Atmospheric Environment 61 (2012) 94–102

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Atmospheric particulate mercury: Concentrations and size distributions

Pyung-Rae Kim [a], Young-Ji Han [a,*], Thomas M. Holsen [b], Seung-Muk Yi [c]

[a] Department of Environmental Science, College of Natural Science, Kangwon National University, 192-1 Hyoja-2-dong, Chuncheon, Kangwon-do 200-701, Republic of Korea
[b] Department of Civil and Environmental Engineering, Clarkson University, 8 Clarkson Ave., Potsdam, NY 13699-5710, USA
[c] Department of Environmental Health, Graduate School of Public Health, Seoul National University, Gwanak 599, Gwanak-ro, Gwanak-gu, Seoul 151-742, Republic of Korea

HIGHLIGHTS

- ► Size distributions of atmospheric particulate Hg (PHg) were measured in urban and rural areas.
- ► The size distribution of PHg was frequently observed to be *uni-modal*.
- ► The fine mode was dominant in winter while the coarse mode became important in summer.
- ► PHg in fine mode increased due to the partitioning of gaseous Hg onto the fine particles in winter.

ARTICLE INFO

Article history:
Received 2 April 2012
Received in revised form
4 July 2012
Accepted 6 July 2012

Keywords:
Particulate mercury
Size distribution
Urban
Rural
Oxidation

ABSTRACT

In this study, the size distributions of atmospheric particulate mercury (PHg) were measured in both urban and rural areas during the summer, fall, and winter. Both PHg concentrations and the contribution of PHg to total PM aerosol were higher at the urban (PHg = 6.8 ± 6.5 pg m^{-3}, PHg/total PM = 0.18 pg μg^{-1}) than at the rural site (PHg = 4.6 ± 2.7 pg m^{-3}, PHg/total PM = 0.06 pg μg^{-1}). Based on size-distribution measurements, the fine mode was the dominant size at both sites in winter while the coarse mode became more important during summer. In winter PHg concentrations in the fine mode increased because of the effective adsorption of gaseous Hg onto the fine particles at the low temperature and increased Hg oxidation reactions in the presence of high particles concentrations. During winter elevated concentrations of total PHg were measured when the prevailing winds were northwesterly originating in China.

1. Introduction

Mercury (Hg) is a toxic heavy metal of concern throughout the northern hemisphere. Its major anthropogenic sources include coal-fired power plants, non-metal smelters, and waste incinerators. These sources emit 1230–2890 ton yr^{-1} globally (UNEP, 2008). Hg generally exists in inorganic forms in ambient air and does not constitute a direct public health risk at the level of exposure usually found (Driscoll et al., 2007). However, once inorganic Hg is deposited into aquatic systems it can be transformed into methyl mercury (MeHg) by sulfate reducing and other types of bacteria in anoxic sediments and in the water column, and readily bioaccumulate (Fleming et al., 2006; U.S. EPA, 2001). This process results in human exposure to Hg to be due primarily to the consumption of contaminated fish.

Many studies have found that atmospheric deposition of inorganic Hg is the primary indirect source of MeHg found in aquatic systems. Modeling work by Han et al. (2008) indicated that decreased atmospheric Hg deposition contributed to marked decreases in MeHg concentrations in blood of the common loon in south-central New Hampshire. Similarly the long-term METAALICUS (Mercury Experiment to Assess Atmospheric Loading in Canada and the United States) project showed that the Hg concentration in fish generally is highly correlated with variations in atmospheric mercury deposition (Hammerschmidt and Fitzgerald, 2006; Orihel et al., 2007).

Atmospheric Hg generally exists in three forms including gaseous elemental mercury (Hg^0; GEM), gaseous oxidized mercury (Hg^{II}), and particulate mercury (PHg). These three types of Hg have different physical and chemical properties. GEM is the predominant form of Hg in ambient air; however, Hg^{II} and PHg are more important with respect to atmospheric deposition due to their large dry deposition velocities and scavenging coefficients (Shannon and Voldner, 1995). Although atmospheric deposition has been suggested to be a critical mechanism related to MeHg levels in aquatic systems, it is difficult to quantify the total amount of Hg deposited. Direct measurement of total wet Hg deposition is widely measured

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[*] Corresponding author. Tel.: +82 33 250 8579; fax: +82 33 251 3991.
E-mail address: youngji@kangwon.ac.kr (Y.-J. Han).

1352-2310/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.atmosenv.2012.07.014

using rain and snow samplers although individual deposition amounts of Hg^{II} and PHg cannot be determined this way.

There are no widely accepted measurement techniques for Hg dry deposition even though progress has been made using surrogate surfaces (Lyman et al., 2007; Marsik et al., 2007; Lai et al., 2011; Huang et al., 2011) and micrometeorological methods (Lindberg et al., 2002; Poissant et al., 2004). Dry deposition measurements of Hg often have large uncertainties due to the very low air concentration of Hg^{II} and PHg, the uncertainties associated with the use of surrogate surfaces, the small vertical gradients in its concentration, and the effects of fast chemical reactions and advection from local sources (Zhang et al., 2009). Therefore, modeling work is commonly used to estimate Hg dry deposition using a resistance approach.

In order to estimate the dry deposition of a particulate pollutant, particle diameter plays a key role since it affects gravitational settling, aerodynamic resistance, and surface resistance (Zhang et al., 2001). However, there have been few studies investigating the size distribution of PHg in ambient air. Many studies have estimated the depositional flux of PHg based on the assumption of a bi-modal distribution of PHg in which 70% of the mass is 0.68 μm and 30% is 3.5 μm (Landis et al., 2002; Han et al., 2008; Lai et al., 2011). This distribution was first introduced during the Atmospheric Exchange Over Lakes and Ocean Study (AEOLOS) where the size distribution of PHg was measured in downtown Detroit during a short duration in March 1–18, 1994 (Keeler et al., 1995; Landis et al., 2002). In reality the size distribution of PHg changes due to physical and chemical processes including adsorption, nucleation, and other gas-particle partitioning mechanisms, ambient particle concentrations and meteorological conditions. To better understand PHg fate and transport, seasonal variations in size segregated PHg concentrations need to be measured. Two studies measuring the size distribution of PHg were conducted in the major cities, Beijing and Shanghai China (Wang et al., 2006; Xiu et al., 2009); however, a detailed analysis of the full size distribution of PHg was not possible with the limited number of size cuts (1.6, 3.7, 8.0, 18 μm) used.

In Korea the history of atmospheric Hg measurements are relatively shorter than in the USA and Canada. Total gaseous mercury (TGM) was first measured by Kim and Kim (2000) starting in the late 1980s in Seoul, Korea. They reported very high concentrations of 14.4 ± 9.8 ng m^{-3}. More recent studies reported much lower TGM concentrations ranging from 2.1 to 3.9 ng m^{-3} (Kim et al., 2002, 2011; Shon et al., 2008; Gan et al., 2009; Nguyen et al., 2010). Measurements of speciated Hg concentrations in Korea were first reported in 2009 (Gan et al., 2009; Kim et al., 2009; Ahn et al., 2011), and are quite scarce.

This study is one of the first to measure the size distribution of atmospheric PHg in both urban and rural settings during the summer, fall, and winter, in order to identify factors controlling its variability. The seasonal and spatial variations in the size distribution of PHg were identified, and the gas-particle partitioning of Hg is discussed.

2. Materials and methods

2.1. Sampling

Particle samples were collected at two sites using multi-stage impactor. One site is in a small city, Chuncheon, Korea, which is surrounded by mountains which limits the transport of locally emitted air pollutants while the other is located in Seoul, the most urbanized area of Korea (Fig. 1). Chuncheon is located northeast of urban and industrial areas of Korea where large anthropogenic Hg sources are located (Fig. 1); therefore, air pollutants can be transported to Chuncheon when there are prevailing westerly winds.

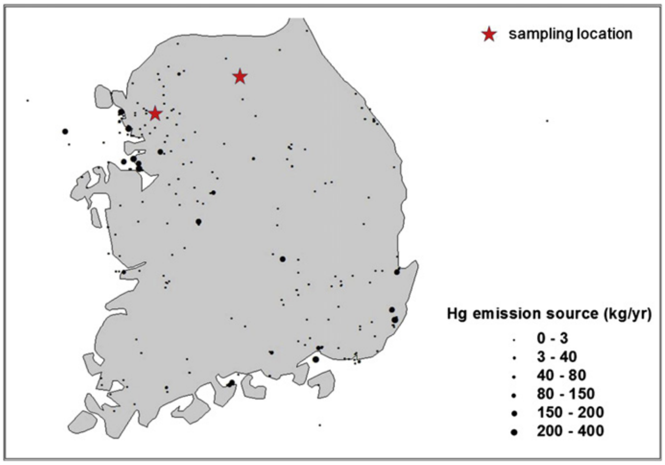

Fig. 1. Anthropogenic Hg sources (circle symbol) in Korea and two sampling sites (cross symbol) in Chuncheon and Seoul (Seo, Personal communication).

Measurements were made using an eight-stage MOUDI (Micro Orifice Uniform Deposit Impactors, Midel M 100R, MSP Corp) with Zeflour filters (Pall corp.) deployed on the roof of the four-story Kangwon National University Sciences building in Chuncheon and on the top of the Graduate School of Public Health in Seoul National University in Seoul. Each 10 sets of size-segregated particles (18–10, ~5.6, ~3.2, ~1.8, ~1.0, ~0.56, ~0.32, and ~0.18 μm) were collected using a MOUDI in Chuncheon and Seoul for 48 h each (00:00–00:00) at a flow rate of 30 L min^{-1} in summer ($N = 5$), fall ($N = 5$), and winter ($N = 10$) (Table 1).

A cascade impactor (Model 20-800, Tisch) with quartz filters (Tisch Environmental, Inc.) was used when the MOUDI was not

Table 1
PHg concentrations and meteorological condition in two cities (Note that * indicates the PHg concentration in PM_{10} while others show the PHg concentration in PM_{18}).

	PHg conc. (pg m^{-3})	PHg/PM (pg $μg^{-1}$)	Wind speed (m s^{-1})	Temp. (°C)	Note
Chuncheon (**rural site**)					
2009/11/05	3.1	0.06	0.70	11.35	Fog 3.5 h
2009/11/09	1.3	0.17	2.15	13.00	
2009/11/17	3.8	0.34	0.90	−1.10	
2009/11/20	6.7	0.21	0.75	0.10	Snow
2009/11/23	6.2	0.09	0.40	4.30	
Fall Avg.	4.2	0.17	0.98	5.53	
2009/12/02	8.5	0.15	0.50	2.75	Fog 1.5 h
2009/12/05	2.9	0.12	2.10	−2.55	Snow
2009/12/08	6.9	0.14	0.40	−0.60	Fog 7 h
2009/12/17	6.6	0.26	1.80	−8.45	
2009/12/20	8.3	0.21	0.95	−6.40	
Winter Avg.	6.7	0.17	1.15	−3.05	
2010/08/17*	2.5	0.07	0.83	27.57	Rain
2010/08/27*	0.9	0.03	0.70	24.83	Rain
2010/08/30*	1.6	0.07	0.83	24.97	Rain
Summer Avg.	1.7	0.06	0.79	25.79	
Seoul (**urban site**)					
2009/12/29	12.2	0.22	3.30	−4.25	
2010/01/01	6.7	0.22	2.95	−5.60	Snow
2010/01/04	8.9	0.43	2.95	−7.90	Snow
2010/01/07	18.9	0.39	1.70	−9.05	Fog 10 h
2010/01/10	14.2	0.27	2.00	−4.30	Fog 20 h
Winter Avg.	12.2	0.31	2.58	−6.22	
2010/07/19	1.6	0.34	3.27	27.57	
2010/07/21	1.3	0.18	3.63	26.43	Rain
2010/07/23	1.3	0.21	2.43	25.33	Rain
2010/07/25	1.5	0.11	2.80	26.10	Rain
2010/07/27	1.1	0.05	2.43	26.90	
Summer Avg.	1.4	0.18	2.91	26.47	