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Pollution characteristics of organic and elemental carbon in $PM_{2.5}$ in Xiamen, China

Fuwang Zhang[1,2], Jinping Zhao[1], Jinsheng Chen[1,*], Ya Xu[1,2], Lingling Xu[1,2]

1. Key Lab of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China. E-mail: fwzhang@iue.ac.cn
2. Graduate University of Chinese Academy of Sciences, Beijing 100049, China

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Abstract

Xiamen, located on the southeastern coastal line of China, is undergoing rapid urbanization and industrialization, so its air quality has a trend of degradation. However, studies on level, temporal and spatial changes of fine particles ($PM_{2.5}$) and their carbonaceous fractions are scarce. In this article, abundance, sources, seasonal and spatial variations, distribution of organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$, were studied at suburban, urban and industrial sites in Xiamen during four season-representative months in 2009–2010. $PM_{2.5}$ samples were collected with middle volume sampler and were analyzed for OC and EC with thermal optical transmittance (TOT) method. Results showed that the annual average $PM_{2.5}$ concentrations were 63.88–74.80 μg/m^3 at three sites. While OC and EC concentrations were in the range of 15.81–19.73 μg/m^3 and 2.74–3.49 μg/m^3, respectively, and clearly presented the summer minima and winter maxima in this study. The carbonaceous aerosol accounted for 42.8%–47.3% of the mass of $PM_{2.5}$. The annual average of secondary organic carbon (SOC) concentrations in Xiamen were 9.23–11.36 μg/m^3, accounting for approximately 56% of OC. Strong correlations between OC and EC was found in spring (R^2 = 0.50) and autumn (R^2 = 0.73), suggesting that there were similar emission and transport processes for carbonaceous aerosols in these two seasons, while weak correlations were found in summer (R^2 = 0.33) and winter (R^2 = 0.41). The OC/EC ratios in $PM_{2.5}$ varied from 2.1 to 8.7 with an annual average of 5.7, indicating that vehicle exhaust, coal smoke and biomass burning were main source apportionments of carbonaceous fractions in Xiamen.

Key words: fine particle; carbonaceous aerosol; organic carbon; elemental carbon; Xiamen

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Introduction

Carbonaceous aerosol is a significant component in fine particles (aerodynamic diameter less than 2.5 μm, $PM_{2.5}$), accounting for up to 40% of $PM_{2.5}$ mass in urban atmosphere (Seinfeld and Pandis, 1998), which is usually classified into organic carbon (OC) and elemental carbon (EC). EC, as a primary pollutant, derives from incomplete combustion of carbon contained materials, while OC can be either released directly into the atmosphere or produced from gas-to-particle reactions (Pandis et al., 1992). EC plays an important role on global climate change by affecting radiative forcing (Jacobson, 2001) and chemical reactions by forming new pollutants. OC consists of a mixture of hundreds of organic compounds (Rogge et al., 1993), and exerts a negative climate forcing influence as a scattering medium. Despite the evident significance of EC and OC in the process of air chemistry and physics, information concerning their spatial and seasonal variability is still limited.

Carbonaceous aerosol has drawn special attention in recent years due to its adverse impacts on environment, human health and climate change (Qiu and Yang, 2000; Jacobson, 2002; Hansen et al., 2005). China is a major global source of carbonaceous aerosol due to its high rates of usage of fossil-fuels and bio-fuels (Cao et al., 2006; Junker and Liousse, 2008). There were several studies focusing on the field measurements of carbonaceous fractions in $PM_{2.5}$ in China, such as Beijing (He et al., 2004; Duan et al., 2006), Shanghai (Feng et al., 2006, 2009), Guangzhou (Cao et al., 2004; Duan et al., 2007), Hong Kong (Cao et al., 2004; Ho et al., 2006), and other cities (Cao et al., 2004; Yang et al., 2005; Meng et al., 2007; Li and Bai, 2009). Moreover, researches about carbonaceous fractions in $PM_{2.5}$ abroad were also carried out (Lewtas et al., 2001; Viidanoja et al., 2002; Fan et al., 2003, 2004; Salma et al., 2004; Viana et al., 2007). However, systematic studies about the abundances, sources, spatial and seasonal variations, distributions of carbonaceous aerosols in $PM_{2.5}$ are still seldom.

* Corresponding author. E-mail: jschen@iue.ac.cn

Xiamen is a subtropical climate city in southeastern China, with an area of 1565.1 km^2 and a population of approximately 2.5 million. The main industries of Xiamen include electronics, machinery and chemicals. With rapid development of economy, like many other cities in China, Xiamen also suffers from air pollution problems (Xiamen Environmental Protection Bureau, 2008). The purposes of this study were: (1) to monitor seasonal and spatial variations of OC and EC concentrations in $PM_{2.5}$; (2) to investigate the relationship and distribution for carbonaceous fractions; (3) to identify the possible sources and factors affecting carbonaceous fractions in Xiamen.

1 Methodology

1.1 Sites and sampling

Carbonaceous aerosol samples were collected at the three environmental function areas in Xiamen, China (Fig. 1): suburban (Jimei University town in Jimei District, JM), urban (Xianyue residential area in Siming District, SM) and industrial area (Lulian hotel in Haicang District, HC).

JM, as a suburban sampling site, is located in suburban of Jimei District with rapid urbanization, which is surrounded by highway, schools, residential buildings and the Xinglin Bay. The sampler was installed at rooftop of laboratory building, about 30 m above the ground.

SM, as an urban sampling site, is arranged in Siming District, which represents mixed area of residential, traffic, and commercial environments in urban. The sampler was placed on the rooftop of a residential building, about 15 m height above the ground.

HC as the industrial sampling site is situated in Haicang District, which is main base of petrochemical and power sources in Xiamen. The sampler was set on the rooftop of a four-story hotel, about 15 m above the ground.

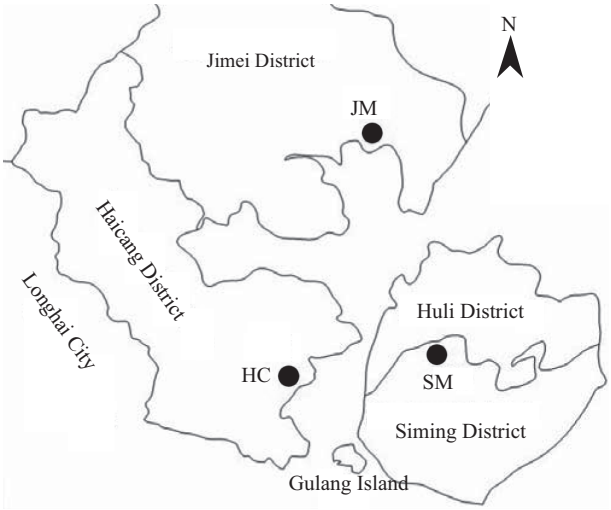

Fig. 1 Location of the sampling sites.

The 24-hr samples were performed from April 2009 to January 2010. Samples were collected for five consecutive days in every season at each site, and then 60 samples were got in this study. Middle volume samplers (Tianhong TH-150C III, China) were employed for collecting samples at a flow rate of 100 L/min. The particulates were retained on Whatman quartz fiber filters (whatman QFFs Ø90 mm, UK), which were previously annealed for 5 hr at 450°C in a furnace to remove residual carbon, then they were kept in baked aluminum foil within sealed polyethylene plastic bags. During sampling periods the meteorological parameters, including ambient temperature, relative humidity, wind speed and wind direction, are also recorded in Table 1.

All the filters were weighted before and after exposure with an analytical microbalance (Sartorius T-114, Germany) after stabilizing under constant temperature (25°C and relative humidity (52%) in a chamber. All samples were stored in refrigerator at –20°C for late analysis.

1.2 Analysis methods

OC and EC concentrations in $PM_{2.5}$ were measured by carbon analyzer (Sunset Lab Model-4, USA) with the thermal optical transmission (TOT) method following the National Institute for Occupational Safety and Health (NIOSH) protocol (Birch and Cary, 1996).

A small standard size punch (1.5 cm^2) from a QFF was placed in the sample oven, where the transmittance of red light (λ = 660 nm) through the filter could be monitored during the analysis. There were three steps of analytic procedure for OC and EC. Firstly, the sampler was heated under pure helium (He) atmosphere up to 850°C after a temperature ramp, all carbon compounds were converted into CO_2 by manganese dioxide (MnO_2) in the oxidation oven, and the CO_2 was swept out of the oxidizing oven with the He stream and measured directly by a self-contained non-dispersive infrared (NDIR) detector system. Secondly, the sample oven was cooled to 550°C and reheated to a final temperature of 870°C in a mixture of He (98%) and O_2 (2%) atmosphere.

The second temperature ramp was initiated in an oxidizing gas stream. EC was oxidized off the filter into the oxidation oven, converted into CO_2 and detected by NDIR as OC. Thirdly, an external standard gas (methane gas) was injected by a fixed volume loop for calculation at the end of every analysis. Every result was correlated by methane standard gas. The split point of OC and EC was defined

Table 1 Meteorological parameters during different sampling periods

Sampling period	Temperature (°C)	RH (%)	Wind speed (m/sec)	Wind direction	Visibility (km)
April 15–30, 2009	18.1–25.7 (20.9)	41–78 (56)	5.0–21.7 (9.8)	E-EN-N	7.7–24.6 (14.6)
July 1–15, 2009	25.7–32.2 (28.5)	55–87 (74)	3.8–19.7 (7.3)	W-WS-S	10.9–26.6 (20.0)
October 15–31, 2009	21.5–27.7 (24.4)	31–61 (47)	6.1–25.3 (10.6)	E-EN-N	9.2–25.0 (16.1)
January 1–15, 2010	10.6–16.3 (12.1)	52–84 (68)	4.1–20.6 (8.1)	E-EN-N	8.4–18.3 (12.1)

Ranges of daily variation with average are given in parentheses.

as the point at which the light transmittance of the sample returns to the initial value. The carbon evolved before the split point was considered as OC, and that evolved after the split point was EC correspondingly.

1.3 Quality assurance and quality control (QA/QC)

The analyzer was calibrated with blank filters and standard sucrose solutions every day. The results were corrected by the average concentrations of OC and EC in the blank samples, which were 0.97 μg/m^3 and zero, respectively. Replicate analyses were performed with 20% of total samples, and the differences indicated by replicate analyses was within 5% for OC, 10% for EC. Field blanks for each site were also collected and determined to examine operational contamination of the field samples in four seasons. Generally, the concentrations of OC and EC on the field blanks were less than 1% of the sample batches, and were not subtracted from the samples. The detection limit for EC and OC was 0.1 μg/m^3.

2 Results and discussion

2.1 Concentrations of $PM_{2.5}$ and OC and EC

Table 2 summarizes the concentrations of $PM_{2.5}$ at the three sampling sites. From Table 2, it was found that the mass of $PM_{2.5}$ in Xiamen was much higher than 15 μg/m^3 limited by USA National Ambient Air Quality Standard. The annual averaged concentration of $PM_{2.5}$ in JM was a little lower than that in SM, and the highest appeared in HC. Table 2 also shows that concentrations of $PM_{2.5}$ ranked in the order of summer < spring < autumn < winter. The results suggested that surrounding environment for each functional area, as well as the meteorological factors were responsible for the differences.

Table 2 Statistical concentrations of the $PM_{2.5}$ at the three sampling sites

Season	JM (μg/m^3)	SM (μg/m^3)	HC (μg/m^3)
Spring	54.04 ± 6.78	64.41 ± 4.77	75.37 ± 8.12
Summer	38.11 ± 4.68	34.26 ± 5.17	38.76 ± 6.32
Autumn	63.44 ± 8.56	80.62 ± 9.55	83.33 ± 7.02
Winter	99.92 ± 5.17	117.08 ± 10.12	101.73 ± 9.92
Annual	**63.88 ± 26.20**	**72.12 ± 34.23**	**74.80 ± 26.44**

Data are presented as mean ± deviation (n = 5).
JM, SM, and HC are sampling sites.

The average concentrations of OC, EC, and total carbonaceous aerosol (TCA), as well as OC/EC ratios and TCA/$PM_{2.5}$ ratios are listed in Table 3. The concentrations of OC, EC, and TCA showed similar trend to PM mass (Table 2). However, there was a different variation between TCA/$PM_{2.5}$ ratios and PM mass. In this study, TCA was calculated by the sum of EC and organic matter (OM), which was estimated to be 1.6 times of OC (Turpin and Huntzicker, 1995). TCA/$PM_{2.5}$ ratios could reflect the source apportionment of carbonaceous fractions and PM mass in some degree. As shown in Table 3, TCA accounted for an annual averaged 42.8% ± 7.6% (JM), 46.6% ± 8.3% (SM) and 47.3% ± 8.7% (HC) of $PM_{2.5}$, with the seasonal rank of spring < autumn < winter < summer. The data in Table 3 also suggested that TCA/$PM_{2.5}$ ratios were about 30% in spring and 50% in the other three seasons. The distinct lowest contribution of TCA/$PM_{2.5}$ ratio in spring could account for dust storms which occurred frequently in Northwest China during this season, thereby affecting the air quality of Southeastern China by long distant transportation in some degree, the studies of air quality impacted by dust storms in Hong Kong (Wai et al., 2005) and Taiwan (Fang et al., 2002) have been reported.

Various techniques were used for OC and EC measurements other than TOT, such as TOR (thermal optical reflection) etc. Although there were good agreements for total carbon (TC, sum of OC and EC) values generally compared with other methods, OC and EC concentration usually had some deviations between different analysis methods (Watson et al., 2005). Thus this study compared the carbonaceous aerosol in $PM_{2.5}$ in Xiamen with those in other cities detected only by TOT method. Urban areas are mainly residence, work, education and amusement places for people, thereby, where the carbonaceous aerosol has a significant effect on the environment and health.

Table 3 Average concentrations of OC, EC, OC/EC ratios and TCA/$PM_{2.5}$ ratios

Sampling site	Season	OC (μg/m^3)	EC (μg/m^3)	OC/EC	TCA (μg/m^3)	TCA/$PM_{2.5}$ (%)
JM (suburban)	Spring	10.14 ± 0.73	1.78 ± 0.52	6.1 ± 1.8	18.01 ± 1.28	33.3 ± 2.4
	Summer	9.64 ± 0.67	2.20 ± 0.50	4.6 ± 1.4	17.63 ± 0.69	46.3 ± 1.8
	Autumn	14.47 ± 1.82	2.46 ± 0.63	6.1 ± 1.1	25.62 ± 3.41	40.4 ± 5.4
	Winter	28.99 ± 4.30	4.53 ± 0.44	6.5 ± 1.2	50.91 ± 6.79	51.0 ± 6.8
	Annual	**15.81 ± 9.05**	**2.74 ± 1.22**	**5.8 ± 0.8**	**28.04 ± 15.68**	**42.8 ± 7.6**
SM (urban)	Spring	12.91 ± 0.91	2.16 ± 0.47	6.2 ± 1.3	22.82 ± 1.72	35.4 ± 2.7
	Summer	9.90 ± 0.67	2.34 ± 0.52	4.4 ± 1.4	18.19 ± 0.81	53.1 ± 2.4
	Autumn	24.24 ± 1.42	3.71 ± 0.42	6.6 ± 0.8	42.51 ± 2.28	52.7 ± 2.8
	Winter	30.06 ± 3.02	4.99 ± 0.58	6.1 ± 1.1	53.09 ± 4.74	45.3 ± 4.1
	Annual	**19.28 ± 9.48**	**3.30 ± 1.32**	**5.8 ± 1.0**	**34.15 ± 16.45**	**46.6 ± 8.3**
HC (industrial)	Spring	14.58 ± 1.66	2.18 ± 0.51	6.7 ± 1.7	25.88 ± 2.57	34.3 ± 3.4
	Summer	11.27 ± 0.55	2.46 ± 0.51	4.6 ± 0.4	20.50 ± 0.80	52.9 ± 2.1
	Autumn	23.55 ± 0.71	4.11 ± 0.32	5.7 ± 0.3	41.80 ± 1.46	50.2 ± 1.8
	Winter	29.53 ± 2.94	5.20 ± 0.48	5.7 ± 0.4	52.46 ± 5.03	51.6 ± 4.9
	Annual	**19.73 ± 8.34**	**3.49 ± 1.42**	**5.7 ± 0.9**	**35.16 ± 14.66**	**47.3 ± 8.7**

Values are represented as average ± standard deviation.
TCA means total carbonaceous aerosol (TCA = 1.6×OC + EC) (Turpin and Huntzicker, 1995).
OC: organic carbon; EC: elemental carbon.

Table 4 summarizes the OC and EC concentrations in $PM_{2.5}$ measured by TOT method in urban areas in Xiamen and other cities.

From Table 4, it could be found that EC concentrations in $PM_{2.5}$ ranked in the following order: Xiamen < Hong Kong < Nanjing < Taiyuan < Guangzhou < Beijing. However, OC concentrations in $PM_{2.5}$ did not have a regular rank, the reason was that OC abundances were not only affected by exhaust of local pollutants, but also impacted by meteorological factors. In a word, Xiamen, locating in subtropical coast region, where OC concentrations were higher and EC concentrations were lower than those of other cities in China, but both OC and EC concentrations were higher than those of Europe and North America.

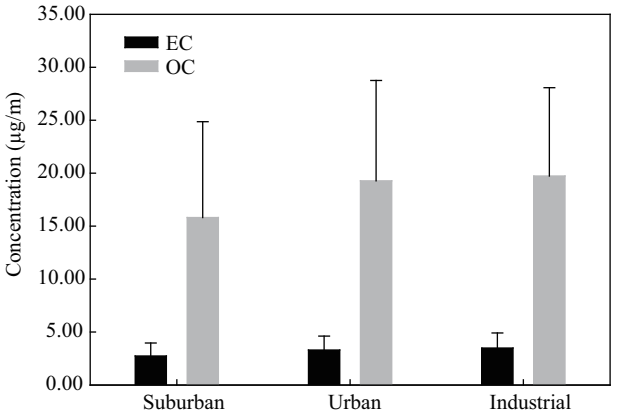

Fig. 2 Spatial variations of organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$.

2.2 Seasonal and spatial variations of OC and EC

Table 3 shows strong seasonal variations of OC and EC in $PM_{2.5}$ in Xiamen. The seasonal average OC and EC concentrations were higher in autumn and winter, whereas lower in spring and summer. The lowest OC concentration occurred in summer (9.64 $\mu g/m^3$) and the highest OC concentration appeared in winter (30.06 $\mu g/m^3$). There was a slight difference for EC in different seasons, the average of which in spring (seasonal lowest) and winter (seasonal highest) were 2.04 and 4.91 $\mu g/m^3$ concurrently. The seasonal OC concentrations ranked in order of summer < spring < autumn < winter as that of $PM_{2.5}$ mass, while EC took a turn of spring < summer < autumn < winter. The highest value of OC and EC were about four and two times than that of the lowest one, respectively. OC and EC concentrations in $PM_{2.5}$ were inclined to be lower during the warm seasons while they were higher during the cold seasons, this trend was consistent with what had been reported by the study (Cao et al., 2007) conducted in other cities in China.

The seasonal characteristics of OC and EC concentrations in $PM_{2.5}$ in Xiamen could be explained as the combined impact of meteorological conditions. During marine monsoon seasons of Xiamen, usually from June to August, clean air mass coming from the oceans could dilute ambient air pollution to a great extent. So the carbonaceous aerosol pollution in Xiamen was very limited during summer. However, during the other three seasons, winds mainly blew from the inland of China, where air masses were polluted during long distant transportation. Therefore, the carbonaceous aerosol pollution in Xiamen was heavier during autumn and winter, and the high OC and EC concentrations in winter had been also linked to particularly meteorological conditions, such as the increased stability of the lower troposphere. However, it was not so severe during the spring due to the frequent dust storms that brought more PM mass with low OC and EC.

Figure 2 shows the spatial variations of OC and EC. It could be found that OC concentrations in $PM_{2.5}$ ranked in the order of suburban < urban < industrial, in accord with pollutant emissions in Xiamen. There was only slight difference for EC in three sampling sites. Local emissions in Xiamen increased sharply due to rapid urbanization and industrialization in recent years, Xiamen consumed more than 10 million tons of coal annually for industrial and residential purposes (Xiamen Environmental Protection Bureau, 2008). There were several power plants, municipal incinerators, and petrochemical plants, etc. in Xiamen, and the number of motor vehicles reached 600 thousands by the

Table 4 Organic carbon (OC), elemental carbons (EC) concentrations in $PM_{2.5}$ and OC/EC ratio in Xiamen and other cities measured by TOT method

Location	Sampling period	OC ($\mu g/m^3$)	EC ($\mu g/m^3$)	OC/EC	Reference
Xiamen, China	Apr 2009	12.9	2.2	6.2	This study
Xiamen, China	Jul 2009	9.9	2.3	4.4	This study
Xiamen, China	Oct 2009	24.2	3.7	6.6	This study
Xiamen, China	Jan 2010	30.1	5.0	6.1	This study
Beijing, China	Jan 2002–Jul 2003	16.9	5.9	2.9	Feng et al., 2006
Shanghai, China	Oct 2005–Aug 2006	14.7	2.8	5.0	Feng et al., 2009
Guangzhou, China	Jul–Nov 2002	21.4	5.7	3.8	Feng et al., 2006
Nanjing, China	Feb–Sep 2001	13.2	3.7	3.6	Yang et al., 2005
Taiyuan, China	Dec 2005–Feb 2006	28.9	4.8	7.0	Meng et al., 2007
Hong Kong, China	Aug 2004–Mar 2005	12.0	3.4	3.5	Duan et al., 2007
Seattle, America	Apr–May 1999	5.7	0.9	6.1	Lewtas et al., 2001
Toronto, Canada	Jul 2001	7.3	0.7	10.5	Fan et al., 2003
Vancouver, Canada	Aug 2001	3.6	0.3	11.2	Fan et al., 2004
Helsinki, Finland	Jul 2000–Jul 2001	3.0	1.2	2.5	Viidanoja et al., 2002
Barcelona, Spain	Jul–Dec 2004	5.3	2.1	2.6	Viana et al., 2007
Ghent, Belgium	Jun 2004–Feb 2005	4.1	1.0	4.1	Viana et al., 2007
Amsterdam, Netherlands	Jul 2005–Feb 2006	5.3	1.8	2.9	Viana et al., 2007
Milan, Italy	Aug 2002–Dec 2003	9.2	1.4	6.6	Lonati, et al., 2007
Budapest, Hungary	Apr–May 2002	6.8	3.3	2.1	Salma et al., 2004

end of 2009 (Xiamen Environmental Protection Bureau, 2008). Therefore, vehicular exhaust and industrial emission were the major sources of carbonaceous pollution in Xiamen, which was consistent with the studies conducted in other cities (Cao et al., 2004; Feng et al., 2006).

2.3 Carbon distribution

The direct separation and quantification of primary organic carbon (POC), and secondary organic carbon (SOC) are difficult, although there are many methods for quantification of TOC. Nowadays, the minimum OC/EC ratio method, which relies mainly on ambient measurements of OC and EC, has been used to estimate the SOC formation widespread (Turpin and Huntzicker, 1995; Castro et al., 1999). This approach suggests that samples having the lowest OC/EC ratio contain almost exclusively POC. So the concentration of SOC can be estimated by the following Eqs. (1) and (2):

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

$$OC_{pri} = EC \times (OC/EC)_{min} \quad (2)$$

where, OC_{sec} is the secondary organic carbon, OC_{tot} is the total organic carbon, OC_{pri} is the primary organic carbon, $(OC/EC)_{min}$ is the value of the lowest OC/EC ratio.

Since the ratios of OC/EC can be affected by many factors such as meteorology, local sources and long-range transport of pollutants. Therefore, the measurements of POC and SOC are semi-quantitative. The $(OC/EC)_{min}$ in $PM_{2.5}$ used in this study was 2.4, which was close to that of Guangzhou, China (2.3–4.5) (Duan et al., 2007), and Shanghai, China (2.4–4.7) (Feng et al., 2009), but higher than that of Budapest, Hungary (1.1–2.9) (Salma et al., 2004), and Helsinki, Finland (1.1) (Viidanoja et al., 2002).

The carbon fractions were calculated for each season, and the proportions of POC, SOC, and EC relative to TC (TC = OC + EC, OC = POC + SOC) are illustrated in Fig. 3. Seasonal concentrations of TC were 14.64 μg/m^3 (spring), 12.61 μg/m^3 (summer), 24.18 μg/m^3 (autumn) and 34.43 μg/m^3 (winter), respectively, with the seasonal rank of summer < spring < autumn < winter. The carbon distribution of POC, SOC, and EC accounted for 45.2%, 36.3%, and 18.5% of TC in summer, respectively, while the SOC proportion increased with the POC and EC proportion decreased in the other three seasons. The difference between the two patterns was mainly resulted from meteorological conditions during each sampling period, especially the wind direction. In summer, the prevailed wind direction was W-WS-S, under the influence of the Asian monsoon, clean air masses from the oceans brought low OC fraction to Xiamen. The result of this study was

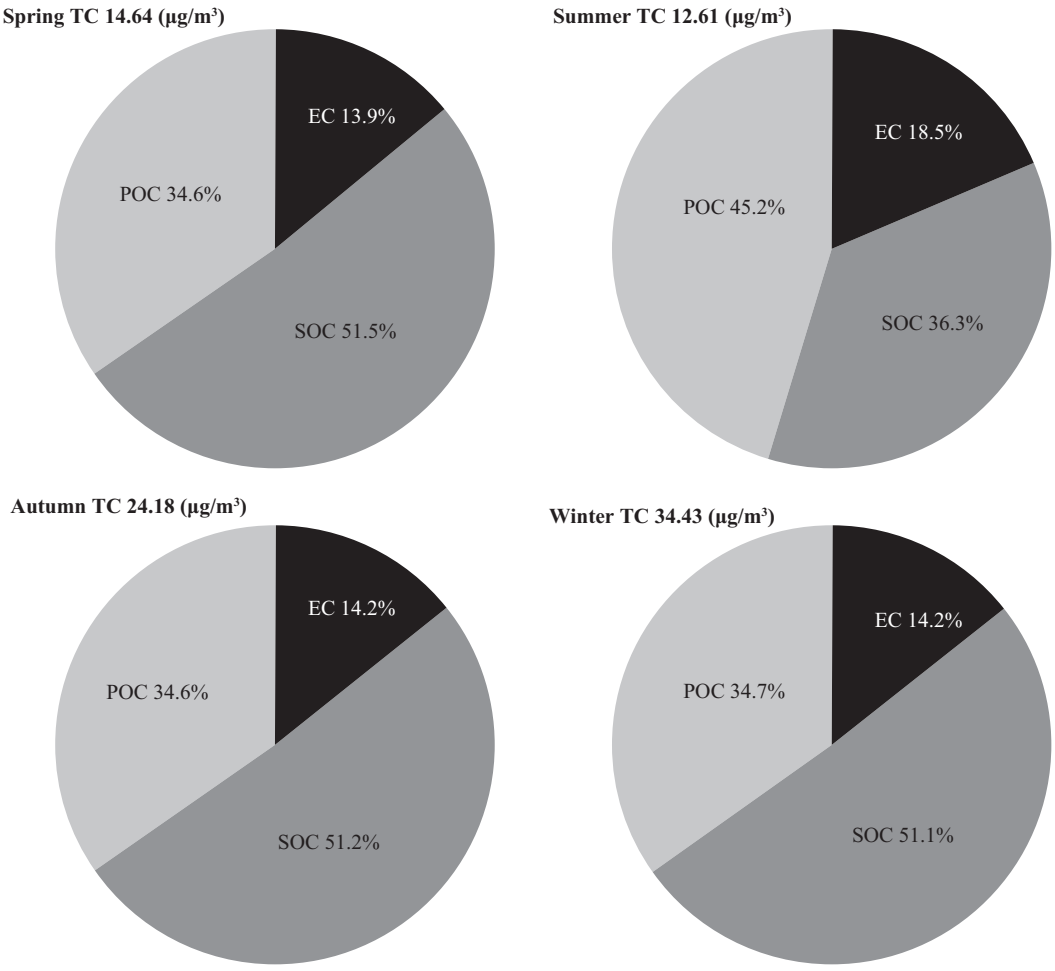

Fig. 3 Carbon distributions of OC, EC and TC in $PM_{2.5}$ for four seasons. POC: primary organic carbon; SOC: secondary organic carbon.

consistent with other study on 14 cities in China (Cao et al., 2007).

Based on Eqs. (1) and (2), it could be estimated that seasonal average concentrations of SOC in Xiamen were (7.65 ± 1.74), (4.67 ± 0.60), (12.53 ± 3.53) and (17.75 ± 0.61) μg/m^3 in spring, summer, autumn, and winter, which accounted for 60.6%, 45.4%, 60.2% and 60.1% of OC, respectively. It illuminated that SOC was an important component of OC mass in Xiamen, presenting a significant trend of second transformation.

SOA (SOA = 1.6 × SOC) (Turpin and Huntzicker, 1995) plays an important role on physical and chemical properties of the atmosphere, relating to haze, visibility, climate, and health. The annual average concentrations of estimated SOA in the three sampling sites in Xiamen were 14.77–18.18 μg/m^3, covering 23.1%–25.2% of $PM_{2.5}$ mass, which indicated that SOA also contributed a major fraction of $PM_{2.5}$ mass in Xiamen.

2.4 Relationship between OC and EC

Generally, the relationship between OC and EC concentrations could reflect the origin of carbonaceous fractions (Chow et al., 1996). If major fractions of OC and EC were emitted from a primary source, the correlation between the OC and EC concentrations should be strong, because the correlated rates of EC and OC emission would be proportional to each other (Na et al., 2004).

Figure 4 describes the correlations between OC and EC in all $PM_{2.5}$ samples. It presented strong correlations between OC and EC in spring (R^2 = 0.50) and autumn (R^2 = 0.73), which suggested that the same emission and transport process affecting the two carbonaceous fractions, whereas correlations between OC and EC were weak in summer (R^2 = 0.33) and winter (R^2 = 0.41), indicating other influences of subtropical monsoon climate discussed above, except for emission and transport process. In summer intense sunlight and high temperature produce high diffusion and chemical reaction rates, so vegetation releases large amounts of biogenic volatile organic compounds (Guenther et al., 1995), which generates SOA by photochemical reaction (Hallquist et al., 2009).

Since carbonaceous aerosol represented a mixture of various emission sources, the OC/EC ratios also could be used to distinguish different origin and transformation characteristics (Chu, 2005). Typical emission sources of carbonaceous fractions commonly included vehicle exhaust (OC/EC: 2.5–5.0) (Schauer et al., 2002), coal smoke (OC/EC: 2.5–10.5) (Chen et al., 2006), kitchen emissions (OC/EC: 4.3–7.7) (See and Balasubramanian, 2008), and biomass burning (OC/EC: 3.8–13.2) (Zhang et al., 2007), etc. It should be noted that the OC/EC ratios presented above were measured by TOT method, which were comparatively higher than those by TOR method (Watson et al., 2005). Overall, the OC/EC ratios in this study varied from 2.1 to 8.7 with an annual average of 5.7, which illuminated that vehicle exhaust, coal smoke and biomass burning were possible sources of carbonaceous fractions in Xiamen.

Except for emission of carbonaceous fractions, which was discussed above, the OC/EC ratios were also affected by atmospheric conditions. Average seasonal OC/EC ratios were higher in spring (6.3), autumn (6.1) and winter (6.1) while lower in summer (4.5), which implied that

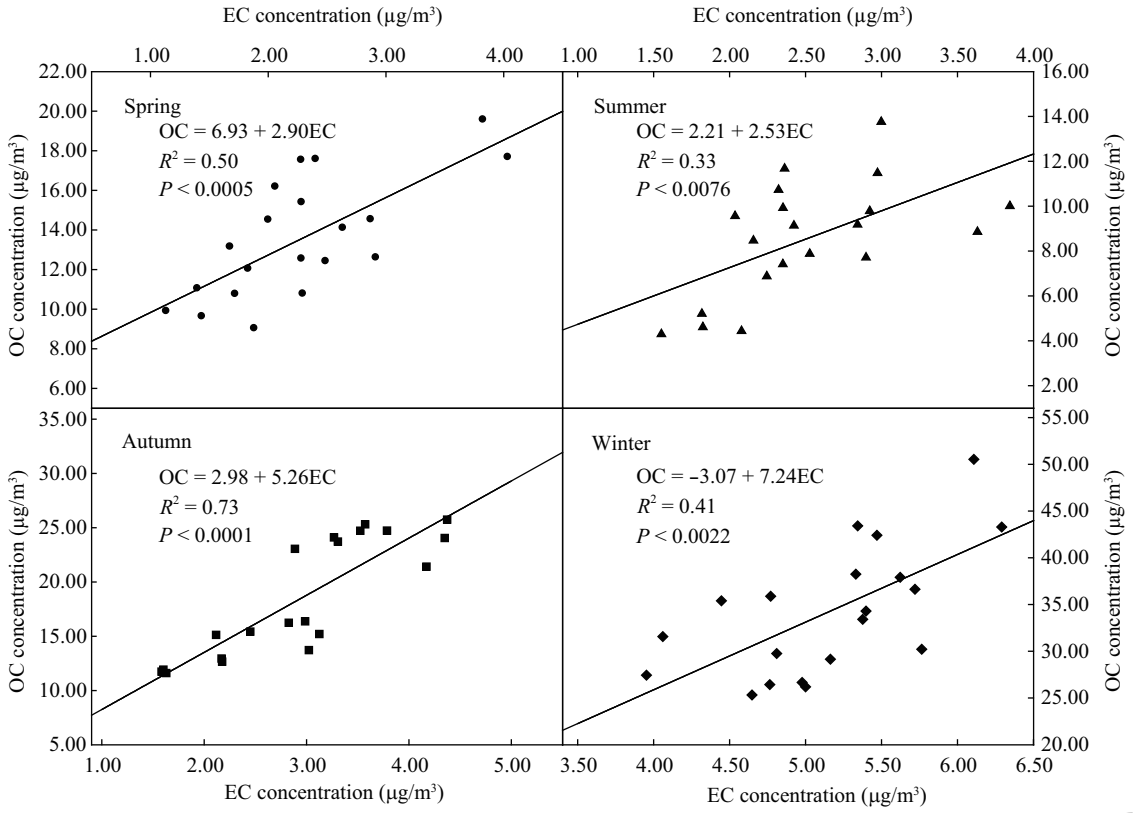

Fig. 4 Relationships between OC and EC in $PM_{2.5}$ during the four seasons.

meteorology may be also an main factor to influence the ratio of OC/EC. For example, inversion layer occurred frequently in winter would increase accumulation of OC (Sheehan and Bowman, 2001). In addition, prevailing wind direction during four seasons, excluding summer, was E-EN-N (Table 1), which could carry pollutant plume from northern China, by long-range transportation maybe also a factor to lead higher ratio OC/EC. This result was similar with other study (Duan et al., 2007).

3 Conclusions

This study was conducted at three representative sites in Xiamen during four seasons to characterize pollution of OC and EC in $PM_{2.5}$.

(1) Seasonal $PM_{2.5}$ concentrations in Xiamen ranged from 38.11 to 117.08 $\mu g/m^3$, indicating heavy fine particle pollution in Xiamen. Results of OC and EC in $PM_{2.5}$ suggested that OC concentrations were higher and EC concentrations were lower than those of other cities in China, but both OC and EC concentrations were higher than those of Europe and North America.

(2) The concentrations of OC and EC tended to be lower in warm seasons and higher in cold seasons, which implied that meteorological conditions was a main factor to result in these differences. While OC and EC concentrations in $PM_{2.5}$ took a turn of suburban < urban < industrial, which suggested that local emissions, such as vehicle exhaust and industrial emission, was another factor to influence the carbonaceous pollution in Xiamen.

(3) Annual average OC concentrations accounted for about 85% in TC, which illuminated that OC was the main fraction of TC. Moreover, annual average SOC concentrations accounted for about 56% in OC, which obviously exhibited that there was high transformation of carbonaceous fractions in this coastal city.

(4) Strong correlations between OC and EC in spring and autumn suggested that there were similar sources and transportation processes in spring and autumn, while weak correlations occurred in summer and winter. The annual average value of OC/EC ratios in this study was 5.7, which indicating that carbonaceous fractions in Xiamen were emitted from mixed sources such as vehicle exhaust, coal combustion, and biomass combustion, etc.

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