



The implication of carbonaceous aerosol to the formation of haze: Revealed from the characteristics and sources of OC/EC over a mega-city in China

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ABSTRACT

The characteristics and sources of organic carbon (OC) and elemental carbon (EC) in PM_{2.5} in 2006–2007 as well as their impact on the formation of heavy haze in Shanghai were investigated. Daily average concentrations of OC and EC ranged from 1.8 to 20.1 $\mu\text{g m}^{-3}$ and 0.5–7.8 $\mu\text{g m}^{-3}$ with averages of 7.2 and 2.8 $\mu\text{g m}^{-3}$, respectively. The carbonaceous aerosol (OC plus EC) contributed to ~27.2% of the total mass of PM_{2.5} on annual average. Obvious seasonal variation was observed in both OC and EC. The percentage of secondary organic carbon (SOC) contributed to OC was in a range of 2.4–66.8%, with an average of 40.1%. Three types of haze were classified based on their chemical composition. OC, EC, SO₂/NO₂ (in turn, SO₄²⁻/NO₃⁻) were responsible for the formation of the three types of haze, respectively. The carbonaceous aerosol was one of the key factors in the formation of haze. Local emissions were the dominant sources of OC and EC in warm seasons, and long-range transport had a significant contribution to OC and EC in PM_{2.5} in spring and winter in Shanghai.

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1. Introduction

Carbonaceous species constitute a significant fraction of ambient respirable suspended particulates (RSP or PM₁₀) and fine particles (PM_{2.5}), ranging from ~10% in remote areas to ~40% in urban areas [1–5]. Generally, the carbonaceous species in aerosols are classified into two categories: organic carbon (OC) and elemental carbon (EC). EC aerosols are mainly emitted from combustion sources, while OC aerosols may be derived from both primary source and chemical reactions between primary gaseous OC species in atmosphere [6–8]. OC and EC play important role in various atmospheric processes. EC generally exhibits a positive climate forcing as it absorbs solar radiation, whereas OC overall shows a negative climate forcing as it is mainly a scattering medium [9,10]. OC may contain those organic compounds that are potentially mutagenic and carcinogenic (e.g. PAHs, PCBs, PCDDs and PCDFs) and therefore have an adverse impact on human health. Cooke et al. [11] and Streets et al. [12] estimated that EC generated in China accounted for 1/4 of the global yield. Menon et al. [13] simulated the direct radiative forcing of aerosols in the region of China and India using a climate model, and found that EC generated in China and India enhanced summer floods in southern China and drought in northern China.

Shanghai is one of the biggest cities in the world, located in the eastern coast of China with 16.74 million people and over 5800 km²

area. It is a strong commercial and industrial base with the largest petrochemical complex, steel output, and other major industries in China. Shanghai also receives huge anthropogenic emissions from East Asia under the influence of monsoon system, particularly in spring and winter. As a result, Shanghai is experiencing a heavy haze in the past decade. Haze is defined as the weather phenomenon which leads to atmospheric visibility less than 10 km due to the suspended solid or liquid particulates, smoke and vapor in the atmosphere. Haze formation is closely related to meteorological conditions and air pollution [14]. Haze is a worldwide phenomenon that has attracted a lot of attention for its significant effects on visibility, cloud formation, public health, and climate system. Although several studies on the chemical composition of PM_{2.5} have been carried out in Shanghai [15–21], the relations between its chemical characteristics and the formation of haze have not been investigated. In order to better understand haze formation and sources of OC and EC, we measured the carbonaceous species with other elements and ions in PM_{2.5} in normal days and haze episodes in 2006–2007 in Shanghai, investigated the haze types, the visibility, and their relation to the different key pollutants, and demonstrated the implication of carbonaceous aerosol to the formation of haze.

2. Experiment

2.1. Sampling

A total of 73 PM_{2.5} samples were collected in four seasons from April 2006 to January 2007 in Shanghai. The samples in spring (April 12–27, 2006), summer (August 1–21, 2006), autumn (Octo-

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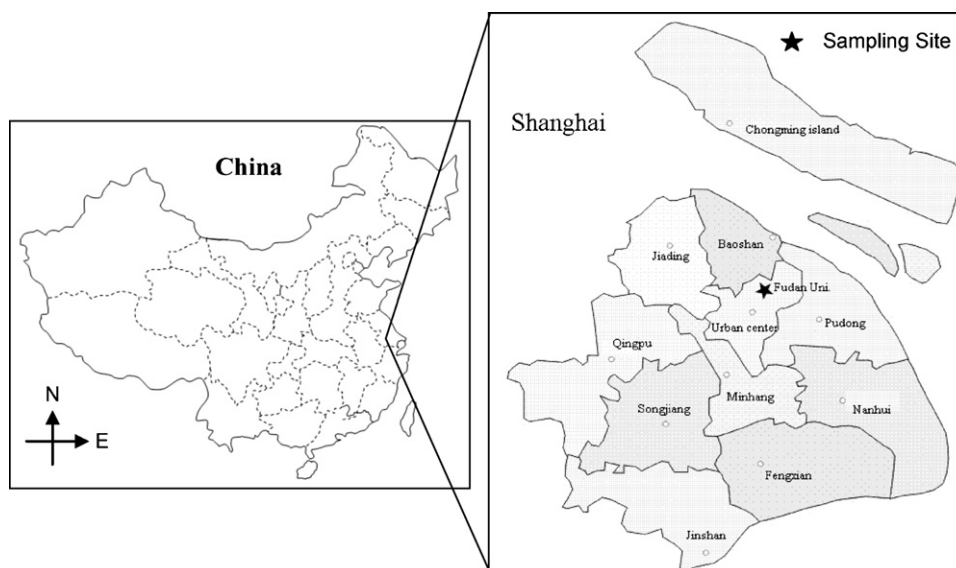


Fig. 1. Location of sampling site and surrounding regions in Shanghai, China.

ber 13–29, 2006) and winter (January 5–21, 2007) were collected on the roof of No. 4 teaching building at Fudan University. The sampling location is the representative of urban Shanghai that is under the impact of the traffic, industrial, and residential activities (Fig. 1). $PM_{2.5}$ was collected on quartz filters ($\Phi 90$ mm, Whatman Company, UK) using a middle-flow impact aerosol sampler (Beijing Geological Instrument-Dickel Co., Ltd., model: (TSP/ PM_{10} / $PM_{2.5}$)-2, flow rate: 77.59 L min^{-1}). The sampling time was generally 24 h. The quartz filters were preheated at 500°C for 5 h to remove the residual OC prior to sampling. All filters were weighed before and after sampling using an analytical balance (Sartorius 2004MP, reading precision $10 \mu\text{g}$) after stabilizing under constant temperature ($20 \pm 1^\circ\text{C}$) and humidity ($40 \pm 1\%$). The samples were stored in a refrigerator at -20°C for late analysis. SO_2 and NO_2 were monitored by API 200 (Advanced Pollution Instrumentation, Inc., USA) or TE43C (Thermo Electron Corporation Environmental Instruments Division, USA) and API 300 or TE42C, respectively. The daily QC/QA is implemented by professional staff of Shanghai Environmental Monitoring Center according to the Technical Guideline of Automatic Stations of Ambient Air Quality in Shanghai, which was developed partially on the basis of guidelines established by the US EPA (1998) [22].

2.2. OC and EC analyses

OC and EC in aerosol samples were measured using Thermal/Optical Carbon Analyzer (Desert Research Institute (DRI) Model 2001, Atmoslytic Inc., Calabasas, CA, USA). A 0.5 cm^2 punch of each sample was analyzed for eight carbon fractions following the IMPROVE TOR protocol [23,24]. Four OC fractions (OC1, OC2, OC3, and OC4 at 120°C , 250°C , 450°C , and 550°C , respectively, in a helium atmosphere), and three EC fractions (EC1, EC2, and EC3 at 550°C , 700°C , and 800°C , respectively, in a 2% oxygen/98% helium atmosphere) were produced. During volatilization of organic carbon, part of organic carbon was converted pyrolytically to EC (this fraction of OC was named as OP). A He-Ne laser was employed to monitor the sample reflectance. As pyrolysis occurs, the reflectance decreases. Then, as EC is removed from the filter, the reflectance will increase until all carbon is removed from the filter. IMPROVE OC is operationally defined as $\text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OP}$ and EC is defined as $\text{EC1} + \text{EC2} + \text{EC3} - \text{OP}$. The detailed procedures were described in literatures [25,26]. 10 blank filters were analyzed fol-

lowing the same procedures and the sample results were corrected by the average blank concentrations of 1.8 and $0.6 \mu\text{g m}^{-3}$ for OC and EC, respectively.

2.3. Ions analysis

One-fourth of each sample and blank filter was extracted ultrasonically by 10 ml water, which was deionized previously to resistivity of $18 \text{ M}\Omega \text{ cm}^{-1}$. After passing through microporous membranes (pore size of $0.45 \mu\text{m}$; diameter of 25 mm; made by the affiliated plant of Beijing chemical school), the pH of the filtrates was measured with a pH meter (model, Orion 818). Each filtrate was stored at 4°C in a clean glass tube prior to analysis. 8 anions (F^- , CH_3COO^- , HCOO^- , $\text{C}_2\text{O}_4^{2-}$, Cl^- , SO_4^{2-} , NO_3^- , and PO_4^{3-}) and 5 cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and NH_4^+) were analyzed by Ion Chromatography (IC, model, Dionex 600) consisting of a separation column (Dionex Ionpac AS11 for anion and CS12A for cation), a guard column (Dionex Ionpac AG 11 for anion and AG12A for cation), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50), and a gradient pump (Dionex Ionpac GP50). The gradient weak base eluent ($76.2 \text{ mM NaOH} + \text{H}_2\text{O}$) was used for anion detection, while the weak acid eluent (20 mM MSA) used for cation detection. The recovery of each ion was in the range of 80–120%. The relative standard deviation of each ion was less than 5% for reproducibility test. The detection limits ($S/N=3$) were less than 0.04 mg L^{-1} for anions and 0.006 mg L^{-1} for cations. The quality assurance was routinely carried out by using Standard Reference Materials (GBW 08606) produced by National Research Center for Certified Reference Materials, China. The details were given elsewhere [19].

3. Results and discussion

3.1. Concentrations of carbonaceous species

Average concentrations of $PM_{2.5}$, OC, EC and TC (total carbon, sum of OC and EC) in four seasons in 2006 are presented in Table 1 and their daily concentrations are plotted in Fig. 2. $PM_{2.5}$ mass concentrations ranged from 4.1 to $87.6 \mu\text{g m}^{-3}$ with an average of $41.0 \mu\text{g m}^{-3}$ during the sampling period, which was almost three times higher than the National Ambient Air Quality Standard (NAAQS) of $15 \mu\text{g m}^{-3}$ (US EPA, 1997). The daily ave-

Table 1
Average concentrations of PM_{2.5}, OC, EC, and TC in four seasons in 2006.

Season (N ^b)	Concentration ^a (μg m ⁻³)				Percentage ^a (%)			
	PM _{2.5}	OC	EC	TC	OC	EC	TC	OC/EC
Spring (18)	47.3 ± 17.1	8.4 ± 2.2	3.7 ± 0.9	12.1 ± 3.1	18.2 ± 3.8	8.0 ± 1.9	26.3 ± 5.5	2.5 ± 1.3
Summer (21)	15.1 ± 6.1	3.8 ± 1.6	1.1 ± 0.45	4.9 ± 1.9	30.1 ± 10.6	9.3 ± 3.7	39.5 ± 13.5	3.5 ± 0.9
Autumn (17)	36.1 ± 17.1	6.5 ± 2.6	2.1 ± 0.8	8.5 ± 3.2	19.3 ± 5.9	6.4 ± 2.4	25.6 ± 7.6	3.2 ± 0.8
Winter (17)	65.4 ± 16.8	10.9 ± 4.5	4.4 ± 1.8	15.3 ± 6.2	17.0 ± 5.9	6.9 ± 2.3	24.0 ± 7.9	2.2 ± 0.2

^a Values represent average ± standard deviation.

^b Numbers of samples.

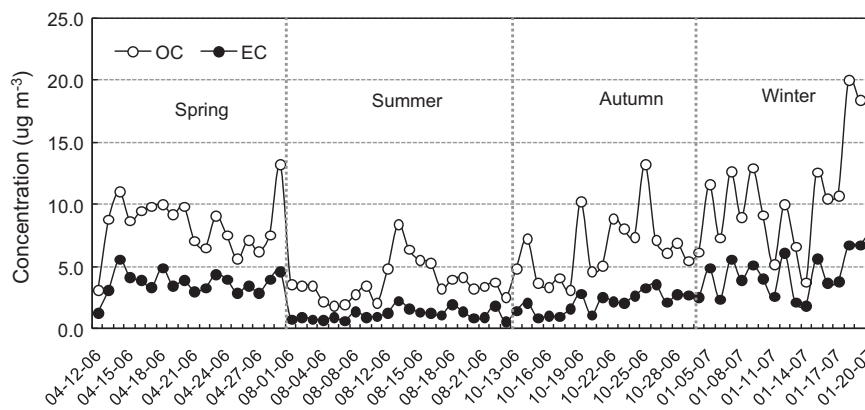


Fig. 2. Daily average concentrations of OC and EA in four seasons, 2006–2007 in Shanghai.

rage concentration of OC varied from 1.6 μg m⁻³ in summer to 20.1 μg m⁻³ in winter with an average of 7.0 μg m⁻³. EC levels increased from the minimum of 0.4 μg m⁻³ in summer to the maximum of 7.8 μg m⁻³ in winter with an average of 2.7 μg m⁻³. TC contributed to 5.5–71.5% of PM_{2.5} mass with an average of 28.9%, indicating the significance of carbonaceous species in PM_{2.5} in Shanghai. Obvious seasonal variations were observed of OC and EC in PM_{2.5} in 2006. The average concentrations of OC and EC were 5.2 and 1.6 μg m⁻³ in warm seasons (summer, autumn) and 9.1 and 4.1 μg m⁻³ in cold seasons (spring, winter), respectively. The average fraction of OC in PM_{2.5} was approximately 21.1% with the lowest of 3.8% in winter and the highest of 54.7% in summer. The average fraction of EC in PM_{2.5} was 7.6% with the lowest of 1.9% in winter and the highest of 16.8% in summer, and this was consistent with the observations reported in previous studies [19–22]. A large amount of mineral dust along with pollutant aerosol is brought into Shanghai in winter, which could decrease the proportion of OC and EC in PM_{2.5} in winter [19].

As the concentration of OC and EC measured are operationally defined, and the concentrations would be related to the method applied, it is difficult to compare their concentrations from different studies. Here we normalized the concentrations of OC and EC by the PM_{2.5} mass concentration and compared the OC and EC fractions observed at different sites. Fig. 3 shows the OC and EC fractions in total PM_{2.5} mass (OC% and EC%) at different sampling sites located in China and in foreign cities. It can be seen from Fig. 3 that the average percentage of OC and EC in PM_{2.5} in Shanghai were much higher than most of the cities shown in the figure, such as Gwangju, South Korea [6], Kyoto, Japan [3], Diamond bar, USA [26], Kaohsiung, Taiwan [27], Ulan-Bator, Mongolia [4], and Beijing, China [28], but Los Angeles, USA [26]. The results indicated that air pollution related to carbonaceous species in PM_{2.5} was rather severe in Shanghai.

3.2. Correlation between OC and EC

EC is a good indicator of primary anthropogenic sources, and the correlation between OC and EC has often been used as a tra-

cer of primary OC, as the chemical transformations of EC, such as chemical reaction or phase change in the aerosol, are very limited. The origins of carbonaceous particles can be estimated based on the correlation between organic and elemental carbon [29,30]. Fig. 4 shows the correlations between OC and EC in four seasons in Shanghai. Strong correlations between OC and EC were observed in spring ($R^2 = 0.67$), and winter ($R^2 = 0.84$), suggesting they were likely attributed to a common source, e.g. the combustion of fossil fuel and vehicle emissions. Coal combustion could be the major source of air pollution. In addition, the number of motor vehicles increased substantially from 0.47 million in 1996 to 2.38 million in 2006 in Shanghai, thereby the vehicle emission has become one of the major sources. Thus, it is critical to improve the air-quality to control the emissions from the large number of motor vehicles within this region. The correlation coefficients between OC and EC were lower in summer ($R^2 = 0.54$) and autumn ($R^2 = 0.51$) than those in spring and winter, indicating that there must be additional sources of OC existed other than the common sources with EC. The secondary organic carbon (SOC) formed through chemical reactions may contribute to this part of OC. The formation of SOC is in favor

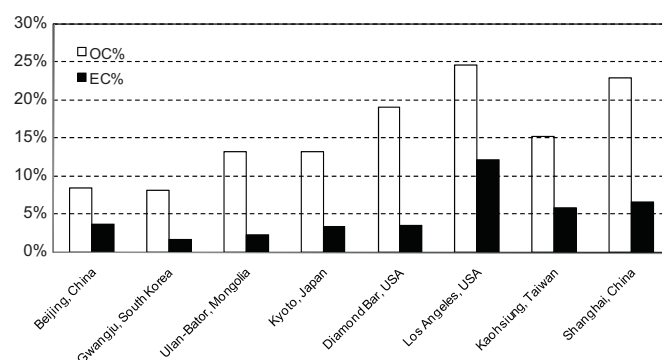


Fig. 3. Comparison of the contributions of OC and EC to PM_{2.5} at different sampling sites over the world.

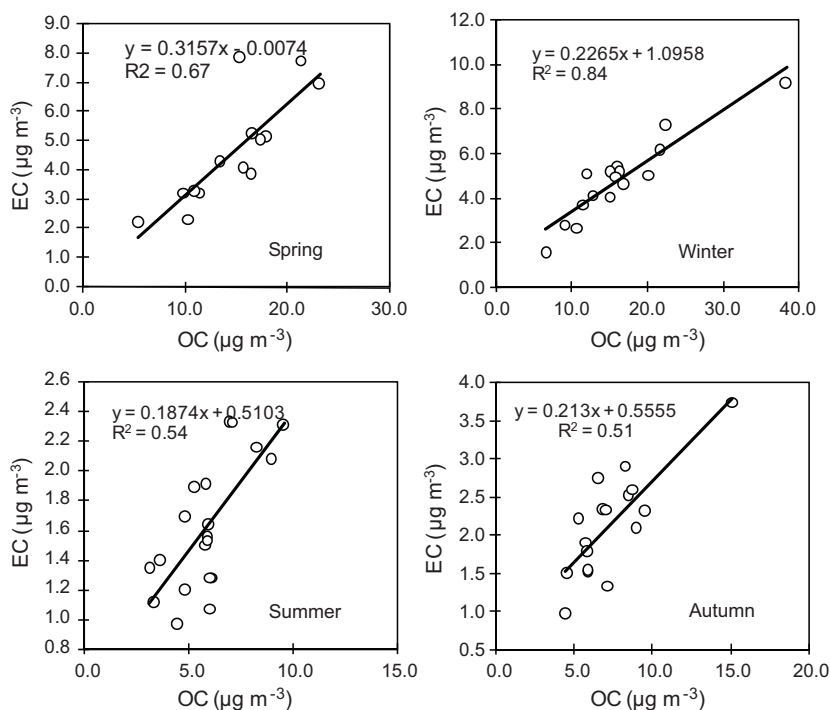


Fig. 4. Correlation between OC and EC in four seasons, 2006, in Shanghai.

of the high temperature and high relative humidity (RH), and also determined by the emission rate and chemical activity of the volatile organic compounds that may undergo atmospheric oxidation [31]. OC concentrations were found to be high under stable weather (low wind speed) conditions in summer and autumn, indicating the contribution of SOC to the total OC is significant in these seasons.

3.3. Estimates of secondary organic carbon (SOC)

EC is essentially a primary pollutant, and OC is resulted from both primary emitted sources and secondary transformation from gaseous precursors [32]. To quantify the contributions of both primary and secondary organic carbon to carbonaceous aerosol, Turpin and Huntzicker [10] used an equation below:

$$OC_{\text{sec}} = OC_{\text{tot}} - OC_{\text{pri}} \quad (1)$$

$$OC_{\text{pri}} = EC \left(\frac{OC}{EC} \right)_{\text{pri}} \quad (2)$$

where OC_{pri} is primary OC, OC_{sec} is secondary OC, OC_{tot} is total OC, and $(OC/EC)_{\text{pri}}$ is the ratio of OC to EC in the primary aerosol. However it is difficult to estimate the ratio $(OC/EC)_{\text{pri}}$ accurately for a given area. Castro et al. [33] suggested that $(OC/EC)_{\text{pri}}$ could be replaced by $(OC/EC)_{\text{min}}$ (the minimum ratio of OC/EC), and the equation could be written as below:

$$OC_{\text{sec}} = OC_{\text{tot}} - EC \left(\frac{OC}{EC} \right)_{\text{min}} \quad (3)$$

$(OC/EC)_{\text{min}}$ of 1.6 in $PM_{2.5}$ was observed in this study, which was comparable to those measured in other urban areas, e.g. $(OC/EC)_{\text{min}}$ of 1.3 in Pearl River Delta Region, China [25] and 1.5 at Long Beach [10]. Based on this $(OC/EC)_{\text{min}}$, the seasonal average concentrations of SOC in $PM_{2.5}$ were listed in Table 2. The concentrations of SOC in summer and autumn were 2.0 and 2.5 $\mu\text{g m}^{-3}$, accounting for 49.5% and 46.6% of OC and 15.2% and 9.1% of total $PM_{2.5}$ mass, respectively. In spring and winter, the concentrations of SOC were 2.5 and 3.8 $\mu\text{g m}^{-3}$, accounting for 29.0% and 33.5% of OC and 5.3% and

5.9% of $PM_{2.5}$, respectively. The results suggested that SOC had a significant contribution to $PM_{2.5}$ in Shanghai, especially in warm season.

3.4. Implication of OC and EC to the formation of haze

Haze, defined for such a weather phenomenon as the atmospheric visibility less than 10 km due to the suspended particles, smoke, has been spread over most areas of China and has generated wide attention [34–36]. Although several studies on the chemical composition of $PM_{2.5}$ were carried out in Shanghai, the implication of carbonaceous species in $PM_{2.5}$ to haze has not been investigated [37,38]. During the sampling period, six heavy haze episodes occurred on April 13–15, April 29, August 12–14, October 20–24, 2006, and January 5–10, January 17–19, 2007. Fig. 5 shows the daily average concentrations of SO_2 , NO_2 , SOC, OC, EC, and visibility during the sampling period, 2006–2007, in Shanghai. Three types of haze were classified according to the relations of visibility with the pollutants in each episode. (1) Haze 1 and haze 3 shown in Fig. 5 were classified as Type I, both haze 1 and 3 were formed mainly because of the accumulation of carbonaceous species; (2) haze 4 was as type II, mainly formed due to the accumulation of SO_2 and NO_2 ; (3) haze 2, 5 and 6 were as type III, formed because of both OC/EC and SO_2/NO_2 . In the previous study of our research group [19,21], we found that atmospheric SO_2 and NO_2 were the main precursors and sources of SO_4^{2-} and NO_3^- in $PM_{2.5}$, and high concentrations of SO_4^{2-} , NO_3^- , and NH_4^+ were responsible for the formation of haze. Table 3 summarizes the average concentrations of OC, EC, SOC, SO_2 and NO_2 in non haze days (NH) and haze days (HD), and the ratios of HD/NH of these species. Those ratios of HD/NH for OC, EC, SOC, SO_2 , and NO_2 were 1.5, 1.7, 1.2, 0.7, and 0.9, respectively in haze 1 and 3 (type I), indicating that the concentrations of OC and EC were elevated during both haze episodes and responsible for the formation of haze. In haze 4 (type II) the ratios of HD/NH for SO_2 , NO_2 , OC, EC, and SOC were 2.0, 1.5, 0.8, 0.7, and 0.9, respectively, indicating that the high concentrations of SO_2 and NO_2 (in turn, of

Table 2
Average concentrations of estimated SOC and its contribution to OC and PM_{2.5}.

Seasons	SOC ($\mu\text{g m}^{-3}$)	SOC/OC (%)	SOC/PM _{2.5} (%)
Spring	2.5	29.0	5.3
Summer	2.0	49.5	15.2
Autumn	2.5	46.6	9.1
Winter	3.8	33.5	5.9

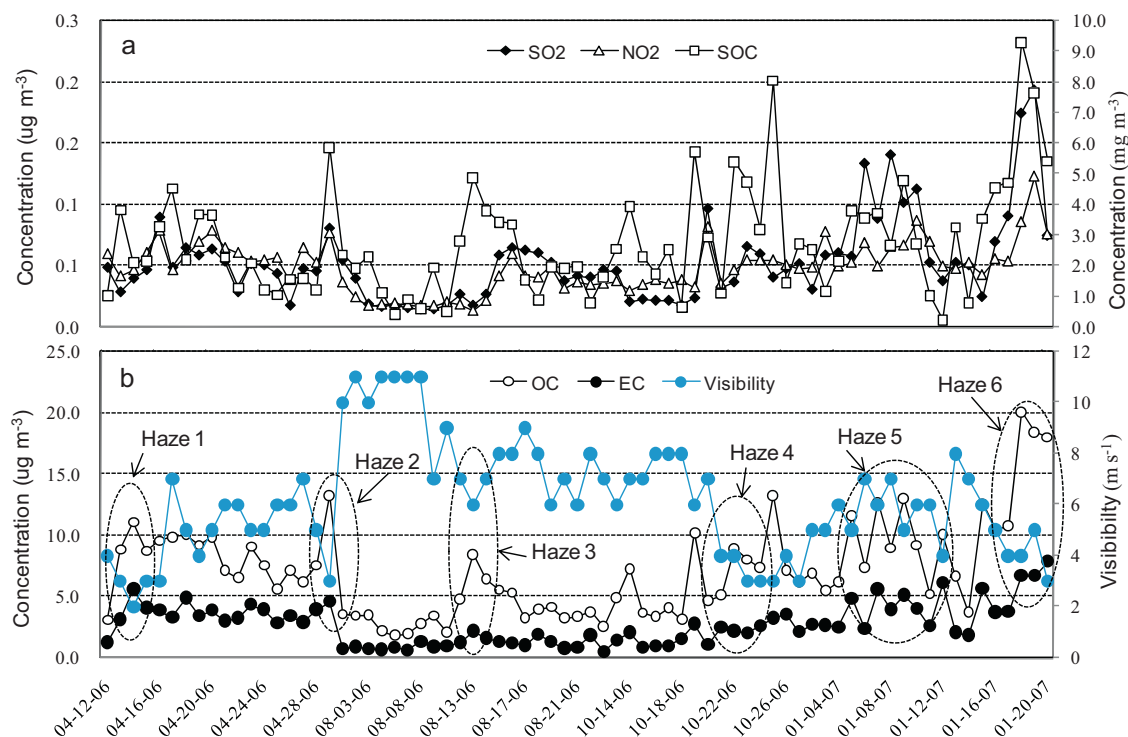


Fig. 5. (a) Daily average concentrations of SO₂, NO₂ and SOC, (b) of OC, EC and visibility during the sampling period, 2006–2007, in Shanghai.

SO₄²⁻ and NO₃⁻, considering the close relationships between SO₂ and SO₄²⁻ and NO₂ and NO₃⁻, may be responsible for the formation of haze. In haze 2, 5, and 6 (type III) the ratios of HD/NH for OC, EC, SOC, SO₂, and NO₂ were all greater than 1.0, indicating that the accumulation of both organic and inorganic species in PM_{2.5} could

be responsible for the formation of haze. It must be noted that two of the three types of haze and five of the six episodes were closely related to the high concentrations of OC and EC, indicating that the carbonaceous aerosol was one of the key factors in the formation of haze.

Table 3
Average concentrations of OC, EC, SOC, SO₂, and NO₂ in non haze days (NH) and haze days (HD), and the ratios of HD/NH of these species.

Species	Type	Type I		Type II		Type III	
		Haze 1	Haze 3	Haze 2	Haze 4	Haze 5	Haze 6
	No ^a	3	3	3	5	6	3
OC ($\mu\text{g m}^{-3}$)	NH	6.3	4.1	6.7	8.5	7.1	8.9
	HD	9.5	6.6	10.4	6.7	10.5	16.4
	HD/NH	1.5	1.6	1.6	0.8	1.5	1.8
EC ($\mu\text{g m}^{-3}$)	NH	2.6	1.1	3.2	2.8	3.7	3.7
	HD	4.3	4.3	4.3	2.0	4.3	5.7
	HD/NH	1.7	3.9	1.3	0.7	1.2	1.5
SOC ($\mu\text{g m}^{-3}$)	NH	2.2	2.3	1.6	3.9	1.2	2.9
	HD	2.7	3.8	3.6	3.6	3.6	7.2
	HD/NH	1.2	1.7	2.3	0.9	3.0	2.5
SO ₂ (mg m^{-3})	NH	0.06	0.04	0.05	0.03	0.05	0.05
	HD	0.04	0.02	0.06	0.06	0.11	0.15
	HD/NH	0.7	0.5	1.2	2	2.2	3
NO ₂ (mg m^{-3})	NH	0.07	0.04	0.03	0.04	0.06	0.05
	HD	0.06	0.02	0.07	0.06	0.07	0.09
	HD/NH	0.9	0.5	2.3	1.5	1.2	1.8

^a Numbers of samples in every haze period.

3.5. Sources

3.5.1. Factor analysis

Principal component analysis (PCA) was used to identify the possible sources of OC, EC, together with 13 ions in the aerosols. The result of factor analysis (after varimax rotation) is shown in Table 4. Three of the major components, interpreting the variation in concentrations of OC, EC and 13 ions in PM_{2.5}, were identified on the basis of the magnitude of Eigenvalues (greater than one), and these three factors accounted for 87.0% of total variance in the entire set of the data. Factor 1 that explained 57.8% of the total system variance was highly loaded by OC, EC, SO₄²⁻, NO₃⁻, NH₄⁺ and moderately loaded by C₂O₄²⁻, HCOO⁻, CH₃COO⁻. This factor appeared to represent industrial and mobile sources. In China, gasoline and diesel fuel contain 0.12% and 0.2% sulfur (by weight), respectively [19]. The estimated ratios of NO_x to SO_x from the emission of gasoline and diesel fuel burning are 13:1 and 8:1, respectively. The sulfur content in coal is ~1% and the estimated ratio of NO_x to SO_x is 1:2 from coal burning. Therefore, it was reasonable to use SO₄²⁻ as an indicator for stationary source and NO₃⁻ for mobile emission in China [19]. Factor 2 was highly loaded by Ca²⁺, Mg²⁺, Na⁺, Cl⁻, and explained about 21.4% of the total system variance. It appeared to represent dust sources, including road dust, marine particles, and dust from long-range transport. Factor 3 accounted for 7.9% of the total system variance and was highly loaded by F⁻, PO₄³⁻ and K⁺. This factor may represent the incineration and biomass burning sources because F⁻ and PO₄³⁻ were derived mainly from incineration and K⁺ was a good tracer of biomass burning. It can be seen from the factor analysis that the industrial and mobile emissions were the main sources for carbonaceous aerosol.

3.5.2. Correlation analysis

Fig. 6(a) and (b) shows the relationships of OC, EC with NO₃⁻ and SO₄²⁻, respectively, in four seasons for all samples collected. Significant correlations were found between OC and NO₃⁻ and between EC and NO₃⁻ with the correlation coefficients of 0.58 and 0.64, respectively. NO₃⁻ has often been used as an indicator of vehicle emissions in an urban area. These results indicated that vehicle emission was an important source of OC and EC in Shanghai. OC and EC were also significantly correlated with SO₄²⁻ with the correlation coefficients of 0.79 and 0.81, respectively, indicating that OC and EC could likely derive from the common sources as SO₄²⁻ did. As much of SO₄²⁻ could be transported into Shanghai in win-

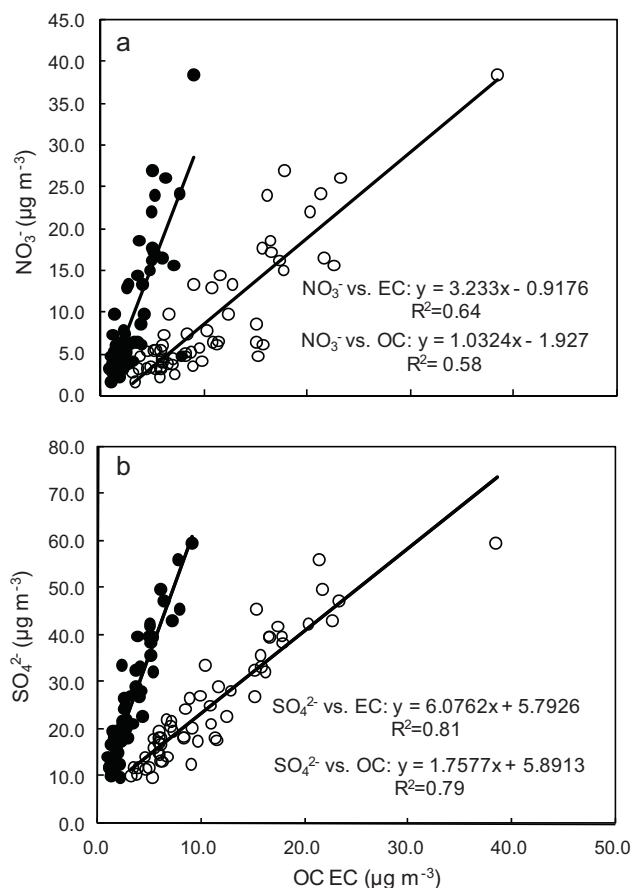


Fig. 6. (a) Correlation of NO₃⁻ with OC (hollow dot) and EC (black dot); (b) Correlation of SO₄²⁻ with OC (hollow dot) and EC (black dot).

ter and spring [38], part of OC and EC could be transported into Shanghai too through the medium- or/and long-range.

3.5.3. Impact of long-range transport

Fig. 7(a) shows the frequency of wind directions in four seasons in 2006, and Fig. 7(b)–(d) illustrates the three typical pathways of air parcels arriving in Shanghai. In winter and spring the prevailing northerly and/or northwesterly wind travels over the continent

Table 4
Primary component analysis of those components in PM_{2.5} in Shanghai.

Species	Factor 1 Industry and motor vehicles	Factor 2 Dust	Factor 3 Incineration and biomass burning
F ⁻	0.1059	0.1644	0.7269
CH ₃ COO ⁻	0.6909	0.3175	0.1042
HCOO ⁻	0.5192	0.4349	0.0291
Cl ⁻	0.0364	0.5843	0.0379
SO ₄ ²⁻	0.8991	0.1840	0.0027
NO ₃ ⁻	0.8754	0.2125	0.0804
C ₂ O ₄ ²⁻	0.5642	0.1045	0.4263
PO ₄ ³⁻	0.2484	0.0654	0.7143
Na ⁺	0.2852	0.5231	0.0700
NH ₄ ⁺	0.6793	0.2232	0.0466
K ⁺	0.1388	0.3486	0.5122
Mg ²⁺	0.1572	0.7315	0.1258
Ca ²⁺	0.2898	0.7063	0.0905
OC	0.9652	0.0372	0.0103
EC	0.8157	0.0127	0.1829
Eigenvalues	6.2	2.8	1.0
% of variance	57.7	21.4	7.9
Cumulative%	57.7	79.1	87.0

Extraction method: principal component analysis and rotation method: varimax with Kaiser normalization. Note: boldface indicates that the factor loading is higher than 0.50.

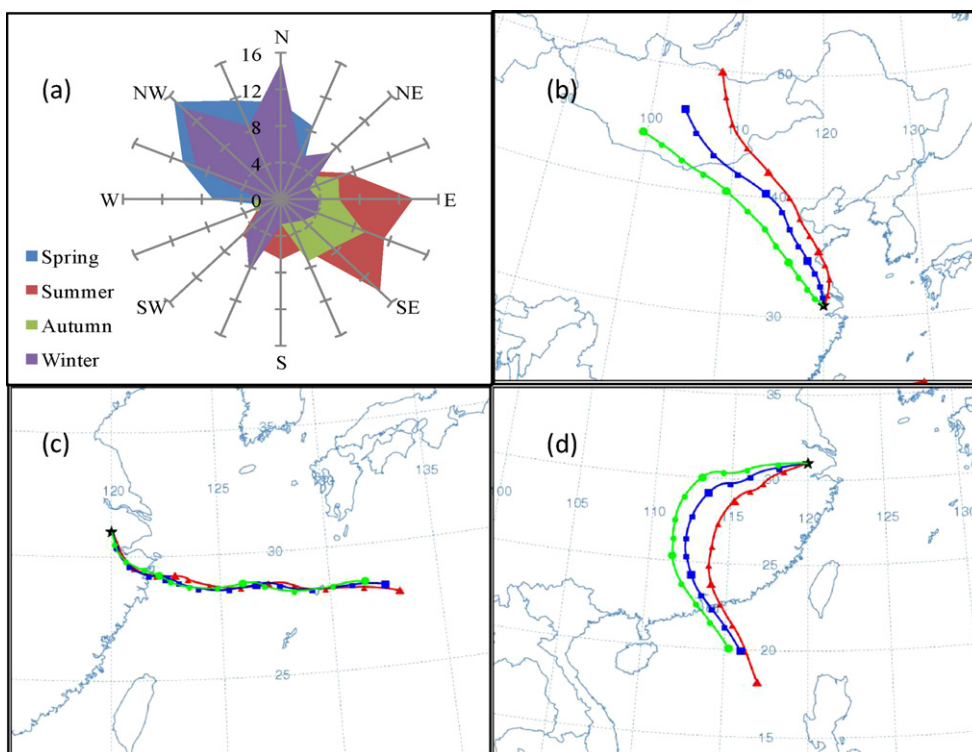


Fig. 7. (a) Wind roses in four seasons, 2006 in Shanghai, (b)–(d) three typical back trajectories in the sampling time in 2006.

before reaching Shanghai, bringing highly polluted air masses to Shanghai. In spring and winter the air masses typically originate from northern or/and northwestern China (Fig. 7(b)). In spring and winter the air masses originated from those deserts and those arid/semi-arid areas would carry much dust, mixed with more pollutants on their pathways, where a lot of coal-mines are located and a large amount of coal is used for heating, and then invaded into Shanghai. Consequently, in spring and winter both local emissions and those transported mixed dust aerosols from outside would have important contribution to fine particles in Shanghai. In summer and autumn, the prevailing southeasterly monsoon wind brings clean air masses from East China Sea to Shanghai (Fig. 7(c)), and the air-pollutants in the fine particles would mainly be from the local emissions. In addition, air parcels could also come from southwest, bringing aged aerosols, and arrive at Shanghai, as it is shown in Fig. 7(d). In the previous study [Wang et al. [39]] of our group, we quantified the contributions of dust aerosols through the long-range transport to Shanghai in spring, and the particulate matter, crustal dust, and secondary aerosols from outside the city could account for 35%, 75%, and 20%, respectively, of those corresponding matters over Shanghai. These results further supported the conclusion that OC and EC in Shanghai could also be partially from the long-range transport.

4. Conclusions

The characteristics and sources of organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ in 2006–2007 as well as their impact on the formation of heavy haze in Shanghai were investigated. Daily average concentrations of OC and EC ranged from 1.8 to 20.1 $\mu\text{g m}^{-3}$ and 0.5–7.8 $\mu\text{g m}^{-3}$ with averages of 7.2 and 2.8 $\mu\text{g m}^{-3}$, respectively. The carbonaceous aerosol contributed to ~27.2% of the total mass of $PM_{2.5}$ on annual average. Obvious seasonal variation was observed in both OC and EC. The percentage of secondary organic carbon (SOC) contributed to OC was in a range of 2.4–66.8%, with an average of 40.1%. Three types of haze were classified based on

their chemical composition. OC, EC, SO_2/NO_2 (in turn, $\text{SO}_4^{2-}/\text{NO}_3^-$) were responsible for the formation of the three types of haze, respectively. The carbonaceous aerosol was one of the key factors in the formation of haze. Local emissions were the dominant sources of OC and EC in warm seasons, and long-range transport had a significant contribution to OC and EC in $PM_{2.5}$ in spring and winter in Shanghai.

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