Simultaneous Measurements of Carbonaceous Aerosol in Three Major Cities in the Beijing-Tianjin-Hebei region, China

Jianfang Jiang\textsuperscript{1,5}, Lili Hou\textsuperscript{1*}, Xing Yan\textsuperscript{2}, Huiyue Liu\textsuperscript{1}, Shuang Sun\textsuperscript{3}, Shanshan Li\textsuperscript{4}, Kai Xiong\textsuperscript{4}, Wenji Zhao\textsuperscript{1*}

\textsuperscript{1}School of Resources, Environment & Tourism, Capital Normal University, Beijing 100048, China
\textsuperscript{2}State Key Laboratory of Remote Sensing Science, College of Global Change and Earth System Science, Beijing Normal University, Beijing 100875, China
\textsuperscript{3}Beijing Municipal Ecological and Environmental Monitoring Center, Beijing 100048, China
\textsuperscript{4}Beijing Municipal Research Institute of Environmental Protection, Beijing 100037, China
\textsuperscript{5}School of Geography and Information Engineering, China University of Geosciences, Wuhan, 430074, China

*Corresponding author
E-mail address: 4973@cnu.edu.cn (Wenji Zhao); lili.hou@cnu.edu.cn (Lili Hou)
Phone: +86-13810707928 (Wenji Zhao); +86-13488730355(Lili Hou)
Postal Address: School of Resources, Environment and Tourism, Capital Normal University, No. 105, West Third Ring North Road, Haidian District, Beijing,100048 (Wenji Zhao, Lili Hou)
Abstract:

Simultaneous observations of carbonaceous aerosols in multiple cities are of great significance for a comprehensive understanding of the level of carbonaceous aerosol pollution in the Beijing-Tianjin-Hebei (BTH) region. In this study, PM$_{2.5}$ samples were collected simultaneously in Beijing (BJ), Tianjin (TJ), and Shijiazhuang (SJZ) during the 2017–2018 heating season, and the contents of organic carbon (OC) and elemental carbon (EC) in the samples were measured. The mean mass concentrations were 10.15–46.23 μg m$^{-3}$ for OC, and 2.13–10.42 μg m$^{-3}$ for EC in three cities. SJZ had more serious carbonaceous aerosols pollution compared with BJ and TJ. The OC and EC levels in three cities, especially in Beijing, were significantly lower than those reported in previous studies, implying the effectiveness of strict air pollution control measures in 2017. Based on the OC/EC minimum ratio method, the mass concentration of secondary organic carbon (SOC) was estimated, and SOC pollution in BJ was relatively light. Analysis of eight carbonaceous components showed that the gasoline vehicle exhaust sources made high contributions to the levels of carbonaceous aerosols in all three cities. Compared with SJZ, the carbonaceous aerosols in BJ and TJ were more affected by road dust pollution. Analysis of backward trajectory indicated that the carbonaceous aerosols in the three cities were affected by pollution transport from the BTH region and surrounding areas, in addition to local sources. In contrast to the other two cities, OC and EC in SJZ were greatly affected by short-distance air mass transport from Hebei Province.

Keywords: The Beijing-Tianjin-Hebei region; Carbonaceous aerosol; PM$_{2.5}$; SOC; Source analysis; Backward trajectory
1 INTRODUCTION

Carbonaceous aerosols, as a group of important chemical components of fine particulate matter (PM$_{2.5}$), attract worldwide attention due to their notable effects on air quality, global and regional climate, water cycle, and human health, etc. (Ding et al. 2016; Huang et al. 2014; Mauderly and Chow 2008). Carbonaceous aerosols are mainly divided into two groups: organic carbon (OC) and elemental carbon (EC) (Chow and Watson 2002; Hao et al. 2019). The list of OC contains many harmful substances, such as polycyclic aromatic hydrocarbons, organic acids, n-alkanes, heterocyclic compounds, carboxyl compounds (aldehydes, ketones), some of which have strong carcinogenicity and considerably impact human health (Mauderly and Chow 2008; Offenberg and Baker 2002). The problems of EC are mainly focused on the significant impact on atmospheric visibility and global climate change due to the strong capability of chemical adsorption and solar radiation absorbing (Feng et al. 2009; Glasius et al. 2018). OC includes not only primary organic carbons (POC) directly emitted from the emission sources, but also secondary organic carbons (SOC) generated by organic gases through photochemical reactions (Guo 2016; Sudheer et al. 2016). It makes sources of OC are normally complex and difficult to identify. Sources of EC are more straightforward. EC is mainly directly discharged by pollution sources due to incomplete combustion of fossil fuels and biomass (Cao et al. 2004). OC and EC can come from both identical sources and distinct emissions. It is of great importance to identify the sources of the carbonaceous aerosols for controlling the PM$_{2.5}$ contents in the air as well as improving the air quality in the city.

Many researches have been conducted on carbonaceous aerosols regarding the contents, spatial and temporal variations, emission sources and potential source region. For example, Yan et
al. (2020) measured the contents of OC and EC in Xinxiang in 2017. The mean mass concentration
of OC and EC were 19.24 and 7.36 $\mu$g m$^{-3}$, accounting for 16.08% and 6.15% of the PM$_{2.5}$ mass
concentration, respectively. Huang et al. (2018) analyzed the seasonal characteristics of
carbonaceous aerosols in Wanzhou city. The results showed that the mass concentrations of OC
and EC were high in spring and winter, and a strong correlation between OC and EC was observed.
Zhou et al. (2017) compared the pollution characteristics of carbonaceous aerosols during haze and
non-haze days in Jinan and found greater SOC apportionment during haze days. Zhang et al. (2017)
analyzed the sources of carbonaceous aerosols in Anshan city, and found that the carbonaceous
aerosols in PM$_{2.5}$ came from a mixture of biomass combustion sources, coal burning sources,
vehicle emissions and road dust sources. Yang et al. (2019) identified the potential source areas of
OC and EC in Nanchong city and found that OC and EC were influenced by both regional transport
and local sources. These studies of carbonaceous aerosol covered a wide range of study areas, from
rural or suburban areas to industrial cities, to modernized metropolitan regions.

The Beijing-Tianjin-Hebei (BTH) region is one of the most advanced metropolitan regions in
China as well as an important industrial base. Air pollution in Beijing and surrounding areas is
notorious so that it has aroused public attention for several decades (Li et al. 2012; Zhao et al. 2013;
Wang et al. 2015, Zhang et al. 2019). In recent years, many activities that are major emissions of
air pollutants such as heating by using coal mine and driving fuel vehicles, have been gradually
eliminated or replaced in the BTH region with the executed of the “Action Plan on Air” (Ji et al.
2019). It is important to understand how these actions impact the concentration and structure of
carbonaceous aerosols, so that updated observation of carbonaceous aerosols in the BTH region is needed.

Moreover, recent measurements of air pollution level in the BTH region were normally conducted by a unit of single city, since clean air measures were firstly taken by separate city governments. For example, Ji et al. (2018) analyzed the seasonal characteristics of carbonaceous aerosol in Beijing and found that the level of carbonaceous aerosol was significantly higher in winter than in other seasons. Unfavorable weather conditions were an important reason for obvious seasonal variations. Cheng et al. (2018) analyzed the sources of carbonaceous aerosols in Tianjin in 2016. The results showed that coal burning and vehicle exhaust were the main source of carbonaceous aerosols. Chen et al. (2017) analyzed the chemical components of PM$_{2.5}$ during haze weather in 2016 in Shijiazhuang. It was found that the mean OC/EC ratio was as high as 10.8, suggesting a great portion of secondary pollution. Potential Source Contribution Function (PSCF) analysis indicated that the potential source areas of PM$_{2.5}$ in Shijiazhuang were not only local emissions but also the border areas between Hebei, Henan, and Shandong Provinces and central Shanxi Province. These studies have mainly focused on the carbonaceous component characteristics in single cities.

Nowadays, collaborating efforts of air clean among different cities in the region, rather than single city efforts, has been enhanced and become a main strategy for air pollution control. A few studies involving synchronous observations in multiple cities have been reported. However, most of the studies focused on the seasonal and diurnal variations of carbonaceous aerosols (Dao et al. ...)
The other study was conducted on the full component analysis of PM$_{2.5}$, and the analysis about carbonaceous aerosols was not comprehensive (Dao et al., 2021). The year of 2017 was the final year of the first phase (Year 2013-2017) of the national “Action Plan on Air” (MEP 2019). In the year, a coordinated work of extraordinary strict pollution control measures in the region was organized. Meanwhile, air clean strategies designed to meet the demand of individual cities were still employed. There is a lack of study that comprehensively assesses the differences and similarities in the concentration levels and sources of carbonaceous aerosols in different cities in the Beijing-Tianjin-Hebei region after strict pollution control measures in 2017.

The objective of this study is to learn (1) to what extent that the air quality of the BTH region has been improved at the end of the first phase of the “Action Plan on Air” in terms of carbonaceous aerosols in PM$_{2.5}$, (2) the similarities and differences of OC and EC in three major cities in the BTH region through a synchronous observation, and (3) how the structure of carbonaceous aerosols can be influenced by regional air quality control measures and city specified conditions. Therefore, carbonaceous aerosols in PM$_{2.5}$ samples during a heating period (Dec. 27th, 2017 - Jan. 19th, 2018) were simultaneously collected and analyzed in cities of Beijing, Tianjin, and Shijiazhuang in the BTH region. The results are expected to provide a scientific basis for governments to carry out PM$_{2.5}$ pollution prevention and control more accurately according to both local conditions and joint efforts in the region.

2 Materials and methods
2.1 Study area and sampling sites

The BTH region was selected as the study area for its elevated pollution level, dense population, and rapidly developed economy. It is one of the most dynamic regions in China. By the end of 2017, the total population of the region was 112.47 million, and the gross regional product (GDP) reached 8058.05 billion yuan (HBBS 2018). The BTH region is located in the North China Plain. It is a typical alluvial fan-coastal plain topography unit, with Taihang Mountain to the west and Bohai Sea to the east. Three cities were selected for collecting PM$_{2.5}$ samples based on a comprehensive consideration of socioeconomic, environmental, and geological conditions: Beijing (BJ), Tianjin (TJ) and Shijiazhuang (SJZ).

Sampling sites were placed to avoid interferences of industry and traffic, with locations shown in Fig. 1. The sampling site in BJ (116°18'E, 39°55'N; Height = 15 m) is located on the 4th floor of a teaching building in the capital normal university, Haidian District, Beijing, surrounded by schools, business, and residential area. The sampling site in TJ (117°5'E, 39°5'N; Height = 15 m) is located on the 4th floor of a teaching building in Tianjin Chengjian University, Xiqing district, Tianjin, surrounded by residential and commercial areas. The sampling site in SJZ (114°51'E, 38°2'N; Height = 7 m) is located in a residential area, on the roof of a resident's room in Gaocheng district.
Fig. 1. Locations of sampling sites in the study area.

2.2 Sample collection and analysis

The samples were collected by PM$_{2.5}$ samplers during the heating season from December 27, 2017 to January 19, 2018 simultaneously in the three cities. PM$_{2.5}$ samples in BJ were collected by a large-flow PM$_{2.5}$ sampler (1.13 m$^3$ min$^{-1}$; TE-6070DV, Tisch, Medford, MA, USA), with 203 mm $\times$ 254 mm quartz fiber filters. PM$_{2.5}$ samples in TJ were collected by a low-flow sampler (16.7 L min$^{-1}$; PQ200, BGI, Cambridge, MA, USA), with 47-mm diameter quartz fiber filters. A medium-flow sampler (100 L min$^{-1}$; TH-150A, Wuhan Tianhong Instruments Co., Ltd., Wuhan, China) was used to collect the PM$_{2.5}$ samples in SJZ, with 90-mm diameter quartz fiber filters. Continuous sampling was conducted from 08:00 to 20:00. A total of 63 samples were used after removing invalid samples due to instrument failure (January 7 to 9, 2018). Prior to sampling, the quartz fiber filters were wrapped with tin foil and baked at 550 °C for 5 h to remove residual organic impurities.
Before and after sampling, each filter was balanced in a constant temperature and humidity chamber for 48 h. After sampling, the filters were wrapped with tin foil and placed in a refrigerator at 4 °C to avoid volatilization. All samples were weighed with a high-precision electronic microbalance. Meteorological data, including air pressure (P), wind speed (WS), temperature (T), and relative humidity (RH) in the three cities were downloaded from China Meteorological Data Network (http://data.cma.cn/) and listed in Table 1. Among the three cities, SJZ has the lowest WS and the highest T, with mean values of 1.3 m s⁻¹ and 0.4 °C; TJ has the highest WS and P, with mean values of 2.6 m s⁻¹ and 1027.3 hPa; and BJ has the lowest RH, with a mean value of 33.3%. No rainfall occurred in the three cities during the monitoring period.

Table 1. Meteorological parameters in BJ, TJ, and SJZ during the sampling period.

<table>
<thead>
<tr>
<th>Statistic</th>
<th>BJ</th>
<th>TJ</th>
<th>SJZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>WS</td>
<td>T</td>
</tr>
<tr>
<td></td>
<td>(hPa)</td>
<td>(m s⁻¹)</td>
<td>(°C)</td>
</tr>
<tr>
<td>Mean</td>
<td>1021.9</td>
<td>1.81</td>
<td>-0.2</td>
</tr>
<tr>
<td>St. Dev.</td>
<td>5.3</td>
<td>0.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Minimum</td>
<td>1013.3</td>
<td>0.9</td>
<td>-5.0</td>
</tr>
<tr>
<td>Median</td>
<td>1021.8</td>
<td>1.7</td>
<td>-0.4</td>
</tr>
<tr>
<td>Maximum</td>
<td>1033.7</td>
<td>3.6</td>
<td>3.3</td>
</tr>
</tbody>
</table>

The OC and EC contents in the samples were quantitatively measured using a thermal/optical carbon analyzer (DRI Model 2001A). The experimental method was based on the thermal optical
reflection (TOR) method specified in the Interagency Monitoring of Protected Visual Environments (IMPROVE) analysis protocol. Samples of 0.539 cm² were taken from the quartz filter membrane and placed in the sample furnace. The protocol consists of three stages. Firstly, the contents of OC1, OC2, OC3, and OC4 were obtained by heating the filtration membrane at 120 °C, 250 °C, 450 °C, and 550 °C in the pure helium oxygen-free environment. Secondly, the contents of EC1, EC2, and EC3 were obtained by further heating at 550 °C, 700 °C, and 800 °C in a helium atmosphere with 2% oxygen. The carbon components generated at the above ambient temperatures were oxidized to CO₂ by MnO₂ catalysis and then reduced to CH₄ in the reduction furnace, which was quantitatively detected by a flame ionization detector (FID). Finally, the content of pyrolysis carbon (OP) was determined by irradiation with 633nm. The final OC was calculated as OC1 + OC2 + OC3 + OC4 + OP, and EC was calculated as EC1 + EC2 + EC3 − OP. For quality control, flow calibration of the sampling instrument was performed before sample collection to ensure stable and accurate data. The instrument was calibrated by CH₄/CO₂ standard gas before and after sample analysis. Before analyzing samples, the instrument was baked at a high temperature and a blank test was performed to ensure that there were no residual impurities in the instrument. In each city, two blank samples were collected during the sampling period, and the determination results of the blank samples were all below the detection limits. One sample was randomly selected from every seven samples for replicate testing, and the error between the two analyses was < 10%.

2.3 Air mass trajectory analysis

The HYSPLIT model was used to compute the daily air mass trajectories at sampling points in BJ, TJ, and SJZ during the sampling period. The model is developed by the National Oceanic
and Atmospheric Administration (NOAA) and the Australian Meteorological Agency to calculate the transport and diffusion trajectories of air pollutants (Draxler and Hess 1998). This model can be used to simulate the movement trajectory of air masses from other regions to the observation points. When the pollution concentration of the observation point corresponding to time was added to each backward trajectory, the effects of air mass trajectories from different directions on pollutants in the study area could be analyzed based on the method of trajectory clustering (Stein et al. 2015).

In this paper, the simulation time was 48 h and the simulation height was 100 m. This height was higher than the urban canopy, therefore, could represent the average low-level atmosphere. Cluster analysis was performed on the trajectories of each city using TrajStat software, (Liu et al. 2017; Wang et al. 2009), and the mean value of carbonaceous components mass concentration, OC/EC ratio, surface meteorological parameters corresponding to different trajectory clusters were statistically analyzed.

3 RESULTS AND DISCUSSION

3.1 OC and EC mass concentration characteristics

To quantitatively evaluate the pollution level of the BTH region in 2017-2018 heating season in terms of carbonaceous aerosols, the variations of OC and EC mass concentrations in three cities (BJ, TJ and SJZ) were measured, as shown in Fig. 2. During sampling days, the mass concentration of OC varied from 3.62 to 77.29 μg m\(^{-3}\) in three cities, with average value of 10.15 ± 5.13 μg m\(^{-3}\) in BJ, 16.83 ± 9.25 μg m\(^{-3}\) in TJ, and 46.23 ± 19.57 μg m\(^{-3}\) in SJZ. The mass concentration of EC
varied from 0.41–16.33 μg m\(^{-3}\), with average value of 2.13 ± 1.39 μg m\(^{-3}\) in BJ, 4.93 ± 3.03 μg m\(^{-3}\) in TJ and 10.42 ± 3.11 μg m\(^{-3}\) in SJZ. The mass concentrations of OC accounted for 17.18%, 20.48%, and 33.37% of PM\(_{2.5}\) in BJ, TJ, and SJZ, respectively. Compared with OC, the mass concentrations of EC accounted for relatively lower proportions, i.e., 3.61%, 6.01%, and 7.52% in BJ, TJ, and SJZ, respectively. It can be seen that the pollution of carbonaceous aerosol is more severe in SJZ than in BJ and TJ, since the mass concentration of total carbon (TC, TC = OC + EC) in SJZ was 4.61 and 2.60 times those in BJ and TJ, respectively. This was mainly associated with the outdated industrial structure and energy consumption as well as unfavorable meteorological conditions in the city. As an industry city, SJZ developed industries such as raw materials, steel, electricity, and cement, and large amounts of OC and EC were emitted from such industrial production (Liu et al. 2018). In addition, WS in SJZ was significantly lower than that in the other two cities, with a mean of 1.3 m s\(^{-1}\). The low WS was not conducive to the dilution of pollutants, which also led to higher OC and EC levels.

**Fig. 2.** Statistics of OC and EC mass concentrations in BJ, TJ, and SJZ during the sampling period.
To estimate the extent to which air quality had been improved and the effectiveness of the control measures taken in recent air clean actions in the BTH region, OC and EC levels obtained in this study were compared with previous ones, as summarized in Table 2. In general, OC and EC levels in the three cities were lower than those reported in previous studies, but the degrees of air quality improvement were different among the three cities. There was a sharp decrease in TC mass concentration in BJ, reduced by approx. 64% from 2010 to 2017. It seems that the rate of decrease in TC was slower at the early stage (~20% decline in 2010-2013), and then accelerated (~40% decline in 2014-2017). The decrease in TJ, however, was small compared with in BJ. The mass concentration of TC declined by approx. 25-40% from 2008 to 2017. TC decrease in SJZ was even lower than TJ, declined by approx. 3.4-25% from 2010 to 2017. It should be mentioned that measurements from different studies could not be compared directly, but the trends can be somewhat meaningful. These decreases in TC in the BTH region indicate that the Clean Air Action is effective, especially in BJ. The first phase of national “Action Plan on Air” was carried on during the year of 2013-2017, and 2017 was the last year of the action. The control measures were strict in BJ and surrounding areas throughout the action, but not very strict in other areas of the BTH region at the beginning of the action, mainly because of differences in levels of development and industrial structures among cities. From 2017, however, stricter measures have been adopted in the whole BTH region to control the pollution caused by loose coal burning, industrial pollution, and exhaust emissions (MEP 2019). The levels of carbonaceous aerosol pollution in 2017 in three cities were significantly lower than that in previous years, especially in 2015-2016. Air pollution control
measures in BJ have started earlier with a comprehensive and effective plan and, therefore, showing
the most significantly reduction in carbonaceous aerosol pollution. Other cities in the BTH region
should continue with the strict measures and detailed control plan could be further discussed to
ensure cleaner air quality.

Table 2. Summarizing OC and EC levels in BJ, TJ, and SJZ in this study and previous studies.

<table>
<thead>
<tr>
<th>Cities</th>
<th>Sampling date</th>
<th>OC (μg m⁻³)</th>
<th>EC (μg m⁻³)</th>
<th>TC (μg m⁻³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BJ</td>
<td>2017–2018 winter</td>
<td>10.2</td>
<td>2.1</td>
<td>12.3</td>
<td>This research</td>
</tr>
<tr>
<td>BJ</td>
<td>2016 winter</td>
<td>26.7</td>
<td>5.2</td>
<td>31.9</td>
<td>Fan et al., 2018</td>
</tr>
<tr>
<td>BJ</td>
<td>2013–2014 winter</td>
<td>18.6</td>
<td>4.4</td>
<td>23.0</td>
<td>Ji et al., 2016</td>
</tr>
<tr>
<td>BJ</td>
<td>2010 winter</td>
<td>26.8</td>
<td>7.1</td>
<td>33.9</td>
<td>Zhao et al., 2013</td>
</tr>
<tr>
<td>TJ</td>
<td>2017–2018 winter</td>
<td>16.8</td>
<td>4.9</td>
<td>21.8</td>
<td>This research</td>
</tr>
<tr>
<td>TJ</td>
<td>2016 winter</td>
<td>25.3</td>
<td>6.1</td>
<td>31.4</td>
<td>Qi et al., 2018</td>
</tr>
<tr>
<td>TJ</td>
<td>2015 winter</td>
<td>18.5</td>
<td>3.4</td>
<td>21.9</td>
<td>Liu et al., 2016</td>
</tr>
<tr>
<td>TJ</td>
<td>2008 winter</td>
<td>22.9</td>
<td>5.6</td>
<td>28.5</td>
<td>Gu et al., 2010</td>
</tr>
<tr>
<td>SJZ</td>
<td>2017–2018 winter</td>
<td>46.2</td>
<td>10.4</td>
<td>56.7</td>
<td>This research</td>
</tr>
<tr>
<td>SJZ</td>
<td>2015–2016 winter</td>
<td>55.8</td>
<td>19.9</td>
<td>75.7</td>
<td>Xie et al., 2019</td>
</tr>
<tr>
<td>SJZ</td>
<td>2010 winter</td>
<td>46.5</td>
<td>12.1</td>
<td>58.6</td>
<td>Zhao et al., 2013</td>
</tr>
</tbody>
</table>

3.2 Correlation analysis, OC/EC ratio and SOC estimation

It is generally considered that EC in the carbonaceous aerosols is a group of inert pollutants,
which mainly come from primary emissions. While OC can be not only emitted from the primary
pollution source, but also generated by photochemical reactions of volatile organic compounds (VOCs). Based on the correlation between OC and EC, whether the two have homological sources can be preliminarily determined (Na et al. 2004). A good correlation indicates that OC and EC come from similar pollution sources or the proportion of SOC in OC is small. A poor correlation indicates that the sources of OC and EC are complex (Turpin and Huntzicker 1995). Linear regression analysis of OC and EC was shown in Fig. 3. The correlation coefficients R² were 0.81, 0.80, and 0.85 in BJ, TJ, and SJZ, respectively, indicating that the sources of OC and EC were all similar in three cities. This result is consistent with previous studies in which strong correlations between OC and EC in winter were found in BJ, Shanghai, and Jinan (Gao et al. 2018; Yang et al. 2005; Zhou et al. 2017). Among the three cities, the correlation in SJZ was greater than in TJ and BJ, indicating a more homological sources of OC and EC in SJZ. The correlations in BJ and TJ were very close, but the value in TJ was a little weaker. This phenomenon was also reported by Qi et al. (2018) who found a weaker correlation between OC and EC in TJ compared with other major cities in the BTH region during the winter of 2016. This may be associated with the formation of SOC (Pachauri et al. 2013). TJ is close to the Bohai Sea in the east, and it is likely that the special meteorological conditions influence the correlation between OC and EC.
EC is often used as a tracer for primary source emissions and the OC/EC ratio can be applied to determine whether secondary pollution exists (Cabada et al. 2004). It is generally believed that SOC can be formed when OC/EC ratio is greater than 2 (Aswini et al. 2018; Chow et al. 1996).

The statistics of OC/EC ratios in BJ, TJ, and SJZ during the monitoring period is shown in Fig. 4. The ratios in the three cities ranged from 2.38‒10.74, demonstrating the existence of SOC. In addition, OC/EC ratios varied by pollution sources. The OC/EC ratios were reported 1.1–5.0 from vehicle exhaust emissions, 2.5‒10.5 from coal combustion, and 4.3‒80 from biomass combustion (Cao et al. 2007; Huang et al. 2018; Watson et al. 2001). Based on the OC/EC range, it is likely that carbonaceous aerosols in the three cities were mainly affected by vehicle exhaust emissions, coal combustion and biomass combustion during the 2017–2018 heating season. This finding is consistent with previous studies on major cities in the BTH region (Qi et al. 2018; Wang et al. 2015).

**Fig. 3.** Relationship between OC and EC in BJ, TJ, and SJZ during the 2017–2018 heating season.
Fig. 4. Statistics of OC/EC ratios in BJ, TJ, and SJZ.

During the monitoring period, the mean OC/EC ratios were 5.56, 3.70, and 4.29 in BJ, TJ, and SJZ, respectively, with the highest ratio in BJ and the lowest in TJ. The high OC/EC value in BJ is probably because of the lower proportion of EC in PM$_{2.5}$ in BJ than in other two cities, as discussed in section 3.1. This phenomenon is probably related to the green taxi policy replacing gasoline-fueled taxis with electric ones. As mentioned, gasoline vehicle exhaust exhibits lower OC/EC ratio than other sources including coal burning and biomass burning, so that the substitution of electric vehicles on gasoline vehicles can probably led to a rise in the OC/EC ratio in BJ.

The mean OC/EC ratios under different pollution levels were analyzed statistically, as shown in Fig. 5. Based on the PM$_{2.5}$ mass concentration, we defined PM$_{2.5} \leq 75$ $\mu$g m$^{-3}$, $75$ $\mu$g m$^{-3} < PM_{2.5} \leq 150$ $\mu$g m$^{-3}$, and PM$_{2.5} > 150$ $\mu$g m$^{-3}$ as clean days, light polluted days, and heavily polluted days, respectively (Li et al. 2018). The relation between OC/EC ratio and PM$_{2.5}$ varied by cities. In SJZ, the OC/EC ratio increased significantly as the pollution level increased, suggesting that the increase in PM$_{2.5}$ pollution in SJZ was more influenced by source emissions of OC than
EC. In contrast, OC/EC ratios in BJ decreased with increased pollution levels, indicating that the increase in PM$_{2.5}$ pollution was more affected by source emissions of EC than OC. This result is consistent with the study by Zhang et al. (2020), which found that compared with OC, the EC mass concentration in BJ increased significantly on pollution days. The OC/EC ratios in TJ did not show obvious trend, with slightly lower values during light and heavily polluted days than during clean days.

**Fig. 5.** Relations between OC/EC ratios and PM$_{2.5}$ levels in BJ, TJ and SJZ.

Carbonaceous aerosols are not only affected by primary emission sources such as coal combustion, biomass combustion, and vehicle exhaust, but also by secondary pollution sources. SOC is formed by complex gas particle reactions of VOCs in the atmosphere. Compared with POC, the formation mechanism of SOC is more complicated. The estimation of SOC can reflect the secondary transformation of carbon components in the region, which is helpful to understand the source of carbon components in the current region, so as to carry out pollution prevention and control in a targeted manner. At present, to the best of our knowledge there is no method to directly distinguish primary organic matter from secondary organic matter in aerosols. Indirect methods are
generally used to estimate the SOC. The OC/EC minimum ratio method is relatively simple and easy to apply (Castro et al. 1999) so that is widely used for SOC estimation (Lim and Turpin 2002; Pachauri et al. 2013; Wang et al. 2020). The calculation is conducted by the equation as follows:

\[
\text{SOC} = \text{TOC} - \text{EC} \times (\text{OC/EC})_{\text{min}}
\]

where OC and EC are the mass concentrations of OC and EC, and \((\text{OC/EC})_{\text{min}}\) is the lowest OC/EC ratio observed.

During sampling period, the lowest OC/EC ratios in BJ, TJ and SJZ were 3.57, 2.38 and 3.09, respectively. According to the Eq. 1, the estimated values of SOC in BJ, TJ, SJZ were 2.55 \(\mu g \, m^{-3}\), 5.10 \(\mu g \, m^{-3}\) and 14.05 \(\mu g \, m^{-3}\), accounting for 25.15%, 30.29% and 30.38% of the OC, respectively.

In winter, the mass concentration of SOC is usually greater, mainly related to the increase in gaseous precursors caused by coal or gas heating as well as adverse weather conditions such as boundary layer subsidence, temperature inversion, and high RH (Dan et al. 2004; Pachauri et al. 2013). Zhou et al. (2017) pointed out that RH plays an important role in the generation of SOC. High RH helps to dissolve water-soluble gases into the liquid aerosol particles, promoting further chemical reactions in these particles (Ji et al. 2018). Among the three cities, both SOC and its proportion in OC were the lowest in BJ. There may be two reasons. On the one hand, compared with TJ and SJZ, BJ has fewer industrial and mining enterprises, leading to lower emissions of gaseous precursors. On the other hand, the RH in BJ was low during the monitoring period, only 33.3% on average, this low RH was not favorable to SOC formation. The mass concentration of SOC in TJ was much lower than that in SJZ, while the proportion of SOC in OC was almost same.
as that in SJZ. The high proportion in TJ is probably related to its geographical location. TJ is close to the Bohai Sea in the east, and unfavorable meteorological conditions such as land and sea breeze and high RH (43.7%) contributed to SOC formation, resulting a greater SOC proportion.

3.3 Source analysis of carbonaceous aerosols

The contents of eight carbonaceous components (OC1, OC2, OC3, OC4, EC1, EC2, EC3, and OP) in PM$_{2.5}$ samples were obtained using TOR method, and the abundances of these carbonaceous components can represent the source spectrum to a certain extent. Previous studies have shown that OC1 mainly comes from biomass combustion; abundant OC2 can be found in coal burning sources; OC3 and OC4 are rich in road dust; abundant EC1 and OP can be found in gasoline vehicle exhaust, and EC2 and EC3 represent the source of diesel exhaust (Chow et al. 2004; Li and Bai 2009; Watson et al. 1994).

To further analyze the sources of carbonaceous aerosols, the mass fractions of eight carbonaceous components were calculated, as shown in Fig.6. The composition of carbonaceous components showed both similarities and differences among the three cities. In terms of mass fraction, the ascending order of carbonaceous components in BJ was OC4 > OC3 > EC1 > OC2 > OC1 > OP > EC2 > EC3. The ascending order of carbonaceous components in TJ was OC4 > EC1 > OC3 > OC2 > OC1 > OP > EC2 > EC3. The ascending order of carbonaceous components in SJZ was EC1 > OP > OC4 > OC3 > OC2 > OC1 > EC2 > EC3. The mass fractions of EC2 and EC3 in all three cities were extremely low, with the totals of EC2 and EC3 all less than 2.50%. This is probably because of the effective control of diesel vehicle transportation in the BTH region. The
structure of carbonaceous components was similar in BJ and TJ. Among all carbonaceous
components, EC1, OC3, and OC4 accounted for the largest proportions, and the totals of the three
were 67.69% and 69.83% for BJ and TJ, respectively, indicating that gasoline vehicle exhaust and
road dust were most likely the main sources of carbonaceous aerosols in these two cities. The mass
fractions of OC1 and OC2 were relatively low; the sum of the two was only 23.44% and 21.99%
in BJ and TJ, respectively. This observation indicates that the contributions of biomass and coal
combustion sources to carbonaceous aerosols were less important than vehicle emission sources.

Similar structure of carbonaceous aerosols was also found in Shanghai and Qingdao (Yao et al.
2020, Yu et al., 2022). In recent years, with the surge in the number of motor vehicles, the
contribution of motor vehicle exhaust emissions to particulate matter has increased. The structure
of carbonaceous aerosols in SJZ was quite different from that in BJ and TJ. In SJZ, the mass
fractions of OC3 and OC4 was significantly lower than in the other two cities, indicating that road
dust pollution in this city was relatively light. The mass fractions of EC1 and OP were significantly
higher than other carbonaceous components, with sums of the two as high as 54.99%. This was
consistent with previous analysis in SJZ conducted by Li et al. (2018). Abundant EC1 and OP
usually come from gasoline vehicle exhaust. However, the number of private cars in SJZ was 2.28
million in 2017, which was about half of the private cars in BJ (BJBS 2018; HBBS 2018). It is
likely that the high mass fractions of EC1 and OP in SJZ may be related to the lower quality of
local vehicle fuel and the existence of other types of pollution sources. In addition, OP has also
been reported to be usually related to secondary sources (Tan et al., 2021). In order to further
analyze the sources of carbonaceous aerosols in the three cities, a correlation analysis was performed on the eight carbonaceous components and SOC. It can be seen from Fig. 7 that SOC in SJZ was not only significantly correlated with OP, but also had a strong correlation with OC1, OC2, EC1, OC3. However, in TJ, among the eight carbonaceous components, only the correlation between OP and SOC was higher than 0.60, indicating that the formation mechanism of SOC in this city may be more complex. SOC and OP in the three cities all showed strong correlations, and the correlation coefficients were 0.88, 0.79 and 0.97, respectively. Among the three cities, SJZ had the strongest correlation between SOC and OP, which was consistent with the analysis result that SJZ had the highest SOC proportion among the three cities.

The sources of carbonaceous aerosols in three cities were analyzed, which provided the basis for taking targeted measures to prevent and control air pollution. According to the source analysis results, the regulating departments of the three cities should actively take measures to prevent and control gasoline vehicle exhaust emissions. The impact of secondary pollution sources on carbonaceous aerosols in the three cities cannot be ignored, especially in SJZ. Measures to control road dust are also needed for BJ and TJ.

**Fig. 6.** Mass fractions of eight carbonaceous components in BJ, TJ, and SJZ.
Fig. 7. Correlation analysis results of SOC and eight carbonaceous components.

3.4 Influence of atmospheric transportation on carbonaceous aerosol contents

Contents of PM$_{2.5}$ and its chemical composition were usually influenced by both local pollution sources and regional pollutant transport. In this study, backward trajectory analysis was applied to identify the air mass transmission paths during the monitoring period. Trajectories in all three cities were clustered into five groups in terms of the directions, as shown in Fig. 8. OC and EC corresponding to different trajectory clusters showed significant differences. Statistics of the surface meteorological parameters corresponding to each trajectory cluster are listed in Table 3.

In BJ, long-distance trajectories in the north and north-west directions (clusters 2, 3, and 4) were dominant, with fewer trajectories in the east direction (cluster 1) and south direction (cluster 5). Among all of the clusters, high mass concentrations of OC and EC were found in clusters 5, 1, and 3. Cluster 5 only accounted for 4.8% of the total trajectories, started from Henan Province, and passed over Hebei Province before reaching BJ. The mass concentrations of OC (18.89 μg m$^{-3}$) and EC (5.18 μg m$^{-3}$) were the highest among all the clusters, probably attributed to the accumulation of pollutants from northern Henan and southern Hebei. These two areas have very...
dense population and industrial distribution, and the air pollution problem has been serious for a long time (Feng et al. 2016; Meng et al. 2016). Cluster 1 accounted for 14.3% of the total trajectories, and came from the sea. This route of air mass easily transfers pollutants from TJ and Langfang to BJ. The mass concentrations of OC (12.10 μg m\(^{-3}\)) and EC (2.63 μg m\(^{-3}\)) were also higher, only after cluster 5. Cluster 3 accounted for the highest proportion (42.9%) of the total trajectories, and passed through Mongolia, the border between Inner Mongolia and Shanxi, and Hebei before reaching BJ. The mass concentrations of OC (11.68 μg m\(^{-3}\)) and EC (2.27 μg m\(^{-3}\)) were also high. It is worth mentioning that the OC/EC ratio in cluster 3 was the highest (5.97) among all clusters, which may be related to the industrial structure of the surrounding areas along the path. Many coal-fired powers plants are distributed in the central and western regions of Inner Mongolia (Ji et al., 2019), and Shanxi is a large coal-producing province, resulting in high OC emissions. The low OC and EC mass concentrations in clusters 2 and 4 were mainly due to lighter pollution along the route and the favorable meteorological conditions (Table 3).
Fig. 8. Cluster analysis of 48-h backward trajectories, with OC and EC mass concentrations corresponding to different clusters.
Compared with BJ, in TJ, the proportion of trajectories in north and northwest directions (clusters 2 and 3) decreased, and the proportion of trajectories from southward (cluster 5) and sea (clusters 1 and 4) increased. Among all the clusters, the mass concentrations of OC and EC were high in clusters 3, 1, and 5. Cluster 3 accounted for 19.1% of the total trajectories, passing through Mongolia, and the border between Inner Mongolia and Shanxi, Hebei Province, and BJ, and had the highest mass concentrations of OC (26.05 μg m$^{-3}$) and EC (6.71 μg m$^{-3}$). Cluster 5 accounted for 23.8% of the total trajectories, widely covered Henan, Shandong, Shanxi, Hebei Province, and the mass concentrations of OC (21.65 μg m$^{-3}$) and EC (7.01 μg m$^{-3}$) were also relatively high. Areas through which clusters 3 and 5 passed were generally densely populated and industrially developed. A large number of pollutants, including OC and EC discharged from industrial production and coal-fired heating in winter, were transmitted to TJ along with the air mass, which intensified the carbonaceous aerosol pollution in TJ. Cluster 1 accounted for 14.3% of the total trajectories, and came from the sea. Possibly affected by the land and sea breeze, this type of air mass corresponded to a high RH (74.6%) and low WS (1.6 m s$^{-1}$), which made it difficult for the pollutants emitted from local and surrounding areas (Hebei, Shandong Province) to be diffused. It is worth mentioning that the OC/EC ratio (2.76) in cluster 1 was the lowest among all clusters. This was probably associated with ship exhaust emissions from the sea. Air masses of clusters 2 and 4 were cleaner, and the mass concentrations of OC and EC were low.

In SJZ, in contrast to the other two cities, short-distance trajectories (cluster 1) in the northeast direction were dominant. The other trajectories were mainly from the northwest directions. Both
the trajectories numbers of cluster1 and the corresponding OC and EC mass concentrations (55.42 μg m\(^{-3}\) and 12.04 μg m\(^{-3}\) respectively) were the highest among all clusters, indicating that this kind of trajectory had the greatest impact on carbonaceous aerosols. The trajectories of cluster 1 were generally very short in distance and mainly covered parts of southern Hebei. The WS corresponding to cluster 1 was low (1.1 m s\(^{-1}\)) and the RH (53.4%) was high, which were likely to cause the accumulation of pollutants from local and nearby cities (Baoding, Cangzhou city). Clusters 2, 3, and 5 accounted for 42.9% of the total trajectories, and the mass concentrations of OC and EC were also relatively high. Affected by the low-lying terrain in the middle of the Taihang Mountains, a high frequency of quiet breezes was found in SJZ, and pollutants from the surrounding areas such as southern Hebei, Shanxi, Henan, and other places were collected in SJZ by means of airflows in various directions (Zhou et al. 2020). In addition, there are many local industrial and mining enterprises in SJZ and their distribution is scattered, so the pollution can be easily accumulated no matter which direction the air mass comes from.

**Table 3.** Meteorological data corresponding to different clusters in three cities.

<table>
<thead>
<tr>
<th>Clusters</th>
<th>BJ</th>
<th>TJ</th>
<th>SJZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WS (m s(^{-1}))</td>
<td>RH (%)</td>
<td>T (°C)</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>50.5</td>
<td>−0.7</td>
</tr>
<tr>
<td>2</td>
<td>2.8</td>
<td>22.3</td>
<td>−2.2</td>
</tr>
<tr>
<td>3</td>
<td>1.6</td>
<td>34.6</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Backward trajectory analysis showed that the carbonaceous aerosols in the three cities may be affected by pollution transport from the BTH region and surrounding areas, including Inner Mongolia, Shanxi, Shandong, and Henan Province. Therefore, a coordinated plan of controlling air pollution should be established and strengthen in the BTH region and surrounding areas, in addition to the current local pollution control measures.

4 CONCLUSIONS

To better understand the pollution characteristic of carbonaceous aerosols in the BTH region after the implementation of strict source emission control measures, PM$_{2.5}$ samples were collected simultaneously in BJ, TJ, and SJZ during the 2017–2018 heating season, and the mass concentrations of OC and EC in the samples were determined and analyzed. Influenced by industrial structure and meteorological conditions, there were significant differences in the levels of OC and EC among three cities. The highest mass concentrations of OC (46.24 ± 19.57 μg m$^{-3}$) and EC (10.42 ± 3.11 μg m$^{-3}$) were found in SJZ, while the lowest concentrations of OC (10.15 ± 5.13 μg m$^{-3}$) and EC (2.13 ± 1.39 μg m$^{-3}$) were measured in BJ. Compared with previous studies, the OC and EC levels in our study were all lower than those reported in previous studies, which was related to the implementation of a series of air pollution prevention measures in 2017. The OC/EC ratios were in the range of 2.38–10.74 in the three cities. In SJZ, the OC/EC ratio increased significantly as the PM$_{2.5}$ pollution level increased. In contrast, OC/EC ratios in BJ decreased with increased PM$_{2.5}$ pollution levels. Among the three cities,
both the mass concentration of SOC and its proportion in OC in BJ were significantly lower than those in the other two cities.

Analysis of eight carbonaceous components showed that the contributions of gasoline vehicle exhaust to carbonaceous aerosol pollution were all relatively high in the three cities. Compared with SJZ, road dust pollution in BJ and TJ was more serious. Backward trajectory analysis showed that the transport characteristics of carbonaceous aerosols were different among the three cities. For BJ, trajectories from the northwest with long pathways were dominant, however, the OC and EC levels were particularly high when controlled by air masses from Henan Province in the southward direction. For TJ, the proportion of trajectories from southward and the sea increased compared with BJ, and the OC and EC levels were particularly high when controlled by long-distance air masses from the northwest area. In contrast to the other two cities, the short-distance trajectory covering parts of cities in local Hebei had a great impact on carbonaceous aerosols in SJZ.

ACKNOWLEDGEMENTS

This research was supported by the National Key R&D Program of China (No.2018YFC0706004, 2018YFC0706000) and Beijing Natural Science Foundation (8202024). We thank all participants for their tireless work and cooperation.

FUNDING

This research was supported by the National Key R&D Program of China (No.2018YFC0706004, 2018YFC0706000) and Beijing Natural Science Foundation


32


Li, X., Li, S., Xiong, Q., Yang, X., Qi, M., Zhao, W., Wang, X. (2018). Characteristics of PM$_{2.5}$ chemical compositions and their effect on atmospheric visibility in urban Beijing, China during the heating season, Int. J. Env. Res. Pub. He. 15, 1924. https://doi.org/10.3390/ijerph15091924


https://doi.org/10.1016/j.atmosres.2015.12.013


https://doi.org/10.1016/j.atmosenv.2003.11.023


https://doi.org/10.1016/S1352-2310(01)00427-7


https://doi.org/10.1016/j.atmosres.2013.03.010


Tan, L. (2021). The pollution characteristics and influencing factors of secondary components in PM$_{2.5}$ in Jinan City. Shandong Jianzhu University. (in Chinese)


