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Characteristics of atmospheric mercury deposition and size-fractionated particulate mercury in urban Nanjing, China

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Abstract

A comprehensive measurement study of mercury wet deposition and size-fractioned particulate mercury (Hg^P) concurrent with meteorological variables was conducted from June 2011 to February 2012 to evaluate the characteristics of mercury deposition and particulate mercury in urban Nanjing, China. The volume weighted mean (VWM) concentration of mercury in rainwater was 52.9 ng L^{-1} with a range of 46.3–63.6 ng L^{-1}. The wet deposition per unit area was averaged 56.5 µg m^{-2} over 9 months, which was lower than that in most Chinese cities, but much higher than annual deposition in urban America and Japan. The wet deposition flux exhibited obvious seasonal variation strongly linked with the amount of precipitation. Wet deposition in summer contributed more than 80 % to the total amount. A part of contribution to wet deposition of mercury from anthropogenic sources was evidenced by the association between wet deposition and sulfates, and nitrates in rainwater. The ions correlated most significantly with mercury were formate, calcium and potassium, which suggested that natural sources including vegetation and resuspended soil should be considered as an important factor to affect the wet deposition of mercury in Nanjing. The average Hg^P concentration was 1.10 ± 0.57 ng m^{-3}. A distinct seasonal distribution of Hg^P concentrations was found to be higher in winter as a result of an increase in the PM_{10} concentration. Overall, more than half of Hg^P existed in the particle size range less than 2.1 µm. The highest concentration of Hg^P in coarse particles was observed in summer while Hg^P in fine particles dominated in fall and winter. The size distribution of averaged mercury content in particulates was bimodal with two peaks in the bins of < 0.7 µm and 4.7–5.8 µm. Dry deposition per unit area of Hg^P was estimated to be 47.2 µg m^{-2} using meteorological conditions and a size-resolved particle dry deposition model. This was 16.5 % less than mercury wet deposition. Compared to Hg^P in fine particles, Hg^P in coarse particles contributed more to the total dry deposition due to higher deposition velocities. Negative correlation between precipitation and the Hg^P concentration reflected the effect of scavenging of Hg^P by precipitation.

ACPD
13, 28309–28341, 2013

1 Introduction

Mercury (Hg) is a toxic and persistent global pollutant that can cause serious negative effects on human health and ecology via bioaccumulation of methylated mercury through the food chain in aquatic systems (Lindqvist, 1991; Schroeder and Munthe, 1998). Atmospheric mercury exists in three forms due to different chemical and physical property: gaseous elemental mercury (GEM), reactive gaseous species (RGM) and particulate mercury (Hg^P). GEM, the predominant form (> 95 %), is very stable in the atmosphere with a lifetime of 0.5 ∼ 2 yr (Schroeder and Munthe, 1998). In contrast, since RGM and Hg^P have significantly higher reactivity, deposition velocities, and water solubility than GEM, deposition of atmospheric mercury is largely dominated by RGM and Hg^P (Fu et al., 2010a). Atmospheric deposition is widely recognized as the main process for scavenging of atmospheric mercury and an important source of mercury to terrestrial and aquatic ecosystems (Lindberg et al., 1998; Miller et al., 2005; Selvendiran et al., 2008; Landis et al., 2002; Rolfhus et al., 2003).

Atmospheric mercury deposition includes through both wet and dry processes; each has their own characteristics (Sanei et al., 2010). The relative importance of the wet and dry deposition pathways varies considerably depending upon location, climate, and human influence (Rea et al., 1996; Sakata and Marumoto., 2005; Miller et al., 2005). Monitoring of the deposition flux and understanding the characteristics of mercury deposition are required for assessment of the environmental risks of mercury. In North America, more than 100 National Atmospheric Deposition Program's (NADP) Mercury Deposition Network (MDN) sites collected data and examined long-term trends in mercury deposition at regional scales (Vanarsdale et al., 2005; Lai et al., 2007; Hall et al., 2005; Prestbo and Gay, 2009). European Monitoring and Evaluation Program (EMEP) suggested that the typical concentrations of total mercury in rainwater and wet deposition flux were quite different across Europe (Wangberg et al., 2007; Yang et al., 2009; Ebinghaus et al., 1999). China has been regarded as one of the largest atmospheric mercury emission sources in the world (Streets et al., 2005; Wu et al., 2006). How-

ACPD
13, 28309–28341, 2013

ever, limited monitoring sites and data are available to understand mercury deposition in China. Measurements of mercury deposition in China have been conducted in remote areas like Changbai Mountain (Wan et al., 2009b) in northeastern China and Fanjing Mountain (Xiao et al., 1998), Leigong Mountain (X. W. Fu et al., 2010), Wujiang River Basin (Guo et al., 2008), Gongga Mountain (X. Fu et al., 2008, 2010) in southwest China. The few measurements of mercury deposition in the urban area of Guiyang (Feng et al., 2002; Tan et al., 2000), Changchun (Fang et al., 2001, 2004) Gongga Mountain suggested much more serious mercury contamination than that in remote areas and most of other countries. Obviously there are still limitations to fully describe temporal and spatial distributions of mercury deposition in China and its relationship to global atmospheric mercury cycling. Long-term continuous measurements of atmospheric mercury in China especially in urban area are greatly needed.

Particulate mercury (Hg^P) is one of the major forms of mercury lost via wet and dry deposition (Sakata and Marumoto, 2002). Particulate mercury is associated with airborne particles, such as dust, soot, sea-salt aerosols, and ice crystal, is likely produced by adsorption of RGM onto atmospheric particles (Lu and Schroeder, 2004). Most research indicates higher Hg^P concentrations and fractions in suspended particles in urban or industrial areas than in rural areas (Kim et al., 2012; Fang et al., 2001a, 2011a, 2012). Also, some measurements of Hg^P were conducted to estimate the dry deposition of mercury onto the particle surface (Fang et al., 2011b, 2011c; Wan et al., 2009b; Keeler et al., 1995; Chand et al., 2008). The deposition rate of Hg^P depends on the particle diameter, especially for dry deposition (Lestari et al., 2003; Peters and Eiden, 1992). Particle diameter plays a key role since it affects gravitational settling, aerodynamic resistance, and surface resistance (Zhang et al., 2001). Xiu et al. (2005) and Wang et al. (2006) studied Hg^P in two major cities in China, Shanghai and Beijing, with four and five size cut stages, respectively. A small number of size cut stages does not reveal a detailed analysis of the full size distribution of Hg^P. Ten size fractions of Hg^P were collected by Feddersen et al. (2012) and Kim et al. (2012) to evaluate the dominant fractions and variability of Hg^P in America and Korea, respectively. The

ACPD
13, 28309–28341, 2013

size distribution of Hg^P changes due to physical and chemical processes including adsorption, nucleation, and other gas-particle partitioning mechanisms, ambient particle concentrations, and meteorological conditions (Kim et al., 2012). To better understand the fate and transport of Hg^P, more seasonal variations in size-segregated Hg^P concentrations need to be determined.

Nanjing, the capital of Jiangsu Province, is located in the northwest of the Yangtze River Delta (YRD) region and more than 200 km west to China Sea, which is one of the most industrialized and urbanized regions in China and potentially affected by marine condition. Nanjing is the second largest city in eastern China with a high population density and large energy consumption. Due to rapid economic development, environmental pollution has become a problem of increasing concern in Nanjing. The containment of atmospheric mercury is one of the most serious environmental problems. As reported in Zhu et al. (2012), the 2011 annual average concentration of total gaseous mercury (TGM) was $7.9 \pm 7.0\,ng\,m^{-3}$, significantly higher than the Northern Hemisphere background value ($\sim 1.5\,ng\,m^{-3}$). However, the level of atmospheric mercury deposition in Nanjing and the YRD region has not been determined until now. In this study, the mercury content in precipitation and atmospheric particles in nine size fractions from $< 0.4\,\mu m$ to $10\,\mu m$ were monitored from June 2011 to February 2012 in urban Nanjing. To the best of our knowledge, this is the first comprehensive study of atmospheric mercury deposition and Hg^P in the YRD urban region.

2 Experimental method

2.1 Sampling site and methods

Deposition of atmospheric mercury and Hg^P were monitored on the top of a 24 storied building (75 m) on the Gulou campus of Nanjing University. Our site (32.05° N, 118.78° E) is located in the heart of the urban area of Nanjing. The climate and land covers in Nanjing and a detail description of our site can be found in Zhu et al. (2012).

ACPD
13, 28309–28341, 2013

The samples of mercury in this study were collected from June 2011 to February 2012, representing summer, fall, and winter. Samples in spring 2012 were contaminated due to sample handling, so the characteristics in spring cannot be used in this study. Simultaneously, meteorological parameters including wind, temperature, precipitation, relative humidity, and solar radiation were measured with the same method described in Zhu et al. (2012).

Wet deposition samples were collected using an automated precipitation sampler. The sampler was open automatically when rain was detected. Otherwise, the collection bottle was sealed to protect Hg^P from depositing. Normally, sample collection bottles were manually changed with a pre-cleaned new one every five days. In total, 22 samples which were all more than 50 mL were collected during the study period. The samples were stored at around 4 °C in a refrigerator before analysis. The total mercury concentration was determined in the Modern Analysis Center of Nanjing University using cold vapor atomic fluorescence spectrometer (CVAFS). The average method detection limit is 0.08 ng L^{-1}, and the relative standard deviation (RSD) ≤ 2 %. Simultaneously, major water-soluble ions in precipitation, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, F^-, oxalate, and formate were analyzed using Wan Tong 850 professional IC chromatography.

An Andersen eight-stage cascade impactor was used to collect size-segregated particles with cut-off sizes of 10–9, ~ 5.8, ~ 4.7, ~ 3.3, ~ 2.1, ~ 1.1, ~ 0.7 and ~ 0.4 µm. The sampler was operated at a flow rate of 28.3 L min^{-1} to maintain maximum efficiency and the air pump was calibrated before sampling. Sample campaigns were conducted semimonthly on random days. Generally sample collection began at noon and continued for 3 days. Each filter was conditioned in desiccator for more than 24 h and weighed by electronic balance three times with a precision of 0.01 mg before and after collection. The mercury content in the particulate matter was also analyzed using cold vapor atomic fluorescence spectrometer (CVAFS).

ACPD
13, 28309–28341, 2013

2.2 Calculation of wet and dry deposition

Wet deposition flux is calculated by multiplying the measured total concentration of mercury concentration in rainwater (THg) by the corresponding precipitation amount (Prec) as Eq. (1).

$$F_w = \mathrm{THg} \times \mathrm{Prec} \quad (1)$$

where F_w represents wet deposition flux of mercury.

Dry deposition flux is calculated as the product of the sum of the size-fractionated concentration of Hg^P and its respective dry deposition velocity as shown in Eq. (2).

$$F_d = \sum C_{HgP} \times V_d \quad (2)$$

where F_d is dry deposition flux of Hg^P, C_{HgP} is the concentration of Hg^P in each size fraction and V_d is the corresponding dry deposition velocity.

A size-resolved particle dry deposition model developed by Zhang et al. (2001) is used to estimate dry deposition velocity for each size fraction. The model uses the same method as Slinn's (1982) for modeling particle dry deposition, but used a simplified empirical parameterization for all deposition processes. This parameterization calculates particle dry deposition velocity as a function of particle size and meteorological variables which are measured at our site. It includes deposition processes, such as turbulent transfer, Brownian diffusion, impaction, interception, gravitational settling and particle rebound. Our estimation of deposition flux should be more accurate than those using a constant deposition velocity in previous studies such as Fang et al. (2012), Wang et al. (2006) and Lombard et al. (2011).

ACPD
13, 28309–28341, 2013

3 Results and discussion

3.1 Concentration of mercury in precipitation and wet deposition

From June 2011 to February 2012, 22 samples of rainwater were collected at our site. The total mercury (THg) concentration in precipitation, daily and 5 day accumulated precipitation amount and the calculated THg deposition flux are displayed in Fig. 1. The maximum THg concentration was 63.6 ng L^{-1} occurring during 1–5 June 2011 and minimum was 46.3 ng L^{-1} sampled during 16–20 October 2011. However, the 5 day accumulated maximum (11.6 µg m^{-2}) mercury wet deposition was collected during 16–20 July 2011, which constituted almost 20 % of the total wet deposition of 9 months. Similarly, both Keeler et al. (2005) and Lombard et al. (2011) reported a single rainfall event contributing approximately 17 % and 14 %, respectively, to the annual wet deposition in America. Table 1 provides a summary of all data during our study period. The volume weighted mean (VWM) concentration of mercury of all samples was 52.9 ng L^{-1} with precipitation depth of 1067.7 mm. The mercury wet deposition calculated as the product of the concentration and amount of precipitation was 56.5 µg m^{-2} over 9 months.

Our study period of 9 months represent summer (June, July, August in 2011), fall (September, October, November in 2011) and winter (December in 2011 and January, February in 2012) respectively. Seasonal variation of mercury wet deposition is apparent in Table 1. Deposition in summer accounted for a substantial portion of the total deposition which contributed more than 80 % with the highest monthly deposition flux of 18.1 µg m^{-2} $month^{-1}$ in June. Correspondingly, the greatest VWM concentration of mercury in precipitation (53.5 ng L^{-1}) was also measured in summer. However, seasonal differences in the VWM concentration were not as significant as those in deposition flux. The correlation coefficient (r) between the VWM concentration and deposition flux was 0.41 compared with 0.99 between precipitation amount and deposition flux. As a result, the seasonal variability in mercury wet deposition was less consistent with that in VWM concentrations while was more strongly linked to that in precipitation amounts. Compared to other seasons the combination of higher relative concentrations and more

ACPD
13, 28309–28341, 2013

precipitation in summer enhanced the overall flux. Similar seasonal patterns were observed in both deposition flux and concentration in remote areas of China (X. Fu et al., 2010; X. W. Fu et al., 2010) and North America (Choi et al., 2008; Mason et al., 2000; Keeler et al., 2005; Sanei et al., 2010; Lombard et al., 2011) with the annual maximum in summer. It was suggested by Keeler et al. (2005) and Mason et al. (2000) that this annual maximum was mainly due to more effective scavenging by rain in summer than by snow in the cold season. Mercury is not incorporated into cold cloud precipitation as efficiently as in warm cloud precipitation (Landis et al., 2002). However, snow hardly occurred in Nanjing during the 2012 winter. The relationship between precipitation and deposition flux suggests that there is a continual source of mercury during a precipitation event. This source is likely the oxidation of GEM via gas-phase and/or in-cloud aqueous reactions (Mason et al., 2000). Enhanced photochemical activities in summer can probably enhance the rate of GEM oxidation (Munthe et al., 1995). Also, as hypothesized by Zhu et al. (2012), mercury released from mercury contaminated soils during the warm season may have caused very high TGM peaks in Nanjing. That may be one of the important sources for mercury wet deposition in summer. On the other hand, a positive correlation between THg concentrations and precipitation amounts (r = 0.32) indicates that RGM and Hg^P may not be scavenged effectively and completely by precipitation from the atmosphere or continuous emission sources in Nanjing.

3.2 Comparison with other sites

A comparison of THg concentrations in precipitation and wet deposition flux between our site in Nanjing and other sites in the world is given in Table 2. Differences among the data at these sites were very distinct. Overall, THg concentrations and wet deposition flux at urban sites were both higher than those at rural sites, which is in line with the point demonstrated by Fang et al. (2004) and Landis et al. (2002) that human activities in urban areas can enhance mercury concentrations in precipitation. THg concentrations in rural China were comparable to most literature data from rural sites in North

ACPD
13, 28309–28341, 2013

America, Europe, and Northeast Asia. However, THg levels in urban China were much higher than those in urban America and even urban Japan which is close to China. Since measurements of mercury deposition in urban China are very limited, the data at our site can be compared only with those from Guiyang and Changchun in China. Table 2 shows that wet deposition of mercury in urban Nanjing was much lower than that in Guiyang and Changchun. Coal burning is one of the most important sources for atmospheric mercury and more coal burning occurs in these two cities than in Nanjing. This difference was enhanced in winter when space heating was practiced in Guiyang and Changchun while not in Nanjing. Moreover, the measurements in Guiyang and Changchun were conducted ten years earlier than this study. During the past ten years, the mercury content in coal decreased notably because the Chinese government enacted a series of policies to control mercury emissions from major coal-fired industrial sources.

In comparison, the wet deposition during the 9 months (56.5 $\mu g\,m^{-2}$) in Nanjing was 3–8 times higher than the value in Japanese and American urban sites, resulting from higher VWM concentrations in Nanjing (52.9 $ng\,L^{-1}$) than the values (3.2–25.9 $ng\,L^{-1}$) at MDN sites (National Atmospheric Deposition Program, 2011). London, an industrial megacity, showed comparable THg concentrations and deposition flux (Yang et al., 2009). This indicates that high population density and industrialization with large energy consumption may be important factors for environmental contamination at urban areas.

3.3 Association between mercury and major ions in precipitation

Major water-soluble ions including H^+, F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, formate, and oxalate in each precipitation sample were analyzed during our study period. Among the ionic constituents sulfate contributed the maximum amount (39.31 %) followed by magnesium (19.16 %), nitrate (16.04 %), and ammonium (6.48 %). The ionic balance of rainwater samples demonstrated a trend as $SO_4^{2-} > NO_3^- > Cl^- >$

ACPD
13, 28309–28341, 2013

$C_2O_4^{2-}$ > $HCOO^-$ for anions and Mg^{2+} > NH_4^+ > Na^+ > K^+ > Ca^{2+} for cations. The total anions contributed 68 % and cations 32 % to the rainwater composition. The pH value of rainwater ranged from 4.62 to 6.58 with an average of 5.86, which was a little more alkaline compared to the reference level 5.6 provided by China Meteorological Administration (2006), due to the dominant contribution from sulfate and nitrate. Table 3 shows correlation coefficients between deposition fluxes of the ions of interest. Better correlations indicate common sources of various ions, and hence association between ions is a useful indicator of their potential sources in rain water.

Sodium and chloride, elements associated with sea water, were highly correlated ($r = 0.98$, $p < 0.01$). The averaged Cl/Na mole ratio was 1.18 in our study, near the ratio of 1.16 in seawater (Seinfeld and Pandis, 2006; Caffrey et al., 2010), so sodium and chloride in rainwater in Nanjing came from sea salt aerosols. However, mercury did not correlate well with sodium and chloride ($r = 0.37$ and 0.23, respectively, with poor significance $p > 0.05$). Little contribution to mercury deposition from sea salt aerosols was suggested although Nanjing is often under the influence from marine condition. It was possibly caused by continental emission sources entrained in marine air masses en route to Nanjing which dominated over the marine air chemical composition interfered with the correlation between mercury deposition and sea salt.

Sulfates and nitrates made the largest contribution to the anions in rainwater and comprised more than 50 % of the total mass. Paired depositions and concentrations of sulfates and nitrates both showed a strong correlation ($r = 0.95$ and $r = 0.90$, respectively). The high correlation coefficients indicated their origin from same regions of their precursors SO_2 and NO_X, which are mainly emitted by anthropogenic sources such as fossil fuel combustion and other high temperature processes. As we know, coal combustion is one of the most important anthropogenic sources for mercury. However, the correlation coefficients between mercury and sulfate as well as nitrate were 0.39 and 0.44, respectively, higher than that between mercury and sea salt aerosol. This suggests that anthropogenic sources contributed more to wet deposition of mercury than sea salt aerosols, but cannot affect the variation of deposition flux remarkably.

ACPD
13, 28309–28341, 2013

Table 3 shows that the ions correlated with mercury most significantly were formate (r = 0.99), calcium (r = 0.93), and potassium (r = 0.88). Formate is indicative of volatile organic compounds mostly emitted from vegetation (Dordevic et al., 2010). Good correlations were seen between calcium and potassium (r = 0.76), calcium and magnesium (r = 0.92), which suggested their crustal origin, namely local resuspended soil and dust from inland cities (Guentzel et al., 1998; Shen et al., 2012; Salve et al., 2006). In view of good correlations of mercury with formate, calcium, potassium, and magnesium (r = 0.73), natural sources including vegetation and resuspended soil should be considered as an important factor influencing the wet deposition of mercury in Nanjing. As suggested in Zhu et al. (2012), natural sources also could make a significant contribution to the higher monthly average levels of TGM in Nanjing especially in summer due to Nanjing and its surrounding areas being one of the largest natural emission regions in summertime China. The re-volatilized mercury from soil and vegetation could be previously deposited anthropogenic mercury.

3.4 Size-fractionated particulate mercury

From June 2011 to February 2012, 17 campaigns of particle sampling in eight size stages were conducted at our site. The average total Hg^P in PM_{10} during our study period was $1.10 \pm 0.57\ ng\,m^{-3}$ with a range of 0.32–2.04 $ng\,m^{-3}$. While the level of Hg^P in Nanjing was much higher than that in rural areas in China (30.7 $pg\,m^{-3}$ in Mt. Gongga, Fu et al., 2008; 77 $pg\,m^{-3}$ in Mt. Changbai, Wan et al., 2009b), it is very close to that in Beijing ($1.18 \pm 0.82\ ng\,m^{-3}$) (Wang et al., 2006) and comparable to that in other Chinese cities such as Shanghai (0.233–0.529 $ng\,m^{-3}$, Xiu et al., 2005) and Changchun (0.022–1.984 $ng\,m^{-3}$, Fang et al., 2001b). Compared globally, the Hg^P concentration in Nanjing was far higher than that in most cities in the world such as Tokyo ($0.098 \pm 0.051\ ng\,m^{-3}$, Sakata and Marumoto, 2002), Detroit ($0.021 \pm 0.030\ ng\,m^{-3}$, Liu et al., 2007), and Seoul ($6.8 \pm 6.5\ pg\,m^{-3}$, Kim et al., 2012). There was a clear seasonal cycle of Hg^P in Nanjing (Fig. 2). The highest monthly averaged concentration was 1.95 $ng\,m^{-3}$ measured in De-

ACPD
13, 28309–28341, 2013

cember, which was a factor of > 4 higher than the lowest one in August (0.46 ng m^{-3}). The seasonal average concentration was the highest (1.82 ng m^{-3}) in winter and low in summer (0.70 ng m^{-3}) and fall (0.87 ng m^{-3}). In our site, the averaged ratio of Hg^P concentration to TGM was measured up to 0.519 which was extremely higher than that in other sites over the world always lower than 0.1 (Mao and Talbot, 2012; Wan et al., 2009a; Valente et al., 2007), while the ratios in summer ranged during 0.042–0.097. One of the most important reasons for the highest concentration and ratios of Hg^P to TGM in winter was the increasing concentration of PM_{10}. The concentration of PM_{10} averaged over our sampling period in winter was 103 µg m^{-3} compared to 63 µg m^{-3} in summer and 69 µg m^{-3} in fall. This may be attributed to the fact that particles are scavenged much less efficiently in winter (Mao et al., 2012). In addition, the concentrations of Hg^P and PM_{10} showed good correlation with a correlation coefficient of 0.67. The concentration of particles appeared to have a large effect on the concentration of Hg^P in the atmosphere.

Fractional measurements were used to characterize the size distribution of Hg^P in Nanjing. Figure 3 illustrates the averaged percentages of Hg^P in each size fraction. More than half of Hg^P existed in the particle size less than 2.1 µm which can be regarded as fine particles. Especially, the Hg^P in the particle size between 0.7 and 2.1 µm contributed 39.8 % to the total Hg^P in PM_{10}. Gas-particle transformation plays a vital role in formation of Hg^P in fine particles as more than 95 % atmospheric mercury exists in gaseous form (Xiu et al., 2005). The other way to form Hg^P in fine particles is adsorption of gaseous mercury on fine particles which are primarily produced by condensation and coagulation of combustion products (Ames et al., 1997). Also, a small peak was found in the particle size between 4.7 and 10 µm which are regard as coarse particle size range. Compared with Hg^P in fine particles, Hg^P in coarse particles may form through adsorption of gaseous mercury on coarse particles commonly generated by natural sources such as salt spray and dust, and mechanical processes from anthropogenic sources (Mamane et al., 2008). Furthermore, quite different size distributions

ACPD
13, 28309–28341, 2013

of Hg^P for seasons are illustrated in Fig. 3. More Hg^P concentrated in the three most coarse size fractions (> 4.7 µm) in summer with percentage of 22.7 %, while higher percentage of Hg^P in fine particles < 2.1 µm were measured in fall and winter (59.6 % and 53.8 % respectively). A possible reason for this shift in particle size was that gas-particle partitioning of atmospheric mercury actively occurred on fine particles during the cold season (Kim et al., 2012). This was demonstrated by a controlled laboratory system designed by Rutter and Schauer (2007) suggesting the partition coefficient K_P (Eq. 3) is inversely correlated with temperature.

$$K_P = \frac{Hg^P/PM}{TGM} \quad (3)$$

where Hg^P is the concentration of particulate mercury. PM represents the particle mass, and TGM is the concentration of gaseous mercury.

Moreover, the mass percentage of Hg^P in the size fraction between 0.7 and 1.1 µm in summer and between 1.1 and 2.1 µm in winter were particularly high, which accounted for 19.2 % and 17.3 % of total Hg^P, respectively. However, the predominant mercury species in these fractions have not been identified. Xiu et al. (2009) suggested all mercury species including Hg^0, $HgCl_2$, $HgBr_2$, $HgSO_4$, HgO, HgS, and methylated mercury may deposit on particles. Data of species are needed to further study the causes for the peaks.

In order to minimize the effect of PM_{10} concentration, the mercury content in particles (Hg^P/PM_{10}) was studied. Figure 4 showed the seasonal variation of the mercury content in each size fraction. The size distributions of averaged mercury content in particles were bimodal during our study period two peaks in the bins of < 0.7 µm and 4.7–5.8 µm. These two peaks were close in magnitude with content both higher than 25 ng mg^{-1} which was unlike the mass distribution. It demonstrated that Hg^P might have come from two different sources or formed via different mechanisms. Since fine particles possess the most surface area per unit mass, the mercury species with low

ACPD
13, 28309–28341, 2013

volatility are preferentially adsorbed on fine particles (Kim et al., 2012). As a result, the lowest mercury content was measured in two largest size fractions (5.8–10.0 µm). However, the mercury content peak in 4.7–5.8 µm need to be studied further. In addition, mercury content in summer in the four finest size fractions below 2.1 µm was 17 ~ 53 % lower than that in fall and winter. A possible explanation was that higher temperature in summer liberated the volatile mercury adsorbed on the particles (Xiu et al., 2005). By contrast, the mercury content in coarse particles in summer was comparable with that in fall and winter. Xie et al. (2008) found that GEM was a significant contributor to Hg^P in large particles. As measured by Zhu et al. (2012), the concentration of TGM was extremely high during summer in Nanjing. Morey TGM in summer might account for part of the mercury content in coarse particles.

3.5 Dry deposition of particulate mercury

Besides wet deposition, dry deposition was the other primary way to scavenge mercury from the atmosphere and deposit it into terrestrial and aquatic ecosystems. The dry deposition flux of Hg^P was calculated using the ambient concentration of Hg^P and the size dependent dry deposition velocity. The concentration of Hg^P was estimated using measurements of PM_{10} at our site during the study period. We assumed that the size distribution of Hg^P and mercury content in PM_{10} remained constant during the time period following the sample collection time window.

Dry deposition of Hg^P per unit area was calculated to be 47.2 µg m^{-2} during nine months in our study period. Estimated Hg^P dry deposition was 16.5 % less than the measured mercury wet deposition (56.5 µg m^{-2}). Table 4 showed the lowest seasonal dry deposition flux was in summer, while fluxes in fall and winter were a little higher. But the seasonal variation of dry deposition flux was not as apparent as that of the wet deposition flux. The seasonal variabilities in mercury wet deposition and Hg^P dry deposition were opposite in phase. The ratios of mercury wet deposition to Hg^P dry deposition ranging from 0.19 in the fall to 3.89 in the summer. The large precipitation

ACPD
13, 28309–28341, 2013

amount and mercury wet deposition and the lowest Hg^P dry deposition in summer possibly reflected the effect of scavenging by precipitation, indicated by every precipitation event followed by decreased Hg^P concentration at our site (Fig. 5). During precipitation events, the Hg^P concentration decreased by 56 % on average, ranging from 16 % to 94 %. Negative correlation between the precipitation amount and Hg^P concentration was statistically significant with $r = -0.25$. Hg^P can be scavenged by rainfall from atmosphere directly, evidenced in lower concentrations of Hg^P during a precipitation event. In addition, precipitation causes higher humidity and the soil is not as easily resuspended, so that the Hg^P bound to wind-blown soil material decreases (Fang et al., 2001b). Furthermore, the relative contribution of Hg^P in different size fractions to the total dry deposition was calculated. Although the mass percentage of Hg^P in coarse particles was much less than Hg^P in fine particles, Hg^P in coarse particles ($> 5.8\,\mu m$) contributed 24.6 % more than Hg^P in fine particles ($< 2.1\,\mu m$) to the total dry deposition due to the extremely high deposition velocity. The dry deposition velocity of particles increased with particle size, so dry deposition of Hg^P in sizes between $9.0 \sim 10.0\,\mu m$ occupied more than 30 % of the total for all seasons. The finest Hg^P contributed around 10 % owing to higher concentrations.

4 Summary

Measurement study of wet and dry deposition of size-fractioned particulate mercury was conducted from June 2011 to February 2012 to characterize mercury deposition and Hg^P in urban Nanjing, China. The VWM concentration of THg of all rainwater samples was $52.9\,ng\,L^{-1}$ during the study period. The mercury wet deposition per unit area was $56.5\,\mu g\,m^{-2}$ over 9 months. Seasonal variation in what was strongly linked to precipitation amount based on a strong correlation ($r = 0.99$) between precipitation and deposition flux. In comparison, wet deposition in urban Nanjing was lower than that in Chinese cities, but much higher than annual deposition in urban areas in Amer-

ACPD
13, 28309–28341, 2013

ica and Japan. The anthropogenic influence on mercy wet deposition was evidenced by the association between wet deposition of mercury and sulfates and nitrates. The ions correlated with mercury in rainwater most significantly were formate, calcium, and potassium, which suggested the importance of natural sources including vegetation and resuspended soil to mercury wet deposition in Nanjing.

Atmospheric particles were sampled in nine size fractions during the study period at our site. The average Hg^P concentration in PM_{10} was $1.10 \pm 0.57\,ng\,m^{-3}$, comparable to that in other Chinese cities but far higher than that in rural areas in China as well as most cities in the world. A distinct seasonal cycle in Hg^P concentrations was found with much higher levels in winter than in summer and fall due to increased concentrations of PM_{10} in winter. More than half of the total Hg^P existed in particle sizes < 2.1 µm and the size distributions of averaged mercury content in particles were bimodal with two peaks in < 0.7 µm and 4.7–5.8 µm. Furthermore, higher percentage of Hg^P in coarse particles was measured in summer while more Hg^P concentrated in fine particles occurred in fall and winter. Dry deposition per unit area of Hg^P was calculated to be $47.2\,\mu g\,m^{-2}$, a little less than mercury wet deposition. Hg^P in coarse particles contributed more to the total dry deposition than Hg^P in fine particles due to its high deposition velocity. A significant negative correlation between precipitation and Hg^P concentration reflected the effect of Hg^P scavenging by rain.

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ACPD
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ACPD
13, 28309–28341, 2013

Table 1. The statistical summary of mercury concentration, precipitation and wet deposition flux.

	VWM concentration ($ng\,L^{-1}$)	Precipiation amount (mm)	Wet deposition flux ($\mu g\,m^{-2}$)
Summer	53.5	872.6	46.7
Fall	49.0	59.2	2.9
Winter	51.0	135.9	6.9
All Data	52.9	1067.7	56.5

ACPD
13, 28309–28341, 2013

Table 2. Summary of wet deposition of mercury in China and other countries.

Locations	Classification	Period	THg (ng L^{-1})	Wet deposition		Reference
Mt.Gongga, China	Rural	May 2005–Apr 2006	9.9 ± 2.8	9.1	$\mu g\,m^{-2}\,yr^{-1}$	Fu et al. (2008)
Mt.Gongga, China	Rural	May 2005–Apr 2007	14.3	26.1	$\mu g\,m^{-2}\,yr^{-1}$	Fu et al. (2010)
Wujiang River, China	Rural	2006	36.0	34.7	$\mu g\,m^{-2}\,yr^{-1}$	Guo et al. (2008)
Mt. Leigong, China	Rural	May 2008–May 2009	4.0	6.1	$\mu g\,m^{-2}\,yr^{-1}$	Fu et al. (2010)
Mt. Fanjing, China	Rural	1996	–	115	$\mu g\,m^{-2}\,yr^{-1}$	Xiao et al. (1998)
Changchun, China	Urban	Jul 1999–Jul 2000	162–697	152.4	$\mu g\,m^{-2}\,yr^{-1}$	Fang et al. (2004)
Guiyang,China	Urban	1997–1998	–	43.8 ± 35.8	$\mu g\,m^{-2}\,month^{-1}$	Tan et al. (2000)
Nanjiang, China	Urban	Jun 2011–Mar 2012	52.9	0.7–18.1	$\mu g\,m^{-2}\,month^{-1}$	This study
Chuncheon, Korea	Rural	Aug 2006–Jul 2008	8.8	9.4	$\mu g\,m^{-2}\,yr^{-1}$	Ahn et al. (2011)
Tokyo,Japan	Urban	Dec 2002–Nov 2003	8.7	16.7	$\mu g\,m^{-2}\,yr^{-1}$	Sakata et al. (2005)
Aichi, Japan	Urban	Apr 2004–Mar 2005	7.8	13.1	$\mu g\,m^{-2}\,yr^{-1}$	Sakata and Asakura (2007)
Hyogo, Japan	Urban	Apr 2004–Apr 2005	9.5	14	$\mu g\,m^{-2}\,yr^{-1}$	Sakata and Asakura (2007)
London, UK	Urban	Jan 1999–Dec 2005	43.8–76.0	15.–45.3	$\mu g\,m^{-2}\,yr^{-1}$	Yang et al. (2009)
Wisconsin, USA	Urban	Jun 2004–May 2005	13.9	6.7	$\mu g\,m^{-2}\,yr^{-1}$	Rutter et al. (2008)
Virginia, USA	Rural	Jun 2006–Sep 2006	6.8	9	$\mu g\,m^{-2}\,yr^{-1}$	Kolker et al. (2008)
New Hampshire, USA	Rural, Costal	Jun 2006–Aug 2009	0.75–65.09	8.41–12.33	$\mu g\,m^{-2}\,yr^{-1}$	Lombard et al. (2011)

ACPD
13, 28309–28341, 2013

Table 3. The correlation coefficients between mercury and major ions in rainwater (bold for $p > 0.05$).

	Hg	H^+	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Formate	Oxalate
Hg	1.00	0.65	0.78	**0.23**	0.44	**0.39**	**0.37**	0.52	0.88	0.93	0.73	0.99	**0.33**
H^+		1.00	**0.40**	**0.04**	**0.15**	**0.05**	**0.15**	**−0.06**	0.53	0.62	0.59	0.71	**0.07**
F^-			1.00	0.75	0.87	0.87	0.82	0.82	0.94	0.75	0.81	0.96	0.89
Cl^-				1.00	0.85	0.94	0.98	0.67	0.63	**0.17**	0.73	0.78	0.90
NO_3^-					1.00	0.95	0.87	0.89	0.72	0.45	0.73	0.71	0.97
SO_4^{2-}						1.00	0.94	0.83	0.71	**0.38**	0.80	0.78	0.99
Na^+							1.00	0.70	0.74	0.29	0.76	0.91	0.91
NH_4^+								1.00	0.70	0.49	0.47	0.59	0.88
K^+									1.00	0.76	0.69	0.97	0.78
Ca^{2+}										1.00	0.92	0.98	**0.36**
Mg^{2+}											1.00	0.89	0.78
Formate												1.00	0.66
Oxalate													1.00

ACPD
13, 28309–28341, 2013

Table 4. Dry deposition fluxes ($\mu g\,m^{-2}$) in each size fraction in each season.

Size (μm)	Summer		Fall		Winter		All Data	
	Flux	Percent	Flux	Percent	Flux	Percent	Flux	Percent
< 0.4	1.0	8.1 %	2.7	17.3 %	1.9	9.8 %	5.6	11.8 %
0.4–0.7	0.4	3.2 %	1.1	6.9 %	1.1	5.5 %	2.5	5.3 %
0.7–1.1	0.9	7.5 %	0.8	5.5 %	1.0	5.2 %	2.8	5.9 %
1.1–2.1	0.4	3.1 %	0.6	4.0 %	1.2	6.0 %	2.2	4.6 %
2.1–3.3	0.7	6.0 %	0.4	2.6 %	0.7	3.6 %	1.8	3.9 %
3.3–4.7	0.7	5.6 %	0.8	4.9 %	1.2	5.9 %	2.6	5.5 %
4.7–5.8	1.5	12.6 %	1.4	9.4 %	2.1	10.8 %	5.1	10.8 %
5.8–9.0	2.4	20.1 %	2.2	14.5 %	4.0	20.1 %	8.6	18.3 %
9.–10.0	4.1	34.0 %	5.4	35.0 %	6.5	33.1 %	16.0	33.9 %
Total	12.0		15.4		19.8		47.2	

ACPD
13, 28309–28341, 2013

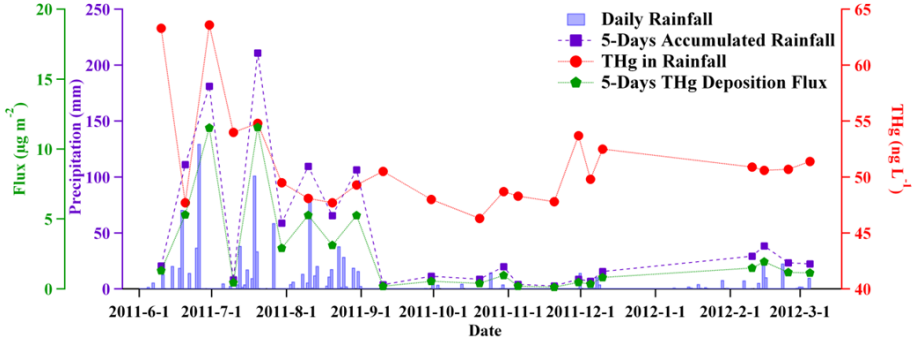
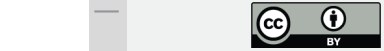


Fig. 1. Time series of mercury concentration in precipitation, wet deposition flux and precipitation.

ACPD
13, 28309–28341, 2013



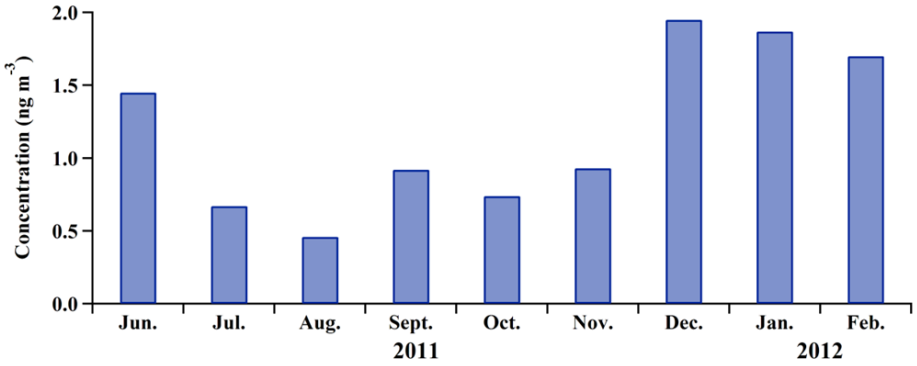


Fig. 2. Monthly variation of Hg^P concentration during June 2011–February 2012.

ACPD
13, 28309–28341, 2013

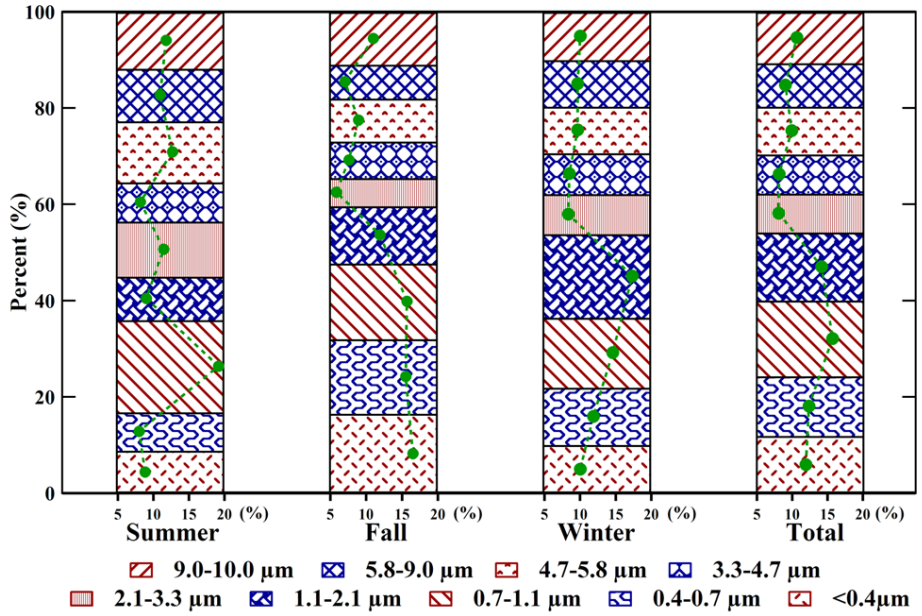


Fig. 3. Size distribution of Hg^P mass in each season and over the whole study period.

ACPD
13, 28309–28341, 2013

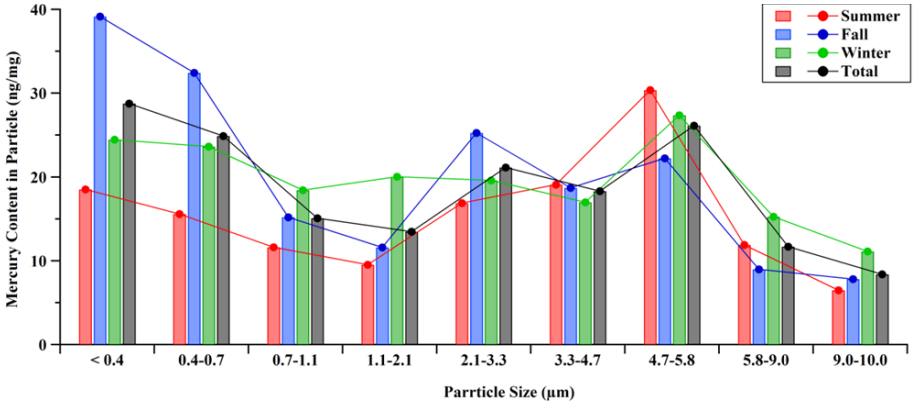


Fig. 4. Mercury content in size-fractioned particles in each season and over the whole study period.

ACPD
13, 28309–28341, 2013

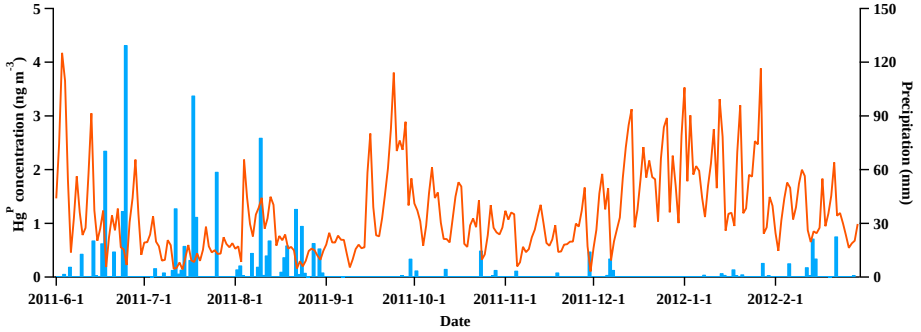


Fig. 5. Hg^P concentration and precipitation during the study period.

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