

Original Research

# Seasonal Variations and Chemical Characteristics of PM<sub>2.5</sub> Aerosol in the Urban Green Belt of Beijing, China

Yu Wang, Hui Zhang, Jiexiu Zhai, Yanan Wu, Ling Cong, Guoxin Yan, Zhenming Zhang\*

College of Nature Conservation, Beijing Forestry University, Beijing 100083, China

Received: 20 December 2018

Accepted: 12 February 2019

## Abstract

Particulate matter (PM) pollution in Beijing is becoming an increasingly serious problem and is thus attracting considerable scientific attention. In order to reveal the characteristics and source of PM<sub>2.5</sub> and its components, observations of PM<sub>2.5</sub>, water-soluble ions, elemental carbon (EC), and organic carbon (OC) were conducted in the urban green belt of Beijing from April 2016 to April 2017. The annual average concentrations of PM<sub>2.5</sub>, EC, OC, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> were found to be 124.02, 10.21, 30.73, 36.84, 27.63, and 16.87 μg/m<sup>3</sup>, respectively. Moreover, the ratios of OC/EC, NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> were 2.58 and 0.75, respectively, and calculated secondary organic carbon concentration was 9.75 μg/m<sup>3</sup>. These results indicate that: 1) PM<sub>2.5</sub> pollution in the urban green belt of Beijing is more serious than in many other cities in China and has increased considerably over a period of five years; 2) there is a considerable variation in both the total PM<sub>2.5</sub> concentration and composition of water-soluble ions throughout different seasons, while the forest belt width has no evident influence on the PM concentration and water-soluble ions; 3) OC and EC concentrations and the ratio of OC/EC shows that traffic emissions during summer are higher than in other seasons and that traffic emissions are the dominant carbon source in Beijing. Furthermore, the carbon contribution to total PM<sub>2.5</sub> is greater than in other cities.

**Keywords:** PM<sub>2.5</sub>, water-soluble ions, carbonaceous species, the urban green belt, Beijing

## Introduction

With the development of urbanization, environmental problems have drawn more attention in China in recent years [1]. In areas with better economic development, fine particulate matter (PM<sub>2.5</sub>)

is listed as one of the most important pollutants in the atmosphere [2]. It causes a reduction in visibility, has an adverse influence on human health, and is known to be related to global climate change [3]. Although it is only a small part of the air, it is considered to be the main component of atmospheric pollutants [4]. PM<sub>2.5</sub> is a combination of many chemical components rather than a single molecule. In order to evaluate the impact of PM<sub>2.5</sub>, it is necessary to conduct in-depth research on its chemical characteristic [5]. Water-soluble ions and

\*e-mail: zhenmingzhang@bjfu.edu.cn

carbonaceous species are two dominant components of  $PM_{2.5}$  [6]. Water-soluble ions, dominated by  $SO_4^{2-}$ ,  $NO_3^-$ , and  $NH_4^+$ , affect the visibility of the atmosphere to a great extent [7]. Atmospheric particulate carbon is usually classified into two main fractions: organic carbon (OC) and elemental carbon (EC). OC mainly results from emissions related to human activity such as coal combustion, automobile exhaust, and biomass combustion [8, 9], and can form secondary organic carbon (SOC) by atmospheric chemical conversion processes involving organic precursors [10, 11]. In contrast, EC is essentially a primary pollutant emitted directly during the incomplete combustion of carbon-containing fuels and has a significant impact in terms of causing a reduction of visibility and aerosol radiative forcing [12].

Recently more and more studies focused on the effect of forests in particle removal [13]. Research in Beijing Olympic Forest Park showed  $PM_{2.5}$  concentration within the forest to be approximately 1.5 times greater than outside, which indicates that the forest may block the pollutants in it [14]. Besides the blocking, trees are also able to efficiently reduce the concentration of PMs by capture, and wooded areas are characterized by higher rates of dry deposition than other land cover types [15, 16]. Urban forests are thus able to improve air quality in relation to a number of different air pollutants and can consequently assist in improving human health [16]. Some studies have analyzed the effectiveness of trees in accumulating particulate matters on leaves and have identified certain tree species that are efficient at

capturing air pollutants. Species with denser leaves and denser hairs on the leaves have better capabilities, of course, and fine particle capture [17-19]. However, most of the studies have only focused on the relationship between accumulation amount and tree traits instead of the forest parameters such as width, while it is the forest that can reduce pollution instead of some individual plant. In addition, systematic studies related to water-soluble species and atmospheric particulate carbon of  $PM_{2.5}$  in relation to urban green belts and different trees remain extremely limited. Therefore, it is crucial to provide a theoretical basis in urban green system planning – especially in some seriously polluted cities such as Beijing.

The present study investigates changes in the concentration of water-soluble ions and carbon components of  $PM_{2.5}$  within the urban green belt in Beijing, and thus the objectives are: (1) to examine spatial and seasonal variations of water-soluble ions and concentrations of OC and EC in the urban green belt; (2) to investigate the relationship between OC and EC, as well as secondary organic carbon (SOC) formation; and (3) to identify the influence of meteorological factors on water-soluble ions and carbon components.

## Material and Methods

### Study Area

The study was carried out at Olympic Forest Park, which is the largest urban green landscape in Asia.

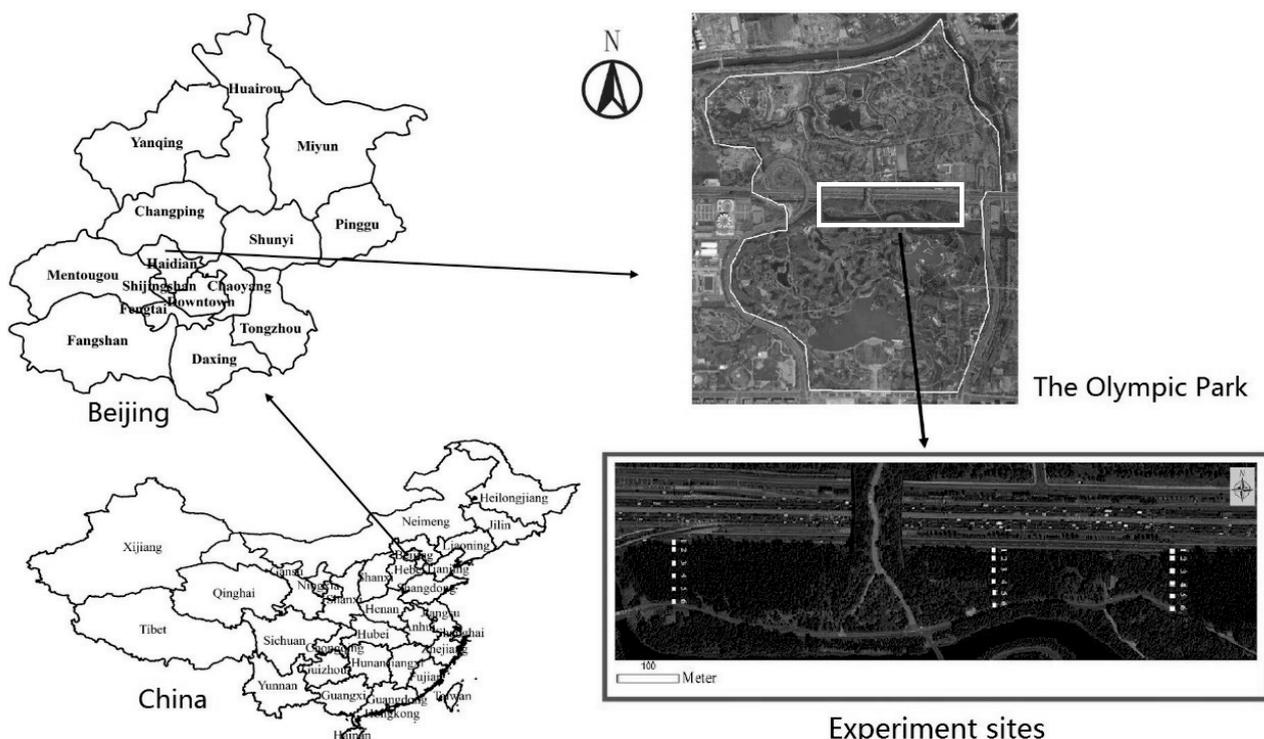


Fig. 1. Research sample and monitoring sites.

Table 1. Forest parameters.

The name of the forest	Tree species	Width (m)	LAI	Height of tree (m)	DBH (m)	Ground diameter (m)
<i>Populoustomentosa</i> forest	<i>Loniceramaackii</i>	3	—	2.34	—	0.020
	<i>Populous tomentosa</i>	60	3.26	12.4	0.167	—
<i>Ulmuspumila</i> forest	<i>Loniceramaackii</i>	3	—	3.07	—	0.034
	<i>Ulmus</i>	57	2.78	7.3	0.169	—
Mingled forest	<i>Loniceramaackii</i>	3	—	2.20	—	0.215
	<i>Populous tomentosa</i>	24	2.87	13.4	0.165	—
	<i>Salix matsudana</i>	35	2.24	7.2	0.190	—

It covers an area of 680 hectares and is located at the north end of the north-south axis of Beijing. The 5<sup>th</sup> Ring Road crosses through the Forest Park and divides the park into two parts: north and south. As shown in Fig. 1, the experimental sites in this study were located in three forest bands dominated by a different tree species, and these were situated at the north edge of the south Olympic Park adjacent to the 5<sup>th</sup> Ring Road. From the left side to the right side, the bands contain tree species of *Populoustomentosa*, *Ulmuspumila*, and mixed forest, which are species widely distributed within Beijing. Table 1 shows the specific parameters in each forest area.

### PM<sub>2.5</sub> Samples

Table 1 shows the specific parameters for each forest, where the width of the *P. tomentosa* forest band was 63 m, that of the *Ulmuspumila* band was 60 m, and that of the mixed forest band was 62 m. The forest belt was adjacent to the 5<sup>th</sup> Ring Road of Beijing, which was considered the main pollutant input in the current study. Six monitoring points were located in each band at distances of 0 m, 3 m, 18 m, 33 m, 48 m, and 63 m from north to south. A Dust Mate particulate matter sampler (Turnkey Co. Ltd, British), a suspended particulate pollutants sampler (TH-150C, Westernization instrument Technology Co., Ltd., Beijing, China), and a small weather station (Kestrel 4000 Pocket Weather Meter, Nielsen-Kellerman, Boothwyn, PA, USA) were installed at each sampling point to collect data relating to the concentration and composition of PM, and meteorological data (temperature, wind speed, relative humidity, and radiation). The Dust Mate monitor recorded the concentration of PM<sub>2.5</sub> every minute; the suspended particulate pollutants sampler could collect PM<sub>2.5</sub> on glass fiber filters (20 L/min) and the meteorological data were collected every 30 minutes [20-22]. And we calibrated our instruments every time before the experiment. Moreover, the base of the filter film and the cutting head were ultrasonically cleaned with deionized water three times before each experiment [23]. Five rain-free days in each season from April 2016 to April 2017 were selected to conduct the experiment. The

sampling time was from 06:00 to 18:00 at each sample point, which ensured that the duration of sampling time was approximately 12 h. A total of 20 PM<sub>2.5</sub> samples were collected at each sampling point during the experiment.

### Water-Soluble Ions Analysis

Water-soluble ion analysis of PM was performed by clipping off a quarter of a sampling filter membrane, dissolving it in 50 ml of deionized water, and performing ICS-2000 ion chromatography to determine the anion and cation content. In this study, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> were selected for analysis (more details can be found in a previous study from Qiu et al. [24]).

### Carbonaceous Species Analysis

A quarter of a quartz filter was clipped off and a DRI Model 2001 organic carbon/elemental carbon analyzer was used to analyze amounts of OC and EC. Four OC sections were heated in an oxygen-free environment (OC1, OC2, OC3, and OC4 at 120°C, 250°C, 450°C, and 550°C, respectively). The sample under a helium environment containing 2% oxygen was heated as EC1, EC2, and EC3 at 550°C, 700°C, and 800°C, respectively. OC was then defined as the total value of OC1+OC2+OC3+OC4+OP according to the IMPROVE protocol (a pyrolyzed carbon fraction determined when reflected or transmitted laser light attains its original intensity after O<sub>2</sub> is added to the analyzer's atmosphere), and EC was defined as the total of EC1+EC2+EC3+OP [25, 26].

## Results and Discussion

### PM<sub>2.5</sub> Mass Concentration

A statistical summary of the mass concentration of PM<sub>2.5</sub> from spring to winter is shown in Fig. 2, where the averages and standard deviations of PM<sub>2.5</sub> in spring, summer, autumn, and winter are shown to be 125.05±46.84 μg/m<sup>3</sup>, 94.91±27.11 μg/m<sup>3</sup>,

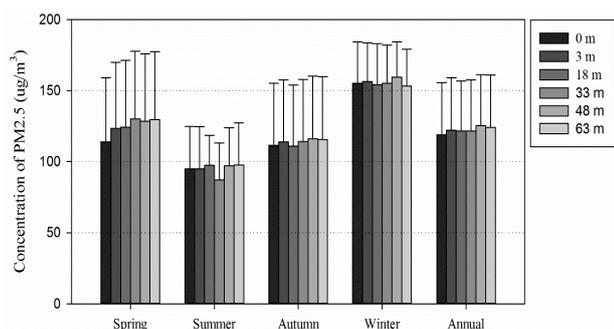


Fig. 2. Variations in  $PM_{2.5}$  concentrations throughout different seasons and within widths of forest bands.

$113.74 \pm 43.6 \mu\text{g}/\text{m}^3$ , and  $155.54 \pm 27.13 \mu\text{g}/\text{m}^3$ , respectively. The mass concentrations of  $PM_{2.5}$  were found to be lower in the summer than in other seasons and the maximum concentration occurred in winter, but variations in concentrations in spring and winter were insignificant ( $P > 0.05$ ). The two-way ANOVA was used to test the effects of season and distance, and significant effects were determined in relation to seasons ( $P < 0.001$ ), but here was no variation found in relation to the sites of differing widths. It is considered that the higher concentration of  $PM_{2.5}$  in winter could be associated with the lower wind speed and is thus attributed to the local crustal materials re-suspended in the atmosphere [20, 21]. During winter the unfavorable synoptic-scale (anti-cyclonic circulation) and meteorological conditions (very low temperature, surface layer inversions) additionally contribute to the occurrence of increased air pollution events. In our study area, dust is derived from northwestern China and transported eastward in winter, which could also contribute to the difference in seasonal variations [27, 28].

The annual average  $PM_{2.5}$  concentration was  $124.02 \mu\text{g}/\text{m}^3$ , which is more than eight times that

of the U.S. National Ambient Air Quality Standard (NAAQS) annual average of  $15 \mu\text{g}/\text{m}^3$ . Forests are considered to be sinks for particles, and they have an impact on the dispersal of  $PM_{2.5}$ ; therefore, the  $PM_{2.5}$  mass concentration in the forest should be higher than that outside of it [29]. For example, it was determined in a previous study that the  $PM_{2.5}$  concentration in a forest near Shanghai ranged from  $58$  to  $150 \mu\text{g}/\text{m}^3$  [30]. Furthermore, Nguyen et al. compared concentrations in and outside of an urban forest in Beijing; the results outside the forest showed the average value to be 25.4% lower than inside [14]. However, in this study, only a slight variation in  $PM_{2.5}$  concentration was determined by the forest belt, which shows that forest width has little effect on the  $PM_{2.5}$  concentration. In addition, it shows that the observed  $PM_{2.5}$  concentration, in all likelihood, reflects that of Beijing. Although an air quality standard for PMs has been established in China, the pollution situation in Beijing is known to be more serious than in other domestic cities (Table 3). For example, the mean concentration of PM in Fuzhou, Guangzhou, Shanghai, and Qingdao is  $44.33 \mu\text{g}/\text{m}^3$ ,  $103 \mu\text{g}/\text{m}^3$ ,  $94.6 \mu\text{g}/\text{m}^3$ , and  $49.58 \mu\text{g}/\text{m}^3$ . In addition, the average concentration of PM in Beijing is twice as high as it was five years ago [31, 32]. The standard deviations imply that the  $PM_{2.5}$  mass concentration has a wider variation range in spring and autumn. Therefore, although the average concentration in these two seasons is relatively lower than in winter, the sharp changes observed in PM mass concentrations could be very harmful to health [24].

#### Concentrations of Water-Soluble Ions

Three water-soluble ions,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ , were selected for detection in this study (Table 2), and average concentrations were found to be  $36.84 \pm 22.78 \mu\text{g}/\text{m}^3$ ,  $27.63 \pm 16.51 \mu\text{g}/\text{m}^3$ , and  $16.87 \pm 14.12 \mu\text{g}/\text{m}^3$ , respectively. The order of

Table 2. Average concentrations of water-soluble ions and carbonaceous species during the monitoring period.

	Spring	Summer	Autumn	Winter	Annual
$\text{SO}_4^{2-}$ ( $\mu\text{g}/\text{m}^3$ )	56.48	42.18	35.85	12.83	36.84
$\text{NO}_3^-$ ( $\mu\text{g}/\text{m}^3$ )	32.48	36.93	21.07	20.03	27.63
$\text{NH}_4^+$ ( $\mu\text{g}/\text{m}^3$ )	14.70	31.73	11.22	9.82	16.87
EC ( $\mu\text{g}/\text{m}^3$ )	9.91	12.62	9.94	8.66	10.21
OC ( $\mu\text{g}/\text{m}^3$ )	28.39	26.36	30.44	37.72	30.73
TC ( $\mu\text{g}/\text{m}^3$ )	38.30	38.97	41.45	51.83	42.64
SOC ( $\mu\text{g}/\text{m}^3$ )	10.41	4.45	10.51	13.62	9.75
EC/ $PM_{2.5}$	0.08	0.13	0.10	0.06	0.09
OC/ $PM_{2.5}$	0.23	0.28	0.27	0.24	0.25
OC/EC	2.87	2.09	2.77	2.67	2.58
$\text{NO}_3^-/\text{SO}_4^{2-}$	0.88	0.58	0.59	1.56	0.75

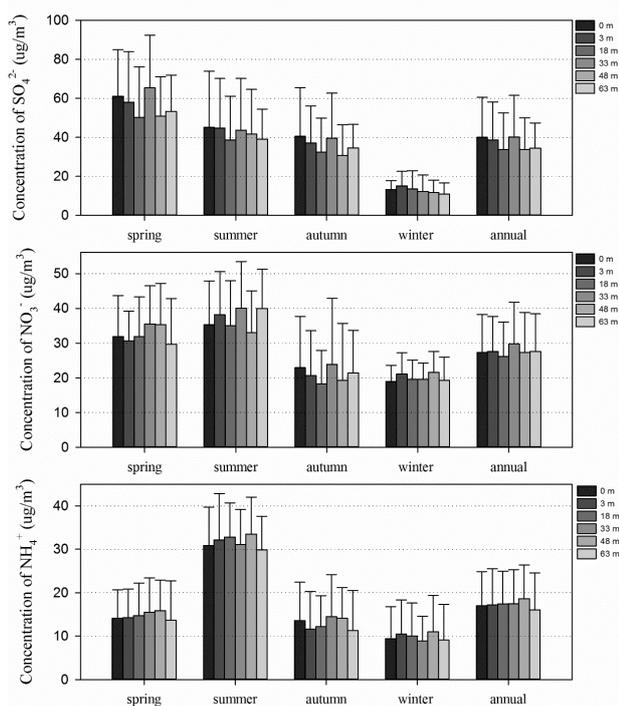


Fig. 3. Variation in ion concentrations throughout different seasons and within various sampling widths of the forested area.

concentration of  $\text{SO}_4^{2-}$  is spring>summer>autumn>winter, with concentrations of  $56.48 \pm 30.21 \mu\text{g}/\text{m}^3$ ,  $42.18 \pm 25.18 \mu\text{g}/\text{m}^3$ ,  $35.85 \pm 28.72 \mu\text{g}/\text{m}^3$ , and  $12.83 \pm 6.98 \mu\text{g}/\text{m}^3$ , respectively. The  $\text{NO}_3^-$  concentrations were higher in spring and summer than in autumn and winter; average  $\text{NO}_3^-$  concentrations were  $32.48 \pm 22.97 \mu\text{g}/\text{m}^3$ ,  $36.93 \pm 13.95 \mu\text{g}/\text{m}^3$ ,  $21.07 \pm 14.18 \mu\text{g}/\text{m}^3$ , and  $20.03 \pm 14.93 \mu\text{g}/\text{m}^3$  in spring, summer, autumn, and winter, respectively.  $\text{NH}_4^+$  concentrations peaked in summer at  $31.73 \pm 33.1 \mu\text{g}/\text{m}^3$  and then decreased to  $14.7 \pm 7.42 \mu\text{g}/\text{m}^3$  in spring. In addition, they were  $11.22 \pm 8.43 \mu\text{g}/\text{m}^3$  in autumn, and the lowest value was found in winter at  $9.82 \pm 7.52 \mu\text{g}/\text{m}^3$ . The concentrations changed slightly in accordance with the different widths of forest sites (see Fig. 3 ( $P > 0.05$ )). For example, peak values were found in 33 m or 48 m sites for all the tree types. Concentrations found in the study forest belt were significantly higher than in other forests. For example, in Changba Mountain forest, China, the  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  concentrations were  $12.9 \mu\text{g}/\text{m}^3$ ,  $0.33 \mu\text{g}/\text{m}^3$ , and  $3.94 \mu\text{g}/\text{m}^3$ ; in Hainan, China, concentrations were  $2.17 \mu\text{g}/\text{m}^3$ ,  $0.13 \mu\text{g}/\text{m}^3$ , and  $0.56 \mu\text{g}/\text{m}^3$ ; and in Lock Rock, USA, concentrations were  $23.1 \mu\text{g}/\text{m}^3$ ,  $10.9 \mu\text{g}/\text{m}^3$ , and  $10.3 \mu\text{g}/\text{m}^3$  [30, 33, 34]. In addition, there were no significant variations ( $P < 0.001$ ) among sites of different widths in the forest. The concentration of  $\text{SO}_4^{2-}$  was higher at a distance of 33 m and 0 m (about  $40.0 \mu\text{g}/\text{m}^3$ ), and in the sites of 33 m the  $\text{NO}_3^-$  was the highest at about  $29.8 \mu\text{g}/\text{m}^3$ . When it comes to  $\text{NH}_4^+$ , concentration of sites at other distances were all lower than that at a distance of 48 m, of which

the concentration was  $18.6 \mu\text{g}/\text{m}^3$ . Although previous studies have proved that plant organs such as foliage and bark are able to accumulate particles and their components [35-38], few researchers can estimate an exact amount of the reduction in concentration in relation to forests at the plot scale. According to the concentration variation results detected in this study, the forest belt whose width is 63 m had little effect on the ion concentrations in the city. Similar unclear concentration variations regularly in the urban area and a nearby forest could also be found in other reports. In Shanghai, China, the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  in a forest on Chongming Island were found to be  $23.1 \mu\text{g}/\text{m}^3$ ,  $10.9 \mu\text{g}/\text{m}^3$ , and  $10.3 \mu\text{g}/\text{m}^3$ , respectively; and concentrations in the Dinghu Mountain Nature Reserve in Guangzhou were  $10.24 \mu\text{g}/\text{m}^3$ ,  $0.47 \mu\text{g}/\text{m}^3$ , and  $3.04 \mu\text{g}/\text{m}^3$ , respectively.

Previous studies have demonstrated that the ratio of  $\text{NO}_3^-/\text{SO}_4^{2-}$  can be efficiently used to assess the contribution of mobile and stationary sources of sulfur and nitrogen in the atmosphere. The emission ration of  $\text{NO}_x$  to  $\text{SO}_x$  was 1:2 from coal burning, while it was 1:8 and 1:13 of gasoline and diesel fuel burning in China [39, 40]. Thus, higher value ratios imply the predominance of stationary sources over mobile source pollutions, and vice versa [31, 40, 41]. In this study, the annual average mass ratio of  $\text{NO}_3^-/\text{SO}_4^{2-}$  was  $0.75 \pm 0.46$  and ranged from 0.42 to 1.79 during the sampling periods, and was 0.88, 0.58, 0.59, and 1.56 in spring, summer, autumn, and winter, respectively. In addition, differences were significant between winter and other seasons. It is considered that higher values in winter and spring may be attributed to the burning of coal in relation to heating. The value determined in this study was much higher than that found in other forest sites, such as on Changbai Mountain (0.03), Chongming Island (0.47), in Dinghu Mountain Nature Reserve (0.05), and on Hainan Island (0.06) and K-pusta (0.2). In addition, when compared to other cities, the ratios found in this study in Beijing were extremely high. For example, ratios in Fuzhou, Hangzhou, Shanghai, and Guangzhou were 0.41, 0.36, 0.35, and 0.79, respectively [40, 42-44]. Hence, the serious PM pollution in Beijing comes from coal combustion, including heating and industry emissions, while traffic emissions might contribute a little (although the vehicles in Beijing were much more numerous than in other cities).

#### Concentrations of OC and EC

The average OC and EC concentrations in different seasons are shown in Fig. 4: the OC concentrations were  $28.39 \mu\text{g}/\text{m}^3$ ,  $26.36 \mu\text{g}/\text{m}^3$ ,  $30.44 \mu\text{g}/\text{m}^3$ , and  $37.72 \mu\text{g}/\text{m}^3$  in spring, summer, autumn, and winter, respectively. Peak concentrations occurred in winter; which is attributed to the growing number of emission sources from residential and commercial incomplete combustion [31, 40]. It is thus considered that

Table 3. Comparison between results of this study and other studies.

Reference	PM <sub>2.5</sub>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup> / SO <sub>4</sub> <sup>2-</sup>	EC	OC	SOC	OC/EC	Study area	Seasons
This study	125.9	36.8	27.6	16.9	0.75	10.2	30.8	9.75	2.6	Beijing	A
Choi et al. (2012)	41.9	5.1	4.58	3.65	0.9	1.72	7.92	4.6	4.6	Korea	A
Xu et al. (2012)	44.3	10.8	4.39	3.89	0.41	2.17	8.5		3.9	Fuzhou	SU, AU, WI
Li and Bai (2009)	117	—	—	—	—	5.1	22.7	12.8	4.4	Tianjin	WI
Zhang et al. (2009)	63.9	—	—	—	—	7.1	13.5	—	2	Beijing	SP
Duan et al. (2005)		—	—	—	—	7.3	21.2	10.8	3	Beijing	AU
Li et al. (2010)	38.8	12.9	0.33	3.94	0.03	0.5	4.9	2.3	9.8	CB	SU
Li et al. (2010)	89.2	23.1	10.9	10.3	0.47	1.6	9.9	4.4	6.2	Shanghai	SU
Li et al. (2010)	30.8	10.2	0.47	3.04	0.05	0.7	5.3	3.4	7.3	DH	SU
Li et al. (2010)	18	2.17	0.13	0.56	0.06	0.2	2.4	—	12	Hainan	SU
Maenhaut et al. (2010)	12.7	2.87	0.57	1.34	0.2	0.3	3.3	—	11	Japan	SU
Tanner et al. (2004)	19	7.7	0.01	1.7	0	0.7	4	—	5.7	Tennessee	A

Note: A: all year, SP: spring; SU: summer; AU: autumn; WI: winter; CB: Changbai Mountain Nature Reserve, Jilin Province, China; DH: Dinghu Mountain Nature Reserve, Guangdong Province, China.

residential heating in winter and late autumn in Beijing may contribute to the relatively high OC concentrations in these two seasons and that the higher concentrations of OC may be caused by ambient industrial areas. According to previous studies (Table 3), the annual average OC concentrations in Tianjin and Beijing near the Chinese capital-industrial zone were higher than those in Qingdao and Fuzhou, where there are fewer industrial emissions [26, 31, 42, 45].

EC concentrations were 9.91  $\mu\text{g}/\text{m}^3$ , 12.62  $\mu\text{g}/\text{m}^3$ , 9.94  $\mu\text{g}/\text{m}^3$ , and 8.66  $\mu\text{g}/\text{m}^3$  for spring, summer, autumn, and winter, respectively. The highest value was therefore in summer, and this is considered to be related to traffic emissions. For example, in spring, a large percentage of the Beijing population return to their hometowns to celebrate the Spring Festival with families, and therefore the population sharply decreases (known as the “Spring Festival Evacuation”). Therefore, the low population density at this time lasts for approximately 20 days, and leads to a reduction in vehicle use. In contrast, many tourists visit Beijing in summer, which causes relatively high traffic emissions.

EC and OC concentrations in urban areas were higher than within the forest, even when the PM<sub>2.5</sub> mass concentration was similar (details are provided in Table 3). Average EC concentrations on Changbai Mountain and Chongming Island, and in Dinghu Mountain Nature Reserve and Jingfengling Nature Reserve were 0.5  $\mu\text{g}/\text{m}^3$ , 1.6  $\mu\text{g}/\text{m}^3$ , 0.7  $\mu\text{g}/\text{m}^3$ , and 0.2  $\mu\text{g}/\text{m}^3$ , respectively, while the average OC concentrations at four forest sites were 4.9  $\mu\text{g}/\text{m}^3$ , 9.9  $\mu\text{g}/\text{m}^3$ , 5.3  $\mu\text{g}/\text{m}^3$ , and 2.4  $\mu\text{g}/\text{m}^3$ , respectively [30]. The average annual concentrations of EC and OC in the forest belt in this study (10.21 and 30.8  $\mu\text{g}/\text{m}^3$ )

were higher than at all the forest sites and the city areas cited above, and both the EC and OC concentrations detected within the different site widths in the forest belt varied slightly ( $P > 0.05$ ). In other words, the observed EC and OC concentrations could be considered as the representative of the situation in Beijing, and the high values could thus be attributed to the sheer number of vehicles in the city. In addition, the OC concentrations in Beijing have doubled in the past five years and this is also attributed to the increase in vehicle numbers in the city; these results are consistent with those of a previous analysis [26].

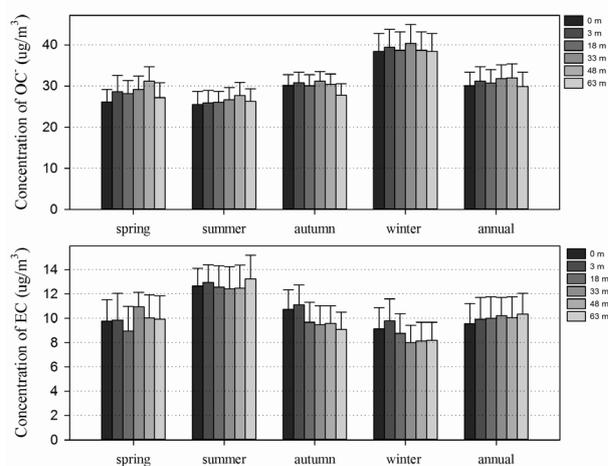


Fig. 4. Variations in EC and OC concentrations throughout different seasons and within various sampling widths of the forested area.

### Analysis of SOC Concentrations

OC consists of a complex intermixture of species from primary and secondary sources. EC is mostly emitted from primary sources and remains inert in the atmosphere; it has frequently been used as a tracer of primary OC to determine SOC concentrations. It is possible to obtain a semi-quantitative estimation of SOC using the following equation:

$$OC_{soc} = OC_{tot} - EC \times (OC/EC)_{MIN} \quad (1)$$

...where  $OC_{soc}$  is secondary organic carbon,  $OC_{tot}$  is total organic carbon, and  $(OC/EC)_{MIN}$  is the minimum  $OC/EC$  ratio of the surrounding aerosol. As listed in Table 2, the estimated SOC concentrations were  $10.41 \mu\text{g}/\text{m}^3$ ,  $4.45 \mu\text{g}/\text{m}^3$ ,  $10.51 \mu\text{g}/\text{m}^3$ , and  $13.62 \mu\text{g}/\text{m}^3$  for spring, summer, autumn, and winter, respectively. The peaks and troughs of SOC occurred in winter and summer, respectively. It is therefore considered possible that the burning of coal for heating during winter and traffic emissions may increase pollutant emissions, including primary carbonaceous particles and organic gases [42, 46]. According to former studies, the annual average SOC concentration in Beijing was higher than in Qingdao and Fuzhou, but was less than in Incheon, Korea [31, 40, 42, 46]. The reason for this may be that OC dominates the composition, and this is related to heating in winter and the large volume of traffic. In addition, industrial emissions also cause an increase in OC.

### Relationship between OC, EC, and $\text{PM}_{2.5}$

The origins of OC and EC can be evaluated by their relationship [46, 47]. As shown in Table 2 and Fig. 5,

the OC/EC ratio has a seasonal variation with a peak value in spring (2.87), followed by autumn (2.77), winter (2.67), and a low value in summer (2.09). EC is formed from the combustion of fuel and thus higher OC/EC value indicates a relative higher proportion of traffic emissions. In summer, as coal combustion is reduced, traffic emissions account for a larger proportion than in winter, and this result is consistent with the analysis of  $\text{NO}_3/\text{SO}_4$ . According to prior studies, OC/EC values are higher within forests. In this respect, the average ratio value at four forest sites was 8.83 in China, the mean value of two forests in the USA was 7.86 [30, 33, 34], and in this study the OC/EC value was 2.6. Beijing is the capital of China and thus is a hub of various emission sources, such as coal combustion, traffic emissions, and industrial emissions. The lower ratio of OC/EC, and the SOC concentration determined in summer indicates that the higher primary carbon, which is mainly emitted from coal burning, more traffic emission in this case. Compared with other cities, Beijing has a higher vehicle density, a lower ratio of OC/EC and concentration of SOC, and a higher EC concentration, which supports our hypothesis.

The sum of averaged OC and EC accounts for 31%, 41%, 37%, and 30% of the total  $\text{PM}_{2.5}$  mass concentrations in spring, summer, autumn, and winter. OC is the major contributor to total carbon and accounts for about 74%, 68%, 90%, and 80% of the amount within the four seasons. The higher percentages in summer are related to the relatively lower  $\text{PM}_{2.5}$  concentrations and the interception of the forest. The higher leaf density in summer and autumn causes a low-dispersion condition and thus more EC and OC is blocked by the forest, causing the higher observed values. In addition, the carbon contributed more to  $\text{PM}_{2.5}$  mass concentration than in other cities [31,

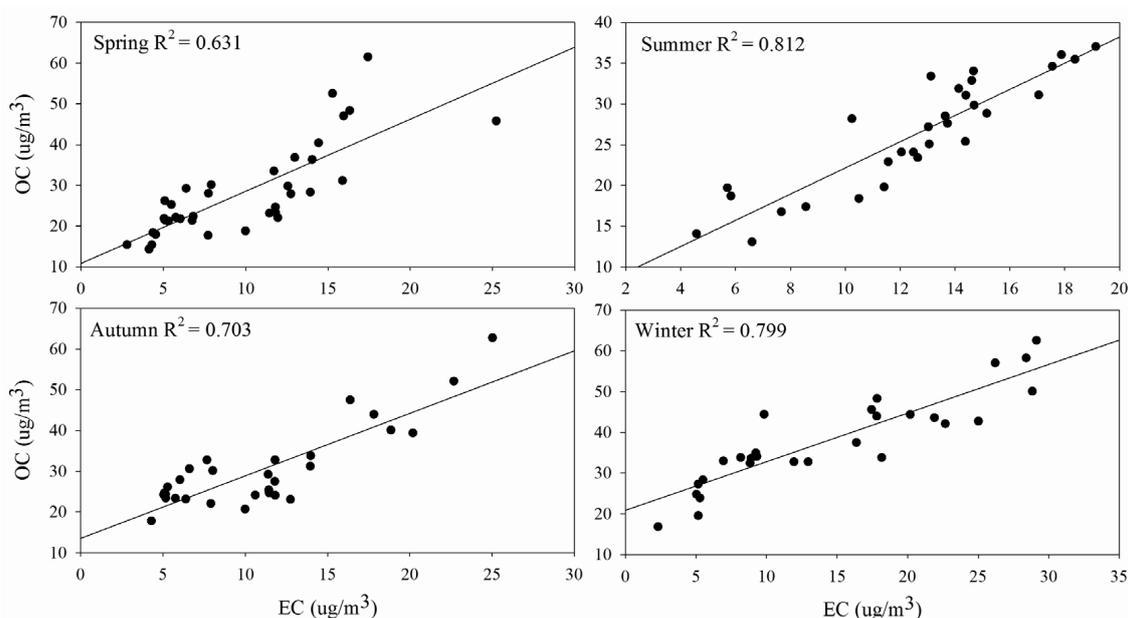


Fig. 5. Relationship between EC and OC in different seasons.

Table 4. Regression analysis of PM<sub>2.5</sub>, EC, and OC using meteorological factors.

Pollutant	Function	R <sup>2</sup>	P
PM <sub>2.5</sub>	PM <sub>2.5</sub> = -179.25WS + 204.57	0.144	0.001
	PM <sub>2.5</sub> = 3.617RH - 16.75	0.674	0.001
EC	EC = -1.957WS + 12.353	0.192	0.099
	EC = 0.211RH + 1.535	0.172	0.098
OC	OC = -3.460WS + 29.182	0.178	0.102
	EC = 0.365RH - 2.414	0.235	0.003

WS: wind speed (ms<sup>-1</sup>); RH: relative humidity (%)

42, 45]. Furthermore, the contribution of EC and OC in the forest were less than 30%, which means the high ration of carbons is related to human activities [34].

### Impact of Meteorological Factors

Table 4 presents the regression functions of PM mass concentrations, OC, EC, and meteorological factors. The results show that PM<sub>2.5</sub> mass concentrations, OC, and EC are negatively correlated with wind speed but positively correlated with RH. These analyses are consistent with previous studies [14, 24, 26], but the correlation coefficient is smaller, which means that wind speed and relative humidity contribute less to PM concentrations and particulate carbon. This difference could be related to various resources used in different studies, such as varying research scales and methods of measurement. For example, previous studies have focused on one season only, usually spring, and have collected meteorological data using a meteorological tower (at a height of over 5 m). However, in this study, data were collected over a period of two years and meteorological data were collected in the forest near the ground (at a height of 1.5 m), thereby giving temporal and spatial heterogeneity, and the variation range in this study is larger. Furthermore, there may be a concentration threshold, which means only when in a specific concentration variation range can the meteorological factors such as wind speed influence the PM concentration effectively. However, further studies are considered necessary in order to prove the hypothesis in this study.

The mass concentration of all the tested particles are lower than Beijing, and a common phenomenon has been found that in summer the concentrations are the lowest during the year while winter and early spring has the highest concentration. The current study indicates that fuel combustion is the major resource of particles, and this result is in accordance with previous studies, which could also explain why the particle pollution situation is more serious in winter. Besides, atmospheric conditions can also influence the transmission of particle matter and thus the atmospheric circulation in

winter might not be conducive for pollutant dispersion. However, further studies are required to support this idea.

### Limitations

Our current study analyzed the concentrations of PM<sub>2.5</sub>, water-soluble ions and carbon composition in forest belts in Beijing and analyzed the spatial-temporal distribution and resources of those air pollutants. However, it is important to highlight that there remain some limitations in our research. First of all, the pollutant concentration and composition outside the forest were not recorded and thus we cannot estimate the effect of particle removal directly. Besides, our resource analysis is based on the ratio of different compositions which comes from empirical theory. Although this method is considered to be correct way and is broadly accepted, there are also some uncertainties in our conclusions. For example, the conclusions drawn regarding the sources of observed aerosol constituents are often based on assumptions (i.e., the role of traffic) and sometimes inconsistent with the data collected (i.e., the role of leaves in OC and EC summer concentrations). The next step should trace exact resources and thus provide more powerful theory support to deal with the serious pollution.

### Conclusions

To reveal characteristics and sources of PM<sub>2.5</sub> and its components, observation of PM<sub>2.5</sub>, water-soluble ions, EC, and OC was conducted in Beijing throughout four seasons over a period of two years. PM<sub>2.5</sub> pollution in the urban green belt of Beijing was found to be much more extensive than in other cities in China, and the annual concentration was more than eight times the NAAQS; furthermore, the amount of pollution was found to have doubled in five years. It is considered that the high concentrations are related to ambient industrial and local traffic emissions. The concentrations of water-soluble ions and EC were higher in summer than in winter, and these results contrast with those

from other cities. The “Spring Festival Evacuation” and the increase in population in relation to summer sightseeing in Beijing may explain this irregularity. In addition, the relationship between  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , and EC and OC also give the same conclusion. The lower ratios of OC/EC and  $\text{SO}_4^{2-}/\text{NO}_3^-$  and the calculated SOC concentrations in the summer indicate the existence of higher amounts of primary carbon, which is mainly derived from coal burning and traffic emissions. In addition, it was found that carbon contributes more to the  $\text{PM}_{2.5}$  concentration in Beijing than in other cities. Compared with other cities, Beijing has a high vehicle density, a lower ratio of OC/EC, a lower concentration of SOC, and a higher concentration of EC. In addition, it was found that there was no significant variation in concentration within the sample site of different widths within the forest, and it is thus considered that the width of a forest belt only has a negligible effect on pollutant concentration.

### Acknowledgements

This research was supported by the Fundamental Research Funds for the Central Universities (2016JX05). The authors acknowledge the constructive comments provided by both the reviewers and editors.

### Conflict of Interest

The authors declare no conflict of interest.

### References

- ZHANG F., WANG Z., CHENG H., LV X., GONG W., WANG X., ZHANG G. Seasonal variations and chemical characteristics of  $\text{PM}_{2.5}$  in Wuhan, central China. *Science of the Total Environment*. **518-519**, 97, **2015**.
- LI R., HARDY R., ZHANG W., REINBOLD G.L., STRACHAN S.M. Chemical Characterization and Source Apportionment of PM in a Nonattainment Rocky Mountain Valley. *Journal of Environment Quality*. **47**, 238, **2018**.
- ZHU L., LIU J., CONG L., MA W., MA W., ZHANG Z. Spatiotemporal Characteristics of Particulate Matter and Dry Deposition Flux in the Cuihu Wetland of Beijing. *PLoS One*. **11**, e158616, **2016**.
- ZHAO L., LUN X., LI R., CAO Y., SUN F., YU X. Deposition of  $\text{PM}_{2.5}$  Sulfate in the Spring on Urban Forests in Beijing, China. *Atmosphere*. **8**, 3, **2017**.
- BEHERA S.N., BETHA R., LIU P., BALASUBRAMANIAN R. A study of diurnal variations of  $\text{PM}_{2.5}$  acidity and related chemical species using a new thermodynamic equilibrium model. *Science of the Total Environment*. **452-453**, 286, **2013**.
- TIAN M., WANG H.B., CHEN Y., YANG F.M., ZHANG X.H., ZOU Q., ZHANG R.Q., MA Y.L., HE K.B. Characteristics of aerosol pollution during heavy haze events in Suzhou, China. *Atmospheric Chemistry & Physics*. **16**, 7357, **2015**.
- ZHANG F., XU L., CHEN J., YU Y., NIU Z., YIN L. Chemical compositions and extinction coefficients of  $\text{PM}_{2.5}$  in peri-urban of Xiamen, China, during June 2009–May 2010. *Atmospheric Research*. **106,150**, **2012**.
- CACHIER H., LIOUSSE C., BUAT-MENARD P., GAUDICHET A. Particulate content of savanna fire emissions. *Journal of Atmospheric Chemistry*. **22**, 123, **1995**.
- DUAN F., LIU X., YU T., CACHIER H. Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing. *Atmospheric Environment*. **38**, 1275, **2004**.
- PANDIS S.N., HARLEY R.A., CASS G.R., SEINFELD J.H. Secondary organic aerosol formation and transport. *Atmospheric Environment*. **26**, 2269, **1992**.
- PANKOW J.F. An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol. *Atmospheric Environment*. **41**, 75, **2007**.
- JACOBSON M.Z. Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature*. **409**, 695, **2001**.
- LIU J., ZHAI J., ZHU L., YANG Y., LIU J., ZHANG Z. Particle removal by vegetation: comparison in a forest and a wetland. *Environmental Science and Pollution Research*. **24**, 1597, **2017**.
- NGUYEN T., YU X., ZHANG Z., LIU M., LIU X. Relationship between types of urban forest and  $\text{PM}_{2.5}$  capture at three growth stages of leaves. *Journal of Environmental Sciences*. **27**, 33, **2015**.
- MCDONALD A., BEALEY W., FOWLER D., DRAGOSITS U., SKIBA U., SMITH R., DONOVAN R. H., HEWITT C., NEMITZ E. Quantifying the effect of urban tree planting on concentrations and depositions of  $\text{PM}_{10}$  in two UK conurbations. *Atmospheric Environment*. **41**, 8455, **2007**.
- PRAJAPATI S. Ecological effect of airborne particulate matter on plants. *Environmental Skeptics & Critics*. **1**, 12, **2012**.
- GAWROŃSKA H. Particulate Matter on Foliage of 13 Woody Species: Deposition on Surfaces and Phytostabilisation in Waxes – a 3-Year Study. *International Journal of Phytoremediation*. **15**, 245, **2013**.
- DZIERZANOWSKI K., POPEK R., GAWROŃSKA H., SAEBÅ A., GAWROŃSKI S.W. Deposition of particulate matter of different size fractions on leaf surfaces and in waxes of urban forest species. *International Journal of Phytoremediation*. **13**, 1037, **2011**.
- SÆBØ A., POPEK R., NAWROT B., HANSLIN H.M., GAWROŃSKA H., GAWROŃSKI S.W. Plant species differences in particulate matter accumulation on leaf surfaces. *Science of the Total Environment*. **427-428**, 347, **2012**.
- LIU J., ZHU L., WANG H., YANG Y., LIU J., QIU D., MA W., ZHANG Z., LIU J. Dry deposition of particulate matter at an urban forest, wetland and lake surface in Beijing. *Atmospheric Environment*. **125**, 178, **2016**.
- LIU J., MO L., ZHU L., YANG Y., LIU J., QIU D., ZHANG Z., LIU J. Removal efficiency of particulate matters at different underlying surfaces in Beijing. *Environmental Science & Pollution Research*. **23**, 408, **2016**.
- LIU J., YANG G., WU Y., WANG Y., ZHANG Z., ZHANG M. Wetlands with greater degree of urbanization improve  $\text{PM}_{2.5}$  removal efficiency. *Chemosphere*. **207**, 601, **2018**.
- SUN F., YIN Z., LUN X., ZHAO Y., LI R., SHI F., YU X. Deposition velocity of  $\text{PM}_{2.5}$  in the winter and spring above

- deciduous and coniferous forests in Beijing, China. *PLoS One*. **9**, e97723, **2014**.
24. QIU D., LIU J., ZHU L., MO L., ZHANG Z. Particulate matter assessment of a wetland in Beijing. *Journal of Environmental Sciences*. **36**, 93, **2015**.
  25. ZHANG R., HO K.F., CAO J., HAN Z., ZHANG M., CHENG Y., LEE S.C. Organic carbon and elemental carbon associated with PM<sub>10</sub> in Beijing during spring time. *Journal of Hazardous Materials*. **172**, 970, **2009**.
  26. WU C., NG W.M., HUANG J., WU D., YU J.Z. Determination of Elemental and Organic Carbon in PM<sub>2.5</sub> in the Pearl River Delta Region: Inter-Instrument (Sunset vs. DRI Model 2001 Thermal/Optical Carbon Analyzer) and Inter-Protocol Comparisons (IMPROVE vs. ACE-Asia Protocol). *Aerosol Science and Technology*. **46**, 610, **2012**.
  27. NATSAGDORJ L., JUGDER D., CHUNG Y.S. Analysis of dust storms observed in Mongolia during 1937-1999. *Atmospheric Environment*. **37**, 1401, **2003**.
  28. QI Z., JIMENEZ J.L., WORSNOP D.R., MANJULA C. A case study of urban particle acidity and its influence on secondary organic aerosol. *Environmental Science & Technology*. **41**, 3213, **2007**.
  29. JIN S., GUO J., WHEELER S., KAN L., CHE S. Evaluation of impacts of trees on PM<sub>2.5</sub> dispersion in urban streets. *Atmospheric Environment*. **99**, 277, **2014**.
  30. WANG, JIALIANG, FENG, ZHANG, HUIJIAN, ZEPING, BANGJIN, WANG, GUOYING. Composition, source, mass closure of PM<sub>2.5</sub> aerosols for four forests in eastern China. *Journal of Environmental Sciences*. **22**, 405, **2010**.
  31. XU L., CHEN X., CHEN J., ZHANG F., HE C., ZHAO J., YIN L. Seasonal variations and chemical compositions of PM<sub>2.5</sub> aerosol in the urban area of Fuzhou, China. *Atmospheric Research*. **104-105**, 264, **2012**.
  32. WU C., NG W.M., HUANG J., WU D., YU J.Z. Determination of Elemental and Organic Carbon in PM<sub>2.5</sub> in the Pearl River Delta Region: Inter-Instrument (Sunset vs. DRI Model 2001 Thermal/Optical Carbon Analyzer) and Inter-Protocol Comparisons (IMPROVE vs. ACE-Asia Protocol). *Aerosol Science & Technology*. **46**, 610, **2012**.
  33. TANNER R.L., PARKHURST W.J., VALENTE M.L., PHILLIPS W.D. Regional composition of PM<sub>2.5</sub> aerosols measured at urban, rural and "background" sites in the Tennessee valley. *Atmospheric Environment*. **38**, 3143, **2004**.
  34. MATSUDA K., FUJIMURA Y., HAYASHI K., TAKAHASHI A., NAKAYA K. Deposition velocity of PM<sub>2.5</sub> sulfate in the summer above a deciduous forest in central Japan. *Atmospheric Environment*. **44**, 4582, **2010**.
  35. GUO L., MAGHIRANG R.G. Numerical Simulation of Airflow and Particle Collection by Vegetative Barriers. *Engineering Applications of Computational Fluid Mechanics*. **6**, 110, **2012**.
  36. PRZYBYSZ A., SÆBØ A., HANSLIN H.M., GAWROŃSKI S.W. Accumulation of particulate matter and trace elements on vegetation as affected by pollution level, rainfall and the passage of time. *Science of the Total Environment*. **481**, 360, **2014**.
  37. TERZAGHI E., WILD E., ZACCHELLO G., CERABOLINI B.E.L., JONES K.C., GUARDO A.D. Forest Filter Effect: Role of leaves in capturing/releasing air particulate matter and its associated PAHs. *Atmospheric Environment*. **74**, 378, **2013**.
  38. YAN G., LIU J., ZHU L., ZHAI J., CONG L., MA W., WANG Y., WU Y., ZHANG Z. Effectiveness of wetland plants as biofilters for inhalable particles in an urban park. *Journal of Cleaner Production*. **194**, 435, **2018**.
  39. WANG Y., ZHUANG G., TANG A., YUAN H., SUN Y., CHEN S., ZHENG A. The ion chemistry and the source of PM<sub>2.5</sub> aerosol in Beijing. *Atmospheric Environment*. **39**, 3771, **2005**.
  40. CHOW J.C., WATSON J.G. Seasonal variations and sources of mass and chemical composition for PM<sub>10</sub> aerosol in Hangzhou, China. *Particology*. **7**, 161, **2009**.
  41. CHOI J.K., HEO J.B., BAN S.J., YI S.M., ZOH K.D. Chemical characteristics of PM<sub>2.5</sub> aerosol in Incheon, Korea. *Atmospheric Environment*. **60**, 583, **2012**.
  42. DUAN F., HE K., MA Y., JIA Y., YANG F., LEI Y., TANAKA S., OKUTA T. Characteristics of carbonaceous aerosols in Beijing, China. *Chemosphere*. **60**, 355, **2005**.
  43. WANG Y., ZHUANG G., ZHANG X., HUANG K., XU C., TANG A., CHEN J., AN Z. The ion chemistry, seasonal cycle, and sources of PM<sub>2.5</sub> and TSP aerosol in Shanghai. *Atmospheric Environment*. **40**, 2935, **2006**.
  44. TAN J.H., DUAN J.C., CHEN D.H., WANG X.H., GUO S.J., BI X.H., SHENG G.Y., HE K.B., FU J.M. Chemical characteristics of haze during summer and winter in Guangzhou. *Atmospheric Research*. **94**, 238, **2009**.
  45. LI W., BAI Z. Characteristics of organic and elemental carbon in atmospheric fine particles in Tianjin, China. *Particology*. **7**, 432, **2009**.
  46. CHOW J.C., WATSON J.G., LU Z., LOWENTHAL D.H., FRAZIER C.A., SOLOMON P.A., THUILLIER R.H., MAGLIANO K. Descriptive analysis of PM<sub>2.5</sub> and PM<sub>10</sub> at regionally representative locations during SJVAQS/AUSPEX. *Atmospheric Environment*. **30**, 2079, **1996**.
  47. TURPIN B.J., HUNTZICKER J.J. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. *Atmospheric Environment*. **29**, 3527, **1995**.