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Four-year record of mercury wet deposition in one typical industrial city in southwest China

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HIGHLIGHTS

- Atmospheric Hg is primarily associated with local emission sources and long-range transport.
- The below-cloud scavenging is the predominant mechanism contributing Hg to precipitation.
- The formation of MeHg in atmosphere and methylation are influenced by the concentration of RHg, besides the local THg load.

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ABSTRACT

During the period from December 2010 to November 2014, long-term monitoring of Hg wet deposition was conducted at three sites in Chongqing. The four-year volume-weighted mean concentrations (VWC) of total mercury (THg) and methylmercury (MeHg) in precipitation were 34.25 ng L^{-1} and 0.48 ng L^{-1}, respectively. The average annual wet deposition fluxes were 37.83 ± 11.53 μg m^{-2} yr^{-1} for THg and 0.61 ± 0.19 μg m^{-2} yr^{-1} for MeHg. Besides, the average proportion of MeHg in THg was 1.41%. These data were well ahead of values observed in most of other areas. The annual VWC of Hg rose remarkably in 2012 and then reached a plateau or climbed mildly in the following 2 years, while its annual wet deposition fluxes saw an upward trend throughout the whole period. In addition, the high figures of Hg concentration were generally found in the non-monsoon seasons, but its elevated wet deposition fluxes normally appeared in the rainy seasons. These characteristics of inter-annual and seasonal changes for VWC and fluxes were observed at every sampling site in this study as well. Besides, there were significantly spatial distributions for VWC and fluxes of THg in the descending order of the downtown (NA), the suburban (BB) and the controlled site (JY). While for MeHg, BB had the largest values, followed by NA and JY. So apart from THg load, the formation of MeHg was influenced by other factors in Chongqing, like the concentration of reactive mercury (RHg) in precipitation. Additionally, particulate bound mercury (PHg) is the dominant form among various Hg species, and atmospheric Hg is effectively eliminated during the initial period of the rain event and the below-cloud scavenging is the predominant mechanism contributing Hg to precipitation.

1. Introduction

Mercury (Hg), the only heavy metal in liquid at normal temperature, can generate a wide range of air pollution across boundaries because of its volatility and long-range transport in the atmosphere. It has been listed as a priority hazardous pollutant by a number of international organizations and has continued to be a hot issue in the related field of environmental science (Wang et al., 2004; Keeler et al., 2005; Wu et al., 2008). Mercury in the atmosphere, unlike other harmful heavy metals which normally exist as a particulate form, presents primarily in the gas phase, which is referred to as gaseous elemental mercury (GEM, Hg^0) accounting for approximately 95% of the total amount (Cohen et al., 2004; Lindberg et al., 2007; Faïn et al., 2009). This Hg species could be effectively scavenged by wet or dry deposition after oxidation and adsorption onto aerocolloid's surface or dissolution in atmospheric

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droplets(Fu et al., 2012; Wang et al., 2014). Two other Hg species in the atmosphere including gaseous oxidized mercury (GOM) and particulate bound mercury (PHg) (Caffrey et al., 2010; Che-Jen and Pehkonen, 2012), constituting about 5% combined of total Hg, can be directly deposited via dry or wet deposition after a short residence time of several hours to a week (Fitzgerald, 1995; Lamborg et al., 2002; Fu et al., 2010) due to their high surface reactivity and water solubility. Atmospheric deposition, especially wet deposition which mainly scavenges GOM and PHg, has a significantly positive effect on wiping off the atmospheric mercury accordingly (Guentzel et al., 2001; Sakata and Marumoto, 2005). Therefore, making an investigation on concentration and deposition flux of Hg in wet deposition has valuable implications to the comprehension of the fate of Hg in the atmospheric, terrestrial and aquatic systems.

Heretofore, numerous monitoring networks have been built to provide accurate and useful data to estimate long-term trends of Hg in atmospheric deposition at regional scales. In North America, for instance, there are 102 active Mercury Deposition Network (MDN) sites to provide services (National Atmospheric Deposition Programme, 2007). And Canadian Atmospheric Mercury Measurement Network (CAMNet), built by Environment Canada, also owned 11 active stations in 1994 (CAMNet, 2006). Studies about mercury in wet deposition become increasingly important for human health and wildlife and have attracted considerable attention of domestic and overseas scholars as well as correlative agencies, but most of study areas mainly focus on outskirts, coastal or remote regions (Xu et al., 2014; Marumoto and Matsuyama, 2014; Gichuki and Mason, 2014; Fu et al., 2010; Choi et al., 2008; Guo et al., 2008a,b). There are less reports related to Hg in wet deposition in industrial city worldwide. With the development of industry, air pollution has been regarded as a detrimental by-product, especially for most developing countries, whose economic and technological abilities cannot ensure optimized discharge of wastes. The concentration of atmospheric Hg has tripled averagely in recent years compered to the preindustrial value (Feng et al., 2009). Through calculation, Asia is considered to be the largest source region of atmospheric Hg (more than 1000t), accounting for up to 50% of global emissions (Pacyna et al., 2006). Combustion of fossil fuel (e.g., coal and petroleum), the main source of energy industrial manufacture needs, has a vital contribution to this high level. China is a large emitter of atmospheric Hg (Fu et al., 2012), and there were already some monitoring researches about Hg in precipitation as well (Liu et al., 2000; Guo et al., 2008a,b; Fu et al., 2010; Wang et al., 2014; Zhao et al., 2015). But the lack of long-term successive research about industrial city in China is a defect, therefore, plenty of work need to be done compared to other countries. After all, Hg pollution in China is still a cause for concern (Pacyna et al., 2006; Fu et al., 2012), especially the southwest of China, where has been recognized as one of the seriously affected areas (Streets et al., 2005). Chongqing, located next to the upper reaches of the Yangtze River and in the eastern Sichuan Basin, is a municipality with typical industry in Southwestern China, so we selected three sampling sites in this city to research and analyze the Hg in precipitation. Several years ago, our study reported the results about the volume-weight mean (VWM) concentrations and deposition fluxes of THg and total methylmercury (MeHg) in precipitation during one year period from July 2010 to June 2011 (Wang et al., 2012, 2014). However, limited data are available in terms of long-term continuous monitoring. Therefore, the field experiment for 4 years in a row was conducted so as to more accurately measure the values of THg and MeHg in wet deposition and depict their patterns of spatial and temporal distributions. Simultaneously, we analyzed other forms of Hg in samples, including dissolved mercury (DHg), particulate bound mercury (PHg), dissolved methylmercury (DMeHg), particulate bound methylmercury (PMeHg) and reactive mercury (RHg), to more deeply understand their change characteristics and contributing factors.

2. Materials and methods

2.1. Sites description

Three representative monitoring sites are located in different kinds of places in Chongqing (Fig. 1). The sampling site of Nanan district (NA; 29°31′36.2″N, 106°33′35.0″E) is in a downtown area with high population density and adjacent to shopping malls and streets. Another site (BB; 29°49′36.2″N, 106°22′42.9″E) with good vegetation cover is situated in Beibei district, and this site is commonly regarded as a representative suburban and residential area. The third one (JY; 29°49′46.1″N, 106°22′42.9″″E) is located in the Jinyun mountain near rural regions and covered by a large area of forest, remote from disturbance of human activities, and thus JY is considered as a typical controlled site. Other complementary descriptions of these monitoring sites are available in our published papers (Wang et al., 2012, 2014).

2.2. The sampler and sampling methods

The automatic precipitation sampler (APS-3A; Changsha Xianglan Scientific Instruments Co., Hunan, China) was installed on unsheltered roof of building at each monitoring site and used to collect rain samples in the current research during the four-year period from December 2010 to November 2014. The components and operating mechanism of the sampler were explained in our former reports (Wang et al., 2012). In brief, it was made up of (from top to bottom) a dust cover, a rain funnel, eight Teflon tubes for connecting the funnel to eight sampling borosilicate bottles and a small portable refrigerator (4 °C) for storing the bottles with rain samples. In addition, there are two essential elements, one is a moisture sensor in the back of the sampler and the other is a rain gauge which was installed in the left. When a precipitation event occurs with rainfall over 5 mm, the moisture sensor is triggered to let the dust cover open and then the rain funnel rises up automatically to collect rainwater. After that, the rainwater flows into one borosilicate bottle via the connective Teflon tube. We set the period from the beginning time of rain to the next 9 am as one rain event and the rainwater collected during this period as one sample. Then another clean tube and bottle would be changed for the next rain event. When the signal of precipitation can not be detected by the sensor for consecutive 20 min, the funnel goes down and the cover is closed avoiding contamination. All trapped rain samples were shipped at 4 °C to our laboratory once a week for further processing.

Every sampler was washed monthly with HCl (10%, v/v) and ultra-pure water (18.2 MΩ cm^{-1}) to insure the funnel and tubes were clean and were not blocked by some small objects like dead insects. Besides, all sampling bottles and other borosilicate glassware were thoroughly cleaned by dipping in dilute nitric (25%, V/V; Chuandong, Chongqing, China) and hydrochloric acids (2%, V/V; Chuandong, Chongqing, China) for at least 24 h. Before using, all of glassware were rinsed with ultra-pure water and then baked for 1 h in the muffle furnace at 500 °C one day in advance.

2.3. Sample disposition and analysis methods

At every sampling site, a certain amount of each rain sample was removed on the spot to measure some related parameters, mainly including the pH and the concentrations of main anions. The remaining sample was divided into two acid-cleaned borosilicate