Aerosol and Air Quality Research, 15: 1485–1493, 2015

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2014.12.0331

Characteristics of Organic Carbon and Elemental Carbon in the Ambient Air of Coking Plant

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ABSTRACT

To investigate the characteristics of organic carbon (OC) and elemental carbon (EC) in the ambient air of coking plant, particulate matter samples were collected and analyzed. The OC and EC mass concentrations were in the range of 104.2–223.2 μg/m^3 and 93.7–237.8 μg/m^3, respectively, which were much higher than those in the ambient air of industry, highway, and urban roadway tunnel. The OC concentrations did not significantly differ at the coke side and the machine side, whereas the EC concentration was significantly higher at the coke side. The OC/EC ratios ranged from 0.74 to 2.35, and coking was the primary source of OC and EC. Carbonaceous aerosol was a large component in the ambient air, and the total carbonaceous aerosol (TCA) accounted for 39.1%–73.0% of the total suspended particulates (TSP). TCA contributions to TSP were consistent at the coke side and the machine side, and both contributions were lower than those at other sampling sites. OC and EC emission control must be strengthened for improving coking plant air quality and reducing health hazards to coke-plant workers. OC–EC correlation was evident, with a correlation coefficient of 0.976 ($p < 0.05$) at the coke-oven top, coke side, and machine side, whereas no significant correlations were observed at sites downwind of the coke oven ($p > 0.05$).

Keywords: Coking; Organic carbon; Elemental carbon; Total carbonaceous aerosol; OC/EC.

INTRODUCTION

Carbonaceous aerosol, which accounts for a substantial fraction of ambient aerosols (Yu and Yu, 2009), profoundly affects air quality, visibility, climate, and human health (Mark, 2001; Ye *et al.*, 2003; Satsangi *et al.*, 2012; Zhang *et al.*, 2012; Cao *et al.*, 2013; Zhang *et al.*, 2013). It is a complex mixture, primarily containing organic carbon (OC) and elemental carbon (EC) (Cao *et al.*, 2003; Satsangi *et al.*, 2012). EC, often called black carbon and soot, which contains pure carbon and graphite carbon (Cao *et al.*, 2003) and originates mainly from coal combustion, vehicle emission, and wood burning (Szidat *et al.*, 2009; Jiang *et al.*, 2011; Shen *et al.*, 2013). OC contains polycyclic aromatic hydrocarbons (PAHs), n-alkanes, organic acids, carbonyl compounds, and heterocyclic compounds (Szewczyńska *et al.*, 2013). Certain OC components, such as PAHs and polychlorinated biphenyls, exhibit carcinogenic, teratogenic, and mutagenic properties (Chen *et al.*, 2005; Ladji *et al.*, 2014). OC originates through two mechanisms: (1) direct emission from sources and (2) secondary OC (SOC) formation from volatile organic compounds (VOCs) and gas-to-particle conversion of semivolatile organic compounds (semi-VOCs) (Turpin and Huntzicker, 1995; Cao *et al.*, 2003). Because of the several hazards associated with OC and EC, carbonaceous aerosol has attracted worldwide attention in recent decades (Cao *et al.*, 2004; Cao *et al.*, 2007; Niu *et al.*, 2012; van Drooge *et al.*, 2012; Pachauri, 2013).

Coal utilization processes emit large quantities of air pollutants, and coking is a prevalent coal conversion process. Coking is a dry distillation process in oxygen-free conditions at high temperatures (Mastral and Callén, 2000). The contaminants emitted during coking include inorganic compounds, heavy metals, OC, and EC (Tsai *et al.*, 2007; Mu *et al.*, 2012; Liu *et al.*, 2013; Mu *et al.*, 2013; Liu *et al.*, 2014). Coke-plant workers are exposed to organic pollutants, leading to high lung cancer mortality (Redmond, 1983; Bertrand *et al.*, 1987). In China's Shanxi province, OC and EC emissions from coking are second only to domestic coal emission and are much higher than those from biomass combustion, power plant and vehicle emissions (Cao *et al.*, 2006).

Previous studies have shown that OC and EC severely affect human health (Ostro *et al.*, 2008; Ostro *et al.*, 2009; Patel *et al.*, 2009; Kelly and Fussell, 2012; Ostro *et al.*, 2015). Ostro *et al.* (2009) found that total hospitalizations

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from childhood respiratory diseases, such as pneumonia, acute bronchitis, and asthma, were mostly associated with OC, EC, and particulates with the diameter less than 2.5 μm ($PM_{2.5}$). On the basis of the species interquartile range, the results showed an excess risk of 3%–7% for many of the respiratory outcomes (Ostro *et al.*, 2009). Siginificant associations were found between cardiovascular disease and OC, EC, and $PM_{2.5}$, with a 3%–5% increase in daily mortality among non-high-school graduates (Ostro *et al.*, 2008). Patel *et al.* (2009) reported that significant relationships were observed between EC and cough in young children during the cold and flu season.

Liu *et al.* (2013) have reported the pollution characteristics and size distributions of OC and EC in the coking plant air and found that the OC and EC concentrations were 377.8 $\mu g/m^3$ and 151.7 $\mu g/m^3$. Based on a literature review, few studies have investigated the distributions of OC and EC in the air surrounding coke ovens, which influence health risk assessments, source apportionments and diffusion mechanisms. In this study, a coking plant located in the outer suburbs of Shanxi, China, was selected as the research location. The objectives of this study are to investigated the (1) OC, EC, and total suspended particulates (TSP) levels in the ambient air of the coke plant, (2) spatial distributions of OC and EC around the coke oven, (3) correlations of OC and EC associated with TSP near and downwind of the coke oven, and (4) contributions of carbonaceous species to the TSP mass. The results will provide basic data for health risk assessment and a foundation for pollution control in the coke plant.

MATERIALS AND METHODS

Sample Collection

A coking plant located in the outer suburbs of Shanxi, China, was selected as the research location. The plant is surrounded by cropland and the ambient air is hardly affected by other industrial sources. Country roads mainly surround the coking plant and vehicular traffic is low. The plant has a JL4350D coke oven with a chamber size of 13080 mm × 500 mm × 4300 mm. Coal is charged through stamp charging; the coking time is 36 h and the daily coke output is 1728 t. A baghouse precipitator with a dust-removal efficiency of 96% is used. Seven sampling sites were chosen according to "emission standard of air pollutants for coke oven" (GB 16171-1996), "technical guidelines for fugitive emission monitoring of air pollutants" (HJ/T 55-2000), and the layout of the coking plant. Because the coke yard and clean coal yard are located west and south of the coke oven, respectively, reference sites were established north of the oven. The locations of the coke plant and the sampling sites are shown in Fig. 1. The sampling sites and their functions are as follows. (A) South of the coke oven, atop a one-story structure near the coke-car track on the coke side, represents the pollution situation of the coke side. (B) North of the coke oven, atop a one-story structure near the charging-car track on the machine side, represents the pollution situation of the machine side. (C) The green area 200 m the north of the coke oven, is the reference site. (D) The grassland near the plant boundary, 450 m northeast of the coke oven, represents the air pollution situation at the factory boundary. (E) Near the transformer room east of the plant, 240 m downwind of the coke oven, represents the leeward pollution situation. (F) The grassland near the southeastern boundary, 320 m downwind of the coke oven, represents the leeward pollution situation and the air pollution situation at the factory boundary. (G) At the coke-oven top, represents the characteristics of the fugitive emission source.

Samples were collected in August and September 2010. The weather was mostly sunny. The average (i.e., arithmetic averages of all values measured during the sampling period) ambient temperature, relative humidity, and atmospheric pressure were 25°C, 74%, and 91.4 kPa, respectively. The dominant wind direction was northwesterly and westerly, with a calm wind frequency of 14.7% during the sampling period. Particulate matter samples were collected using TSP samplers (TH-1000F) made in China, and the particulate samples were collected using glass fiber filters (GFFs; 20.3 cm × 25.4 cm). Three samples were obtained from each sampling site, yielding a total of 21 samples. Each sample was collected over 5 h.

Before sampling, the GFFs were wrapped in aluminum foil and baked at 500°C for 5 h to volatilize any organic contaminants. The GFFs were weighed before and after sampling to determine the amount of particles collected. They were equilibrated for 48 h at 25°C and 50% relative humidity in a temperature and humidity chamber before weighed using a microbalance (Sartorius LA130S-F) accurate to 0.1 mg. After sampling, the GFFs were removed from the sampler, folded with the adsorbed particulate matter on the inner side, and wrapped in aluminum foil. After weighing, all filters were stored at –20°C until analysis.

Organic Carbon and Total Carbon Analysis

The mass concentrations of total carbon (TC) and OC in TSP were analyzed using an Elementar Analysensysteme GmbH vario EL cube made in Germany (Bi *et al.*, 2007; Shi *et al.*, 2011), as follows. Place 4–5 mg membrane samples in the instrument. Heat the samples to 1000°C and feed them oxygen for 10 min for combustion. Separate CO_2 from the generated gas by using a gas chromatographic column and determine the CO_2 concentration by using a thermal conductivity detector (TCD). Finally, convert the CO_2 concentration to a TC mass concentration. Similarly, place another 4–5 mg of the membrane samples in the instrument, heat to 450°C, feed them oxygen for 10 min for combustion, and determine CO_2 concentration by using a TCD; convert the CO_2 concentration to an OC mass concentration.

Quality Control and Quality Assurance

The standard curve is plotted using 18 solid acetanilide standard samples with known carbon content values; the mass of the standard samples ranged from 0.5 to 7 mg. The standard curve is calibrated using the standard samples each time the analyzer is run for verifying instrument stability and ensuring the credibility of the OC and TC measurements. Concentrations of target OC and EC in prepared blank filters were not detected.

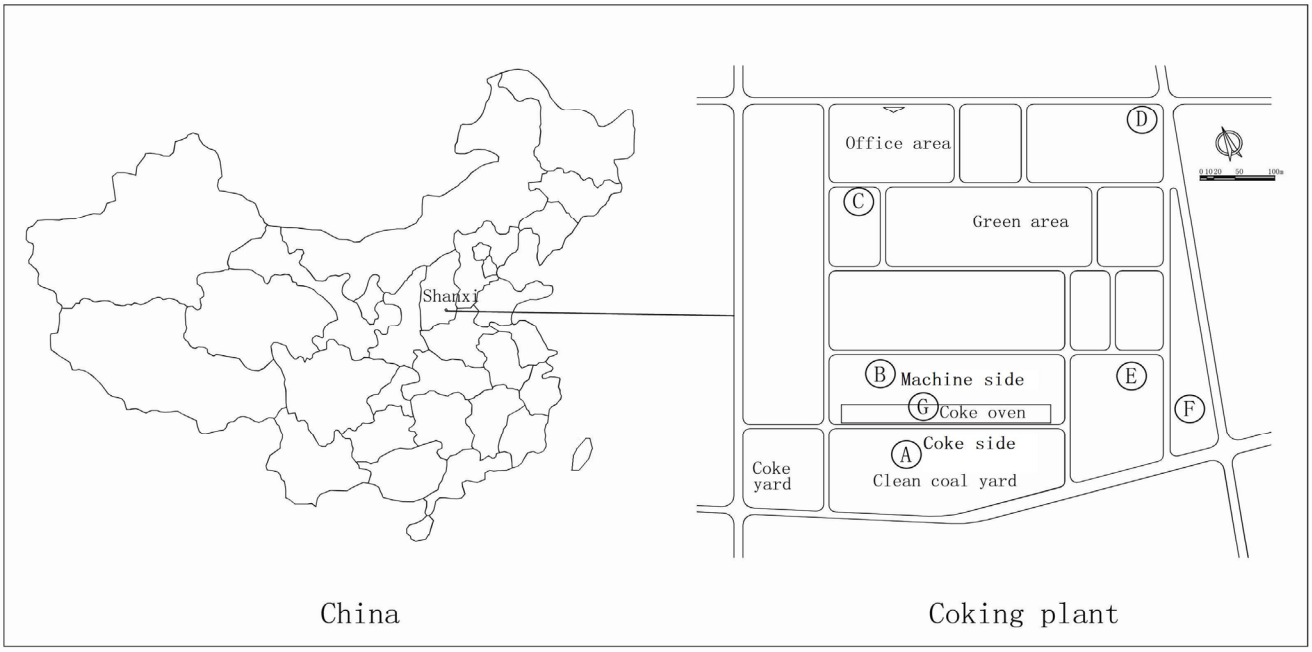

Fig. 1. Locations of the investigated plant in Shanxi, China, and the sampling sites in the coking plant area.

Data Analysis

Inorganic carbon is a small proportion of the TC in ambient air particulate matter (Na *et al.*, 2004; Cao *et al.*, 2007; Yu and Yu, 2009; Niu *et al.*, 2013); therefore Eq. (1) was used to calculate the mass concentration of EC:

$$EC = TC - OC \quad (1)$$

where EC, TC, and OC are mass concentrations (μg/m^3).

Previous studies (Turpin and Lim, 2001; Ram and Sarin, 2011) have reported that organic matter (OM) concentration can be estimated by multiplying the measured OC concentration by conversion factors of 1.6 and 2.1 (used mainly for vegetative detritus, lipids from microorganisms, and biomass combustion) for urban and nonurban aerosols, respectively. The ambient air of the coking plant investigated in this study is more similar to urban atmosphere than nonurban atmosphere according to Turpin and Lim (2001) definition. Therefore, OM can be estimated by multiplying the amount of OC with 1.6. The total carbonaceous aerosols (TCA) are the sum of OM and EC:

$$TCA = (OC \times 1.6) + EC \quad (2)$$

where TCA are mass concentrations (μg/m^3).

RESULTS AND DISCUSSION

Pollution Characteristics of TSP

The mass concentrations of TSP, OC, and EC in the ambient air of the coking plant are listed in Table 1. The TSP mass concentrations were 1317.6, 576.5, 634.6, 571.8, 719.6, and 619.8 μg/m^3 at sites A–F, respectively. The average TSP concentration for sites A–F was 740.0 μg/m^3, which was lower than the coking plant boundary threshold (1000.0 μg/m^3) recommended in the "emission standard of pollutants for coking chemical industry" (GB16171-2012, China). The TSP concentration at site A (1317.6 μg/m^3) slightly exceeded the threshold, whereas those at sites B–F (571.8–719.6 μg/m^3) were lower than the threshold. The TSP concentration at site A was significantly higher than that at site B ($p < 0.05$). Site A was near the coke-car track at the coke side; the higher TSP concentration was caused by dust leakage during coke pushing. The TSP concentrations at sites D, E, and F were 571.8, 719.6, and 619.8 μg/m^3, respectively, suggesting that TSP concentrations in the coking plant were slightly affected by the relative orientations of the coke oven and sampling sites, and that the variations among these three sites were associated with the distance from the oven. The TSP concentrations decreased with increasing distance from the coke oven. The TSP concentrations obtained in this study for coke side and machine side were lower than those obtained by Liberti *et al.* (2004) (2100 and 1700 μg/m^3), possibly because of variation in the oven type and coke output.

Characteristics of OC and EC

The mass concentrations of OC and EC in TSP in the plant's ambient air were in the range of 104.2–223.2 and 93.7–237.8 μg/m^3, with the average being 169.6 and 150.9 μg/m^3, respectively (Table 1). The contributions of coarse particle (≥ 10.2 μm) OC (14.3%) and EC (13.1 %) are low (Liu *et al.*, 2013), therefore, we compared the OC and EC in TSP in the ambient air of the coking plant with those in PM_{10} at other locations. Tian *et al.* (2013) reported that the PM_{10} OC and EC concentrations in the ambient air of Taiyuan, Shanxi, were 25.89 and 6.82 μg/m^3 in summer, respectively. The corresponding values in Lahore, Pakistan were 63 and 21 μg/m^3 (Alam *et al.*, 2014). Samara *et al.* (2014) reported values of 11.3 and 6.56 μg/m^3 at an urban

Table 1. TSP, OC, and EC concentrations and OC/EC ratios at seven sampling sites in the coke plant area.

Sampling sites	Samples	OC (μg/m^3)	EC (μg/m^3)	TSP (μg/m^3)	OC/EC
A	1	130.3	147.3	1374.5	0.88
	2	136.9	294.6	1614.1	0.46
	3	252.5	271.4	964.2	0.93
	Average	173.3	237.8	1317.6	0.76
B	4	114.9	95.8	609.7	1.20
	5	104.2	81.2	558.9	1.28
	6	93.3	105.6	560.7	0.88
	Average	104.2	94.2	576.5	1.12
C	7	286.8	123.3	748.7	2.33
	8	99.3	88.1	519.6	1.13
	9	210.0	199.2	635.5	1.05
	Average	198.7	136.9	634.6	1.50
D	10	201.1	54.2	511.8	3.71
	11	166.8	97.1	712.2	1.72
	12	210.3	129.9	491.6	1.62
	Average	192.7	93.7	571.8	2.35
E	13	92.7	138.6	486.1	0.67
	14	462.3	294.8	1311.8	1.57
	15	114.6	71.1	360.9	1.61
	Average	223.2	168.2	719.6	1.28
F	16	122.0	192.6	593.6	0.63
	17	162.7	151.0	691.0	1.08
	18	91.8	181.0	574.7	0.51
	Average	125.5	174.8	619.8	0.74
G	19	1008.0	923.1	4021.8	1.09
	20	511.4	306.5	2509.7	1.67
	21	1308.5	1058.0	4395.1	1.24
	Average	942.6	762.6	3642.2	1.33

traffic site in Thessaloniki, northern Greece. Clearly, the OC and EC levels in the ambient air of the coking plant are significantly higher than those in urban ambient air.

The OC/EC ratios in the ambient air of the coking plant were in the range of 0.74–2.35 (Table 1). The coke-oven top is the fugitive emission source during coking, and the OC/EC ratio at the coke-oven top was 1.33. The OC and EC pollution in the coking plant area may be contributed to by vehicular emissions on both the country road and the plant's internal roads. Previous studies (Watson *et al.*, 2001; Huang *et al.*, 2006) have reported OC/EC ratios of 2.97, 0.57, 2.70, 15.67, and 12.73 for coal-fired boilers, vehicular emissions, residential coal combustion, forest fires, and paved road dusts, respectively. In contrast to the OC/EC ratios from these pollution sources and considering that the sampling sites were close to the coke oven, the primary source of OC and EC in the coking plant was the coking process.

Table 2 compares the OC and EC concentrations and the OC/EC ratio in the ambient air of the coking plant with those reported in previous studies (Handler *et al.*, 2008; Pio *et al.*, 2011; Ducret-Stich *et al.*, 2013; Alves *et al.*, 2015). OC/EC ratios of 1.29, 1.67, 1.09, and 1.8 were reported for the ambient air of coking plant, highway, urban roadway tunnel, and industry. These ratios all being lower than 2 suggest that the OC and EC pollutions near these sources mainly originated from primary emission (Turpin and Huntzicker, 1995; Chow *et al.*, 1996). OC and EC concentrations were 2.76 and 1.65 μg/m^3 in the highway atmosphere, 29.6 and 27.1 μg/m^3 in the atmosphere of the urban roadway tunnel, and 6.0 and 3.9 μg/m^3 in the industrial air (Pio *et al.*, 2011; Ducret-Stich *et al.*, 2013; Alves *et al.*, 2015). The OC concentration in the coking plant area was 169.6 μg/m^3, which is 61.4 times that of the highway atmosphere, 5.7 times that of the urban roadway tunnel air, and 28.3 times of the industrial air. The EC concentration in the ambient air of the coking plant area was 150.9 μg/m^3, which is 91.5, 5.6, and 38.7 times those of the aforementioned sources' atmosphere, respcetively. The OC and EC concentrations were substantially higher than those in the ambient air of the industry, highway, and urban roadway tunnel. The ambient air of the coking plant was severely polluted by OC and EC emission during coking. Consequently, OC and EC emission control must be strengthened to improve air quality in the coking plant and reduce health hazards to the coke-plant workers.

As shown in Table 1, the spatial distributions of OC and EC in TSP in the ambient air of the coking plant varied. The OC concentration was the highest at sites C, D, and E, followed by site A, with the lowest values at sites B and F. The EC concentration was the highest at site A, followed by sites E and F, with the lowest values at sites B, C, and D. Spatial variation in the concentrations was tested using a two-sample t-test with a confidence interval of 95% and a

Table 2. OC and EC concentrations and the OC/EC ratio in the ambient air of the coking plant and at other locations.

Ambient air[a]	Sampling period	Aerosol	OC (μg/m^3)	EC (μg/m^3)	OC/EC	Analytical method	References
Coking plant	August, September 2010	TSP	169.6[b]	150.9[b]	1.29[b]	Thermal two step combustion	This study
Highway Tunnel	April–May 2005	PM_{10}	–	–	0.9	Thermal two step combustion	Handler *et al.* (2008)
Highway	January–December 2008	PM_{10}	2.76	1.65	1.67	Thermal-optical transmission method	Ducret-Stich *et al.* (2013)
Urban Roadway Tunnel	February 2013	PM_{10}	29.6	27.1	1.09	Thermal-optical transmission method	Alves *et al.* (2015)
Industry	June 1992–2010	PM_{10}	6.0	3.9	1.8	Thermal-optical method	Pio *et al.* (2011)

[a] Ambient air near the pollution sources.
[b] Average value of sampling sites A–F.

significance level of 5% in Origin 8.0. The OC concentrations did not vary significantly between sites A and B ($p > 0.05$), whereas the EC concentration at site A was significantly higher than that at site B ($p < 0.05$). Large amounts of carbonaceous aerosols are emitted from the guide grooves of the quenching car and from the quenching car transporting coke to the quenching tower. Some semi-VOCs have high vapor pressure because of high temperature at the coke side (site A), and mainly exist in gas-phase. The involatile coke is the important component of EC, and its concentration in particles is high though the ambient air temperature is high at the coke side. Consequently, the distributions of OC and EC were varied at the coke side and the machine side.

The OC concentration at site D was significantly higher than that at sites B and F ($p < 0.05$), whereas the EC concentration at site D was significantly lower than that at site F ($p < 0.05$). EC has high chemical stability and remains in the ambient air for a long time; therefore, the spatial distribution of EC around the coke oven is influenced mainly by the distance and relative orientation of the oven. Previous studies (Turpin and Huntzicker, 1995; Chow *et al.*, 1996) have reported that SOC exists when the OC/EC ratio exceeds 2. The OC/EC ratio at site D was 2.35, indicating that secondary pollution exists at site D. Bieniek and Lusiak (2012) reported that coking emits large amounts of SOC precursors such as toluene, m-xylene, and p-xylene. Moreover, coking emits a large amount of semi-VOCs such as PAHs, and gas-to-particle conversion of these compounds influence OC concentrations in the coking plant air (Shi *et al.*, 2011; Mu *et al.*, 2013; Mu *et al.*, 2014). Therefore, the OC distribution in the coking plant air was due to the cumulative effect of coking emissions, atmospheric dispersion and dilution, SOC formation from VOCs, and gas-to-particle conversion of semi-VOCs.

The relationship of OC and EC varied around the coke oven. The correlations of OC and EC in TSP near the coke oven (sites A, B, and G) and downwind of the coke oven (sites E and F) are plotted in Fig. 2. OC and EC exhibited a high correlation, with a correlation coefficient of 0.976 ($p < 0.05$), and the mean OC/EC ratio was 1.27 near the coke oven, as shown in Fig. 2(a). The results suggest that OC at sites near the oven are possibly directly emitted from primary sources, with some of the primary sources being fugitive emissions from the coke oven top and leakage during coal charging and coke pushing. No significant correlations were observed between OC and EC at sites downwind of the coke oven ($p > 0.05$), as depicted in Fig. 2(b). OC and EC at sampling sites E and F are affected not only by fugitive emissions but also by stack emissions from coal charging, coke pushing, and coke-oven gas combustion (Mu *et al.* 2013). Gas- and solid-phase redistribution of semi-VOCs may be another factor that causes poor OC–EC correlation at sites E and F (Liberti *et al.*, 2006; Mu *et al.*, 2014).

Contributions of Carbonaceous Species to the TSP Mass

OC, EC, and TCA contributions to TSP at all sampling sites are plotted in Fig. 3. At the coke-oven top, OC, EC, and TCA contributions to TSP were 25.1%, 19.7%, and 59.9%, respectively. OC and EC contributions to TSP in

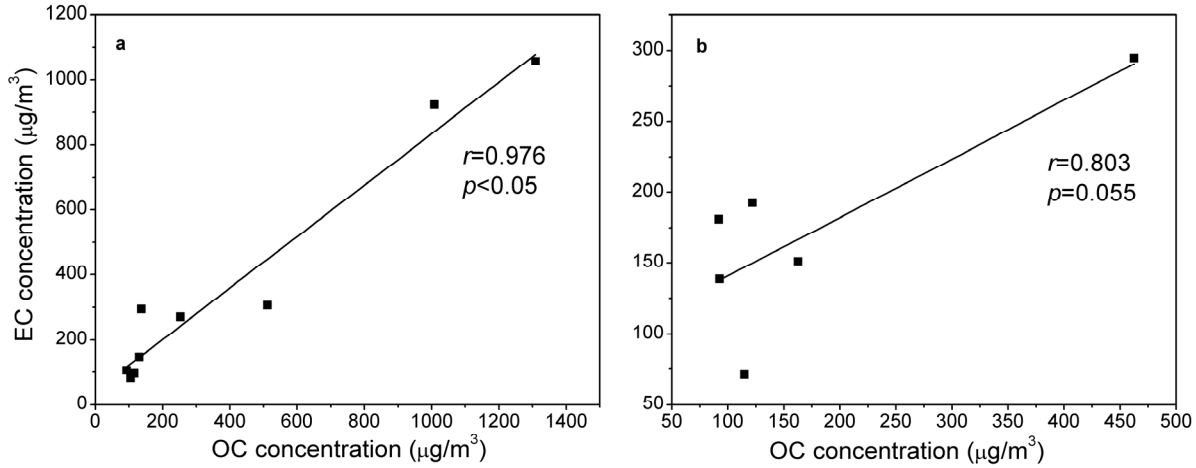

Fig. 2. Correlations of OC and EC with TSP (a) near the coke oven (sites A, B, and G) and (b) downwind of the coke oven (sites E and F).

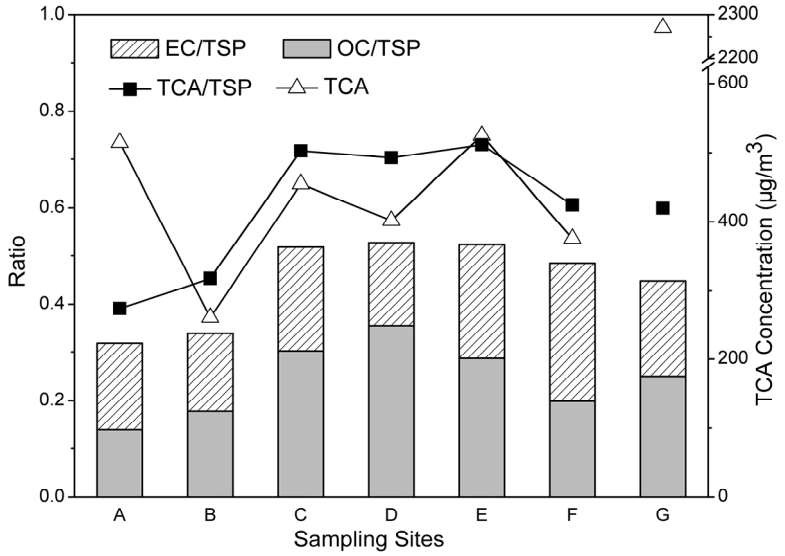

Fig. 3. OC/TSP, EC/TSP, and TCA/TSP ratios and TCA concentrations at all sampling sites in the coking plant area.

the ambient air of the coking plant were in the range of 13.9%–35.5% and 16.1%–28.5%, respectively, which are consistent with OC and EC values at the coke-oven top. The OC/TSP and EC/TSP ratios in the ambient air of the coking plant were similar to the ratios at the coke-oven top, indicating that the OC and EC in the plant area arose mainly during coking. OC and EC contributions to PM_{10} in four cities in Shanxi were in the range of 10.5%–16.9% and 11.7%–21.5%, respectively (Peng *et al.*, 2011). Meng *et al.* (2007) reported that OC and EC accounted for 18.6% and 2.9% of $PM_{2.5}$ in winter in Taiyuan, Shanxi.

EC contributions to TSP varied slightly in the ambient air of the coking plant, with a difference of 12.4% between the maximal and minimal values. The lowest and highest EC/TSP ratios were at sites B and F, respectively. By contrast, OC contribution to TSP varied significantly, with a difference of 21.6% between the maximal and minimal values. The OC/TSP ratio in the plant ambient air was the highest at site D (35.5%), followed by sites C (30.2%) and E (28.7%); the lowest were at sites A (13.9%) and B (17.8%). The OC/TSP ratios at sites D, C, and E were slightly higher than that at the coke-oven top and those at sites A and B were slightly lower than that at the coke-oven top. The highest OC/TSP ratio occurred at site D because of semi-VOCs gas-solid transformation and SOC formation (Bieniek *et al.*, 1993; Chen *et al.*, 1999). At sites A and B, OC/EC ratios were 0.76 and 1.12, indicating less SOC formation at these sites; therefore, the OC in TSP at these two sites was largely primary OC directly emitted during coking. Meanwhile, a large number of coke particles with lower OC emitted during coke pushing, which may be another factor that causes the lowest OC/EC ratio at site A.

The TCA concentrations in the ambient air of the coking plant were in the range of 260.9–525.3 μg/m^3, and TCA accounted for 39.1%–73.0% of TSP. Romundstad *et al.* (1998) reported that carbonaceous particulate concentrations in the coking plant ranged from 900 to 16200 μg/m^3 and that the concentration at the oven side was 7900 μg/m^3. These

values are higher than those in this study, possibly because of differences in coke oven type, dedusting equipment, and environmental management systems. Peng *et al.* (2011) reported that the TCA contributions to PM_{10} in four cites in Shanxi were in the range of 29.8%–40.0%. Therefore, carbonaceous aerosols are a large component in the ambient air of the coking plant. TCA mass concentrations were the highest at sites A and E. TCA/TSP ratios were the highest and the lowest at sites E and A, respectively, as shown in Fig. 3, which were because of the higher and lower TSP concentrations at sites A and E, respectively. The OC concentration at site E was higher than that at site A, which explains the higher TCA/TSP value at site E. The TCA mass concentration at site A, located on the coke side, was twice that at site B, located on the machine side, but the TCA/TSP ratios were similar at these two sites. The TCA/TSP ratios in the ambient air of the coking plant were highest at sites C, D, and E, followed by site F, and the lowest were at sites A and B (Fig. 3). TCA contributions to TSP were lower at sites A and B than those at other sampling sites, and the highest contribution was at site E, located 240 m east of the coke oven. Sites A and B were located at the coke side and the machine side of the oven, respectively. A part of the TSP at site A arose from coke leakage during coke pushing and a part of the TSP at site B may have arisen from coal leakage during coal charging, which explains the lower contributions of TCA to TSP at sites A and B.

CONCLUSIONS

In this study, OC and EC in TSP sampled in a representative coking plant in Shanxi, China, were analyzed and the spatial distribution characteristics of carbonaceous aerosols were discussed.

The TSP concentrations in the coking plant ranged from 571.8 to 1317.6 μg/m^3; all TSP concentrations except that at the coke side were lower than the recommended threshold at the coking plant boundary in the "emission standard of pollutants for coking chemical industry" (GB16171-2012) in China. The TSP concentration at the coke side was significantly higher than that at the machine side ($p < 0.05$). The TSP concentrations were slightly inflected by the relative orientations of the coke oven and sampling sites and closely associated with the distance from the coke oven.

The primary source of OC and EC in the coking plant area was the coking process. The OC and EC mass concentrations in the plant ambient air ranged from 104.2 to 223.2 μg/m^3 and 93.7 to 237.8 μg/m^3, which were much higher than those in the ambient air of industry, highway tunnel, and urban roadway tunnel. The OC concentrations did not vary significantly between the coke side and the machine side ($p > 0.05$), but the EC concentration was significantly higher at the coke side than at the machine side ($p < 0.05$). The OC concentration at the northeastern boundary was significantly higher than at the machine side and the southeastern boundary ($p < 0.05$), whereas the EC concentration at the northeastern boundary was significantly lower than that at the southeastern boundary ($p < 0.05$). The spatial distribution of EC around the coke oven was affected primarily by distance and the relative orientations of the oven and the sites. The OC distribution in the coking plant air was due to the cumulative effect of coking emissions, atmospheric dispersion and dilution, SOC formation from VOCs, and gas-to-particle conversion of semi-VOCs. OC–EC correlation was evident, with a correlation coefficient of 0.976 ($p < 0.05$) at the coke-oven top, coke side, and machine side, whereas no significant correlations were observed between OC and EC at sites downwind of the coke oven ($p > 0.05$).

OC/TSP and EC/TSP ratios in the ambient air of the coking plant ranged from 13.9% to 35.5% and 16.1% to 28.5%, which were consistent with the ratio at the coke-oven top. Carbonaceous aerosol was a large component, and TCA accounted for 39.1%–73.0% of TSP. The TCA contributions to TSP at the coke side and the machine side were consistent. The TCA contributions to TSP were lower at the coke side and machine side than those at other sampling sites. Higher contributions occurred at a certain distance away from the coke oven.

ACKNOWLEDGEMENTS

This research work was supported by the Project of National Natural Science Foundation of China (Grand 41173002, 41373008) and Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (Grand 2014126).

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Received for review, January 5, 2015
Revised, April 12, 2015
Accepted, May 31, 2015