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Characteristics of PM2.5 in Miyun, the northeastern suburb of Beijing: chemical composition and evaluation of health risk

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Abstract In recent years, the fine particulate matter pollution has become increasingly serious in Beijing, the capital of China. Being considered as an environment-friendly district of Beijing, current research concerning air pollution in Miyun area was relatively less. From August 24, 2013 to September 29, 2013, 24-h samples were collected in the urban and rural areas of Miyun, Beijing, so as to better understand the sources contributing to PM2.5 and the risk to human health in this district. The data obtained showed that daily PM2.5 mass concentrations ranged from 35.33 to 318.71 $\mu g\ m^{-3}$ in the urban sampling site, which however were between 12.62 and 292.33 $\mu g\ m^{-3}$ in the rural sampling site. At least 23.5 and 41.2 % of the monitoring data, respectively, exceeded the limit value. The mass concentrations of a number of PM2.5 elements fluctuated significantly in the decreasing order of Zn, Ba, Sr, Cu, Pb, Cr, V, Ni, Sb, and Cd. The daily contribution of three cations (NH_4^+, K^+, and Na^+) and four anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}) to PM2.5 mass simultaneously varied from 27.51 to 44.04 % and from 29.54 to 46.14 %. In addition, significant linear correlations between main constituents of the ions (SO_4^{2-}, NO_3^-, and NH_4^+) at both sites indicated that the majority of NH_4^+ was probably in the form of ammonium sulfate and ammonium nitrate. The risk levels of carcinogenic heavy metals detected in survey region occurred in the order of Cr, Cd, and Ni, of which, Cr may have a potential risk to the environment. High risk levels of both carcinogenic and non-carcinogenic heavy metals were easy to occur on haze–fog days.

Introduction

Recently, atmospheric particulate matter has been one of the major problems having an effect on the atmospheric environment quality of the city, especially the fine particulate (diameter<2.5 μm), which cannot only cause the haze–fog weather that reduces the visibility but also easily go through the bronchus and alveoli into blood where the harmful substance carried by the fine particle is dissolved and lead to a serious threat to human health (Kampa and Castanas 2008). With the adjustment of energy structure and the increase of motor vehicle exhaust, complex air pollution of Beijing area and fine particle pollution are aggravating, especially secondary aerosol pollution. Moreover, an increased health risk could be associated with the exposure to traffic in consideration of a more crowed traffic than before (McCreanor et al. 2007). Therefore, fine particulate matter pollution in Beijing has become a social hot issue and attracted extensive attention from both domestic and foreign academic circles.

More than a decade ago, it was reported that the annual average mass concentration of PM2.5 measured at five different sites in Beijing was 101 and 127 $\mu g\ m^{-3}$ and was displayed at urban residential sites in another study (Zheng et al. 2005; He et al. 2001). What is more, a similar study

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indicated the values of 96.5 and 106.9 $\mu g\ m^{-3}$ at two different sites in Beijing (Duan et al. 2006). Therefore, it can be seen that for a long time, Beijing, the capital of China, has experienced serious fine particulate matter pollution. In the past few years, with the implementation of new National Ambient Air Quality Standard for PM2.5 (hereafter called NAAQS; 75 $\mu g\ m^{-3}$ for a 24-h average, level II; 35 $\mu g\ m^{-3}$ for an annual average, level II) in China, a large number of measures have been devoted to air pollution control in Beijing (PRC National Standard 2012). According to several studies, a summary could be drawn that the annual PM2.5 concentrations in Beijing were between 70 and 100 $\mu g\ m^{-3}$ from 2003 to 2013 (Lang et al. 2013; Zhao et al. 2009). However, this range was still two to three times higher than the limit of level II according to national standard, which, respectively, exceeded the limit level of World Health Organization (hereafter called WHO; 10 $\mu g\ m^{-3}$ for an annual average) and National Ambient Air Quality Standards of the United States (15 $\mu g\ m^{-3}$ for an annual average) by a factor of 7.0–10.0 and 4.6–6.6. Therefore, there were more challenges to improve environmental air quality in Beijing areas (USEPA 2006).

Inductively coupled plasma-mass spectrometry (hereafter referred to as ICP-MS) was universally adopted to measure metal elements in PM2.5 and provide concentration data for epidemiological studies and quantitative source apportionment calculations (Kulkarni et al. 2007). Atmospheric data collected from Beijing demonstrated that under the haze–fog weather, the concentrations of pollution elements (As, Zn, Pb, and Cu) were, respectively, 0.04, 0.79, 0.44, and 0.09 $\mu g\ m^{-3}$ in PM2.5, which were 3.6–10.0 times higher than those in non-haze–fog days (Sun et al. 2006). More seriously, as a developing country similar to China, Hisar Indian has reported a high level of Pb, Ni, Cu, Mn, Fe, and Mg concentrations in the aerosol particle (Haritash and Kaushik 2007). There was significant difference in the metal concentration between different regions. In addition, these heavy metals have been confirmed to be enriched in various sources, such as soil and crustal dust, a number of industrial processes, vehicle emissions, and coal combustion (Tian et al. 2012). Common constituents of inorganic water-soluble ions in PM2.5 included F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, NH_4^+, K^+, Na^+, Ca^{2+}, and Mg^{2+}, among which, NO_3^-, SO_4^{2-}, Cl^-, and NH_4^+ were the main components (Puxbaum et al. 2007; Giugliano et al. 2005; Kim et al. 2006). Moreover, the contribution of these ions to the PM2.5 mass varied from 30 to 50 %, which has been demonstrated in numerous countries and regions (Lonati et al. 2005; Viana et al. 2005; Wang et al. 2004; Wang et al. 2006). In addition to the characteristics mentioned above, there were significant distinctions in the concentration and correlation coefficient of cations and anions between different seasons, especially the main ions (Viana et al. 2005).

Through the respiratory system, particles with smaller diameter have a greater capability to enter into the organism (Sanchez-Rodas et al. 2012). Provincial statistics revealed that municipalities in Beijing have a much higher level of exposure when compared with other provinces (Yao and Lu 2014). Consequently, the health effects of air pollution, especially the pollution caused by fine particle matter, have attracted great attention on account of the high exposure risk, even though concentrations of air pollutants were relative low. Research data showed that due to atmospheric contamination, annual global death toll has reached two million by means of damaging the respiratory system (Shah et al. 2013). Health risk assessment was mainly conducted in seriously polluted areas in China. Research carried out in the zinc-smelting district (northeast of China) manifested that Pb and Cd from street dust were considered as the most possible culprits to health risks (Zheng et al. 2010). In Dongying, China, hazard indexes of As exhibited the highest values in both adult and children. In other words, As could bring a potential threat to human health and lead to a cancer effect (Kong et al. 2011). Being regarded as an effective way, health risk assessment of heavy metals in PM2.5 can provide the theoretical basis for understanding the local air pollution status and implementing early preventive measures.

In order to investigate the current situation of PM2.5 pollution in Miyun, Beijing, a monitoring covering the period of August 24, 2013 to September 27, 2013 was carried out. The chemical composition, including trace metal and water-soluble ions, was obtained. Chemical characteristics of PM2.5 were compared between rural and urban sites. At last, in order to provide theoretical basis for the local government, this study examined the health risks of exposure to the metals in the levels observed to residents in urban and rural Miyun.

Materials and methods

Sampling locations

As the largest district and county of Beijing, Miyun County is considered as an important source of drinking water and an ecological reserve in the development area of Beijing, which is located in the northeast of the capital and belongs to the boundary of Yanshan Mountain and the North China Plain. Miyun was the first national ecological county in north China, whose forest coverage rate reaches up to 62.3 %. Besides, the moist index and water quality rank among the top of the city as well. In Miyun, ambient PM2.5 samples were collected at two different sites simultaneously in this study (Fig. 1). One sampling site (M1, 40° 21′ 46.43″ N, 116° 49′ 27.02″ E) is located at the south of Miyun County. Being located at the northeastern village of Miyun, the other sampling site (M2, 40° 26′ 56.15″ N, 116° 53′ 47.55″ E) is approximately 1.2 km away
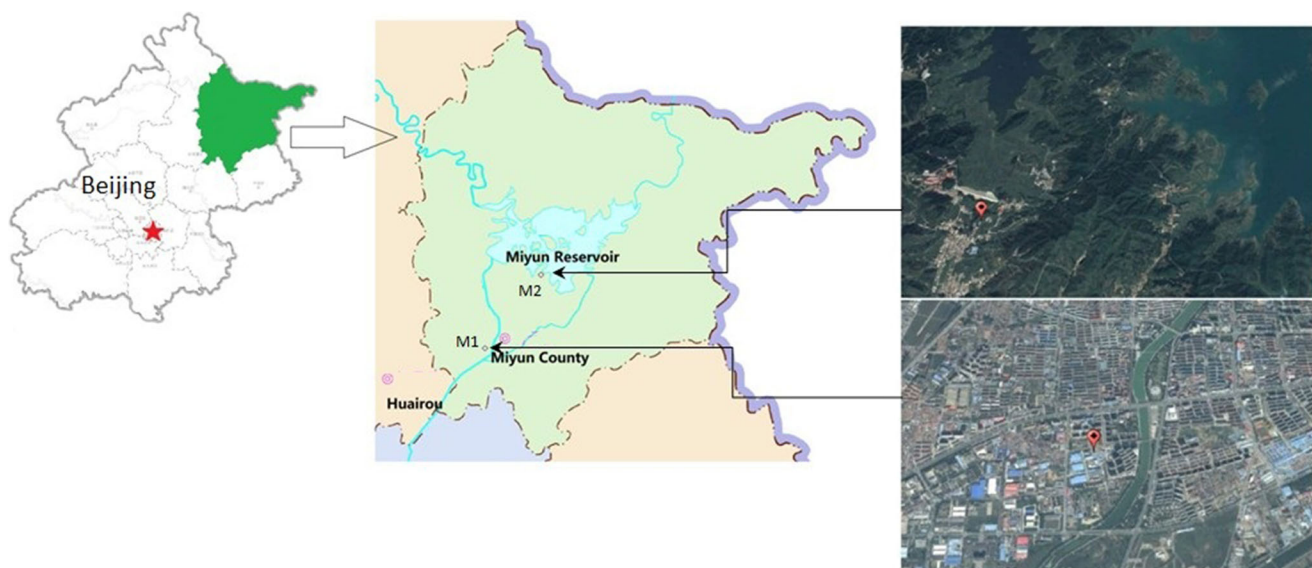
Fig. 1 Location of M1 and M2 in Miyun

from Miyun Reservoir. M1 site was surrounded by three streets and two construction fields, which is primarily affected by residential emissions, construction dust, and motor vehicle exhaust. As there were no major industrial activities surrounding, M2 site can be considered as a background sampling site.

Sampling methods

PM2.5 samples were collected from August 24, 2013 to September 27, 2013. In addition to August 27, August 28, and September 4 (rainy days), all the samples were collected under no-rainy conditions. Sampling was conducted once a day and each sampling event lasted for 24 h (from 8 am to 8 am). During the sampling, a median-volume sampler along with a PM2.5 cutting equipment (manufactured by Laoying, Qingdao, China) was adopted at a flow rate of 100 L min^{-1} to collect the samples, and the flow recorder of the machine could automatically compute each total volume. All the samplers were placed on the roofs of buildings, which were approximately 10 m above the ground. Glass fiber filters were employed as the sampling membrane (a diameter of 88 mm, Beijing Synthetic Fiber Research Institute, Beijing, China). Prior to sampling, the membranes were baked at 60 °C for 2 h, so as to remove volatile substances and other impurities. The scale used for weighing is accurate to 100,000th of a gram (XP105DR, Mettler Toledo, Switzerland). Thirty-four samples were collected at each site, and a total of 68 samples were obtained throughout the process. After sampling, all the filters were airproofed in tin foil packages, which were stored at −20 °C until analysis after being weighed. During the sampling period, meteorological data were also recorded, such as atmospheric pressure, ambient temperature, ambient relative humidity, and wind speed.

Trace element analysis

In order to ensure the accuracy of the experiment, samples were sent to the Beijing Research Institute of Uranium Geology. Clean scissors were employed to cut half of each membrane, and ICP-MS was adopted to identify concentrations of trace metals (Cu, Sr, Cd, Zn, Pb, Ni, Cr, Ba, V, and Sb). After the shredded filters were transferred into a 25-mL polytetrafluoroethylene (PTFE) vial, 7 mL of HNO$_3$ and 3 mL of HClO$_4$ were added to the vial. At last, the vessel was covered with steel jar outside and placed in a microwave digestive system (MK-III, Sinco Institute of Microwave Dissolving and Testing Techniques, China). Pressure and temperature profiles in the vessels were monitored on an external computer to better assess their effects on sample digestion. Effective digestions were achieved by setting the microwave program and power settings so that temperature was always the controlling parameter (Kingston and Haswell 1997). The tank was baked in the microwave digestive system for about 24 h with the temperature being maintained at 100 °C, so as to fully dissolve the sample. And then, the temperature was increased to 260 °C until white smoke appeared. After being digested and cooled, 3 mL of remaining solution was transferred to a 15-mL volumetric flask. In the next step, the flask was calibrated at the final volume by employing buffer solution. Subsequently, the solution was measured through the application of ICP-MS (VG PQ ExCell, Thermo Fisher Scientific Inc., USA). In addition, the method described above was employed to digest and analyze five blank filters with 0.1 g mL^{-1} NIST Standard Reference Material 1648a. The experiment results indicated that the recovery rates were between 85 and 110 %, which were within the error range. The whole experiment process was in strict accordance with "Methods for Chemical Analysis of Silicate Rocks-Part 30:

Determination of 44 Elements" (Wang et al. 2013; PRC National Standard 2010).

Water-soluble ion analysis

One fourth of each filter was employed for the determination of water-soluble ion concentrations. In aqueous extracts of the filters, four anions (SO_4^{2-}, NO_3^-, Cl^-, and F^-) and three cations (Na^+, NH_4^+, and K^+) were detected through the application of ion chromatography (ICS-90, Dionex, USA). By placing the shredded filters (one fourth of each filter) into a separate 20-mL tube, water-soluble species were extracted from the filters. Afterwards, 10 mL of distilled and deionized water with an electrical conductivity of 18.3 MΩ was added to the tube. All the vessels were subjected to ultrasonic agitation for 1 h and then additional shaking (with the help of a mechanical shaker) for 1 h, so that ionic compounds could be extracted completely. The extract solutions were filtered through a hydrophilic membrane (0.45 μm, PTFE, Whatman International Ltd., USA) and stored in pre-cleaned tubes at 4 °C until analysis. Cation concentrations were determined by employing a CS12A column (Dionex Corp.), which were eluted with 20 mmol L^{-1} methanesulfonic acid. On an AS11-HC column (Dionex Corp.), anions were separated and eluted with 3.5 mmol L^{-1} Na_2CO_3 and 1.0 mmol L^{-1} $NaHCO_3$. After that, calibration was performed for each analytical sequence. The detection limits were within the range of 0.0025–0.0124 and 0.0211–0.0677 μg mL^{-1}. Standard reference materials adopted in the experiment were obtained from the National Research Center for Certified Reference Materials, China. Recoveries of ions were greater than 85 %. The method described above was employed to experimentally extract and measure the five blank samples three times. In the end, the average of the blank values was subtracted from sample concentrations measured (Xu et al. 2012).

Methods of health risk assessment

By means of estimating the negative impact of environment factors on human health, assessment of the risk to human health was generally adopted in environmental epidemiology study. The connection between human body exposure (through mouth, breathing, and skin) and pollutant concentrations was explained by the atmospheric pollution exposure from the following three aspects, including pollutant concentration, duration, and frequency (Hertel et al. 2001). According to the USEPA Integrated Risk Information Database (hereafter called IRIS) and International Agency for Research on Cancer (hereafter called IARC), pollutants were divided into non-carcinogens and carcinogens. Among evaluated elements, Cu, Pb, Zn, and V are non-carcinogenic, while Cr, Ni, and Cd are carcinogenic. There are different health risk assessment models for these two types of

pollutants. The health risk assessment model recommended by USEPA (EPA 1989) was adopted in this paper.

Normal average daily dose (hereafter called ADD, mg kg^{-1} day^{-1}) is employed for non-carcinogenic elements, such as Cu, Pb, Zn, and V, while lifetime average daily dose (hereafter called LADD, mg kg^{-1} day^{-1}) is adopted for carcinogenic elements, such as Cr, Ni, and Cd. The exposure dose rate can be calculated according to the following equation:

$$ADD(\text{or LADD}) = (C \text{ X IR XEF X ED}) / (BW \text{ X AT}) \quad (1)$$

where C represents the concentration of pollutants (mg m^{-3}), IR is the respiration rate (m^3 day^{-1}), EF is the exposure frequency (day a^{-1}), ED is the duration of exposure (day), BW is the body weight (kg), and AT is the average exposure time (day).

Risk assessment for non-carcinogenic substances As the measure gauge for non-carcinogenic risks, hazard quotient (hereafter called HQ) can be calculated based on the equation below:

$$HQ = ADD / RfD \quad (2)$$

where RfD represents the reference dose (mg kg^{-1} day^{-1}), and HQ is the hazard quotient for non-carcinogenic risks (dimensionless value). When HQ is greater than 1, the risk of cancer exists; when HQ is less than or equal to 1, less risk exists or the risk can be ignored.

Risk assessment for carcinogenic substances The incremental lifetime cancer risk (hereafter called ILCR) is calculated by using the following equation:

$$ILCR = LADD \text{ X SF} \quad (3)$$

where ILCR is the average annual excess risk of cancer for an individual (dimensionless value), and SF is the slope factor (mg kg^{-1} day^{-1})$^{-1}$. When ILCR is greater than 10^{-4}, the potential risk of cancer exists seriously. When ILCR is less than 10^{-6}, less risk exists or the risk can be ignored.

Results and analysis

Ambient concentrations of PM2.5

Figures 2 and 3 present the mass concentrations of PM2.5 obtained from samples. In the samples collected from M1 site, the PM2.5 concentration fluctuated between 35.33 and 292.33 μg m^{-3} with an average value of 91.61 μg m^{-3}, while that from M2 site varied from 12.62 to 318.71 μg m^{-3} with a mean of 66.70 μg m^{-3}. When compared with the daily average PM2.5 concentration (159 μg m^{-3}, Beijing) observed in 2013, these levels were significantly lower (Huang et al.
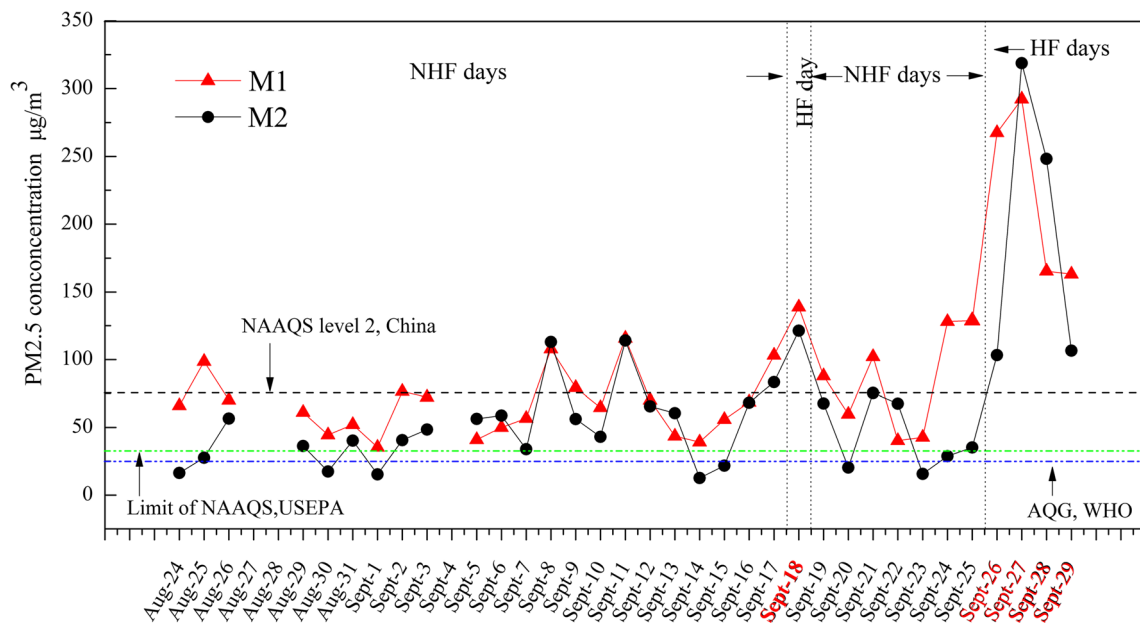
Fig. 2 Daily concentration of PM2.5 in M1 and M2 sampling sites

2014), of which, the average PM2.5 level at M1 site significantly exceeded the outdoor average PM2.5 daily limit (75 μg m^{-3}, level II) according to the Ambient Air Quality Standard of China (GB 3095–2012). Therefore, 41 % of the 24-h data at M1 exceeded the limit, which was 23 % at M2 site. Furthermore, the maximum concentrations occurred on September 27 at the two sites were approximately four times of the relevant limit. In Fig. 2, an obvious concentration increase could be observed at both two sites from September 26 to 29 and on September 18, which was under continuous haze–fog (hereafter called HF) weather. PM2.5 mass concentration also exhibits peak value on September 8, September 11, and September 21 at both sites. However, weather

information which was released to public by the Meteorological Bureau of Beijing manifested September 8, September 11, and September 21 were not under HF weather. There would be particles transported from other regions to Miyun County because of large amount of factories and mines in the adjacent county. Besides, these peaks may be caused by dust generated from construction, for there were many houses being transformed in Miyun County during sampling period. Besides, during the HF period, the average PM2.5 level at M1 and M2 significantly exceeded the value during the non-haze–fog (hereafter called NHF) period by a respective factor of 3.7 and 3.6 (Fig. 3). It is easy to find in Fig. 3 that average PM2.5 concentration of NHF period was under level II of NAAQS

Fig. 3 Monthly average mass concentration of PM2.5 of M1 and M2
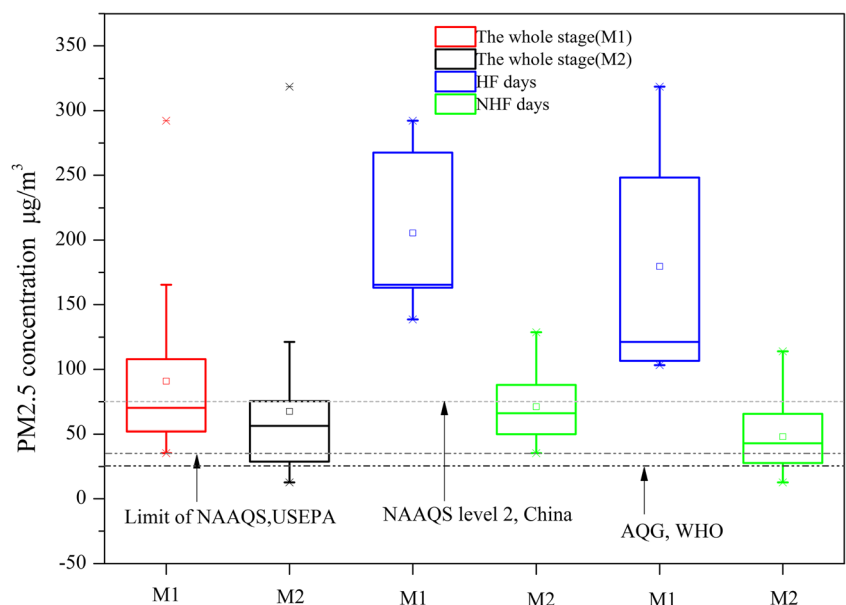
China at both sampling sites in Miyun. PM2.5 level during NHF period still exceeded the limit of NAAQS USEPA and Air Quality Guideline (hereafter called AQG) of WHO. However, when compared with other cities in China, the mean PM2.5 concentration in Miyun that is the suburb of Beijing was lower than the values of 103.1 μg m^{-3} in Shanghai in autumn 2009 (Wang et al. 2013) and 103.0 μg m^{-3} in Guangzhou in autumn 2004 (Andreae et al. 2008), which suggested that PM2.5 pollution in Miyun was slightly lower in autumn when compared with other cities in China.

Weather conditions

Figure 4 displays the daily air temperature and pressure of Miyun areas in August and September, 2013, while Fig. 5 presents the daily wind speed and relative humidity data during sampling stage. It can be seen that the temperature gradually decreased and ranged from 4.9 to 34.5 °C over time. In the following days (August 27–28 and September 4), a rainy weather occurred, and then air temperature presented a downward trend. However, air pressure was similar to that of first rise after the falling trend during this period. Corresponding to weather variation, the daily PM2.5 concentration showed a moderating trend after rainy days as well. This trend was not significant on September 5 at M2. It may caused by the error from sample weighing process.

It is important to note that air was relative calm and only weak winds occurred throughout the sampling periods. As mentioned above, from September 23 to September 29, data collected from both sampling sites suggested an episode of a very high concentration of PM2.5. When it experienced HF weather at the end of September (26–29), the lowest

temperature dropped to 5 °C and air pressure increased when compared with NHF days. Comparison between Figs. 4 and 5 and Fig. 2 concluded that the weather within this period was favorable for the occurrence of such elevated concentrations. Besides, air temperature, wind speed, and inversion layer were low, while air pressure was high (Pastuszka et al. 2010).

Elemental compositions

Being collected daily at each site, half of a sampling membrane was analyzed to investigate metal element compositions. All the 10 estimated trace metals were significantly higher than their instrumental detection limit. The element concentration variations between two sites are given in Table 1 and Figs. 6 and 7. According to M1 site, it was evident that Zn and Ba showed the highest concentration levels in PM2.5, followed by Sr > Cu > Pb > Cr > V > Ni > Sb > Cd with the same trend being found at M2 site. The total of mean concentrations of the 10 measured elements was 1.52 and 1.43 μg m^{-3}, which, respectively, accounted for 1.57 and 2.51 % of PM2.5 monthly average concentrations. Figures 6 and 7 showed that the mass concentrations of various elements in PM2.5 fluctuated significantly at M1 and M2 sites. The mass concentration of Zn and Ba at both sites varied with consistency, especially on NHF sampling days (Fig. 7). This result indicated that the two sampling sites may be affected by the same source, especially under NHF weather. Cr, V, Ni, Sb, and Cd detected in M1 samples exhibited slightly higher average concentrations than those in M2 (Table 1). Furthermore, the statistics of the points on Fig. 6 concluded that there were 22 days in M1, of which concentration of Sr was higher than that of M2. Similarly, during the entire sample period, the
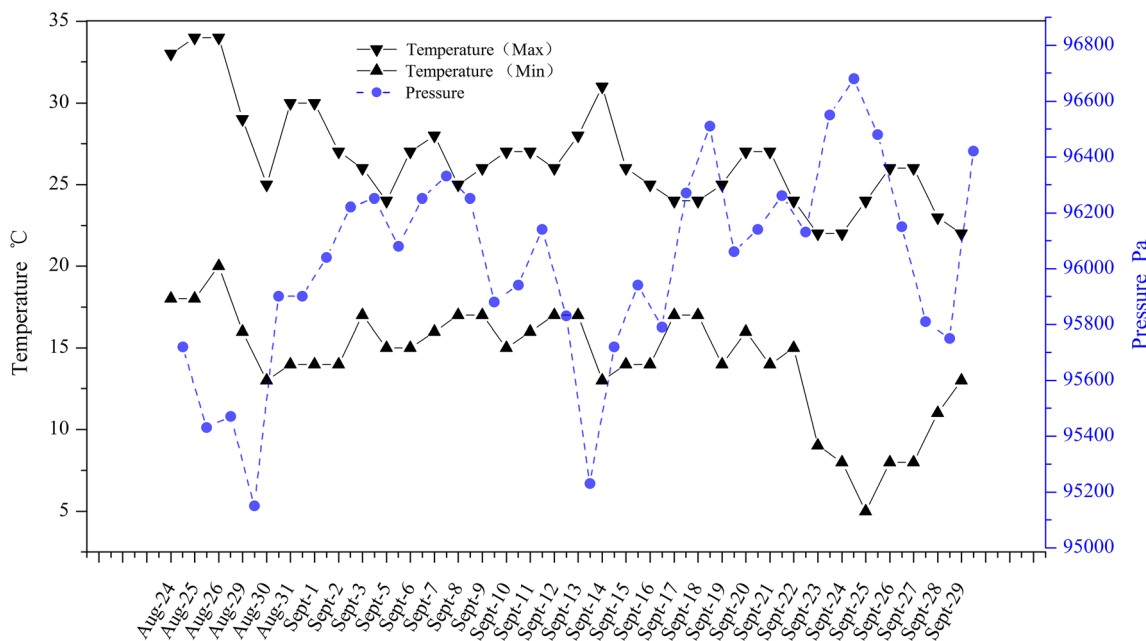
Fig. 4 Ambient air temperature and pressure during sampling period
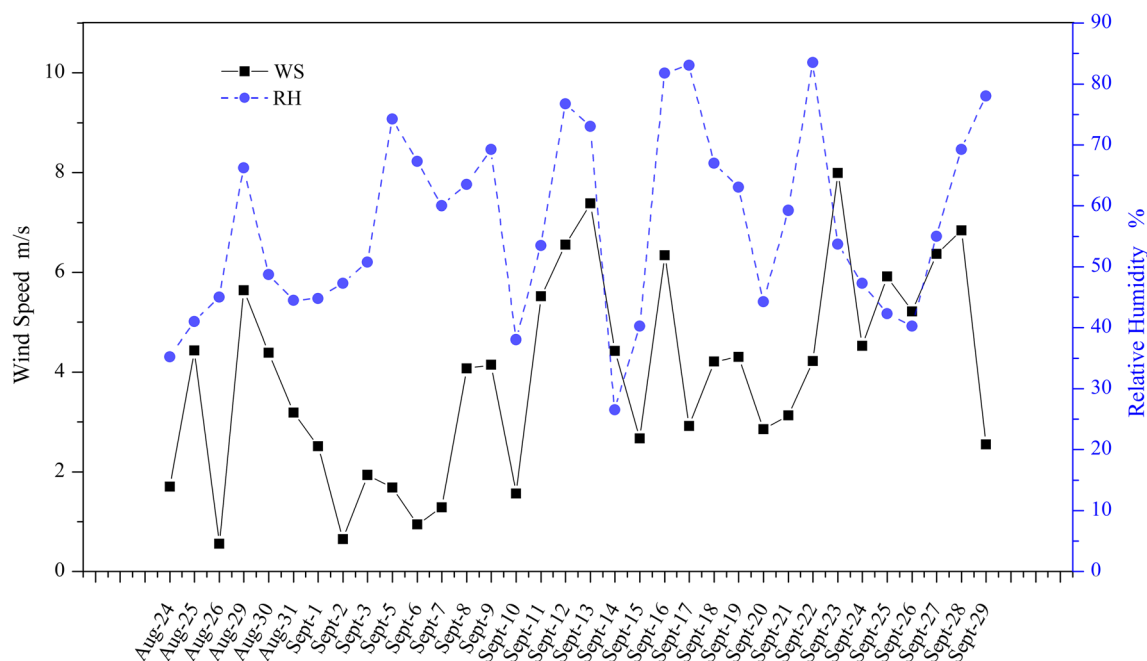
Fig. 5 Relative humidity and wind speed of ambient air in August and September

daily level of Pb in M1 exceeded the value in M2 for more than 20 days. What is more, Pb and Cu detected in M1 exceed the level in M2 for more than 85 % of NHF days. Rural site exhibited a slightly higher level of Pb than urban only on September 8, 11, and 13. These results may be due to urban motor emissions and industrial emissions located nearby M1 site in Miyun County. When compared with NHF days,

concentrations of M1 target elements underwent a substantial increase during HF days with the same tendency being found at M2 site. Rural site exhibited a higher level of Cu than urban, especially on September 8, 11, 13, 18, 22, 27, 28, and 29. Dates mentioned above all exhibited high PM2.5 levels. The potential reason may be the higher relative humidity and lower ventilation indices under HF conditions. Besides, there may be particles transported from other regions. For example, M2 site was closer to the adjacent Kailuan County where large amount of factories and mines exist. When particle was transported from the northeast industrial area, the rural Miyun seems easier to be affected. However, further studies are needed on the influence mechanism. Compared with other cities, daily mean concentrations of Cu, V, Cr, and Pb in Miyun were equal to those in Milan, and average values of other metals were significantly lower than those in most cities in China and other Asian countries (Vecchi et al. 2004; Deng et al. 2006).

Table 1 Mean concentrations of PM2.5, metals, and water-soluble ions during the sampling period

Parameter	Unit	M1	M2
PM2.5	µg/m³	96.61±62.42	66.69±60.43
F^-	µg/m³	0.12±0.02	0.10±0.01
Cl^-	µg/m³	1.54±1.08	1.56±1.22
NO_3^-	µg/m³	6.62±4.19	4.60±4.02
SO_4^{2-}	µg/m³	13.80±6.89	10.70±7.64
Na^+	µg/m³	1.52±0.96	1.25±0.89
K^+	µg/m³	1.98±1.19	1.54±1.29
NH_4^+	µg/m³	5.53±3.87	3.84±3.71
V	ng/m³	0.66±0.44	0.51±0.50
Cr	ng/m³	1.02±0.65	0.78±0.75
Ni	ng/m³	0.29±0.18	0.22±0.20
Cu	ng/m³	3.80±1.88	3.52±3.80
Zn	µg/m³	0.78±0.55	0.65±0.77
Sr	ng/m³	9.26±5.24	7.86±8.25
Cd	ng/m³	0.06±0.05	0.04±0.03
Sb	ng/m³	0.25±0.17	0.16±0.17
Ba	µg/m³	0.72±0.35	0.77±0.90
Pb	ng/m³	3.52±2.74	2.21±1.87

Ionic characteristics

In PM2.5 samples, three cations (NH_4^+, K^+, and Na^+) and four anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}) were measured. Due to the high blank values in the glass filters, Ca^{2+} and Mg^{2+} were not determined. It was observed that SO_4^{2-} was the predominant ionic component throughout the sampling period. At both sampling sites, average concentrations of cations and anions were decreased in the same order, namely $SO_4^{2-} > NO_3^- > Cl^- > F^-$ and $NH_4^+ > K^+ > Na^+$ (Table 1). The daily contribution of all the ions to PM2.5 mass at M1 varied from 27.51 to 44.04 %. However, the value at M2 ranged from 29.54 to
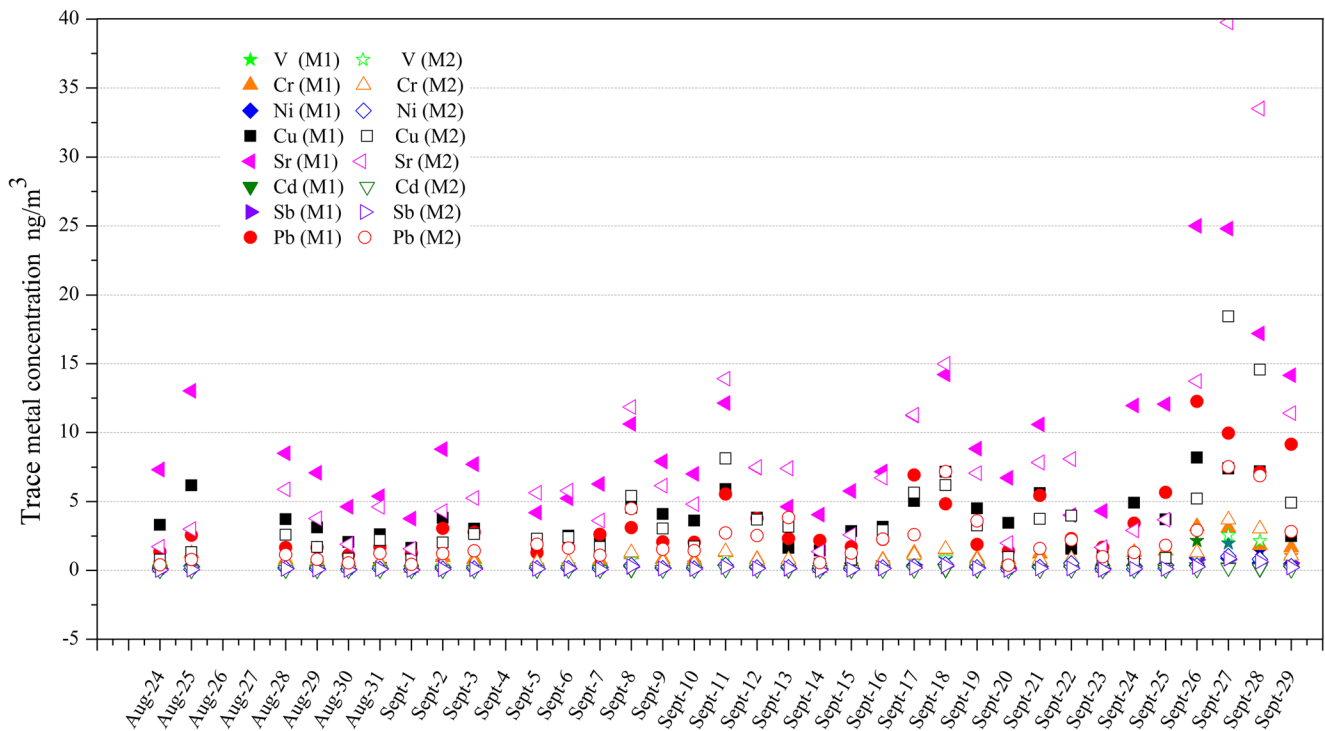
Fig. 6 Variety of daily metal concentration at M1 and M2

46.14 %, which was slightly higher than that at M1 and much greater than that in Kanpur, India (Ram and Sarin 2011). In addition, the 24-h average concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ at M1 were, respectively, in the range of 5.4–35.34, 1.77–21.45, and 0.98–19.49 μg m^{-3}, while the corresponding values at M2, respectively, varied from 2.81 to 34.98 and 0.29 to 19.95 to 0.34 to 16.08 μg m^{-3} (Table 1). Simultaneously, the daily average contribution of SO_4^{2-}, NO_3^-, and NH_4^+ to all water-soluble ions was approximately 45.79, 20.99, and 16.84 % at M1 site and 47.76, 17.95, and 14.18 % at M2 site.

Fig. 7 Daily concentration of Zn and Ba in M2 site

The conclusion could be drawn that in Miyun, SO_4^{2-}, NO_3^-, and NH_4^+ were the main constituents of water-soluble ions in PM2.5, which was consistent with the results obtained in Nanjing, Shanghai, Beijing, and Thessaloniki (Wang et al. 2002; Yao et al. 2002; Tolis et al. 2014).

Correlation between water-soluble ions

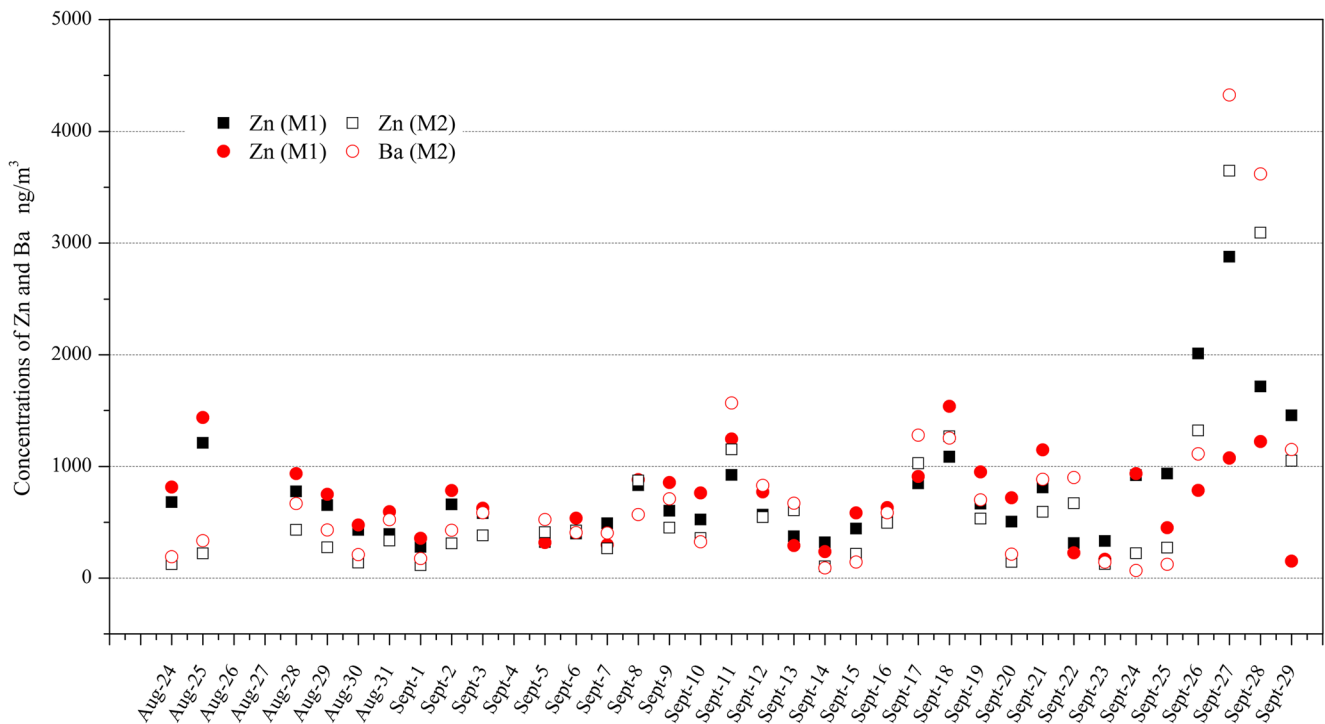IBM SPSS Statistics 21 was employed to analyze correlations between ion components in PM2.5. Table 2 suggested that at M1 and M2 sampling sites, there were significant linear correlations among NO_3^-, SO_4^{2-}, and NH_4^+, which indicated that the majority of NH_4^+ was probably in the form of ammonium sulfate and ammonium nitrate and NO_3^- and SO_4^{2-} which were likely derived from the same source. Evident distinctions between statistical results from M1 and M2 could be observed. At M1 site, the correlations between Cl^- and NO_3^-, Cl^- and NH_4^+, and Na^+ and NH_4^+ were significant. However, the corresponding correlation coefficient for these ions at M2 was less than that in M1. The correlation between NO_3^- and NH_4^+ exhibited a maximum value, which suggested that NH_4^+ might mainly exist as nitrate instead of sulfate at M2. The urban sampling site was more closely surrounded by local industrial and residential areas. Thus, compared with rural site, urban site was easier influenced by sulfur compounds in factory flue gas. In the atmospheric PM2.5, ammonium nitrate and sodium chloride were the two most common components and, at high temperatures, nitrate could volatilize and decompose into nitrate acid and ammonia (Viana et al. 2005). Even in early autumn, high temperature in Miyun County led part of the acid to react with sodium chloride in the aerosol and form hydrochloric acid, which resulted in Cl^- volatilization in the form of HCl. Nitrate existing in ambient PM2.5 was possibly favorable for the chloride conservation. At the end of August and early September, chemical reactions probably occurred in aerosol in Miyun. More correlations within Cl^-, NO_3^-, NH_4^+, and Na^+ mentioned above and significant correlations between Na^+ and K^+ implied that the enriched nitrate in PM2.5 was beneficial to chloride stabilization at M1 site in autumn as well. Besides, it was possible that K^+ was in the form of

chloride and sulfate instead of nitrate in the aerosol. When compared with M2 site, the complicated correlation at M1 may be affected by the evaporation of relevant components from sewage disposal plant nearby the urban sampling site. Moreover, the influence mechanism needs to further researched.

Heavy metal risk assessment

Tables 3 and 4 exhibited relevant exposure and reaction parameters for metals entering the human body through the respiratory system. Due to the lack of basic data of local exposure parameters, USA's parameters were generally adopted in previous researches to conduct health risk assessment. However, with the development of studies concerning Chinese exposure parameter, a number of parameters have been modified to adapt to local population in China. To guarantee that the target population exposure dose is closer to the actual result and makes the result of the health risk assessment more reasonable and more accurate, suitable exposure parameters were chosen from *Exposure Factors Handbook* and existing researches in this study for Chinese population (EPA 2011; Wang et al. 2009; Li et al. 2013).

Table 5 indicated that at M1 and M2 sampling sites, the monthly average risk level of non-carcinogenic heavy metals for exposure through the respiratory system, respectively, was 2.35×10^{-5} (V for women) to 8.31×10^{-4} (Zn for children), 1.78×10^{-5} (V for women), and 6.96×10^{-4} (Zn for children). Whether it was for men, women, or children, the maximum risk level in urban and rural Miyun all occurred on HF days (September [26] and September 27). However, when it underwent NHF days, the HQ of both sites exhibited low values. For example, non-carcinogenic metals had a minimum value of HQ on August 30 September 1, September 14, and September 20 of which the PM2.5 mass concentration was under AQG WHO (Fig. 2). Although HQ of M1 was slightly higher than that of M2, all the values calculated at both sites were significantly lower than 1. This result could reflect less atmospheric environment pollution in rural suburb than in urban. The monthly average risk levels of non-carcinogenic

Table 2 Correlation between different water-soluble ions in M1 and M2 sampling sites

	M1						M2					
	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+
SO_4^{2-}	1	0.61[a]	0.21	0.51[a]	0.19	0.01	1	0.47[a]	0.08	0.54[a]	−0.18	0.29
NO_3^-		1	0.55[a]	0.63[a]	−0.03	−0.12		1	0.34	0.77[a]	−0.17	0.07
Cl^-			1	0.60[a]	0.36	0.27			1	0.02	0.49	0.35
NH_4^+				1	0.53[a]	0.35				1	−0.13	0.34
Na^+					1	0.57[a]					1	0.02
K^+						1						1

[a] Good correlativity

Table 3 Exposure parameters for uptake through the respiratory system

Group	Men	Women	Children
IR/m^3 day^{-1}	19.2	14.17	5
BW/kg	62.7	54.4	15
EF/day a^{-1}	350	350	350
ED/a	30	30	6
AT (for carcinogens)/day	70×365	70×365	70×365
AT (for non-carcinogens)/day	30×365	30×365	6×365

IR respiration rate, *BW* body weight, *EF* exposure frequency, *ED* duration of exposure, *AT* average exposure time

heavy metals occurred in the decreasing order of Zn, Pb, Cu, and V. What is more, non-carcinogenic substances posed the greatest cancer risk to children, followed by men and then women.

As shown in Table 6, at M1 and M2 sampling sites, the monthly average risk level of carcinogenic heavy metals for exposure through the respiratory system, respectively, ranged from 6.68×10^{-9} (Ni for children) to 5.33×10^{-6} (Cr for men), 5.16×10^{-9} (Ni for children), and 4.09×10^{-6} (Cr for men). Being detected at M1 and M2, the risk levels of carcinogenic heavy metals occurred in the order of Cr > Cd > Ni. Of which, the ILCR of Cd and Ni was obviously lower than 10^{-6}, while the corresponding value of Cr was between 10^{-6} and 10^{-4}, which suggested that the risk levels of Cd and Ni were under average risk acceptance and, to some extent, Cr may have a potential risk to the environment. High ILCR value of carcinogenic heavy metals was easy to occur on HF days, which is similar with the analysis of non-carcinogenic heavy metals. When compared with non-carcinogenic heavy metals, the risk levels of carcinogenic heavy metals to adults and children were different. In addition to Ni (due to its low risk level), Cr could cause harm to men more easily, followed by women and then children, while Cd could have an effect on women more easily than men and children, especially in the urban district. Different risk tendencies to men, women, and children between carcinogenic and non-carcinogenic can be demonstrated by individual differences in respiration rate, outdoor

Table 4 Reaction parameters for heavy metals entering the human body through the respiratory system

Element	Nature	SF [mg(kg day)$^{-1}$]$^{-1}$	RfD mg(kg day)$^{-1}$
Cd	Carcinogenic	8.4	
Cr	Carcinogenic	42.0	
Ni	Carcinogenic	0.84	
Pb	Non-carcinogenic		3.5×10^{-3}
Cu	Non-carcinogenic		1.43×10^{-2}
Zn	Non-carcinogenic		0.3
V	Non-carcinogenic		7×10^{-3}

Table 5 The risk associated with non-carcinogenic heavy metal components of PM2.5 for different demographic groups

	Men			Women			Children		
M1	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
V	1.01×10^{-5} September 1	8.96×10^{-5} September 1	2.73×10^{-5}	8.65×10^{-6} September 26	7.70×10^{-5} September 26	2.35×10^{-5}	1.11×10^{-5} September 1	9.85×10^{-5} September 1	3.00×10^{-5}
Cu	2.48×10^{-5} September 23	1.67×10^{-4} September 23	7.73×10^{-5}	2.13×10^{-5} September 23	1.43×10^{-4} September 26	6.64×10^{-5}	2.73×10^{-5} September 23	1.83×10^{-4} September 23	8.49×10^{-5}
Zn	2.71×10^{-4} September 1	2.79×10^{-3} September 27	7.56×10^{-4}	2.33×10^{-4} September 1	2.39×10^{-3} September 27	6.49×10^{-4}	2.98×10^{-4} September 1	3.06×10^{-3} September 27	8.31×10^{-4}
Pb	9.27×10^{-5} August 30	1.02×10^{-3} September 26	2.93×10^{-4}	7.96×10^{-5} August 30	8.75×10^{-4} September 26	2.51×10^{-4}	1.02×10^{-4} August 30	1.12×10^{-3} September 26	3.22×10^{-4}
M2	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
V	3.44×10^{-6} September 14	1.07×10^{-4} September 27	2.07×10^{-5}	2.96×10^{-6} September 14	9.20×10^{-5} September 27	1.78×10^{-5}	3.78×10^{-6} September 14	1.18×10^{-4} September 27	2.28×10^{-5}
Cu	9.50×10^{-6} September 14	3.75×10^{-4} September 27	7.16×10^{-5}	8.16×10^{-6} September 14	3.22×10^{-4} September 27	6.15×10^{-5}	1.04×10^{-5} September 14	4.12×10^{-4} September 27	7.87×10^{-5}
Zn	1.01×10^{-4} September 14	3.54×10^{-3} September 27	6.33×10^{-4}	8.69×10^{-5} September 14	3.04×10^{-3} September 27	5.44×10^{-4}	1.11×10^{-4} September 14	3.89×10^{-3} September 27	6.96×10^{-4}
Pb	3.11×10^{-5} September 20	6.24×10^{-4} September 27	1.83×10^{-4}	2.67×10^{-5} September 20	5.36×10^{-4} September 27	1.57×10^{-4}	3.42×10^{-5} September 20	6.86×10^{-4} September 27	2.01×10^{-4}

Table 6 The risk associated with carcinogenic heavy metal components of PM2.5 for different demographic groups

M1

	Men			Women			Children		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Cr	2.04×10^{-6} September 1	1.67×10^{-5} September 26	5.33×10^{-6}	1.75×10^{-6} September 1	1.43×10^{-5} September 26	4.58×10^{-6}	4.48×10^{-7} September 1	3.67×10^{-6} September 26	1.17×10^{-6}
Ni	1.07×10^{-8} September 1	9.64×10^{-8} September 26	3.04×10^{-8}	9.21×10^{-9} September 1	8.28×10^{-8} September 26	2.61×10^{-8}	2.46×10^{-9} September 1	2.12×10^{-8} September 26	6.68×10^{-9}
Cd	2.08×10^{-8} September 1	2.58×10^{-7} September 26	6.72×10^{-8}	1.79×10^{-8} September 1	2.21×10^{-7} September 26	5.77×10^{-8}	4.57×10^{-9} September 1	5.67×10^{-8} September 26	1.48×10^{-8}

M2

	Men			Women			Children		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Cr	7.60×10^{-7} September 14	1.92×10^{-5} September 27	4.09×10^{-6}	6.53×10^{-7} September 14	1.66×10^{-5} September 27	3.51×10^{-6}	1.67×10^{-7} September 14	4.24×10^{-6} September 27	8.98×10^{-7}
Ni	4.20×10^{-9} September 14	1.09×10^{-7} September 27	2.34×10^{-8}	3.61×10^{-9} September 14	9.33×10^{-8} September 27	2.01×10^{-8}	9.24×10^{-10} September 14	2.39×10^{-8} September 27	5.16×10^{-9}
Cd	7.71×10^{-9} September 1	1.85×10^{-7} September 27	4.55×10^{-8}	6.62×10^{-9} September 1	1.59×10^{-7} September 27	3.90×10^{-8}	1.69×10^{-9} September 1	4.07×10^{-8} September 27	9.99×10^{-9}

exposure, and body weight. In Miyun, the risk posed by carcinogenic and non-carcinogenic metals was significantly lower than that in numerous cities in China and other Asian cities (Sharma and Maloo 2005).

Conclusions

Through the analysis of data from the two sampling sites, PM2.5 pollution in rural Miyun was slightly lower in September in comparison with urban. Compared with other cities in China, fine particle pollution in Miyun atmosphere was relatively slightly lower in autumn. Zn and Ba were the most enriched metals among the 10 measured elements. The metal concentration at both sites ranged in the same order: Sr, Cu, Pb, Cr, V, Ni, Sb, and Cd. NO_3^-, SO_4^{2-}, and NH_4^+ were not only the major water-soluble ions in the aerosol but also had significant linear correlations at both rural and urban sampling sites. The risk levels for the non-carcinogenic heavy metals detected at M1 and M2 occurred in the decreasing order, Zn, Pb, Cu, and V, while the carcinogenic heavy metals for the following order: Cr > Cd > Ni. Among the carcinogenic heavy metals, Cr may have potential risk to environment to some extent.

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