Impact of air pollution control measures and regional transport on carbonaceous aerosols in fine particulate matter in urban Beijing, China: Insights gained from long-term measurement

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Abstract As major chemical components of airborne fine particulate matter (PM$_{2.5}$), organic carbon (OC) and elemental carbon (EC) have vital impacts on air quality, climate change, and human health. Because OC and EC are closely associated with fuel combustion, it is helpful for the scientific community and policymakers assessing the efficacy of air pollution control measures to study on the impact of the control measures and regional transport on the OC and EC levels. In this study, hourly mass concentrations of OC and EC associated with PM$_{2.5}$ were semi-continuously measured from March 2013 to February 2018. The results showed that annual mean OC and EC concentrations declined from 14.0 to 7.7 μg/m$^3$ and from 4.0 to 2.6 μg/m$^3$, respectively, from March 2013 to February 2018. In combination with the data of OC and EC in previous studies, an obvious decreasing trend in OC and EC concentrations was found, which was caused by clean energy policies and effective air pollution control measures. However, no obvious change in the ratios of OC and EC to the PM$_{2.5}$ mass (on average, 0.164 and 0.049, respectively) was recorded, suggesting that inorganic ions still contributed a lot to PM$_{2.5}$. Based on the seasonal variations of OC and EC, it appeared that higher OC and EC concentrations were still observed in the winter months, with the exception of winter of 2017-2018. Traffic policies executed in Beijing resulted in nighttime peaks of OC and EC, caused by heavy-duty vehicles and heavy-duty diesel vehicles being permitted to operate from 0:00 to 6:00. In addition, the fact that there was no traffic restriction in weekends led to higher concentrations in weekends compared to weekdays. Significant correlations between OC and EC were observed throughout the study period, suggesting that OC and EC originated from common emission sources, such as exhaust of vehicles and fuel combustion. OC and EC levels increased with enhanced SO$_2$, CO and NO$_x$ concentrations while the O$_3$ and OC levels enhanced simultaneously when O$_3$ concentrations were higher than 50 μg/m$^3$. Nonparametric wind regression analysis was performed to examine the sources of OC and EC in the Beijing area. It was found that there were distinct hot spots in the northeast wind sector at wind speeds of approximately 5 km/h, as well as diffuse signals in the southwestern wind sectors, highlighting probable trans-boundary transport from highly industrialized regions upwind of the Hebei province, such as Baoding, Shijiazhuang and Handan, which were the most polluted cities in China. This was consistent with their higher potential as source areas, as determined by the potential source contribution function (PSCF) analysis. A high-potential source area was precisely pinpointed, which was located in the
northwestern and southern areas of Beijing in 2017 instead of solely in the southern areas of Beijing in 2013. This work shows that improvement of the air quality in Beijing benefits from strict control measures; however, joint prevention and control of regional air pollution in the regions is needed for further improving the air quality. The results provide a reference for controlling air pollution caused by rapid economic development in developing countries.

Key words air pollution control measures, regional transport, organic carbon, elemental carbon, Beijing
1 Introduction

Worldwide attention on atmospheric organic carbon (OC) and elemental carbon (EC) has been paid by the public and the scientific community because OC and EC have vital effects on air quality, atmospheric visibility, climate, and human health (Bond et al., 2013; Boucher et al., 2013; World Health Organization (WHO), 2012). OC is composed of thousands of organic compounds and occupies 10-50% of the ambient PM$_{2.5}$ mass (Seinfeld and Pandis, 1998) while EC, which is emitted from fuel combustion, represents 1-13% of the ambient PM$_{2.5}$ mass (Shah et al., 1986; Tao et al., 2017; Malm et al., 1994). Considering that OC and EC occupy high fractions of the PM$_{2.5}$, a decline in OC and EC concentrations will improve air quality. Due to the light scattering potential of OC and the light absorption ability of EC, high concentrations of OC and EC can impair the atmospheric visibility. In addition, OC and EC can affect the atmospheric energy balance through scattering and absorbing incoming and outgoing solar and terrestrial radiation (direct effect) and through modifying the microphysical properties of clouds, like influencing cloud condensation nuclei and/or ice nuclei (indirect effects). Direct and indirect effects of OC and EC remain one of the principal uncertainties in estimates of anthropogenic radiative forcing (Boucher et al., 2013). In particular, black carbon (BC also called EC) coated with secondary particles can enhance aerosol radiative forcing (Wang et al., 2013; Zhang et al., 2008). BC is found to aggravate haze pollution in megacities (Ding et al., 2016; Zhang et al., 2018). Most of all, OC and EC adversely affect human health. As important constituents of OC, polycyclic aromatic hydrocarbons (PAHs) are well known as carcinogens, mutagens, and teratogens and therefore pose a serious threat to the health and the well-being of humans (Boström et al., 2002). Short-term epidemiological studies provide sufficient evidence of all-cause and cardiovascular mortality and cardiopulmonary hospital admissions associated with daily variations in BC concentrations; besides, cohort studies proved that all-cause and cardiopulmonary mortality are linked with long-term average BC exposure (WHO, 2012). Thus, long-term continuous observations of OC and EC are a prerequisite to further study air quality, atmospheric visibility, climate effects, and human health. However, long-term continuous observations of OC and EC in China are scarce.

In the world, China is considered as one of the regions of high emissions of OC and EC due to high energy consumption and increasing vehicle population, accompanying rapid economic growth.
development and urbanization for decades (http://www.stats.gov.cn/tjsj/ndsj/2017/indexch.htm). As the capital of China, Beijing with a residential population of 21.7 million, domestic tourists of $2.9 \times 10^3$ million and foreign tourists of approximately 3.3 million in 2017 (http://tjj.beijing.gov.cn/English/AD/) faces severe air pollution problems, which have attracted worldwide attention. A series of studies on OC and EC have already been performed in Beijing. Lang et al. (2017) indicated that OC showed a downward trend and EC had almost no change before 2003, both increased from 2003 to 2007, but decreased after 2007. The decline in OC concentrations was associated with coal combustion and motor vehicle emission control measures, while that in EC was caused by the replacement of fossil fuel and control of biomass emissions. Tao et al. (2017) stated that the nearly 30% reduction in total carbon (TC) in recent years in Beijing can be taken as a real trend. Lv et al. (2016) found that the concentrations of OC and EC remained unchanged from 2000 to 2010 in Beijing. Yang et al. (2011a) conducted a long-term study of carbonaceous aerosol from 2005 to 2008 in urban Beijing and found a decline in the ratio of carbonaceous species to the PM$_{2.5}$ mass in contrast to what was observed 10 years earlier, which indicated that the importance of carbonaceous species in PM$_{2.5}$ had decreased. In addition, pronounced seasonal variations were recorded with the highest concentrations occurring in winter and the lowest ones in summer. Overall, these previous researches seem somewhat inconsistent with each other and they seldom focused on studying the impact of air pollution control measures and regional transport on the carbonaceous aerosol levels in detail.

Notably, a series of the strictest measures on emission abatement and pollution control were implemented in China from September 2013 (Jin et al., 2016). Substantial manpower and material resources have been put into improving the air quality in the past five years and significant measures are being taken for the atmospheric environment and ecosystem (Gao et al., 2017). To evaluate the effectiveness of air pollution control measures, it is necessary to conduct a long-term continuous observation of OC and EC and to study their long-term variation. Most of the previous studies showed average information for certain periods based on filter sampling and laboratory analysis and did not reflect the dynamic evolution processes of OC and EC with hourly resolution, which can provide important and detailed information for the potential health risk in the area with frequent occurrence of air pollution episodes. In addition, long-term measurements in urban areas of China
with high population density were scarce (Yang et al., 2005, 2011a; Zhang et al., 2011; Li et al., 2015; Chang et al., 2017) and the knowledge on long-term continuous hourly observations is still lacking, which is yet important for recognizing the influence of source emissions on air quality. Based on the above-mentioned background, it is necessary to perform a long-term continuous hourly observation to explore the characteristics of OC and EC, to examine the relationship between OC and EC and with major air pollutants and their sources so as to better assess the influence of emission control measures on the OC and EC levels. In this study, inter-annual, seasonal, weekly and diurnal variation of OC and EC were investigated. The influence of local and regional anthropogenic sources was evaluated using non-parametric wind regression (NWR) and potential contribution source function (PSCF) methods. This study will be helpful for improving the understanding of the variation and sources of OC and EC associated with PM$_{2.5}$ and assessing the effectiveness of local and national PM control measures and it provides a valuable dataset for atmospheric modelling study and assessing the health risk. It also is the first time that a continuous hourly measurement for a 5-year period based on the thermal-optical method is reported for urban Beijing.

2 Experimental

2.1 Description of the site

The study site (39°58′28″ N, 116°22′16″ E, 44 m above ground) was set up in the second floor in the campus of the State key laboratory of atmospheric boundary physics and atmospheric chemistry of the Institute of atmospheric Physics, Chinese Academy of Science (Fig. 1). The site is approximately 1 km south from the 3rd Ring Road (main road), 1.2 km north from the 4th Ring Road (main road), 200 m west of the G6 Highway (which runs north-south) and 50 m south of the Beitucheng West Road (which runs east-west), respectively. The annual average vehicular speeds in the morning and evening traffic peaks were approximately 27.8 and 24.6 km/h, respectively, in the past five years. During the whole study period the level of traffic congestion is mild based on the traffic performance index published by the Beijing Traffic Management Bureau (http://www.bjtrc.org.cn/), which indicated 1.5-1.8 times more time will be taken to publicly travel during traffic peaks than during smooth traffic. The study site is surrounded by residential zones, a street park and a building of ancient relics without industrial sources. The experimental campaign

2.2 Instrumentation

Concentrations of PM$_{2.5}$-associated OC and EC were hourly measured with semi-continuous thermal-optical transmittance method OC/EC analyzers (Model 4, Sunset Laboratory Inc. Oregon, United States of America (USA)). The operation and maintenance are strictly executed according to standard operating procedures (SOP, https://www3.epa.gov/ttnamt1/spesunset.html). Volatile organic gases are removed by an inline parallel carbon denuder installed upstream of the analyzer. A round 16-mm quartz filter is used to collect PM$_{2.5}$ with a sampling flow rate of 8 L/m. A modified NIOSH thermal protocol (RT-Quartz) is used to measure OC and EC. The sampling period is 30 min and the analysis process lasts for 15 min. Calibration is performed according to the SOP. An internal standard CH$_4$ mixture (5.0%; ultra-high purity He) is automatically injected to calibrate the analyzer at the end of every analysis. In addition, off-line calibration was conducted with an external amount of sucrose standard (1.06 μg) every three months. The quartz fiber filters used for sample collection were replaced by new ones before the laser correction factor dropped below 0.90. After replacement, a blank measurement of the quartz fiber filters is carried out. The uncertainty of the TC measurement has been estimated to be approximately $\pm 20\%$ (Peltier et al., 2007). A US Environmental Protection Agency Federal Equivalent Method analyzer of PM$_{2.5}$ (SHARP 5030, Thermo-Fisher Scientific, Massachusetts, USA) was used to monitor PM$_{2.5}$ and $\pm 5\%$ for 24 h is the accuracy of the measurements. The operation, maintenance and calibration are strictly executed according to the instruction manual of the Model SHARP 5030 PM$_{2.5}$ analyzer (Ji et al., 2016). The data were processed using an Igor-based software (Wu et al., 2018) and the commercial software of Origin.

2.3 NWR and PSCF methods

2.3.1 NWR method

NWR is a source-to-receptor source identification model, which provides a meaningful
allocation of local sources (Henry et al., 2009; Petit et al., 2017). Wind analysis results using NWR were obtained using a new Igor-based tool, named ZeFir, which can perform a comprehensive investigation of the geographical origins of the air pollutants (Petit et al., 2017). The principle of NWR is to smooth the data over a fine grid so that concentrations of air pollutants of interest can be estimated by any couple of wind direction ($\theta$) and wind speed ($u$). The smoothing is based on a weighing average where the weighing coefficients are determined using a weighting function $K(\theta, u, \sigma, h) = K_1(\theta, \sigma) \times K_2(u, h)$ (i.e., Kernel functions). The estimated value ($E$) given $\theta$ and $u$ is calculated by the following equations (1)-(3):

$$E(\theta|u) = \frac{\sum_{i=1}^{N} Ci \times K_1(\frac{\theta-\Theta}{\sigma}) \times K_2(\frac{u-U}{h}) \times Yi}{\sum_{i=1}^{N} K_1(\frac{\theta-\Theta}{\sigma}) \times K_2(\frac{u-U}{h})}$$  \hspace{1cm} (1)

$$K_1(x) = \frac{1}{\sqrt{\pi} \sigma} e^{-0.5x^2} \quad -\infty < x < \infty$$  \hspace{1cm} (2)

$$K_2(x) = 0.75(1-x^2) \quad -1 < x < 1$$  \hspace{1cm} (3)

where $\sigma$ and $h$ were smoothing parameters, which can be suggested by clicking on the button of suggest estimate in the software of Zefir; $Ci$, $Wi$, and $Yi$ are the observed concentration of a pollutant of interest, resultant wind speed and direction, respectively, for the $i$th observation in a time period starting at time $t_i$; $N$ is the total number of observations.

After the calculation, graphs of the estimated concentration and the joint probability are generated. The NWR graph of the air pollutant of interest, acquired directly via the NWR calculation, represents an integrated picture of the relationship of estimated concentration of the specific pollutant, wind direction and wind speed. The graph of the joint probability for the wind data, equivalent to a wind rose, shows the occurrence probability distribution of the wind speed and wind direction.

2.3.2 PSCF method

The PSCF method is based on the residence time probability analysis of air pollutants of interest (Ashbaugh et al., 1985). Source locations and preferred transport pathways can be identified (Poirot and Wishinski, 1986; Polissar et al., 2001; Lupu and Maenhaut, 2002). The potential locations of the emission sources are determined using backward trajectories. A detailed description can be found in Wang et al. (2009). In principle, the PSCF is expressed using equation (4):

$$PSCF(i, j) = w_{ij} \times \frac{m_i}{n_j}$$  \hspace{1cm} (4)
where $w_{ij}$ is an empirical weight function proposed to reduce the uncertainty of $n_{ij}$ during the study period, $m_{ij}$ is the total number of endpoints in $(i, j)$ with concentration value at the receptor site exceeding a specified threshold value and $n_{ij}$ is the number of back-trajectory segment endpoints that fall into the grid cell $(i, j)$ over the period of study. In this study, the domain for the PSCF was set in the range of (30-70 °N, 65-150 °E) with the grid cell size of 0.25 × 0.25°.

3 Results and discussion

3.1 Levels of OC and EC

Statistics for the OC and EC concentrations from March 1, 2013 to February 28, 2018 are summarized in Table 1. Benefiting from the Air Pollution Prevention and Control Action Plan, a decline in annual average concentrations is on the whole recorded. In detail, the annual average concentrations of OC peaked in 2014 and then declined from 14.5 to 7.7 μg/m$^3$, whereas those of EC also peaked in 2014 and then declined from 4.3 to 2.6 μg/m$^3$ during the study period. The decline in OC and EC concentrations is closely associated with decreasing coal consumption, increasing usage of natural gases and the implementation of a strict vehicular emission standard (Table 2).

Knowledge of the relative contribution of OC and EC to PM$_{2.5}$ is important in formulating effective control measures for ambient PM (Wang et al., 2016a). The ratios of OC and EC to PM$_{2.5}$ varied little during the whole study period. The ratios of OC to PM$_{2.5}$ ranged from 15.5 to 17.8 % with the average of 16.4 %, while those of EC to PM$_{2.5}$ ranged from 4.5 to 5.2 % with the average of 4.9 %.

OC accounted, on average, for 77.0 ± 9.3 % of the total carbon (TC, the sum of OC and EC), while EC amounted for 23.0 ± 9.3 % of the TC. These results are consistent with those in previous studies (Wang et al., 2016a; Tao et al., 2017, Lang et al., 2017). The contribution of TC to PM$_{2.5}$, 21.3 ± 15.8 %, is also similar to those reported in previous studies, listed in Table S1, for example, at urban sites of Hongkong, China (23.5-23.6 % in 2013), Hasselt (23 %) and Mechelen (24 %) in northern Belgium, rural sites in Europe (19-20 %) and some sites in India (on average, 20 %, Bisht et al., 2015; Ram and Sarin, 2010; Ram and Sarin, 2012), but lower than those observed historically at multiple sites in China (on average 27 %, Wang et al., 2016a), with Beijing (27.6 %, from March 2005 to Feb 2006), Chongqing (28.3 %, from March 2005 to February 2006), Shanghai (34.5 %, from March 1999 to May 2000) and Guangzhou (26.4 %, December 2008 to February 2009), in Budapest (40 %), Istanbul (30 %), and many sites in the USA, like Fresno (43.2 %), Los Angeles
(36.9 %) and Philadelphia (33.3 %) (Na et al., 2004). Compared to previous studies, the ratio of TC to PM$_{2.5}$ became smaller, indicating a smaller contribution of carbonaceous aerosols to PM$_{2.5}$. A higher ratio of TC to PM$_{2.5}$ suggests that there is a lower contribution from secondary inorganic ions to PM$_{2.5}$. The carbonaceous aerosol (the sum of multiplying the measured OC by a factor of 1.4 and EC) represented on average, 27.7 ± 16.7 % of the observed PM$_{2.5}$ concentration, making it a dominant contributor to PM$_{2.5}$.

Table 2 lists recently published results for OC and EC mass concentrations in major megacities. Although the observation periods were not same, a comparative analysis of OC and EC concentrations between different megacities could show the status of energy consumption for policymakers, drawing lessons and experience from other countries. It is obvious that the PM$_{2.5}$-associated OC and EC levels in the megacities in the developing countries were far higher than those in the developed countries. The PM$_{2.5}$-associated OC and EC concentrations in Beijing were higher than those in Athens, Greece (2.1 and 0.54 μg/m$^3$), Los Angeles (2.88 and 0.56 μg/m$^3$) and New York (2.88 and 0.63 μg/m$^3$), USA, Paris, France (3.0 and 1.4 μg/m$^3$), Seoul, South Korea (4.1 and 1.6 μg/m$^3$), Tokyo, Japan (2.2 and 0.6 μg/m$^3$) and Toronto, Canada (3.39 and 0.5 μg/m$^3$). That is because clean energy has widely been used and strict control measures are taken to improve the air quality step by step in the developed countries. Of the megacities in the developing countries, OC and EC concentrations in Beijing were lower than those in most other megacities, like Mumbai and New Delhi, India, and Xi’an and Tianjin, China, but close to those in Shanghai and Hongkong, China, and higher than those in Lhasa, China. These differences/similarities indicate that OC and EC gradually declined in Beijing and that a series of measures had progressive effects. However, to further improve the air quality, more synergetic air pollution abatement measures of carbonaceous aerosols and volatile organic compounds (VOCs) emissions need to be performed.

Fig. 2 shows the mass fractions of carbonaceous aerosols in different PM$_{2.5}$ levels classified according to PM$_{2.5}$ concentrations during the whole study period. There were 571, 561, 310, 169, 142 and 74 days for excellent, good, slightly polluted, moderately polluted, heavily polluted and severely polluted air quality levels during the whole period. It was obvious that OC and EC concentrations increased with the degradation of air quality. OC and EC concentrations were 6.3
and 1.7, 10.2 and 2.9, 13.7 and 4.1, 17.3 and 5.3, 24.6 and 7.9 and 35.5 and 11.3 μg/m³ for excellent, 
good, slightly polluted (LP), moderately polluted (MP), heavily polluted (HP) and severely polluted 
(SP) air quality days, respectively. However, the percentages of OC and EC accounting to PM$_{2.5}$ 
decreased with the deterioration of air quality. OC and EC made up for 31.5 % and 8.3 %, 18.9 % 
and 5.4 %, 14.7 % and 4.4 %, 13.4 % and 4.1 %, 12.9 % and 4.2 % and 11.4 % and 3.6 % during 
excellent, good, slightly polluted, moderately polluted, heavily polluted and severely polluted air 
quality days, respectively. The percentage for OC decrease from 31.4 to 11.4 % while that for EC 
decreased from 8.3 to 3.6 % with the deterioration of air quality, indicating that other PM$_{2.5}$ 
constituents than OC and EC contributed more to the increased PM$_{2.5}$ levels. This is consistent with 
previous studies showing that secondary inorganic ions play a more important role in the increase 
in PM$_{2.5}$ concentrations (Ji et al., 2014, 2018).

### 3.2 Inter-annual variation of OC and EC

To evaluate the effect of the clean air act over a prolonged period, our OC and EC data were 
combined with the data of previous studies for Beijing. As shown in Figs. 3 and 4, a decreasing 
trend in OC and EC concentrations is on the whole observed. The decline in OC and EC 
concentrations was closely associated with a combined effect of stricter standards for vehicle 
emissions, the increase in usage of natural gases and electricity consumption and the decreasing 
consumption of coal and diesel oil, although the gross domestic product, population, energy 
consumption and vehicular population rapidly increased (Table 2). In particular, there is an obvious 
dividing line of OC and EC concentrations in 2010. After 2010, the OC and EC concentrations were 
lower than those observed previously. This is because that Shougang Corporation, which is one of 
the China's largest steel companies, moved out of Beijing and highly polluted factories on the 
Beijing outskirts relocated in 2010 (http://www.china.org.cn/business/2011- 
01/13/content_21731198.htm) in addition to the gradual reduction of coal consumption and 
increasing usage of clean energy like natural gases and electricity. In addition, all the small coal 
mines in Beijing shut down and plenty of yellow label (heavy-polluting) vehicles were forced off 
road. It resulted in an obvious decline in OC and EC concentrations from 2011. Note that the OC 
and EC levels in 2008 and 2009 were also somewhat lower, which was caused by a series of 
measures to improve the air quality for the Olympic Games in 2008 and a decline in industrial
production because of China’s exports crash in 2009, respectively. It suggests that a stringent clean
air act and rectifying industry played important roles in the air quality improvement.

Similar to OC and EC, the annual mean \( \text{SO}_2 \) and \( \text{NO}_2 \) concentrations also showed a decreasing
trend. As well-known, \( \text{SO}_2 \) originates from coal combustion and the usage of sulfur-containing oil
(Seinfeld and Pandis, 1998). With the replacement of coal combustion for industrial production,
residential heating and cooking by clean energy (e.g., natural gases, electricity and lower sulfur
content in oil), a clear decline in annual \( \text{SO}_2 \) concentrations was observed in the Beijing area starting
from 2002. Compared with \( \text{SO}_2 \), OC and EC came from vehicular emission and biomass burning
besides coal combustion. Thus, the decline in coal consumption only played a partial role in the
decline in the annual mean OC and EC concentrations. The rapid increase of vehicle population
partly offset the great effort in eliminating coal consumption, although standards for vehicle
emissions were also raised. As important products of vehicular emission, OC and EC did not decline
as \( \text{SO}_2 \). Similar to \( \text{NO}_2 \), which comes from the direct emission of vehicles or the oxidation of NO
from vehicular exhaust, OC and EC declined gradually but at a lower rate. It suggests that further
control of vehicular emissions will be useful to lower the OC and EC concentrations. Note also that
the effective control of biomass burning contributed a lot to the decrease in OC and EC
concentrations. As shown in Fig. 3, the decline in the number of fire spots was somehow correlated
with decreasing OC and EC concentrations in the past five years.

3.3 Monthly and seasonal variations

Fig. S1 shows the monthly mean OC and EC concentrations at our study site for the whole 5-
year period. Similar variations are observed with generally higher mean OC and EC levels in the
colder months (from November to February) and lower ones in the warm months (from May to
October). The highest average OC and EC concentrations were \( 24.1 \pm 18.7 \mu \text{g/m}^3 \) in December 2016
and \( 9.3 \pm 8.5 \mu \text{g/m}^3 \) in December 2015, respectively. However, the lowest OC and EC levels were
not observed in the warm months; they were \( 5.0 \pm 4.6 \mu \text{g/m}^3 \) in January, 2018 and \( 1.5 \pm 1.7 \mu \text{g/m}^3 \)
in December, 2017, respectively; this was associated with both frequent occurrence of cold air mass
and the implementation of a winter radical action plan in Beijing from November, 2017. Overall,
the increased fuel consumption for domestic heating in addition to unfavorable meteorological
conditions in the colder months is considered to lead to higher OC and EC levels (Ji et al., 2014).
In the warm months no energy is consumed for domestic heating and the wet scavenging by frequent precipitation occurring in these months gives rise to lower OC and EC levels. In the warm months, the monthly mean OC and EC concentrations decreased almost year by year. In contrast, in the cold months no decline in the monthly mean OC and EC concentrations could be seen. The interquartile ranges of OC and EC in the warm months was narrower than those in cold months, indicating that there was more substantial variation in concentration in these months. The larger variation in the colder months was caused by the cyclic accumulation and scavenging processes (Ji et al., 2012). The successive accumulation processes were closely associated with unfavorable meteorological conditions, which gave rise to higher OC and EC concentrations, while scavenging processes by cold fronts led to lower levels.

As to the seasonality in OC and EC, similar seasonal variations are observed in the various years with generally higher mean concentrations in autumn and winter and lower levels in spring and summer (Fig. 5). The seasonal variations are explained by both changes in emission strength and in meteorology (Cao et al., 2007). The high concentrations in winter are thought to be mainly associated with emission from residential heating (biomass burning for heating occasionally occurred in autumn and winter although biomass burning has been prohibited by the national laws, regulations and policies.) along with unfavorable meteorological conditions such as lower mixing layer height, temperature inversion, calm wind leading to less pollutant transport and a higher relative humidity promoting secondary conversion of air pollutants (Ji et al., 2014, Zheng et al., 2015). In addition, the lower air temperature in winter led to shifting the gas-particle equilibrium of semi-volatile organic compounds (SVOCs) into the particle phase, resulting in the higher OC levels. In autumn and winter, the cold start of vehicles (5.64 million vehicles in Beijing at the end of 2017) also increased the emission of OC. On the other hand, the higher planetary boundary layer (PBL) and larger wind speeds in spring and summer led to higher ventilation and more dispersion of pollutants. In spring and summer, the higher temperature shifted the gas-particle equilibrium of semi-volatile organic compounds towards the gas phase. In addition, OC and OC can also be effectively scavenged by frequent precipitation in summer.

Remarkably, the OC and EC concentrations in the autumn and winter of 2017 were lower than those in the previous years. This was due to the combined effect of controlling anthropogenic
emissions strictly and the favorable meteorological conditions. Since September 2017, a series of
the most stringent measures within the Action Plan on Prevention and Control of Air Pollution were
implemented to improve the air quality; these measures included restricting industrial production
by shutting down thousands of polluting plants, suspending the work of iron and steel plants in 28
major cities and limiting the use of vehicles and reducing coal consumption as a heating source in
northern China. In addition, the air quality improvement in the autumn and winter of 2017 was
closely tied to frequent cold fronts accompanied by strong winds, which was favorable for
dispersing the pollutants. The average OC and EC concentrations in the winter were 1.69 and 1.14,
2.17 and 1.93, 1.49 and 2.14, 2.41 and 2.29 and 2.29 and 0.80 and 0.88 times higher than those in the summer
for 2013, 2014, 2015, 2016 and 2017, respectively. The difference in the ratios for 2017 was due to
the series of the most stringent measures taking effect and the favorable meteorology. The Beijing
municipal government in particular has made great efforts to replace coal by natural gases and
electricity-powered facilities. Besides, new energy vehicles are increasingly used to replace the
gasoline vehicles.

3.4 Diurnal variation and weekly pattern for OC and EC

As can be seen in Figs. S2 and S3, a clear diurnal variation is observed for both OC and EC in
each year. This variation is closely tied to the combined effect of diurnal variation in emission
strength and evolution of the PBL. The pattern for EC with higher concentrations in the nighttime
(from 20:00 to 4:00) and lower levels in the daytime (from 9:00 to 16:00) is largely linked to the
vehicular emissions. The EC concentrations increased starting from 17:00, corresponding with the
evening rush hours, emission from nighttime heavy-duty diesel trucks (HDDT) and heavy-duty
vehicles (HDV) and the formation of a nocturnal stable PBL. As regulated by the Beijing Traffic
management Bureau (http://www.bjjtgl.gov.cn/zhuanti/10weihao/), HDV and HDDT are allowed to
enter the urban area inside the 5th Ring Road from 0:00 to 06:00 (local Time). At other times, both
the higher PBL height and lower traffic intensity resulted in lower EC concentrations. The amplitude
of the diurnal variation in the EC concentrations was smaller in the last three years. The maximum
peak concentration (22:00-7:00) was 1.68, 1.62, 1.43, 1.40 and 1.40 times higher than that observed
in the valley period (13:00-15:00) for 2013, 2014, 2015, 2016 and 2017, respectively. Similar to EC,
the diurnal pattern for OC was also characterized by concentrations in the nighttime (from 20:00 to
4:00) and lower levels in the daytime (from 14:00 to 16:00). However, the formation of secondary organic carbon from gas-phase oxidation of VOCs with increased solar radiation during midday gave rise to a small additional peak of OC. Like for EC, the amplitude of the diurnal variation in the OC concentrations was smaller in the last three years. The maximum peak concentration (19:00-3:00) was 1.47, 1.47, 1.30, 1.34 and 1.26 times higher than that observed in the valley period (14:00-16:00) for 2013, 2014, 2015, 2016 and 2017, respectively. Separate diurnal variations of OC and EC for each season in each year are shown in Figs S4 and S5. Similar patterns are observed in in the four seasons but the difference between peak and valley levels is larger in the winter than in the other three seasons. The larger variation in the winter is due to the additional emission from residential heating and more unfavorable meteorological conditions (Ji et al., 2016).

The difference in diurnal pattern between weekdays and weekends was also examined, see Figs. S6 and S7. Similar diurnal variations are found on weekdays and weekend days. The maximum peak concentration for EC (22:00-7:00) was 1.55, 1.43, 1.55, 1.51, 1.51, 1.46 and 1.59 times higher than the valley concentration (13:00-15:00) for Monday, Tuesday, Wednesday, Thursday, Friday, Saturday and Sunday, respectively, while the maximum peak concentration for OC (19:00-3:00) was 1.41, 1.32, 1.38, 1.43, 1.37, 1.31 and 1.43 times higher than the valley concentration (14:00-16:00) for Monday, Tuesday, Wednesday, Thursday, Friday, Saturday and Sunday, respectively. In contrast to previous studies (Grivas et al., 2012; Jeong et al., 2017; Chang et al., 2017), OC and EC exhibited higher concentrations on weekends than on weekdays. The average OC and EC concentrations on Saturday and Sunday were 13.2 ± 1.8 μg/m³ and 3.9 ± 2.7 μg/m³ and 12.0 ± 10.4 μg/m³ and 3.7 ± 3.6 μg/m³, respectively, whereas the average OC and EC levels during the weekdays were 11.8 ± 1.8 μg/m³ and 3.6 ± 3.5 μg/m³, respectively. This indicates that there is no significant decline in anthropogenic activity in the weekends compared to weekdays. In fact, enhanced anthropogenic emissions could be caused by no limit on driving vehicles based on license plate on weekends. The larger OC and EC concentrations in the weekend are thus mainly attributed to enhanced traffic emissions, which is consistent with higher NO₂ and CO concentrations in the weekend (on average 56.6 ± 35.9 μg/m³ for NO₂ and 1.16 ± 1.18 mg/m³ for CO on weekdays (number of samples = 29492); 57.8 ± 37.0 μg/m³ for NO₂ and 1.25 ±1.18 mg/m³ for CO on weekends (number of samples = 11881)).
The relationship between particulate OC and EC is an important indicator that can give information on the origin and chemical transformation of carbonaceous aerosols (Chow et al., 1996).

Fig. 6 presents the regression between the OC and EC concentrations for the PM$_{2.5}$ samples of the separate years 2013 to 2017. Significant correlations ($R^2$ ranging from 0.87 to 0.66) were observed with the slopes declining from 3.6 to 2.9 throughout the study period. The significant correlations suggest that in most cases OC and EC originated from similar primary sources. The slopes are consistent with the OC/EC ratios ranging from 2.0 to 4.0 for urban Beijing in previous studies (He et al., 2001; Dan et al., 2004; Zhao et al., 2013; Ji et al., 2016). In addition, the average OC/EC ratios observed in this study are comparable to those observed at other urban sites with vehicular emission as a dominant source in China and foreign countries, but lower than those in cities where coal is an important source of the energy needed (Table 4). The decline in the OC/EC ratio may be caused by decline in coal consumption and restriction in biomass burning. Coal combustion, biomass burning and secondary formation give rise to higher OC/EC ratios while vehicular emission result in lower ones (Cao et al., 2005).

EC and part of the OC originate from primary anthropogenic emissions, including fossil fuel combustion and biomass burning (Bond et al., 2013), and secondary OC is formed along with ozone formation. Hence, long-term and concurrent measurement of OC, EC, SO$_2$, NO$_x$, CO and O$_3$ is helpful for understanding the emission features or formation processes and for providing tests to current emission inventories. The variation in the OC and EC as a function of the SO$_2$, NO$_x$, CO and O$_3$ concentration is shown in Fig. 7. There is a clear increase in OC and EC with increasing SO$_2$, NO$_x$, and CO, suggesting that the latter played a role in the enhancement of the former and that these various species shared common sources although they have a different lifetime. OC and EC increased, on average, by approximately 8.9 μg/m$^3$ and 5.7 μg/m$^3$, respectively, with an increase of 2 mg/m$^3$ in CO. Considering that CO has a long lifetime (Liang et al., 2004) and that its increase depends on source strength and meteorology, high CO concentrations usually occur in the heating season when unfavorable meteorological conditions prevail. At very high CO concentrations, the increase in OC becomes slower than that in EC. This can be explained by that local emissions became dominant because the unfavorable meteorological conditions corresponding with the high
CO concentrations resulted in a weak exchange of air on the regional scale. The OC/EC ratio declined at very high CO concentrations. This could be because vehicular emissions became the dominant pollution source and gradually replaced the industrial emissions in Beijing (http://language.chinadaily.com.cn/2018-05/15/content_36203449.htm). As documented by previous studies (Schauer et al., 2002, Na et al., 2004), emission of gasoline vehicles results in an OC/EC ratio varying from 3 to 5 while that of diesel vehicles is below 1. The above results are consistent with previous studies which showed that gasoline and diesel vehicles give rise to higher CO emissions (Wu et al., 2016).

Given that NO$_x$ and CO have some common emission sources (Hassler et al., 2016), the OC and EC levels were also analyzed in different intervals of NO$_x$ concentrations. Both OC and EC are enhanced with increasing NO$_x$ concentrations. Their enhancements were 5.0 μg/m$^3$ and 2.1 μg/m$^3$, respectively, for an increase in NO$_x$ concentration of 40 μg/m$^3$. Although NO$_x$ are highly reactive and have a short lifetime (Seinfeld and Pandis, 1998) in contrast to CO, the OC/EC ratio also declined at very high NO$_x$ concentrations, be it to a lesser extent than was the case at very high CO concentrations. As was the case for high CO concentrations, more stable meteorological conditions and local emissions became prevailed when higher concentrations of NO$_x$ were observed. In fact, 63.5 % of all NO$_x$ emissions comes from vehicular emissions based on the statistical data of air pollutant emissions in Beijing (http://www.bjepb.gov.cn/bjhrb/xxgk/ywdt/zlkz/hjtj37/827051/index.html).

Examining the variation of OC and EC for different intervals of SO$_2$ concentrations allows us to further study the impacts of industrial production or coal combustion on the OC and EC levels. Similar to the relationship between CO and the carbonaceous species, the OC and EC concentrations enhanced with increasing SO$_2$ concentrations. Their enhancements were 2.8 μg/m$^3$ and 0.7 μg/m$^3$, respectively, for an increase in SO$_2$ concentration of 10 μg/m$^3$. An increase in the OC/EC ratio occurred at large SO$_2$ concentrations, suggesting that coal consumption provided a substantial contribution to the OC and EC levels in Beijing. Because oil with a low sulfur content has been widely used in Beijing since 2008 and little coal was used in the urban areas of Beijing, the SO$_2$ mostly originated from industrial production in the surrounding areas of Beijing and from coal combustion for residential heating in the suburban and rural areas of Beijing. Previous studies also
showed that a higher OC/EC ratio is due to coal consumption and not from vehicular emissions (Cao et al., 2005). Hence, coal combustion (for industrial production) on the regional scale led to the enhancement of both the OC/EC ratio and SO$_2$ concentrations in Beijing via long-range transport.

Emissions of primary air pollutants lead to the formation of ozone and secondary organic carbon (SOC) through multiple pathways (Seinfeld and Pandis, 1998), both of which are the principal components of photochemical smog. Thus, the relationship of OC and O$_3$ is helpful for understanding the variation and formation of OC and O$_3$. The OC concentrations were highest for an O$_3$ concentration of 50 μg/m$^3$, which is approximately the average O$_3$ concentration in Beijing in winter (Cheng et al., 2018). For O$_3$ concentrations above 100 μg/m$^3$, the O$_3$ and OC concentrations enhanced simultaneously. This was because that the increased O$_3$ formation in favorable meteorological conditions enhanced atmospheric oxidation and thereby the generation of SOC. This gave rise to a concurrent increase in O$_3$ and OC concentrations. However, OC declined for O$_3$ concentrations increasing from 50 to 100 μg/m$^3$. Lower O$_3$ concentrations were observed when unfavorable meteorological conditions or scavenge processes occurred. Usually lower O$_3$ concentrations accompanying lower OC concentrations are caused by scavenging processes such as rainfall and strong winds. However, the unfavorable meteorological conditions led to the loss of O$_3$ via titration of NO trapping in the lower mixed layer height and accumulation and conversion of OC. In addition, scattering and absorbing effects of aerosols that were trapped in lower mixed layer led to less solar radiation reaching the ground and further restrained the O$_3$ formation (Xing et al., 2017; Wang et al., 2016b).

3.6 Impact of atmospheric transport on the OC and EC concentrations

Figs. 8 and 9 show the results of the NWR analysis applied to 1-h PM$_{2.5}$-associated OC and EC concentrations measured from 2013 and 2017 in Beijing. Fig. S8 presents the gridded emissions of OC and BC for the Beijing-Tianjin-Hebei (BTH) region and China, based on emission inventory (Zheng et al., 2018). The NWR results exhibit distinct hot spots (higher concentrations) in the northeast wind sector at wind speeds of approximately 0-6 km/h, which were closely associated with local emissions under stagnant meteorological conditions (low wind speed), as well as diffuse signals in the southwestern wind sector, highlighting probable trans-boundary transport from highly industrialized regions upwind of the Hebei province of China, such as Baoding, Shijiazhuang and
Handan, which were the most polluted cities in China. Previous studies found high loadings of OC and EC in Baoding, Shijiazhuang and Handan (http://english.mee.gov.cn/Resources/Reports/soe/).

The joint probability data in Figs. 14 and 15 show prevailing winds were from N to E and from S to W with wind speeds of approximately 1-6 km/h and of approximately 4-9 km/h, respectively.

Note further that the hot spots of OC are broader than those of EC in the graphs of estimated concentrations; this might be due to the fact that the VOCs (the precursors of SOC) emitted from upwind areas, including the SW wind sector, led to an increase in OC concentrations at the receptor site during the atmospheric transport while the EC concentrations slowly declined due to dilution and deposition during the atmospheric transport.

Considering that the NWR analysis can only provide an allocation of local sources, the PSCF analysis is a helpful complement to investigate potential advection of pollution over larger geographical scales. Fig. 10 presents the PSCF results for OC and EC for the years 2013 to 2017.

Similar to the NWR analysis, the PSCF results indicated that local emissions and regional transport from southerly areas were important contributors to the OC and EC loadings during the whole study period. Only slight differences in the potential source regions are observed between the different years. In 2013, a clear high potential source area was recorded for both OC and EC; it was located in the southern plain areas of Beijing, particularly in the adjacent areas of the Hebei, Henan, Shandong, Anhui and Jiangsu provinces. This was because there were intensified anthropogenic emissions from those in 2013. The high pollutant emissions were caused by rapid economic growth, urbanization and increase in vehicle population, energy consumption and industrial activity in the southern plain areas of Beijing (Zhu et al., 2018), which resulted in a high aerosol loading in the downwind areas. This result is consistent with previous studies (Ren et al., 2004; Wu et al., 2014; Ji et al., 2018). In contrast to 2013, in the years 2014 to 2017 the high potential source regions for OC and EC stretched to the juncture of Inner Mongolia and the Shaanxi and Shanxi provinces, and even to the juncture of Inner Mongolia and the Ningxia Hui Autonomous Region and of Inner Mongolia and the Gansu province. This is consistent with coal power plants being abundant in the above areas (Liu F. et al., 2015). As well known, coal power plants are also important emitters of SO₂, and those emissions were seen in satellite images (Li et al., 2017; Zhang et al., 2017), thus proving evidence for those sources. The potential source areas for OC and EC were similar in 2013 and 2014. Overall,
the potential source areas were more intense for OC than for EC. The emission of OC precursors (i.e., volatile organic compounds) from the Hebei, Henan, Shandong, Anhui, Jiangsu, Shanxi and Shaanxi provinces led to OC concentrations downwind via chemical conversion during the atmospheric transport. The widest potential source areas for OC and EC were recorded in 2016 and they expanded into the eastern areas of Xinjiang Uyghur Autonomous Region. They are probably associated with the economic boom in the western areas of China. In 2015, the potential source areas were like in 2013 and 2014 also more intense for OC than for EC. Although the winter action plan was enforced in Beijing, Tianjin and 26 surrounding cities (the so-called “2+26 cities”), whereby the industrial output was curtailed, inspections of polluting factories were ramped up and small-scale coal burning was banned at the end of 2017, there was still a clear spatial difference in emission of air pollutants, with relatively higher PM$_{2.5}$ concentrations in the southern areas of Beijing. Hence, these areas still contributed substantially to OC and EC loading in Beijing.

As found in earlier studies (Ji et al., 2018; Zhu et al., 2018), the southern areas of Beijing were main source areas. Despite the ever-stringent air pollution control measures, which are enforced in key areas of China, the economic booming in the western areas of China gave rise to substantial air pollution in the adjacent areas of several provinces and the northwestern areas of China. To further improve the air quality in Beijing, strict emission restrictions should be launched in the above areas and joint control and prevention of air pollution should be enforced on the regional scale. It should be avoided that polluted enterprises, which are closed in key regions, are moved to the western areas of China or to areas where there is no supervision and control of the emission of air pollutants.

4 Conclusions

In this study, hourly mass concentrations of OC and EC in PM$_{2.5}$ were semi-continuously measured from March 1, 2013 to February 28, 2018 at a study site in Beijing. The inter-annual, monthly, seasonal and diurnal variations in OC and EC are presented, the relationship between the carbonaceous species and other pollutants was examined and the source regions were assessed using both NWR and PSCF analysis. The impact of the air pollution control measures and of the regional transport on carbonaceous species in the fine particulate matter was investigated. The following main conclusions can be drawn:

(1) OC and EC occupied a high fraction of the observed PM$_{2.5}$ concentrations, making it a dominant
contributor of PM$_{2.5}$. Their concentrations increased with the degrading air quality whereas their percentage in PM$_{2.5}$ declined, which was consistent with previous studies showing that secondary inorganic ions played a relatively more important role in increasing PM$_{2.5}$ concentrations.

(2) A clear decline in OC and EC levels was observed after a series of energy policies for air pollution abatement and control had been implemented. To further improve air quality, more synergistic air pollution abatement measures of carbonaceous aerosols and VOCs emissions are needed.

(3) OC and EC showed marked seasonal, monthly, weekly and diurnal variations. The seasonal patterns were characterized by higher concentrations in the colder months (from November to February) and lower ones in the warm months (from May to October) of the various years. Because of stringent measures for air pollution abatement, the difference between the winter and summer levels decreased. The EC diurnal pattern was characterized by higher concentrations in the nighttime (from 20:00 to 4:00) and lower ones in the daytime (from 9:00 to 16:00). The higher OC and EC levels during the weekend can be attributed to the traffic regulation in Beijing. The diurnal fluctuation in OC and EC was closely tied to a combined effect of change in emission sources and evolution of the PBL.

(4) Significant correlations between OC and EC were observed throughout the study period, suggesting that OC and EC originated from common sources, such as vehicle exhaust, coal combustion, etc. The contribution of coal combustion and biomass burning decreased and this resulted in lower OC/EC ratios. The OC and EC concentrations increased with higher SO$_2$, CO and NO$_x$ levels, while the O$_3$ and OC concentrations increased simultaneously for O$_3$ levels above 50 µg/m$^3$.

(5) Local emissions and regional transport played an important role in the OC and EC concentrations. Higher concentrations were observed for winds from the northeast sector at wind speeds of approximately 5 km/h, but there were also diffuse signals in the southwestern wind sectors, highlighting probable transboundary transport from highly industrialized regions upwind of the region of the Hebei province. The potential source regions of OC and EC stretched to the broader areas in northwestern and western regions where coal and coal power plants are abundant. Some slight differences in the potential source regions were observed from 2013 to 2017, which was...
closely associated with the economic boom in the western areas of China. In addition, the southern areas of Beijing still contributed a lot to OC and EC loading in Beijing.

In summary, this study will be helpful for improving the understanding the sources of OC and EC associated with PM$_{2.5}$ and for assessing the effectiveness of local and national PM control measures. In addition, it provides valuable datasets for modelling studies and for assessing the health risk.

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Author contributions

D.S., W.M. and Y.S. designed the research. D.S., W.M., J.H., Z.W., W. K., W.P., Y.S., J.Y., B.H. and Y.S. performed the research. D.S., Z.W., and W.M. analyzed the data. D.S., J.H., and W.M. wrote and edited the manuscript. All other authors commented on the manuscript.

References


Li, C., McLinden, C., Fioletov, V., Krotkov, N., Carn, S., Joiner, J., Streets, D., He, H., Ren, X., Li, Z., and Dickerson, R.: India is overtaking China as the world’s largest emitter of anthropogenic sulfur dioxide, Scientific Reports, DOI:10.1038/s41598-017-14639-8, 2017.


Liu, G., Li, J., Wu, D., and Xu, H.: Chemical composition and source apportionment of the ambient PM$_{2.5}$ in Hangzhou, China, Particuology, 18, 135-143, 2015.


air pollution sources. 5. C1-C32 organic compounds from gasoline-powered motor vehicles,


Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate


Sharma, S. K. and Mandal, T. K.: Chemical composition of fine mode particulate matter (PM$_{2.5}$) in
an urban area of Delhi, India and its source apportionment, Urban Clim., 21, 106-122,

Quantification of long-term primary and secondary source contributions to carbonaceous aerosols,
Environ. Pollut. 219, 897-905, 2016.

Sofowote, U. M., Rastogi, A. K., Debosz, J., and Hopke, P. K.: Advanced receptor modeling of
near–real–time, ambient PM$_{2.5}$ and its associated components collected at an urban–industrial site

PM$_{2.5}$ in Beijing using principal component analysis/absolute principal component scores and

composition of PM$_{2.5}$ at an urban site of Chengdu in southwestern China, Adv. Atmos. Sci., 30,
1070-1084, 2013.

Tao, J., Gao, J., Zhang, L., Zhang, R., Che, H., Zhang, Z., Lin, Z., Jing, J., Cao, J., and Hsu, S. C.:
PM$_{2.5}$ pollution in a megacity of southwest China: source apportionment and implication, Atmos.

Tao, J., Zhang, L., Cao, J., and Zhang, R.: A review of current knowledge concerning PM$_{2.5}$
chemical composition, aerosol optical properties and their relationships across China, Atmos. Chem.

Villalobos, A. M., Amonov, M. O., Shafer, M. M., Devi, J. J., Gupta, T., Tripathi, S. N., Rana, K. S.,
McKenzie, M., Bergin, M. H., and Schauer, J. J.: Source apportionment of carbonaceous fine


Zhang, F., Zhao, J., Chen, J., Xu, Y., and Xu, L.: Pollution characteristics of organic and elemental carbon in PM$_{2.5}$ in Xiamen, China, J. Environ. Sci., 23(8), 1342-1349, 2011.


Zhao, P., Dong, F., and Yang, Y.: Characteristics of carbonaceous aerosol in the region of Beijing, Tianjin, and Hebei, China, Atmos. Environ., 71, 389-398, 2013.


Fig. 1. Map with location of the sampling site (the trapezoidal symbol in the right figure indicates the sampling site).
Fig. 2. Variation of OC, EC, and PM$_{2.5}$ concentrations and of the percentages of OC, EC, and other components in PM$_{2.5}$ for different air quality levels.
Fig. 3. Inter-annual variation in the annual mean OC and EC concentrations in PM$_{2.5}$ from 2002 to 2018 in Beijing. The variation in NO$_2$ and SO$_2$ concentrations and in the number of fire spots is also shown.
Fig. 4. Interannual variation of OC and EC during the whole study period.
Fig. 5. Seasonal variations of OC and EC concentrations from March 2013 to February 2018.
Fig. 6. Relationship between OC and EC using the Deming regression method from 2013 to 2017 (the dashed line indicates a OC/EC ratio of 3:1).
Fig. 7. OC and EC concentrations as a function of the SO$_2$, CO, NO$_x$ and O$_3$ concentration.
Fig. 8. Wind analysis results using NWR on 1-h OC concentrations measured in Beijing from 2013 to 2017 (Unit of wind speed: km/h).
Fig. 9. Wind analysis results using NWR on 1-h EC concentrations measured in Beijing from 2013 to 2017.
Fig. 10 Potential source areas for OC and EC in Beijing from 2013 to 2017. The color code denotes the PSCF probability. The measurement site is indicated with a . The identification of the provinces is given in Fig. S9.
Table 1. Statistics for the OC and EC concentrations (in μg/m³) from March 2013 to February 2018.

<table>
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<th></th>
<th>OC</th>
<th>Stdev</th>
<th>EC</th>
<th>Stdev</th>
<th>PM$_{2.5}$</th>
<th>Stdev</th>
<th>OC/PM$_{2.5}$</th>
<th>EC/PM$_{2.5}$</th>
<th>TC/PM$_{2.5}$</th>
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<td>14.0</td>
<td>11.7</td>
<td>4.0</td>
<td>3.3</td>
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<td>82.9</td>
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<td>4.0</td>
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<td>4.4</td>
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<td>11.3</td>
<td>3.6</td>
<td>3.7</td>
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<td>0.150</td>
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<td>whole study period</td>
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<td>10.6</td>
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<td>3.6</td>
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<td>77.6</td>
<td>0.164</td>
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Table 2. Annual variations of gross domestic product, population, total energy consumption, population of vehicles, consumption of gasoline, diesel oil, coal, natural gas and vehicle emission standards in Beijing.

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<td>6164</td>
<td>7141</td>
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<td>12419</td>
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Vehicular emission

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Table 3. Mean or median OC and EC mass concentrations observed in the major megacities of the world published in the literature and recorded in this study (in μg/m³).

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<td>7.7</td>
<td>2.6</td>
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<td>2.88</td>
<td>0.56</td>
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*https://aqs.epa.gov/api
Table 4. The ratios of OC/EC in main domestic and foreign cities.

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*https://aqs.epa.gov/api