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# A two-year study of carbonaceous aerosols in ambient $PM_{2.5}$ at a regional background site for western Yangtze River Delta, China

Dong Chen [a], Hongfei Cui [a], Yu Zhao [a,b,*], Lina Yin [a], Yan Lu [a], Qingeng Wang [a,b]

[a] State Key Laboratory of Pollution Control & Resource Reuse and School of the Environment, Nanjing University, 163 Xianlin Ave., Nanjing, Jiangsu 210023, China
[b] Jiangsu Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (CICAEET), Nanjing University of Information Science & Technology, Jiangsu 210044, China

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ABSTRACT

To analyze the characteristics of regional background carbonaceous aerosols in western Yangtze River Delta (YRD), hourly organic carbon (OC) and elemental carbon (EC) in fine particular matter ($PM_{2.5}$) were measured with a semi-continuous carbon analyzer at a suburban site in upwind Nanjing from June 2013 to May 2015. Relatively low OC, EC and OC/EC were observed compared to other studies conducted in Nanjing. The reasons include the limited primary emissions around the observation site, the improved emission controls in recent years, and the use of denuder to reduce positive artifact in OC measurement. Resulting from the stable atmosphere conditions and emission variations, the highest concentrations of carbonaceous aerosols were found in both winters, with average OC and EC observed at 11.8 ± 10.0 and 5.9 ± 3.4 μg/m$^3$ for the first one, and 8.1 ± 5 and 4.5 ± 2.4 μg/m$^3$ for the second one, respectively. Compared to 2013, reduced OC and EC were found in summer and autumn 2014, demonstrating the benefits of emission control polices implemented for the Nanjing Youth Olympic, while elevated OC observed in spring 2015 was attributed probably to the increased biomass burning. For the hazy event in winter 2013, the back trajectories of air masses suggested that heavy pollution were from eastern Jiangsu, northern Anhui and Jiangsu, downtown Nanjing, and Shanghai. Secondary aerosol formation played an important role indicated by the larger mass fraction of OC and increased OC/EC in $PM_{2.5}$ during the heavy pollution period. In the harvest season, biomass burning was estimated to contribute 51% and 16% of OC and EC concentrations, respectively.



## 1. Introduction

As a main component of $PM_{2.5}$ (particles with aerodynamic diameters <2.5 μm), carbonaceous aerosols including organic carbon (OC), elemental carbon (EC) and carbonate (CC) (Birch and Cary, 1996; Chow et al., 2001) play vital roles in visibility, radiative forcing and human health (Wilson and Spengler, 1996). EC (sometimes referred to as black carbon, BC) originates mainly from incomplete combustion of biomass and fossil fuels, and is an important factor in climate studies for its optical characteristic of solar radiation absorption (Bond and Bergstrom, 2006). OC contains hundreds of individual organic compounds and it typically comprises 10–50% of ambient $PM_{2.5}$ mass (Seinfeld and Pandis, 1998). OC comes both directly from combustion sources (described as primary organic carbon, POC) and chemical reactions in which gaseous volatile organic compounds (VOCs) are converted to pollutants in the particle phase (described as secondary organic carbon, SOC). Attributed only to local source, CC is much smaller in the mass fraction (Chow et al., 2005).

Relatively high concentrations of OC and EC were found in China for decades (Novakov et al., 2005; Cui et al., 2015). Located in eastern China, Yangtze River Delta (YRD) is one of the country's regions with the most developed city cluster and the heaviest air pollution (Yao et al., 2002; Chan and Yao, 2008). A series of field measurements on ambient carbonaceous aerosols were conducted in YRD cities including Shanghai (Feng et al., 2009; Zhao et al., 2015a; Wang et al., 2015a), Hangzhou (Cao et al., 2009) and Nanjing (Zhuang et al., 2014; Li et al., 2015; Wang et al., 2015b). Most previous studies, however, were based on filter-sampling and off-line measurement without diurnal variations, and missed information of dynamic evolution processes of carbonaceous aerosols within one day (Hu et al., 2012). In addition, current measurements in YRD regions were conducted mainly in urban areas or downwind from cities, and the results could be largely influenced by local sources (Yang et al., 2005a, 2005b; Zhang et al., 2011; Li et al., 2015). The knowledge on regional background of carbonaceous aerosols for YRD, which is important for understanding the impacts of emissions

* Corresponding author at: State Key Laboratory of Pollution Control & Resource Reuse and School of the Environment, Nanjing University, 163 Xianlin Ave., Nanjing, Jiangsu 210023, China.
*E-mail address:* yuzhao@nju.edu.cn (Y. Zhao).

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on regional air quality, is still lacking. Recently, series of measures on emission abatement and pollution control have been conducted in YRD cities (Zhao et al., 2015b), while their effects on ambient OC and EC have seldom been analyzed. In this case, long-term observation with high temporal resolution is necessary in the region to explore the characteristics and sources of ambient carbonaceous aerosols and to reflect the influence of emission controls on those aerosols, for the period with pollution control gradually implemented.

In this work, therefore, we conducted a more than two-year observation on hourly concentrations of ambient OC and EC in Nanjing, the capital city of Jiangsu province located in the western YRD (Fig. S1a in the supplement), to improve the understanding of the sources and formation of OC and EC in fine particles, and to indicate the effectiveness of local and regional PM controls in YRD. Nanjing is the second largest city in central east China following Shanghai, with a total area of 6587 $km^2$ and population of 8 million in 2012 (NJNBS, 2013). Coal is the dominant pollution source in Nanjing, and the heavy industries including coal-fired power, cement, steel and refinery plants accounted for 96% of the city's total coal consumption (Zhao et al., 2015b). Traffic is another important anthropogenic source due to the rapid growth in vehicle population since 2010 (Qiu, 2015), and the number reached 1.7 million in 2014 (NJNBS, 2015). It was the first time that real-time measurement based on thermal-optical method was applied at a site that can be representative for regional background of YRD (Ding et al., 2013). Inter-annual and seasonal of OC and EC were characterized at the site. The contributions of SOC formation to $PM_{2.5}$ were investigated with EC-tracer method. The influence of given anthropogenic sources on carbonaceous aerosols were further evaluated combining other air quality and meteorology information.

## 2. Methods

### 2.1. Site description

As shown in Fig. S1a, ambient OC and EC were measured at a suburban site in the Xianlin Campus of Nanjing University in northeast Nanjing, roughly 20 km away from downtown (118°57′10″E, 32°07′14″N, NJU site). The site is set at the roof of the School of the Environment building (about 30 m above the ground level), and is about 300 m away from the G25 highway. Shown in Fig. S2 in the supplement are the precipitation and temperature data collected from Jiangsu Provincial Meteorological Bureau (data source: http://www.jsmb.gov.cn), and Fig. S3 the monthly wind data measured at NJU site (note data were missed at the end of 2014 and the first half of 2015 due to instrument malfunction). Given the prevailing winds from southeast and northeast, the site is located upwind Nanjing with limited effects of the local emissions in the downtown. Besides the site is downwind of the most developed YRD region including the mega city Shanghai and the Suzhou–Wuxi–Changzhou city cluster (Fig. S1b-d), thus it is representative for the regional level of western YRD (Ding et al., 2013).

Due to the technical problems of the instruments at NJU site, other species in the atmosphere including ozone ($O_3$), carbon monoxide (CO), sulfur dioxide ($SO_2$), nitrogen dioxide ($NO_2$), $PM_{2.5}$ and $PM_{10}$ were routinely measured and reported at a state-operated monitoring site (Xianlin site), 4.5 km west from the NJU site (Fig. S1a). To evaluate the observation discrepancies at two sites, available simultaneous measurements on $PM_{2.5}$ mass concentrations at the two sites were collected and compared for July-Oct 2014 and Dec 2014, as shown in the Fig. S4. The hourly $PM_{2.5}$ concentrations were satisfyingly consistent with each other, and high correlation coefficients were calculated for both periods. Given the relatively close distance between the two sites, therefore, we assume that there was no significant difference in the air quality between NJU and Xianlin site, and the data at Xianlin sites could then be applied as an approximation for NJU.

### 2.2. OC and EC measurement

The OC and EC measurement was conducted continuously for two years from June 2013 to May 2015, covering summer: June–August of 2013 and 2014; autumn: September–November of 2013 and 2014; winter: December to February of 2013, 2014 and 2015; spring: March–May of 2014 and 2015. We refer the period of June 2013–May 2014 and that of June 2014–May 2015 as the first and the second year, respectively.

Hourly ambient concentrations of OC and EC in $PM_{2.5}$ were sampled and measured by semi-continuous carbon analyzer (Model-4, Sunset Lab, USA). The analyzer applies the thermal-optical transmittance (TOT) method and uses a modified protocol of the National Institute of Occupational Safety and Healthy (NIOSH 5040) as its default protocol. The airborne particles are first inhaled into a $PM_{2.5}$ cyclone at a flow rate of 8.0 l/min, with the collection time set at 40 min for each cycle. $PM_{2.5}$ then passes through a carbon impregnated multichannel parallel-plate diffusion denuder which removes the gas-phase organic compounds that may transform to solid-phase organic carbon to increase the positive artifact (Turpin et al., 2000). OC and EC were collected on two quartz filters to save the losing gas-phase organic compounds that originate from solid-phase under the destruction of gas-solid equilibrium (Huebert and Charlson, 2000; Cheng et al., 2009; Cheng et al., 2010). $PM_{2.5}$ on the filters were then analyzed following the NIOSH protocol and TOT method for carbon factions, including four OC fractions in a helium atmosphere and six EC fractions in a 2% oxygen/98% helium atmosphere. The correction for the pyrolyzed carbon (PC) converted from OC to EC was performed by monitoring the transmittance of a pulsed He-Ne diode laser beam at 660 nm through the quartz fiber filter during the sample analysis. At last, all the carbon components (OC and EC) were converted to $CO_2$ and detected with a non dispersive infrared (NDIR) absorption $CO_2$ sensor. OC and EC were automatically quantified by dividing their peak areas by the internal calibration peak made by methane gas (5% $CH_4$ in He). The resultant OC was the sum of OC fractions and PC, and EC was defined as EC fractions minus PC. The details of quality control and assurance are described in the supplement. In addition to thermal EC, an optical measurement of EC was also provided by the Sunset analyzer. The optical EC is calculated using the light attenuation (ATN) through the quartz filter monitored throughout the sampling time. The optical OC is calculated by subtracting optical EC from TC. However, to our knowledge, the light attenuation is not only caused by EC but also by brown carbon (BrC), and the optical EC may overestimate the true value. Thus the thermal EC and OC were applied to this study.

The original hourly OC and EC concentrations were judged according to the data before and after the moment. Outliers of OC and EC were excluded when it was ten times higher than the nearest two time points. Moreover, the averaged OC positive artifact in this study (0.89 μgC/$m^3$) was at the similar level with that by Lin et al. (2009) (0.94 μgC/$m^3$). The detection limit for OC and EC of the instrument were 2.0 μgC/$m^3$ and 0.5 μgC/$m^3$ according to Lin et al. (2009), thus the measured OC and EC concentrations lower than the detection limit were screened out in this study. Totally ~14,834 h of OC and EC valid data were available after screening.

In order to investigate the influence of sampling and analytical methods on results, 16 off-line daily $PM_{2.5}$ samples were collected using a four-channel sampler (TH-16 A, Tianhong Company, Wuhan, China) during March 5–23 in 2015, and were analyzed using the same protocol as the on-line measurement. In addition, 36 off-line $PM_{2.5}$ samples were collected in summer (August 13–September 4, 2013), winter (December 26–29, 2013), and spring (April 18–May 1, 2014) using TH-16 A, and were analyzed using a DRI Model 2001 Thermal/Optical Carbon Analyzer. The analyzer applies thermal-optical reflectance (TOR) method under Interagency Monitoring of Protected Visual Environments (IMPROVE_A) protocol (Chow et al., 2001). The results are compared with those from on-line measurements.