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Spatial-temporal distributions of gaseous element mercury and particulate mercury in the Asian marine boundary layer

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HIGHLIGHTS

- Spatial-temporal distributions of GEM and Hg^P in the Asian MBL were discussed.
- Size distributions of Hg^P were bi-modal in spring and uni-modal in fall.
- The coarse mode was dominant in spring while the fine mode was dominant in fall.
- The coarse particles contributed more than 90% to the total dry deposition of Hg^P.

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ABSTRACT:

We determined the concentrations of gaseous element mercury (GEM) and particulate mercury (Hg^P) in the Asian marine boundary layer (MBL) during the spring and fall of 2013 and 2014 to investigate the spatial-temporal distributions of GEM and Hg^P. A cascade impactor was used to collect Hg^P in nine size fractions ranging from 10 μm to <0.4 μm. The concentrations of Hg^P in PM_{10} (hereafter referred to as HgP 10) tended to decrease from the land to the open sea both in spring and fall. The mean (±SD) concentrations of HgP 10 during spring and fall were 15.3 ± 9.1 and 15.8 ± 4.4 pg m^{-3} respectively, while the mean GEM concentration during the entire study period was 2.02 ± 1.08 ng m^{-3} (N = 12,341), which was much higher than those of other remote oceans. Moreover, the size distributions of Hg^P was bi-modal during spring, and Hg^P was found mainly (57%) in coarse fractions (2.1–10 μm), while Hg^P was dominated by fine particles (<2.1 μm) during fall. The concentrations of GEM and HgP 10 in the Bohai Sea (BS) were generally higher than those in the Yellow Sea and East China Sea. Furthermore, the HgP 10 concentrations were slightly higher during fall than during spring except the data measured in the BS for its specific location. The average dry deposition fluxes of Hg^P were calculated to be 2.77 ng m^{-2} d^{-1} during spring and 1.92 ng m^{-2} d^{-1} during fall, respectively, which were comparable to those measured at rural sites in North America, but considerably lower than those measured in urban cities in China. Additionally, compared to fine particles, coarse particles contributed more than 90% to the total dry deposition of Hg^P due to higher deposition velocities.

1. Introduction

Mercury (Hg) is considered to be a global persistent pollutant due to its ability to undergo long range transport in the atmosphere (Schroeder and Munthe, 1998). Moreover, the bioaccumulation and biomagnification of methylmercury in the food chain is a primary ecotoxicological concern related to Hg in the global environment (Ci et al., 2011c). Hg is emitted into the atmosphere from various natural and anthropogenic sources (Pacyna et al., 2003, 2006, 2010; Schroeder and Munthe, 1998; Zhang et al., 2015). The fate and transport of Hg released into the atmosphere are determined by its physical and chemical properties and transformation processes. Atmospheric Hg exists mainly in three operationally defined forms, including gaseous elemental Hg (GEM or Hg^0), reactive gaseous Hg (RGM = $HgCl_2$ + $HgBr_2$ + HgBrOH + …), and particulate Hg (Hg^P) (Choi et al., 2008; Gabriel et al., 2005; Schroeder and Munthe, 1998). The ratios of GEM, RGM, and Hg^P to total atmospheric Hg (THg^a = GEM + RGM + Hg^P) vary geographically depending on

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different land surface types, chemical environments, and human influences. However, very little is known about Hg^P in comparison to GEM and RGM, and even less is known about the size-fractionated Hg^P in the atmosphere. Generally, Hg^P constitutes a small percentage of THg^a at rural sites (Feddersen et al., 2012; Kim et al., 2012; Mao and Talbot, 2012; Xu et al., 2013), but it contributes a significant portion of the deposition of Hg to the land and ocean. Previous studies in China, Japan, Europe, and North America showed that the dry deposition of Hg^P was similar in magnitude to the wet deposition of Hg (Gencarelli et al., 2014; Landis and Keeler, 2002; Sakata and Marumoto, 2005; Zhu et al., 2014). Hg^P may actually play a disproportionately large role in the deposition of atmospheric Hg.

In recent decades, research on the sources, transport, and deposition of Hg^P has gained increasing attention as it is critical in fully understanding the behavior and cycling of Hg in the environment. Although the size distribution of Hg^P has been reported in many studies, most of them concentrated on urban or rural sites, for example, the Hg^P measurements at urban and suburban sites in Beijing showed that the highest Hg concentration was found in the size fraction less than 1.1 μm (Wang et al., 2006). Tsai et al. (2003) reported that the Hg^P in PM_{10} (hereafter referred to as HgP 10) measured in Tainan showed regular daily variation with the higher values at daytime and lower values at nighttime, and there was more Hg^P in fine particles (<2.5 μm) than in coarse particles (2.5–10 μm) (generally > 70%). Xiu et al. (2005) studied the size-fractionated Hg^P in Shanghai and found that Hg^P mainly concentrated on fine particles and approximately 50–60% of Hg in PM_8 concentrated on $PM_{1.6}$. Nine and ten size fractions of Hg^P were collected by Feddersen et al. (2012), Kim et al. (2012), Xu et al. (2013), and Zhu et al. (2014) to evaluate the dominant fractions and variability of Hg^P in North America, South Korea, and China, respectively, where the size distribution of Hg^P changes due to different meteorological conditions, physical and chemical processes (e.g., adsorption and nucleation), and sources of ambient particles.

Atmospheric emissions of Hg from East Asia are much higher than those from other continents in global emission inventories (Pacyna et al., 2006, 2010). China is the largest contributor to global atmospheric Hg, and anthropogenic Hg emissions are likely to further increase with the expansion of nonferrous production and coal combustion (Streets et al., 2005; Wu et al., 2006; Zhang et al., 2015). Several atmospheric GEM measurements had been conducted in the downwind regions and sites of East Asia, including the Yellow Sea (YS), East China Sea (ECS), and some coastal sites of the YS and ECS (Ci et al., 2011a, b; 2015; Friedli et al., 2004; Jaffe et al., 2005; Nguyen et al., 2007, 2010; Xia et al., 2010). However, there is little documentation on the GEM levels in the Bohai Sea (BS) and ECS. Besides, little equivalent information on the spatial and size distributions of Hg^P in the Asian marine boundary layer (MBL) is available. The descriptions of source, spatial and size distributions, and removal processes of Hg^P in the MBL are the prerequisite to assess its impact on marine environment. Additionally, atmospheric deposition is the main source of Hg to the open ocean and plays a large role in determining the pool of Hg^{II} available for reduction (Mason and Sheu, 2002). Therefore, this paper aims to identify the spatial distributions of GEM and Hg^P in the Asian MBL, compare the seasonal variability of GEM and Hg^P, and estimate the dry deposition flux of Hg^P based on the concentrations of each size-fractioned Hg^P. To our knowledge, this is the first comprehensive study of the size distributions of atmospheric Hg^P in the Asian MBL. Through the data presented here, we hope to provide fundamental data for the further research on GEM and Hg^P cycling in the marine environment.

2. Materials and methods

2.1. Study area

Fig. 1 shows the sampling regions, including the majority areas of the BS, YS, and ECS. The BS is an inner sea, while the YS and ECS are semi-enclosed marginal seas. In addition, the sampling regions are located in the downwind of the East Asia, which contributed about half to the global Hg emission from anthropogenic sources (Pacyna et al., 2006, 2010), thus the study regions may be significantly influenced by the anthropogenic emissions of Hg (e.g., fossil fuel combustion, nonferrous metals smelting, and cement production) from China, Korean Peninsula, and Japan (Pacyna et al., 2006, 2010; Wu et al., 2006; Zhang et al., 2015).

2.2. Sampling and analytical methods

2.2.1. Atmospheric Hg^P measurements

Two oceanographic cruises onboard the R/V *Kexue* III were conducted in the ECS during the spring (21 June to 19 July) and fall (27 October to 18 November) of 2013. An Andersen cascade impactor was deployed on the top deck of the R/V at a height of 15.5 m above the sea level (a.s.l.). Another two campaigns onboard the R/V *Dongfanghong* II were carried out in the YS and BS during the spring (27 April to 20 May) and fall (5–24 November) of 2014. The impactor was mounted on the top of the R/V at a height of 17.0 m a.s.l.. To reduce the contamination from exhaust plume of the ships as little as possible, we stopped sampling when R/V arrived at sampling stations.

The Andersen impactor has been widely used to collect Hg^P in the atmosphere (Feddersen et al., 2012; Kim et al., 2012; Zhu et al.,

Fig. 1. The location of the sampling regions (Bohai Sea, Yellow Sea, and East China Sea) during the spring and fall cruises of 2013 and 2014.