Annual variations of black carbon over the Yangtze River Delta from 2015 to 2018

Yue Tan¹, Honglei Wang¹,²,³*, Shuangshuang Shi¹, Lijuan Shen¹, Chen Zhang¹, Bin Zhu¹, Song Guo², Zhijun Wu², Ziyi Song¹, Yan Yin¹, Ankang Liu¹

¹Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disasters, Key Laboratory for Aerosol-Cloud-Precipitation of China Meteorological Administration, Nanjing University of Information Science & Technology, Nanjing 210044, China
²State Key Joint Laboratory of Environment Simulation and Pollution Control (Peking University) College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China
³State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

ARTICLE INFO

Article history:
Received 8 November 2019
Revised 13 April 2020
Accepted 13 April 2020
Available online 26 May 2020

Keywords:
Black carbon (BC)
Absorption Ångström exponent (AAE)
Meteorological elements
Temporal characteristics

ABSTRACT

In this study, the black carbon (BC) measurements in the atmosphere of Nanjing, China were continuously conducted from 2015 to 2018 using a Model AE-33 aethalometer. By combining dataset of PM₂.₅, PM₁₀, CO, NO₂, SO₂, O₃ and meteorological parameters, the temporal variations and the source apportionment of BC were given in this study. The results showed that the PM₂.₅ mass concentrations decreased in Nanjing, with an average annual rate of variation of 6.50 μg/(m³·year). Differently, the annual average concentrations of BC increased with an average annual variation rate of 214.71 ng/(m³·year). The seasonal variations showed the pattern of BC mass concentrations in winter > autumn > spring > summer. The diurnal variations of BC mass concentrations showed a double-peak in all four seasons. The first peak occurred at approximately 7:00 in spring, summer and autumn and around 8:00 in winter. The second peak took place after 18:00. The average AAE (absorption Ångström exponent) was 1.26 with a maximum of 1.35 during wintertime and the lowest (1.12) during summertime. In addition, the AAE was smaller in the daytime than that at night, with a minimum occurring between 13:00 and 14:00. BC and visibility show a good power-function relationship at different humidity levels. The average values of the visibility thresholds of the BC mass concentrations in spring, summer, autumn and winter were 1.326, 5.522, 1.340 and 0.708 μg/m³, respectively. The greater the relative humidity, the smaller the visibility threshold for the BC mass concentrations was.

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

Black carbon (BC) is one of the most important absorbers of visible light in the atmosphere. It absorbs solar radiation in the visible band and alters regional and global radiation budgets, leading to regional and global climate change (Bond et al., 2013; Ramanathan and Carmichael, 2008). BC particles are exposed in the atmosphere and mixed with other particles, resulting in their aging and, in turn, affecting their capacity for radiative forcing, visibility impairment and modifying cloud formations (Chen et al., 2017a). BC has a dome effect and plays an important role in the interaction between aerosols and the stratosphere. The heating effect of BC at the top of the stratosphere and the cooling effect on the earth’s surface inhibit the development of the atmospheric boundary layer, leading to pollutants being limited to lower heights and, thus, exacerbating regional pollution (Ding et al., 2016; Wang et al., 2018). In addition, BC causes great harm to human health. BC has a unique structure that is loose and porous, and it can readily adsorb various toxic and harmful substances onto its surfaces. The BC particle size is small, and it is easily absorbed into the respiratory system as a significant component of PM2.5 (Ji et al., 2019b). Geng et al. (2013) concluded that BC is significantly associated with cardiovascular and total mortality but that it is not related to respiratory mortality. Ravindra (2019) found that the average BC concentrations for indoor, outdoor and semi-open kitchens were 14.54, 14.28 and 24.69 μg/m³ in northern India, respectively, and semi-open kitchens were associated with higher cancer risks than indoor and outdoor kitchens.

The sources of BC can be classified into two types: anthropogenic and natural sources. Globally, biomass burning is the largest source of atmospheric BC (Bond et al., 2013). However, in urban areas, the average ratio of the contribution of fossil-fuel combustion and biomass (or wood) burning to BC is estimated to be 2.90 ± 1.47 at 880 nm (Dunkma et al., 2018). In other words, regional BC concentrations in urban areas are closely related to transportation (oil burning). The contributions of different vehicle types to the BC concentrations vary. For example, the BC emission contribution rates from heavy-duty diesel vehicles are approximately 4 times those from light-duty gasoline-powered vehicles (Miranda et al., 2019). The main BC sinks include dry and wet deposition (e.g., rain, snow, hail, sleet) (Begam et al., 2016; Bibi et al., 2017; Wu et al., 2018). BC is deposited directly onto the receptor surfaces by dry deposition and, in most cases, accounts for 15%–40% of total sedimentation. (Textor et al., 2006). Wet deposition (rainfall) is a dominant pathway for BC removal over the oceans and land. (Barrett et al., 2019; Taylor et al., 2014). The long-term trend of BC shows clear seasonal and daily variations, and there are variations with precipitation patterns and BC sources. The observations of carbonaceous aerosols from 2005 to 2016, at Syowa Station, coastal Antarctica revealed that the equivalent BC (EBC) concentrations were highest in September–October and were lowest in February–April, and the absorption Ångström exponent (AAE) ranged from 0.5 to 1.0 in April–October and from 1.0 to 1.5 in December–February (Hara et al., 2019). BC is transmitted between regions. Real-time observations of the BC levels in the Brahmaputra River Valley and the Himalayas have shown that vehicles contributed more than 85% of the ambient BC, and BC transmission and subsidence occurred almost throughout the year, within which the maximum subsidence usually took place before and during the monsoon; additionally, it was found that temperatures, wind speeds and solar radiation had negative correlations with BC concentrations, while relative humidity showed a positive correlation (Barman and Gokhale, 2019).

China is a major global emitter of BC, and its large emissions account for approximately one quarter of global anthropogenic emissions (Bond et al., 2013). The regions with relatively high BC emissions are mainly distributed in Beijing-Tianjin-Hebei (BTH), the Yangtze River Delta (YRD) and the Pearl River Delta (PRD) (Chen et al., 2014; Liu et al., 2019a; Ran et al., 2016; Tan et al., 2016; Yang et al., 2019; Zhang et al., 2009). In view of the specific progress of social development and the variations of regional development models, the main BC sources vary across regions and historical periods. Gao et al. (2018) identified the history of regional BC sources over the past 150 years using the PAH component of peatlands and the Sanjiang Plain and found that BC emissions in the two areas increased due to the rapid development of the environment. This study found that the proportion of BC emissions from coal burning in the most BC-emitting regions increased in recent years and is an environmental problem. The proportion of BC emissions from transportation sources has increased; in addition, transportation has become an important BC source in the Sanjiang Plain since the 1990s. Severe air pollution caused by coal-fired heating in winter in urban areas of northern China will lead to increased BC absorption. Enhancement of BC absorption is primarily related to the photochemical production of city-scale nitrate and sulfate aerosols. As the sulfate levels increase, regional-scale haze plumes strengthen absorption enhancement (Chen et al., 2017b). The BC concentrations in the PRD region were still high in 2017 although a series of air quality control policies have been implemented (Ji et al., 2019b), but an obvious decreasing trend in BC concentrations was found in Beijing from 2013 to 2018, with no obvious change in the ratios of BC to the PM2.5 mass, suggesting that inorganic ions still contributed a lot to PM2.5 (Ji et al., 2019b, 2017, 2016). Zheng et al. (2012) developed a high-resolution regional emissions inventory for BC and organic carbon (OC) for the Pearl River Delta (PRD) region of China and found that the primary OC/BC ratios in underdeveloped cities are higher, while those of the developed areas in the central and southern regions of the PRD are lower. Liu et al. (2019b) studied the relationships between BC and heavy metals and the magnetic properties in the soil near a cement plant and found that the BC concentrations in the PRD region were still high. The Xuzhou Cement Plant were significantly positively correlated with the concentrations of Cd, Co, Cu, Pb and Zn, indicating that these heavy metals are likely to be retained by BC.

The Yangtze River Delta, located on the western coast of the Pacific Ocean and at the east edge of the Asian continent, is one of the fastest growing regions in China and in the world. Rapid urbanization, industrialization and population movement have had very large impacts on the region’s energy, resources and land use types. The emissions of air pollutants, such as motor vehicle exhaust, industrial exhaust gas and atmospheric aerosols continue to increase, which not only degrades the urban air quality but also has a great impact on the atmospheric chemical composition of the region. Besides, a large number of the atmospheric pollutants arriving by long-distance transmission to the Yangtze River Delta can be transmitted farther to the coastal and western Pacific regions, seriously affecting the regional atmospheric environment and regional climate change. In recent years, a large number of researchers have conducted in-depth research on BC in the Yangtze River Delta. Zhuang et al. (2014) found that the annual average BC concentration of Nanjing in 2012 was 4.157 ± 2.626 ng/m³ and showed five seasonal patterns, namely, being high in spring and autumn and low in winter; the diurnal variation of the BC concentrations was also obvious, and it was high in peak traffic hours and low in the afternoon. Lu et al. (2019b) studied the vertical profiles of BC and the planetary boundary layer (PBL) structures from February
14, 2016 to January 4, 2017 and identified four distinct types of BC vertical distributions. Wang et al. (2014) studied the concentrations of BC ($m_{BC}$) under different weather conditions from April 2007 to March 2010 in Shanghai and found a positive correlation between haze intensity and monthly averaged $m_{BC}$. However, long-term continuous observations of BC in the Yangtze River Delta region are still rare. Nanjing is a central city in the Yangtze River Delta and East China, and its atmosphere contains complex pollutants, which mainly consist of carbonaceous aerosols from traffic, industrial and residential sources. In this study, BC levels were continuously observed from January 1, 2015 to December 31, 2018 in Nanjing using a Model AE-33 aethalometer. Combined with the data for PM (PM$_{2.5}$ and PM$_{10}$), pollutant gases (NO$_x$, CO, SO$_x$, and O$_3$) and meteorological elements, the sources and temporal variations, such as annual, monthly and diurnal variations, of BC were examined. Besides, the effects of meteorological conditions on the BC pollution characteristics were also evaluated. Subsequently, the spectral dependence of BC absorption was also discussed, and AAE was calculated to analyse its temporal variations and main influencing factors.

### 1. Data and methods

#### 1.1. Observation site and times

The observation site for the black carbon (BC) mass concentrations is located on top of the meteorological building (32.20°N, 118.71°E) on the campus of Nanjing University of Information Science and Technology, with an altitude of approximately 60 m. To the northeast of the observation site is an industrial zone, which includes petrochemical, steel and chemical energy polluting enterprises. In addition, transportation around the observation site is developed, and there are numerous roads. Approximately 500 meters to the east of the observation site is the Ningliu Highway. The observation period was from January 1, 2015 to December 31, 2018. In a few specific months, there were fewer valid data points due to instrument failures. Therefore, data from the following four months were not considered: February 2015, August 2015, January 2018 and March 2018. The effective days of BC concentration measurements from 2015 to 2018 were 269, 363, 360 and 306, respectively.

1.1.1. Observation instruments and methods

BC was observed with a Model AE-33 aethalometer (Magee Scientific, USA). It uses two-point measurement technology and dynamic zero-point calibration to provide continuous observations at fixed points at seven wavelengths (370, 470, 520, 590, 660, 880, 950 nm). Model AE-33 uses PM$_{2.5}$ cutting heads with a sampling flow of 5 L/min and a time resolution of 1 min. Considering that the absorption characteristics of other light-absorbing aerosols (such as brown carbon and mineral dust) at 880 nm are not obvious, the data measured at 880 nm are taken as the mass concentration values of BC (Drinovec et al., 2015). The absorption coefficient $Abs_\lambda$ (mm$^{-1}$) of carbonaceous aerosols is calculated by Eq. (1):

$$Abs_\lambda = \sigma_{eq} \cdot M_{BC} \cdot 10^{-3}$$

where, $\sigma_{eq}$ (m$^2$/g) is the mass absorption coefficient of the dispersed carbonaceous aerosols and $M_{BC}$ (ng/m$^3$) is the mass concentration of the carbonaceous aerosols.

The relationship between the absorption coefficient $Abs_\lambda$ and the wavelength $\lambda$ for carbonaceous aerosols is expressed as Eq. (2):

$$Abs_\lambda = \lambda^{-AAE}$$

where, AAE represents the aerosol absorption Ångström exponent, which was imported to represent the spectral dependence of $Abs_\lambda$ by a fitted power-law relationship for seven channels and $\lambda$ is the wavelength. The absorption coefficients of 7 wavelengths were used to fit the exponential function curve to obtain the AAE values. AAE is a reliable indicator to evaluate the size and source of particles (Schuster et al., 2016).

Additionally, meteorological factors such as wind speed and direction, visibility and precipitation were provided by the CAWS600 automatic observation station on the campus of Nanjing University of Information Science and Technology (NUIST). The mass concentrations of air pollutants such as PM$_{2.5}$, PM$_{10}$, NO$_2$, SO$_2$, CO and O$_3$ were provided by the national real-time publishing platform for urban air quality (http://106.37.208.233:20035/).

### 2. Results and discussion

#### 2.1. Temporal variations of BC

2.1.1. Annual variation of BC

Fig. 1a shows that the BC concentrations in Nanjing from 2015 to 2018 initially decreased and then increased. The lowest BC mass concentration was only 1.33 μg/m$^3$ in 2016, which is 58.2%, 61.63% and 45.43% of that in 2015, 2017 and 2018, respectively. Fig. 1a shows that the total annual precipitation in 2016 was 2,815.5 mm, which is 1.14–1.94 times that for the other years. Precipitation has an effective removal effect for atmospheric pollutants (Barrett et al., 2019). In addition, according to Fig. 1a, the average wind speed in 2016 was 1.95 ± 0.98 m/sec, which was 1.08–1.11 times that of the other
years. The greater wind speeds are more conducive for the diffusion of atmospheric pollutants, which explains that the BC concentrations in 2016 were the lowest.

Referring to the statistical bulletin of the national economic and social development of Nanjing from 2015 to 2018, we obtained data for car ownership, electricity consumption and freight volumes in Nanjing from 2015 to 2018, as shown in Table 1. According to Table 1, the BC sources continued to increase every year. Therefore, the BC concentrations in 2018 were 1.36 times higher than those in 2017 under similar meteorological conditions such as precipitation and wind speed in 2017 and 2018, as shown in Fig. 1a.

Air Pollution Prevention and Control was published in October, 2013, declaring that the Beijing-Tianjin-Hebei, Yangtze River Delta, and Pearl River Delta regions plan to reduce fine particle concentrations by 25%, 20%, and 15% respectively by 2017, and Regulations of Jiangsu Province on the Prevention and Control of Atmospheric Pollution was also published in February, 2015. As shown in Fig. 1b and Fig. 2, with the implementation of the air quality control measures mentioned above, the mass concentrations of PM$_{2.5}$ in Nanjing have been decreasing yearly, and they were 64.8 μg/m$^3$ in 2016 and were only 41.4 μg/m$^3$ in 2017. Since then, the PM$_{2.5}$ mass concentrations increased slightly to 45.3 μg/m$^3$ in 2018. However, the trend of BC/PM$_{2.5}$ shown in Fig. 1a is similar to that of BC. BC accounted for the lowest proportion of PM$_{2.5}$ in 2016, and was only 2.63%. After that, BC increased gradually and accounted for 7.18% of PM$_{2.5}$ in 2018. BC increased by 35.66% in 2018 compared to 2017, while PM$_{2.5}$ increased by only 9.57%. In other words, although the air quality control measures in Nanjing caused the mass concentrations of PM$_{2.5}$ to decrease yearly, the impact on BC in atmosphere was not significant. This outcome has led to yearly increases in the proportion of BC in PM$_{2.5}$.

### 2.1.2. Monthly variations of BC

The BC mass concentrations revealed seasonal characteristics, mainly caused by seasonal variations of meteorological factors. Fig. 3a shows that the mass concentrations of BC ranged from 0.6573 to 3.927 μg/m$^3$, with the lowest value in May 2016 and the highest value in November 2018. The BC mass concentrations were generally low in spring and summer and were high in autumn and winter; however, in the spring and summer of certain years (such as 2016 and May–August 2017), the BC mass concentrations increased sharply during these periods, due low wind speeds that were not conducive for the diffusion of pollutants. The Yangtze River Delta region is affected by the warm and wet Pacific currents that are brought by the southeast monsoon in June and July of every year (Wang et al., 2017). The precipitation in Nanjing is distributed mostly in June–October (Fig. 3a). As an extreme case,
the total precipitation in June 2015 was 859.70 mm, which is more than twice that in the other months of the year.

The PM$_{2.5}$ mass concentrations were low in spring and summer and high in autumn and winter and reached a minimum in August for all years except 2016. In 2017, the PM$_{2.5}$ mass concentration reached a minimum of 26.05 $\mu$g/m$^2$. In October 2016, the mass concentrations of PM$_{2.5}$ decreased abnormally and were only 79.25% in August of the same year. This outcome may be due to the heavy precipitation and the strong wet PM$_{2.5}$ deposition in October of that year.

The ratio of BC/PM$_{2.5}$ is closely related to both precipitation and wind speed and showed clear peaks in spring and summer. For example, from May to August 2017, there were low wind speeds and heavy precipitation (Fig. 3a). The low wind speeds led to a decrease in BC diffusion, and increased the BC concentrations in the region. Heavy precipitation caused large particles in PM$_{2.5}$ to settle to the ground and a decrease in large particles in the atmosphere, causing the BC/PM$_{2.5}$ ratio to increase and present obvious peaks. Precipitation removes pollutants, and wind speed diffuses and dilutes pollutants; however, their effects on BC and PM$_{2.5}$ are different. Considering precipitation intensities and wind speeds, it can be seen that the ratio of BC/PM$_{2.5}$ was larger and once reached approximately 10%, for those cases with both heavy precipitation and high wind speeds, such as May–August 2018 (the wind speeds were between 2 and 2.5 m/sec and the precipitation reached 300 mm). When the precipitation was strong but the wind speeds were low, as in May–August 2017 (the wind speeds were less than 2 m/sec, the maximum precipitation reached 500 mm), the ratio of BC/PM$_{2.5}$ was also high, with a maximum of approximately 9%. For the case of little precipitation and high wind speeds, as in March–April 2018 (the wind speeds were approximately 2.5 m/sec, the precipitation was only approximately 60 mm), the ratio of BC/PM$_{2.5}$ was small and approximately 3%. When the precipitation was little and the wind speeds were low, such as for December 2015 (the wind speed was approximately 1.6 m/sec, and the precipitation did not exceed 20 mm), the BC/PM$_{2.5}$ ratio was also low and with the ratio of only 2.3%. Therefore, the BC/PM$_{2.5}$ ratio was larger when the precipitation was heavy, and the BC/PM$_{2.5}$
Fig. 4 – Diurnal variation of (a) BC mass concentration, (b) BC/PM$_{2.5}$, (c) relative humidity (RH) and (d) wind speed in different seasons.

Fig. 5 – Diurnal variation of mass concentrations of (a) PM$_{2.5}$, (b) PM$_{10}$, (c) NO$_2$, (d) SO$_2$, (e) CO and (f) O$_3$. 
ratio was smaller when the precipitation was little, but the BC/PM$_{2.5}$ ratio exhibited little correlation with wind speeds. In other words, the influence of precipitation on the BC/PM$_{2.5}$ ratio was much greater than that of wind speed.

The BC/PM$_{2.5}$ ratio can be also used to analyze the sources of BC. The ratio of BC/PM$_{2.5}$ from mobile sources (5.9%–74.0%) is usually higher than that from industrial sources (0.46%–3.0%) and the BC/PM$_{2.5}$ ratio from oil combustion is 3%–13.6% (Zheng et al., 2019). As seen from Fig. 3b, the BC/PM$_{2.5}$ ratio ranged from 1.41%–10.05%. In January, March, December 2015 and January–May, August–September 2016, the ratio of BC/PM$_{2.5}$ (1.41%–3%) was in the range of industrial sources (0.46%–3.0%) while the ratio of BC/PM$_{2.5}$ in the remaining 34 months was 3%–10.05%, which is in the range of oil combustion (3%–13.6%). Generally, oil combustion is the main BC source in most months in Nanjing.

2.1.3. Diurnal variation of BC

The diurnal variation of BC concentrations is closely related to meteorological factors, as well as the diurnal variations of other pollutants in the atmosphere and the patterns of human production and living activities. Fig. 4a shows that the diurnal variations of the BC mass concentrations show a double peak in all four seasons. The trend of BC mass concentrations is similar in spring, summer and autumn. The first peak occurs at approximately 7:00 and gradually reaches the second peak after 18:00; while the first peak in winter is delayed by one hour and occurs at approximately 8:00. The first peak is highest in winter at 3.1 $\mu$g/m$^3$, which is 1.33 times higher than in the lowest season. The second peak is also highest in winter and is 2.681 $\mu$g/m$^3$, which is also 1.33 times than in the lowest season.

 Meteorological factors have an important influence on the diurnal variations of the BC mass concentrations. From the diurnal variations of relative humidity (Fig. 4c), it can be seen that the relative humidity at night is higher than in the daytime. From Fig. 4d, we can see that the wind speeds peak in the afternoon. Under the relatively stable weather conditions at night, the wind speed in Nanjing maintains a relatively fixed value of 1.5 m/sec. However, after sunrise at 7:00 (spring, summer and autumn) or 8:00 (winter), the circulation from the urban heat island becomes stronger due to enhancement by radiation, and the wind speed increases gradually and finally reaches its maximum of approximately 2.5 m/sec at 13:00–15:00 during the period of strongest radiation during the day. Strong winds are conducive for the diffusion of pollutants, resulting in minimum BC concentrations at 13:00–15:00. It is worth noting that the BC concentrations did not decrease after the end of the rush hour, which may be due to the special climatic conditions in Nanjing. Nanjing area has a high frequency of temperature inversion at night and it usually forms after dusk (Lu et al., 2019), which also causes the second peak in BC diurnal variation in the Nanjing area to be not remarkable.

In addition to the meteorological factors, the BC mass concentrations are also affected by pollution sources. Fig. 5c, e show that the diurnal variations of NO$_2$ and CO exhibit a bimodal structure. The NO$_2$ concentrations reach two peaks at 8:00–9:00 and at 20:00–21:00. The CO concentrations reached peaks at 8:00 and 20:00 in spring, summer and autumn, and the first peak is delayed by two hours in winter, taking place at 10:00. As analysed above, the two peaks in the BC diurnal variations occur at the same times as the two peaks for NO$_2$ and CO, and the delay for the first peak in winter is also the same, indicating that BC is closely related to NO$_2$ and CO. Considering the pollution sources, NO$_2$ and CO are both products of incomplete combustion. The main source of NO$_2$ emissions in cities is vehicle exhaust and CO mainly comes from
coal and car exhaust, while BC is the product of incomplete combustion of fossil fuels, biofuels and biomass (Bond et al., 2013). Combined with the law of life of the citizens, we draw the conclusion that exhaust emissions in the morning and evening rush hours are also one of the main reasons for the bimodal occurrence of diurnal variations in the BC mass concentration.

2.2. Spectral dependence of aerosol absorption: absorption Ångström exponent (AAE)

From the relationship between absorption coefficients and wavelengths in the four seasons shown in Fig. 6, the AAE in Nanjing is greatest in winter and reaches 1.35, and it is lowest in summer and drops to 1.12. The chemical composition of BC directly determines the size of the AAE and the chemical composition of BC is directly related to its sources. Studies have shown that AAEs close to 1 indicate that carbonaceous aerosols are mainly produced by exhaust emissions (liquid fuels), while AAEs close to 2 are mainly attributed to coal combustion and biomass combustion (solid fuels) (Jing et al., 2019). From the diurnal (Fig. 7a), monthly (Fig. 7b) and seasonal variations of the AAE (Fig. 6), although the monthly averages of the AAEs in some specific months are greater than 1.5, the seasonal and time averaged AAEs are all less than 1.4, which is closer to 1 than to 2. Therefore, we conclude that the carbonaceous aerosols in Nanjing are probably mainly derived from vehicle exhaust generated by liquid fuels such as petroleum. Besides, the mass concentrations of SO$_2$ in winter, as is shown in Fig. 5d, are higher than those in the other three seasons. SO$_2$ mainly comes from coal combustion (solid fuel), which also explains why the AAEs are generally higher in winter (Fig. 7b).

Moreover, Fig. 6 shows that the absorption coefficients of the atmospheric aerosols in autumn and winter are larger than in spring and summer. The contribution of non-BC to atmospheric light absorption is greater, but the absorption by BC still plays a dominant role. This outcome is different from the situation that the contribution rate of non-BC in winter is higher than that of BC in northern China, which may result from coal-fired heating leading to a significant increase in non-BC in winter in the North (Ran et al., 2016).

The monthly AAE variations, demonstrated in Fig. 6a, show that the average AAE is 1.26 and ranges from 0.63 to 1.56. Among these, the lowest value was in October 2017, and the highest was in October 2015. The average AAE is greater than 1 for almost every month, except in June 2016 and July–October.
2017. For the diurnal AAE variations, Fig. 7b shows that the AAEs in the daytime are lower than those at night and reach their minimum values between 13:00 and 14:00. This outcome may result from the strong convective mixing during daytime by causing aging aerosols in the upper layer to cause the newly formed BC aerosols to be more easily covered by carbonaceous aerosols, thus accelerating the aging and increases in particle size. Thus, the AAEs decreased. For the seasonal differences in the diurnal variations, the AAEs follow a pattern of winter > spring > autumn > summer, indicating that the particle sizes of carbon aerosols in summer are the largest, followed by spring and autumn, and the smallest sizes occur in winter.

2.3. Effects of meteorological elements on BC mass concentrations and AAEs

2.3.1. The effect of wind speed and wind direction on BC. Low wind speeds are not conducive for the diffusion of pollutants. Clean cases of BC are defined as BC concentrations less than 3.5 μg/m³ which are one-tenth of the national standard for PM2.5, indicating good air quality (Ran et al., 2016). Fig. 8 shows that the BC-polluted area (BC > 3.5 μg/m³) in Nanjing is mostly concentrated in the wind speed circle of less than 4 m/sec, while the BC seriously-polluted area (BC > 8 μg/m³) only appears in the wind speed circle of less than 2 m/sec.

The wind dependence of BC is different for different seasons. During the observation period, serious BC pollution events occurred in spring and autumn (BC > 8 μg/m³). Specifically, serious BC pollution events appeared in spring with southeast winds less than 1 m/sec and BC mass concentrations greater than 8.25 μg/m³ and appeared in autumn with southwest winds less than 1 m/sec and BC mass concentrations greater than 8.95 μg/m³. It is worth noting that the high BC concentrations in autumn even reached 10.97 μg/m³. Because convective motion was inhibited in autumn and BC does not easily diffuse, the area of high BC values in autumn was more prominent than in the other three seasons. In addition, there was no serious BC pollution in summer and winter, but the average mass concentrations of BC in summer and winter (1.82 μg/m³, 1.86 μg/m³, respectively) were higher than those in spring and autumn (1.55 μg/m³, 1.42 μg/m³, respectively) in the wind speed circle of 1–4 m/sec. In the view of the probability of pollution occurrences, BC pollution (BC > 3.5 μg/m³) occurred more frequently in summer and winter.
2.3.2. Relation between AAEs and wind
Fig. 9 shows that the AAEs for the four seasons are positively correlated with wind speed, and in the low wind speed circle (usually less than 2 m/sec), the AAEs are extremely small; in addition, some are even less than 1. The relationship between AAEs and wind speed is mainly related to the aging speeds of carbonaceous aerosols. Particles readily diffuse at high wind speeds, which are not conducive for the process of collision growth. The aging speed of particles decreases, and the particle size is smaller, leading to increasing AAEs.

Additionally, there was a large area of high AAEs in summer and autumn, and the highest values were more than 2.5, which is mainly distributed in the wind speed circle of 2–4 m/sec with northeast winds. In contrast, the AAEs in spring and winter reached high values only in a few small areas, and most of these values were less than 2. Aside from the large areas of high AAEs, there were large areas with low AAEs in summer. The overall average AAE was only 1.11 in summer, while in spring, autumn and winter, it was 1.30, 1.36 and 1.31, respectively. Therefore, the AAEs in summer were significantly lower than those in the other three seasons because the high-speed winds in summer were not conducive for particle aging and resulted in smaller particle sizes for the carbonaceous aerosols.

2.3.3. The relationship between BC and visibility under different relative humidity (RH)

The fitting of BC and visibility at different RH levels shows that BC and visibility are in good agreement with the power function relationship (Fig. 10, Table 2). Fig. 10 shows that the points corresponding to RH greater than 90% in spring, autumn and winter were mainly distributed in a visibility range of less than 5 km in the lower left corner, while the red dotted dense area in summer was larger and could be extended to the visibility range of less than 10 km. Table 2 shows that the $\beta$ values of the fitting function were negatively correlated with RH, but no rigorous regularity for $\beta$ was found.

Fig. 10 shows that when the BC concentrations were below a certain threshold, the atmospheric visibility decreased sharply with increasing BC concentrations, and the rate of decrease slowed down gradually. When the BC concentrations were quite large, the visibility tended to be flat. Ten kilometers is the threshold to distinguish between hazy days and non-hazy days, so 10 km was used to determine the visibility threshold of the BC mass concentrations. $\text{Vis} = 10 \text{ km}$ was substituted into the fitting equation to calculate the mass concentration threshold of BC under different RH. According to the threshold values of the BC mass concentrations in different seasons, shown in Table 2, the mean values of the BC mass
concentrations in spring, summer, autumn and winter were 1.326, 5.522, 1.340 and 0.708 μg/m³, respectively. These were highest in summer and lowest in winter, indicating that the visibility in winter would be smaller for the same conditions of RH and BC.

In addition, higher RH values mean smaller visibility thresholds of the BC mass concentrations. For higher RH conditions, the visibility was reduced to less than 10 km even with very little BC, such as the conditions in spring with RH > 50, summer with RH > 70, autumn with RH > 70 and winter with RH > 50. For those four situations, even if the BC concentrations were less than 1 μg/m³, the visibility was lower than 10 km. As an extreme case, when the spring RH > 90, the visibility threshold of the BC concentrations was reduced to nearly zero.

This analysis provides theoretical guidance for solving the problem of improving visibility in the decision-making process for atmospheric environmental control: At a certain RH, reducing the BC mass concentrations can significantly improve visibility when the BC mass concentration is lower than the corresponding threshold, which can be viewed as the BC-sensitive area for visibility; when the mass concentration of BC is above the threshold, reducing the mass concentration of BC has little effect on improving visibility. Therefore, efforts should be made to reduce other components, which affect atmospheric visibility.

3. Conclusions

In this study, the black carbon (BC) measurements in the atmosphere of Nanjing, China were continuously conducted from 2015 to 2018 using a Model AE-33 aethalometer (Magee Scientific, USA). By combining dataset of PM$_{2.5}$, PM$_{10}$, CO, NO$_x$, SO$_2$, O$_3$ and meteorological parameters, the temporal variations and the source apportionment of BC were given in this study.

The results showed that the mass concentrations of PM$_{2.5}$ in Nanjing were 64.83 ± 21.62, 52.12 ± 19.45, 41.36 ± 18.06 and 45.32 ± 17.33 μg/m³ from 2015 to 2018, respectively, with annual variation rates of 12.71%, -10.76%, and 3.96 μg/(m³·year), respectively. Previous measurements for air quality control mainly focus on PM$_{2.5}$, but BC, as part of PM$_{2.5}$, is rarely studied separately. The annual average concentrations of BC were measured in this study from 2015 to 2018 as 2,290.4 ± 466.6, 1,333.1 ± 650.7, 2,163.1 ± 459.9 and 2,934.5 ± 604.7 ng/m³, respectively, and the annual variation rates were -957.29, 829.96 and 771.45 ng/(m³·year), respectively. The seasonal variations showed the pattern of BC mass concentrations in winter > autumn > spring > summer. The highest concentration (3,927.24 ng/m³) was found in November 2018 and the lowest concentration (657.33 ng/m³) occurred in May 2016.

![Fig. 10 – The relationship between BC and visibility in different seasons and at different levels of RH in (a) Spring, (b) Summer, (c) Autumn and (d) Winter.](image-url)
The diurnal variations of the BC mass concentrations showed a double-peak in all four seasons. The first peak occurred at approximately 7:00 in spring, summer and autumn and occurred around 8:00 in winter. The second peak took place after 18:00. The influence of precipitation on the BC/PM$_{2.5}$ ratio was much greater than that of wind speed. The BC/PM$_{2.5}$ ratio was larger when precipitation was heavy, while the BC/PM$_{2.5}$ ratio showed little correlation with wind speed.

The AAE is closely related to emission sources. Oil combustion is the main source of BC for most months in Nanjing. The average AAE value was 1.26 with a maximum of 1.35 during wintertime and the lowest (1.12) during summertime. Besides, the AAEs were lower in the daytime than at night, with minimum values occurring between 13:00 and 14:00. The influence of the winds in different seasons on the regional concentrations of BC and AAE varied greatly. Low wind speeds (less than 2 m/sec) are not conducive for the diffusion of BC, and the AAEs are positively correlated with wind speeds. The BC and visibility demonstrate a good power-function relationship at different humidity levels. The average values of the visibility threshold of the BC mass concentrations in spring, summer, autumn and winter were 1.326, 5.522, 1.340 and 0.708 μg/m$^3$, respectively. Higher relative humidity means smaller visibility thresholds for the BC mass concentrations.

**Declaration of Competing Interest**

We declare that we have no financial and personal relationships with other people or organizations that can inappropriate influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled "Annual variations of black carbon over the Yangtze River Delta from 2015 to 2018".

**Acknowledgments**

This study was supported by the National Natural Science Foundation of China (Nos. 91664224 and 41805096), the special fund of State Key Joint Laboratory of Environment Simulation and Pollution Control (No. 19K03ESPCC), the Natural Science Foundation of Jiangsu Province (No. BK20180801) and the Natural Science Research Project for Universities of Jiangsu Province, China (No. 18KJB170011).

**REFERENCES**


