Concentrations and chemical compositions of PM$_{10}$ during hazy and non-hazy days in Beijing

Xianchu Wu$^{1,2}$, Bin Chen$^{1,3,*}$, Tianxue Wen$^1$, Ammara Habib$^1$, Guangyu Shi$^1$

1. Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China
2. University of Chinese Academy of Sciences, Beijing 100049, China
3. Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disasters, Nanjing University of Information Science & Technology, Nanjing 210044, China

ARTICLE INFO

Article history:
Received 26 November 2018
Revised 22 March 2019
Accepted 26 March 2019
Available online 4 June 2019

Keywords:
PM$_{10}$
Haze
Beijing
Chemical composition
Air mass

ABSTRACT

In order to study the concentrations of major components, characteristics and comparison in hazy and non-hazy days of PM$_{10}$ in Beijing, aerosol samples were collected at urban site in Beijing from December 29, 2014 to January 22, 2015. Heavy metals like Zn, Pb, Mn, Cu, As, V, Cr and Cd were deeply studied considering their toxic effects on human being; nine water-soluble inorganic ions (SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Na$^+$, K$^+$, Cl$^-$, Ca$^{2+}$ and Mg$^{2+}$) and carbon fractions (OC and EC) were also analyzed. The concentrations of heavy metals were 1.03–1.98 times higher in hazy days than those in non-hazy days, mainly due to biomass burning and coal burning. The trends in total heavy metals concentrations were basically consistent with the trends in PM concentrations except for two obvious periods (12.29–12.30; 1.14–1.15); but when air masses accumulated locally or around Beijing, trends in PM concentrations and heavy metals were opposite. The proportion for NO$_3^-$/SO$_4^{2-}$ indicated that mobile sources such as automobiles were important reasons for haze in Beijing. Correlation between OC and EC during non-hazy days was strong ($R^2 = 0.95$) but it was low ($R^2 = 0.67$) during hazy days, and large variations for OC/EC values occurred in hazy days. The calculated mass concentration of SOC is 2.58 $\mu$g/m$^3$, which only accounted for 10.1% of the OC concentration.

© 2019 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Atmospheric pollution constitutes a big challenge for densely populated urban areas and mega-cities in particular. China is the most populated and fastest developing country in the world. Over the past several decades, it has suffered from poor air quality caused by fine particles(diameter ≤ 2.5 $\mu$m), as a consequence of rapid economic growth and a drastic increase in the number of vehicles. As the capital, political, economic and cultural center of China, Beijing, with a population of about 27 million, has suffered over-concentration of population, which brought heavy natural, ecological, and social resources pressure; it makes urban environmental problems more and more prominent, especially the concentration of air pollutants. In recent years, hazy days have been occupying more than 100 days per year, and the annual average visibility has been lower than 15 km. The average number concentration of particles less than

* Corresponding author. E-mail: chen_bin@mail.iap.ac.cn (Bin Chen).

https://doi.org/10.1016/j.jes.2019.03.021
1001-0742 © 2019 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.
100 nm could reach up to 30,000 cm$^{-3}$ in the urban area of Beijing, which is much higher than Wu’s studies (27,000 cm$^{-3}$) (Wu et al., 2008). It is known that aerosols can not only reduce the visibility, but also have an adverse effect on the human respiratory and cardiovascular systems. The World Health Organization (WHO) estimated that air pollution was associated with approximately 300,000 premature deaths per year in China (Duan et al., 2014).

Beside the mass concentration and the particle size, the concentration of potential toxic metals of aerosols plays a decisive role for the assessment of atmospheric pollution and the hazards to human health (Limbeck et al., 2012; Sato et al., 2008). Atmospheric heavy metals are continually being deposited into the ground by dry and wet deposition, from where they could be absorbed by plant roots and stems or impact soil enzyme activity, biological activity and biodiversity, resulting in persistent negative impacts on the ecosystem biogeochemical cycles. The long-term existence of heavy metals may pose a great potential threat to the environment, it can invade the respiratory system, induce heart disease, lung disease, reduce lung function, and even cause cancer (Fang, 2010). As, Cr, Ni, Pb and Cd have some carcinogenic capacity, As and Cd have potent teratogenic effects on the human body, and Pb and Hg are toxic to the fetus (Hu et al., 2012). High anthropogenic emissions of heavy metals enter into the biosphere in China, and these emissions far exceed those of other countries with increasing trend (Pacyna and Pacyna, 2001). Studies have shown that about 70%–80% of metal elements in the atmosphere are adsorbed on fine particles (Lv et al., 2005; Mohanra et al., 2004).

The scattering and extinction effects of atmospheric aerosols are affected by its own physical properties (including particle size distribution, mass concentration, etc.) and chemical composition. Water-soluble compounds (nitrates, sulfates, ammonium salts, etc.), organic and elemental carbon (OC and EC) are the main chemical components that reduced visibility in hazy days. Nitrates and sulfates are one of the most important extinction components in the atmosphere, the visibility will significantly reduce with the increasing of concentration. Concentrations of nitrates and sulfates have a close relationship with the acidity of atmospheric precipitation. Water-soluble ions have strong hygroscopic property; they can promote the formation of cloud condensation nuclei, and also affect the size, composition, number, acidity and life time of aerosols due to their strong hygroscopic property (Xiang et al., 2017). In the case of high relative humidity, the moisture-absorbing growth of water-soluble ions will enhance the extinction effect of aerosols, which will lead to a decrease in visibility.

Carbonaceous species are also important fraction in PM$_{10}$. Based on thermal and optical properties, carbonaceous aerosols can be divided into EC and OC. OC is emitted by fossil fuel combustion or is formed by a complex process of secondary formation, including of a vast array of individual organic species, such as formaldehyde, acetone and PAHs (Cao et al., 2003; Tang et al., 2006; Yang et al., 2011). EC, which is important for radiative forcing, can be emitted directly by incomplete combustion of, e.g., biomass and fossil fuel (Xiang et al., 2017), mainly from primary emissions. Carbonaceous species have a significant impact on the atmospheric environment and regional climate, but also have an important hazard to human health.

Prior research on the chemical composition of particles in Beijing was mainly focused on fine particles, and it was also mainly focused on some specific species in China and abroad in recent years (Pathak et al., 2009; Ianniello et al., 2011), the size distribution of aerosol chemical species (Guo et al., 2010; Li et al., 2012), particle number concentration (Yue et al., 2011) and new particle formation processes (Gao et al., 2012) have also been discussed. There were few measurements of PM$_{10}$, especially comprehensive analysis of the different chemical compositions of particles. To fully understand concentrations and chemical compositions of atmospheric particles in Beijing, daily PM$_{10}$ samples were collected at an urban site in Beijing during December, 2014-January, 2015. The concentrations of major components, their characteristics and comparison in hazy and non-hazy days of PM$_{10}$ were discussed in detail. The studies presented are expected to be useful in making future PM pollution control policies.

1. Experimental design

1.1. Sample collection

The sampling site was located on the roof of an office building at the IAP (Institute of Atmospheric Physics, Chinese Academy of Sciences) campus (116°22′ E, 39°58′ N) in the Haidian District, Beijing, which is about 6 m above the ground. The site is in the middle of the North Third Ring Road and the North Fourth Ring Road in Beijing, which is about 150 m eastern from the east-west urban traffic main road, North Tucheng Road, and is about 200 m from the Badaling Expressway (Fig. 1). It is surrounded by high-density roads, residential buildings and office buildings. There are no obvious industrial sources of aerosols in the vicinity. Therefore, it can be considered as a typical urban site.

Sampling was conducted from December 29, 2014 to January 22, 2015 by a sampler (VFC-PM10, Thermo, USA). There was no precipitation during observation period. The quartz filters were baked at 800°C for 3 hr before using to remove absorbed organic vapors. The sampling duration was 24 hr and filters were changed at about 9:00 am. Two sets of samplers were used to take samples in turn. After collecting, the sampler was ultrasonically cleaned and dried, and was left for use the next day. The concentrations of all species were calculated by mass divided by sampling air flow rate.

1.2. Chemical analysis

After sampling, all the samples were wrapped in aluminum foil and stored in a refrigerator (−18°C) to avoid sunlight and analyzed for chemical species in less than a month. Prior to extraction and digestion, each filter was cut into three equal parts. One of them was digested with nitric acid, hydrogen peroxide, and hydrofluoric acid at 180°C for 6 hr. The reagents were all Merk ultra-pure reagents (6 mL HNO$_3$ + 2 mL H$_2$O$_2$ + 0.1–1 mL HF Mixed acid system). After the permeation solution passed through a filter (pore size: 0.45 μm, Membrana, Germany, Micro PES), an inductively coupled
plasma-mass spectrometry (ICP-MS, Agilent 7700X, USA) was used for analysis of elements. Strict quality control was performed throughout the experimental process, and a collision cell and shield torch were used to ensure the accuracy of the measurement elements. Another part of filter was used for extraction with de-ionized water for an hour, then water-soluble inorganic ions were analyzed by ICS-90 ion chromatography (Dean, USA). The carbon fractions were measured by a thermo-optical carbon analyzer (DRI-2001A, Atmoslytic, USA), following the IMPROVE protocol (Chow et al., 2007).

1.3. Meteorological condition and PM concentration

PM$_{2.5}$ and PM$_{10}$ hourly mass concentrations were collected by Quartz fiber on iron tower (next to the office building; 1 m above ground) at IAP campus. Meteorological hourly data at Beijing Olympic Sports Center (temperature (T), visibility (M) and relative humidity (RH), etc.) were from the Beijing Meteorological Bureau. The distance between two sites is 1.5 km.

1.4. Air mass back trajectories

Air mass backward trajectories were conducted by the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) 4.0 Model to generate backward trajectories at three altitudes of 100, 500 and 1000 m above ground level (AGL).

2. Results and discussion

2.1. Metals in atmospheric particles

As shown in Fig. 2, Zn, Pb, Mo, Mn, and Cu are elements with high abundance among all tested elements (expected for crustal elements). The average concentrations of crustal elements (Al, Fe, Ca, Mg, Na, Ti, Ba, and Sr) accounted for 23.8% of PM$_{10}$ mass. Crustal elements are mainly from fugitive dust influenced by the overall level of urban sanitation, greening cover, human earthmoving activities, and dust control. The crustal elements had strong correlations (almost more than 0.8). Considering the maturity of research at home and abroad, eight heavy metal elements such as Zn, Pb, Mn, Cu, As, V, Cr and Cd were selected to be discussed. During the experimental period, the average concentrations of the eight heavy metals were 415.413, 183.587, 105.227, 82.368, 16.098, 7.998, 49.795 and 4.529 ng/m$^3$. Zn and Pb were the most abundant heavy metals in PM$_{10}$ in Beijing.

Fig. 1 – Location of sampling site (https://map.baidu.com/).

Fig. 2 – Mass distribution of non-crustal elements in particles.
Haze is defined as a weather phenomenon in which the deterioration of visibility (less than 10 km) due to blurring of atmospheric turbidity at a relative humidity of less than 90%. During the observation period, there were a total of 10 days of hazy days and 15 days of non-hazy days. The concentrations of Zn, Pb, Mn, Cu, As, V, Cr, Cd, and Ti in hazy and non-hazy days are listed in Table 1. They were 1.83, 2.43, 1.28, 1.66, 1.98, 1.36, 1.03, 2.85, and 1.21 times higher than that in non-hazy days, indicating that the concentration of heavy metals has increased in hazy days, mainly due to biomass burning and coal burning. Cd had the highest growth multiple, which is consistent with Wang's conclusion (Wang et al., 2015). Cd is mainly derived from the waste gas produced by coal burning, garbage burning, etc. It can enter the human liver and kidney, and it has the carcinogenic effect. It is also observed that except for Cr, the concentration of V, Mn, and Ti also varies slightly. V and Mn are mainly derived from petroleum combustion and steel smelting. Beijing government has strictly controlled industrial production after entering the heavy pollution season, so industrial emissions are not any more the main factor for heavy metal pollution in winter. As for Ti, it is consistent with the conclusion obtained by Zhang Dan (Zhang et al., 2007) that the daily variation of the crust elements is not obvious.

WHO (2000) developed guidelines for heavy metals in atmospheric particulate matters. In 2012, China revised the new standard (NAAQS) (GB3095-2012) based on the original Ambient Air Quality Standard (GB3095-1996). There are limits of heavy metals concentrations such as Pb, As, Cd, Hg, and Cr (VI) in the standard. As shown in Table 1, comparing the average concentration during the observation period with the reference values, it can be found that the mass concentrations of Pb, Mn and Cd did not exceed the limits of the two standards, while As exceeds the current air quality standards in China and the World Health Organization 2.68 and 2.44 times. Most atmospheric Cr exists in two forms of inorganic Cr (III) and Cr (VI). Cr (VI) can do harm to the kidneys and heart, and have a carcinogenic effect (Duan and Tan, 2013). Both the ambient air quality standard and the WHO standard only list the limit of Cr (VI) concentration. The existence of Cr in the atmosphere and the conversion between different valence states still require further study. Moreover, the average mass concentration of Cd in hazy days exceeds the limits of ambient air quality standard and the air quality standard of WHO. But GB2095-2012 is for “Total Suspended Particulate (TSP)”, average concentration for Cd is 4.529 which is very close to the limit of 5 for TSP. Therefore, it is possible that Cd concentration also exceeds the NAAQS standards during entire observation period.

In Table 2, the concentrations of heavy metals in this study are compared with concentrations in spring, and it’s obvious that heavy metal pollutions in winter was more serious. Comparing with the concentrations of heavy metals during the observation period and the concentrations of heavy metals of PM_{2.5} in Beijing and the concentrations in the 44 major cities in China over the past decade, the situation of heavy metals pollutions had improved significantly. This is related to a series of measures, such as the promotion and use of unleaded gasoline throughout the country, the implementation of new ambient air quality standards and the “Air Pollution Prevention Action Plan.”

As shown in Fig. 3, during the observation period, daily average mass concentrations of PM_{2.5} and PM_{10} ranged from 10.3 to 327.7 and 47.1 to 453.4 μg/m³, respectively. The average concentrations of PM_{2.5} and PM_{10} were 100.4 and 161.4 μg/m³, respectively, which were much higher than the concentration limits in NAAQS (35 and 70 μg/m³, respectively, annual average). And they are 10.04 and 8.07 times of WHO guidelines, respectively, indicating that Beijing has serious atmosphere particle pollution in winter. The ratio of mass concentration of PM_{2.5} to PM_{10} in hazy days and non-hazy days were 0.79 and 0.66, respectively. The proportion of fine particles in PM_{10} increases in hazy days, indicating that there were a large number of new particles generated in hazy days and fine particles play a significant role in forming haze. The concentration of heavy metals will increase significantly during heavy pollution periods (Duan et al., 2014; Sun et al., 2013). The trends in total heavy metals concentrations were basically consistent with the trends in PM concentrations, indicating that the prevention and control of heavy metal pollution in Beijing should focus on the control of particulate emissions; however, there are two obvious periods (12.29–12.30; 1.14–1.15) which trends in PM concentrations and heavy metals were opposite. Thus, the characteristics of pollutions (Based on HYSPLIT; back trajectories; 48 hr; 100, 500, 1000 m

<table>
<thead>
<tr>
<th>Table 1 – Comparison of heavy metal concentrations in observation period with those in hazy days, non-hazy days and the concentration limits of different guidelines.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy metals</td>
</tr>
<tr>
<td>Zn (ng/m³)</td>
</tr>
<tr>
<td>Pb (ng/m³)</td>
</tr>
<tr>
<td>Mn (ng/m³)</td>
</tr>
<tr>
<td>Cu (ng/m³)</td>
</tr>
<tr>
<td>As (ng/m³)</td>
</tr>
<tr>
<td>V (ng/m³)</td>
</tr>
<tr>
<td>Cr (ng/m³)</td>
</tr>
<tr>
<td>Cd (ng/m³)</td>
</tr>
<tr>
<td>Ti (ng/m³)</td>
</tr>
</tbody>
</table>

In the concentration limits of Cr of the two guidelines, the Cr is Cr (VI).

<table>
<thead>
<tr>
<th>Table 2 – Comparison of heavy metal element concentrations in different studies.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy metals</td>
</tr>
<tr>
<td>Zn (ng/m³)</td>
</tr>
<tr>
<td>Pb (ng/m³)</td>
</tr>
<tr>
<td>Mn (ng/m³)</td>
</tr>
<tr>
<td>Cu (ng/m³)</td>
</tr>
<tr>
<td>As (ng/m³)</td>
</tr>
<tr>
<td>V (ng/m³)</td>
</tr>
<tr>
<td>Cd (ng/m³)</td>
</tr>
</tbody>
</table>

b Zhao et al. (2013). PM_{2.5}; Winter.
c Duan and Tan (2013).
and wind directions of four different periods were analyzed in Table 3. When air masses were transported from the outside where far from Beijing, the trends in PM concentrations were consistent with heavy metal concentrations; however, when air masses accumulated locally or around Beijing, trends in PM concentrations and heavy metals were opposite. Air masses from near north-west and near west of mainland brought PM with abundant heavy metals.

2.2. Water-soluble inorganic ions

Water-soluble inorganic ions are an important component of atmospheric particles. $\text{SO}_4^{2-}$, $\text{NO}_3^-$, and $\text{NH}_4^+$ account for 77.6% ± 17% of the total concentration of all ions, and it also shows that secondary pollution in the atmosphere of Beijing in winter was serious. The concentrations of these three kinds of ions are related to the mass concentration of corresponding gaseous precursors ($\text{SO}_2$, $\text{NH}_3$, $\text{NO}_x$), also affected by atmospheric humidity and temperature. The average concentrations of several important water-soluble ions $\text{NO}_3^-$, $\text{SO}_4^{2-}$, $\text{NH}_4^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Cl}^-$, $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$ were 12.39, 10.24, 11.76, 1.35, 1.51, 7.51, 6.06 and 0.74 $\mu g/m^3$. As shown in Fig. 4, the ratio of concentrations of hazy days and non-hazy days were 1.81, 1.60, 2.01, 1.42, 1.14, 1.21, 1.44 and 1.31 times, which are higher than the concentration ratio of hazy days and non-hazy days of PM$_{10}$. The ratio of water soluble ions in hazy and non-hazy days accounted for 40.2% ± 13% and 38.93% ± 9% of concentration of PM$_{10}$, respectively, and accounted for 54% ± 9% and 50% ± 16%, respectively. Huang et al. (2013) once pointed out that the concentration ratio of $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{NH}_4^+$ in summer was 3.0, 1.6 and 3.1 times, respectively, and was mainly distributed in fine particles.

In atmospheric aerosols, the mass ratio of $\text{NO}_3^-$/$\text{SO}_4^{2-}$ can be used to compare the contribution of stationary and mobile sources to NO$_2$ and SO$_2$ in the atmosphere (Xiao and Liu, 2003). The greater the $\text{NO}_3^-/\text{SO}_4^{2-}$, the greater the contribution of mobile sources such as automobile to NO$_2$ and SO$_2$, and the smaller $\text{NO}_3^-/\text{SO}_4^{2-}$, the greater the contribution of stationary source such as coal burning to NO$_2$ and SO$_2$. In developed countries, $\text{NO}_3^-/\text{SO}_4^{2-}$ is between 1.33 and 2.20. Since coal accounts for more than 70% of total energy in China, and the vehicle ownership is lower than that of developed countries, $\text{NO}_3^-/\text{SO}_4^{2-}$ is often less than 1, mainly 0.13–0.67 (Yang et al., 2007). During the experiment period, the proportion for $\text{NO}_3^-/\text{SO}_4^{2-}$ in Beijing was 1.31 and 1.16 in hazy days and non-hazy days, respectively. The value greater than 1.0 for $\text{NO}_3^-/\text{SO}_4^{2-}$ in winter in Beijing was consistent with previous studies by Huang et al. (2016). Both the rapidly

### Table 3 – Comparison of characteristics of pollutions and wind directions in different periods.

<table>
<thead>
<tr>
<th>Period</th>
<th>Trends in concentration</th>
<th>Characteristics of pollutions</th>
<th>Wind direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.29-12.30</td>
<td>PM ↓ Heavy Metals ↑</td>
<td>29: External transportation 30: Local accumulation 14: Local accumulation 15: External transportation</td>
<td>29: None 30: None 14: Northwest 15: None</td>
</tr>
<tr>
<td>1.14-1.15</td>
<td>PM ↑ Heavy Metals ↓</td>
<td>16: External transportation 17: External transportation</td>
<td>16: None 17: None</td>
</tr>
<tr>
<td>1.16-1.17</td>
<td>PM ↑ Heavy Metals ↓</td>
<td>4: External transportation 5: External transportation</td>
<td>4: None 5: North</td>
</tr>
<tr>
<td>1.4-1.5</td>
<td>PM ↓ Heavy Metals ↑</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

None: No sustained wind direction.
increasing vehicle numbers and the recent introduction of a strict implementation of flue gas desulfurization in coal-fired power plants for the reduction of atmospheric SO$_2$ would result for the increase of the NO$_3^−$/SO$_4^{2−}$ value (Zhang et al., 2016). So, one of important reasons for haze is the emission of automobile exhaust gas. Therefore, the government should strengthen the measures such as controlling car ownership, restrictions based on the last digit of license plate numbers, and phasing out high-polluting vehicles.

Compared with SO$_4^{2−}$, NO$_3^−$ and NH$_4^+$, the mass concentrations of Na$^+$, K$^+$, Cl$^-$, Ca$^{2+}$ and Mg$^{2+}$ are relatively low. Many studies have found that the abundance of K$^+$ in PM$_{2.5}$ can serve as a diagnostic tracer for biomass burning sources (Watson et al., 2001). Chloride is usually considered from anthropogenic emissions such as biomass burning, coal combustion, and vehicle exhaust fine fraction and from sea water in coarse fraction (He et al., 2001; Li et al., 2012; Watson et al., 2001). In hazy days, the linear relationship between K$^+$ and Cl$^-$ was acceptable ($R^2 > 0.8$), but the relationship during non-hazy days was poor ($R < 0.3$), which indicates that Cl$^-$ is mainly from biomass combustion in atmospheric particles in Beijing during the winter. Ca$^{2+}$ and Mg$^{2+}$ mainly from the wind dust and building dust (Zhang and Iwasaka, 1999). The large increase in the ratio between concentrations of hazy days and non-hazy days indicates that formation of haze was in separable from dust which was from construction sites and exposed soil in winter in the Beijing.

### 2.3. OC and EC

In hazy days, the average mass concentrations of OC and EC were 37.71 and 23.01 μg/m$^3$, respectively, counting for 20.6% ± 12.9% and 12.6% ± 6.8% of the PM$_{10}$ mass concentration, respectively; whereas in non-hazy days, the average mass concentrations of OC and EC were 17.46 and 8.01 μg/m$^3$, which were counted for 17.4% ± 11.2% and 8.0% ± 5.5% of the PM$_{10}$ mass concentration, respectively. The content of carbonaceous species in atmospheric particles rose significantly during the hazy days, and it had the same tendency as heavy metals and water-soluble ions, which may be caused by coal burning and emission of automobile exhaust gas.

The source of EC and OC is complicated. By researching the relationship between OC and EC, the source of carbonaceous species can be distinguished in a way. If the correlation of OC and EC is good, it can be considered that most of them come from the same pollution source, so the source of carbonaceous species can be qualitatively analyzed by using the correlation of OC and EC. A linear regression (confidence 99%) was performed on the OC and EC in the PM$_{10}$ samples collected during the experiment period. As shown in Fig. 5, not surprisingly, correlation during non-hazy days was strong ($R^2 = 0.95$), but it was low ($R^2 = 0.67$) during hazy days, implying that OC and EC tended to be mainly from the same primary sources and were controlled by similar processes after being emitted (Zhang et al., 2016) in non-hazy days, but the source of carbonaceous species is relatively complex and there may be reactions of secondary aerosols in hazy days. The ratio of OC/EC also can reflect the emission and conversion characteristics of carbonaceous species in aerosols. Usually, the ratio of OC/EC was 4.0–16.3 obtained from stationary source such as fossil fuel combustion, residential coal combustion and biomass burning, while 1.1 for vehicular emission (Watson et al., 2001; Zhang et al., 2008). During the observation period, OC/EC ratio ranged from 1.39 to 2.18 with an average of 1.68 in hazy days, from 1.65 to 3.66 with an...
average value of 2.55 in non-hazy days. Large variations for OC/EC values indicate that carbonaceous species may come from different sources, especially in hazy days.

The correlation coefficient between OC/EC and K⁺ is negative (\( R = -0.15 \) at hazy days and \( R = -0.23 \) at non-hazy days), indicating that the high ratios of OC/EC are mainly due to other sources than biomass combustion. EC are mainly from primary emissions, and OC forms secondary organic carbon (SOC) due to photochemical reactions, which increases OC/EC ratio. Previous studies have shown that there may be the existence of SOC, when OC/EC is greater than 2.0 (Castro et al., 1999).

According to the formula of the minimum OC/EC ratio method proposed by Turpin and Huntzicker (1995):

![Fig. 5 – Correlations of EC and OC during haze days and non-haze days.](image)

![Fig. 6 – Air mass backward trajectories during non-hazy and hazy days.](image)


$$\text{OC}_{\text{sec}} = \text{OC}_{\text{tot}} - \text{EC} \times (\text{OC/EC})_{\text{min}},$$

where $\text{OC}_{\text{sec}}, \text{OC}_{\text{tot}}$ and $\text{EC}$ is mass concentration of SOC, OC and EC in the sample, and $(\text{OC/EC})_{\text{min}}$ is the minimum value of OC/EC during the observation period. Because of the low temperature during the observation period in Beijing, the photochemical reaction is not active affected by the temperature. Thus the calculated mass concentration of SOC is 2.58 $\mu$g/m$^3$, which only accounted for 10.1% of the OC concentration, therefore the high OC/EC ratio is mainly derived from primary emissions. But the SOC pollution was relatively serious in non-hazy days with an average value of 2.55 during the observation period.

2.4. Back trajectories

The air mass back trajectories (72 hr, 500 m AGL) during the non-hazy and hazy days are shown in the Fig. 6. It can be seen that the air masses from the far north-west decreased PM in Beijing and they were relatively clean. It originated from the Siberian region, passed through Mongolia, Inner Mongolia, Hebei and Tianjin. In contrast, air masses from the near east, south-east and south of the mainland increased PM and were dirty. These air masses have passed through heavily polluted areas with heavy industrial density and high population density in the Northeast, Shandong, Hebei, Tianjin and Henan, bringing with a large amount of atmospheric particles, which in turn aggravated pollution of heavy metal and water-soluble ions. The conclusion was consistent with previous study by Zhang et al. (2016) that air masses from the south and southeast directions will increase pollution, while air masses from the northwest will be relatively clean and beneficial to the quality of the atmospheric environment.

3. Conclusions

In this study, chemical components and concentrations of PM$_{10}$ were analyzed in winter in Beijing. Daily mass concentrations of PM$_{2.5}$ and PM$_{10}$ ranged from 10.3 to 327.7 and 47.1 to 453.4 $\mu$g/m$^3$, respectively. The concentrations of heavy metals were 1.03–1.98 times higher than that in non-hazy days. Among these heavy metals, only the level of As exceeded the reference values of National Ambient Air Quality Standard. The trends in total heavy metals concentrations were basically consistent with trends in PM concentrations expect for two obvious periods (12.29–12.30; 1.14–1.15). When air masses accumulated locally or around Beijing, trends in PM concentrations and heavy metals were opposite. Air masses from near north-west and near west of mainland brought particulate matters with abundant heavy metals. SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were greatly enhanced during hazy days, the proportion for NO$_3$/SO$_4^{2-}$ indicated that the rapidly increasing vehicle numbers was an important reason for haze. OC and EC tended to be mainly from the same primary sources and were controlled by similar processes after being emitted in non-hazy days, but the source of carbonaceous species is relatively complex and there may be reactions of secondary aerosols in hazy days. The calculated mass concentration of SOC is 2.58 $\mu$g/m$^3$, which only counted for 10.1% of the OC concentration. Air masses from the far north-west decreased PM in Beijing and they were relatively clean; however, those from the near east, south-east and south of the mainland increased PM and were dirty.

Acknowledgments

This work was supported by the International Partnership Program of Chinese Academy of Sciences (IPP) (No.134111KYSB20180021), the National Natural Science Foundations of China (No. 41590871), the National Key R&D Program of China (no. 2017YFB0504600), the National Natural Science Foundations of China (No. 41475136) and the International Science & Technology Cooperation Program of China (No. 2013DFG22820).

REFERENCES


He, K.B., Yang, F.M., Ma, Y.L., Zhang, Q., Yao, X.H., Chan, C.K., et al., 2001. The characteristics of PM$_{2.5}$ in Beijing, China. Atmos. Environ. 35 (29), 4959–4970.


