Effects of forest belt in park on the chemical composition for PM$_{2.5}$

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Abstract. This paper represents results on the effects of forest belt on seasonal variation on the main chemical components for PM$_{2.5}$ in the park environment in Beijing. PM$_{2.5}$ samples were collected inside and outside a conifer forest simultaneously for 1 year in Beijing Olympic Forest Park. Chemical components including organic carbon (OC), elemental carbon (EC), water-soluble ions and elements in PM$_{2.5}$ were measured. Results indicated that forest belt had significant impacts on PM$_{2.5}$ chemical compositions of park. Organic matter, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and crustal matter were the dominant components of PM$_{2.5}$. The measured OC was divided into primary OC (POC) and second OC (SOC) parts following the method of EC tracer. Concentrations of OC, SOC, as well as SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and K$^+$ in PM$_{2.5}$ inside of forest were markedly higher than those outside of forest. The highest concentrations of OC, EC, and SO$_4^{2-}$ were observed in winter and the lowest values were found in summer. In contrast, the highest concentrations of most crustal elements were observed in spring, and the highest levels of pollutant elements were found in winter. Among these elements, annual mean concentrations of As and Cr exceeded WHO standard during monitoring period.

1. Introduction

Liquid or solid particles suspended in the air are called airborne particulate matter (PM) [1-2]. PM$_{2.5}$ is defined as those particles with aerodynamic diameter smaller than 2.5 μm, which has potential effects on human health, climate, radiation balance and visibility [3-5]. Beijing, the capital of China has a population of more than 21 million and almost 5.3 million vehicles [6], which is surrounded by high mountains in the north, west and south directions. The air pollution due to the natural geographical conditions and insufficient environmental capacity in Beijing has become an increasing public health concern [7-8].

Previous researches have indicated that trees/forests can mitigate PM$_{2.5}$ pollution through removal and subsequent lowering the concentrations of PM$_{2.5}$ [9-13]. However, it should also be noticed that plants may be sources of particles and an obstacle to air flow [14]. At this point, the formation of PM$_{2.5}$ is evidently influenced by plants’ effect resulting from biogenic volatile organic compounds (BVOC) emission of trees at forest area [15-16]. Typically, chemical components including carbonaceous matters, water soluble ions and elements accounting for 65% to 85% of the measured PM mass in most urban and non-urban areas [17]. The carbonaceous aerosol is formed by a complex mixture of organic carbon (OC) and elemental carbon (EC), which is emitted from combustion sources with graphitic-like structure. Since EC almost does not undergo chemical change, it is a good indicator
as primary anthropogenic air pollutant. However, OC species can be emitted from either anthropogenic or biogenic sources, which could be also generated from photochemical reactions among primary gaseous in the air [18]. Generally, NH$_4^+$, SO$_2^-$ and NO$_3^-$ are the main water-soluble ions in PM$_{2.5}$ [19], whose precursor gases are also the most important factors (SO$_2$, NO$_x$, NH$_3$ or HNO$_3$), resulting in secondary aerosols through photochemical reactions. Some elements presented in PM$_{2.5}$ are regarded as carcinogens for human or animal and less prone to chemical transformations [17], thus studies on their pollution levels and potential emission sources are required for protecting public health [7-8].

Many studies on chemical compositions of aerosol at forest area have been conducted in North America and Europe [20-21]. In Asia, a few studies on this issue have also been conducted. Cheng et al. (2007) compared the mass concentrations and ions contents of PM$_{2.5}$ between an urban site and a forest site in central Taiwan [22]. Li et al. (2010) determined the sources and mass closures of aerosol collected in four Chinese forest areas, and comparing the results with those with other forest areas across the world [23]. However, these studies are mainly focused on the characteristics of organic compounds or inorganic ions. The whole fractions of PM$_{2.5}$ chemical composition in forest area is still limited. In addition, the temporal and spatial variations on the concentrations of PM$_{2.5}$ and chemical components in urban forest areas are rarely studied and poorly understood.

2. Materials and Methods

2.1. Sample collection and site description

PM$_{2.5}$ was sampled at two sites in Beijing Olympic Forest Park which is sited in the north-south axis’ northern end in the city, approximately 680 hectares in size. It has become the largest public park and a natural landscape resort for Beijing citizen after 2008 Beijing Olympic. Besides, sites in this park are located in the urban area of Beijing and samples collected in this sampling site could present trends in air pollution at urban area of Beijing [3]. Site 1 was inside a conifer forest (116°23.824′E, 40°01.032′N). The forest was constituted mainly of Platycladus orientalis and Sabina chinensis which are also the native tree species of Beijing, and tree density is 53 per acre. Site 2 was outside the forest on the middle of a garden road with width of 6 m. The distance between the two sites was about 20 m. Two sampling sites are depicted in Figure 1.

![Figure 1. Sampling locations in Beijing Olympic Forest Park.](image)

A medium flow rate sampler (KC-120H, LSDZ Corporation) was placed at each site to collect PM$_{2.5}$ at a flow rate of 99 min L$^{-1}$. The inlet tube was installed about 1.5 m above the ground, a height that is especially correlative with human exposure. PM$_{2.5}$ samples were collected simultaneously at the both sites at 5-day intervals (six samples per month) in January, April, July, and October 2014. Each sample was collected over a 12 h period with starting at 7:00 a.m., and a total of 48 PM$_{2.5}$ samples were collected. All samples were collected on quartz microfiber filters (Whatman 1851-090 Grade QM-A Circles, d=90 mm). After sampling, the filters were sealed in a polystyrene box and stored at −18 °C prior to analysis. Blank field samples were also collected before and after sampling by installing a filter on the sampler for 5 min without pumping into any air.

2.2. Mass concentration analysis

Samples and field blanks were weighed before and after sampling with an analytical balance (AL-104IC, reading precision 10 μg). Before weighing, conditioning the filters at a temperature of (25 ±
2°C and a relative humidity of (45 ± 2)\% for 24 h. All the steps were strictly quality controlled to avoid sample contamination.

2.3. Analysis of carboneous aerosols
Mass loadings of OC and EC on the filter samples were analyzed using a RT-4 OCEC aerosol analyzer, following the IM-PROVE thermo/optical reflectance (TOR) protocol [24]. About 1.5 cm² punch aliquot of a sample quartz filter was heated gradually at different temperatures. The released carbon fraction at each temperature is oxidized to carbon dioxide (CO₂), then reduced to methane (CH₄) for quantification by flame ionization on detector. The detection limits for EC and OC are below 0.1 μg cm⁻².

2.4. Water-soluble ion analysis
Samples were analyzed for eight water-soluble ions, including NH₄⁺, Ca²⁺, K⁺, Mg²⁺, Na⁺, SO₄²⁻, NO₃⁻, and Cl⁻. 1/4 filter was extracted in 25 mL deionized water (18.2 MΩ·cm) for 30 min in a sonicating bath, then filtered through a syringe filter with a pore size of 0.45 μm. Cations were analyzed by ion chromatography (ICS 90, DIONEX Corporation), using an analytical column (CS12A) and a suppressor (CS-RS II) with MSA (22 mmol L⁻¹) as the eluent. The detection limits were 0.004, 0.008, 0.002, 0.002, and 0.002 mg L⁻¹, respectively. Anions were analyzed by an ion chromatograph (ICS 2000, DIONEX Corporation), using an analytical column (AS11-HC), and a suppressor (ASRS 300) with KOH (30 mmol L⁻¹) as the eluent. The detection limits were 0.02, 0.02, and 0.01 mg L⁻¹, respectively.

2.5. Element analysis
The sample filters were digested with concentrated nitric acid (ultra-pure) at 180 °C for 6 hours in a high-pressure Teflon digestion container with concentrated hydrofluoric acid (ultra-pure) and concentrated hydrogen peroxide (ultra-pure). 16 elements (Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Cd, Ba, Pb) in the samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, 7700x, Agilent Corporation). The detection limits for element analysis, when converted to atmospheric concentration in μg L⁻¹, were 0.004 (Na), 0.0003 (Mg), 0.0007 (Al), 0.01 (K), 0.048 (Ca), 0.001 (Cr), 0.0006 (Mn), 0.009 (Fe), 0.002 (Ni), 0.0004 (Cu), 0.001 (Zn), 0.0004 (As), 0.00004 (Sr), 0.00008 (Cd), 0.0002 (Ba) and 0.0002 (Pb). All standards and blanks were matched with samples in the same analysis process to calibrate the analysis results.

2.6. Data analysis
All obtained data were grouped with seasons. Further statistical analysis including average value, paired t-test, coefficient of divergence (CD) and linear fits were calculated in Microsoft Excel 2010 and STATISTICA[25].

3. Results and discussion

3.1. Concentration of PM₁.5 and meteorological data
Table 1 Comparison of annual mean concentration of PM₂.5 and meteorological data at sampling sites.

|          | IF(n=24)  | OF(n=24)  | IF/OF  |
|----------|-----------|-----------|--------|
|          | Mean      | S.D.      | Mean   | S.D.   |        |
| PM₁.5 (μg·m⁻³) | 112.1     | 75.26     | 57.56  | 39.84  | 1.95*  |
| Wind speed (m·s⁻¹)| 0.7       | 0.3       | 1      | 0.5    | 0.7*   |
| Temperature (°C) | 13.43     | 10.04     | 13.51  | 10.79  | 0.99   |
| Relative humidity (%) | 50.27     | 12.09     | 46.27  | 11.71  | 1.09*  |
| Pressure (kpa)    | 102.8     | 1.15      | 102.2  | 1.04   | 1.01*  |

*Denote the ratio has statistical significance at p<0.05
Table 1 presents the annual average concentrations of PM$_{2.5}$ and meteorological data at inside forest site (IF) and outside forest site (OF). The average concentration of PM$_{2.5}$ at IF site was 112.1 μg m$^{-3}$, which is higher than that (57.56 μg m$^{-3}$) at OF site. The mass differences between inside forest site (IF) and outside forest site (OF) were probably due to the differences in meteorological condition. The lower wind speed and higher relative humidity and pressure at IF were observed compared with those at OF, resulting in the PM$_{2.5}$ mass differences. Our results are in agreement with the findings from Sun et al. (2006) and Zhao et al. (2014) that PM$_{2.5}$ concentrations were positively correlated with relative humidity and strongly negatively correlated with wind speed [26-27].

3.2. Chemical species in PM$_{2.5}$
Table 2 lists the average concentrations of PM$_{2.5}$ and its chemical constituents by season at IF site. The differences in mean chemical composition between IF and OF sites are also shown in this table. At the both sites, the main contributors to PM$_{2.5}$ mass (generally>0.5μg m$^{-3}$) were OC, EC, NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, Na, Ca, K, Mg, Al, and Fe in every season [28]. OC was the most abundant species, ranging from 14.4% to 26.27% of the average seasonal mass at IF site, and 15.39% to 20.78% at OF site. While the sum of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ concentrations accounted for 18.8-36.66% of PM$_{2.5}$ mass concentration at IF site, and 16.09-29.46% of PM$_{2.5}$ mass concentration at OF site. PM$_{2.5}$ and its dominating chemical species (OC, EC, NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$) displayed strong seasonal variations with the highest values in winter or autumn and the lowest values in summer at both sites. In four seasons, the concentrations of PM$_{2.5}$ mass and dominant chemical components were higher at IF site than those at OF site. Furthermore, that concentrations of PM$_{2.5}$, OC, NO$_3^-$, SO$_4^{2-}$, NH$_4^+$ and K$^+$ at IF site were markedly higher according to the value of IF/OF (Table 2), which are 1.35-2.58 times, 1.51-3.22 times, 1.21-4.02 times, 1.28-3.07 times, 1.1-3.24 times and 1.04-3.64 times higher than those at OF site, respectively. This result might be explained by high biogenic VOC emission [15,29], high relative humidity in favor of the secondary aerosol formation [30] and poor diffusion condition against the air exchange in the forest compared with non-vegetated area. More detail analysis will be illustrated in the following sections.

Figure 2 measures the spread degree about the average concentrations of each chemical component at two sampling sites in different seasons using the coefficient of divergence (CD), a self-normalizing parameter:

$$CD_k = \sqrt{\frac{1}{p} \sum_{i=1}^{p} \frac{(x_{ij} - x_{ik})^2}{x_{ij} + x_{ik}}}$$

![Figure 2](image-url) Comparison of average concentrations of chemical components for PM$_{2.5}$ mass at IF and OF sites during winter (a), spring (b), summer (c), and autumn (d).

Where $j$ and $k$ stand for IF and OF sampling sites, $p$ is the number of studied components, and $x_{ij}$ and $x_{ik}$ represent the average mass concentrations of a chemical component $i$ at sites $j$ and $k$ [30-31].
The CD values were 0.33, 0.18, 0.27 and 0.1 for winter, spring, summer and autumn, respectively. Greater differences in the chemical composition between IF and OF sites in winter and summer were observed based on the values and scatter plots in Figure 2, which are likely due to lower wind speed in winter and summer resulting in the decreases of the air exchange and favored the accumulation of pollutants inside the forest. In addition, the deposition mass flow is lower as a result of low wind speed, reducing the effect of the particle removal through plants [32-33].

Table 2: Statistical summary of PM2.5 measurements (µg m⁻³) at IF site and the differences of mean chemical composition between IF and OF sites in different seasons.

|               | Winter (n=6) | Spring (n=6) | Summer (n=6) | Autumn (n=6) |
|---------------|-------------|--------------|--------------|--------------|
| **Mean**      |             |              |              |              |
| Mass          | 189.64      | 68.85        | 2.58*        | 109.34       | 33.79        | 2.03*        | 42.22        | 17.96        | 1.8*         | 107.24       | 69.05        | 1.35*        |
| OC            | 49.17       | 15.30        | 3.22*        | 15.75        | 1.48        | 1.9*         | 11.09        | 3.38         | 1.77*        | 19.95        | 4.11         | 1.51*        |
| EC            | 7.82        | 4.07         | 2.62*        | 2.75         | 0.66        | 1.61         | 1.68         | 1.17         | 1.79*        | 4.02         | 1.78         | 1.45         |
| NO₃⁻          | 24.7        | 12.82        | 4.02*        | 9.53         | 5.76        | 1.71*        | 2.18         | 0.69         | 2.09*        | 8.4          | 4.98         | 1.21*        |
| SO₄²⁻         | 31.3        | 15.68        | 3.07*        | 13.45        | 5.63        | 2.08*        | 4.54         | 3.2          | 2.41         | 12.85        | 6.49         | 1.28*        |
| Cl             | 3.6         | 1.81         | 2.03         | 0.94         | 0.91        | 1.71         | 0.22         | 0.18         | 1.57         | 1.71         | 1.48         | 1.1          |
| NH₄⁺          | 13.52       | 4.45         | 3.24*        | 6.00         | 3.35        | 1.79*        | 1.22         | 0.19         | 1.42*        | 7.12         | 6.68         | 1.1*         |
| Na⁺           | 1.10        | 0.19         | 2.56*        | 0.62         | 0.16        | 1.44*        | 0.061        | 0.022        | 1.42*        | 0.73         | 0.46         | 1.18         |
| K⁺            | 2.51        | 0.78         | 3.64*        | 0.92         | 0.41        | 1.96*        | 0.07         | 0.067        | 1.75*        | 1.2          | 1.1          | 1.04*        |
| Ca²⁺          | 1.49        | 0.49         | 1.34         | 2.42         | 2.07        | 1.1          | 0.15         | 0.087        | 1.15         | 1.89         | 0.58         | 1.15         |
| Mg²⁺          | 0.23        | 0.10         | 0.67         | 0.39         | 0.36        | 1.26         | 0.028        | 0.0019       | 1.45         | 0.33         | 0.095        | 1.38         |
| Na             | 1.03        | 0.58         | 0.91         | 1.4          | 0.49        | 1.23         | 0.91         | 0.31         | 1.2          | 1.7          | 0.4          | 0.99         |
| Mg             | 0.92        | 0.36         | 0.99         | 1.56         | 0.88        | 0.83         | 0.94         | 0.3          | 0.98         | 1.29         | 0.32         | 0.84         |
| Al             | 0.87        | 0.11         | 0.86         | 1.45         | 0.36        | 0.94         | 0.79         | 0.41         | 1.3          | 1.83         | 0.58         | 1.09         |
| K              | 1.28        | 0.61         | 1.39         | 1.53         | 0.65        | 1.47         | 1.03         | 0.47         | 1.47         | 1.95         | 1.3          | 1.2          |
| Ca             | 1.19        | 0.44         | 0.78         | 2.86         | 1.26        | 0.87         | 1.21         | 0.52         | 0.95         | 2.49         | 0.5          | 0.84         |
| Cr             | 0.057       | 0.055        | 0.59         | 0.056        | 0.042       | 0.78         | 0.11         | 0.089        | 2.89         | 0.075        | 0.042        | 1.39         |
| Mn             | 0.08        | 0.0095       | 1.7          | 0.08         | 0.032       | 1.14         | 0.08         | 0.07         | 4           | 0.063        | 0.04         | 1.07         |
| Fe             | 1.19        | 0.19         | 1.11         | 1.75         | 0.81        | 1.01         | 0.96         | 0.26         | 1.37         | 1.79         | 1.23         | 1.23         |
| Ni             | 0.0057      | 0.0038       | 0.25         | 0.038        | 0.031       | 1.06         | 0.041        | 0.04         | 4.3          | 0.011        | 0.0088       | 1.74         |
| Cu             | 0.026       | 0.0057       | 1.13         | 0.024        | 0.011       | 1.2          | 0.011        | 0.0065       | 2.24*        | 0.059        | 0.014        | 1.09         |
| Zn             | 0.46         | 0.15         | 1.35         | 0.27         | 0.097       | 1.17         | 0.17         | 0.056        | 1.55*        | 0.32         | 0.22         | 1.19*        |
| As             | 0.023       | 0.015        | 1.77         | 0.01         | 0.0064      | 1.43         | 0.0064       | 0.0038       | 1.52         | 0.0065       | 0.0054       | 1.18         |
| Sr             | 0.027       | 0.004        | 1.35         | 0.05         | 0.017       | 1.09         | 0.015        | 0.0058       | 1.5          | 0.022        | 0.0084       | 1.1          |
| Cd             | 0.0022      | 0.00059      | 1.69*        | 0.0016       | 0.00082     | 1.33         | 0.0005       | 0.00046      | 1.67         | 0.0019       | 0.00042      | 1.18         |
| Ba             | 0.048       | 0.0091       | 1.67         | 0.042        | 0.027       | 1.11         | 0.043        | 0.026        | 2.7          | 0.079        | 0.077        | 1.72         |
| Pb             | 0.2         | 0.072        | 1.81*        | 0.11         | 0.068       | 1.53         | 0.044        | 0.051        | 1.91         | 0.15         | 0.081        | 1.16         |

*Denote the ratio has statistical significance at p<0.05

3.3. Carbonaceous contents in PM2.5

Both sampling sites in Beijing Olympic Forest Park showed consistent seasonality in the concentrations of OC and EC (Figure 3). The lowest concentrations were observed in season and the highest concentrations were found in the wintertime. The lowest level of air pollution in the summer season was most likely due to the increased mixing depth [34] and more rainy days resulting in washing out the particulate matters in the atmosphere [35]. In addition, high proportion of coal burning for heating in winter could also increase the concentrations of OC and EC [36]. Comparisons of OC and EC concentrations, mass percentages in PM2.5, and OC/EC ratios between this study and other studies in Beijing are shown in Table 3. It has been seen clearly that mass percentages of OC in
PM$_{2.5}$ at IF site during winter and summer were higher or comparable with those in the other studies, while mass percentages of EC were the lowest among all those locations. This result suggests higher ratio of OC/EC was observed at IF site, which was likely due mainly to secondary organic aerosols (SOA) formation.

Figure 3. Seasonal mean concentrations of OC and EC in PM$_{2.5}$ and OC/EC ratios at IF site (a) and OF site (b).

| Location          | Period       | Concentration ($\mu$g m$^{-3}$) | Mass percentage (%) | OC/EC | References          |
|-------------------|--------------|----------------------------------|---------------------|-------|---------------------|
| Urban forest park (IF) | Winter 2014  | 49.17±15.3                       | 7.82±4.07           | 25.93 | 6.29                | This study |
|                   | Summer 2014  | 11.09±3.38                       | 1.68±1.17           | 26.27 | 3.98                |           |
| Semi-urban site   | Winter 2012  | 21.91±12.0                       | 5.03±2.58           | 24.16 | 5.55                |           |
| Urban site        | 2008         | 19.1                             | 8.45                | 17.37 | 7.68                |           |
| Rural site        | 2008         | 9.96                             | 4.52                | 16.07 | 7.29                |           |
| Urban sites       | Winter 2002  | 36.7±19.4                        | 15.2±11.1           | 26.7  | 10.6                |           |
|                   | Summer 2002  | 10.7±3.6                         | 5.7±2.9             | 12.2  | 6.2                 |           |
| Urban site        | Winter 1999  | 31.49                            | 11.08               | 17.9  | 6.3                 |           |
|                   | Summer 1999  | 13.42                            | 6.27                | 18.14 | 8.47                |           |

Table 3. Literature values of OC and EC for PM$_{2.5}$ in various areas of Beijing.

OC is comprised of primary and second source. Primary sources include combustions of fossil fuels and biomass. Gas-to-particle conversions and condensations of volatile organic compounds are considered as secondary source of OC [36]. Since EC is only formed through incomplete combustion of carbonaceous fuel and mostly inert in the atmosphere, it is usually used as a tracer of primary OC because of their typical emitting together [37-38]. Furthermore, OC-to-EC ratio has been used to determine the SOA presence when the ratio exceeds 2 [39]. In this study, the ratio ranged from 2.98 to 9.48 at IF site, from 2.7 to 7.04 at OF site, and the seasonal average ratios of OC/EC at both sites were all greater than 4 with higher ratios appearing at IF site (Figure 3). This result confirmed that one major source of OC inside the forest in Beijing Olympic Forest Park was SOA. A principle for estimating the second OC (SOC) is that EC-tracer method. The prime OC/EC (\((OC/EC)_{pri}\)) is considered to be the representative of a given area based on the fact that EC and primary OC, especially in fine particles, often have the same source. When the measured OC/EC in environmental aerosols is higher than \((OC/EC)_{pri}\), the extra OC is considered as secondary organic carbon [36]. Turpin and Huntzicker (1995) suggested an equation below to identify the SOC based on the hypothesis mentioned above:

\[
OC_{sec} = OC_{tot} - EC \times (OC/EC)_{pri}
\]

where \(OC_{sec}\) is the SOC, \(OC_{tot}\) is total OC, and the formula \(EC \times (OC/EC)_{pri}\) is used to [40].

Calculate the primary organic carbon \((OC_{pri})\). However, it is difficult to accurately estimate the ratio \((OC/EC)_{tot}\) for a given region. Since the ratio \((OC/EC)_{pri}\) varies with various sources and is affected by meteorological conditions, it is assumed that ratio is impacted by the diurnal and seasonal fluctuations [40]. Then an adjusted equation has been adopted to estimate \(OC_{pri}\) in some studies [35-36,39], the equation could be written as below:

\[
OC_{pri} = \frac{OC_{tot} - EC \times (OC/EC)_{tot}}{1 - EC \times (OC/EC)_{tot}}
\]
OC_{sec} = OC_{tot} - EC \times (OC/EC)_{min}, where (OC/EC)_{min} is the minimum ratio observed. This equation would be reasonable if the minimum ratios are stable and reproducible at various locations in different seasons. The (OC/EC)_{min} of 2.7 was observed in this study because lack of sun and unstable air mass could weaken the photochemical activity, leading to the minimal of SOC formation. The calculated average concentrations of SOC at both sampling sites in four seasons are given in Table 4. As the data indicated, SOC in Beijing Olympic Forest Park contributed to the total OC, accounting for mostly more than 40% with the maximum of 59.1%. SOC/OC exhibited a bimodal pattern with the highest in winter and the second mode in summer. The high SOC/OC values observed in summer may be due to the increase of oxidant levels, which enhances the in-situ photochemical formation of secondary organic aerosols [35]. However, in this case, the appearance of the winter maxima was contradictory in this context. This might be due to more emissions of semi-volatile organic compound and organic gas, as well as the lower mixing heights during winter allowing accumulation of SOA precursors and acceleration of SOA formation [37]. The higher SOC concentrations and mass percentages at IF site than those at OF site can also be seen in Table 4, which is mainly due to stronger photochemical activity and more VOC emissions inside of the forest.

**Table 4.** Values of secondary organic carbon (SOC) and organic matter (OM) percentages.

|          | IF                  |              |              |          |          |          |
|----------|---------------------|--------------|--------------|----------|----------|----------|
|          | SOC (μg m⁻³)        | SOC/OC (%)   | OM/PM₂.₅ (%) | SOC (μg m⁻³) | SOC/OC (%) | OM/PM₂.₅ (%) |
| Winter   | 28.06               | 57.06        | 41.48        | 7.22     | 47.31     | 33.25     |
| Spring   | 8.33                | 53           | 23.05        | 3.67     | 44.27     | 24.63     |
| Summer   | 6.55                | 59.1         | 42.03        | 2.22     | 46.64     | 32.41     |
| Autumn   | 6.61                | 45.59        | 29.77        | 2.93     | 43.51     | 26.58     |

Since the chemical composition of the organic fraction of PM₂.₅ is largely unknown, a method to estimate the mass concentrations of this portion is needed. According to Turpin and Lim, multiple factors OC-to-POM (particle organic matter) of 1.6 ± 0.2 for urban and 2.1 ± 0.2 for non-urban aerosols [41]. Tao et al. (2009) have regarded that conversion factors between 1.2 and 1.6 are generally used for urban aerosols [39]. In view of the above situation, we assumed that the conversion coefficient of OC-to-POM is relatively high, which is 1.6 for both sampling sites, since the objects we studied were urban forest aerosols. Hence, in this study, organic matter (OM) contributed 23.05% - 42.03% at IF site, and 24.63% - 33.25% for PM₂.₅ at OF site, during four seasons, as seen in Table 4.

### 3.4. Water-soluble ions in PM₂.₅

Mass percentages of each water-soluble ion for total ions at IF and OF sites in different seasons are shown in Figure 4. The gradient of ion species at IF site was: SO₄²⁻ > NO₃⁻ > NH₄⁺ > Ca²⁺ > Cl⁻ > K⁺ > Na⁺ > Mg²⁺ in spring and autumn; SO₄²⁻ > NO₃⁻ > NH₄⁺ > Cl⁻ > Ca²⁺ > K⁺ > Na⁺ > Mg²⁺ in summer; and SO₄²⁻ > NO₃⁻ > NH₄⁺ > Cl⁻ > K⁺ > Ca²⁺ > Na⁺ > Mg²⁺ in winter. SO₄²⁻, NO₃⁻ and NH₄⁺ were the dominant ion species, each season contributes 79.53-92.65% of the total mass of water-soluble ions. Similar situation was observed for OF site. Concentrations of the three major ions were much higher in winter than those in summer at both sites. High content of SO₄²⁻ in winter could be related to high concentrations of its precursor SO₂, which may be due to the increase of coal consumption and poor dispersion during heating period. The highest concentrations of NO₃⁻ observed in winter are mainly due to the low temperatures (<15 °C) favoring a shift from the gas phase as nitric acid (HNO₃) to the particle phase as ammonium nitrate (NH₄NO₃) [42]. At IF site, the sum concentrations of Na⁺, Mg²⁺, and Ca²⁺ were 2.82 in winter, 3.43 in spring, 0.24 in summer and 2.95 in autumn, with the highest concentration appearing in spring. The similar seasonal variation on sum of these three ions was observed at OF site. This spring peak is largely dependent on the crustal sources of the three ions (e.g. re-suspended road dust, soil dust, and construction dust) and the frequency dust events occurred in Beijing in this season. Cl⁻ is usually considered to be from coal combustion, and K⁺ is from biomass burning [19], thus the two ions showed higher concentrations in heating period at both sites.
The mass ratio of NO$_3$/$\text{SO}_4^{2-}$ could be used to analyze the relative importance of mobile vs. stationary sources of sulfur and nitrogen in the atmosphere \cite{32}. This ratio ranged from 0.48 to 0.79 at IF site, and 0.55 to 0.86 at OF site, with the mean value of 0.67 measured in different seasons, which matched the result studied by Wang et al. \cite{47}, suggesting that stationary sources were likely more important than mobile sources in Beijing Olympic Forest Park. Seasonal NO$_3$/$\text{SO}_4^{2-}$ showed the lower value in summer (0.55, 0.48) at IF and OF, compared with that in winter (0.79, 0.6), spring (0.71, 0.86) and autumn (0.65, 0.69).

### 3.5. Chemical elements in PM$_{2.5}$

The sources of elements in PM$_{2.5}$ were estimated according to the calculated enrichment factors (EF) shown in Table 5. Al is used as the reference of crustal sources and the crustal abundance of each element in China’s Environment Monitoring Station is adopted \cite{43}. EF is defined as $\text{EF} = (X/\text{Al})_{\text{aerosol}}/(X/\text{Al})_{\text{crust}}$, where $(X/\text{Al})_{\text{aerosol}}$ is the concentration ratio of X to Al in aerosol sample, and $(X/\text{Al})_{\text{crust}}$ is the average concentration ratio of X to Al in crust. Based on EF of each species, the 16 elements measured can be divided into crustal, pollutant, and mixed groups. The crustal group includes Al, Fe, Na, K, Mg, Ca, Mn, and Ba, of which the average enrichment factor of each element was below 10 \cite{44-45}. Concentrations of these crustal elements were higher in spring and autumn than those in winter and summer at both sites, as shown in Table 2. The pollutant group includes As, Zn, Pb, and Cd, of which the EF of each species was up to hundreds to thousands \cite{45}. High enrichment of these elements indicates that the main sources for these elements are non-crustal and various pollution emissions may lead to their loads in the ambient air, thus, obvious seasonal changes were observed in the pollutant group. All the pollutant elements in winter have the highest concentrations and in summer have the lowest values at both sites (Table 2), which may be explained by the more local sources of emissions, such as emission from the heating in winter, while less sources of emissions and better dispersion of the motor-vehicles emissions due to the high temperature. Table 5 clearly shows that the highest EFs of those pollution elements were in winter at the both sites, which further confirmed the serious air pollution in winter. Sr, Ni, Cr and Cu are defined as the mixed elements, as their EFs were within 100 and they show the characteristics of both crustal and pollutant species. Since As, Cr, Ni, Pb, and Cd have carcinogenic effects \cite{46-47}, these toxic elements should attract more attention. Annual mean concentrations of As, Cr, Ni, Pb, and Cd were 0.011, 0.075, 0.024, 0.13, and 0.0016 $\mu$g m$^{-3}$ at IF site, and 0.0074, 0.065, 0.014, 0.084, and 0.0011$\mu$g m$^{-3}$ at OF site, respectively, in which, except As and Cr, concentrations of the other elements were all less than WHO standard 0.025, 0.5, and 0.005 $\mu$g m$^{-3}$\cite{48}. The values of As at IF site and OF site were 1.67 and 1.12 times than WHO standard 0.0066 $\mu$g m$^{-3}$. Since only the standard value of Cr$^{6+}$ was formulated in WHO, the conversion factors 0.13 \cite{48} of Cr to Cr$^{6+}$ was used here, then the concentrations of Cr$^{6+}$ at IF and OF were 0.0096 and 0.0085 $\mu$g m$^{-3}$, respectively, much larger than WHO limit 0.00025 $\mu$g m$^{-3}$.

Nriagu and Davidson \cite{1986} illustrated that Cr likely reflects a variety of pollution sources \cite{49}, in particular coal combustion and sewage sludge incineration. The sources of As in Beijing were industry and motor vehicles emission \cite{47}. Since Beijing Olympic Forest Park is adjacent to Fifth Ring Road, one of the busiest roads in Beijing, the observed As is assumed to mainly originate from motor

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.png}
\caption{Percentage of water-soluble ions attributable to the total ions during different seasons at IF site (a) and OF site (b).}
\end{figure}
vehicles emission. Between the two sampling sites, there was no significant difference for pollution elements in PM$_{2.5}$ (two sample t-test, p>0.05), although slightly higher (13.3–41.67%) concentrations of As, Cr, Ni, Pb, and Cd at IF site than at OF site were observed during the whole sampling periods.

Table 5. Enrichment factors of elements in PM$_{2.5}$ in different seasons at IF and OF sites.

|        | Winter | Spring | Summer | Autumn | Winter | Spring | Summer | Autumn |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Fe     | 3.23   | 2.84   | 2.86   | 2.3    | 2.49   | 2.67   | 2.7    | 2.03   |
| Na     | 6.34   | 5.16   | 6.15   | 7.87   | 4.95   | 3.98   | 5.16   | 5.46   |
| K      | 5.35   | 3.83   | 4.72   | 3.86   | 3.29   | 2.45   | 2.08   | 3.51   |
| Mg     | 5.86   | 5.93   | 6.55   | 3.89   | 5.05   | 6.73   | 8.66   | 5.08   |
| Ca     | 6.33   | 9.09   | 7.04   | 6.25   | 6.94   | 9.85   | 9.65   | 8.15   |
| Mn     | 9.15   | 5.48   | 10.43  | 3.43   | 4.57   | 4.51   | 2.44   | 3.49   |
| Ba     | 7.59   | 3.82   | 7.08   | 5.68   | 3.9    | 3.25   | 3.78   | 3.57   |
| Sr     | 10.91  | 11.95  | 6.57   | 4.16   | 6.83   | 10.34  | 5.67   | 4.08   |
| Ni     | 15.76  | 56.35  | 123.19 | 15.29  | 55.5   | 46.09  | 36.75  | 9.93   |
| Cr     | 67.11  | 39.7   | 140    | 42.13  | 97.92  | 48     | 49.37  | 32.76  |
| Cu     | 90     | 49.09  | 41.62  | 95.71  | 68.2   | 38.47  | 23.67  | 94.5   |
| As     | 194.01 | 50.36  | 58.38  | 25.43  | 90.08  | 32.94  | 49.06  | 23.39  |
| Zn     | 361.61 | 128.92 | 142.29 | 111.74 | 226.35 | 100.87 | 120.06 | 108.53 |
| Pb     | 624.49 | 201.46 | 152.4  | 219.32 | 307.79 | 128.66 | 108.27 | 207.05 |
| Cd     | 1893.28| 298.79 | 580.11 | 1059.31| 1101.09| 200.79 | 403.89 | 996.23 |

3.6. Mass reconstruction

Figure 5. Mass reconstruction of chemical composition for PM$_{2.5}$ in different seasons at IF site (a) and OF site (b),

In this study, PM$_{2.5}$ can be divided into eight main components: organic matter, EC, nitrate, sulfate, ammonium, other ions, crustal matter and trace species (Figure 5). Four aggregate variables were calculated from determination of chemical species. The first was organic matter, and the related oxygen and hydrogen mass is estimated by multiplying the OC concentration by 1.6 [39-40]; the second, other ions, was calculated as the sum of Cl$^-$, Na$^+$, K$^+$, and Ca$^{2+}$; the third was crustal matter calculated as the sum of the oxides of Al, Fe, Ca, Mg[10]. The fourth was trace species calculated by summing up all the elements after subtracting the crustal matter mentioned above plus Mg$^{2+}$ [19]. The reconstructed chemical composition estimates the distribution of each component based on the average concentration of PM$_{2.5}$ mass at the both sites. Its contribution was comparable to or larger than that of the major water-soluble ions. The sum of the two components reconstructs mass concentration by 49.56-78.14% for PM$_{2.5}$ at IF site and 48.5-61.15% at OF site in different seasons. The crustal matter abundance averaged 4.49-30.76% in the PM$_{2.5}$ mass, which is also the major component at both sites. The lowest percentages of crustal matter appeared in winter period at both sites, although their concentrations were not the lowest, because the concentrations of total PM$_{2.5}$ in winter were much higher than the other seasons. In addition, the contributions of crustal matter were all lower at IF site than those at OF site in four seasons, as their concentrations were close between the two sites, while the concentrations of total PM$_{2.5}$ were higher at IF site. The unexplained portion averaged 6.83-25.98% and 0.34-12.81% of PM$_{2.5}$ mass at IF site and OF site, respectively. The larger range and higher average values of unexplained portion at IF site suggest that there may be more bound water in
gravimetric mass for PM$_{2.5}$ inside the forest compared to outside the forest during plants’ growing season [50].

4. Conclusion

Organic matter, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and crustal matter were the dominant components for PM$_{2.5}$. OC could account for the most of the total PM$_{2.5}$ mass concentration. OC and those three dominant ions showed obvious seasonal trend, with the highest concentrations in winter and the lowest values in summer. In contrast, the highest levels of most crustal elements were found in spring, and the highest levels of pollutant elements were observed in winter.

Forest belt had significant impacts on the chemical compositions of PM$_{2.5}$ in park. The measured OC was split into primary OC (POC) and second OC (SOC) counterparts following the EC tracer method. Concentrations of OC, SOC, as well as SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and K$^+$ in PM$_{2.5}$ inside of forest were markedly higher than those outside of forest. SOC inside of forest contributed to the total OC in a greater measure, which is mainly due to the stronger photochemical activity and more VOC emissions inside the forest.

Among these pollutant elements, annual mean concentrations of As and Cr exceeded WHO standard during monitoring period, which were consistent with previous studies [47-48,51].

Further work is required to analyze the organic compounds supposed to be secondary products and the extent of the atmospheric oxidation of volatile organic compounds into secondary products to confirm the characterization of PM$_{2.5}$ in urban forest air.

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