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Characterization of Atmospheric Organic Carbon and Element Carbon of $PM_{2.5}$ and PM_{10} at Tianjin, China

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ABSTRACT

Concentrations of organic carbon (OC) and elemental carbon (EC) in atmospheric particles were measured in Tianjin during January, April, July and October in 2008. The 24-h $PM_{2.5}$ (particles with aerodynamic diameters less than 2.5 micrometer [μm]) and PM_{10} (particles with aerodynamic diameters less than 10 micrometer [μm]) samples were simultaneously collected every day during sampling periods. These samples were analyzed for OC/EC by thermal/optical reflectance (TOR) following the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol. The annual average concentration was 109.8 ± 48.5 μg/m^3 in $PM_{2.5}$, and 196.2 ± 86.1 μg/m^3 in PM_{10}, respectively. The average ratio of $PM_{2.5}/PM_{10}$ was 57.9%, indicating the $PM_{2.5}$ had been one of the main contaminations affecting urban atmospheric environmental quality in Tianjin. The concentrations of OC and EC in $PM_{2.5}$ and PM_{10} were all relatively higher in winter and fall and lower in summer and spring. This seasonal variation could be attributed to the cooperative effects of changes in emission rates and seasonal meteorological conditions. The annual average concentration of the estimated secondary organic carbon (SOC) was 14.9 μg/m^3 and occupied 61.7% of the total OC in $PM_{2.5}$, while those in PM_{10} were 23.4 μg/m^3 and 61.2%, respectively, indicating SOC had been an important contributor to organic aerosol in Tianjin. The distribution of eight carbon fractions (OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OP) was also reported and found that the biomass burning, coal–combustion and motor-vehicle exhaust were all contributed to the carbonaceous particles in Tianjin.

Keywords: $PM_{2.5}$; PM_{10}; Organic carbon (OC); Elemental carbon (EC); Tianjin.

INTRODUCTION

Carbon is one of elements in atmospheric particulate matter, which occupies about 20–60% of $PM_{2.5}$ concentration and mainly exists in the form of organic carbon (OC) and element carbon (EC). Atmospheric EC is directly emitted from primary anthropogenic sources, while OC can be directly emitted from sources such as primary particulates and secondary organic carbon can be formed from the products of atmospheric chemical reactions through the low vapor pressure, proper temperature and sunlight in the atmosphere. OC and EC in particulate matter play important roles in global climate effects, visibility degradation and human health (Vedal, 1997; Chan, 1999; Cooke *et al.*, 1999; Kirkevag *et al.*,1999; Lighty *et al.*,2000; Menon *et al.*, 2002; Waston, 2002; Barnett *et al.*, 2005).

China is a major emission source of global carbonaceous aerosol due to its high rates of usage of coal and biofuels (Cao *et al.*, 2006; Junker and Liousse, 2006). Several studies concerning OC and EC in PM had been done in coastal or relatively developed cities like Beijing, Shanghai, Guangzhou and Hong Kong (Cao *et al.*, 2003; Cao *et al.*, 2004; Dan *et al.*, 2004; Yang *et al.*, 2005). But limited measurements of OC and EC are conducted in Tianjin (Cao *et al.*, 2007).

Tianjin is the largest coastal city in north China, and is located about 120 km southeast of Beijing. It has a total population of over 10 million and an area of 11919.7 km^2. Major industries in Tianjin include automobile, petrochemical, metallurgy, energy, electronics and medicine. Like many other well-developed coastal cities, such as

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Shanghai, Guangzhou, and Hong Kong (He *et al.*, 2001; Cao *et al.*,2003; Ye *et al.*, 2003; Cao *et al.*, 2004; Louie *et al.*, 2005a, 2005b), Tianjin is also faced with the serious problems of particulate matter pollution and poor visibility.

In order to figure out chemical composition of atmospheric particles and to make emission control policies in Tianjin, observation of OC and EC in $PM_{2.5}$ and PM_{10} were simultaneously conducted. The primary objectives of this study are to (1) examine seasonal variations of PM and OC and EC, (2) conclude relationship between OC and EC, (3) estimate secondary organic carbon (SOC), (4) analyze contributions of eight carbon fractions so as to identify possible sources and factors affecting carbonaceous species in Tianjin.

SAMPLING AND ANALYSIS

Sampling Site

The 24-h (0900 to 0900 local time) $PM_{2.5}$ and PM_{10} samples were simultaneously collected at an urban sampling site (Fig. 1). This site situates at the Atmospheric Boundary-layer Observation Station of Tianjin, which is located in a commercial-residential area and approximately 200m away from a major roadway. There are not high buildings and factories around, and it has natural ventilation and no special contamination. The sampling devices of particulate were situated on the second floor (about 10 m from ground) of the meteorological observation tower (the height of 225 m).

Sample Collection

Four seasons are very distinct based on local meteorological characteristics of Tianjin. Four sampling periods in 2008 were chosen to present winter–January 1st to 25th, spring–April 1st to 25th, summer–July 1st to 25th, and fall–October 1st to 25th, respectively.

In the four sampling periods, daily $PM_{2.5}$ and PM_{10} samples were collected on 90 mm Pallflex #2500 Quartz-fiber filters using middle-flow impact samplers (TH 150A Ⅱ) operating at a flow rate of 100 L/min. The quartz filters were pre-heated in a muffle furnace at 900°C for three hours before sampling to remove the residual carbon. Before and after sampling, the filters were equilibriumed in the dessicator (a temperature between 20°C and 23°C and a relative humidity (*RH*) between 35% and 45%) for forty-eight hours, and then weighed on an electronic microbalance with a ±1 μg sensitivity (Mettler Toledo, Switzerland) to determine the PM mass. Each filter was weighted at least three times before and after sampling, and the net mass was obtained by subtracting the pre-sampling weights from the post-sampling weights. Different among replicate weights were <10 μg for blanks and <20 μg for samples. After weighing, the samples were placed in refrigerator at −18°C until analysis. In this study, a total of 75 $PM_{2.5}$ and 75 PM_{10} samples were collected during the ambient sampling periods.

Thermal/Optical Carbon Analysis

OC and EC were analyzed by Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) following the IMPROVE (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol (Chow *et al.*, 1993, 2001; Fung *et al.*, 2002; Chow *et al.*, 2004a, 2005). In the analysis procedure, a 0.5 cm^2 punch from the filter was analyzed and the four OC fractions (OC1, OC2, OC3, and OC4) were respectively obtained at 120°C, 250°C, 450°C, and 550°C in a He atmosphere; the pyrolyzed carbon fraction (OP) was determined when a reflected laser light attained its original intensity after O_2 was added to the analysis atmosphere; and three EC fractions (EC1, EC2, and EC3) were respectively obtained at 550°C, 700°C, and 800°C in a 2% O_2/98% He atmosphere. Based on the IMPROVE protocol, OC is defined as OC1 + OC2 + OC3 + OC4 + OP and EC is defined as EC1 + EC2 + EC3 − OP. Every day the analyzer was calibrated with known quantities of CH_4. One sample per group of 10 samples was analyzed repeatedly. The difference determined from replicate analyses was smaller than 5% for TC and 10% for OC and EC. In the all procedure, the blank filters were also analyzed

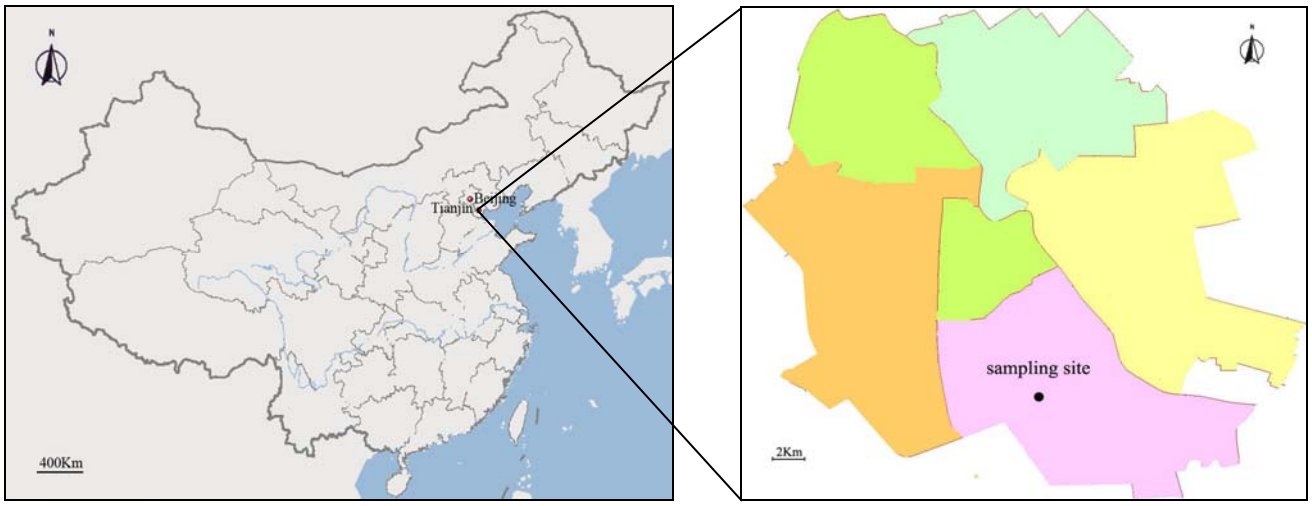


Fig. 1. Location of the sampling site at Tianjin, China.

to get the blank OC and EC concentrations. The average blank concentrations were used to correct the sample results.

RESULTS AND DISCUSSION

$PM_{2.5}$ and PM_{10} Concentrations and Ratios

The all valid observations of 24-h $PM_{2.5}$ and PM_{10} concentrations were summarized in Table 1. From this table, the results indicated:

The diurnal average concentration varied from 34.7 μg/m^3 to 296.8 μg/m^3 in $PM_{2.5}$, 55.7 μg/m^3 to 462.3 μg/m^3 in PM_{10}, respectively. Compared to the Ambient Air Quality Standards (AAQS) of Class II (150 μg/m^3) for PM_{10} applicable to residential and common industrial area and promulgated by State Environmental Protection Agency of China (SEPA) in 2000. In the sampling periods, 52 samples in 75 PM_{10} samples exceeded the standard of SEPA, furthermore, the pollution level of PM_{10} exceeded standards of SEPA by 1.0–3.1 times. However, SEPA hadn't established the standard for $PM_{2.5}$. While in 1997, USEPA, for the first time, had promulgated National Ambient Air Quality Standards for $PM_{2.5}$ with a diurnal average of 65 μg/m^3. In the sampling periods, 61 samples in 75 $PM_{2.5}$ samples exceeded the standard of USEPA, furthermore, the pollution level of $PM_{2.5}$ in Tianjin exceeded the standard of USEPA by 1.0–4.6 times. So the pollution of $PM_{2.5}$ and PM_{10} were very serious in Tianjin and could not be ignorable in the future.

The seasonal average concentration of $PM_{2.5}$ was 107.5 ± 42.5 μg/m^3 in spring, 87.0 ± 33.5 μg/m^3 in summer, 111.0 ± 48.7 μg/m^3 in fall and 133.7 ± 69.4 μg/m^3 in winter, respectively. While the seasonal average concentration of PM_{10} was 196.5 ± 77.0 μg/m^3 in spring, 156.6 ± 55.1 μg/m^3 in summer, 203.4 ± 98.5 μg/m^3 in fall and 228.1 ± 113.8 μg/m^3 in winter, respectively. In the four seasons, the average concentrations of $PM_{2.5}$ and PM_{10} were always the highest in winter and the lowest in summer. This seasonal variation could be attributed to the cooperative effects of changes in emission rates and seasonal meteorological conditions. In spring, the weather was windy and dry and was favorable for dispersion of PM, at the same time the low humidity might not favor to secondary particle formation. In summer, the rainfall was very plentiful and the PM could be efficiently removed by wet scavenging. In fall, the enhanced emission from biomass burning mainly resulted in higher concentration of PM. In winter, the high concentration of PM could be attributed to the enhanced emission from coal combustion for heating and unfavorable meteorological conditions (e.g. low mixing layer height, frequent inversion, etc.).

The ratios of $PM_{2.5}/PM_{10}$ ranged from 21.5% to 87.2% in spring, from 25.5% to 78.3% in summer, from 37.7% to 78.3% in fall and from 28.8% to 93.2% in winter, respectively. The annual average ratio of $PM_{2.5}/PM_{10}$ was 57.9% during 2008. Compared to other Chinese cities, the percentage of $PM_{2.5}$ in PM_{10} was: Hong Kong, 2001—71.7% (Cao *et al.*, 2003); Guangzhou, 2001—67.9% (Cao *et al.*, 2003); Shenzhen, 2001—73.3% (Cao *et al.*, 2003); Zhuhai, 2001—70.8% (Cao *et al.*, 2003); Chongqing, 1997—65.1% (Wei *et al.*, 1999); Wuhan, 1997—60.5% (Wei *et al.*, 1999); Lanzhou, 1997—51.9% (Wei *et al.*, 1999); Xi'an, 2003—60.4% (Wei *et al.*, 1999); Beijing, 1999–2000—64% (He *et al.*, 2001). Although the percentage of $PM_{2.5}/PM_{10}$ in South was quite different from that in North, the percentage in South was higher than that in North. The $PM_{2.5}$ had been one of main contamination affecting urban atmosphere environmental quality in Tianjin. The pollution degree of PM_{10} in northern cities exceeded that in southern cities. The main reason possibly was owing to the north – dry and rainless climate and sandstorm from the northwest.

Concentrations and Seasonal Variations of TC, OC and EC

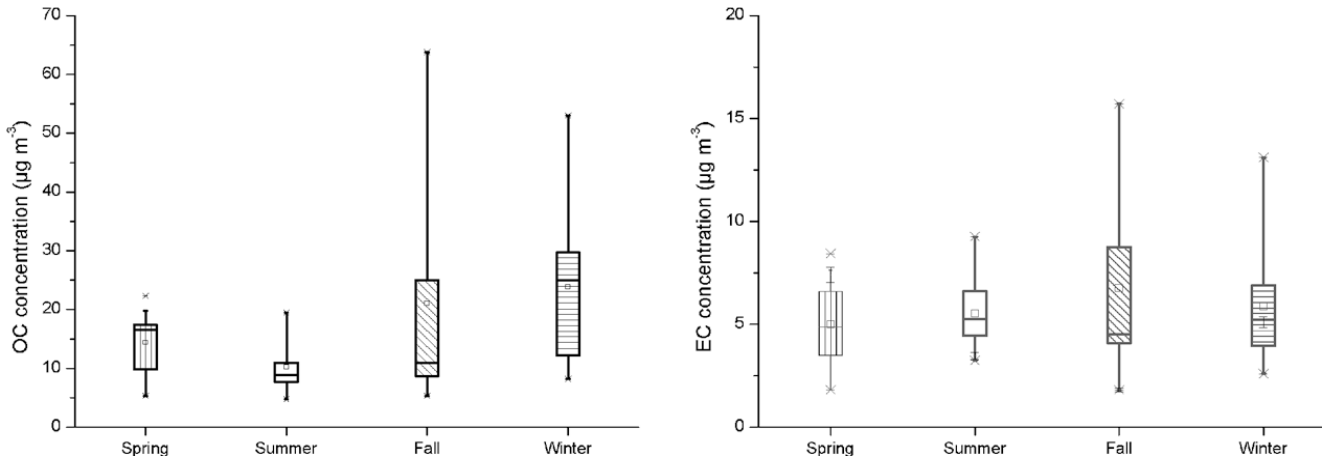
A summary of the measurement results for 24-h average concentrations of OC and EC in Tianjin were given in Fig. 2. The annual average concentrations of OC and EC were 16.9 ± 10.5 μg/m^3 and 5.7 ± 2.7 μg/m^3 in $PM_{2.5}$, 30.8 ± 18.2 μg/m^3 and 8.9 ± 4.4 μg/m^3 in PM_{10}, respectively.

The concentrations of TC and OC in $PM_{2.5}$ obviously varied with the change of the season and their gradation was summer < spring < fall < winter, while the EC concentration of $PM_{2.5}$ was in the order of spring < summer < winter < fall. The TC and EC concentrations of PM_{10} were in the order of summer < fall < spring < winter, OC in the order of summer < spring < fall < winter. The smallest concentrations of OC and EC were all in summer. Because of without heating in summer, the decreasing consumption for coal and meteorological conditions aided the dispersion and mitigated the carbonaceous pollution. Excepting EC in $PM_{2.5}$, the highest concentrations of carbonaceous species were in winter. This could be attributed to the enhanced emissions from coal combustion heating and unfavorable atmospheric dispersion (e.g. low mixing layer height, frequent inversion, etc.). While the highest concentration of EC in $PM_{2.5}$ was in fall, the highest concentration of EC

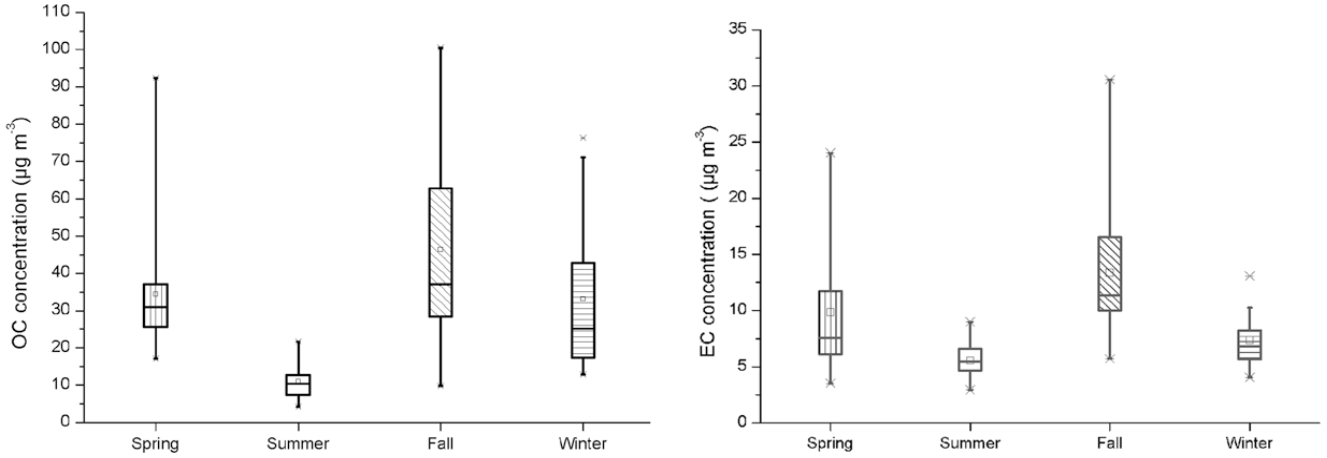
Table 1. $PM_{2.5}$ and PM_{10} concentrations of four seasons in Tianjin, China.

Season	Sample numbers		$PM_{2.5}$ Concentration (μg/m^3) [a]			PM_{10} Concentration (μg/m^3) [a]			$PM_{2.5}/PM_{10}$ (%)		
	$PM_{2.5}$	PM_{10}	Min	Max	Average	Min	Max	Average	Min	Max	Average
Spring	20	20	34.7	159.2	107.5 ± 42.5	55.7	365.7	196.5 ± 77.0	21.5	87.2	57.2 ± 19.6
Summer	17	17	35.6	138.2	87.0 ± 33.5	80.2	275.5	156.6 ± 55.1	25.5	78.3	57.0 ± 16.4
Fall	18	18	41.1	190.1	111.0 ± 48.7	81.9	444.1	203.4 ± 98.5	37.7	78.3	55.9 ± 10.1
Winter	20	20	53.4	296.8	133.7 ± 69.4	78.7	462.3	228.1 ± 113.8	28.8	93.2	61.3 ± 17.7

[a] values represent average ± standard deviation



(a) $PM_{2.5}$



(b) PM_{10}

Fig. 2. Average concentrations of TC, OC and EC at Tianjin, China.

in PM_{10} was in winter. Possibly, the contribution of biomass burning to $PM_{2.5}$ in fall was more important than that to PM_{10}.

Comparison TC, OC and EC with other Asian Cities

As shown in Table 2, the TC, OC, and EC concentrations in this study were compared with those measured in other Asian cities.

In spring, the OC and EC concentrations of $PM_{2.5}$ were higher than those measured in Chonju and Kosan, but lower than those measured in Beijing and Shanghai. In summer, the OC and EC concentrations of $PM_{2.5}$ were higher than those measured in Shanghai, Chonju and Kosan, but lower than those measured in Beijing. Otherwise, the OC concentration was higher than that in Seoul, but the EC concentrations was lower than that in Seoul. In fall, the OC and EC concentrations of $PM_{2.5}$ were higher than those measured in Chonju, Kosan, but lower than those measured in Beijing and Xi'an. Otherwise, the OC concentration was higher than that in Shanghai, but the EC concentration was lower than that in Shanghai. In winter, the OC concentration was higher than that in Guangzhou, Shenzhen, Zhuhai, Hong Kong, Shanghai, Chonju, Kosan, but lower than that in Beijing, Xi'an and Taiyuan. While the EC concentration was higher than that in Guangzhou, Shenzhen and Taiyuan, but lower than that in Beijing, Zhuhai, Hong Kong, Xi'an, Shanghai, Chonju and Kosan.

The OC and EC concentrations in PM_{10} were higher than those measured in Seoul in summer; Beijing and Uji in fall; Uji in winter. The average OC and EC concentrations respectively were 30.8 μg/m^3 and 8.9 μg/m^3 in this study and higher those measured in Kaohsiung and Hangzhou.

In summary, the OC concentration of PM in Tianjin was much higher than that measured in overseas cities and similar to those in Beijing, Guangzhou, Shenzhen, Zhuhai, Hong Kong, Xi'an, Taiyuan – all heavily polluted cities. The EC concentration in Tianjin was at a moderate level and comparable to those in most other cities. These indicated the severity of carbonaceous particles in China urban atmosphere.

Relationship between OC and EC

There were main artificial letting sources of OC and EC, which were commercial coal combustion, motor-vehicle exhaust and biomass burning. The relationship between OC

Table 2. Comparison of TC, OC, and EC at Tianjin with other Asian cities.

City	Period	Sample category	TC ($\mu g/m^3$)	OC ($\mu g/m^3$)	EC ($\mu g/m^3$)	OC/EC	Measure method	Reference
Tianjin, China	Spring 2008	$PM_{2.5}$	19.4	14.4	5	3	IMPROVE_TOR	This study
	Summer 2008	$PM_{2.5}$	15.7	10.2	5.5	1.8	IMPROVE_TOR	This study
	Fall 2008	$PM_{2.5}$	22.6	20.2	6.5	2.8	IMPROVE_TOR	This study
	Winter 2008	$PM_{2.5}$	28.5	22.9	5.6	3.8	IMPROVE_TOR	This study
Beijing[1], China	Spring, 24 Sep. 1999–28 Sep. 2000	$PM_{2.5}$	24.88	18.21	6.67	2.73	IMPROVE_TOR	He *et al.* (2001)
	Summer,24 Sep. 1999–28 Sep. 2000	$PM_{2.5}$	19.69	13.42	6.27	2.14	IMPROVE_TOR	He *et al.* (2001)
	Fall,24 Sep. 1999–28 Sept. 2000	$PM_{2.5}$	39.02	28.79	10.23	2.81	IMPROVE_TOR	He *et al.* (2001)
	Winter,24 Sep. 1999–28 Sep. 2000	$PM_{2.5}$	42.57	31.49	11.08	2.84	IMPROVE_TOR	He *et al.* (2001)
Guangzhou, China	Jan.–Feb. 2002	$PM_{2.5}$	17.3	12.2	5	2.4	IMPROVE_TOR	Cao *et al.* (2003)
Shenzhen, China	Jan.–Feb. 2002	$PM_{2.5}$	14.4	9.6	4.7	2.3	IMPROVE_TOR	Cao *et al.* (2003)
Zhuhai, China	Jan.–Feb.2002	PM_{25}	23.2	16.3	6.9	2.4	IMPROVE_TOR	Cao *et al.* (2003)
Hong Kong	Jan.–Feb. 2002	$PM_{2.5}$	25.1	17	8.1	2.1	IMPROVE_TOR	Cao *et al.* (2003)
Shanghai[2], China	Spring 1999	$PM_{2.5}$	21.37	16.1	5.27	3.06	IMPROVE_TOR	Ye *et al.* (2003)
	Summer 1999	$PM_{2.5}$	14.23	9.62	4.61	2.09	IMPROVE_TOR	Ye *et al.* (2003)
	Fall 1999	$PM_{2.5}$	22.01	15.22	6.81	2.23	IMPROVE_TOR	Ye *et al.* (2003)
	Winter 1999	$PM_{2.5}$	24.56	16.4	8.16	2.01	IMPROVE_TOR	Ye *et al.* (2003)
Xi'an,China	Fall 2003	$PM_{2.5}$	45.4	34.1	11.3	3.3	IMPROVE_TOR	Cao *et al.* (2005)
	Winter 2003	$PM_{2.5}$	74.2	61.9	12.3	5.1	IMPROVE_TOR	Cao *et al.* (2005)
Taiyuan,China	Winter, Dec. 2005, Jan.–Feb. 2006	$PM_{2.5}$	33.5	28.9	4.8	7.0	IMPROVE_TOR	Meng *et al.* (2007)
Chonju, Korea	Spring 1995	$PM_{2.5}$	8.42	4.83	3.59	1.35	IMPROVE_TOR	Lee and Kang (2001)
	Summer 1995	$PM_{2.5}$	7.41	4.04	3.37	1.2	IMPROVE_TOR	Lee and Kang (2001)
	Fall 1995	$PM_{2.5}$	12.35	6	6.35	0.94	IMPROVE_TOR	Lee and Kang (2001)
	Winter 1995	$PM_{2.5}$	9.31	4.99	4.32	1.16	IMPROVE_TOR	Lee and Kang (2001)
Kaohsiung, Taiwan	Nov. 1998–Apr. 1999	$PM_{2.5}$	14.4	10.4	4	2.6	Elemental analyzer	Lin and Tai (2001)
Seoul, Korea	Jul. and Aug. 1994	$PM_{2.5}$	17.54	9.97	7.57	1.3	Selective thermal oxidation	Kim *et al.* (1999)
Kosan, Korea	20 Jul.–1 Aug. 1995	$PM_{2.5}$	2.46	2.36	0.1	23.6	Selective thermal oxidation	Kim *et al.* (2000)
	28 Feb.–13 Mar. 1996	$PM_{2.5}$	3.29	2.97	0.32	9.3	Selective thermal oxidation	Kim *et al.* (2000)
	26 Sep.–6 Oct. 1997	$PM_{2.5}$	3.98	3.56	0.42	8.5	Selective thermal oxidation	Kim *et al.* (2000)
	9–20 Jan. 1997	$PM_{2.5}$	3.54	3.31	0.23	14.4	Selective thermal oxidation	Kim *et al.* (2000)
Tianjin, China	Spring 2008	PM_{10}	42.5	32.9	9.6	3.8	IMPROVE_TOR	This study
	Summer 2008	PM_{10}	17	11.2	5.7	1.9	IMPROVE_TOR	This study
	Fall 2008	PM_{10}	40.5	33.2	7.4	3.7	IMPROVE_TOR	This study
	Winter 2008	PM_{10}	58.7	46	12.7	4.3	IMPROVE_TOR	This study
Uji, Japan	Sep.–Oct. 1998	PM_{10}	19.4	13.9	5.5	2.5	R&P 5400	Holler *et al.* (2002)
	Nov.–Dec. 1998	PM_{10}	18	12.8	5.2	2.5	R & P 5400	Holler *et al.* (2002)
Seoul, Korea	Jul. and Aug. 1994	PM_{10}	19.49	11.1	8.39	1.32	Selective thermal oxidation	Kim *et al.* (1999)
Beijing, China	Sept. 8–Nov. 30 2002	PM_{10}	30.1	21.2	8.9	2.4	R & P 5400	Zhang *et al.* (2007)
Kaohsiung, Taiwan	Nov. 1998 to Apr. 1999	PM_{10}	20.6	14.5	6.1	2.4	Elemental analyzer	Lin and Tai (2001)
Hangzhou, China	Sept. 2001–Aug.t 2002	PM_{10}	25.47	21.41	4.06	5.27	TOT	Cao *et al.* (2009)

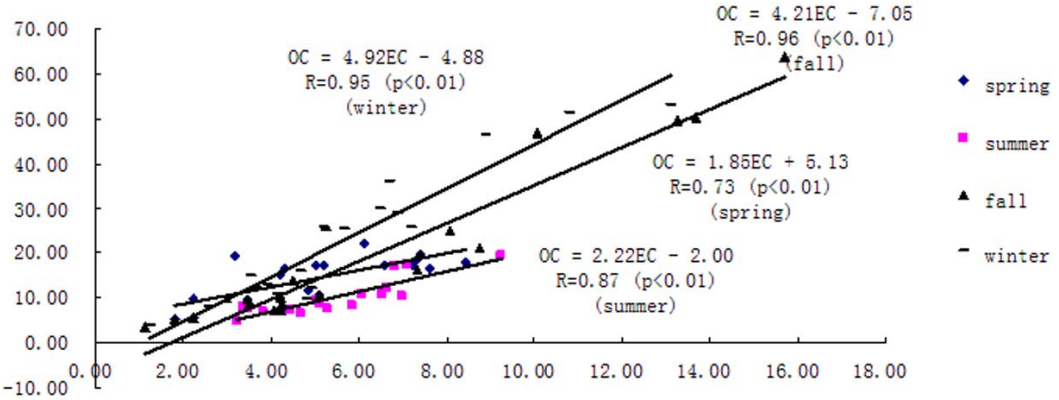
[1] Chegongzhuang site. [2] Tongji University site.

and EC could help identify the origins of carbonaceous $PM_{2.5}$ (Gray *et al.*, 1986; Turpin *et al.*, 1991; Chow *et al.*, 1996). Therefore, the mass ratio of OC to EC (OC/EC) had been used to study emission and transformation characteristics of carbonaceous aerosol.

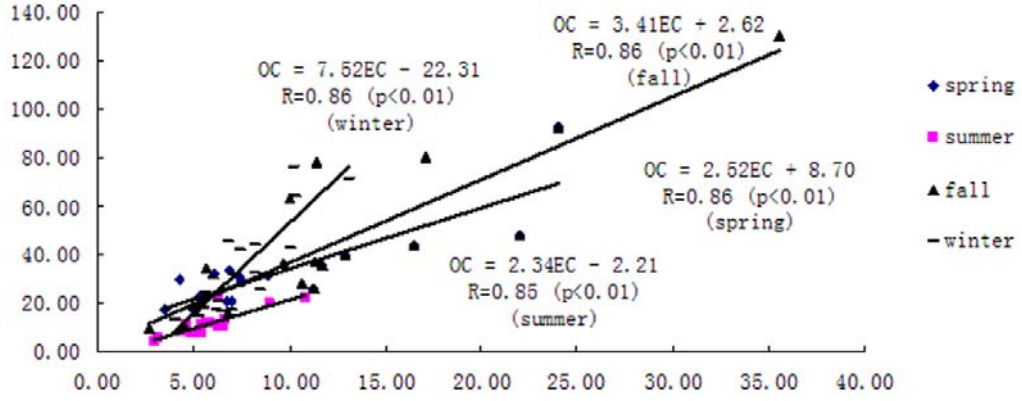
As shown in Fig. 3, the correlation coefficients (R) of OC/ EC were 0.87, 0.73, 0.96 and 0.95 in $PM_{2.5}$ for spring, summer, fall and winter, respectively. The correlation coefficients were higher in winter and fall than those in spring and summer. It showed that in winter and fall the sources of OC and EC in $PM_{2.5}$ were relatively simple. Possibly, the commercial coal combustion and motor-vehicle exhaust were responsible for that in winter, while the motor-vehicle exhaust and biomass burning were responsible for that in fall. The correlation coefficients (R) of OC/EC were 0.86, 0.85, 0.86 and 0.86 for spring, summer, fall and winter in PM_{10}, respectively. These correlation coefficients were very similar in the four seasons, which showed that the sources of OC and EC in PM_{10} were similar and complicated in the four seasons.

As shown in Table 2, the ratios of OC/EC ranged from 2.1 to 6.1, 1.4 to 2.5, 1.7 to 4.7 and 2.0 to 5.4, respectively, in $PM_{2.5}$ and 2.2 to 6.9, 1.4 to 3.5, 2.2 to 6.8 and 2.5 to 7.5, respectively, in PM_{10} for spring, summer, fall and winter. The ratios of OC/EC in $PM_{2.5}$ and PM_{10} in this study were compared with other measurements in Table 2. It appeared that the ratios of OC/EC for most of the urban sites were between 1.0 and 4.0. Because these urban sites were designed not being close to any major primary OC/EC emission sources such as motor vehicles, industrial sources and avoided being unduly influenced by them. But in winter at Tianjin, there were the elevated seasonal average OC/EC ratios (3.8 in $PM_{2.5}$ and 4.3 in PM_{10}) which might be attributed to several reasons. First, coal consumption for winter heating contributed more to OC than EC, and also increased the emission of volatile organic precursors. Secondly, low temperature led to the adsorption and condensation of semi-volatile organic compounds onto existing solid particles. Thirdly, the low mixing layer height in winter would enhance the SOC formation.

Because the organic carbon could be derived from emitted particles as well as secondary organic aerosol, it was very important to confirm the contributions of the primary and secondary organic carbon to carbonaceous aerosol for controlling of particulate pollution. Owing to there was no simple direct analytical technique to analysis secondary organic carbon. Several indirect methodologies had been applied to attain the evaluation of secondary organic carbon in ambient aerosols (Turpin and Huntzicker, 1991; Pandis *et al.*, 1992; Turpin and Huntzicker, 1995; Castro *et al.*, 1999). Following the Castro's equation, the concentration of SOC could be calculated by the experiential equation.



(a) $PM_{2.5}$



(b) PM_{10}

Fig. 3. Relationship between OC and EC concentrations of $PM_{2.5}$ and PM_{10}.

$$SOC = OC - EC(OC/EC)_{\min} \quad (1)$$

In this study, 75 $PM_{2.5}$ samples and 75 PM_{10} samples were simultaneously collected during the sampling periods. The observed minimum ratios of OC/EC were 2.1, 1.4, 1.7 and 2.0, respectively, in $PM_{2.5}$ and 2.2, 1.4, 2.2 and 2.5, respectively, in PM_{10} for spring, summer, fall, and winter.

According to above the equation, the average concentrations of SOC in $PM_{2.5}$ and PM_{10} were calculated and shown in Table 3. The average concentrations of SOC in $PM_{2.5}$ and PM_{10} were all the highest in fall and the lowest in summer. The percentages of SOC/OC in $PM_{2.5}$ and PM_{10} were all higher in summer and fall, while lower in winter and spring. It was possibly due to that SOC in the atmosphere was controlled by temperature. When the temperature was higher, the SOC more easily came into being. The average percentages of SOC/OC were 61.7% in $PM_{2.5}$ and 61.2% in PM_{10}, respectively. It implied that SOC was an important component of OC and SOC might be a significant contributor to atmospheric particles in Tianjin.

OC, EC and TCA Contributions to $PM_{2.5}$ and PM_{10}

As shown in Table 4, the percentages of OC and EC to $PM_{2.5}$ mass accounted for 13.9% and 4.9% for spring, 13.0% and 7.0% for summer, 15.2% and 5.1% for fall, 19.8% and 5.2% for winter, respectively. While the percentages of OC and EC to PM_{10} mass accounted for 18.5% and 5.5% for spring, 8.5% and 4.3% for summer, 21.0% and 6.0% for fall, 16.2% and 3.8% for winter, respectively. Because the relative abundances of OC and EC determined the relative amounts of scattering and absorption, it implied that light scattering of carbonaceous aerosol should be one of the major factors causing visibility impairment in Tianjin. On average, the annual average OC and EC accounted for 17.0% and 5.7% of $PM_{2.5}$ and 16.1% and 4.9% of PM_{10}, respectively. It indicated that more carbonaceous species enriched in fine particles.

The amount of urban organic matter might be estimated by multiplying the amount of OC by 1.6 (Turpin and Lim, 2001). Thus, the total carbonaceous aerosol (TCA) was calculated by the sum of organic matter and elemental carbon (TCA = OC × 1.6 + EC). Total carbonaceous aerosol accounted for an averaged 32.8% of $PM_{2.5}$ mass and 30.6% of PM_{10} mass. Although the percentage of TCA in PM_{10} was lower than in $PM_{2.5}$, the carbonaceous fraction accounted for about one-third of the $PM_{2.5}$ and PM_{10} mass in Tianjin.

The Analysis of Eight Carbon Fractions

The IMPROVE-TOR method step by step upgraded the temperature to measure each sample, and eight carbon fractions (OC1、OC2、OC3、OC4、EC1、EC2、EC3、OP) were provided. Carbon abundances in each of these fractions differed from carbon sources (Waston *et al.*, 1994; Chow *et al.*, 2004b). The abundance of eight carbon fractions in the source sample showed certain character of source composition. Eight carbon fractions had been used to identify the source apportionment of carbonaceous aerosol (Kim *et al.*, 2003a, b; Kim and Hopke, 2004). For example, OC1 was abundant in the sample of biomass burning. The abundance of OC3 and OC4 relatively were in the road dust profile (Chow *et al.*, 2004). OC2 was abundant in the sample of coal-combustion. EC1 was enriched in motor-vehicle exhaust sample (Cao *et al.*, 2005). EC2 and EC3 were carbon fractions of coal–combustion and motor-vehicle exhaust. A larger OP fraction for polar organic compounds was extracted in water (Yu *et al.*, 2002). Therefore, the sources of pollution were identified on the basis of the above mention.

The percentages of carbon fractions collected at Tianjin during the sampling periods were shown in Fig. 4. The average abundances of OC1, OC2, OC3, OC4, EC1-OP, EC2, EC3 and OP were 9.3%, 14.6%, 14.3%, 12.1%, 24.1%, 1.9%, 0.2%, and 23.5%, respectively, in $PM_{2.5}$ TC, while 8.1%, 13.1%, 14.9%, 13.3%, 20.6%, 2.5%, 0.4% and

Table 3. Levels of secondary organic carbon (SOC) estimated from minimum OC/EC ratios.

Season	SOC Concentration (μg/m^3)		Percentage (SOC/OC, %)	
	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}
Spring	8.1 ± 4.8	12.0 ± 8.5	50.3 ± 23.1	37.4 ± 17.2
Summer	7.7 ± 3.8	8.6 ± 4.8	72.3 ± 8.4	73.2 ± 8.7
Fall	16.3 ± 17.3	39.5 ± 30.9	64.4 ± 22.1	75.8 ± 18.1
Winter	16.1 ± 13.0	23.4 ± 15.9	59.8 ± 16.1	58.3 ± 8.5
Average	12.1 ± 9.7	20.6 ± 15.0	61.7 ± 17.4	61.2 ± 13.1

Table 4. Statistical summary of the percentages of TCA, OC and EC in $PM_{2.5}$ and PM_{10}[a].

Season	TCA (%)		OC (%)		EC (%)	
	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}
Spring	27.1 ±6.8	35.1 ± 13.6	13.9 ± 3.8	18.5 ± 6.9	4.9 ± 1.3	5.5 ± 3.0
Summer	28.0 ± 13.1	17.9 ± 12.5	13.0 ± 6.2	8.5 ± 6.2	7.1 ± 3.4	4.3 ± 2.7
Fall	29.4 ± 17.5	39.5 ± 19.9	15.2 ± 9.6	21.0 ± 10.8	5.1 ± 2.5	6.0 ± 3.1
winter	37.0 ± 12.2	29.8 ± 9.2	19.8 ± 7.0	16.2 ± 5.4	5.2 ± 1.5	3.8 ± 1.1
Average	32.8 ± 13.7	30.6 ± 13.8	17.0 ± 7.4	16.1 ± 7.3	5.7 ± 2.2	4.9 ± 2.5

[a] values represent average ± standard deviation

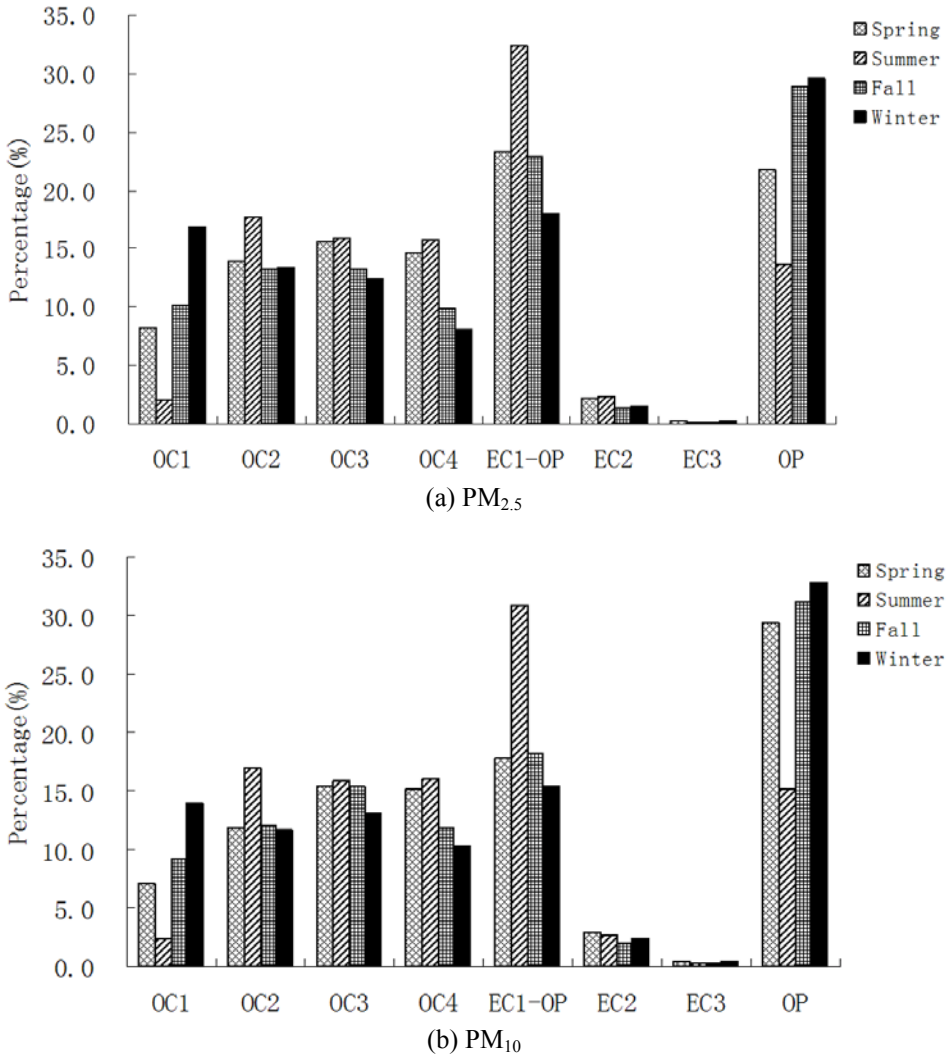


Fig. 4. The abundance of eight carbon fractions of 2008 in Tianjin.

27.1%, respectively, in PM_{10} TC. The percentages of EC3 were the lowest in both $PM_{2.5}$ and PM_{10} TC, because there was very little high-temperature (800°C) EC3 in any of these samples. The percentages of EC2 were the secondary lowest. Because the gasoline-fueled vehicle was the primary one in Tianjin, While EC2 was the most abundant species in the exhaust of diesel-fueled vehicles. With the change of the season, the percentages of OC1 ranged from 2.5% in summer to 14% in winter. This indicated that, apart from the enhanced emissions of biomass burning for heating supply, more semi-volatile OCs tend to condense on pre-exist aerosols under low temperature contributing to the high wintertime OC1 concentration. The percentage of OC2 was the highest in summer, which possibly associated with photochemical SOC formation. The increases of OC3 and OC4 in spring and summer might be indicated the impacts of road dust. The abundance of EC1, mainly from motor-vehicle exhaust, was relatively stable in all the seasons. The high OP fraction, (23.5% in $PM_{2.5}$ TC and 27.1% in PM_{10} TC), implied that substantial water-soluble polar compounds might present in Tianjin atmosphere. Although there was a substantial seasonal variety of eight carbon fractions in $PM_{2.5}$ and PM_{10}, the OC1, OC2, OC3, OC4, EC1, and OP were generally the most abundant species and their percentages were all over 9.0%. This indicated that the biomass burning, coal–combustion and motor-vehicle exhaust were all contributed to the high eight carbon fractions. To accurate source apportionment of carbonaceous aerosol, the source profiles of 8 carbon fractions in Tianjin would be necessary in the future.

CONCLUSIONS

In 2008, Continuous observations were conducted in Tianjin to gain the characterization of organic and elemental carbon. Major results were as follows:

1. The annual average concentrations of $PM_{2.5}$ and PM_{10} were 109.8 ± 48.5 μg/m^3 and 196.2 ± 86.1μ/m^3, respectively. The annual average ratio of $PM_{2.5}/PM_{10}$ was 57.9%. It indicated that $PM_{2.5}$ had been one of the main contaminations affecting urban atmosphere environmental quality in Tianjin.
2. The highest carbon concentration and OC/EC ratios in winter resulted from enhanced emissions from coal

combustion for heating and coupled with poor atmospheric dispersion (e.g. low temperature the low mixing layer height, etc.). In summer, the abundant rainfall removed carbonaceous aerosol by wet scavenging and led to the lowest carbon concentrations and OC/EC ratios.

3. The annual average SOC concentrations were 12.1 ± 9.7 μg/m^3 in $PM_{2.5}$ and 20.6 ± 15.0 μg/m^3 in PM_{10}, respectively. The annual average percentages of SOC/OC were 61.7% in $PM_{2.5}$ and 61.2% in PM_{10}, respectively. It indicated that SOC was an important contributor to PM in Tianjin.
4. Although there was a substantial seasonal variety of eight carbon fractions in $PM_{2.5}$ and PM_{10}, the OC, EC1 and OP were generally the most abundant species, accounting for over 9.0%. This indicated that the biomass burning, coal–combustion and motor-vehicle exhaust were all contributed to the high carbon species.

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