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Seasonal variation of urban carbonaceous aerosols in a typical city Nanjing in Yangtze River Delta, China



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HIGHLIGHTS

- The seasonal character of carbonaceous aerosols was provided.
- Emission sources were discussed as reasons for OC/EC seasonal variation.
- Biomass burning is one of the major contributors to both OC and EC.
- Meteorological condition affected SOC level and its contribution in OC.

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ABSTRACT

The Yangtze River Delta (YRD) is one of the regions with the most dynamic economy and severe atmospheric pollution in China. In order to characterize the particle features, especially the carbonaceous component in the YRD, particulate matter smaller than 2.5 μm ($\text{PM}_{2.5}$) and 10 μm (PM_{10}) samples in each season were collected in urban Nanjing, a typical city that locates in the west part of the YRD. The organic carbon (OC) and elemental carbon (EC) was differentiated using the thermal optical reflectance method. The average concentrations of $\text{PM}_{2.5}$, OC and EC during the study periods were observed to be 117.6, 13.8, and 5.3 $\mu\text{g}/\text{m}^3$ respectively, with all the highest levels in winter. The mass fraction of the Total carbonaceous aerosol (TCA) in $\text{PM}_{2.5}$ was estimated at 23% on average, lower than those reported for other cities in the YRD. The OC and EC correlated well in all the seasons, especially in spring and winter, implying that OC and EC were attributed to common emission sources. Good correlation was observed between OC and estimated K^+ from biomass burning in the harvest season in autumn and summer, indicating biomass burning a significant source of carbonaceous aerosols. This could also be confirmed by the lower fraction of $\text{OC}_3 + \text{OC}_4$ in OC during autumn and summer. The secondary organic carbon (SOC) estimated by EC-tracer method was the highest in winter (7.3 $\mu\text{g}/\text{m}^3$) followed by autumn (6.7 $\mu\text{g}/\text{m}^3$), summer (3.7 $\mu\text{g}/\text{m}^3$) and spring (2.0 $\mu\text{g}/\text{m}^3$). However, the SOC/OC in winter was not as high as that in summer and autumn, implying the high concentration of OC in winter was probably due to the stable weather but not mainly caused by SOC formation. The high SOC/OC ratio in summer was attributed to stronger oxidation, which could be suggested by higher sulfur oxidation ratio (SOR).

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1. Introduction

Carbonaceous aerosols, including organic carbon (OC) and elemental carbon (EC), come mainly from incomplete fuel combustion of industrial boilers/kilns and residential stoves, iron & steel production, and vehicles (Bond et al., 2007). Additionally secondary organic particle formation is also an important source of OC (Pandis et al., 1992; Turpin and Huntzicker, 1995). The adverse

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effect of carbonaceous aerosols on human health has been confirmed by epidemiological studies, by the increased morbidity and mortality of respiratory and cardiovascular diseases with the enhanced exposure to OC and EC (Valavanidis et al., 2008; Cao et al., 2012). Additionally EC has ineligious effect on regional and even global climate by influencing the precipitation and enhancing the green house effect (Menon et al., 2002; Jacobson, 2001).

The carbonaceous aerosols are one of the major pollutants in China (Wang and Hao, 2012; Zhang et al., 2012). In particular, Yangtze River Delta (YRD) in eastern China was one of the three regions (YRD, Beijing–Tianjin–Hebei and Pearl River Delta) suffering the highest particle concentrations and the longest pollution episodes (Wang et al., 2014). The total amount of OC and EC has been reported at 17.5–20.5 $\mu\text{g}/\text{m}^3$ and the total carbonaceous aerosol (TCA), i.e., sum of EC and organic matter (OM, calculated as $1.6 \times \text{OC}$) contributed about 30% of particulate matter smaller than 2.5 μm ($\text{PM}_{2.5}$) in Shanghai, the biggest city in the YRD (Feng et al., 2009). In Hangzhou, another big city in the YRD, the total amount of OC and EC was observed at 25.5 $\mu\text{g}/\text{m}^3$, about 28.5% of particulate matter smaller than 10 μm (PM_{10}) (Cao et al., 2009).

Located in the west part of the YRD, Nanjing (31°14'–32°37' N, 118°22'–119°14' E) is the capital city of Jiangsu province with the population of 8.2 million. Due to the high pollutant emissions (Qiu et al., in preparation) and the unfavorable terrain for pollutant diffusion, the city had haze days increased since 1980s and remained at a high level since 2001 (Cheng et al., 2013a). It is reported that Nanjing had 226 haze days in 2012 (data provided by Nanjing Meteorological Bureau), using the definition of haze day by Wu et al. (2012) (the meteorological optical range is less than 10 km while the daily average relative humidity is less than 90%, with precipitation and other occasions that may lead to low visibility excluded).

The purpose of this study is to assess the seasonal variation of the carbonaceous aerosols in urban Nanjing, representative for the pollution caused by industrial, transport, straw burning etc. in the YRD. There are some studies focusing on the particle mass and organic compounds in the city: Wang et al. (2003) and Wang and Kawamura (2005) have reported the levels of N-alkanes, PAHs,

and water soluble carbon in PM_{10} and $\text{PM}_{2.5}$ in Nanjing. Several researchers studied the particle mass and organic compounds during specific periods, e.g., straw burning seasons and haze episodes (Kang et al., 2013; Wang et al., 2009). Those studies, however, covered only specific periods, and the seasonal differences in the carbonaceous aerosols levels, carbon fractions and sources has not been fully evaluated. In particular, some other chemical indicators, e.g., K^+ and SO_4^{2-} , were seldom applied to help understanding the anthropogenic sources of carbonaceous aerosols in a complex pollution system. Moreover, the secondary organic aerosol (SOA) is the most uncertain and complicated part of particulate matter (PM), while its concentration levels and the reasons affecting the SOA formation in Nanjing have not been well investigated. It is thus important to analyze the seasonal characteristics of OC, EC, OC/EC ratios and secondary organic carbon (SOC) levels, for better understanding the sources, formation mechanisms, and control strategy of carbonaceous aerosols in the typical polluted city.

2. Methods

2.1. Sampling

As shown in Fig. 1, the sampling site is located in the western downtown of Nanjing, on top of the building of Jiangsu Provincial Academy of Environmental Science, 21 m above the ground. It is surrounded by residences, schools, offices and shops, with light traffic. The site is considered representing the pollution condition in the urban area, since it is just downwind of the dominant wind direction (east wind) and there is no obvious emission source nearby.

The 24-h $\text{PM}_{2.5}$ and PM_{10} samples were collected using a four-channel sampler at a rate of 16.7 l/min (TH-16A, Tianhong Company, Wuhan, China), using $\Phi 47$ mm Quartz and Teflon filters. The samples were collected for about 20 days in each season, i.e., autumn (Nov 10–28, 2011), spring (Mar 12–31, 2012), summer (Jun 11–28, 2012) and winter (Dec 5–19, 2013, Dec 24, 2013 and Jan 23–Feb 1, 2014, only $\text{PM}_{2.5}$ samples were collected). The meteorological data during sampling periods can be obtained from the National Climatic

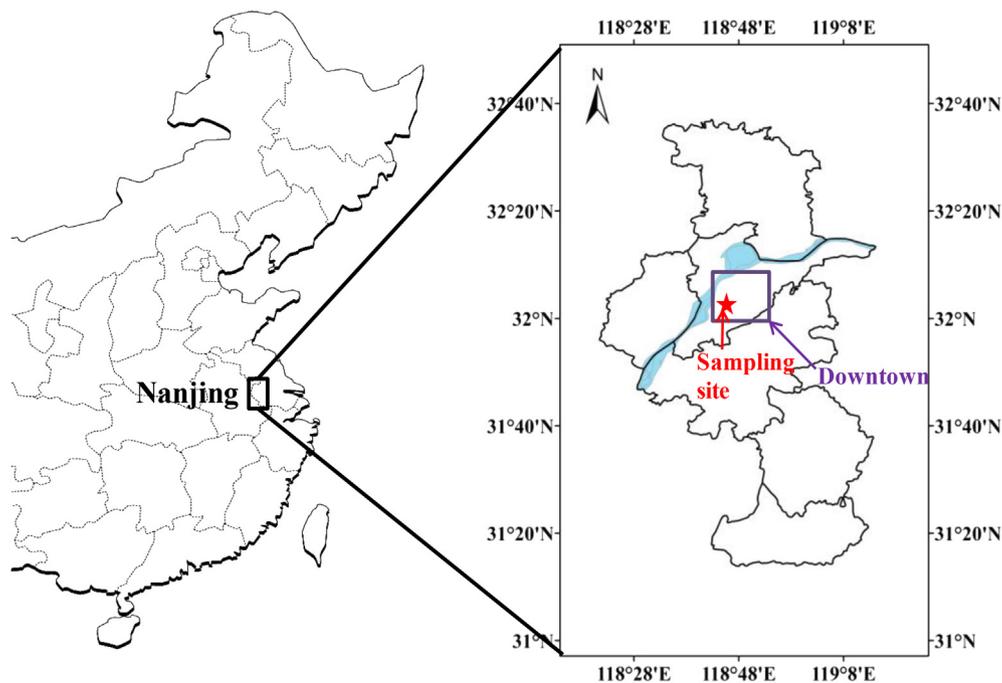


Fig. 1. Location of sampling site in Nanjing.

Data Center of National Oceanic and Atmospheric Administration (NOAA) (<http://www.ncdc.noaa.gov/cdo-web/>). The particle mass was measured by weighing the Teflon filters before and after sampling. The filters were weighed using a high precision digital balance (XP105DR, Mettler-Toledo, Switzerland). All the samples were stored under $-20\text{ }^{\circ}\text{C}$ for later chemical measurements.

The sampler flow rate calibration was done annually using multi-point verification method. The quartz filter was baked at $450\text{ }^{\circ}\text{C}$ for four hours before sampling to minimize the background of organic carbon.

2.2. Measurements

OC and EC collected by Quartz filter were analyzed with a DRI Model 2001 Thermal/Optical Carbon Analyzer, using the IMPROVE_A (Interagency Monitoring of Protected Visual Environments) protocol (Chow et al., 2001) to measure the carbon fractions. The quartz filter was heated stepwise to temperatures of $120\text{ }^{\circ}\text{C}$, $250\text{ }^{\circ}\text{C}$, $450\text{ }^{\circ}\text{C}$, and $550\text{ }^{\circ}\text{C}$ in a pure helium environment to determine OC1, OC2, OC3 and OC4 respectively. Then the environment was shifted to 2% $\text{O}_2/98\%$ He, and the filter continuously heated stepwise to $550\text{ }^{\circ}\text{C}$, $700\text{ }^{\circ}\text{C}$ and $800\text{ }^{\circ}\text{C}$ to determine EC1, EC2 and EC3 respectively. The pyrolysis OC (POC) is defined as the carbon combusted after the initial introduction of oxygen and before the laser reflectance signal achieves its original value (Chow and Watson, 2002) and the POC is assigned to the OC fraction. Therefore, OC is defined as $\text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{POC}$ and EC is defined as $\text{EC1} + \text{EC2} + \text{EC3} - \text{POC}$. For calibration and quality control, measurement with pre-fired filter blank, standard sucrose solution and replicate analysis were performed. Field blanks were collected in each season and the concentration levels of OC and EC were $0.8\text{--}0.9$ and $0\text{--}0.02\text{ }\mu\text{g}/\text{cm}^2$, less than 4% and 1% of the samples, respectively. The samples were corrected by the averaged concentration of the blanks. The detect limit for OC and EC is $0.45\text{ }\mu\text{g}/\text{cm}^2$ and $0.06\text{ }\mu\text{g}/\text{cm}^2$ respectively.

Besides OC and EC, certain other atmospheric chemical compositions were analyzed with various instruments, to provide further information on the sources and formation of carbonaceous aerosols. Water soluble inorganic ions (SO_4^{2-} and K^+) collected on the Teflon filters were analyzed by an Ion Chromatography (Dx-120, Dionex Ltd., USA). Element Fe was extracted using a microwave system (ETHOS, Milestone) and measured using an inductively coupled plasma-atomic emission spectrometer (ICPAES, Intrepid II, Thermo Electron). The concentrations of SO_4^{2-} , K^+ and Fe in field blanks consisted less than 3%, 7% and 1% of the samples, respectively. The detect limit for SO_4^{2-} , K^+ and Fe was 0.02, 0.05 and 0.2 ppm respectively. More detailed analytical procedure can be referred to Bi et al. (2007). The SO_2 concentration was measured and reported by Nanjing Environmental Monitoring Central Station

with Thermal Scientific 43i.

3. Results and discussion

3.1. OC and EC in $\text{PM}_{2.5}$ and PM_{10}

The seasonal averaged concentrations of particle mass, OC, EC, total carbon (TC), and TCA are summarized and listed in Table 1. The averaged $\text{PM}_{2.5}$ mass was 85.48, 77.46 and $95.70\text{ }\mu\text{g}/\text{m}^3$, contributing 64%, 74% and 71% of PM_{10} (132.74 , 104.15 and $134.03\text{ }\mu\text{g}/\text{m}^3$) for spring, summer and autumn, respectively. The concentrations of OC in $\text{PM}_{2.5}$ were 8.50, 7.57 and $15.72\text{ }\mu\text{g}/\text{m}^3$, accounting for 81%, 82% and 77% of that in PM_{10} in spring, summer and autumn, respectively, and the analogue numbers for EC (3.81, 3.09 and $5.90\text{ }\mu\text{g}/\text{m}^3$) were 82%, 86% and 86% in each season. The clear enrichment of carbonaceous composition in smaller particle size, particularly for EC, indicates the important roles of certain combustion sources of anthropogenic origin (e.g., diesel vehicles and biomass burning), from which OC and EC were confirmed to be concentrated in finer particles (Zhang et al., 2009; Li et al., 2007). Since the sampling site was located just downwind of the downtown, in particular, it can be influenced by the intensive vehicle emissions from downtown region.

As listed in Table 1, the mean concentrations of OC and EC had similar seasonal pattern as the $\text{PM}_{2.5}$ and PM_{10} , in the order of winter > autumn > spring > summer. The concentration of OC in $\text{PM}_{2.5}$ in winter was 2.7, 3.0 and 1.4 times the amount in spring, summer and autumn, respectively, and the analogue numbers for EC were 2.2, 2.7 and 1.4. An important reason for the high OC and EC concentrations in winter was probably the more stable atmospheric conditions attributed to lower wind speed and less precipitation. The wind directions and speeds in different seasons are shown in Fig. 2. The averaged wind speed in winter was 2.1 m/s, lower than 3.3, 3.1 and 2.5 m/s in spring, summer and autumn respectively. The precipitation in winter was also less than other seasons: the numbers of precipitation days during the sampling periods were 8 out of 20, 9 out of 20, 3 out of 19, and 3 out of 22 days for spring, summer, autumn and winter respectively. Besides meteorological conditions, other reasons for the seasonal difference such as emission sources and secondary organic aerosol (SOA) formation will be discussed later in Section 3.2 and 3.3, respectively.

Table 2 listed the averaged $\text{PM}_{2.5}$, OC, EC, TCA concentrations with the ratios of TCA/ $\text{PM}_{2.5}$ and OC/EC in Nanjing, compared with studies in YRD big cities as well as two mega cities in China, Beijing and Guangzhou. The $\text{PM}_{2.5}$, OC and EC concentrations were observed to increase in recent years compared to those in Yang et al. (2005): the $\text{PM}_{2.5}$ concentration increased by 104% and 200%, OC by 46% and 44%, and EC by 47% and 55% in autumn and

Table 1
Concentrations of particle mass, OC, EC, TC, TCA and the ratios of OC to EC in $\text{PM}_{2.5}$ and PM_{10} .

| | Season | PM mass | OC | EC | TC | OC/EC | TCA |
|-------------------|---------|------------------------------|--------------------------------|--------------------------------|--------------------------------|-----------------|------------------------------|
| | | ($\mu\text{g}/\text{m}^3$) | ($\mu\text{g C}/\text{m}^3$) | ($\mu\text{g C}/\text{m}^3$) | ($\mu\text{g C}/\text{m}^3$) | | ($\mu\text{g}/\text{m}^3$) |
| $\text{PM}_{2.5}$ | Spring | 85.48 ± 35.54 | 8.50 ± 4.12 | 3.81 ± 2.01 | 12.31 ± 6.08 | 2.34 ± 0.39 | 17.41 ± 8.55 |
| | Summer | 77.46 ± 36.16 | 7.57 ± 3.99 | 3.09 ± 1.40 | 10.66 ± 5.25 | 2.53 ± 0.68 | 15.20 ± 7.63 |
| | Autumn | 95.70 ± 32.60 | 15.72 ± 8.40 | 5.90 ± 2.49 | 21.62 ± 10.39 | 2.76 ± 0.87 | 31.05 ± 15.39 |
| | Winter | 201.14 ± 97.17 | 22.54 ± 9.63 | 8.24 ± 3.13 | 30.78 ± 12.54 | 2.74 ± 0.66 | 44.31 ± 18.30 |
| | Average | 117.58 ± 77.97 | 13.75 ± 9.32 | 5.32 ± 3.11 | 19.07 ± 12.24 | 2.59 ± 0.68 | 27.32 ± 17.81 |
| PM_{10} | Spring | 132.74 ± 51.30 | 10.52 ± 5.39 | 4.64 ± 2.73 | 15.16 ± 8.05 | 2.39 ± 0.43 | 21.47 ± 11.27 |
| | Summer | 104.15 ± 39.37 | 9.25 ± 4.64 | 3.61 ± 1.63 | 12.86 ± 6.08 | 2.66 ± 0.78 | 18.42 ± 8.84 |
| | Autumn | 134.03 ± 40.07 | 20.49 ± 9.63 | 6.89 ± 2.79 | 27.38 ± 11.81 | 3.09 ± 0.88 | 39.68 ± 17.53 |
| | Winter | NA | NA | NA | NA | NA | NA |
| | Average | 123.28 ± 45.48 | 13.18 ± 8.32 | 4.98 ± 2.75 | 18.16 ± 10.74 | 2.70 ± 0.76 | 26.07 ± 15.70 |

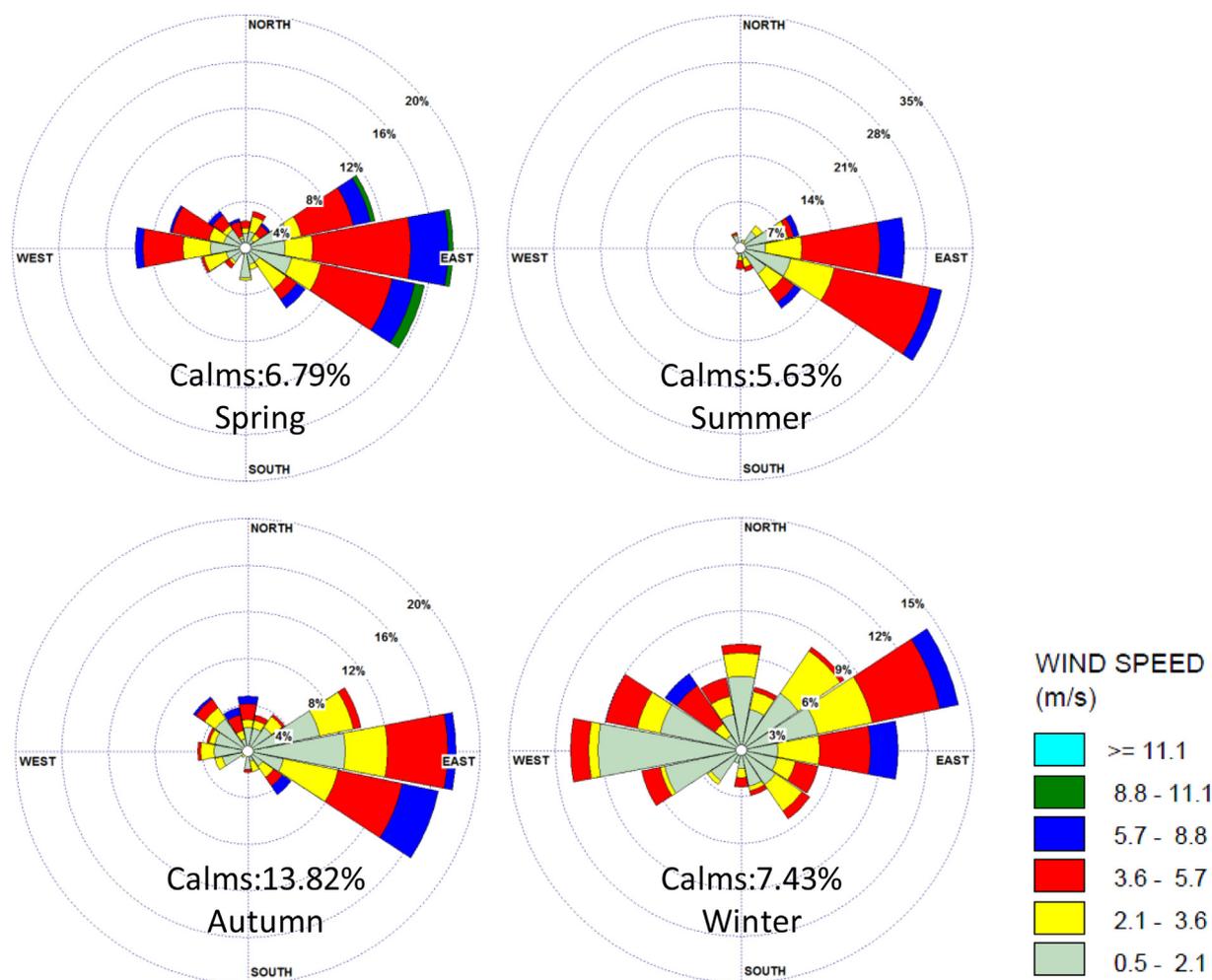


Fig. 2. Plot of wind rose in four seasons.

winter, respectively. The faster growth of $PM_{2.5}$ than OC or EC could be partly due to the increased construction sites area, which was 5,086, 11,247 and 12,016 ha in 2005, 2011 and 2012 respectively (Nanjing Bureau of Statistics, 2006, 2012, 2013). The annual averaged concentrations of OC and EC in Nanjing are lower than 42% and 17% of the YRD values cited here, respectively, and they are generally lower or comparable with the levels of Beijing and Guangzhou. The OC/EC ratio of Nanjing observed in this work ranged between 2.3 and 2.8 for all the seasons, with an average value of 2.6, smaller than 70% of the cited values in Table 2. The contribution of carbonaceous aerosols to $PM_{2.5}$ is relatively low in Nanjing; the fractions of TCA in $PM_{2.5}$ were 20%, 20%, 32% and 24% for spring, summer, autumn and winter respectively, lower than all the other results in the YRD. Generally, based on the chemical composition in $PM_{2.5}$ collected in spring, summer and autumn, the small percentage of carbonaceous aerosols in Nanjing is probably due to more soil dust (17% of $PM_{2.5}$ mass) than Shanghai (less than 3%) (Pathak et al., 2011), more water soluble ions (44% of $PM_{2.5}$ mass) than Hangzhou (32.9% of PM_{10} mass) (Cao et al., 2009) and more undefined matter (16%) than both Hangzhou (4% of PM_{10} mass) and Shanghai (less than 3%) (Pathak et al., 2011; Cao et al., 2009).

3.2. Seasonal variation trend of OC/EC

As shown in Fig. 3, good correlation was found between OC and

EC for all the seasons, with the highest correlation coefficients calculated for spring (0.97) and winter (0.91) respectively, suggesting the common emission sources of OC and EC. The largest OC to EC slope was estimated at 2.80 for winter, followed by 2.53, 2.47 and 1.97 for autumn, summer and spring, respectively. According to Table 1, the ambient OC to EC ratio (OC/EC) was higher in autumn (2.76) and winter (2.74) than that in summer (2.53) and spring (2.34), consistent with observation results conducted in other cities across the country. Feng et al. (2009) reported OC/EC of $PM_{2.5}$ in winter was about two times higher than summer in Shanghai. Gu et al. (2010) also found the highest OC/EC in winter in Tianjin. The higher OC/EC in autumn and winter is probably due to 1) relatively stable atmospheric conditions, which provided longer residence time for the photochemical reaction, as well as the lower temperature which enhanced condensation of volatile SOA (Cao et al., 2007; Li and Bai, 2009); and 2) varied emission patterns by sector. For example, the small residential stoves for heating could enhance coal and other fossil fuel consumption in autumn and winter, although the seasonal usage of fossil fuels has not been officially recorded yet. Those sources would generate a higher OC to EC emission ratio (2.7) compared to big industrial boilers (0.4), iron and steel plants (0.9), or cement kilns (2.5), based on updated emission inventory results in China (Lu et al., 2011; Lei et al., 2011; Zhao et al., 2013, 2014). Regarding transportation, the diesel vehicles, which dominate the emissions of carbonaceous aerosols, were estimated to have 7.6 times more OC under 30 °F than that at 70 °F,

Table 2
Comparison of PM_{2.5}, OC, EC and OC/EC between different cities.

| City | PM _{2.5} (μg/m ³) | OC (μg C/m ³) | EC (μg C/m ³) | OC/EC | TCA | TCA/PM _{2.5} | Reference |
|---------------------|--|------------------------------|------------------------------|-------|------|-----------------------|---------------------|
| YRD | | | | | | | |
| Nanjing | 117.6 | 13.8 | 5.3 | 2.6 | 27.3 | 0.23 | This study |
| Nanjing (Winter) | 67.1 | 15.6 | 3.3 | 4.7 | 28.3 | 0.42 | Yang et al., 2005 |
| Nanjing (Autumn) | 46.9 | 10.8 | 4.01 | 2.7 | 21.3 | 0.45 | Yang et al., 2005 |
| Shanghai | 40.3 | 6.8 | 1.86 | 3.9 | 12.7 | 0.32 | Cao et al., 2013 |
| Shanghai | 67.0 | 16.9 | 10.0 | 1.7 | 37.0 | 0.55 | Pathak et al., 2011 |
| Shanghai (Spring) | 47.3 | 8.4 | 3.7 | 2.5 | 17.1 | 0.36 | Hou et al., 2011 |
| Shanghai (Summer) | 15.1 | 3.8 | 1.1 | 3.5 | 7.2 | 0.48 | Hou et al., 2011 |
| Shanghai (Autumn) | 36.1 | 6.5 | 2.1 | 3.2 | 12.5 | 0.35 | Hou et al., 2011 |
| Shanghai (Winter) | 65.4 | 10.9 | 4.4 | 2.2 | 21.8 | 0.33 | Hou et al., 2011 |
| Shanghai (Winter) | 151.1 | 28.6 | 8.3 | 3.9 | 54.1 | 0.36 | Cao et al., 2007 |
| Shanghai (Summer) | 52.2 | 13.3 | 2.9 | 5.2 | 24.2 | 0.46 | Cao et al., 2007 |
| Hangzhou (Winter) | 168.6 | 30.6 | 9.3 | 3.3 | 58.3 | 0.35 | Cao et al., 2007 |
| Hangzhou (Summer) | 90.6 | 17.1 | 3.6 | 5.2 | 31.0 | 0.34 | Cao et al., 2007 |
| Other cities | | | | | | | |
| Beijing | 68.0 | 8.2 | 4.9 | 2.2 | 18.0 | 0.27 | Pathak et al., 2011 |
| Beijing (Winter) | 126.5 | 27.2 | 7.1 | 3.7 | 50.6 | 0.40 | Cao et al., 2007 |
| Beijing (Summer) | 117.2 | 17.2 | 4.6 | 4.4 | 32.1 | 0.27 | Cao et al., 2007 |
| Guangzhou | 59.0 | 14.9 | 10.5 | 1.6 | 34.3 | 0.58 | Pathak et al., 2011 |
| Guangzhou (Winter) | 156.0 | 41.1 | 14.5 | 2.8 | 80.3 | 0.51 | Cao et al., 2007 |
| Guangzhou (Summer) | 49.1 | 10.6 | 3.2 | 3.6 | 20.2 | 0.41 | Cao et al., 2007 |

while the EC emissions were similar under the two circumstances (Zielinska et al., 2012). In harvest seasons, moreover, ambient OC/EC could also be enhanced by increased biomass burning, the ratios of which were measured at 5 and 12 for wheat and maize straw burning in China, respectively (Li et al., 2007). It can be confirmed through the association between OC and typical biomass burning tracer, as discussed below.

Since the sampling period in November (autumn) and June (summer) was in crops harvest and the straw burning period (Qu et al., 2012), large contribution from straw burning to ambient carbonaceous aerosols can be expected, and it can be estimated through the relationship between OC and K⁺, an important composition from biomass burning. However, K⁺ has multiple sources (e.g. soil, sea salt, coal fire and industry), and thus complicates the carbonaceous aerosols contribution estimation. In order to minimize the influence of other sources of K⁺, a method for estimating K⁺ from biomass burning has been developed by Pachon et al. (2013), based on the regression analysis between K⁺ and other species which shares similar sources with K⁺ except biomass burning. The improved method is followed in this work and K⁺ from biomass burning is calculated using the following equation (Pachon et al., 2013):

$$K_{\text{biomass burning}}^+ = K^+ - 0.37 \times [\text{Fe}] \quad (1)$$

Where K_{biomass burning}⁺ is the concentration of potassium ion from biomass burning, K⁺ is the measured concentration of potassium ion, and [Fe] is the concentration of iron. The K_{biomass burning}⁺ in spring was calculated at 0.22 μg/m³, 57% lower than that in summer and autumn, suggesting less contribution from biomass burning in spring. It has to be noted that the OC contributed by biomass burning does not include SOA, which is formed by the oxidation of VOCs emitted from biomass burning. The correlation between OC and K_{biomass burning}⁺ is illustrated in Fig. 4. The correlation factors were 0.88 and 0.95 for summer and autumn respectively, larger than the value of 0.64 in spring. The good correlation indicated the biomass burning to be an important source of OC. By detecting OC, EC and other compositions variation with a high resolution aerosol mass spectrometer (AMS) and a single particle soot photometer (SP2) during summer and winter campaign, Huang et al. (2013) also

concluded that biomass burning was a significant source of atmospheric OC and EC in another city Jiaxing in the YRD. The OC contributed by biomass burning observed by Cheng et al. (2014a) was 71%, higher than that in our study, probably because our study covered a longer period and included sampling days with less biomass burning.

The percentage of OC contributed by biomass burning can be roughly calculated by Eq. (2) (Zheng et al., 2005).

$$\text{OC}\% = \frac{\left(\text{OC}/K_{\text{biomass burning}}^+\right)_{\text{slope}} \times K_{\text{biomass burning}}^+}{\text{OC}} \times 100\% \quad (2)$$

The OC percentages from biomass burning were calculated at 38%, 58% and 47% for spring, summer and autumn respectively, confirming the biomass burning a dominant source of the OC in the two seasons.

Besides K⁺, levoglucosan can also be used as tracer of biomass burning. K⁺ has been observed to be comparable with levoglucosan during straw residual burning period (Cheng et al., 2013b; Viana et al., 2008), whereas the K⁺ showed non-linear relationship with levoglucosan in some occasions due to additional K⁺ sources (Cheng et al., 2013b). Indicated by larger correlation coefficient between levoglucosan and K_{biomass burning}⁺ than that between levoglucosan and total K⁺ based on observation at a typical downtown site in the United States, the method we adopted in this work was believed to better separate biomass burning from soil dust and vehicle emissions (Pachon et al., 2013). However, the local sources and emission characteristics of K⁺ could be different in the YRD, and uncertainty might exist in estimation of K_{biomass burning}⁺ for Nanjing. Therefore the estimation of OC contributed from biomass burning needs to be improved in the future once more information of specific biomass burning tracers (e.g., levoglucosan) gets available for the YRD.

It can be inferred, therefore, that prohibiting straw open burning in the harvest season is the priority for carbonaceous aerosols control in Nanjing, and this action could be expected to decrease the OC by a half (Qu et al., 2012). Eliminating the small residential stoves for heating in autumn could also benefit, since the residential coal combustion have OC and EC emission factors 174 to

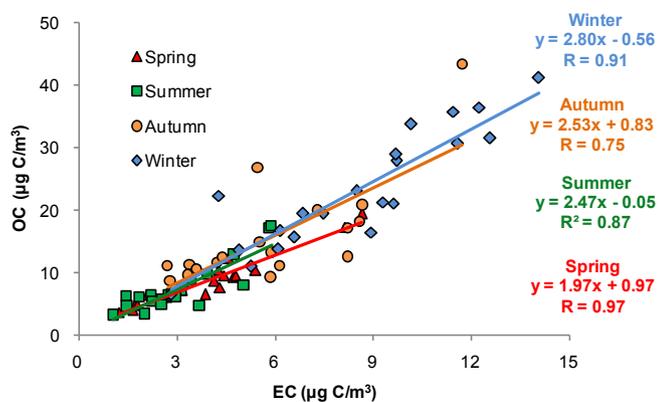


Fig. 3. Correlation between EC and OC in different seasons.

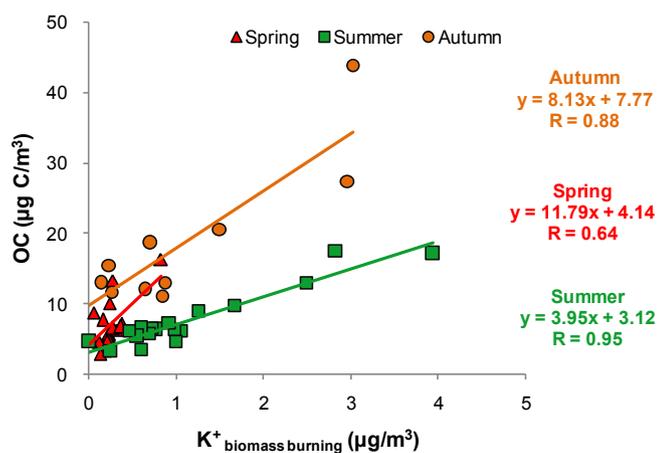


Fig. 4. Correlation between OC and K^+ biomass burning in autumn and summer.

1567 times more than that for industrial combustors (Zhang et al., 2008). Therefore, the central heating should be considered to reduce the carbonaceous aerosol emissions from small and inefficient coal and biofuel stoves.

3.3. SOA of $PM_{2.5}$

The concentration of secondary organic carbon (SOC) was estimated using EC-tracer method (Snyder et al., 2009). We assumed that the non-combustion particle OC was negligible (Castro et al., 1999; Duan et al., 2005). Moreover, the primary OC to EC ratio, $(OC/EC)_{\text{primary}}$, was simplified as the smallest ratio of particle OC to EC in each season, representing primary OC and EC emissions. The values of SOC and OC in each sampling day are shown in Fig. 5.

The order of averaged SOC was winter ($7.3 \mu\text{g}/\text{m}^3$) > autumn ($6.7 \mu\text{g}/\text{m}^3$) > summer ($3.7 \mu\text{g}/\text{m}^3$) > spring ($2.0 \mu\text{g}/\text{m}^3$), while that of SOC/OC was summer (0.46) > autumn (0.39) > winter (0.30) > spring (0.25). The SOC/OC in Nanjing was comparable with Shanghai (e.g., 0.41–0.495 in summer, Pathak et al., 2011; Hou et al., 2011); and the seasonal pattern of SOC/OC in Nanjing was consistent with other YRD cities where higher ratios were also found in summer than other seasons (Hou et al., 2011; Cao et al., 2007). The lower SOC/OC in winter and spring resulted partly from the higher $(OC/EC)_{\text{primary}}$ (1.85 for winter and 1.70 for spring) than that in summer (1.27) or autumn (1.53) from observation. As indicated in Section 3.2, relatively large OC emissions would be expected from small residential stoves and diesel vehicles in cold seasons.

Dynamic oxidation process is another important factor determining the SOC formation level. With similar formation pathway (e.g., aqueous-phase reaction) as water soluble OC, an indicator for SOA formation, particulate SO_4^{2-} was used to represent secondary aerosol formation (Cheng et al., 2014b; Zhou et al., 2012). The magnitude of secondary SO_4^{2-} formation could be quantified by the sulfur oxidation ratio (SOR), which was higher when more gaseous species become oxidized (Sun et al., 2006). Yang et al. (2012) compared SOR and SOA formation levels indicated by acetic to formic acid ratio at two different sites, and revealed that higher SOR occurred with stronger SOA formation. Thus they implied that SOR can be applied to indicate SOA level to some extent. The SOR can be calculated with Eq. (3) as below:

$$\text{SOR} = n\text{SO}_4^{2-} / (n\text{SO}_4^{2-} + n\text{SO}_2) \quad (3)$$

where n is the molar concentration.

In this work the SOR was calculated at 0.21, 0.31 and 0.31 for spring, summer and autumn respectively, consistent with lower SOC/OC in spring, as shown in Fig. 5. The results confirmed the stronger oxidation in summer and autumn. However, SOR did not have synchronized variation trend with SOC or SOC/OC, indicating the complex of SOC and/or sulfate formation. The aqueous-phase transformation of SO_2 to sulfate mainly includes several pathways of reactions with O_3 , H_2O_2 and O_2 catalyzed by metals. Those reactions can be influenced by factors that have little association with SOC, e.g., SO_2 concentration (Voutsas et al., 2014). Thus unsynchronized trend of SOR and SOC could be induced.

The ratio of SOC/OC during polluted days was relatively higher. During Dec 5–8, 2013 and Jan 27–31, 2014, the averaged $PM_{2.5}$ concentration was $258.4 \mu\text{g}/\text{m}^3$, significantly higher than the averaged $PM_{2.5}$ ($161.5 \mu\text{g}/\text{m}^3$) in the rest sampling days in winter. Meanwhile the averaged SOC concentration and the SOC/OC during the polluted days was $11 \mu\text{g}/\text{m}^3$ and 0.40 respectively, larger than the averaged concentration and ratio ($4.7 \mu\text{g}/\text{m}^3$ and 0.23) of the rest sampling period, respectively. Similar trend has been observed during spring (Mar 26–30, 2012), summer (June 11–13, 2012) and autumn (Nov 10–14 and Nov 25–28, 2011), when the SOC concentration during the polluted days were 3.6 , 8.9 and $9.9 \mu\text{g}/\text{m}^3$, higher than the value of 1.5 , 2.7 and $4.1 \mu\text{g}/\text{m}^3$ for the rest of each sampling periods. At the same time, the SOC/OC ratios during polluted days were 0.27, 0.56 and 0.42 respectively for spring, summer and autumn respectively, which were higher than the ratio of 0.25, 0.44 and 0.36 for the rest of the sampling periods. The results indicate that the formation of SOA could be an important reason for severe hazy pollution, and it can be supported by the campaign for four mega-cities during the haze event across the country in Jan 2013 (Huang et al., 2014).

3.4. Carbon fractions characteristics

The concentrations and seasonal variation of carbon fractions in $PM_{2.5}$ and PM_{10} has been studied. Although the carbon fractions are operationally defined, different evaporation/oxidation temperature represents their unique characteristics, which can help to identify the source or to tell the different feature of the particles in each season. The carbon fractions in $PM_{2.5}$ in each season have been plotted in Fig. 6, in which the EC1 has been adjusted by subtracting POC from the original EC1.

The most abundant carbon fractions were EC1 and OC3, followed by OC4 and OC2. The amount of EC2 and EC3 was limited, with no EC3 observed in summer. POC was detected only in several samples in each season. The relatively high averaged POC value in winter and autumn was due to two or three extremely polluted day

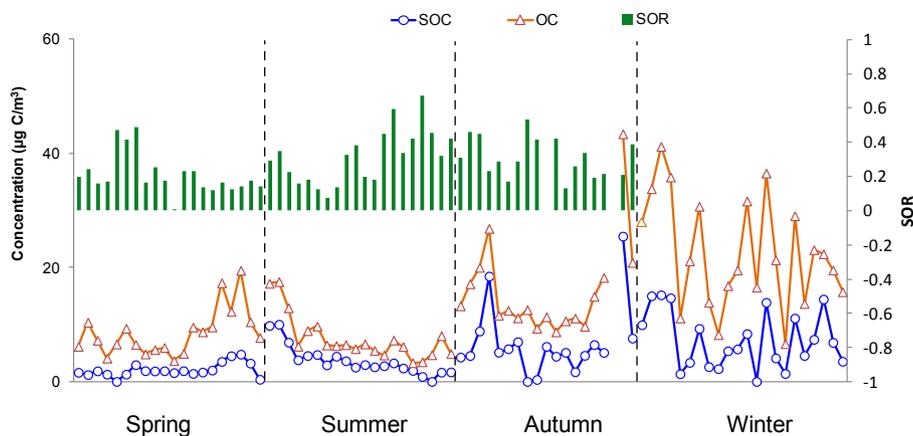


Fig. 5. Daily SOC and OC concentrations, and SOR estimated with Eq. (3) by season. Every dot and column represent a single sampling day.

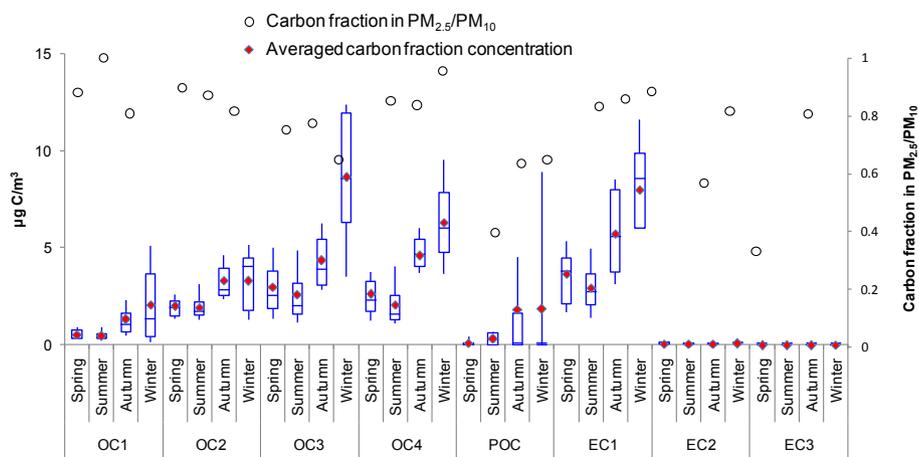


Fig. 6. Carbonaceous fractions concentration and ratio in $PM_{2.5}/PM_{10}$ in each season. The red diamond is the averaged concentration of carbon fractions. The blue box indicates the median, with percent 25% and 75%. The blue line indicates percent 10% and 90%. The black circle is the ratio of carbon fractions in $PM_{2.5}/PM_{10}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in autumn and winter.

Since OC1 and OC2 evaporate at the temperature less than 250 °C, they are usually identified as volatile and semi-volatile (Duan et al., 2012). The fractions of OC1 + OC2 in OC were 31%, 33%, 30% and 24% for spring, summer, autumn and winter respectively, indicating lower percentage of volatile and semi-volatile substances in winter. The fraction of OC3 + OC4 in OC in autumn (58%) and summer (63%) was lower than spring (68%) and winter (67%). Because OC3 and OC4 were related to road dust emissions (Chow et al., 2004), this lower ratio in autumn and summer was in accordance with larger effects of biomass burning.

The ratio of each carbon fraction in $PM_{2.5}$ to that of PM_{10} has also been illustrated in Fig. 6. This ratio was higher than 80% for OC1, OC2, OC4 and EC1, indicating the carbon fractions were mainly concentrated in $PM_{2.5}$. The ratio for OC3 was lower than 80% for all the studied seasons (60%, 75% and 77% in autumn, spring and summer respectively), indicating that OC3 was distributed more on coarser particles. This bi-mode distribution of OC3 has also been reported by Duan et al. (2012), in which the OC3 in the fine mode was probably emitted from combustion sources and the OC3 in the coarse mode could come from the grinding of biomass debris.

The carbon fractions of EC could be used to explore the contribution of combustion sources in Nanjing. Char-EC and soot-EC are defined as EC1 and EC2 + EC3 respectively (Han et al., 2010). Char-

EC represents carbon emitted from pyrolysis or partially burned residue, while soot-EC from by high temperature burning process. The char-EC and soot-EC in this study were lower than those observed in Xi'an (Han et al., 2010) or Beijing (Duan et al., 2012). Moreover, the ratio of char-EC/soot-EC in Nanjing was 36, 32, 64 and 84 for spring, summer, autumn and winter respectively, much higher than the ratios in Xi'an (2.17–6.69) (Han et al., 2010) or Daihai (0.91–2.72) (Han et al., 2008), but close to the results by Duan et al. (2012) in Beijing (35–52). The EC concentration in Nanjing was 5.3 $\mu\text{g}/\text{m}^3$ on average, which was lower than other big cities (e.g., 22.3 $\mu\text{g}/\text{m}^3$ in Beijing, Duan et al., 2012, and 8.41 $\mu\text{g}/\text{m}^3$ in Xi'an, Han et al., 2010). However the incomplete combustion at relatively lower temperature or biomass burning contributed the dominant part of EC in Nanjing. This result was consistent with the correlation analysis of OC and K^+ , implying biomass burning is an important source of carbonaceous aerosol in Nanjing, and was also consistent with higher char-EC/soot-EC ratio during winter with lower environment temperature.

4. Conclusion

Carbonaceous aerosols in ambient $PM_{2.5}$ and PM_{10} were collected and characterized for four seasons in Nanjing, a city in the west part of Yangtze River delta with serious haze pollution

problem. The concentrations of OC, EC and PM_{2.5} were found to be higher in winter and lower in summer. The concentration of TCA was comparable with other cities in YRD, but the TCA/PM_{2.5} was relatively low. Common sources of OC and EC were indicated for the city by good correlation with each other. The seasonal pattern of OC and EC depended largely on variation of emission sources and weather condition. In particular, biomass burning was one of the most important sources of carbonaceous aerosols during harvest season, although Nanjing is an industrialized city. It could be confirmed by good correlation between OC and K⁺_{biomass burning}, as well as relatively low level of OC3 and OC4. The SOC contributed to OC from 25% to 46% for different seasons, with higher fractions during haze days. Higher SOC/OC and SOR were found in summer resulting from stronger atmospheric oxidation, while the absolute SOC concentration was the highest in winter, indicating meteorological condition played an important role in pollutants accumulation. In order to improve the contribution of biomass burning to carbonaceous aerosols, specific tracing compounds needs to be further investigated in the future work. Better understanding of char-EC formation and its source contribution is of great interest to evaluate the primary sources of carbonaceous aerosols in the YRD.

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