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Stable isotope composition of mercury forms in flue gases from a typical coal-fired power plant, Inner Mongolia, northern China

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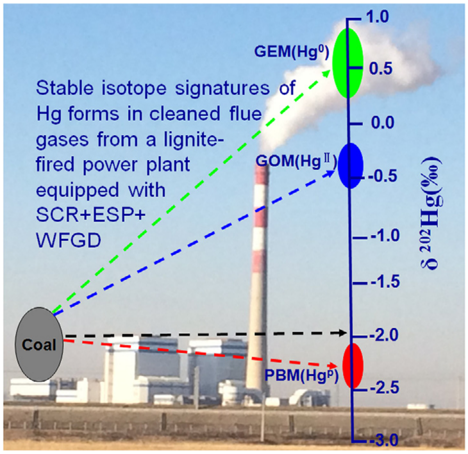
HIGHLIGHTS

- The first speciated Hg isotope ratios in coal combustion flue gases are presented.
- Significant Hg isotope kinetic MDF was observed during Hg forms transformation.
- Emitted gaseous Hg highly enriches in heavy Hg isotopes relative to feed coal.

GRAPHICAL ABSTRACT



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ABSTRACT

Mercury forms emitted from coal combustion via air pollution control devices are speculated to carry different Hg isotope signatures. Yet, their Hg isotope composition is still not reported. Here, we present the first onsite Hg isotope data for gaseous elemental Hg (GEM) and gaseous oxidized Hg (GOM) of flue gases from a typical lignite-fired power plant (CFPP). Significant mass dependent fractionation (MDF) and insignificant mass independent fractionation (MIF) are observed between feed coal and coal combustion products. As compared to feed coal (δ^{202}Hg = −2.04 ± 0.25‰), bottom ash, GEM and GOM in flue gases before and after wet flue gas desulfurization system significantly enrich heavy Hg isotopes by 0.7–2.6‰ in δ^{202}Hg, while fly ash, desulfurization gypsum and waste water show slight but insignificant enrichment of light Hg isotopes. GEM is significantly enriched heavy Hg isotopes compared to GOM and Hg in fly ash. Our observations verify the previous speculation on Hg isotope fractionation mechanism in CFPPs, and

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suggest a kinetically-controlled mass dependent Hg isotope fractionation during transformation of Hg forms in flue gases. Finally, our data are compared to Hg isotope compositions of atmospheric Hg pools, suggesting that coal combustion Hg emission is likely an important atmospheric Hg contributor.

1. Introduction

Mercury (Hg) is a toxic pollutant, which is released from both natural and anthropogenic sources [1–3]. Hg emitted from natural sources is thought to be mainly in the form of gaseous elemental Hg (GEM), whereas anthropogenically emitted Hg has a large portion of gaseous oxidized mercury (GOM) and particle-bound mercury (PBM) [4]. GEM has a relatively long atmospheric residence time (~1 year), and can be transported globally [4,5]. GOM and PBM are readily scavenged from atmosphere, and deposit in the vicinity of emission sources [4,6]. Modern industrialization has increased Hg loading into the surface environment by a factor of 2–5 [7,8]. Coal combustion is the main anthropogenic Hg source, reaching 700–900 tons/year into atmosphere [1,2,9]. Coal-fired power plants are considered to be the largest point Hg sources in most countries. However, the identification and quantification of Hg emitted from coal-fired power plants are still challenged.

Mercury stable isotope has a potential in tracing sources of Hg and geochemical processes [10–13]. A series of physicochemical reactions involving Hg, such as biotic and photochemical reduction [14–18], methylation [19–21], demethylation [22,23], volatilization [24], evaporation [25,26], and adsorption [27,28] can systematically seperate Hg isotopes via mass dependent fractionation (MDF) and mass independent fractionation (MIF). Previous studies have shown >10‰ variations in both MDF (indicated by δ^{202}Hg) and MIF of odd Hg isotopes (indicated by Δ^{199}Hg) in natural samples [10,29–33].

Biswas et al. [34] first showed that the MDF and MIF signatures of Hg isotopes in coal could be used as a diagnostic tool for “fingerprinting” Hg emissions from different coal sources by using a step heating combustion procedure to preconcentrate Hg in an oxidizing solution of 1% $KMnO_4$ and 1.8 M H_2SO_4. The distinguishability of different world regional coals by Hg isotope composition is further explored in Sun et al. [35] However, the air pollution control devices(APCDs) and speciated Hg conversion process possibly shifts the isotope composition of emitted Hg relative to combusted coal [35,36]. This would obscure the source tracing of Hg emissions from coal combustion [37,38]. By measuring Hg isotope composition in feed coal and its combustion products (i.e., bottom ash, fly ash and desulfurization gypsum), Sun et al. [36] estimated that the emitted total Hg from a typical CFPP enriched heavy Hg isotopes by ~0.3‰ in δ^{202}Hg relative to feed coal, and suggested that different Hg species in CFPP flue gasses might carry contrasting MDF signatures. Further, Sun et al. [35] developed a double-Rayleigh MDF model for Hg species in CFPP flue gasses, and predicted that GEM is enriched heavy isotope compared to GOM and PBM. Similarly, significant isotope fractionation is also observed in CFPP for other elements like S and Zn [39,40]. Direct Hg isotope measurement on different Hg species in CFPP flue gases is still lacking, which limit our ability to trace the contribution of coal combustion in atmospheric Hg pools [41–43].

In this study, we present the first onsite Hg isotope measurement on gaseous Hg (GEM and GOM) in flue gases of a CFPP from Inner Mongolia, North China. Our aims are to: (1) examine speciated Hg isotope shifts of coal combustion emissions relative to feed coal; (2) understand Hg isotope fractionation mechanisms during coal combustion and transport of flue gases through post-combustion APCDs; (3) test if the previous CFPP Hg isotope fractionation models can correctly predict our observations on Hg forms.

2. Experimental section

2.1. Configuration of CFPP and sampling sites

The sampling was carried out in a typical 300 MW subcritical CFPP fed by pulverized lignite in a power plant, Mongolian, China. The studied CFPP is installed with a selective catalytic reduction system (SCRs) to control NOx emissions, followed by electrostatic precipitators (ESPs) to remove particles and wet limestone flue gas desulfurization systems (WFGD) to control SO_2 emissions. During the sampling period, the studied CFPP was operated under normal conditions. The configuration of the studied CFPP and sampling sites are showed in Fig. 1.

2.2. Sampling and processing

A C-5000 source sampling system (Environmental Supply Company, USA) was used to sample Hg forms in flue gases at the inlet and outlet of WFGD according to the Ontario Hydro Method [44] in the field because of high percentage of PBM in flue gas before the ESPs that can be absorbed on the filter and seriously affected mercury forms of the sampling flue gas and frequently blocked the sampling device. The Hg forms in coal combustion flue gases were withdrawn iso-kinetically into the sampling train through a probe/filter system maintaining at 120 °C. PBM was recovered from the particle captured in the filter. However, due to >99.6% particle removal efficiency of ESPs for the studied power plant[45], we did not collect enough particle samples on the filter for Hg isotope measurement. Gaseous Hg was collected in the sampling train composed of a series of impingers in an ice bath at the inlet (i) and outlet (o) of WFGD. The first three impingers filled with 1.0 mol/L KCl solution were used to collect GOM. GEM is collected in the subsequent impingers including one impinger containing a mixture of 5% HNO_3 and 10% peroxide H_2O_2, and three impingers, each containing a mixture of 4% $KMnO_4$ and 10% H_2SO_4 [34,37]. After each sampling campaign, the three combined KCl solution, one $HNO_3-H_2O_2$ solution and three combined $H_2SO_4+KMnO_4$ solution were immediately transferred into three 250 ml pre-cleaned boron silicon glass bottles as GOMi/o (KCl), GEMi/o (HNO_3–H_2O_2) and GEMi/o ($KMnO_4$–H_2SO_4), respectively. The Hg concentrations in collected solutions were initially measured in the field by Lumex R915 M. According the results, we adjusted appropriate sampling flow rates and sampling time to collect enough Hg for isotope measurement.

Feed coal was sampled from the pneumatic conveying duct connected to the CFPP. Limestone and fresh processing water were collected from the inlet of WFGD. Bottom ash from the grate below the boiler, fly ash from all hoppers of ESPs, desulfurization gypsum and desulfurization recycling waste water for WFGD, were collected shortly after combustion of feed coal. The solid samples were stored in polyethylene bags, and water samples were stored in 1 l PTFE bottles. The sampling frequency of solid and water samples (generally 2–3 times a day) was determined by the sampling arrangement of the flue gases. The total sampling duration is