the current study.

For the first method, based upon the concentration of total mercury in the samples, about 10–150 mg of sample was weighed. The sample was digested with 5 mL aqua regia solution at 90 °C for 12 h. After cooling to room temperature, the sample was diluted to 20 mL with ultrapure deionized water and then, was filtered with a 0.22 μm filter membrane. Finally, the sample was preserved in the dark at 4 °C before further use.

The second method was based on a previous study (Sun et al., 2013a) and is illustrated in Fig. 2. A quartz tube (I.D.: 26 mm; O.D.: 28 mm; Length: 350 mm) was embedded in two tube furnaces (Xingyuan Electric Appliance Factory, China) in series. Oxygen gas (purity > 99.99%; Fuzhou Xinhang Industrial Gas Co., China.) was passed through the quartz tube with a flow rate of 12 mL/min, while the outlet of the quartz tube was immersed into a solution of 0.06% (m/v) KMnO_4 with 10% (v/v) H_2SO_4 . The weighed sample was placed in the quartz tube in furnace A. Furnace B was heated to and maintained at a temperature of 900 °C. Then, Furnace A was slowly

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