Characterization of Atmospheric Organic and Elemental Carbon of PM$_{2.5}$ in a Typical Semi-Arid Area of Northeastern China

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ABSTRACT

In the spring of 2006, daily particulate matter (PM$_{2.5}$) aerosol samples were collected in Tongyu, a semi-arid area in northeastern China. The concentrations of organic carbon (OC) and elemental carbon (EC) were determined with a thermal/optical carbon analyzer in the filter samples. The average concentrations of OC and EC in PM$_{2.5}$ were 14.1 ± 8.7 and 2.0 ± 1.3 μg/m^3, respectively. A good correlation between OC and EC was observed during the spring season, suggesting that they might be derived from similar sources. The correlation between OC and K$^+$ was high (R = 0.74), and the K$^+$/OC ratio, as determined from their linear regression slope, reached 2.57. The good correlation and high K$^+$/OC ratio indicated that biomass-burning was probably one of the major sources of OC in this region. The concentrations of estimated secondary organic carbon (SOC) in PM$_{2.5}$ in Tongyu ranged from below the detection limit to 26.1 μg/m^3 (mean, 5.9 μg/m^3). The percentages of SOC in OC and in PM$_{2.5}$ mass were 42.0% and 2.1%, respectively. The SOC concentrations during dust storm (DS) periods were higher than those during non-dust storm (NDS) ones, suggesting that chemical reaction processes involving gas-particle conversion occurred during the long-distance transport of aerosol particles.

Keywords: Semi-arid area; Organic carbon; Elemental carbon; Dust storm.

INTRODUCTION

Carbonaceous materials, including organic carbon (OC) and elemental carbon (EC), are major components of ambient aerosols in urban and rural atmospheres (He *et al*., 2001; Wang *et al*., 2001; Cao *et al*., 2004; Duan *et al*, 2005; Chen and Yu, 2007) and play important roles on radiative transfer, health effects, and atmospheric chemistry (Andreae, 1983; Crutzen and Andreae, 1990; Menon *et al*., 2002; Wu *et al*., 2004; Zhang *et al*., 2009). For example, EC may be the second most important component (after CO$_2$) of global warming in terms of directly affecting global warming trends (Jacobson, 2002) and OC might cause mutagenic and carcinogenic effects due to its polycyclic aromatic hydrocarbons components. The major sources of EC are incomplete burning of biomasses and fossil fuels (Cao *et al*.,

2003) while OC can be directly emitted from sources or produced from chemical reactions involving gaseous organic precursors (Pandis *et al*., 1992; Shen *et al*., 2007).

Asian dusts are referred to mineral dust originated from hyper-arid, arid and semi-arid lands located in the northwest and northern China, southern Mongolia, and eastern Russia (Wang *et al*., 2000; Zhou and Zhang, 2003; Fan and Wang, 2004; Huang *et al*., 2006a; Shen *et al*., 2006; Fan and Wang, 2007; Shen *et al*., 2009; Huang *et al*., 2012). Due to human activities, desert areas in China have expanded to 1.61 × 10^6 km^2, accounting for 16.7% of the total landmass in China (Yuan *et al*., 2006). Long-range transport of Asian dust is one of the important sources of atmospheric aerosols in the downwind regions, particularly during the dust seasons. Asian dusts can influence ecosystems, environments, and climates (Sokolik and Toon, 1996; Sokolik *et al*., 2001; Han *et al*., 2004; Cao *et al*., 2005; Huang *et al*., 2006b, 2008). Some Asian dust may settle on the ocean's surface and provide nutrients (e.g., Fe^{2+}) to the oceanic biosphere (Zhuang *et al*., 1992). Some investigations have also reported that soil dusts were mixed with anthropogenic materials

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even in arid and semi-arid regions, and were then transport to downwind areas (Alfaro *et al.*, 2003; Arimoto *et al.*, 2004; Shen *et al.*, 2007).

Air pollution in Asia has increased significantly at the regional, continental, and global scales during the past several decades. Carbonaceous aerosols contributed 20–50% to the total aerosol mass from urban to regional scales in China (He *et al.*, 2001; Cao *et al.*, 2003; Lee *et al.*, 2006; Cao *et al.*, 2007). The mass fraction of organic aerosols ranged from 10–70% in fine modes (Andrews *et al.*, 2000). To develop emission control measures, there is a need to better understand the contributions of carbonaceous aerosols to the total aerosol mass and to identify the sources of the aerosols. Although many studies on carbonaceous aerosols have been undertaken recently in China, especially in urban areas (He *et al.*, 2001; Cao *et al.*, 2003; Ho *et al.*, 2006; Cao *et al.*, 2007; Duan *et al.*, 2007; Zhang *et al.*, 2007), studies in semi-arid regions are still very limited (Shen *et al.*, 2007).

In the present study OC and EC data collected in a spring season in a semi-arid area in northeastern China has been analyzed. The objectives of this study are (1) to investigate the compositions and sources of carbonaceous aerosols in fine particles and to evaluate the OC and EC fractions during dust storm events (DS) and Non dust storm periods (NDS); (2) to investigate daily variations of highly absorbing aerosols (EC and dust) and OC; (3) to identify the transport pathways and possible sources for the carbonaceous aerosols during NDS; and (4) to estimate SOC with respect to transport time and direction in this region during the spring period.

DATA SAMPLING AND ANALYSIS

Sampling Sites and Sample Collection

The sampling site was located in a rural area (Xinhua's town area) of Tongyu (44°25'N, 122°52'E, 184 m above sea level), Jilin Province (Liu *et al.*, 2008; Zhang *et al.*, 2008; Shen *et al.*, 2011). This area is located on the east margin of Horqin sand land (one of the four largest sand-lands in Northern China). The population of Tongyu is 362,500 and the annual precipitation in this area is 332.4 mm. There were no major industrial activities surrounding the sampling location. Coal and wheat and/or maize stalks were used for cooking and heating (from Nov to late April).

A frmOMNI™ Ambient Air Sampler (BGI Incorporated, USA, www.bgiusa.com) was used to collect $PM_{2.5}$ samples with a flow rate of 5 L/min. The sampler was set up on grassland about 3 m above the ground level. The sampler was equipped with a solar power battery to avoid power failure. Samples were collected daily from 14 April to 23 June 2006. Each sample lasted 24-h period from 08:00 a.m. any day to 08:00 a.m. the next day. A total of 53 aerosol samples were collected during the spring of 2006.

24-h $PM_{2.5}$ samples were collected on 47-mm Whatman quartz microfiber filters (QM/A). The filters were pre-heated at 800°C for 3 h prior to sampling to remove organic artifacts or impurities. The exposed filters were placed in petri dishes which were wrapped with aluminum foil and then placed in zip lock bags. All samples were stored in a refrigerator at about 4°C until chemical analysis was conducted to prevent the evaporation of volatile components. Field blank filters were also collected to subtract the positive artifacts due to the absorption of gas-phase organic components onto the filter during and/or after sampling. However, negative artifacts from the volatilization of particle-phase organics from particle samples were not quantified in this study due to our limited resources.

Mass Analysis

The aerosol mass concentrations were determined gravimetrically using a Sartorius MC5 electronic microbalance with 1-μg sensitivity (Sartorius, Göttingen, Germany) at the Institute of Earth Environment, Chinese Academy of Sciences. Before weighed, the quartz filters were equilibrated for 24 h at a constant temperature of 23°C and a relative humidity between 35% and 45%. Each filter was weighed at least three times before and after the sampling by a 24-h equilibration. The mean net mass for each filter was obtained by averaging the mass differences between the pre- and the post-weighting data. The precision of the weighing process was < 10 μg for the blank filters and < 20 μg for the filter samples. Therefore, the precision of weight measurements should be 20 μg for filter samples.

Carbonaceous Aerosol Analysis

The OC/EC concentrations were analyzed using DRI Model 2001 (Thermal/Optical Carbon Analyzer). The IMPROVE_A thermal/optical reflectance (TOR) protocol (Chow *et al.*, 1993, 2001, 2004b) was used for the carbon analysis. The protocol heats a 0.526-cm^2 punch aliquot of a sample quartz filter stepwise at temperatures of 140°C (OC1), 280°C (OC2), 480°C (OC3), and 580°C (OC4) in a non-oxidizing helium (He) atmosphere. Ramping to the next temperature or atmosphere begins when the flame ionization detector (FID) response returns to baseline or a constant value – subject to the condition that the time spent in any segment (OC1, OC2, etc.). When this condition has been reached in the OC4 segment, the 2% O$_2$/98% He atmosphere is introduced and peaks are integrated at 580°C (EC1), 740°C (EC2), and 840°C (EC3). The carbon that evaporates at each temperature is oxidized into carbon dioxide (CO$_2$), then reduced to methane (CH$_4$) for quantification with a flame ionization detector. As the temperature increases in the inert helium, some of the organic carbon is pyrolized into black carbon, resulting in the darkening of the filter deposit. This darkening is monitored by a reflectance of 633 nm of light from a He–Ne laser. When oxygen is added, the original and pyrolized black carbon combusts and the reflectance increases. The amount of carbon that is measured after the oxygen is added until the reflectance achieves its original value is reported as optically detected pyrolyzed carbon (OP). The eight fractions, OC1, OC2, OC3, OC4, EC1, EC2, EC3, and OP, are reported separately in the data sheet. The IMPROVE protocol defines OC as OC1 + OC2 + OC3 + OC4 + OP and EC as EC1 + EC2 + EC3 – OP.

The analyzer was calibrated with known quantities of CH$_4$ every day. Replicate analyses were performed at the rate of one per group of 10 samples. Sixteen blank filters

were also analyzed, and the sample results were corrected by the average of the blank concentrations, which were 1.72 and 0.62 μg/m³ for OC and EC, respectively. The difference determined from the replicate analyses was smaller than 5% for the total carbon (TC, OC + EC) and 10% each for OC and EC.

Elemental Analysis

The elemental concentrations of the $PM_{2.5}$ samples were analyzed directly using a proton-induced X-ray emission (PIXE) method using the 2.5-MeV protons with a 50-nA beam at the Institute of Low Energy Nuclear Physics, Beijing Normal University (Zhu and Wang, 1998; Zhang *et al.*, 2005). All of the concentrations were corrected based on the background data obtained from blank filters. Eighteen elemental concentrations were determined for each sample, including S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr, and Pb. The concentrations of the elements were determined by PIXE in 20 aliquots of a standard reference material from National Bureau of Chemical Exploration Analysis, China. The quality control and quality assurance showed that the analyses for the elements

were within 20% of the standards. Replicate analyses were performed at the rate of one per group of 10 samples, guaranteeing the stability and precision of instrument. Detailed methods were provided by Zhang *et al.* (1993).

Dust Classification

Dust events are classified into four categories in weather observations made by the China Meteorological Administration (CMA). They are defined based on the horizontal visibility, that is, less than 10 km, 1 to 10 km, 500 to 1000 m and less than 500 m, respectively, for the four categories of dust in suspension, blowing dust, dust storm and severe dust storm.

RESULTS AND DISCUSSION

Concentrations of Carbonaceous Aerosols during DS and NDS Periods

The 24-h mean concentrations of OC, EC and the total carbon (TC = OC + EC) at the Tongyu site during the spring 2006 are shown in Fig. 1. The concentrations of OC ranged from 2.7 to 50.6 μg/m³ with an average of 14.1 ± 8.7
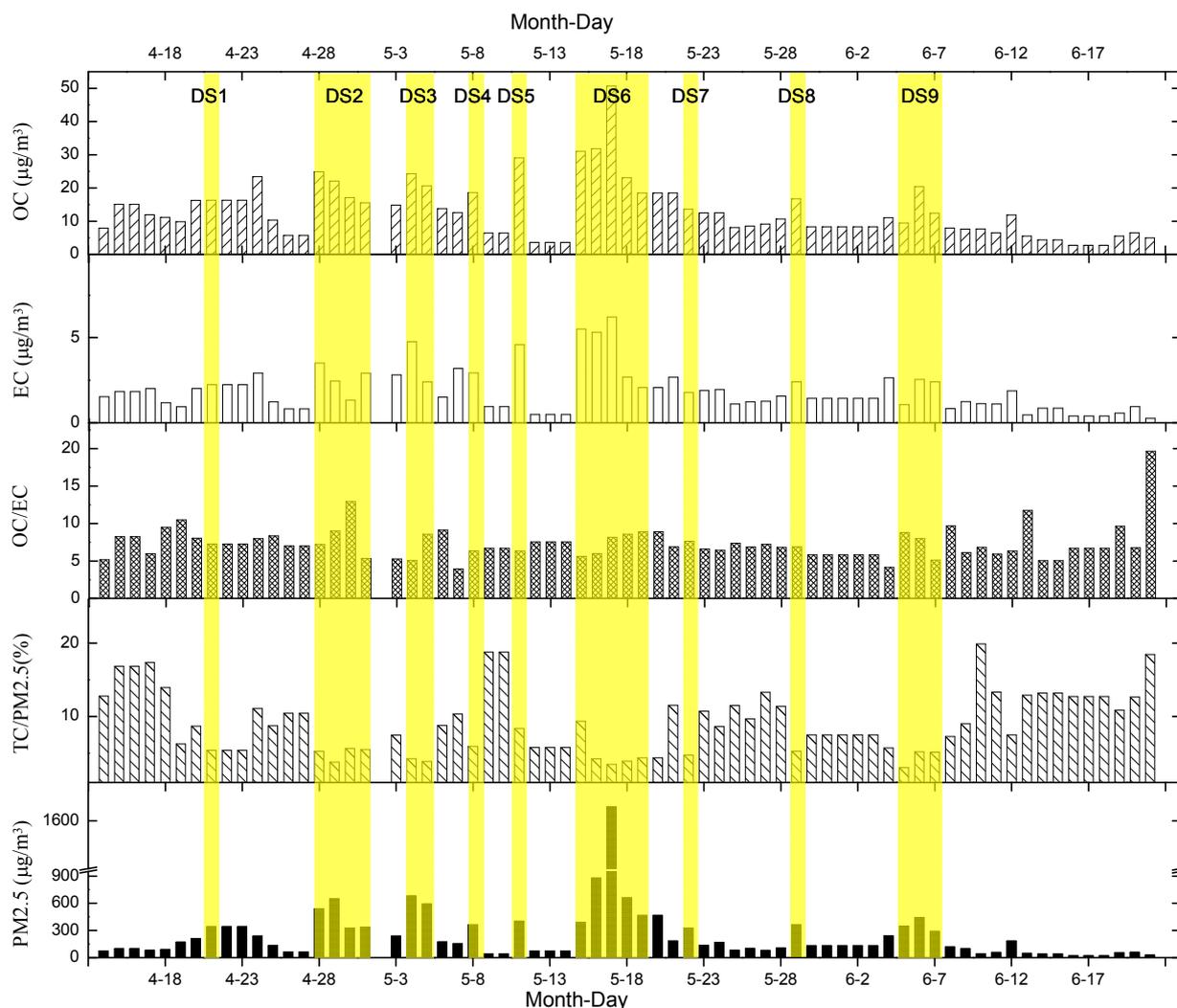

Fig. 1. Time series of OC, EC, OC/EC, TC/$PM_{2.5}$, and $PM_{2.5}$ in the spring at Tongyu.

$\mu g/m^3$, whereas the concentrations of EC ranged from 0.3 to 6.2 $\mu g/m^3$ with an average of 2.0 ± 1.3 $\mu g/m^3$ (Table 1). OC contributed 87.0 ± 3.8% to TC and 5.4 ± 4.7% to $PM_{2.5}$ and EC contributed 13.0 ± 3.8% to TC and 0.8 ± 0.6% to $PM_{2.5}$. On average, carbonaceous aerosols, one of the major components of fine particles in Tongyu, accounted for 6.2 ± 4.8% in $PM_{2.5}$.

The OC concentrations in $PM_{2.5}$ in Tongyu were similar to the mean average concentration in Tongliao (background site, 15.7 $\mu g/m^3$) (Shen *et al.*, 2007), Anaheim (urban site, 13.9 $\mu g/m^3$) (Chow *et al.*, 1994), Kaosiung (urban site, 10.4 $\mu g/m^3$) (Lin and Tai, 2001), and Seoul (urban site, 10.3 $\mu g/m^3$) (Park *et al.*, 2001). These concentrations were higher than those measured at Chongju (urban site, 5.0 $\mu g/m^3$) (Lee and Kang, 2001) and at background site of Cheju island in Korea (3.7 and 2.4 $\mu g/m^3$) (Kim *et al.*, 1999, 2000), but were lower than those measured in Beijing (urban site, 25.3 $\mu g/m^3$) (He *et al.*, 2001), Fresno (urban site, 20.0 $\mu g/m^3$) (Chow *et al.*, 1999), Los Angeles, (urban site, 18.5 $\mu g/m^3$) (Chow *et al.*, 1994), and Athens (urban site, 16.9 $\mu g/m^3$) (Scheff and Valiozis, 1990).

The EC levels in Tongyu in the spring were lower than those measured at Pearl River Delta Region (PRDR) (urban site, 6.1 $\mu g/m^3$), Beijing (urban site, 9.4 $\mu g/m^3$), Seoul (urban site, 8.4 $\mu g/m^3$), Los Angeles/Fresno (urban site, 7.3 $\mu g/m^3$), Anaheim (urban site, 5.5 $\mu g/m^3$), Chongju (urban site, 4.4 $\mu g/m^3$), Athens (urban site, 4.2 $\mu g/m^3$), Kaosiung (urban site, 4.0 $\mu g/m^3$), and Tongliao (3.3 $\mu g/m^3$) (background site, Shen *et al.*, 2007), but higher than those in Cheju island in Korea (0.3 $\mu g/m^3$ in 1999 and 0.1 $\mu g/m^3$ in 2000).

The average $PM_{2.5}$ level during the nine dust storm (DS) events was nearly five times of that during the non-dust storm (NDS) periods (528.0 ± 302.7 versus 111.6 ± 63.4 $\mu g/m^3$, as shown in Table 1). As a result, OC and EC loadings were also higher during the DS events than the NDS periods (Table 1 and Fig. 1). The mean concentrations of OC and EC during the DS events were 21.9 ± 9.0 $\mu g/m^3$ (ranging from 2.7 to 50.6 $\mu g/m^3$) and 3.1 ± 1.4 $\mu g/m^3$ (ranging from 0.3 to 6.2 $\mu g/m^3$), respectively, about two times higher than the mean values during the non-dust storm (NDS) periods (OC = 9.8 ± 4.4 $\mu g/m^3$, ranging from 2.7 to 23.4 $\mu g/m^3$; EC = 1.4 ± 0.8 $\mu g/m^3$, ranging from 0.3 to 3.2 $\mu g/m^3$). According to Turpin and Lim (2001), the amount of urban organic matter (OM) can be estimated by multiplying the amount of OC by 1.6. Thus, total carbonaceous aerosol (TCA) was calculated by the sum of OM and EC (TCA = 1.6 × OC + EC). Although the levels of carbonaceous species during DS were higher than those in NDS, their contributions to $PM_{2.5}$ were actually declined. For example, the percentages of OC, EC and TCA in $PM_{2.5}$ during DS

were only 4.5%, 0.6% and 7.8%, respectively, in comparison to 10.1%, 1.4% and 16.8% during the NDS periods. This implies that other aerosol components increased more than carbonaceous species during DS events.

Biomass-burning emissions are generally characterized by water-soluble K^+ content (Andreae and Merlet, 2001; Duan *et al.*, 2004). The K^+/OC ratio can therefore be used to distinguish biomass burning from other OC sources. In this study, the K^+/OC ratio ranged from 0.04 to 0.24 in $PM_{2.5}$. A good correlation (Fig. 2, R = 0.74) between OC and K^+ was observed (except some outliner). Since most aerosol particles produced from biomass burning are typically present in the fine mode (Tian *et al.*, 2009; Hosseini *et al.*, 2010), the correlation between OC and K^+ in $PM_{2.5}$ suggests that biomass-burning was one of the important sources of the aerosol content in the northeastern China. Stalk burnings by local residents for cooking and heating (from Nov. to late April) should have contributed to carbonaceous aerosols in these areas.

Moreover, the ratios of OC/Fe and EC/Fe against Fe concentration are presented in Figs. 3(a) and (b). Fe can be used as an indicator of crustal elements; thus, high concentrations of Fe were observed during DS events (Zhang *et al.*, 2008). The ratios of OC/Fe and EC/Fe varied much more during the NDS than those during DS. During DS, the ratios of OC/Fe and EC/Fe reached a low constant value at high Fe concentrations, indicating carbonaceous species transported with mineral dust from dust origins. In contrast, the ratios varied greatly during the NDS period at low Fe concentrations. The differences of OC/EC ratios between NDS and DS implied that OC and EC were influenced heavily by the anthropogenic source in NDS in comparison with DS.

Several investigators used the ratio of OC/EC to study emissions (Gray *et al.*, 1986; Turpin *et al.*, 1990; Chow *et al.*, 1996; Cao *et al.*, 2003). Prior studies showed that the OC/EC primary ratios for coal combustion, motor vehicle emissions, and biomass burning were 2.7, 1.1, and 9.0, respectively (Cachier *et al.*, 1989; Watson *et al.*, 2001). A study of Chinese sources by Cao *et al.* (2005b) similarly showed that the OC/EC ratios from coal combustion and biomass burning were much higher than those from motor vehicle emissions. At Tongyu, the OC/EC ratios varied between 3.9 and 12.9, with an average of 7.5. It was noticed that there was no difference of OC/EC ratios between DS and NDS. The high OC/EC ratios observed at Tongyu samples support the notion that biomass burning apparently contributed to the carbonaceous aerosols. It should be pointed out that coal combustion is also an important source to carbonaceous aerosols in this region considering the

Table 1. Concentration and percentage contribution of OC, EC and TC in $PM_{2.5}$ during the whole observation, DS, and NDS periods.

Observation Period	Concentration ($\mu g/m^3$)				Percent (%)		
	OC	EC	OC/EC	$PM_{2.5}$	$OC/PM_{2.5}$	$EC/PM_{2.5}$	$TC/PM_{2.5}$
Whole observation	14.1 ± 8.7	2.0 ± 1.3	7.5 ± 2.7	260.9 ± 274.4	5.4	0.8	6.2
DS (19)	21.9 ± 9.0	3.1 ± 1.4	7.5 ± 1.8	528.0 ± 302.7	4.2	0.6	4.7
NDS (34)	9.8 ± 4.4	1.4 ± 0.8	7.5 ± 2.4	111.6 ± 63.4	8.8	1.3	10.1

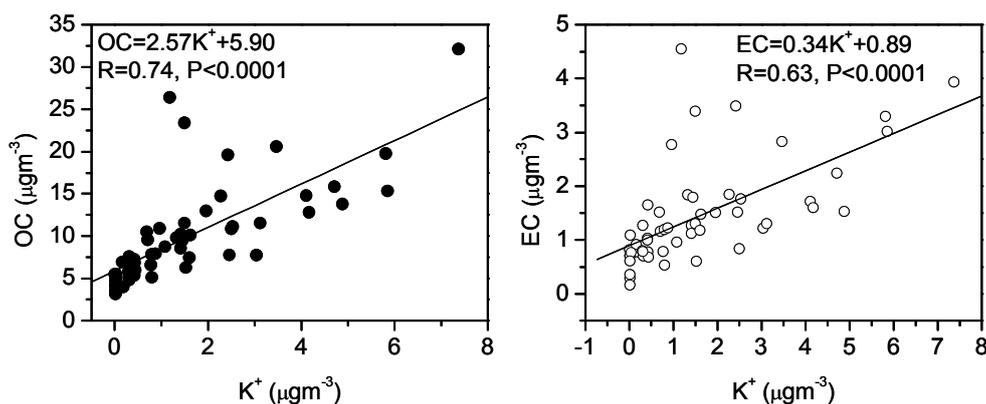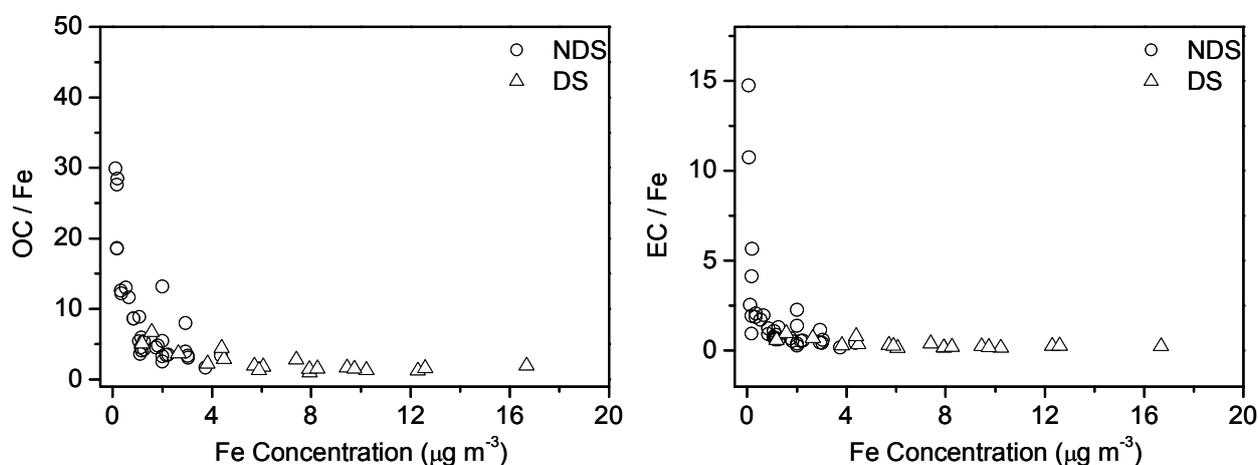**Fig. 2.** Scatter plots of OC and EC against K$^+$.

Fig. 3. Ratio of OC and EC to Fe versus Fe in PM$_{2.5}$ in Tongyu.

large amount of coal consumed and the high concentrations of sulfate and element S observed (Zhang *et al.*, 2008; Shen *et al.*, 2011), which are linked to coal combustion.

Air Mass History during the Aerosol Sampling Period

Because EC is predominately emitted from combustion sources, it has often been used as a tracer of primary OC (Turpin and Huntzicker, 1995). The origins of carbonaceous particles can be estimated on the basis of the relationship between OC and EC. The relationship between OC and EC in PM$_{2.5}$ in Tongyu is shown in Fig. 4. Strong correlations were observed between OC and EC during both DS (R = 0.88) and NDS (R = 0.84) periods. This suggests that the emission of OC and EC in Tongyu was attributed to similar carbonaceous sources. As mentioned above, coal combustion emission may be one of the air pollution sources. Previous studies at different sampling sites also showed good correlations between OC and EC (Chow *et al.*, 1994, 1996; Kim *et al.*, 2000; He *et al.*, 2001; Lee and Kang, 2001; Cao *et al.*, 2003, Dan *et al.*, 2004).

The standard meteorological parameters, including wind speed and direction, air temperature, and relative humidity, were routinely measured. Wind speed did not vary significantly between DS and NDS periods although some differences in wind direction were found. Fig. 5 presents

the wind rose diagram measured at a 20-m level of the meteorological tower. Air masses mainly came from the south, southeast, and northwest sectors during the NDS periods and mainly from southeast, south, west, and northwest sectors during the DS periods.

One of the objectives of this study is to identify the transport pathways and possible sources for the carbonaceous aerosols during NDS (during DS, the origins of air masses were mainly from several dust sources around Tongyu). Therefore, only 24-h air mass back trajectories arriving at 1,000 m above ground level at 06 UTC were calculated for the Tongyu station using the NOAA HYSPLIT 4 trajectory model to investigate the transport pathways and their origins. During the 33 NDS in the spring of 2006, five groups (A through E) of air mass trajectories were identified reaching Tongyu (Fig. 6). Group A represents the air masses from the northwest direction, which passed over Gobi in northern China and the desert regions of Mongolia, Group B from the southwest, Group C from the northeast, Group D from the west, which also passed over Gobi in northern China, and Group E from the southeast. In general, air masses in groups B and C were related to high concentrations of carbonaceous aerosols and had average OC levels of 8.6 ± 6.8 μg/m^3 and 9.7 ± 7.1 μg/m^3, respectively, and EC levels of 1.3 ± 1.0 μg/m^3 and 1.4 ± 1.2 μg/m^3, respectively. On the
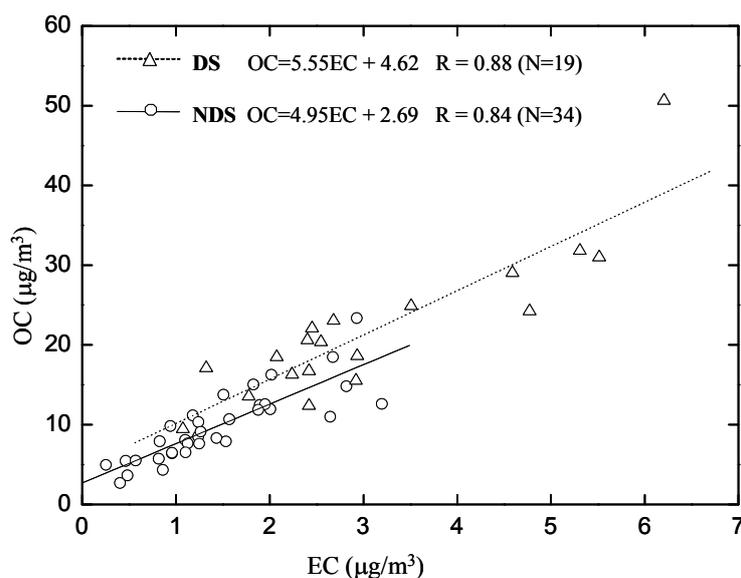
Fig. 4. Scatter plots of OC against EC concentrations in PM$_{2.5}$ samples during the dust and non-dust periods in the spring at Tongyu.
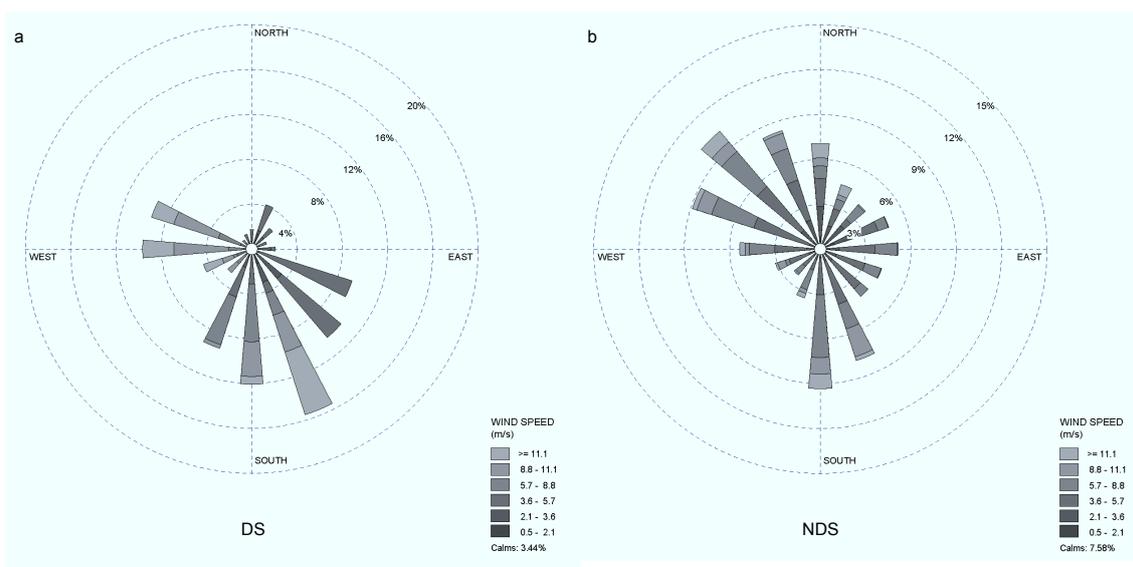

Fig. 5. Wind rose diagram during the sampling period at Tongyu, a: dust storm; b: Non dust storm.

contrary, relatively low carbonaceous aerosol levels were observed in groups A, D, and E, in which the mean OC concentration were 6.0 ± 2.3, 6.3 ± 2.8, and 6.9 ± 1.6 μg/m^3 and EC concentrations were 0.8 ± 0.3, 1.2 ± 1.0, and 1 ± 0.2 μg/m^3, respectively. The southwest area of Tongyu is relatively more urbanized than the areas in the northwest and the south. High emissions of carbonaceous aerosols from the southwest area of Tongyu were prevalent during the episode days. It should be noticed that the standard deviation of groups B and C were much higher than those in groups A, D, and E, indicating the sources of carbonaceous aerosol were more complicated even the transport pathways were similar.

The Characterization of Eight Carbon Fractions

One of the unique features of the IMPROVE TOR protocol is that it can provide the concentrations of eight fractions for carbonaceous aerosol particles (Chow *et al.*, 1993, 2001). The abundances in each of these fractions have been utilized in the source profile study to distinguish different emission sources of carbonaceous aerosol (Chow *et al.*, 2003, 2004a).

The percentages of eight carbon fractions in PM$_{2.5}$ and their comparisons with those in PRDR (Cao *et al.*, 2004) are shown in Fig. 7. The mean abundances of OC1, OC2, OC3, OC4, EC1-OP, EC2, EC3, and OP in TC were 7.3%, 13.2%, 25.5%, 22.8%, 7.6%, 3.3%, 1.8%, and 18.6%, respectively. In general, OC2, OC3, OC4, and OP were the most abundant species in Tongyu. A previous study in PRDR by Cao *et al.* (2004) also described that OC2 and OC3
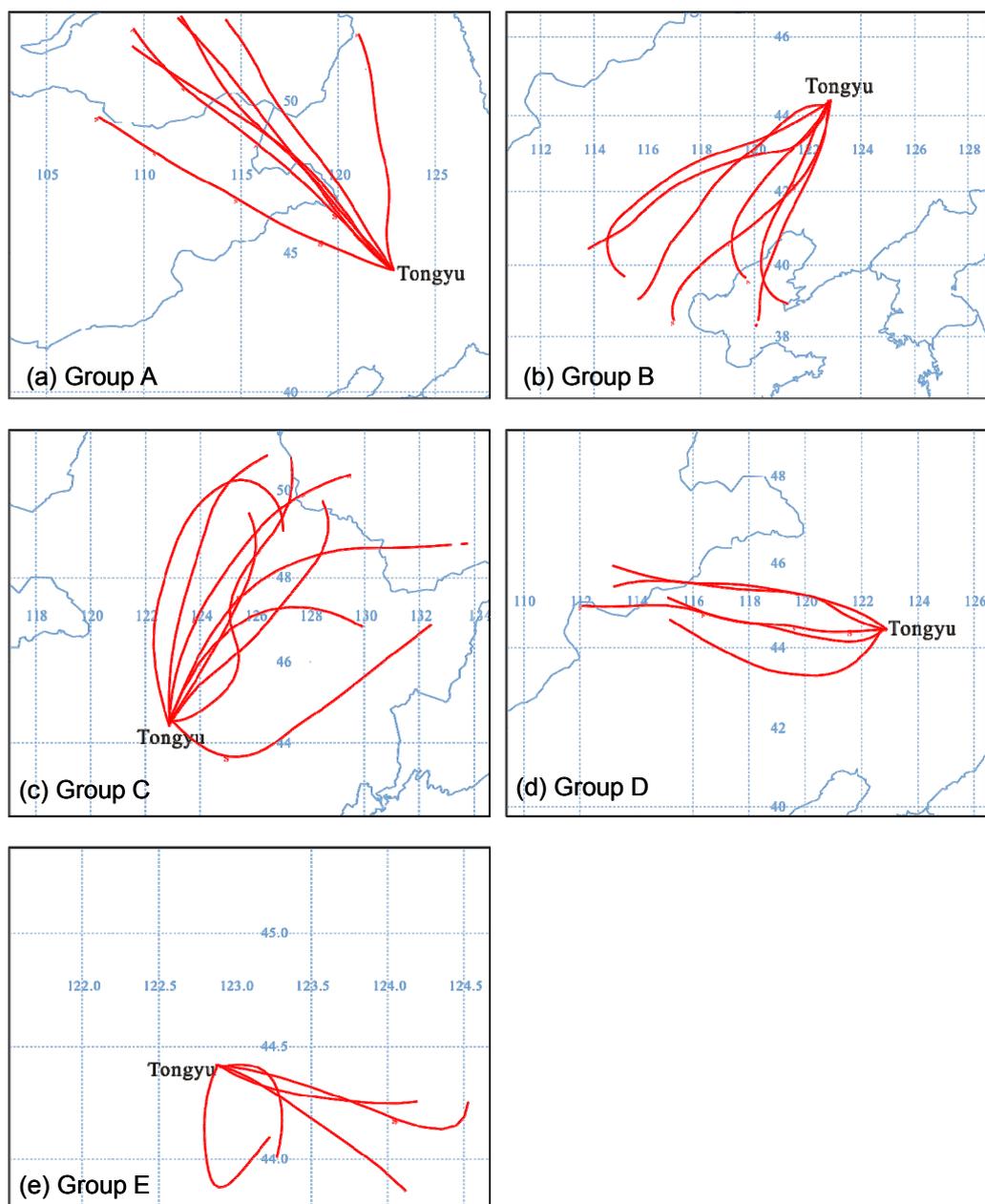
Fig. 6. 24-h air mass back-trajectory analysis for normal days in Tongyu.

were more abundant at the background site in comparison with urban sites. As mentioned above, SOC can be formed during long-distance transport from source regions to sampling sites, and might be abundant in the background areas. Therefore, the abundance of OC2 and OC3 might be associated with the SOC and biomass-burning sources. OP is another important component in Tongyu. Yang and Yu (2002) reported that OP increased with water-soluble organic carbon (WSOC) content, and WSOC contributed to 13–66% of OP. Thus, substantial water-soluble organic components are expected in a semi-arid atmosphere.

Estimation of Secondary Organic Carbon Concentrations

EC is relatively stable in comparison with OC and mainly comes from primary sources. OC can be emitted as primary

particles from combustion processes, but SOC can be formed through atmospheric photochemical reactions. The ratios of OC/EC larger than 2.0 have been used to identify the presence of SOC. In the present study, the OC/EC ratios in $PM_{2.5}$ in Tongyu varied between 3.9 and 12.9 with an average of 7.5 during the whole observation period. The high OC/EC ratio suggests that OC measured here was not only from the direct emissions of particles as primary pollutants but also in the form of secondary organic carbon formed by chemical reactions or produced by residential biomass burning and coal combustion. Since SOC was usually formed during long distance transport, the ratios at rural and background sites were mostly larger than 4.0 (Kim *et al*., 1999, 2000). The high ratios of OC/EC in $PM_{2.5}$ from the present study are compared with other measurements in
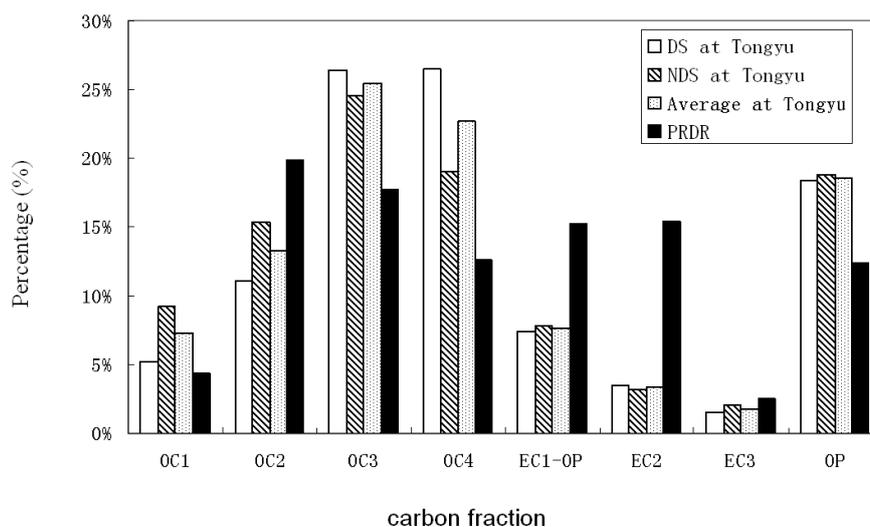
Fig. 7. Percentage of total carbon in $PM_{2.5}$ contributed by eight carbon fractions at the eight sampling sites during the spring at Tongyu and PRDR (Cao *et al.*, 2004).

Asia. It is apparent that the ratios of OC/EC for most of the urban cities fall between 1.0 and 4.0 (He *et al.*, 2001; Lee and Kang, 2001; Cao *et al.*, 2003, Dan *et al.*, 2004).

Separating and quantifying primary and secondary OC from the total measured OC is difficult due to the lack of simple direct or indirect methods. Several indirect methods have been developed in earlier studies to derive SOC, including the organic tracer-based receptor model, the reactive chemical transport model, the nonreactive transport model, and the semi-empirical EC tracer method. The EC tracer method requires ambient measurements of both OC and EC and is easy to apply (Gray *et al.*, 1986; Turpin *et al.*, 1990; Chow *et al.*, 1996; Cao *et al.*, 2003). This method is also used here. As EC is resistant to chemical reactions, it is a good indicator of primary anthropogenic pollutants and has been used to estimate the SOC (Turpin and Huntzicker, 1991; Lin and Tai, 2001; Cao *et al.*, 2003, 2004). Castro *et al.* (1999) suggested an equation to evaluate the production of SOC as follows:

$$OC_{sec} = OC_{total} - EC \times (OC/EC)_{min}, \qquad (1)$$

where OC_{sec} is the secondary OC (SOC), OC_{total} is the total OC (TOC), and $(OC/EC)_{min}$ is the minimum ratio of OC to EC concentration monitored. The major challenge in this method is the accuracy of $(OC/EC)_{min}$ since it could be influenced by meteorological conditions and emission fluctuations.

In this study, among the 53 samples collected during the sampling period, the minimum ratio of OC/EC was 3.9 in Tongyu. This minimum OC/EC ratio in background area had some apparent differences with the values observed in the urban regions. For example, the minimum OC/EC ratios at PRDR (Cao *et al.*, 2003), Long Beach (Turpin and Huntzicker, 1995), and Beijing (Dan *et al.*, 2004) were 1.3, 1.5, and 1.6, respectively. Castro *et al.* (1999) showed the minimum OC/EC ratios at Aveiro, Coimbra, Oporta, and Birmingham as 1.1, 1.1, 1.2, and 1.3, respectively.

The estimated SOC in $PM_{2.5}$ in Tongyu during the whole measurement period ranged from below detection limit to 26.1 $\mu g/m^3$ with an average of 5.9 $\mu g/m^3$. This was also the range for the estimated SOC during the DS periods, although with a different average value of 9.6 $\mu g/m^3$. The estimated SOC during the NDS had a smaller range from BDL to 12.0 $\mu g/m^3$ and lower average of 4.2 $\mu g/m^3$. This suggests that the chemical reaction processes involving gas-particle conversions occurred during the long-distance transportation of the aerosol particles. The estimated SOC concentrations suggested that SOC was an important component of organic aerosols. The percentages of SOC in OC and $PM_{2.5}$ concentrations were 42.0% and 2.1%, respectively. The SOC concentrations in Tongyu were close to the values observed at other urban sites. For instance, the estimated SOC concentration in $PM_{2.5}$ at PRDR was 6.8 $\mu g/m^3$, accounting for 42.6% of the OC (Cao *et al.*, 2003).

SUMMARY

Measurement data on aerosols and associated carbonaceous components (OC and EC in particular) for the semi-arid area of northeastern China were limited and the present study aimed to fill some gap on this issue. The average concentrations of OC and EC in $PM_{2.5}$ in spring season were 14.0 ± 8.3 and 2.1 ± 1.3 $\mu g/m^3$, respectively, at Tongyu, a semi-arid site in northeastern China. The ratios of OC/EC in DS, NDS, and during the observational period were: 7.47 ± 1.83, 7.53 ± 2.71, and 7.51 ± 2.46, respectively. Strong correlations between OC and EC were observed, suggesting they were produced from similar sources. A high $\Delta K^+/\Delta OC$ ratio of 12.3 in $PM_{2.5}$ highlights the significant contributions of biomass-burning emissions. The estimated SOC in $PM_{2.5}$ varied from below detection limit to 26.1 $\mu g/m^3$ with an average of 5.9 $\mu g/m^3$. The percentage of the SOC in OC and $PM_{2.5}$ was 42.0% and 2.1%, respectively. The SOC concentrations during DS were higher than those during NDS, suggesting the occurrence of chemical processes

involving gas-particle conversation during the long-distance transportation of aerosol particles. The impact of biomass-burning and anthropogenic emissions on carbonaceous aerosols in this region certainly deserves more scientific attention.

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