Characteristics and potential sources of atmospheric particulate mercury in Jinan, China

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Abstract

Measurements of atmospheric particulate mercury (PHg) were conducted at a suburban site in Jinan, China from June 2014 to December 2015. The average PHg concentration was 508.5 ± 402.7 pg m⁻³, and the average Hg content in PM_{2.5} (particles with a diameter of 2.5 μm or less) was 6.60 ± 5.82 μg g⁻¹. Both PHg and Hg content in PM_{2.5} aerosols were comparable to levels in some cities in China and were much higher than in cities in North America and Europe. Weak correlations were found between PHg and meteorological parameters. The correlations between PHg and other pollutants in ambient air, including SO₂, CO and NO_x, together with their wind dependence were used for source analysis, which suggested coal-fired industries, cement plants and traffic emissions as potential local sources for the site. Cluster analysis of 36-h backward trajectories suggested that the regional transport from southwestern Shandong Province also contributed to PHg in Jinan.

Keywords: Atmospheric particulate mercury; Source analysis; Meteorological parameter; Cluster analysis; Jinan

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1. Introduction

Mercury (Hg) is a highly toxic heavy metal that attracts global concern due to its persistence and bioaccumulation in food chains. It can endanger both human health and the environment. The atmosphere plays a dominant role in mercury transformation in various environments and allows mercury to enter remote areas through long-range transportation (Pirrone and Mahaffey, 2005; Wängberg et al., 2001). Mercury can be released into the atmosphere from both natural sources (e.g., volcanoes, forest fire, geothermal vents and evaporation from soil and water surfaces) and anthropogenic sources (e.g., coal combustion, non-ferrous metal production, cement production and waste incineration) (Pacyna et al., 2010; Pirrone et al., 2010; Zhang et al., 2015a).

Atmospheric mercury generally exists in three forms: gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particulate mercury (PHg). Each mercury species has different physical and chemical properties and, therefore, different behaviors. GEM is the predominant form of atmospheric mercury, has a residence time of several months to a year and can be transported over long distances (Schroeder and Munthe, 1998). RGM has a much shorter residence time (hours to several days) compared with GEM due to its high solubility and reactivity (Laurier et al., 2003). PHg has high solubility, deposition velocity and scavenging coefficients. PHg residence time generally ranges from hours to several weeks depending on the particle size (Schroeder and Munthe, 1998). Although PHg accounts for a small part of total atmospheric mercury (less than 10%), it plays a vital role in the deposition of atmospheric mercury and therefore the global mercury biogeochemical cycle.

However, long-term monitoring studies of PHg are limited, and their relationships with physical and chemical parameters indicated PHg levels were mostly related to local emission, air mass transport, meteorological parameters and chemical transformation. For example, Mao et al. (2012) suggested that PHg was influenced by wind speed, solar radiation and temperature, whereas relative humidity and precipitation had negligible impact on PHg based on their 1.5 year PHg monitoring study in New England, USA. Poissant et al. (2005) conducted a one-year PHg measurement campaign in southern Quebec, Canada and found that PHg was correlated significantly with solar radiation and wind speed. They also found that PHg was associated with air mass transport and transformation from Hg^0 . Two-year PHg dataset collected from Lyman and Gustin (2009) exhibited that PHg was impacted primarily by local sources and by meteorological conditions in Reno, USA. These studies measured PHg on $\text{PM}_{2.5}$ (particles with a diameter of 2.5 μm or less) using Tekran 1135, instead of manual sampling and analysis.

In recent decades, mercury contamination has become a serious problem in China. Previous studies have shown that approximately two-thirds of global anthropogenic mercury emissions are from Asia and that China is the largest worldwide contributor (Pacyna et al., 2010; Pirrone et al., 2010). Higher emissions may lead to higher atmospheric mercury levels. Several atmospheric mercury measurements have been conducted in Chinese cities and remote areas (Fang et al., 2004; Feng et al., 2004; Fu et al., 2011; Fu et al., 2008; Fu et al., 2012; Wang et al., 2016; Wang et al., 2006; Xiu et al., 2009; Xiu et al., 2005; Xu et al., 2015; Zhang et al., 2015b; Zhu et al., 2014). All of these studies reported much higher mercury species concentrations than studies in developed countries. However, only a few of them focused on PHg in comparison to GEM and RGM.

The updated anthropogenic mercury emission inventories show that Shandong Province ranks second of all of the provinces in China because of the contributions of industrial coal

consumption and cement production (Zhang et al., 2015a). Jinan, the capital of Shandong Province, is a typical area that suffers severe air pollution especially particulate matter contamination. This area could be regarded as an important pathway of mercury transport in eastern China. Studies related to PM_{2.5} have been conducted in Jinan and improve our understanding of the chemical and physical characteristics, sources, and health impacts of PM_{2.5} (Gao et al., 2011; Wang et al., 2012; Yang et al., 2013; Yang et al., 2012). However, no atmospheric particulate mercury data in Jinan has been reported.

To our knowledge, this study is the first long-term monitoring study of PHg in this area. The purposes of this study are to: (1) report the levels of PHg concentration and the mercury content in PM_{2.5} in Jinan; (2) investigate the relationship between PHg and meteorological parameters, as well as other pollutants in the ambient air; (3) discuss the impact of long-range transport on PHg; and (4) attempt to identify the potential sources of PHg in Jinan.

2. Methods

2.1. Site description

The experiment was conducted in Jinan in eastern China (Fig. 1), a typical medium-sized city with increasing population and heavy pollution. The sampling site (36.67°N, 117.03°E) was on the roof of a two-story building in Environmental Monitoring Central Station of Shandong Province, approximately 7 m above ground. It is a suburban site, surrounded by a main road with heavy traffic, residential communities and farmlands. There are a few large industries near the site.

Fig. 1. Location of sampling site in Jinan and the distribution of main industries.

2.2. PM_{2.5} collection

In this study, PM_{2.5} samples were collected using a Thermo Scientific Partisol 200i sampler (Thermo Scientific, USA) with Teflon filters (47 mm, 1 μm pore size) at a flow rate of 16.7 L min⁻¹. Each sample was collected for 23 h, from 10:00 am to 9:00 am the next morning.

Before sampling, Teflon filters were baked at 100 °C for 3 h to remove any deposited

compounds, conditioned in a desiccator for 24 h, and then weighed with a 0.01 mg precision microbalance. After sampling, the filters were equilibrated in a desiccator for 24 h prior to weighing and stored at -18 °C until analysis. Petri dishes were used to store and transport the filters.

The sampling campaign started on 3 June 2014 and ended on 28 December 2015. A total of 357 samples were collected during the sampling period.

2.3. Particulate mercury analysis

To analyze PHg, a Teflon filter was put into a 20 mL brown high-borosilicate glass bottle and soaked by 5 mL BrCl for 24 h. All mercury-containing compounds were oxidized by a digestion solution to soluble Hg^{II} species. Then 15 mL ultrapure water was added to the bottle, which diluted the sample to 0.5% BrCl. Prior to analysis, 0.1 mL $\text{NH}_2\text{OH}\cdot\text{HCl}$ was pipetted into the sample to reduce the halogens. Atomic Fluorescence Spectrometry (AFS) was applied to determine the concentration of mercury after the Hg^{II} in the extract was reduced by KBH_4 to form Hg^0 . This analysis method was used previously by Talbot et al. (2011).

2.4. Backward trajectories analysis

To identify the source of long range transport and regional transport of PHg and to study the impact of air mass movements on PHg, the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by the National Ocean and Atmospheric Administration (NOAA) (Draxler and Rolph, 2003) was used with the Global Data Assimilation System (GDAS) meteorological dataset (spatial resolution 1°). We calculated 36-h backward air mass trajectories ending at the sampling site with a starting height of 1,000 m above ground level. Then, we performed cluster analysis of trajectories.

2.5. Meteorological parameters and criteria pollutants data

Hourly meteorological data for the sampling site, including wind direction, wind speed, air temperature, relative humidity and surface pressure and air pollutants data including O_3 , SO_2 , CO, NO, NO_2 and NO_x were provided by Environmental Information and Monitoring Center of Shandong Province.

2.6. Quality assurance

Field blank filters were measured to reduce the artifacts. The field blank filters were treated similarly to other samples. Field blanks include the filter blanks, reagent blanks, transportation blanks and storage blanks; therefore, field blanks were subtracted from the measured values.

To prevent contamination, the collector head was cleaned with ethyl alcohol before use. The tweezers, scissors, beakers, pipettes and sample bottles were soaked in 20% HNO_3 solution, 5% BrCl, and 5% HCl solution in sequence, for more than 24 h respectively, and then were rinsed five times with ultrapure water.

3. Results and discussion

3.1. Concentrations of PHg in ambient air

The average concentration of PHg in PM_{2.5} during the study period was 508.5 ± 402.7 pg m⁻³, with the median concentration of 441.3 pg m⁻³. Table 1 summarized some studies of PHg worldwide. The PHg concentration in Jinan was over ten times higher than that in remote areas of China and was of the same order of magnitude as in other cities in China. It was lower than that of Beijing and Nanjing. However it should be noted that the particulate matter collected in our study was PM_{2.5}; whereas PHg measured in Beijing and Nanjing were referred to TSP and PM₁₀, respectively. PHg in Jinan was slightly higher than that of cities such as Guiyang and Shanghai but was nearly three-fold higher than coastal cities such as Xiamen, which are relatively cleaner than inland cities. Compared globally, the level of PHg in Jinan significantly exceeded that of most cities in East Asia, Europe and North America by nearly two orders of magnitude. This may result from the differences in energy structures, industrial structures and pollution control technologies between China and developed countries. Only the values observed from areas that were heavily impacted by strong anthropogenic sources (e.g., Zabrze and Mexico City) such as cement production, petroleum refining, non-ferrous metal refining and waste incineration could be comparable. It is speculated that Jinan, as well as other cities in China, probably has more Hg emission sources than developed countries.

Table 1

Comparison of PHg concentration at various locations worldwide

Location	Classification	Time	Cutoff size	PHg (pg m ⁻³)	Reference
Jinan, China	Suburban	Jun 2014-Dec 2015	PM _{2.5}	508.5 ± 402.7	This study
Beijing, China	Urban	Jan, Feb, Sep 1998	TSP	1180 ± 820	Wang et al. (2006)
Nanjing, China	Urban	Jun 2011-Feb 2012	PM ₁₀	1100 ± 570	Zhu et al. (2014)
Guiyang, China	Urban	Aug-Dec 2009	PM _{2.5}	368 ± 676	Fu et al. (2011)
Shanghai, China	Urban	Nov 2013-Oct 2014	PM _{2.5}	300 ± 310	Duan et al. (2016)
Xiamen, China	Coastal	Mar 2012-Feb 2013	PM _{2.5}	174.4 ± 280.6	Xu et al. (2015)
Mt. Gongga, China	Remote	May 2005-Apr 2006	TSP	30.7	Fu et al. (2008)
Mt. Waliguan, China	Remote	Sep 2007-Sep 2008	PM _{2.5}	19.4 ± 18.1	Fu et al. (2012)
Seoul, Korea	Urban	Feb 2005-Feb 2006	PM _{2.5}	23.9 ± 19.6	Kim et al. (2009)
Cape Hedo, Japan	Remote	Mar-May, 2004	PM _{2.5}	3.0 ± 2.5	Chand et al. (2008)
Nova Scotia, Canada	Urban	Jan 2010-Dec 2011	PM _{2.5}	2.3 ± 3.1	Cheng et al. (2013)
Thompson Farm, USA	Coastal	Feb 2009-Aug 2010	PM _{2.5}	0.19-1.14 ^a	Mao and Talbot (2012)
Rochester, USA	Suburban	Dec 2007-Nov 2009	PM _{2.5}	8.7 ± 12.8	Choi et al. (2013)
Chicago, USA	Urban	Jul-Nov 2007	PM _{2.5}	9 ± 20	Gratz et al. (2013)
Zabrze, Poland	Urban	Oct 2006-Apr 2007	PM _{2.5}	100.4	Pyta et al. (2008)
Mexico City, USA	Urban	Mar 2006	PM _{2.5}	187 ± 300	Rutter et al. (2009)

^a The range of median concentrations in different seasons.

Fig.2. Time series of PHg and PM_{2.5} concentrations in Jinan during the study period.

Fig. 2 shows the time series of PHg and PM_{2.5} concentrations during the study period. PHg showed significant variability with some extremely high concentration episodes; this may indicate that the study site was impacted by strong nearby sources. The PHg concentrations showed higher levels during cold months compared with warm months. Similar monthly variations were observed by previous studies in China (Fang et al., 2004; Fu et al., 2008; Fu et al., 2012; Xiu et al., 2009; Xu et al., 2015) and are consistent with some observations outside of China (Cheng et al., 2013; Choi et al., 2013). This can be explained by more favorable condition for the formation of particle-phase mercury and more coal consumption in heating period during winter, along with divergent meteorological conditions between cold and warm seasons (Feng et al., 2004; Kim et al., 2012; Lyman and Gustin, 2009; Rutter and Schauer, 2007). The concentrations of PHg and PM_{2.5} showed significant positive correlation ($r = 0.358$, $p < 0.01$), which revealed that the PHg concentration in the atmosphere was greatly influenced by the concentration of particles. It also suggested some common emission sources for PHg and PM_{2.5}.

3.2. Hg content in PM_{2.5}

To eliminate the effect of PM_{2.5} concentration, the mercury mass content in PM_{2.5} (PHg/PM_{2.5}) was calculated by dividing the mass of Hg on the filter (μg) by the mass of particulate matter on the filter (g). During the study period, the average PHg/PM_{2.5} was $6.60 \pm 5.82 \mu\text{g g}^{-1}$ and the median was $5.26 \mu\text{g g}^{-1}$. Compared with the mercury content in other sources, such as $0.019 \mu\text{g g}^{-1}$ in the soil of Shandong Province (CEM, 1990) and $0.18 \mu\text{g g}^{-1}$ in the coal from Shandong Province (Streets et al., 2005), PM_{2.5} in Jinan appeared to have a strong enrichment of mercury. PHg/PM_{2.5} in Jinan was significantly higher than values reported from other cities domestically and abroad. Previous studies found that Hg content in fine particles was $0.2 \mu\text{g g}^{-1}$ in Okinawa (Chand et al., 2008), $1.23\text{--}4.28 \mu\text{g g}^{-1}$ in Shanghai (Xiu et al., 2009), and $3.5 \mu\text{g g}^{-1}$ in Zabrze (Pyta et al., 2008). The elevated Hg content in Jinan may reflect the strong anthropogenic mercury emission sources here.

Fig.3. Relationship between Hg mass content in PM_{2.5} and PM_{2.5} concentration.

A power function existed between PHg/PM_{2.5} and PM_{2.5} concentration ($p < 0.05$) (Fig. 3). The highest values of PHg/PM_{2.5} were seen when PM_{2.5} concentrations were at low levels ($< 70 \mu\text{g m}^{-3}$). Then PHg/PM_{2.5} decreased rapidly as PM_{2.5} concentrations increased. When PM_{2.5} concentrations reached extremely high levels ($> 250 \mu\text{g m}^{-3}$), PHg/PM_{2.5} values appeared to be relatively constant at very low values. One possible explanation is that particle size could affect PHg/PM_{2.5} value. Study of PM_{2.5} size distribution has been conducted in Jinan. Xu (2011) reported that in Jinan when PM_{2.5} concentrations were elevated (i.e., haze days), particles tended to consist of coarser sizes; when PM_{2.5} concentrations were low (i.e., clear days), it was favorable for the existence of ultrafine particles. Previous studies demonstrated that mercury largely accumulated on ultrafine particles. Xiu et al. (2009) found that 47-60% of mercury in PM₈ concentrated on PM_{1.6} in Shanghai, China. Kim et al. (2012) showed that 55-91% of mercury in PM₁₈ accumulated on PM_{1.8} in Seoul, Korea. In Jinan, on hazy days PM_{2.5} concentrations were elevated but Hg content in PM_{2.5} were low, whereas on clear days PM_{2.5} was comprised of more ultrafine particles with high Hg content. The ultrafine particles have larger surface area and could adsorb mercury more easily.

Considering the elevated values of PHg concentration and Hg content in Jinan, more attention should be paid to the influencing factors and sources of PHg.

3.3. Influences of meteorological parameters

As previous studies suggested, the temporal variation of PHg could be dependent on meteorological conditions. Table 2 shows the correlations between PHg concentration and meteorological parameters.

There was a significant negative correlation between PHg and temperature, especially during winter ($r = 0.300$, $p < 0.01$). The fundamental reason was the impact of gas-particle partitioning, which plays an essential role in the formation of PHg in fine particles (Xiu et al., 2005). Gas-particle partitioning is highly dependent on temperature. Adsorption of gaseous Hg onto a fine particle is more efficient at low temperature; there is a widely recognized equation in Rutter and Schauer (2007) illustrating the anticorrelation between the partitioning coefficient and

temperature. Also the increased emissions during wintertime heating periods should not be neglected, as coal combustion is commonly used for space heating, which emits both Hg and PM_{2.5}. Higher particle concentrations also provided more room for increased GEM oxidation reactions to produce PHg.

Table 2

Summary of Spearman's coefficients between PHg and meteorological parameters.

	PM _{2.5}	Content	Wind Speed	Pressure	Humidity	Temperature
PHg	0.358**	0.781**	-0.114*	0.164**	0.122*	-0.148**
PM _{2.5}		-0.217**	-0.314**	-0.003	0.299**	0.015
Content			0.062	0.154**	-0.067	-0.139**
Wind Speed				-0.003	-0.251**	0.001
Pressure					-0.266**	-0.883**
Humidity						0.234**

** : the p-value < 0.01

* : the p-value < 0.05

Surface pressure was positively correlated with PHg concentrations, which was in line with the negative correlation between temperature and PHg. It has reached an agreement that low (high) pressure was normally coupled with high (low) temperature and elevated (lowered) planet boundary layer height. Low pressure, along with high temperature and increased planet boundary layer height, could accelerate air mass exchange and mixing (Xu et al., 2015) and dilute PHg concentration in ambient air assuming constant emissions as a result.

PHg showed positive correlation with RH. Liquid water or droplets tend to form at higher RH. Several studies illustrated that mercury transformation could be accelerated by aqueous reactions or heterogenic reaction in the liquid phase. For example, Lin and Pehkonen (1999) reported that the weak acidic environment in droplets was favorable to reactions between gaseous mercury and ions such as SO₃²⁻, SO₄²⁻, Cl⁻, HS⁻, S²⁻ and H₂O₂. Subir et al. (2011) also summarized from the literature that gaseous elemental mercury was unlikely to react with O₃ or OH in the gas phase due to the low reaction constant; however, gaseous elemental mercury could be converted to gaseous oxidized mercury by fast oxidation in the aqueous phase. Gaseous oxidized mercury behaves similarly to semi-volatile organic compounds and has been shown to partition onto aerosols at high RH (Pankow, 1993). These studies pointed to the pathway that PHg was formed via gaseous mercury adsorption onto particles followed by oxidation in aqueous phase at high RH.

The inverse correlation between PHg concentration and wind speed revealed that high PHg events were likely to occur at relatively low wind speed, alluding to the predominant effect of local emissions. The relationships between PHg concentration and wind speed and wind direction will be discussed further in Section 3.5.

The correlations between PHg and the meteorological parameters listed above were all significant. However, the relationships were weaker than in other studies in Holland (Gratz et al., 2013), Shanghai (Xiu et al., 2009) and Rochester (Choi et al., 2013). This may, in part, reflect that anthropogenic source emissions contributed more to PHg in the ambient air compared to the meteorological impacts.

3.4. Correlations with other pollutants in the ambient air

Table 3 shows the correlations between PHg and other gaseous pollutants, including SO₂, CO, O₃, NO, NO₂ and NO_x. The strongest positive correlation was between PHg and SO₂, the marker pollutant from coal burning, especially during winter ($r = 0.451$, $p < 0.01$), consistent with the fact that coal burning is the largest anthropogenic mercury emission source to the atmosphere (Pacyna et al., 2010; Streets et al., 2005; Zhang et al., 2015a). China is the largest contributor to global anthropogenic Hg emissions by a large margin (Pacyna et al., 2010), and unlike cities in Europe and North America, coal burning is the main energy source in Jinan. Except for municipal space heating in cold seasons and industrial needs such as coal-fired power plants and coal-fired steel plants that operate all year round, equal attention should be paid to coal burning for producing heat and cooking food in small residential units of rural areas.

Table 3

Summary of Spearman's coefficients between PHg and other pollutants in the ambient air.

	PM _{2.5}	Content	SO ₂	CO	O ₃	NO	NO ₂	NO _x
PHg	0.358**	0.781**	0.360**	0.304**	-0.094	0.178**	0.261**	0.241**
PM _{2.5}		-0.217**	0.349**	0.696**	-0.073	0.106*	0.398**	0.305**
Content			0.150**	0.104*	-0.070	0.102	0.009	0.043
SO ₂				0.339**	-0.278**	0.390**	0.585**	0.546**
CO					-0.237**	0.307**	0.433**	0.414**
O ₃						-0.506**	-0.517**	-0.566**
NO							0.658**	0.850**
NO ₂								0.944**

** : the p-value < 0.01

* : the p-value < 0.05

The traffic emission tracers, CO and NO_x, were both positively correlated with PHg, which indicates traffic is another emission source in Jinan. Gasoline powered vehicles were found to emit various mercury species to the atmosphere, although not as much as from coal combustion (Won et al., 2007), which indicates that traffic emissions should be considered as an Hg source in the areas near heavy-duty roads. CO showed a strong positive correlation with PM_{2.5} in addition to the positive correlation with PHg which could be ascribed to combustion. Apart from coal combustion, other combustion such as mobile oil combustion is considered to emit Hg to the atmosphere (Zhang et al., 2015a). Moreover, PM_{2.5} was found to be contributed in part to traffic emissions in a previous study conducted in Jinan (Yang et al., 2013). This result supports our original assumption.

We did not find any correlation between PHg and O₃ at our site. Positive correlations with O₃, temperature and solar radiation, as well as negative correlation with relative humidity, could be an indication of the presence of photochemical processing (Xu et al., 2015) by which Hg⁰ could be efficiently converted into Hg^{II} and deposited onto the particles. We could not find any similar correlations to those mentioned above. Future work is needed to demonstrate photochemical processes of mercury in Jinan.

3.5. Wind rose and PHg rose

The wind rose at the sampling site during the study period is shown in Fig. 4A. The prevailing wind direction at our site was E-SSW, which accounted for 72% of the entire study period. The wind speed was generally low; 63% was under 1.5 m s^{-1} .

Fig.4. (A) Wind rose covering the whole study period; (B) PHg rose covering the whole study period; (C) PHg concentration versus wind speed

The PHg concentration under different wind speeds and wind directions is shown in Fig. 4B. The average PHg concentrations under wind speeds of $<1.5 \text{ m s}^{-1}$, $1.5\text{--}3.5 \text{ m s}^{-1}$, and $>3.5 \text{ m s}^{-1}$ were 532.72 pg m^{-3} , 468.61 pg m^{-3} , and 300.12 pg m^{-3} , respectively (Fig. 4C). It is notable that the PHg concentration under the condition of lower wind speed was evidently higher than that under higher wind speed and it fluctuated more strongly. Additionally, more than 80% of the high-PHg events (above the 90th percentile value) were observed at low wind speed ($<1.5 \text{ m s}^{-1}$). Apart from the strong mixing of air masses by wind at high speeds, this result indicates that nearby sources emissions may be the major contributors to PHg at our site. The industries adjacent to the site are of main concern. As listed in Fig. 1, an oil refinery and a steel plant are closely located to the north

of the site. They are in an old industrial area and receive much attention because of their great consumption of coal, various emissions of air pollutants and relatively close distance to the urban area. Abdelhafez and Li (2015) showed that industrial activities contaminated the surrounding area with heavy metals. The city of Jinan is located in a basin, and hence air masses from all sources in the basin had been mixed at one point or the other in time, and thus those industrial sources in the northern parts of the city most likely impacted PHg measurements at the site. Traffic emission was another source. The road extremely close to the site is one of the broadest and most congested roads in Jinan, especially at rush hours in the morning and in the evening on weekdays. This increased the possibility for PHg emitted from gasoline powered vehicles to be observed at the site. Moreover, the local residential source should not be neglected. As our site is located in a suburban area, small residential units that produce heat and food with energy from coal combustion used low-grade coal mostly probably leading to significant Hg emissions.

PHg showed wind directional dependence in Jinan. Approximately 60% of the high PHg values were observed under NE-SE winds, and 37.5% were under S-W winds. High PHg values associated with high wind speed were observed under these directions. This result corresponded to the distribution of large point sources (Fig. 1). A power plant, a thermal power plant and a foundry-forge plant were the main point sources situated in the NE-E of the monitoring site, and two thermal power plants and a cement plant to the W-SW. These industrial plants were all coal-fired and have been identified as primary anthropogenic mercury sources (Pacyna et al., 2010; Zhang et al., 2015a). However, there were no apparent large point sources to the south and yet there were high concentrations of PHg, which could be caused by regional transport.

In summary, coal-fired industrial plants, cement plants and traffic emissions were the dominant local sources of PHg in Jinan. Residential sources contributed a smaller but non-negligible portion. This is consistent with the results from Section 3.4.

3.6. Backward trajectories analysis

To further investigate the regional transport of PHg and its impact on PHg in Jinan, the 36-h air mass backward trajectories for a whole year (2015) were clustered and categorized into 4 sections, as shown in Fig. 5.

Cluster 1, cluster 2 and cluster 3 illustrated three major pathways for long-range transport. Cluster 1 originated from the Badain Jaran Desert in the west of Inner Mongolia and accounted for 7%. Cluster 2 originated from Mongolia and southern Russia and accounted for 12%. Cluster 3 originated from the Otindag Sand Land located in middle Inner Mongolia and accounted for 21%. The origins of these clusters are widely recognized as the main sources of Asian dust. In air masses from these dust sources there were a large proportion of coarse particles that had weak adsorption of mercury. And the transport speed was high. Taken together, these conditions did not favor accumulation of mercury on particles. As a result, the concentration of PHg from cluster 1 was the lowest (309.15 pg m^{-3}). However, cluster 2 and cluster 3 did not show a similar pattern with low PHg concentration. The PHg concentration from cluster 2 was 476.53 pg m^{-3} and from cluster 3 was 454.40 pg m^{-3} . This result can be explained by the transport pathways. All three clusters originated from dust sources area of low mercury. When travelling on the pathway, air masses entrained particles from the heavy pollution areas increasing PHg concentrations. One of the most polluted areas, the Beijing-Tianjin-Hebei region, was on the path of cluster 2 and cluster

3. The region was reported to have heavy PHg pollution because of a dense population and intensive industry (Streets et al., 2005; Wang et al., 2006), which allowed particles passing through to adsorb mercury. Therefore, high values of PHg were observed from these two clusters.

Cluster 4 accounted for 60% of the total trajectories and represented transport from the southwestern part of Shandong Province, which has been reported to be a major mercury contributor of the Province due to its dense distribution of coal-fired plants (Xiong et al., 2016). Cluster 4 originated in and passed through mercury polluted areas. Combined with the short transport distance and therefore long residence in polluted areas, mercury was accumulated on particles. This could explain the highest PHg concentration from cluster 4 (491.96 pg m^{-3}). Therefore, cluster 4, the regional transport source, contributed to PHg in Jinan in addition to the local emission sources. Moreover, cluster 4 could be one possible explanation for the unidentified source of the high PHg concentrations in southerly wind noted in Section 3.5.

Fig. 5. Cluster analysis of HYSPLIT 36-h backward trajectories of air masses in Jinan.

4. Conclusions

During June 2014 to December 2015, PHg and Hg content in PM_{2.5} were measured at a suburban site in Jinan. The average PHg concentration and Hg content were $508.5 \pm 402.7 \text{ pg m}^{-3}$ and $6.60 \pm 5.82 \text{ } \mu\text{g g}^{-1}$, respectively. Both PHg and Hg content were significantly higher than in cities in Europe and North America and were comparable to that in cities with heavy air pollution in China, which points to strong local emission sources.

PHg showed negative correlations with temperature and wind speed, and positive correlations with surface pressure and relative humidity. The correlations with meteorological parameters were all significant, albeit relatively weak.

For source identification, the positive correlations of PHg with SO₂, CO, and NO_x and the wind direction suggested that coal-fired industries, cement plants and traffic emissions from nearby congested roads were the major local sources. 36-h air mass back trajectories suggested that PHg in Jinan was less impacted by long-range transport originating from dust sources. In contrast, transport from southwestern part of Shandong Province could have contributed to the PHg levels observed in Jinan.

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Table 1

Comparison of PHg concentration at various locations worldwide

Location	Classification	Time	Cutoff size	PHg (pg m ⁻³)	Reference
Jinan, China	Suburban	Jun 2014-Dec 2015	PM _{2.5}	508.5±402.7	This study
Beijing, China	Urban	Jan, Feb, Sep 1998	TSP	1180±820	Wang et al. (2006)
Nanjing, China	Urban	Jun 2011-Feb 2012	PM ₁₀	1100±570	Zhu et al. (2014)
Guiyang, China	Urban	Aug-Dec 2009	PM _{2.5}	368±676	Fu et al. (2011)
Shanghai, China	Urban	Nov 2013-Oct 2014	PM _{2.5}	300±310	Duan et al. (2016)
Xiamen, China	Coastal	Mar 2012-Feb 2013	PM _{2.5}	174.4±280.6	Xu et al. (2015)
Mt. Gongga, China	Remote	May 2005-Apr 2006	TSP	30.7	Fu et al. (2008)
Mt. Waliguan, China	Remote	Sep 2007-Sep 2008	PM _{2.5}	19.4±18.1	Fu et al. (2012)
Seoul, Korea	Urban	Feb 2005-Feb 2006	PM _{2.5}	23.9±19.6	Kim et al. (2009)
Cape Hedo, Japan	Remote	Mar-May, 2004	PM _{2.5}	3.0±2.5	Chand et al. (2008)
Nova Scotia, Canada	Urban	Jan 2010-Dec 2011	PM _{2.5}	2.3±3.1	Cheng et al. (2013)
Thompson Farm, USA	Coastal	Feb 2009-Aug 2010	PM _{2.5}	0.19-1.14 ^a	Mao and Talbot (2012)
Rochester, USA	Suburban	Dec 2007-Nov 2009	PM _{2.5}	8.7±12.8	Choi et al. (2013)
Chicago, USA	Urban	Jul-Nov 2007	PM _{2.5}	9±20	Gratz et al. (2013)
Zabrze, Poland	Urban	Oct 2006-Apr 2007	PM _{2.5}	100.4	Pyta et al. (2008)
Mexico City, USA	Urban	Mar 2006	PM _{2.5}	187±300	Rutter et al. (2009)

^a The range of median concentrations in different seasons.

Table 2

Summary of Spearman's coefficients between PHg and meteorological parameters.

	PM _{2.5}	Content	Wind Speed	Pressure	Humidity	Temperature
PHg	0.358**	0.781**	-0.114*	0.164**	0.122*	-0.148**
PM _{2.5}		-0.217**	-0.314**	-0.003	0.299**	0.015
Content			0.062	0.154**	-0.067	-0.139**
Wind Speed				-0.003	-0.251**	0.001
Pressure					-0.266**	-0.883**
Humidity						0.234**

** : the p-value < 0.01

* : the p-value < 0.05

Table 3

Summary of Spearman's coefficients between PHg and other pollutants in the ambient air.

	PM _{2.5}	Content	SO ₂	CO	O ₃	NO	NO ₂	NO _x
PHg	0.358**	0.781**	0.360**	0.304**	-0.094	0.178**	0.261**	0.241**
PM _{2.5}		-0.217**	0.349**	0.696**	-0.073	0.106*	0.398**	0.305**
Content			0.150**	0.104*	-0.070	0.102	0.009	0.043
SO ₂				0.339**	-0.278**	0.390**	0.585**	0.546**
CO					-0.237**	0.307**	0.433**	0.414**
O ₃						-0.506**	-0.517**	-0.566**
NO							0.658**	0.850**
NO ₂								0.944**

**: the p-value < 0.01

*: the p-value < 0.05