**Atmospheric
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Spatial and temporal distributions of total and methyl mercury in precipitation in core urban areas, Chongqing, China

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Abstract. The spatial and temporal distribution patterns of mercury (Hg) in precipitation were investigated in the core urban areas of Chongqing, China. During the period from July 2010 to June 2011, total mercury (THg) and methyl mercury (MeHg) concentrations in precipitation were analysed from three sampling sites. Our results suggested that the volume-weight mean THg and MeHg concentrations in precipitation were 30.67 ng l^{-1} and 0.31 ng l^{-1}, respectively. The proportion of MeHg in THg ranged from 0.1 % to 7.6 % with a mean value of 1.3 %. THg and MeHg concentrations showed seasonal variations, while the highest THg value was measured in winter. Contrarily, the highest MeHg concentration was observed in autumn. Additionally, a geographically gradual decline of THg concentration in precipitation was observed from the downtown to the suburb, then to the controlled site in the city. 5 mm rainfall might be a threshold for the full wash-out capability. Rainfall above 5 mm may have a diluting effect for the concentrations of THg. Moreover, the current research implies that the coal combustion and motor vehicles could be the dominant sources for Hg in the precipitation.

1 Introduction

Mercury (Hg) pollution, a global issue, poses potential threats to human health and wildlife (National Research Council, 2000). Hg species, including gaseous element mercury (Hg^0), reactive gaseous mercury (RGM), and partic-

ulate mercury (PHg), are commonly represented in the atmosphere (Lindberg et al., 2007). The primary mechanisms for wet deposition are: (1) in-cloud oxidation of Hg^0 by O$_3$, (2) gas-phase oxidation of Hg^0 by ·OH and O$_3$ followed by cloud-droplet uptake. Dissolved mercury (DHg) and PHg are the major forms of Hg in precipitation, where the later one can be deposited through cloud-droplet/precipitation scavenging activity (Lindberg et al., 2007).

MeHg generally accounts for ∼ 0.5–3.0 % of THg in precipitation (Mason et al., 2000; St. Louis et al., 2005; Nguyen et al., 2005; Munthe et al., 1995a, b), but the proportion can be > 10 % in single event (St. Louis et al., 2005; Hall et al., 2005). At present, the understanding on the sources of MeHg in atmosphere or precipitation is very limited (Hammerschmidt et al., 2007). Previous studies speculated that MeHg in precipitation could originate from the capture of MeHg from atmosphere as well as the oxidation of dimethyl mercury to MeHg (Brosset and Lord, 1995). However, the extents of both processes are typically confined within the atmosphere. Recently, Hammerschmidt et al. (2007) found that MeHg in precipitation could be derived from the aqueous phase methylation through a reaction between labile Hg(II) complexes and (an) unknown methylating agent(s).

Deposition is one of the most important steps of Hg biogeochemical cycle in the atmosphere. Numerous studies suggested that atmospheric deposition is the primary source of Hg to terrestrial and aquatic ecosystems (Lombard et al., 2011), such as Great Lakes (Fitzgerald et al., 1991; Landis and Keeler, 2002), remote inland lakes (Sorensen et al.,

1990) and forested catchments (Munthe et al., 1995a). Some other studies considered atmospheric deposition of MeHg to be a minor contributor to the aquatic ecosystem (Mason et al., 2000), while some investigators argued that wet deposition could be an important source of MeHg for certain ecosystems (Munthe et al., 1995b; Rolfhus et al., 2003), such as upland watershed at the ELA (St. Louis et al., 1994).

Investigating the distributions of Hg deposition is of significant importance to the understanding of the fate of Hg in the environment. Therefore, numerous long-term monitoring stations have already been set up worldwide, like the Mercury Deposition Network (MDN, with more than 100 active stations by now) (National Atmospheric Deposition Program, 2007). Environment Canada also operated Canadian Atmospheric Mercury Measurement Network (CAMNet) which had 11 sampling sites in 1994 (CAMNet, 2006). Only a few monitoring studies of Hg deposition have been carried out at remote and suburban locations in China. Guo et al. (2008) and Fu et al. (2010b) reported that the annual mean Hg concentrations in precipitation were higher in some semi-remote and remote Chinese areas, when compared to some areas in other countries (Guentzel et al., 2001; Sakata and Marumoto, 2005). Although China is recognised as one of the biggest emitters of atmospheric Hg (Zhang and Wong, 2007; Jiang et al., 2006), there lacks long-term Hg research networks capable to depict temporal and spatial distribution of Hg in precipitation. Therefore, it is very urgent to conduct long-term continuous measurements of Hg concentrations in precipitation and its deposition fluxes in China.

Anthropogenic Hg emissions in China show a clear pattern in regional distribution (Wu et al., 2007), while the southwestern China is considered as a seriously affected area (Streets et al., 2005). Chongqing, locates in southwestern China, is regarded as a traditional industrial city. With heavy industry as the main player in the local economy, it has a large demand on energy, about 70 % of which is derived from coal in which the average mercury concentration is $0.32 \, \mathrm{mg \, kg^{-1}}$ (Wang et al., 2006). Previous studies showed that a large amount of Hg emitted into the atmosphere was associated with coal combustion (Wang et al., 1999). The industries locate in the core urban areas are the major sources of Hg pollution to ambient air (Yang et al., 2009). Chongqing, with a complex terrain, is surrounded by hills and mountains, where the average wind speed is as slow as $0.95 \, \mathrm{m \, s^{-1}}$ (Li et al., 2010). Thus, the area is prone to high atmospheric stability and radiation, inhibiting the spreading of mercury to the ambient. In addition, the urban heat island effect also decreases the speed of air flow, resulting in higher atmospheric Hg level in core urban area. It was reported that the annual mean concentration of Hg^0 in main districts of Chongqing ($6.74 \pm 0.37 \, \mathrm{ng \, m^{-3}}$) was three folds higher than the global background level (Yang et al., 2009). With the process of precipitation, the increased Hg which entered the terrestrial ecosystem could endanger the living creature. In ad-

dition, acid deposition is also more serious in Chongqing, which results in high washout ratio and MeHg formation.

To investigate the spatial and temporal distribution patterns of Hg in precipitation in Chongqing, THg and MeHg concentrations in precipitation at three typical sites (including the downtown, suburban and controlled sites in the city) were determined from July 2010 to June 2011. The objectives of this study were: (1) to quantify the concentrations of THg and MeHg in core urban areas in Chongqing; (2) to provide fundamental data for Hg cycling on a global scale.

2 Materials and methods

2.1 Study area and sampling sites

The Chongqing Municipality locates in the upstream of the Yangtze River with a population of 33 030 000 in 2010. Its topography is characterised by valley, hills and mountains; the elevation ranges from 145 to 2797 m above sea level. In addition, it has a typical subtropical humid monsoon climate with an annually average temperature of 18.8° and average annual rainfall of 1200 mm (Yang et al., 2009).

Three sampling sites were selected for monitoring precipitation in Chongqing city, which were located in the downtown, suburban and controlled sites in the city, respectively. Detailed descriptions of the three stations are provided in Table 1. In addition, the locations of the sampling points are illustrated in Fig. 1.

2.2 Sampling methods

The rain samples were collected by automatic precipitation sampler (APS-3A, Changsha Xianglan Scientific Instruments Co., Hunan, China) which was situated on unshadowed building roof at each sampling site. The sampler consisted of one tipping-bucket rain gauge, one moisture sensor, one automatic cover, one funnel, eight sampling borosilicate bottles, eight Teflon tubes connecting the funnel to the sampling bottles and one portable fridge for cold storage (4°) of the rain samples. The moisture sensor would activate the electric pathway allowing automatic removal of the funnel cover during the rain event. Each precipitation event was sampled from each site during the period from July 2010 to June 2011. In a precipitation event, we defined the period of rain as since the triggering of moisture sensor to the next day 09:00 a.m. Then the sampling borosilicate bottle was altered automatically for the next precipitation event.

The water samples were divided into two bottles in the sampling field. One bottle was used for the measurement of pH and the concentrations of major anions. The other bottle was further separated into two samples, one filtered through 0.45 μm microfilters (Millipore, USA) for analyses of dissolved total mercury (DHg) and dissolved methylmercury (DMeHg); the other was unfiltered for analyses of THg and total methylmercury (MeHg). All the samples analysed for

Table 1. Description of sampling sites in core urban areas, Chongqing, China.

Site	Type	Descript
Nanan District (NA)	Downtown	A crowed place with lots of markets and high population density (2294 people per square kilometre)
Beibei District (BB)	Suburban site	A residential area with good vegetation cover, population density (843 people per square kilometre)
Jinyun Mountain (JY)	Controlled site	Near rural regions, covered by extensive forest with little human activities
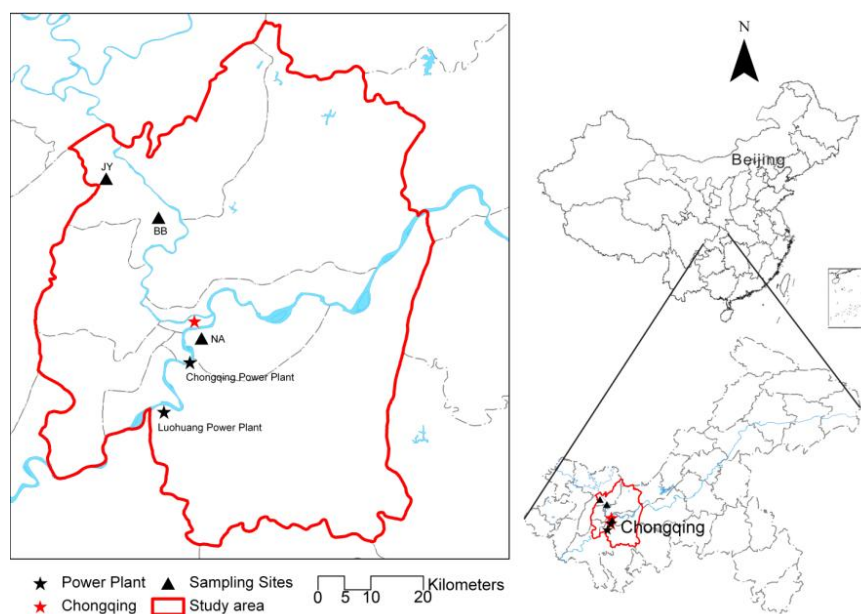
Fig. 1. The locations of study area and sampling sites.

species of Hg were acidified to 5 % (v/v) using concentrated hydrochloric acid (HCl). The rain samples were transported to the lab on ice, and then stored in a refrigerator at $+4°$ in the dark until analysis.

The water samples were transferred from sampler to acid cleaned borosilicate glass bottles. These bottles were initially soaked in 10 % (v/v) HNO$_3$ for at least 48 h, followed by rinsing with ultra-pure water (18.2 MΩ cm^{-1}), and baked for one hour in a muffle furnace at 500°. Finally, they were doubly bagged and stored in wooden boxes until use. All operations were performed in accordance with ultraclean sample handing protocols.

2.3 Sample analysis

For THg and DHg determinations, the samples were analysed (following the EPA Method 1631) by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS, Brooks Rand model III, Brooks Rand Laboratories, Seattle, WA) after oxidation, reduction and trap (US EPA, 2002). Complying with the EPA Method 1630, samples for MeHg and DMeHg determinations went through distillation, ethylation and gas chromatographic (GC) separation before CVAFS analyses (US EPA, 2001).

The major anions: nitrate (NO$_3^-$), nitrite (NO$_2^-$), sulfate (SO$_4^{2-}$), chloride (Cl$^-$), phosphate (PO$_4^{3-}$) in precipitation were measured using Dionex DX-120 Ion Chromatograph according to EPA method 300.0 (US EPA, 1993). Phosphate and nitrate concentrations were often below detection limits (0.03 mg l^{-1} PO$_4^{3-}$ and 0.02 mg l^{-1} NO$_2^-$), thus, not included in our discussion. After transporting the samples to lab, pH was immediately measured.

2.4 Quality control and statistical analysis

Quality controls for THg and MeHg determinations included method blank, blank spikes, duplicates and matrix spikes. The method detection limits ($3 \times \sigma$) of THg and MeHg were 0.02 ng l^{-1} and 0.01 ng l^{-1}. The method blank was lower than the detection limits in all cases. The average relative standard deviation for the duplicate analyses of THg and MeHg were 5.2 % and 5.4 %, respectively. Recoveries for matrix spikes ranged from 95 to 110 % for THg, 85 to 108 % for MeHg. The equipment blanks of automatic precipitation sampler for THg and MeHg were 0.04 ng l^{-1} and 0.02 ng l^{-1}, respectively.

Table 2. Comparison of THg and MeHg concentration in precipitation measured in Core urban area, Chongqing, China and those at other sites.

	Rainfall (mm)	Concentration (ng l^{-1})		Time	Classification	Reference
		THg	MeHg			
Main urban area, Chongqing, China	921	30.67 (5.81–157.58)	0.31(0.04–1.94)	Jul 2010 to Jun 2011	Urban	This study
Wujiang, Guizhou, China	963	36.0 (7.5–149.1)[a]	0.19 (0.08–0.82)[a]	Jan to Dec 2006	Semi-remote	Guo et al. (2008)
Mt.Leigong, Guizhou, China	1533	4 (1.2–30.8)	0.04 (< detection level to 0.15)	May 2008 to May 2009	Remote	Fu et al. (2010a)
Mt.Gongga, Sichuan, China	1818	14.3 ± 7.7	0.16 ± 0.08	May 2005 to Apr 2007	Remote	Fu et al. (2010b)
Mt.Changbai, Jilin, China		11.5–15.9		Aug 2005 to Jul 2006	Remote	Wan et al. (2009)
Caryville, Tennessee, USA	1410 ± 100	10 ± 1		1995–1996	Town	Guentzel et al. (2001)
Underhill, Veront, USA	1091[b]	7.8–10.5[c]		1993–2004	Remote	Keeler et al. (2005)
Newcomb, New York, USA		4.9 (0.2–28.5)		Dec 2004 to Dec 2006	Remote	Choi (2008)
Great Lake Region		13.5 (10–60)	0.097 (0.01–0.85)	May 1997 to Dec 2003		Hall et al. (2005)
ELA, Northwestern Ontario, Canda	835.8	4.04 (0.95–9.31)	0.052 (0.010–0.179)	1992–1993	Remote	St. Louis et al. (1995)
Coweeta Hydrologic Laboratory, North Carolin, USA	139.7	5.75-25	< 0.025–0.16	11 Jun–14 Jul 1994	Remote	Allan et al. (1998)

[a] Precipitation Hg concentrations in Wujaing, China probably overestimate the "real" levels of precipitations semi-rural areas of Guizhou province for its measurements impacted by dry depositions.
[b] Mean rainfall for 11 yr.
[c] The range of annual VMW concentration for 11 yr.

Statistical analyses were performed using SPSS 13.0 software. The differences among sites as well as seasons were tested by the analysis of variation (ANOVA). 0.05 was used as the level of significance for these analyses.

Volume-weighted (VMW) mean concentration is calculated by the following formula (Acid Deposition Monitoring Network in East Asia, 2012):

$$\text{VMW} = (X_1 \times V_1 + X_2 \times V_2 + \cdots + X_t \times V_t) /$$

$$(V_1 + V_2 + \cdots + V_t) = \sum (X_t \times V_t) / \sum V_t$$

where, X_t is the ion concentration of each precipitation event (ng l^{-1}), V_t is the rainfall (mm).

3 Results

3.1 Total mercury in precipitation

Concentrations of THg in precipitation at the three sites from July 2010 to June 2011 ranged from 5.81 to 157.58 ng l^{-1}, with an annual volume-weighted (VMW) mean concentration of 30.67 ng l^{-1} ($n = 258$) (Table 2). Table 2 also shows a comparison of THg concentrations in some other sites in China or other countries. The mean concentration of THg in core urban area, Chongqing was close to that reported in Wujiang River Basin, Guizhou, China (Guo et al., 2008), but significantly higher than those reported in some remote areas such as Mt. Leigong, Guizhou, China (Fu et al., 2010a), Mt. Gongga, Sichuan, China (Fu et al., 2010b), Mt. Changbai, Jilin, China (Wan et al., 2009), Underhill, Veront, USA (Keeler et al., 2005) and Great Lake Region (Hall et al., 2005).

Additionally, most of the mercury in precipitation was associated with particulates, which accounted for 8.3 % to 92.7 % (mean 63.3 %) of total mercury, suggesting that PHg was dominant among the different mercury species. The high correlation ($r = 0.968$, $p = 0.000$) was also observed between PHg and THg concentrations indicating that the THg concentration in precipitation may be influenced by the PHg concentration.

In order to evaluate the spatial and temporal distribution of THg, all the measurements were grouped by seasons and sites (Fig. 2). The seasonal variations of THg in precipitation were obvious with higher mean THg concentrations in winter (December, January, and February) at all sampling sites.

This finding was similar to the seasonal variations of THg in precipitation in Wujiang River Basin, Guizhou, China; but in contrast to the observations in North America (Landis and Keeler, 2002), Adirondacks (Choi et al., 2008) and Great Lakes region (Hall et al., 2005), which found increased THg concentration during summer months.

A spatial trend of decreasing THg concentrations in precipitation was observed from the downtown (NA) to suburban site (BB) and then to the controlled site (JY) in the city. Anthropogenic influences (discuss in Sect. 3.5) and urban heat-island effect can be considered as possible explanations for this trend. THg concentrations at the downtown (NA) (VMW mean concentration 35.95 ng l^{-1}) is statistically significantly higher than that at suburb (BB) ($p = 0.018$) and controlled site (JY) ($p = 0.000$), while no significant difference between BB and JY was observed ($p = 0.060$). In order to further understand the spatial variations of THg concentrations in precipitation, all the samples collected at three sites were divided into six groups based on their initial concentrations: < 10 ng l^{-1}, 10–20 ng l^{-1}, 20–40 ng l^{-1}, 40–60 ng l^{-1}, 60–80 ng l^{-1}, > 80 ng l^{-1} (Fig. 3). The majority of all events at NA, BB, and JY were in the range of 20–40 ng l^{-1}. More than 10 % of all events at NA had THg concentration exceeding 80 ng l^{-1}, all observed in winter months (December, January); contrarily, less than 5 % of events at BB (three events) and JY (three events) had concentrations that high.
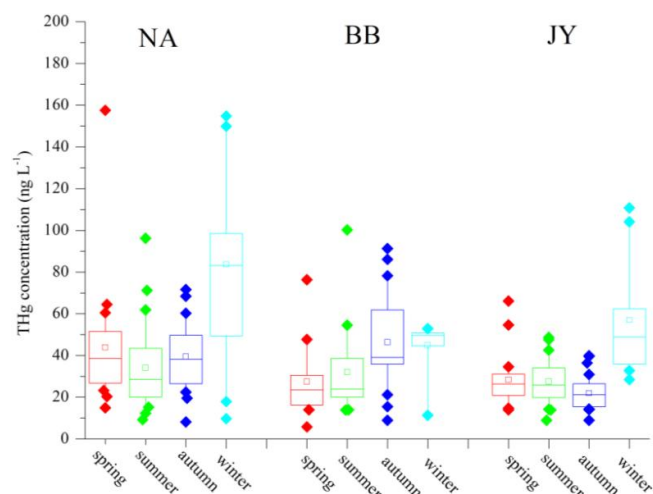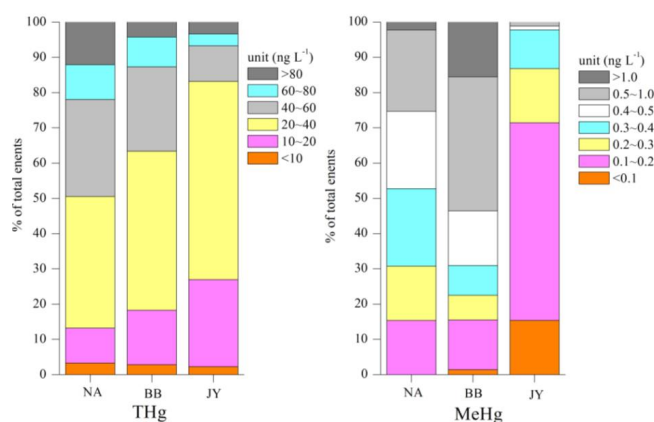
Fig. 2. THg concentrations in all precipitation samples at three sampling sites over time. Box plot showing median (solid line), mean (small square), 25th and 75th percentiles (box boundary), 10th and 90th percentiles (whiskers).

At all three sites, events with THg concentrations less than 10 ng l^{-1} were the rarest.

3.2 Methyl mercury in precipitation

From Table 2, measured MeHg concentrations at the three sites were ranged in 0.04–1.94 ng l^{-1}, the annual VMW mean MeHg concentration was 0.31 ng l^{-1}. When compared to other researches (Table 2), it was much higher than the levels reported in rural area in Wujiang Basin and Mt.Leigong, Guizhou, China (Guo et al., 2008; Fu et al., 2010a), Great lake regions (Hall et al., 2005) and ELA, Canada (St. Louis et al., 1994). It was also determined that 6.2–91.9 % (mean 40.5 %) of the measured MeHg was associated with particles and the correlation between MeHg and PMeHg concentrations was strong ($r = 0.527$, $p = 0.005$).

Percentage of MeHg in THg (%MeHg) in precipitation was 0.1–6.9 % (mean 1.3 %), 0.1–1.8 % (mean 0.7 %), and 0.2–7.6 % (mean 1.9 %) in NA, BB, JY, respectively. Figure 4 shows the %MeHg in all the samples at the three sites from July 2010 to June 2011. The majority of %MeHg was around 1.0 % which was comparable to those reported in northern Wisconsin (mean 1.3 %) (Lamborg et al., 1995) and Great lakes region (most of %MeHg below 1 %) (Hall et al., 2005); but was higher than that reported in Wujiang Basin, China (mean 0.7 %) (Guo et al., 2008). However, when compared with %MeHg in estuarine and marine waters (less than 5 %) or freshwater lakes and rivers (up to 30 %) (Coquery et al., 1997; Leermakers et al., 1996; Mason and Sullivan, 1999; Meili, 1997), it showed a lower MeHg production in precipitation. Higher %MeHg was discovered from September 2010 to November 2010, due to increased MeHg and decreased THg concentrations in autumn. There were only a small num-

**Fig. 3.** The frequency distribution for THg and MeHg concentrations at three sites during one year period.
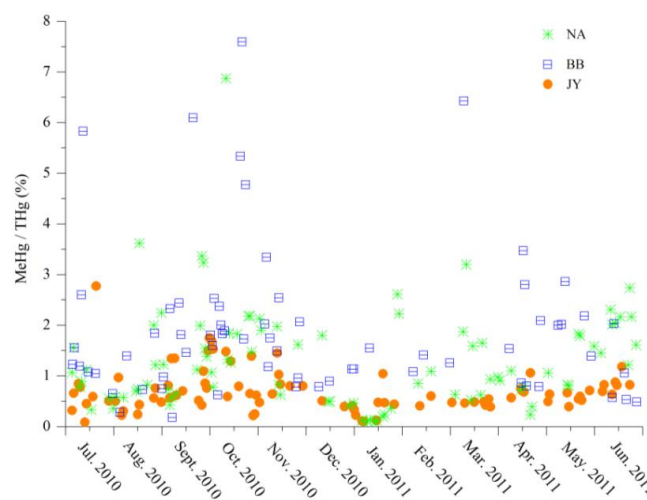
Fig. 4. The percent of THg present as MeHg in all precipitation events at 3 sites.

ber of events with %MeHg beyond 4 %, most of them appeared at BB except one at NA site (in October 2010).

There were significant seasonal variations of mean MeHg concentration. The highest arithmetic mean MeHg concentration occurred in autumn months (VMW mean concentration 0.45 ng l^{-1}) (Fig. 5), which was significantly higher than those sampled in other seasons (spring VMW 0.28 ng l^{-1}, $p = 0.000$; summer VMW 0.27 ng l^{-1}, $p = 0.000$; winter VMW 0.38 ng l^{-1}, $p = 0.001$). This finding about the temporal distribution of MeHg in precipitation is not consistent with observations in many regions which showed increased MeHg concentration during winter months (Guo et al., 2008; Bloom et al., 2004). In spring, summer and winter, MgHg concentrations did not show clear seasonal trend, especially at JY sites the MeHg concentrations in those three seasons were similar. The spatial variation in MeHg concentrations was obvious, the highest mean value (1.94 ng l^{-1})

Table 3. The consumption of total energy and coal (10 000 tons of Standard Coal Equivalent) and the percentage of coal consumption to total energy consumption from 2001 to 2010 in Chongqing.

year	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
coal consumption	1700.4	1929.9	2206.4	2505.1	3151.7	3381.9	3832.3	4049.0	4499.8	4857.6
total consumption of energy	2573.7	2823.1	3137.9	3668.4	4464.6	4881.6	5512.4	5895.1	6431.6	7117.4
coal %	66.1 %	68.4 %	70.3 %	68.3 %	70.6 %	69.3 %	69.5 %	68.7 %	70.0 %	68.3 %
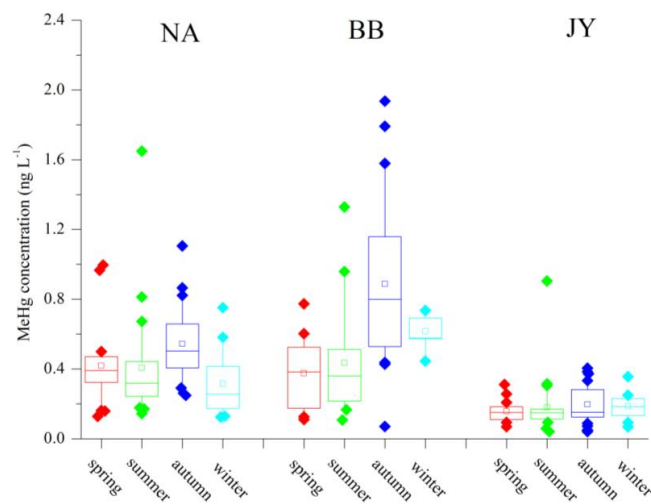
Fig. 5. MeHg concentrations in all precipitation samples at three sampling sites over time.

was observed at BB (suburb) while the lowest ($0.04\,\mathrm{ng\,l^{-1}}$) was observed at JY (control site).

The yearly frequency of events with MeHg concentrations among 0.1–$0.2\,\mathrm{ng\,l^{-1}}$, 0.2–$0.3\,\mathrm{ng\,l^{-1}}$, 0.3–$0.4\,\mathrm{ng\,l^{-1}}$, 0.4–$0.5\,\mathrm{ng\,l^{-1}}$, and 0.5–$1.0\,\mathrm{ng\,l^{-1}}$ at NA is similar (Fig. 3). Events with MeHg concentrations under $0.1\,\mathrm{ng\,l^{-1}}$ were recorded at JY, accounted for about 15 % of all events. At JY, events with lower MeHg concentration were more frequent, about 60 % of all fall into the 0.1–$0.2\,\mathrm{ng\,l^{-1}}$ range. At least 15 % of all events at BB had MeHg concentrations exceeding $1.0\,\mathrm{ng\,l^{-1}}$ which was not observed at JY.

4 Discussion

4.1 Relationship between mercury concentrations in precipitation and rain depth

THg, MeHg concentrations as well as the corresponding precipitation amount of every rain event at the three sites were shown in Fig. 6. Our results show that the THg and MeHg concentrations varied with rain amount. Significant negative correlations between THg and rain amount ($r = -0.176$, $p = 0.005$), as well as MeHg and the rain amount ($r = -0.151$, $p = 0.016$) were also observed. In our research, lower rain amount in winter (47.8 mm, about one-tenth of

that in summer) may be one possible reason for the highest THg concentration.

Frequent plum rains (continuous light rain) in autumn may explain the highest MeHg concentration. Light rain tends to have higher MeHg concentrations than does heavy rain, considering the similar amount of total MeHg sharing in different study sites. Statistically significant difference in MeHg was observed between spring and autumn ($p = 0.520$), although the precipitation amount was similar in spring (263.5 mm, 20 events) and autumn (207.1 mm, 28 events).

We grouped the measurements at the three sites according to the rainfall (China Meteorological Administration): light rain 0–$10\,\mathrm{mm\,d^{-1}}$; moderate rain 10–$25\,\mathrm{mm\,d^{-1}}$ and heavy rain 25–$50\,\mathrm{mm\,d^{-1}}$ (Fig. 7). Torrential rains (50–$100\,\mathrm{mm\,d^{-1}}$) and downpours ($> 100\,\mathrm{mm\,d^{-1}}$) were not taken into our consideration due to low frequencies. Figure 7 shows that lighter rain events exhibit higher THg and MeHg concentrations. THg concentrations measured in rainfalls less than 2 mm were significantly higher than those from heavier rains (2–$5\,\mathrm{mm}$, $p = 0.001$; 5–$10\,\mathrm{mm}$, $p = 0.000$; 10–$25\,\mathrm{mm}$, $p = 0.000$; 25–$50\,\mathrm{mm}$, $p = 0.000$). 25–$50\,\mathrm{mm}$ rainfall showed statistically significant difference in THg concentration when compared to $< 2\,\mathrm{mm}$ ($p = 0.000$) and 2–$5\,\mathrm{mm}$ rainfall ($p = 0.042$). However, there was no significant difference observed when compared to 5–$10\,\mathrm{mm}$ ($p = 0.277$) and 10–$25\,\mathrm{mm}$ ($p = 0.188$) rainfall. These results support the perspective that atmospheric mercury is effectively scavenged during the early part of the rain event (Guo et al., 2008; Hall et al., 2005). As described above, it is likely that the PHg in precipitation accounted for about 63.3 % of THg in our research, being consistent with that the scavenging of PHg by precipitation contributed significantly to mercury wet deposition at urban site (Sakata and Marumoto, 2005).

In addition, our research also preliminarily indicates that 0–$5\,\mathrm{mm}$ rainfall plays a dominant role in scavenging atmospheric Hg and 5 mm may be a threshold value for the biggest wash-out capability to Hg. The part of rain exceeding 5 mm may play a dilution role in term of concentration, instead of washing out.

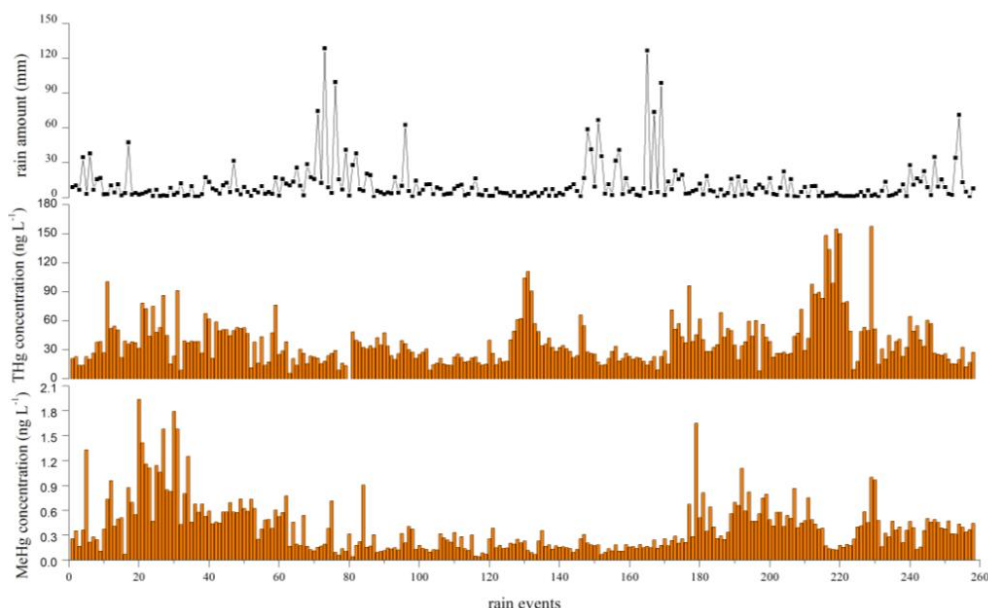However, no statistically significant difference was observed between rainfall and MeHg concentrations.

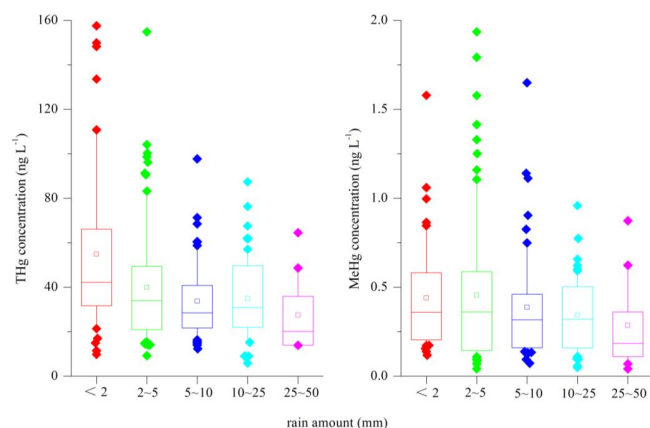**Fig. 6.** The relationship between THg and MeHg concentrations with rain amount.

Fig. 7. THg and MeHg concentrations in precipitation collected from three sampling sites grouped together according to different rain amount.

4.2 Anthropogenic influence on mercury distribution in precipitation

In order to investigate the anthropogenic contributions to precipitative Hg, we examined the correlations between THg and major anions in precipitation. It is interesting that a highly significant correlation was observed between THg and SO_4^{2-} ($r = 0.306$, $p = 0.000$), and between THg and NO_3^- ($r = 0.314$, $p = 0.000$) concentrations in precipitation. SO_4^{2-} and NO_3^- in precipitation mainly come from the washout of SO_2, NO_x in atmosphere, which are indicators for anthropogenic influences (Mao et al., 2008).

SO$_2$ is emitted primarily from the combustion of coal. Coal combustion emission of Hg (about $5\,\mathrm{t\,yr^{-1}}$) contributes to about 57 % of total anthropogenic emissions in Chongqing (Wang et al., 2006). In recent 10 yr, with the industrial developments in Chongqing, the coal consumption increased from 17.0×10^6 tons of Standard Coal Equivalent (SCE) in 2001 to 48.6×10^6 tons in 2011 (Chongqing Statistics Yearbook, 2011). In addition, sulfur-rich coal makes a large proportion in the coal consumption in Chongqing, which unleashes increasing SO_2 into the atmosphere (as shown in Fig. 8, SO_4^{2-} accounts for about 75 % in all anions), and results in serious acid rain, which affects biogeochemical behaviours of Hg, leading to a high washout ratio and formation of MeHg (Branfireun et al., 1999; Wong et al., 2006). In our research, the pH ranged from 2.88 to 7.27, with an acid rain (pH < 5.6) frequency up to 80 %. However, there was no significant correlation between pH and THg/MeHg concentrations ($p = 0.587$; $p = 0.530$). Thereafter, we preliminarily presume that the coal combustion is a main source for mercury wet deposition in Chongqing. Similarly, in Eastern Ohio, USA (Keeler et al., 2006) the dominant contributor to mercury wet deposition was found to be coal combustion ($\sim 70\%$). Thus, the increased coal combustion for domestic activities may also explain the high THg in precipitation in winter, besides the decreased rain amount (as discussed in Sect. 3.4). Guo et al. (2008) also pointed out that maximum THg concentrations in rain in winter may be related to coal burning in domestic activities.

NO_x in atmosphere is emitted directly from the combustion of fossil fuels (such as coal) and transportation sources (Caffrey et al., 2010; Lynam and Keeler, 2006; Lombard et al., 2011). NO_x exhibits peak concentrations in the morning,
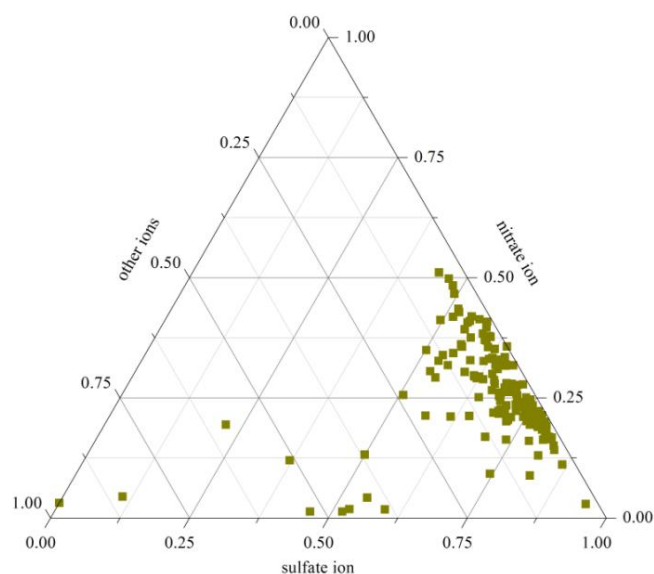
Fig. 8. The percent of main anions in precipitation.

typically associated with the morning commute emissions (Touma et al., 2006). In addition, transportation sources are considered as one of the contributors to atmospheric Hg in urban setting (Lyman and Gustin, 2008), and hourly averaged total gaseous mercury (TGM) concentrations were positively correlated with NO_x ($y = 7.0\,NO_x$ in ppm $+ 1.9$, $r^2 = 0.59$, $p < 0.0001$) (Stamenkovic et al., 2007). Motor vehicles were one of the most important contributors to atmospheric Hg in Chongqing (Yang et al., 2009). In Chongqing, the number of civil motor vehicles had increased for 5.8 folds from 2000 to 2010 (Chongqing Statistics Yearbook, 2001–2011). NO_3^- in precipitation made up 30 % of all measured anions (Fig. 8). Hence, besides coal combustion, mobile transportation sources may also influence the Hg distribution patterns within the urban areas Chongqing.

Higher THg levels at NA site were probably owing to the dense population centres and heavy transportation. The sampling site in NA district is about 5 km away from the Chongqing thermal power plant and 15 km away from the Luohuang thermal power plant (Fig. 1) which will be removed from Chongqing core urban areas by the end of 2013. By generating abundant Hg-containing particles (accounting for 62.6 % of THg at NA site), these two power plants greatly influenced the precipitation Hg concentration. PHg, generally depicted as regional and local pollutant for shorter atmospheric lifetime, deposits by wet and dry deposition within roughly 50 to 500 miles. Thus, Hg in precipitation at NA site might be related to Hg emissions in the surrounding area.

Unlike the NA site which locates in a relatively densely populated and crowded transport area, there is no major mercury emission source around the BB sampling site. Even though JY is relatively isolated from human activities (locates near rural areas and is generally characterised by ex-

tensive forest cover), the results showed no significant difference between BB and JY sampling sites. Long range atmospheric transport of Hg from surrounding areas may be the predominant source for Hg in JY.

Increased atmospheric loadings of Hg could lead to enhanced MeHg in precipitation (Hammerschmidt et al., 2007). However, there was no significant correlation between concentrations of MeHg and THg in precipitation in our research, indicating that they may come from different sources, and not related with anthropogenic source. Sampling is ongoing at these sites, and further researches will be able to identify the long-term trend and sources of MeHg in atmosphere or precipitation.

5   Conclusions

From July 2010 to June 2011, THg and MeHg concentrations in precipitation were investigated in the core urban areas of Chongqing, a traditional industrial city consuming large amount of coal as the major fuel source (70 % of energy consumption). The annual mean THg and MeHg concentrations in precipitation were 30.67 ng l^{-1} and 0.31 ng l^{-1}, respectively. The proportion of MeHg in THg ranged from 0.1 % to 7.6 % with a mean value of 1.3 %. An obvious seasonal variation of THg concentration was observed in precipitation, with highest value in winter and lowest in summer. This could attribute to the rain amount and the seasonal variations in anthropogenic emission sources, especially the coal combustion, a main source of mercury wet deposition in Chongqing. However, the highest MeHg value was observed in autumn. A geographic trend of decreasing THg concentrations in precipitation was also observed from the downtown to the suburb, and then to the controlled site in the city, which was related to regional and local emission sources and long range transport of Hg. Furthermore, 5 mm rainfall may be a threshold for the full wash-out capability, rainfall exceeding 5 mm may have a diluting effect.

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