# Characterization, Meteorological Influences and Source Identification of Carbonaceous Aerosols during the Autumn-winter Period in Tianjin, China

**Peng-hui Li[1], Bin Han[1,3], Jing Huo[1], Bing Lu[1], Xiao Ding[1], Li Chen[1], Shao-fei Kong[1], Zhi-peng Bai[1,2*], Bin Wang[4]**

[1] *State Environmental Protection Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control, Nankai University,Tianjin, China*
[2] *Chinese Research Academy of Environmental Sciences, Beijing, China*
[3] *College of Mathematics Science, Nankai University, Tianjin, China*
[4] *Tianjin Environmental Monitoring Center, Tianjin, China*

## ABSTRACT

Organic and elemental carbon (OC and EC) were measured in $PM_{2.5}$ and $PM_{10}$ at urban and suburban sites in Tianjin, China, from September 2009 to February 2010. Average $PM_{2.5}$ and $PM_{10}$ mass levels were 124 and 243 μg/m$^3$, respectively, with 53% of the $PM_{10}$ mass present as $PM_{2.5}$. The average OC and EC concentrations in $PM_{2.5}$ were 14.5 and 4.3 μg/m$^3$, respectively, while those in $PM_{10}$ were 33 and 6.1 μg/m$^3$, respectively. Relation of OC and EC to the trace elements As, Zn, K and Pb and principal component analysis indicated that multiple sources contributed to the OC and EC. Secondary organic carbon was found to constitute 46% and 66% of the total organic carbon in $PM_{2.5}$ and $PM_{10}$, respectively, in autumn and 41% and 56%, respectively in winter.

*Keywords:* Organic carbon; Element carbon; $PM_{2.5}$; $PM_{10}$; Tianjin.

## INTRODUCTION

Ambient particulate matter (PM), especially in urban and highly industrialized areas, contains an important fraction of carbonaceous material (Nunes and Pio, 1993; Castro *et al*., 1999; Ho *et al*., 2003; Dan *et al*., 2004; Cao *et al*., 2006; Meng *et al*., 2007). Atmospheric particulate carbon is comprised of a complex mixture of substances containing carbon atoms, in two main fractions: organic carbon (OC) and elemental carbon (EC). EC is mainly emitted from anthropogenic combustion sources and does not undergo chemical transformations. It is used as a good indicator of primary anthropogenic air pollutants (Larson and Cass, 1989; Kim *et al*., 2000; Lin and Tai, 2001). OC, containing PAHs, PCBs and other components with potential mutagenic and carcinogenic effects, has both a primary and secondary origin (Cao *et al*., 2003; Cao *et al*., 2005; Ram *et al*., 2008). Primary organic carbon (POC) is formed during combustion and emitted in particulate form, while secondary organic carbon (SOC) is formed in the atmosphere through gas-to-particle conversion processes of volatile organic compounds,

either as result of the condensation of low vapor pressure volatile organics or chemical adsorption of gaseous species on aerosol particle surfaces (Pandis *et al*., 1992; Pankow, 1994; Turpin and Huntzicker, 1995). Formation of SOC has frequently been observed during laboratory investigations in smog chamber experiments from light irradiation of gaseous mixtures containing organic compounds (McMurry and Grosjean, 1985; Stern *et al*., 1987; Pankow, 1994).

Rapid industrialization and economic development has occurred in China during recent years and may increase the emission of various pollutants. Lack of extensive and effective pollution-control measurement means that the amount of particulate matter emitted into atmosphere will increase and impact the health of the public. Many studies have been performed in the world focusing on carbonaceous species of PM, however, limited studies have been done in China (Cao *et al*., 2003; Dan *et al*., 2004). To date, research on carbonaceous particles in $PM_{2.5}$ and/or $PM_{10}$ in China were reported only in few cities, such as Taiwan (Lin and Tai, 2001), Xian (Cao *et al*., 2005), Taiyuan (Meng *et al*., 2007), the Pear River Delta Region (Cao *et al*., 2003) and Beijing (Dan *et al*., 2004). As far as Tianjin is concerned, rare studies have been reported. Tianjin is considered as one of the most developed region of China, and high PM levels and poor visibility have become a serious problem (Cao *et al*., 2003). Coal and biomass burning, vehicle exhaust and industrial emissions all contribute to the ambient PM in

---

* Corresponding author. Tel.: 86-22-2350-3397;
 Fax: 86-22-2350-3397
 *E-mail address:* zbai@nankai.edu.cn

Tianjin. Therefore, observations for OC and EC analysis are needed for Tianjin.

In this paper the concentrations and distributions of particulate elemental and organic carbon in Tianjin are presented. The paper is aimed to quantify the contribution of carbonaceous species to $PM_{2.5}$ and $PM_{10}$, identify potential sources and meteorological influences, and estimate SOC production during the sampling period. Information obtained in this study will also allow evaluation of the changes in air quality in Tianjin and help to develop further pollution control strategies for particulate matter.

## MATERIALS AND METHODS

### *Sampling Sites and Description*

Tianjin is a typical metropolis in northern China, with a

population of approximately 10 million, covering a land area of about 11,919 $km^2$. It is located to the southeast of Beijing, on the lower reaches of the Haihe River and adjacent to the Bohai Sea. As one of the most rapidly developing regions in China, Tianjin has been suffering from severe particulate matter pollution problems during recent years.

Eight sampling sites were chosen in this study as shown in Fig. 1. DongLi monitoring station site (DL) and BeiChen monitoring station site (BC) were chosen to represent suburban sites in Tianjin. The other six sites were located in the urban area. Detailed information about sampling sites is given in Table 1.

### *PM Sampling*

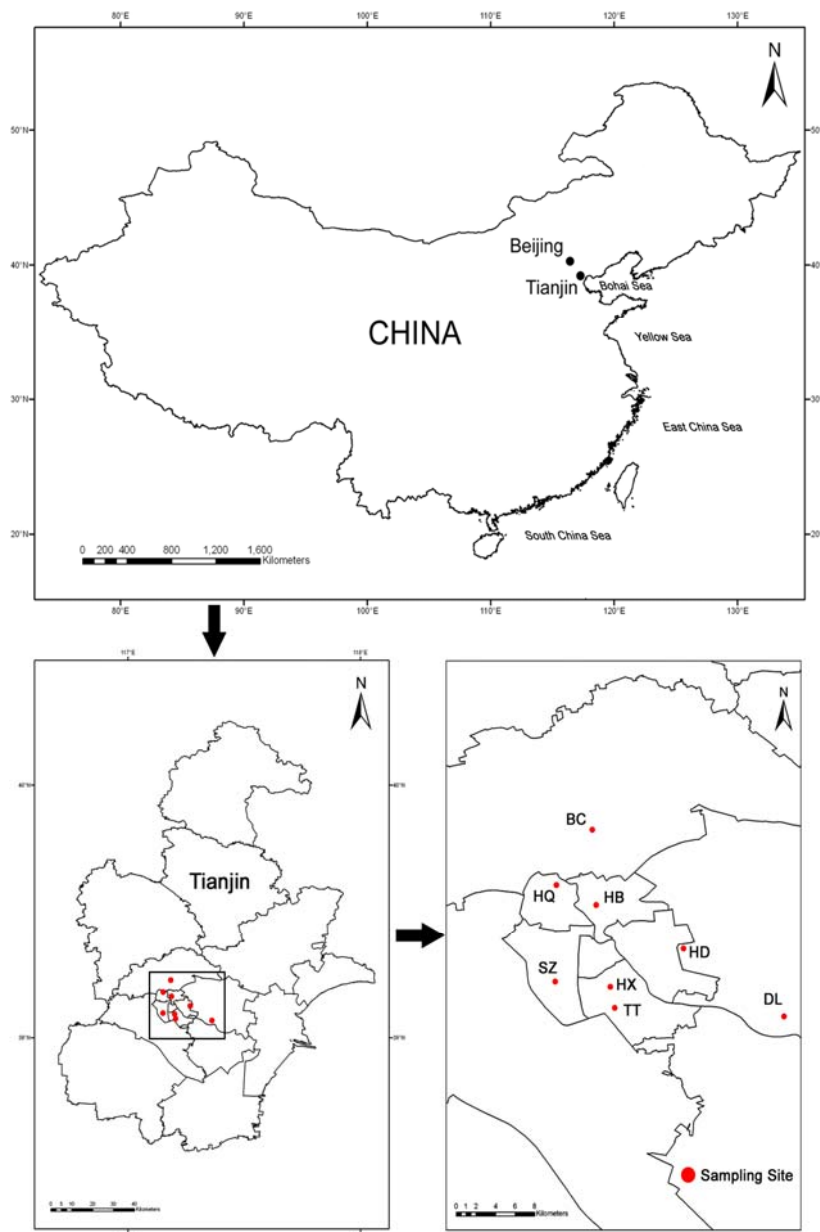PM samples were collected at 8 sites from September, 2009 to February, 2010. $PM_{2.5}$ samples were collected



**Fig. 1.** Location of eight sampling sites in Tianjin.

**Table 1.** Descriptions of sampling sites.

| | Sampling sites | Sites location | Sites description |
|---|---|---|---|
| Suburban sites | DongLi monitoring station site (DL) | N39°4'3.37"<br>E117°21'41.86″ | The site was situated at about 12 m above ground level in the environmental monitoring station of DongLi District |
| | BeiChen monitoring station site (BC) | N39°13'33.60"<br>E117°11'6.10" | The site was situated at about 10 m above ground level in the Tianjin BeiChen hi-tech industrial park. |
| Traditional urban sites | HeXi monitoring station site (HX) | N39°5'33.39"<br>E117° 12'6.23″ | The site was situated at about 10 m above ground level in the environmental monitoring station of HeXi District. |
| | HeBei- environmental protection bureau site (HB) | N39°9'44.70"<br>E117°11'18.80" | The site was situated at about 15 m above ground level in the environmental protection bureau of HeBei District |
| | HongQiao- monitoring station site (HQ) | N39°10'45.7"<br>E117°09'07.1″ | The site was situated at about 16 m above ground level in the Environmental monitoring station of HongQiao District |
| | HeDong-residential area site (HD) | N39° 7'30.10"<br>E117°16'8.90" | The site was situated at about 16 m above ground level in the residential building of HeDong District |
| | SZ | N39°5'48.91"<br>E117°9'4.71" | The site was situated at about 15 m above ground level in the environmental monitoring station of Tianjin. |
| | TT | N39°4'29.40"<br>E117°12'20.62" | The site was situated at about 15 m above ground level in the meteorological observatory tower of Tianjin |

simultaneously at 3 sites (TT, SZ and DL). The sampling span was six days and sampling was for 24 h. Middle-volume air samplers were deployed to collect PM samples at a flow rate of 100 L/min (TH-150C, Tianhong Intelligent Instrument Plant of Wuhan, China).

PM samples were collected using Pall quartz fiber filters (90 mm in diameter, type 2500QAT-UP, Pall Life Sciences, U.S.A.) over 24 h. After sampling, the exposed filters were stored in a refrigerator at about 4°C until chemical analysis to limit losses of volatile components. To reduce the carbonaceous species background level in the filter, quartz filters were pretreated at 900°C for 180 min and then placed in clean polyethylene Petri dishes. The Petri dishes were then wrapped with Teflon tape and aluminum foil, and stored in a freezer until field measurement. The filters were maintained under conditions of 40% relative humidity (RH) and 25°C for over 48 h, and were weighed using an electronic microbalance with ± 1 mg sensitivity before and after sampling. In this study, a blank filter of each site was treated with the same procedure as the sampling filter during the sampling and analytical processes. The blank filter was exposed to the same environments as the sampling filter except for being used as a particle sampling filter. Then the OC content of the blank filter was subtracted from the sampling filter OC content to correct the positive artifacts due to adsorption of gas-phase organics onto the filter during and/or after sampling collection. However, negative artifacts due to volatilization of particle-phase organics from the particle sample were not quantified in this study and the OC values obtained can be considered as conservative results. In all, 231 $PM_{10}$ samples and 81 $PM_{2.5}$ samples were collected in the observation period.

*Experimental Procedure for Analysis of Carbonaceous Species*

The samples were analyzed for OC/EC using DRI Model 2001 (Thermal/Optical Carbon Analyzer). The IMPROVE A thermal/optical reflectance (TOR) protocol 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, and 580°C (EC1), 740°C (EC2), and 840°C (EC3) in an oxidizing atmosphere of 2% oxygen in a balance of helium. The carbon that evolves at each temperature is oxidized to carbon dioxide ($CO_2$), and then reduced to methane ($CH_4$) for quantification with a flame ionization detector. As temperature increases in the inert helium, some of the organic carbon pyrolyzes to elemental carbon, resulting in darkening of the filter deposit. This darkening is monitored by reflectance of 633 nm light of a He–Ne laser. When oxygen is added, the original and pyrolyzed elemental carbon combusts and the reflectance increases. The amount of carbon measured after oxygen is added until the reflectance achieves its original value is reported as optically detected pyrolyzed carbon (OPC). The eight fractions OC1, OC2, OC3, OC4, EC1, EC2, EC3, and OPC are reported separately in the data sheet. The IMPROVE protocol defines OC as OC1 + OC2 + OC3 + OC4 + OPC and EC as EC1 + EC2 + EC3 – OPC. 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. Blank filters were also processed, similar to the protocol used for samples, in order to assess the analytical detection limits. Concentrations of carbonaceous species in the blanks

were below the detection limits in all analysis.

While the TOR method employed in this study is commonly used for PM measurements, it should be recognized that other methods of determining the OC and EC fractions can give different results (Chow *et al.*, 2001).

The elements of $PM_{10}$ and $PM_{2.5}$ collected simultaneously by polypropylene filters (90 mm in diameter, Beijing Synthetic Fiber Research Institute, China) using the same model air sampler were analyzed by ICP-AES. For the detailed procedures see Kong *et al.* (2011). Meteorological data of the sampling period were obtained from the Tianjin Meteorological Bureau.

## RESULTS AND DISCUSSION

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

Descriptive statistics for all valid observations of $PM_{2.5}$ and $PM_{10}$ concentrations from 8 sites in Tianjin operating from September 2009 to February 2010 are summarized in Table 2. The average daily concentration of $PM_{10}$ at the 8 sites ranged from 53 to 1024 $\mu g/m^3$, with an average and standard deviation of 243 ± 151 $\mu g/m^3$. Among the 8 sites, the HD site where $PM_{10}$ samples were collected only in the winter period had the highest mass concentration of 285 ± 218 $\mu g/m^3$. For the other 7 sites sampled both in autumn and winter, average $PM_{10}$ mass at the HB site were the highest (283 ± 185 $\mu g/m^3$). In contrast, the average $PM_{10}$ mass concentration analyzed at the SZ site was the lowest, with a mean concentration of 201 ± 144 $\mu g/m^3$. DL and BC sites, two suburban sites undergoing urbanization, affected by increasing emission sources distributed around the regions, have $PM_{10}$ mean concentrations of 221 ± 126 and 246 ± 139 $\mu g/m^3$, respectively. The average concentrations of $PM_{10}$ at HX, TT and HQ sites were 227 ± 114, 215 ± 104 and 256 ± 127 $\mu g/m^3$, respectively. In the present study, the daily average $PM_{10}$ concentrations of the 8 sites all exceeded the Class 3 of Chinese $PM_{10}$ standard of 150 $\mu g/m^3$, indicating serious particulate emissions in this period in Tianjin.

$PM_{2.5}$ samples were simultaneously collected at three sites: two traditional urban sites (TT and SZ) and one suburban site (DL). The average 24-h $PM_{2.5}$ concentration was 124 $\mu g/m^3$, with a large standard deviation of 83 $\mu g/m^3$, indicating a serious fine particulate pollution and multi-source contribution to airborne $PM_{2.5}$ in this period in Tianjin. Among the 3 sites, unlike the distribution of $PM_{10}$ concentrations, the highest levels of $PM_{2.5}$ appeared at the SZ site, at which the site average concentration of $PM_{10}$ was the lowest in the present study. DL had a similar level of $PM_{2.5}$ at 129 ± 74 $\mu g/m^3$. The TT site had lower $PM_{2.5}$ concentrations, with a mean concentration of 117 ± 73 $\mu g/m^3$. The $PM_{2.5}$ mass concentrations analyzed in Tianjin were higher than those detected in Europe (Van Dingenen *et al.*, 2003; Saarnio *et al.*, 2008; Pindado *et al.*, 2009; Putaud *et al.*, 2010) and Brazil (12 $\mu g/m^3$) (Bourotte *et al.*, 2005); and higher than Cao's study during the same period in the Pearl River Delta Region (73 $\mu g/m^3$) of China (Cao *et al.*, 2003), but were much lower than that found in Taiyuan (193 $\mu g/m^3$), China (Meng *et al.*, 2007). Although there is no specific legislation for $PM_{2.5}$ levels in China,

**Table 2.** Statistical description of the concentrations of $PM_{2.5}$, $PM_{10}$, OC, EC, TC, OC/EC and EC/TC during Semptember 4, 2009–February 25, 2010 at Tianjin of China.

| Sample category | Sampling site | Number of samples | Mass concentrations (µg/m³) Mean ± Standard deviation | Percentile 25th | 50th | 75th | OC (µg/m³) Mean ± standard deviation | Percentile 25th | 50th | 75th | EC (µg/m³) Mean ± standard deviation | Percentile 25th | 50th | 75th | TC (µg/m³) | OC/EC | EC/TC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $PM_{10}$ | SZ | 30 | 201 ± 144 | 113 | 179 | 237 | 23.1 ± 13.5 | 11.7 | 21.3 | 32.3 | 5.2 ± 2.1 | 4.0 | 4.7 | 6.1 | 28.3 ± 15.2 | 4.4 | 0.20 |
| | TT | 29 | 215 ± 104 | 158 | 192 | 258 | 27.4 ± 13.8 | 19.8 | 25.6 | 32.1 | 6.2 ± 2.5 | 4.6 | 5.9 | 7.2 | 33.6 ± 15.9 | 4.5 | 0.20 |
| | DL | 33 | 221 ± 126 | 124 | 187 | 266 | 33.6 ± 24.3 | 14.4 | 26.9 | 46.0 | 6.5 ± 3.7 | 3.9 | 5.5 | 7.9 | 40.1 ± 27.1 | 5.3 | 0.19 |
| | HX | 37 | 227 ± 114 | 150 | 207 | 270 | 30.3 ± 21.4 | 15.5 | 25.7 | 35.9 | 6.3 ± 3.0 | 4.3 | 5.4 | 7.5 | 36.6 ± 24.0 | 4.7 | 0.19 |
| | BC | 28 | 246 ± 139 | 163 | 206 | 325 | 37.0 ± 20.8 | 18.4 | 34.2 | 51.2 | 7.1 ± 3.8 | 4.5 | 6.8 | 8.4 | 44.1 ± 23.8 | 5.3 | 0.18 |
| | HB | 29 | 283 ± 185 | 185 | 249 | 298 | 34.4 ± 20.2 | 17.9 | 30.7 | 43.2 | 6.1 ± 2.7 | 4.2 | 5.8 | 6.8 | 40.4 ± 22.0 | 5.7 | 0.17 |
| | HQ | 29 | 256 ± 127 | 183 | 212 | 338 | 36.4 ± 21.7 | 17.2 | 34.3 | 48.1 | 5.8 ± 2.2 | 4.0 | 5.4 | 7.1 | 42.2 ± 23.3 | 6.0 | 0.16 |
| | HD* | 16 | 285 ± 218 | 193 | 230 | 310 | 42.1 ± 23.9 | 27.7 | 37.1 | 44.4 | 4.9 ± 1.5 | 3.8 | 4.5 | 5.5 | 47.0 ± 24.7 | 8.9 | 0.12 |
| | average | | 243 ± 151 | 155 | 207 | 283 | 32.6 ± 20.6 | 16.9 | 27.7 | 41.2 | 6.1 ± 2.9 | 4.1 | 5.5 | 7.2 | 38.6 ± 22.7 | 5.4 | 0.18 |
| $PM_{2.5}$ | SZ | 26 | 144 ± 119 | 55 | 89 | 170 | 12.4 ± 9.8 | 7.1 | 9.7 | 14.4 | 3.7 ± 3.0 | 2.1 | 2.8 | 5.0 | 16.1 ± 12.5 | 3.8 | 0.23 |
| | TT | 23 | 117 ± 73 | 78 | 111 | 119 | 13.9 ± 11.7 | 7.5 | 10.6 | 14.6 | 4.9 ± 3.2 | 2.8 | 4.4 | 6.8 | 18.8 ± 14.1 | 3.1 | 0.28 |
| | DL | 32 | 129 ± 74 | 85 | 116 | 155 | 17.4 ± 12.4 | 9.2 | 12.7 | 20.8 | 4.3 ± 2.4 | 2.3 | 4.3 | 5.4 | 21.7 ± 14.1 | 4.3 | 0.22 |
| | average | | 124 ± 83 | 77 | 110 | 156 | 14.5 ± 11.2 | 8.0 | 10.6 | 17.8 | 4.3 ± 2.9 | 2.2 | 4.1 | 5.6 | 18.8 ± 13.4 | 3.7 | 0.24 |

* The HD site only collected samples in winter period.

the average daily concentration of $PM_{2.5}$ (124 μg/m$^3$) in Tianjin during the measurement period exceeded the 24-h National Ambient Air Quality Standard (NAAQS) of the USA (35 μg/m$^3$). In order to build an ecological city in Tianjin, further control measures should be conducted to reduce particulate emissions. However, the anthropogenic emissions contributions were considered to be highest during the year of the observation period, and lower $PM_{2.5}$ and $PM_{10}$ mass concentrations may be found on warmer days in Tianjin and further analysis will be done.

The ratios of average 24-h $PM_{2.5}$ to $PM_{10}$ concentrations at the 3 sites were almost at the same level, ranging from 50% (TT site) to 56% (SZ site), with an average of 53%. This study showed that in Tianjin, $PM_{2.5}$ concentrations tend to be little higher than the coarse particle ($PM_{2.5-10}$) concentrations, with the average $PM_{2.5}/PM_{2.5-10}$ ratio of 1.14. The $PM_{2.5}/PM_{10}$ ratio (0.53) in the present study in

Tianjin was comparable with samples from the other urban cities of Lanzhou, China (0.52) (Wei *et al.*, 1999), Azusa, USA (0.51) (Chow *et al.*, 1994), and Montreal, Canada (0.52) (Brook *et al.*, 1997), and was generally lower than those in other Chinese urban cities of PRDR (0.70) (Cao *et al.*, 2003), Nanjing (0.63–0.77) (Wang *et al.*, 2003), Wuhan (0.61) and Chongqing (0.65) (Wei *et al.*, 1999).

### Concentrations of Carbonaceous Species

A summary of the measurement results for 24-h average concentrations of OC, EC and TC from 8 sites of Tianjin are given in Table 2 and their seasonal variations are summarized in Fig. 2. The average OC concentrations in $PM_{2.5}$ and $PM_{10}$ were 14.5 ± 11.2 and 32.6 ± 20.6 μg/m$^3$, respectively and the average EC concentrations in $PM_{2.5}$ and $PM_{10}$ were 4.3 ± 2.9 and 6.1 ± 2.9 μg/m$^3$, respectively. Particulate carbon species (TC, calculated by the sum of OC and EC) accounted



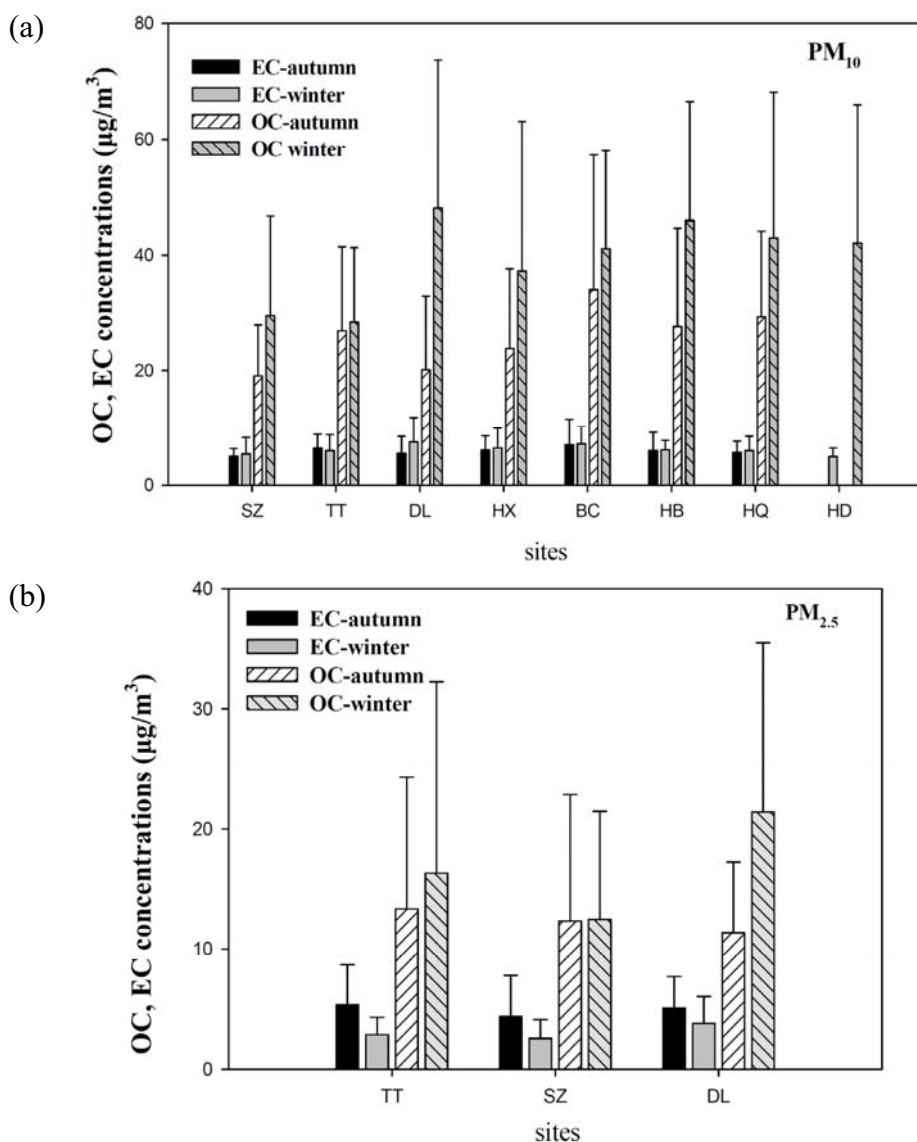**Fig. 2.** Seasonal variation of EC, OC abundances (μg/m$^3$) of $PM_{10}$ (a) and $PM_{2.5}$ (b) at different sampling sites in Tianjin during September 2009–February 2010. The seasons have been presented in terms of two different time periods: autumn (Sep.–Nov.) and winter (Dec.–Feb.).

for an averaged 15.2% of the fine particulate ($PM_{2.5}$) mass loading and 15.9% of $PM_{10}$. $PM_{2.5}$ consisted of 11.7% organic carbon and 3.5% elemental carbon, while $PM_{10}$ consisted of 13.4% organic carbon and 2.5% elemental carbon. EC is confined to sub-micron size particles and has a longer lifetime in the atmosphere. In previous studies (Venkataraman and Friedlander, 1994; Offenberg and Baker, 2000), the ambient distribution of EC was found to be associated with fine particles and contained almost 75% of the total EC in polluted urban areas. In this study, 71% of EC was associated with fine particle mode and 29% of EC was associated with coarse particle mode on average. Our study is in agreement with prior research. However, it is different from some previous research (Pickle *et al.*, 1990; Offenberg and Baker, 2000), which showed that the accumulation of organic compounds was mainly in the sub-micrometer (< 1 μm diameter) particle size range, 44% of OC was found to associate with the fine particle ($PM_{2.5}$) mode and 56% of OC was associated with the coarse particle mode in Tianjin.

Seasonal variability of carbonaceous concentrations has been analyzed in many studies. Higher concentrations are always found in the colder period, because of enhanced consumption of coal, biomass burning and gasoline fuel and typical meteorological conditions (lower intensity of sunshine, lower inversion height and less efficient photochemical decomposition).

The concentration of TC (calculated by the sum of OC and EC) measured in $PM_{10}$ samples in this study was higher in winter (from December to February), with a mean concentration of 46.1 μg/m³, and was lower in autumn (from September to November), with a mean concentration of 31.5 μg/m³, showing an evident seasonal variation, which was consistent with the normal seasonal trend of prior research (Castro *et al.*, 1999; Dan *et al.*, 2004). OC had higher concentrations in winter compared to autumn, with average concentrations of 40.0 and 25.5 μg/m³, respectively. The relatively high abundance of OC during the wintertime was attributed to the enhanced contribution from local emissions and meteorological conditions (lower mixing height and trapping of pollutants due to temperature inversion).

For $PM_{2.5}$ samples collected in 3 sites, higher concentration levels of OC were also found in the winter period, however, higher EC concentrations were found in the autumn season rather than that in winter.

OC and EC concentrations varied among the observation sites, indicating that carbonaceous aerosols in Tianjin were influenced more or less by local factors at various types of sampling sites. Except for the HD site where samples were collected in winter only, the highest concentrations of OC and EC in $PM_{10}$ samples (37.0 ± 20.8 and 7.1 ± 3.8 μg/m³, respectively) were observed at the BC site: a suburban site undergoing urbanization, with some factory emissions. Another suburban site (DL) also had higher TC concentrations of $PM_{10}$ samples compared to sites including TT, SZ and HX. For $PM_{2.5}$ samples, the highest OC and EC concentrations were observed at the DL site, higher than that collected at TT and SZ. The results showed that serious carbonaceous pollution was not only in traditional urban sites, but also in suburban sites undergoing urbanization.

Epidemiological studies have demonstrated stronger exposure–response relationships for mortality and morbidity outcomes in association with fine particles than coarse fractions (Saarnio *et al.*, 2008; Li *et al.*, 2009). $PM_{2.5}$ can effectively penetrate into the respiratory system and deposit deep in the bronchioles and alveoli of the lungs. In this study, we used published data of OC and EC concentrations of $PM_{2.5}$ collected in fall-winter days for comparison (Table 3). The OC concentrations in $PM_{2.5}$ in this research (14.5 μg/m³) were comparable with the mean concentrations reported in PRDR, China (14.7 μg/m³) (Cao *et al.*, 2003), were generally higher than those in Anaheim, USA (13.9 μg/m³) (Chow *et al.*, 1994), Seoul, Korea (10.2 μg/m³) (Kim *et al.*, 2007), Chongju, Korea (5.0 μg/m³) (Lee and Kang, 2001) and Milan, Italy (9.2 μg/m³) (Lonati *et al.*, 2007), but were much lower than those in Los Angeles (18.5 μg/m³) (Chow *et al.*, 1994), Shanghai, China (17.0 μg/m³) (Ye *et al.*, 2003), Taiyuan, China (28.9 μg/m³) (Meng *et al.*, 2007), and Xian, China (61.9 μg/m³) (Cao *et al.*, 2005). The EC levels in the above cities in decreasing order were Xian, China (12.3 μg/m³), Shanghai, China (8.1 μg/m³), Los Angeles (7.3 μg/m³), PRDR, China (6.1 μg/m³), Anaheim (5.5 μg/m³), Taiyuan, China (4.8 μg/m³), Tianjin, China (4.3 μg/m³), Chongju, Korea (4.3 μg/m³), Seoul, Korea (4.1 μg/m³) and Milan, Italy (1.4 μg/m³). Although the conditions of these studies were different, they may provide an overall picture of OC and EC associated with fine particles in different regions.

Compared to other cities in the world, the cities of China

**Table 3.** Comparison of OC and EC of $PM_{2.5}$ at Tianjin with other cities.

| City | period | OC | EC | OC/EC | reference |
|---|---|---|---|---|---|
| Tianjin[a] | September 2009–February 2010 | 14.5 | 4.3 | 3.7 | this research |
| PRDR, China[a] | January–February, 2002 | 14.7 | 6.1 | 2.4 | Cao *et al.* (2003) |
| Los Angeles, USA[a] | November 1987–December 1987 | 18.5 | 7.3 | 2.5 | Chow *et al.* (1994) |
| Anaheim, USA[a] | November 1987–December 1987 | 13.9 | 5.5 | 2.5 | Chow *et al.* (1994) |
| Milan, Italy[b] | August 2002–December 2003 | 9.2 | 1.4 | 6.5 | Lonati *et al.* (2007) |
| Taiyuan, China[b] | December 2005–February 2006 | 28.9 | 4.8 | 7.0 | Meng *et al.* (2007) |
| Seoul, Korea[b] | March 2003–February 2005 | 10.2 | 4.1 | 2.5 | Kim *et al.* (2007) |
| Chongju, Korea[a] | January–February 1996 | 5.0 | 4.3 | 1.2 | Lee *et al* (2001) |
| Shanghai, China[a] | Winter, 1999 | 17.0 | 8.1 | 2.1 | Ye *et al.* (2003) |
| Xian, China[a] | December 2003–February 2004 | 61.9 | 12.3 | 5.1 | Cao *et al.* (2005) |

Measurement method: a, thermal/optical reflectance (TOR); b thermal optical transmission (TOT).

always had much higher OC and EC concentrations in fine particles, therefore a high health risk could exist in China. High OC and EC concentrations (14.5 and 4.3 µg/m$^3$) of PM$_{2.5}$ samples analyzed in the present study indicated that severity of the pollution of carbonaceous particles in Tianjin atmospheric environment.

***Correlations and Sources of Carbonaceous Species***

EC is known as a primary anthropogenic particulate constituent, mainly emitted from combustion processes of biomass or fossil fuels, while OC can be directly emitted to the atmosphere in particulate form along with EC or can be produced by gas to particle conversion processes as secondary sources (Lin and Tai, 2001; Dan *et al.*, 2004; Ram *et al.*, 2008). Since primary OC and EC are mostly generated from the same sources, emission and transformation characteristics of carbonaceous aerosol can be estimated based on the relationship between organic and elemental carbon (Kim *et al.*, 2000; Lin and Tai, 2001).

Linear regression analysis between OC and EC is useful to assess the primary nature of carbonaceous aerosols. As shown in Fig. 3, good OC–EC correlations, differentiated according to seasons, were obtained for PM$_{2.5}$ samples (r = 0.85 for autumn, p < 0.0001; r = 0.93 for winter, p < 0.0001) and PM$_{10}$ samples (r = 0.81 for autumn, p < 0.0001; r = 0.69 for winter, p < 0.0001) collected in Tianjin, indicating the primary nature of the OC in this region. The different linear regression equations in two seasons could be related to the seasonal fluctuation of source emissions and SOC formation.

Elevated OC/EC ratios were found in winter compared to autumn, and this could be attributed to several reasons. First, coal consumption for winter heating contributes more to OC than EC, and also increases the emission of volatile organic precursors. Second, low temperature leads to the adsorption and condensation of semi-volatile organic compounds onto existing solid particles. Third, the low mixing layer height in winter would enhance the SOC
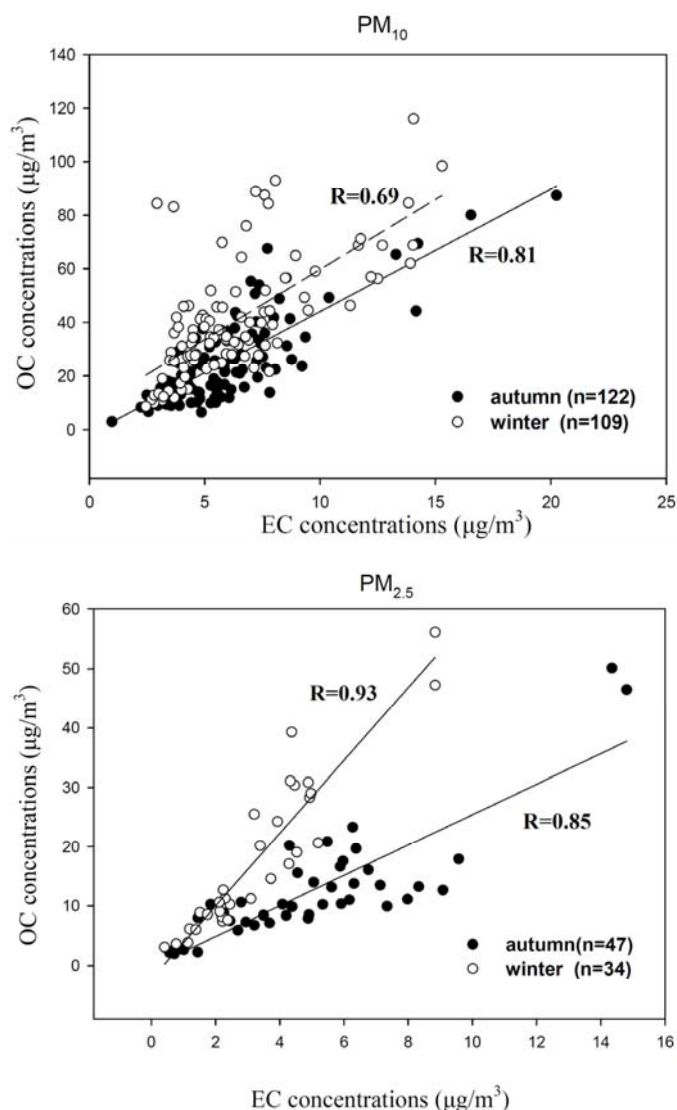


**Fig. 3.** Relationship between organic carbon and elemental carbon concentrations in PM$_{2.5}$ and PM$_{10}$ samples in Tianjin (n: the number of samples).

formation (Strader *et al.*, 1999). This seasonal pattern of higher wintertime OC/EC ratio was also observed in studies in Beijing (Dan *et al.*, 2004), Guangzhou and Hong Kong (Duan *et al.*, 2007).

The HD site, where samples were only collected in winter, had the highest OC/EC ratio for $PM_{10}$ samples (8.9). Among the other sites, the OC/EC ratios of $PM_{10}$ had similar levels between 4.4 and 6.0. HQ had the higher OC/EC ratio (6.0) and SZ had the lowest OC/EC ratio (4.4) for $PM_{10}$ samples. For $PM_{2.5}$ samples, the DL site had a higher OC/EC ratio (4.3) compared to SZ (3.8) and TT (3.1) sites.

The ratios of OC to EC concentrations in $PM_{2.5}$ for this study are compared with other measurements in the world in Table 3. Together with the present study in Tianjin, Chongju (Korea) (Lee and Kang, 2001), Shanghai (China) (Ye *et al.*, 2003), PRDR (China) (Cao *et al.*, 2003), Los Angeles (USA), Anaheim (USA) (Chow *et al.*, 1994) and Seoul (Korea) (Kim *et al.*, 2007) had a OC/EC ratio that ranged from 1.2 to 3.7, consistent with the results of $PM_{2.5}$ observation of western interagency monitoring of protected visual environment (IMPROVE) sites in USA (Richard *et al.*, 2002). And the ratios of OC/ EC at Milan (Italy) (Lonati *et al.*, 2007), Taiyuan (China) (Meng *et al.*, 2007) and Xian (China) (Cao *et al.*, 2005) were larger than 4.0.

Several authors have used EC/TC ratio as an indicator to differentiate the dominant contributor among fossil fuel burning and biomass burning. The relatively lower ratios (0.1–0.2) are used as typical of biomass burning sources and higher ratios (~0.5) indicate contribution from fossil fuel combustion sources (Gillies *et al.*, 2000; Gillies *et al.*, 2001; Ram *et al.*, 2008; Sudheer and Sarin, 2008). The EC/TC ratios of $PM_{10}$ samples were always less than 0.2 at the sites throughout the sampling period. And for $PM_{2.5}$ samples, EC/TC ratios were a little higher than 0.2, which could also represent biomass burning contribution. Biomass burning in residential consumption and open fire was suggested as one of the most important carbonaceous emission sources in China (Cao *et al.*, 2006; Liu and Shao, 2007). In the analysis of Beijing, biomass burning was the largest source of EC, accounting for 40% of the total (Liu and Shao, 2007).

However, it is not sure if these ratios reflect emission characteristics accurately as emission patterns in China may be different from that in other countries. Source apportionment analysis conducted in Tianjin previously indicated that coal combustion fly ash was an important contributor to ambient particles (Bi *et al.*, 2007). In order to further characterize the carbonaceous emission sources in Tianjin, OC and EC were compared with pollution elements from ICP-AES analysis. The relationship of elements including As, Zn, K and Pb, with OC and EC at sampling sites is shown in Table 4. As has long been recognized as coal combustion makers, Zn and Pb are known as tracers of motor vehicle emission, and K is usually considered to relate to biomass combustion (Meng *et al.*, 2007; Dan *et al.*, 2004). OC and EC of $PM_{10}$ and $PM_{2.5}$ samples collected at different sampling sites all have significant positive correlations with Zn and most have positive correlations with Pb, suggesting that vehicle

**Table 4.** Pearson product-moment correlation coefficients between OC, EC concentrations in $PM_{2.5}$ and $PM_{10}$ samples and As, Zn, K and Pb at sampling sites in Tianjin.

| Sample category | Species | K | Zn | As | Pb |
|---|---|---|---|---|---|
| $PM_{10}$ (n = 231) | HX-OC | 0.775** | 0.746** | 0.874** | 0.734** |
| | HX-EC | 0.286 | 0.766** | 0.652** | 0.729** |
| | SZ-OC | 0.736** | 0.571** | 0.849** | 0.655** |
| | SZ-EC | 0.494** | 0.506** | 0.627** | 0.570** |
| | TT-OC | 0.433* | 0.434* | 0.433* | 0.433* |
| | TT-EC | 0.474* | 0.476* | 0.474* | 0.474* |
| | DL-OC | 0.663** | 0.388* | 0.719** | 0.497** |
| | DL-EC | 0.469** | 0.640** | 0.643** | 0.587** |
| | BC-OC | 0.818** | 0.448* | 0.575** | 0.727** |
| | BC-EC | 0.617** | 0.549** | 0.312 | 0.595** |
| | HB-OC | 0.833** | 0.849** | 0.666** | 0.866** |
| | HB-EC | 0.496** | 0.585** | 0.209 | 0.675** |
| | HQ-OC | 0.370 | 0.579** | 0.613** | 0.308 |
| | HQ-EC | 0.150 | 0.399* | 0.281 | 0.207 |
| | HD-OC | 0.734** | 0.698** | 0.731** | 0.653** |
| | HD-EC | 0.113 | 0.735** | 0.543* | 0.528* |
| $PM_{2.5}$ (n = 81) | TT2.5-OC | 0.443 | 0.554* | 0.421 | 0.510* |
| | TT2.5-EC | 0.220 | 0.482* | 0.194 | 0.309 |
| | SZ2.5-OC | 0.722** | 0.683** | 0.617** | 0.588** |
| | SZ2.5-EC | 0.524* | 0.671** | 0.436* | 0.401 |
| | DL2.5-OC | 0.632** | 0.513** | 0.773** | 0.627** |
| | DL2.5-EC | 0.219 | 0.375* | 0.464* | 0.387* |

emission was a main contributor of TC burden. Good positive correlations were also usually found between carbonaceous compounds and K and As, indicating that biomass burning and coal combustion were the main sources of OC and EC in Tianjin. Particular matter for the $PM_{2.5}$ analysis at the TT site and $PM_{10}$ analysis at the HQ site, OC and EC only have good correlations with Zn, showing enhanced vehicle emission contributions.

Principal component analysis (PCA) had been applied for source analysis in many studies (Cao *et al.*, 2005; Moon *et al.*, 2006; Li *et al.*, 2010; Wang *et al.*, 2010), eight carbon fraction concentrations were identified by PCA to quantify source contributions (Table 5, Table 6). For $PM_{2.5}$ samples, three factors accounted for 93.80% of the total variance in the data. Factor 1, which explained 68.37% of the variance, showed high loading for OC1, OC2, OC3, EC1 and OPC. OC1 was enriched in biomass burning; OC2 could point to coal combustion; EC1, OC3 and OPC were considered markers of gasoline motor-vehicle exhaust (Cao *et al.*, 2005). Thus, factor 1 represented multi-source emissions including coal combustion, biomass burning and gasoline motor-vehicle exhaust. Factor 2, which explained 17.07% of the variance, had high loadings for EC2 and EC3, reflected the contribution of diesel-vehicle exhaust (Watson *et al.*, 1994). Factor 3, which explained 8.36% of the variance, had high loadings for OC4. OC4 are enriched in the road dust profile (Chow *et al.*, 2004). For $PM_{10}$ samples, three factors accounted for 90.26% of the total variance in the data. Factor 1, explaining 60.76% of the variance, showed high loading for OC1, OC2, OC3 and

**Table 5.** PCA analysis for PM$_{2.5}$ samples (n = 81).

| Species | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| OC1 | 0.930 | | |
| OC2 | 0.926 | | |
| OC3 | 0.727 | | 0.549 |
| OC4 | | | 0.952 |
| EC1 | 0.913 | | |
| EC2 | | 0.704 | |
| EC3 | | 0.965 | |
| OPC | 0.907 | | |
| Percentage of the variance | 68.37% | 17.07% | 8.36% |

**Table 6.** PCA analysis for PM$_{10}$ samples (n = 231).

| Species | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| OC1 | 0.971 | | |
| OC2 | 0.916 | | |
| OC3 | 0.730 | 0.592 | |
| OC4 | | 0.902 | |
| EC1 | | | 1.000 |
| EC2 | | 0.864 | |
| EC3 | | 0.863 | |
| OPC | 0.846 | | |
| Percentage of the variance | 60.76% | 17.13% | 12.38% |

OPC, indicated the emissions from coal combustion, biomass burning and gasoline motor-vehicle exhaust. Factor 2, which explained 17.13% of the variance, had high loadings for OC4, EC2 and EC3, represented diesel-vehicle exhaust. The high loading of EC1 in factor 3 reflected the contribution of motor-vehicle exhaust.

In the present study, multi-source contribution to OC and EC was found in this period in Tianjin, however, much work needs to be done to thoroughly apportion OC and EC sources.

### Correlations of OC, EC and TC Levels with Meteorological Parameters

Meteorological conditions, including air pressure, wind speed (WS), temperature (Temp.), and relative humidity (RH), may affect concentrations of OC and EC. Correlation coefficients for relationships between OC and EC concentrations (average concentrations of sampling sites) and meteorological parameters collected during the observation period were evaluated and are listed in Table 7. In some studies, wind speed was found to influence pollution concentrations due to its cleanup function (Pindado *et al.*, 2009). Good negative correlations were found between wind speed and OC and EC of PM$_{10}$ and PM$_{2.5}$ fractions in the present study, supporting the cleanup function of wind. TC and OC of PM$_{10}$ samples had good negative correlations with temperature; this could be caused by elevated emissions in colder days. Pressure varied little during the sampling period and did not show evident correlations with OC and EC of particles. No significant correlation was observed between OC and EC concentrations and RH in this research.

**Table 7.** Pearson product-moment correlation coefficients between OC, EC and TC concentrations in PM$_{2.5}$, PM$_{10}$ samples and meteorological parameters. Carbonaceous concentration used average concentration of sampling sites.

| Sample category | Species | Pressure | Temp. | RH | WS |
|---|---|---|---|---|---|
| PM$_{10}$ | TC | 0.119 | −0.448[**] | 0.097 | −0.325[*] |
| | OC | 0.119 | −0.462[**] | 0.075 | −0.309[*] |
| | EC | 0.075 | −0.166 | 0253 | −0.351[*] |
| PM$_{2.5}$ | TC | −0.149 | −0.116 | 0.160 | −0.408[*] |
| | OC | −0.075 | −0.223 | 0.076 | −0.375[*] |
| | EC | −0.445 | −0.399[*] | 0.504 | −0.458[**] |

### Estimation of Secondary Organic Carbon Concentrations

While elemental carbon is essentially a primary pollutant, OC consists of a complicated mixture of species from both primary sources and secondary sources. SOCs are produced in the atmosphere via various chemical and physical transformation processes involving the oxidation of volatile organic reactive gases (VORGs) with reactive species such as ozone, hydroxyl and NO$_x$ radicals followed by coagulation/condensation onto the pre-existing aerosol particles becoming a part of aerosols already present in the atmosphere (Ram *et al.*, 2008). The importance of SOC related to haze, visibility, climate and heath has been known for decades, but not enough research has been done (Cao *et al.*, 2003). Although several constraints and uncertainty exist, the OC/EC ratios were adopted in many studies as an indicator to identify SOC formation. For control strategies for particulate matter, it is necessary to quantify the contributions of the primary and secondary organic carbon to carbonaceous aerosol.

The direct measurement of secondary organic carbon (SOC) is not possible as they are derived from the various physical and chemical transformation processes. Rather, they are estimated either by counting the primary organic carbon, using EC as a tracer, and then subtracting it from the total organic carbon measured (Turpin and Huntzicker, 1995; Castro *et al.*, 1999; Ram *et al.*, 2008) or by summing up the concentrations of all such oxidation products found in the aerosols (Schauer *et al.*, 1996). Since the abundances of VORGs and reactive radicals vary on temporal and spatial scales, SOCs are also considered to vary in the same manner (Ram *et al.*, 2008).

In this research, SOC was estimated by subtracting the primary organic carbon from total organic carbons, using the following equation:

$$OCsec = OCtot − EC × (OC/EC)pri \qquad (1)$$

where OCsec is the secondary OC (SOC), OCtot is the total OC (TOC), and (OC/EC)pri is the primary ratio estimate.

In this study, a total of 231 PM$_{10}$ samples and 81 PM$_{2.5}$ samples were collected during the sampling period. Average SOC concentrations of PM$_{2.5}$ and PM$_{10}$ are listed in Table 8. The estimated SOC concentrations for PM$_{2.5}$ were 5.8 and 7.4 μg/m$^3$, accounting for 46% and 41% of the total OC, was 4.9% and 5.6% compared to the particle mass in

**Table 8.** Levels of secondary organic carbon (SOC) at 8 sites in Tianjin estimated from primary OC/EC ratios.

| Sample category | Sampling site | Autumn | | | winter | | |
|---|---|---|---|---|---|---|---|
| | | SOC (μg/m$^3$) | SOC/OC, % | SOC/Mass, % | SOC (μg/m$^3$) | SOC/OC, % | SOC/Mass, % |
| PM$_{10}$ | SZ | 12.5 | 66 | 6.3 | 14.3 | 49 | 7.0 |
| | TT | 18.4 | 69 | 8.0 | 11.6 | 44 | 6.0 |
| | DL | 13.0 | 65 | 6.9 | 27.1 | 56 | 10.5 |
| | HX | 15.8 | 67 | 7.6 | 19.2 | 51 | 7.8 |
| | BC | 17.8 | 52 | 6.8 | 18.0 | 44 | 8.1 |
| | HB | 19.7 | 72 | 7.3 | 28.9 | 63 | 9.5 |
| | HQ | 21.8 | 75 | 8.8 | 26.2 | 61 | 10.0 |
| | HD | - | - | - | 28.3 | 67 | 9.9 |
| | average | 16.9 | 66 | 7.4 | 22.3 | 56 | 9.0 |
| PM$_{2.5}$ | TT | 6.1 | 46 | 5.4 | 8.7 | 53 | 6.6 |
| | SZ | 6.5 | 52 | 4.8 | 4.1 | 33 | 3.8 |
| | DL | 4.5 | 40 | 4.4 | 9.1 | 42 | 6.2 |
| | average | 5.8 | 46 | 4.9 | 7.4 | 41 | 5.6 |

- Not sampled and analyzed in this research.

the autumn and winter, respectively. For PM$_{10}$, the average concentrations of estimated SOC were 16.9 and 22.3 μg/m$^3$, accounting for 66% and 56% of OC concentrations, was 7.4% and 9.0% compared to the particle mass in the autumn and winter, respectively. The results suggested that SOC was an important component of organic carbon and particle mass. Due to emission and meteorological characters, SOC concentrations were higher in winter than in autumn, specifically 1.32 times higher for PM$_{10}$ and 1.28 times higher for PM$_{2.5}$. However, SOC contributed more to OC in autumn than winter, was 66% in contrast to 56% and 46% in contrast to 41% for PM$_{10}$ and PM$_{2.5}$, respectively. In Castro *et al.*'s (1999) study, SOC was reported to contribute to a minimum of about 17% of TOC during winter contrast to the maximum 78% in summer in Portugal. Also Na *et al.* (2004) reported that the contribution of SOC to the TOC burden tends to be lower during the season with lower photochemical activity than that during the time of enhanced photochemical activity. The present research supported this view to some degree.

The relative amount of secondary organic carbon ranged from 52 to 75%, 44 to 67% with an average of 66% and 56% of the TOC for PM$_{10}$ in autumn and winter season, respectively. And it ranged from 40 to 52%, 33 to 53%, with an average of 46% and 41% of TOC for PM$_{2.5}$ in autumn and winter, respectively. The concentration ratio of secondary organic carbon in PM$_{2.5}$ to that in PM$_{10}$ sampled simultaneously indicated that 34% and 33% of the secondary organic carbon was distributed in PM$_{2.5}$ in autumn and winter, respectively. This showed that the secondary organic particles observed in this research were associated more with the coarse particle mode.

In some research in other urban areas, Cao *et al.* (2003) analyzed SOC accounting for 43% and 38% of organic carbon concentrations in winter for PM$_{2.5}$ and PM$_{10}$ in PRDR, respectively. Castro *et al.* (1999) obtained SOC accounting for 17%, 39%, and 37% of OC at Birmingham, Oporto, and Coimbra in winter for PM$_{10}$. Lin and Tai (2001) found SOC contributed to 40% and 32% of OC for PM$_{2.5}$ and PM$_{10}$ in Kaohsiung, respectively. The estimations

of SOC in this research were in agreement with those in urban areas.

Formation of SOA involves two different processes: production of condensable organic compounds through oxidation reactions (chemical) and subsequent nucleation/ condensation on the pre-existing aerosols (physical) (Ram *et al.*, 2008). However, their formation mechanism needs to be further analyzed in order to assess their contribution to aerosols and their atmospheric chemistry and environment effects on a regional scale.

**CONCLUSIONS**

PM$_{2.5}$, PM$_{10}$ and carbonaceous aerosol were investigated at eight sites in Tianjin from September 2009 to February 2010. Average PM$_{2.5}$ and PM$_{10}$ concentrations were 124 and 243 μg/m$^3$, respectively, with PM$_{2.5}$ constituting 53% of the PM$_{10}$ mass. The average OC concentrations in PM$_{2.5}$ and PM$_{10}$ were 14.5 and 33 μg/m$^3$, respectively and the average EC concentration in PM$_{2.5}$ and PM$_{10}$ were 4.3 and 6.1 μg/m$^3$, respectively. The average OC/EC ratios for PM$_{2.5}$ and PM$_{10}$ in the Tianjin were 3.7 and 5.4, respectively. OC and EC in Tianjin were found to be strongly correlated, which indicated that the dominant source of OC and EC was primary emission. Comparisons of OC and EC with trace elements including As, Zn, K, and Pb and PCA analysis demonstrated multi-sources contributions to carbonaceous species in Tianjin. Good negative correlations were found between wind speed and OC and EC of PM$_{10}$ and PM$_{2.5}$ fractions, indicating the cleanup function of wind. Estimating by primary OC/EC ratio, secondary organic carbon was found to constitute 46% and 66% of the total organic carbon in PM$_{2.5}$ and PM$_{10}$, respectively in autumn and 41% and 56% respectively in winter period. To formulate effective control strategies for air pollutant and build an ecological city in Tianjin, further studies of the origin and composition of the primary and secondary particles are needed.

## REFERENCES

Bi, X., Feng, Y., Wu, J., Wang, Y. and Zhu, T. (2007). Source Apportionment of $PM_{10}$ in Six Cities of Northern China. *Atmos. Environ.* 41: 903–912.

Bourotte, C., Forti, M., Taniguchi, S., Bicego, M. and Lotufo, P. (2005). A Wintertime Study of PAHs in Fine and Coarse Aerosols in Sao Paulo City, Brazil. *Atmos. Environ.* 39: 3799–3811.

Brook, J., Dann, T. and Burnett, R. (1997). The Relationship among TSP, $PM_{10}$, $PM_{2.5}$, and Inorganic Constituents of Atmospheric Particulate Matter at Multiple Canadian Locations. *J. Air Waste Manage. Assoc.* 47: 2–19.

Cao, G., Zhang, X. and Zheng, F. (2006). Inventory of Black Carbon and Organic Carbon Emissions from China. *Atmos. Environ.* 40: 6516–6527.

Cao, J., Lee, S., Ho, K., Zhang, X., Zou, S., Fung, K., Chow, J. and Watson, J. (2003). Characteristics of Carbonaceous Aerosol in Pearl River Delta Region, China during 2001 Winter Period. *Atmos. Environ.* 37: 1451–1460.

Cao, J., Wu, F., Chow, J., Lee, S., Li, Y., Chen, S., An, Z., Fung, K., Watson, J., Zhu, C. and Liu, S. (2005). Characterization and Source Apportionment of Atmospheric Organic and Elemental Carbon during Fall and Winter of 2003 in Xi'an, China. *Atmos. Chem. Phys.* 5: 3127–3137.

Castro, L., Pio, C., Harrison, R. and Smith, D. (1999). Carbonaceous Aerosol in Urban and Rural European Atmospheres: Estimation of Secondary Organic Carbon Concentrations. *Atmos. Environ.* 33: 2771–2781.

Chow, J., Watson, J., Crow, D., Lowenthal, D. and Thomas, M. (2001). Comparison of IMPROVE and NIOSH Carbon measurements. *Aerosol Sci. Technol.* 34: 23–24.

Chow, J., Watson, J., Fujita, E., Lu, Z., Lawson, D. and Ashbaugh, L. (1994). Temporal and Spatial Variations of $PM_{2.5}$ and $PM_{10}$ Aerosol in the Southern California Air Quality Study. *Atmos. Environ.* 28: 2061–2080.

Chow, J.C., Watson, J.G., Kuhns, H., Etyemezian, V., Lowenthal, D.H., Crow, D., Kohl, S.D., Engelbrecht, J.P. and Green, M.C. (2004). Source Profiles for Industrial, Mobile, and Area Sources in the Big Bend Regional Aerosol Visibility and Observational Study. *Chemosphere* 54: 185–208.

Dan, M., Zhuang, G., Li, X., Tao, H. and Zhuang, Y. (2004). The Characteristics of Carbonaceous Species and their Sources in $PM_{2.5}$ in Beijing. *Atmos. Environ.* 38: 3443–3452.

Duan, J., Tan, J., Cheng, D., Bi, X., Deng, W., Sheng, G., Fu, J. and Wong, M. (2007). Sources and Characteristics of Carbonaceous Aerosol in Two Largest Cities in Pearl River Delta Region, China. *Atmos. Environ.* 41: 2895–2903.

Gillies, J. and Gertler, A. (2000). Comparison Chemically Speciated Mobile Source $PM_{2.5}$ Profiles. *J. Air Waste Manage. Assoc.* 50: 1459–1480.

Gillies, J., Gertler, A., Sagebiel, J. and Dippel, W. (2001). On-road Particulate Matter ($PM_{2.5}$ and the Sepulveda Tunnel, Los Angeles, California. *Environ. Sci. Technol.* 35: 1054–1063.

Ho, K., Lee, S., Chan, C., Yu, J., Chow, J. and Yao, X. (2003). Characterization of Chemical Species in $PM_{2.5}$ and $PM_{10}$ Aerosols in Hong Kong. *Atmos. Environ.* 37: 31–39.

Kim, H., Huh, J., Hopke, P., Holsen, T. and Yi, S. (2007). Characteristics of the Major Chemical Constituents of $PM_{2.5}$ and Smog Events in Seoul, Korea in 2003 and 2004. *Atmos. Environ.* 41: 6762–6770.

Kim, Y., Moon, K. and Hoon Lee, J. (2000). Organic and Elemental Carbon in Fine Particles at Kosan, Korea. *Atmos. Environ.* 34: 3309–3317.

Kong, S., Lu, B., Bai, Z., Zhao, X., Chen, L., Han, B., Li, Z., Ji, Y., Xu, Y., Liu, Y. and Jiang, H. (2011). Potential Threat of Heavy Metals in Re-suspended Dusts on Building Surfaces in Oilfield City. *Atmos. Environ.* 45: 4192–4204.

Larson, S. and Cass, G. (1989). Characteristics of Summer Midday Low-visibility Events in the Los Angeles Area. *Environ. Sci. Technol.* 23: 281–289.

Lee, H. and Kang, B. (2001). Chemical Characteristics of Principal $PM_{2.5}$ Species in Chongju, South Korea. *Atmos. Environ.* 35: 739–746.

Li, P., Wang, Y., Li, Y., Wang, Z., Zhang, H., Xu, P. and Wang, W. (2010). Characterization of Polycyclic Aromatic Hydrocarbons Deposition in $PM_{2.5}$ and Cloud/Fog Water at Mount Taishan (China). *Atmos. Environ.* 44: 1996–2003.

Li, Z., Sjodin, A., Porter, E., Patterson Jr, D., Needham, L., Lee, S., Russell, A. and Mulholland, J. (2009). Characterization of $PM_{2.5}$-bound Polycyclic Aromatic Hydrocarbons in Atlanta. *Atmos. Environ.* 43: 1043–1050.

Lin, J. and Tai, H. (2001). Concentrations and Distributions of Carbonaceous Species in Ambient Particles in Kaohsiung City, Taiwan. *Atmos. Environ.* 35: 2627–2636.

Liu, Y. and Shao, M. (2007). Estimation and Prediction of Black Carbon Emissions in Beijing City. *Chin. Sci. Bull.* 52: 1274–1281.

Lonati, G., Ozgen, S. and Giugliano, M. (2007). Primary and Secondary Carbonaceous Species in $PM_{2.5}$ Samples in Milan (Italy). *Atmos. Environ.* 41: 4599–4610.

McMurry, P. and Grosjean, D. (1985). Photochemical Formation of Organic Aerosols: Growth Laws and Mechanisms. *Atmos. Environ.* (1967) 19: 1445–1451.

Meng, Z., Jiang, X., Yan, P., Lin, W., Zhang, H. and Wang, Y. (2007). Characteristics and Sources of $PM_{2.5}$ and Carbonaceous Species during Winter in Taiyuan, China. *Atmos. Environ.* 41: 6901–6908.

Na, K., Sawant, A., Song, C. and Cocker, D. (2004). Primary and Secondary Carbonaceous Species in the Atmosphere of Western Riverside County, California. *Atmos. Environ.* 38: 1345–1355.

Nunes, T. and Pio, C. (1993). Carbonaceous Aerosols in Industrial and Coastal Atmospheres. *Atmos. Environ.*

*Part A* 27: 1339–1346.

Offenberg, J. and Baker, J. (2000). Aerosol Size Distributions of Elemental and Organic Carbon in Urban and Overwater Atmospheres. *Atmos. Environ.* 34: 1509–1517.

Pandis, S., Harley, R., Cass, G. and Seinfeld, J. (1992). Secondary Organic Aerosol Formation and Transport. *Atmos. Environ. Part A* 26: 2269–2282.

Pankow, J. (1994). An Absorption Model of the Gas/Aerosol Partitioning Involved in the Formation of Secondary Organic Aerosol. *Atmos. Environ.* 28: 189–193.

Pickle, T., Allen, D. and Pratsinis, S. (1990). The Sources and Size Distributions of Aliphatic and Carbonyl Carbon in Los Angeles Aerosol. *Atmos. Environ. Part A* 24: 2221–2228.

Pindado, O., Perez, R., Garcia, S., Sanchez, M., Galan, P. and Fernandez, M. (2009). Characterization and Sources Assignation of $PM_{2.5}$ Organic Aerosol in a Rural Area of Spain. *Atmos. Environ.* 43: 2796–2803.

Putaud, J.P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H.C., Harrison, R.M., Herrmann, H., Hitzenberger, R., Hüglin, C., Jones, A.M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T.A.J., Löschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., Brink, H. ten, Tursic, J., Viana, M., Wiedensohler, A. and Raes, F. (2010). A European Aerosol Phenomenology - 3: Physical and Chemical Characteristics of Particulate Matter from 60 Rural, Urban, and Kerbside Sites Across Europe. *Atmos. Environ. 4*4: 1308–1320.

Ram, K., Sarin, M. and Hegde, P. (2008). Atmospheric Abundances of Primary and Secondary Carbonaceous Species at Two High-altitude Sites in India: Sources and Temporal Variability. *Atmos. Environ.* 42: 6785–6796.

Richard, T., Hildemann, L., Kamens, R., Lee, S., Malm, W.C., Pandis, S., Pankow, J., Schauer, J., Watson, J.G. and Zielinska, B. (2002). Secondary Organic Aerosols Research Strategy to Apportion Biogenic/Anthropogenic Sources: An Outcome of the First Secondary Organic Aerosols Workshop, February 4–5, 2002, Desert Research Institute, Reno, NV, Fort Lewis College, Durango, CO. http://ocs.fortlewis.edu/aerosols/index.htm.

Saarnio, K., Sillanp, M., Hillamo, R., Sandell, E., Pennanen, A. and Salonen, R. (2008). Polycyclic Aromatic Hydrocarbons in Size-segregated Particulate Matter from Six Urban Sites in Europe. *Atmos. Environ.* 42: 9087–9097.

Schauer, J., Rogge, W., Hildemann, L., Mazurek, M., Cass, G. and Simoneit, B. (1996). Source Apportionment of Airborne Particulate Matter Using Organic Compounds as Tracers. *Atmos. Environ.* 30: 3837–3855.

Stern, J., Flagan, R., Grosjean, D. and Seinfeld, J. (1987). Aerosol Formation and Growth in Atmospheric Aromatic Hydrocarbon Photooxidation. *Environ. Sci. Technol.* 21: 1224–1231.

Strader, R., Lurmann, F. and Pandis, S. (1999). Evaluation of Secondary Organic Aerosol Formation in Winter. *Atmos. Environ.* 33: 4849–4863.

Sudheer, A. and Sarin, M. (2008). Carbonaceous Aerosols in MABL of Bay of Bengal: Influence of Continental Outflow. *Atmos. Environ.* 42: 4089–4100.

Turpin, B. and Huntzicker, J. (1995). Identification of Secondary Organic Aerosol Episodes and Quantitation of Primary and Secondary Organic Aerosol Concentrations during SCAQS. *Atmos. Environ.* 29: 3527–3544.

Van Dingenen, R., Raes, F., Putaud, J.P., Baltensperger, U., Charron, A., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Hansson, H.C., Harrison, R.M., Hüglin, C., Jones, A.M., Laj, P., Lorbeer, G., Maenhaut, W., Palmgren, F., Querol, X., Rodriguez, S., Schneider, J., ten Brink, H., Tunved, P., Tørseth, K., Wehner, B., Weingartner, E., Wiedensohler, A. and Wåhlin, P. (2004). A European Aerosol Phenomenology. 1: Physical Characteristics of Particulate Matter at Kerbside, Urban, Rural and Background Sites in Europe. *Atmos. Environ.* 38: 2561–2577.

Venkataraman, C. and Friedlander, S. (1994). Size Distributions of Polycyclic Aromatic Hydrocarbons and Elemental Carbon. 2. Ambient Measurements and Effects of Atmospheric Processes. *Environ. Sci. Technol.* 28: 563–572.

Wang, G., Wang, H., Yu, Y., Gao, S., Feng, J., Gao, S. and Wang, L. (2003). Chemical Characterization of Water-soluble Components of $PM_{10}$ and $PM_{2.5}$ Atmospheric Aerosols in Five Locations of Nanjing, China. *Atmos. Environ.* 37: 2893–2902.

Wang, Y., Li, P., Li, H., Liu, X. and Wang, W. (2010). PAHs Distribution in Precipitation at Mount Taishan: China. Identification of Sources and Meteorological Influences. *Atmos. Res.* 95: 1–7.

Watson, J.G., Chow, J.C., Lowenthal, D.H., Pritchett, L.C., Frazier Gary, R., Clifton, A. and Robbins, R. (1994). Differences in the Carbon Composition of Source Profiles for Diesel-and Gasoline-powered Vehicles. *Atmos. Environ.* 28: 2493–2505.

Wei, F., Teng, E., Wu, G., Hu, W., Wilson, W., Chapman, R., Pau, J. and Zhang, J. (1999). Ambient Concentrations and Elemental Compositions of $PM_{10}$ and $PM_{2.5}$ in Four Chinese Cities. *Environ. Sci. Technol.* 33: 4188–4193.

Ye, B., Ji, X., Yang, H., Yao, X., Chan, C., Cadle, S., Chan T. and Mulawa, P. (2003). Concentration and Chemical Composition of $PM_{2.5}$ in Shanghai for a 1-year Period. *Atmos. Environ.* 37: 499–510.