Characteristics of atmospheric organic and elemental carbon aerosols in urban Beijing, China

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HIGHLIGHTS

- Semi-continuous measurements of carbonaceous aerosols were obtained in Beijing.
- Seasonal, weekly and diurnal variations of OC and EC are reported.
- Clean energy strategies resulted in an effective reduction of OC and EC.
- High SOC concentrations were observed in autumn and winter.
- Biomass burning emissions accounted for 18.4% of OC.

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ABSTRACT

Organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ were measured hourly with a semicontinuous thermal-optical analyzer in urban Beijing, China, from Mar 1, 2013 to Feb 28, 2014. The annual mean concentrations of OC and EC in Beijing were 14.0 ± 11.7 and 4.1 ± 3.2 $\mu g/m^3$, respectively. The concentrations observed in this study were lower than those of other reports over the past ten years; however, the concentrations were higher than those reported from most of the megacities in North America and Europe. These findings suggest that OC and EC remained at high levels despite the implementation of strict control measures to improve air quality. The OC and EC concentrations exhibited strong seasonality, with high values in the autumn and winter but low values in the spring and summer in Beijing. The diurnal OC and EC cycles were characterized by higher values at night and in the morning because of primary emissions, accumulations and low boundary-layer heights. Due to increasing photochemical activity, a well-defined OC peak was observed at approximately noon. The OC and EC concentrations followed typical lognormal patterns in which more than 75% of the OC samples had concentrations between 0.9 and 18.0 $\mu g/m^3$ and 75% of the EC samples had concentrations between 0.4 and 5.6 $\mu g/m^3$. An EC tracer method and combined EC tracer and K^+ mass balance methods were used to estimate the contributions from secondary formation and biomass burning, respectively. High secondary organic carbon (SOC) concentrations were found in the autumn and winter due to low temperatures, which are favorable for the absorption and condensation of semi-volatile organic compounds on existing particles. High correlations were found between the estimated SOC in $PM_{2.5}$ and the observed OOA (oxidized organic aerosol) in PM_1; thus, the method proved to be effective and reliable. The annual average $OC_{Biomass\ burning}$ (OC_{bb}) contribution to the total OC concentration was 18.4%, suggesting that biomass burning is a substantial pollution factor in Beijing.

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1. Introduction

Carbonaceous aerosols are of increasing concern because of their complex impacts on human health, the environment and

climate change (IPCC AR5, 2013; World Health Organization, 2000; Duan et al., 2005; Cao et al., 2003). Despite the importance of carbonaceous aerosols in atmospheric chemistry, physics and climate change, it is challenging to characterize the complex nature of carbonaceous aerosols based on measurements (Hand et al., 2013). Carbonaceous aerosols, containing different and unidentified compounds, are typically divided into OC (organic carbon) and EC (elemental carbon) (Turpin et al., 2000). The classification of OC and EC is empirical and highly method-dependent, and their differentiation is still not clear. Among the commonly accepted OC/EC determination methods, the thermal-optical analysis (TOA) method is one of the most well-known methods (Zhang et al., 2012). The widely used TOA methods include the National Institute of Occupational Safety and Health (NIOSH) thermal-optical transmission (TOT) (Birch and Cary, 1996) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal-optical reflectance (TOR) (Chow et al., 1993) protocols. In using the thermal-optical transmission method, a semi-continuous TOA analyzer is advantageous compared with an off-line one because the former provides a high sampling resolution. More importantly, the semi-continuous TOA analyzer makes it possible to capture detailed fluctuations in OC and EC emissions, understand the sources and processes affecting the evolution of OC and EC, assess the impact of human activity on atmospheric environment and recognize their atmospheric transport/transformation mechanisms.

The Beijing-Tianjin-Hebei (BTH) region is one of the most developed city clusters in China. It is located in northern China and is heavily influenced by anthropogenic emission. A series of studies on carbonaceous aerosol was carried out, and high concentrations were typically recorded in the BTH region, particularly in Beijing (Ji et al., 2014; Cheng et al., 2013; Andersson et al., 2015). However, most of the studies on OC and EC were carried out over short periods or during air pollution episodes, which do not fully reflect the long-term temporal characteristics of OC and EC. Moreover, most of the previous studies were based on filter sampling with a low time resolution and were therefore susceptible to filter-sampling artifacts, and few previous studies have been carried out with high temporal resolutions and one-year study periods (Lin et al., 2009; Zhao et al., 2013). Therefore, high time-resolved, continuous, *in situ* measurements are required to study aerosol evolution and transport, understand the sources and processes affecting the evolution of carbonaceous aerosol components and explore primary emissions and secondary formation. In addition, a quantitative understanding of the variations in Beijing is vital for constraining the role of carbonaceous aerosols in global climate models because Beijing is located in a large source area in northern China (Han et al., 2009; Bond et al., 2013).

The Strategic Priority Research Program of Formation, Mechanism and Control Strategies of Haze in China was initiated by the Chinese Academy of Sciences in Dec 2012, and both OC and EC were observed by the semi-continuous Sunset OC/EC instrument from Mar 1, 2013 to Feb 28, 2014. It was the first time that hourly averaged time-resolution concentrations of OC and EC in Beijing were measured for one year after the 2008 Olympic Games. Energy structure and policy changed substantially in Beijing (http://www.bjstats.gov.cn/sjfb/bssj/tjnj/) since the 2008 Olympic Games. In this study, the OC and EC levels in PM$_{2.5}$ were observed at an urban site in Beijing, which represents a typical urban city in the BTH region. The OC and EC pollution characteristics and their seasonal and diurnal variations are presented. Frequency and probability distributions of OC and EC are studied. The OC and EC relationship is explored. In addition, this study also reports the sources of carbonaceous aerosols based on an EC tracer method and a combined EC tracer with K$^+$ mass balance method. The results would distinguish

and quantify the contributions of primary, secondary and biomass burning sources to carbonaceous aerosol.

2. Description of experiment

2.1. Measurement site

The sampling site (39°58′28″ N, 116°22′16″ E) was located between North 3rd Ring Road and North 4th Ring Road (Fig. 1). The site is approximately 1 km from the 3rd Ring Road, 200 m west of the G6 Highway (which runs north-south) and 50 m south of Beitucheng West Road (which runs east-west). The annual average vehicular speeds in the morning and evening traffic peaks were 27.4 and 24.3 km/h, respectively. No industrial sources were located in the vicinity of the sampling site. The experimental campaign was launched from Mar 1, 2013 to Feb 28, 2014.

2.2. Instrumentation

The OC and EC levels in PM$_{2.5}$ were measured with a thermal optical transmission OC/EC analyzer (RT-4, Sunset Laboratory Inc. Oregon, USA). An inline parallel carbon denuder that removes volatile organic gases was installed on the analyzer. Aerosol particles were collected on a round 16-mm quartz filter with a sampling flow rate of 8 L/m. After 30 min of collection, the oven of the instrument was purged with helium and the temperature was increased in multiple programmed steps based on the selected thermal protocol. Particulate organic carbon was then thermally volatilized and oxidized to carbon dioxide (CO$_2$), which was quantified using a non-dispersive infrared (NDIR) detector. The oven was cooled prior to the second part of the analysis, when the oven was purged with a mixture of 5% oxygen in helium; the sample was again heated incrementally. During this stage, all of the remaining carbon on the filter, including elemental carbon, was oxidized to CO$_2$, which was detected using the NDIR. Each analytical process was performed in approximately 15 min. For charring correction a He–Ne laser beam monitored the sample transmittance throughout the heating process. When the laser signal returned to its initial value, the split point between OC and EC was determined (Birch and Cary, 1996). The standard procedure for calibrating was conducted as recommended by Sunset Laboratory Inc. The quartz fiber filters used for sample collection were changed every 5 days, always before the laser correction factor dropped below 0.90. Calibration with an instrument blank was conducted every 5 days. The analyzer was automatically calibrated at the end of every analysis by injecting an internal standard CH$_4$ mixture (5.0%; ultra-high purity He balance). A further off-line calibration was conducted at the beginning and the end of each campaign with an external source of sucrose standard (86 μg). The uncertainty of the TC measurement was estimated to be approximately 7% as determined by the standard error of the sucrose calibration and the routine methane calibration (Han et al., 2009). Uncertainties of the EC-to-OC split, which may depend on the temperature protocols, can lead to additional errors (Boparai et al., 2008).

PM$_{2.5}$ was determined with a synchronized hybrid ambient real-time particulate monitor (SHARP 5030, Thermo-Fisher Scientific, MA, USA), which is a US EPA Federal Equivalent Method analyzer. The accuracy of the measurements was ±5% for 24 h. Calibration and glass fiber filter tape changes were performed every 6 months.

Organic aerosols were measured with an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, DeCarlo et al., 2006). At the beginning, middle and end of the field campaign, the ionization efficiency, inlet flow and particle sizing of HR-ToF-AMS were calibrated following standard protocols (Jimenez et al., 2003; Drewnick et al., 2005). Positive matrix factorization