Atmospheric Research 104-105 (2012) 227–236

Contents lists available at SciVerse ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

Characteristics of carbonaceous aerosol in $PM_{2.5}$: Pearl Delta River Region, China

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ARTICLE INFO

Article history:
Received 16 November 2010
Received in revised form 27 September 2011
Accepted 26 October 2011

Keywords:
$PM_{2.5}$
Organic carbon
Elemental carbon
WSOC
Pearl River Delta

ABSTRACT

Simultaneous measurements of atmospheric organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC) were made at four sampling sites, namely Guangzhou (GZ), Zhaoqing (ZQ), PolyU Campus (PU) and Hok Tsui (HT), in the Pearl River Delta (PRD) region between 14 August 2006 and 28 August 2007. The highest concentrations of total carbon (TC) were found at the medium-scale roadside site (PU) and the lowest were found at the regional-scale site (HT). Among the four sampling sites, the average WSOC at ZQ showed the highest concentrations, while the lowest were seen at HT. OC and EC concentrations revealed spring/summer minima and autumn/winter maxima at all sites except PU, which had a consistently high EC concentration all over the year. The highest WSOC/OC ratio was found at ZQ with an average of 0.41, suggesting that the OC was more oxidized in the atmosphere of the semi-rural site. The lowest WSOC/OC was found at the roadside site of PU. Moreover, the WSOC/OC ratio increased in autumn, when the photochemical reactions are the most active in the PRD region. This can be attributed to aging and atmospheric processing of the organic compounds during their transportation, or to the formation of secondary organic aerosol (SOA). Average annual secondary organic carbon (SOC) concentrations in $PM_{2.5}$ were estimated to be 2.2 and 3.5 μg m^{-3} for GZ and ZQ, comprising 33.5% and 42.8% of the corresponding OC concentrations, respectively. The results indicate that SOC is significant in the PRD region, and its formation mostly occurs within the region.

1. Introduction

The Pearl River Delta (PRD) region in southern China covers nine prefectures of Guangdong province, namely Guangzhou, Shenzhen, Zhuhai, Dongguan, Zhongshan, Foshan, Huizhou, Jiangmen and Zhaoqing, and the Special Administrative Regions of Hong Kong and Macau. The area has a population of 40 million. Its climate is mainly dominated by the Asian monsoon, with a northerly wind prevailing in winter and a southerly wind prevailing in summer. The PRD is one of the three fastest economy development regions in China. With extremely rapid urbanization, the area has been facing increasingly severe pollution issues and has become one of the four worst haze regions in China, together with the Yangtze River Delta, Beijing–Tianjin–Tangshan and Chongqing (Fu et al., 2008). The increases of anthropogenic emissions as well as unique geographical and

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doi:10.1016/j.atmosres.2011.10.016

climatological conditions have led to complex regional air pollution problems such as photochemical smog and haze over the PRD region (Zhang et al., 2008; Zheng et al., 2010). Recently, increased attention has been drawn to particulate matter less than 2.5 μm in diameter ($PM_{2.5}$) in China (Yang et al., 2005; Feng et al., 2006; Li et al., 2008). The fine particles can enter the human respiratory system and can also greatly affect visibility and radiation intensity in the atmosphere (Penner and Novakov, 1996; Menon et al., 2002; Wilkening et al., 2000; Nel, 2005). The adverse health, environment, and climate effects of $PM_{2.5}$ are derived from its chemical composition and properties.

Carbonaceous aerosol, which comprises organic carbon (OC) and elemental carbon (EC), constitutes a major fraction of PM in the atmosphere (Chow et al., 1993; Ho et al., 2002; Ho et al., 2003). Given that organic aerosols form 10–70% of the total fine aerosol by mass (Andrews et al. 2000), fully understanding the sources of OC is thus important. OC, including hundreds or thousands of different individual organic species, can be emitted from both natural and anthropogenic sources (Kanakidou et al., 2005). EC can be directly emitted from combustion sources and undergoes little chemical transformations, and is thus a good indicator of primary anthropogenic air pollutants (Ho et al., 2006). Water-soluble organic carbon (WSOC) is particularly important and typically constitutes a significant fraction, ranging from 20% to 60% to the OC (Decesari et al., 2001; Yu et al., 2004a; Yang et al., 2005; Feng et al., 2006). The WSOC can alter the hygroscopicity of aerosols and influence cloud formation and lifetime (Saxena et al. 1995; IPCC, 2001; Temesi et al., 2003; Viana et al., 2007). In general, secondary organic aerosol (SOA) compounds are water-soluble because they have polar functional groups (e.g., hydroxyl, carbonyl, and carboxyl) produced by the oxidation reaction (Saxena and Hildemann, 1996). A major source of WSOC is considered to be secondary organic aerosols (SOA), formed by the oxidation of volatile organic compounds (VOCs) followed by condensation on existing particles and/or nucleation. Recent studies have demonstrated that the WSOC and estimated SOA have similar chemical characteristics and properties in samples collected in urban areas (Miyazaki et al., 2006; Kondo et al., 2007). Saxena and Hildemann (1996) and Miyazaki et al. (2006) reported that WSOC was associated with a major fraction of SOA. Although some WSOC can be produced by primary emission such as biomass burning (Mayol-Bracero et al., 2002), the source contribution to WSOC is not well understood. In addition, WSOC plays an important role in the heterogeneous chemistry that occurs in fog and cloud water (Fuzzi et al. 2002; Cappiello et al. 2003), which has implications for local and regional air qualities.

The OC and EC concentrations have been widely reported in the PRD region (Cao et al., 2003; Ho et al., 2004; Duan et al., 2007; Huang et al., 2007). However, seasonal and spatial variations of WSOC have not yet been studied. Also, there is a lack of any long-term studies of carbonaceous aerosol in the PRD region. To gain a better understanding of the characteristics of the fine particles, aerosol filter samples were acquired at four sampling locations in the PRD region, namely Guangzhou (GZ), Zhaoqing (ZQ), PolyU Campus (PU) and Hok Tsui (HT), simultaneously on selected dates from 14th August 2006 to 28th August 2007. The main objectives of this study were: (1) to determine the spatial and seasonal variations of carbonaceous species and (2) to explore their source implications.

2. Experimental method

2.1. Sample collection

Four sampling sites were selected in the PRD region, namely Sun Yat-Sen University in Guangzhou (GZ), Zhaoqing University (ZQ) in Zhaoqing, Hok Tsui (HT) and Hong Kong Polytechnic University (PU) in Hong Kong (Fig. 1). The detailed information of the sampling sites were shown in Table 1. These four sites were representative of different characteristics (urban: GZ; semi-rural: ZQ; rural: HT; roadside: PU). Twenty-four-hour integrated $PM_{2.5}$ samples were collected at the four sampling sites simultaneously every sixth day from 14 August 2006 to 28 August 2007. A total of 208 $PM_{2.5}$ valid samples were obtained for carbonaceous analyses. The $PM_{2.5}$ was acquired on pre-fired (800 °C, 3 h) 90 mm quartz micro-fiber filters (QM-A, Whatman, Clifton, NJ) with medium-volume samplers at a flow rate of 113 L min^{-1}. The sampler consisted of a Bendix/Sensidyne 240 cyclone followed by a plenum, a differential pressure flow control and a sampling pump. The sampling flows were checked before and after sampling with a mass flowmeter (Model 4040, TSI, Shoreview, MN). The aerosol loaded filters were stored in a refrigerator at 4 °C before chemical analysis to prevent any loss of volatile components. However, this temperature does not totally prevent the loss of very volatile components and does not avoid some microbial processing. Approximately 5% of field blanks were collected to subtract positive artifacts that resulted from adsorption of gas-phase organic compounds onto the filter during and/or after the sampling.

2.2. OC, EC and WSOC analysis

The OC and EC were measured on a 0.526 cm^2 punch from each filter by thermal optical reflectance (TOR) following the IMPROVE protocol with a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA) (Chow et al., 2004, 2005; Cao et al., 2003). This produced four OC fractions [OC1, OC2, OC3, and OC4 at 120 °C, 250 °C, 450 °C, and 550 °C, respectively, in a pure helium (He) atmosphere], a pyrolyzed carbon fraction [OP, determined when reflected laser light attained its original intensity after oxygen (O_2) was added to the combustion atmosphere], and three EC fractions (EC1, EC2, and EC3 at 550 °C, 700 °C, and 800 °C, respectively, in a 2% O_2/98% He atmosphere). The IMPROVE OC is operationally defined as OC1 + OC2 + OC3 + OC4 + OP, whereas the EC is defined as EC1 + EC2 + EC3 − OP. The minimum detection limits (MDL) for the carbon analysis were 0.8 and 0.4 μgC cm^{-2} for the OC and EC, respectively, with a precision better than 10% for total carbon (TC).

For analysis of the WSOC fraction, five punches (total area of 2.63 cm^2) were taken from each filter and placed into a 15 mL screw-capped vial to which 10 mL of distilled deionized water (DDW) was added. Samples were extracted in a sonication bath for 1 h. Filter debris and suspended insoluble particles were removed from the water extracts using a syringe filter (0.2 mm PTFE membrane). One hundred microliters (100 mL) of the extract was automatically injected into a high-sensitivity Shimadzu TOC-V CPH total carbon analyzer (Columbia, MD, USA) to determine the WSOC content. Each

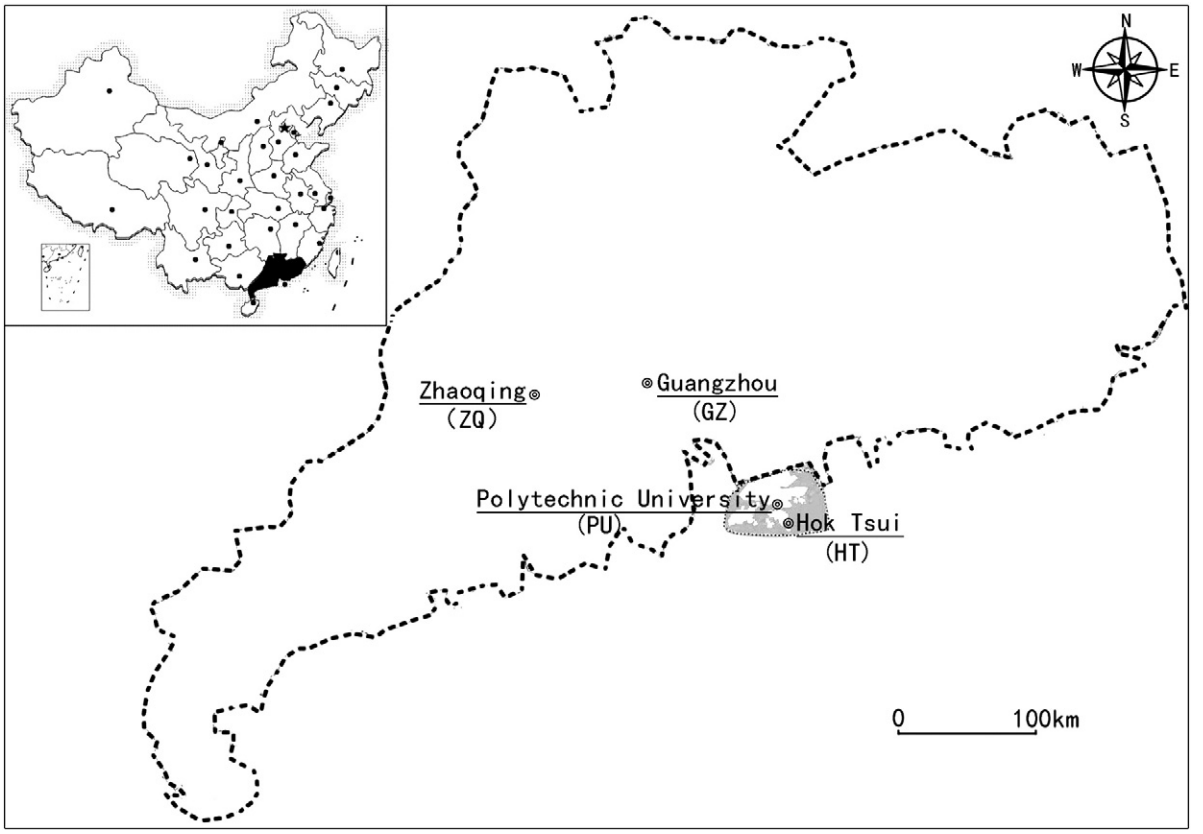

Fig. 1. Map showing locations of the four sampling sites in the PRD region (GZ: Guangzhou; ZQ: Zhaoqing University in Zhaoqing; HT: Hok Tsui; and PU: Hong Kong Polytechnic University in Hong Kong).

extract was analyzed three times to take the mean TOC value. The TC and inorganic carbon (IC) standard solutions were prepared with reagent grade potassium hydrogen phthalate (KHC8H4O4) and sodium hydrogen carbonate (NaHCO3), respectively. The MDL for the method was 15 μg L^{-1}, with a precision of ±5%. All samples were found to have insignificant amounts of IC.

3. Results and discussion

3.1. Spatial and seasonal distribution of OC and EC

Concentrations of OC and EC in the aerosol loaded filter samples collected in the PRD region are listed in Table 2. Large variations in concentrations were seen among the four sites. The concentrations of OC ranged from 1.1 to 24.3 μg m^{-3}, with an average of 6.9 ± 4.2 μg m^{-3}, while the concentrations of EC ranged from 0.42 to 21.7 μg m^{-3}, with an average of 5.9 ± 5.3 μg m^{-3}. The OC concentrations in $PM_{2.5}$ ranked in the ascending order HT<GZ<PU≈ZQ, while the EC concentrations ranked in the order HT<ZQ≈GZ<PU (Fig. 2). Among the four sites, the semi-rural site ZQ had the highest OC concentrations, which is attributable to a mixed contribution from both nearby emission sources and secondary formation processes. The highest EC concentration was seen at PU, which is attributable to high primary automobile emissions. The lowest OC and EC

Table 1
Site information.

Monitoring station	City	Abbreviation	Area type	Above ground
Sun Yat-Sen University	Guangzhou	GZ	Urban	12 m
Zhaoqing University	Zhaoqing	ZQ	Semi-rural	12 m
The Hong Kong Polytechnic University	Hong Kong	PU	Roadside	1.5 m
Hok Tsui	Hong Kong	HT	Rural	1.5 m

Table 2
Concentrations of OC, EC, TC and WSOC in $PM_{2.5}$ (in μg m^{-3}) at the four sampling sites in the PRD region.

Average (range)	Sampling sites				
	GZ	ZQ	PU	HT	Overall PRD region
OC	7.1 ± 3.3 (2.1–20.1)	8.2 ± 5.0 (2.6–24.3)	7.9 ± 3.8 (3.2–19.1)	4.1 ± 3.0 (1.1–14.1)	6.9 ± 4.2 (1.1–24.3)
EC	4.0 ± 2.5 (0.7–15.5)	3.9 ± 2.0 (1.2–8.8)	13.5 ± 3.5 (8.2–21.7)	1.8 ± 1.2 (0.4–5.6)	5.9 ± 5.3 (0.4–21.7)
TC	11.1 ± 5.1 (2.8–35.5)	12.0 ± 6.8 (4.0–31.0)	22.2 ± 6.0 (12.4–36.7)	6.0 ± 4.1 (1.7–19.7)	12.8 ± 8.2 (1.7–36.7)
WSOC	2.0 ± 1.2 (0.4–5.4)	3.3 ± 2.3 (0.5–10.3)	1.8 ± 1.1 (0.4–4.9)	1.3 ± 1.1 (0.2–4.4)	2.1 ± 1.7 (0.2–10.3)
WSOC/OC	28.3%	40.9%	21.1%	28.8%	30.2%

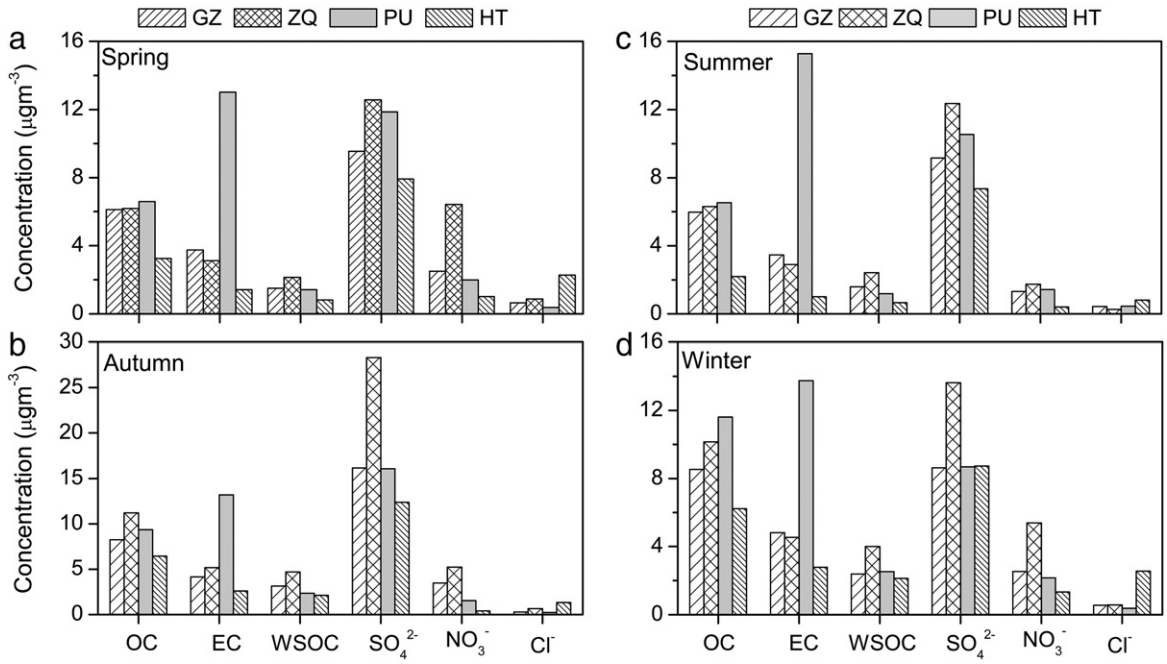

Fig. 2. Seasonal variations of OC, EC, TC and WSOC concentrations in the PRD region.

concentrations were both found at HT, which is a background site in Hong Kong in an upwind position relative to the anthropogenic emission sources. In addition, huge differences in the carbon concentrations were seen for PU and HT, even though their locations are relatively close. This further suggests that the local fueled engine emission strongly dominated carbon concentrations at the roadside site PU. Considering that the EC fraction in the aerosol mass is mostly emitted by motor vehicles (Watson et al., 1994), the order of the ambient EC levels is consistent with the number of vehicles accessing the sites, which is HT<ZQ<GZ<PU. The EC fraction in TC is also the highest at PU (61%), compared with only 30% at HT.

Seasonal distributions of OC and EC are illustrated in Fig. 2. The concentrations of OC and EC were minimum in spring/summer but maximum in autumn/winter at all the sites, except EC at PU. The PU site is located at the exit of a cross-harbor tunnel. The levels of local automobile emissions at PU remained steady throughout the four seasons since the tunnel usage was constant. However, this roadside station is at an upwind position in winter, so influences from ship emissions in the Victoria Harbor were considerably limited. Yu et al. (2004) claimed that PU might receive the plume from ship emissions when the wind direction was from the south in spring and summer. This explains the reverse seasonal trend of EC found at PU and provides further evidence that the seasonality of EC is dependent upon the distance from, and relative location to, the heavy shipping container ports in Hong Kong. The average OC and EC concentrations in the autumn/winter were 1.2 to 2.3 times higher than those in spring/summer in the PRD region. In order to investigate the transport and the source region of air pollutants, 2-day air mass back trajectory analyses were conducted using NOAA HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory, NOAA/ARL) with a starting elevation of 100 m. In winter, prevailing northeasterly wind travels across South China before reaching Hong Kong. The northeasterly winter monsoon brings polluted air masses from China (over the ground). In contrast, the lower carbon concentrations were found in summer, when prevailing southwesterly wind brings warm and damp air masses from the South China Sea through Hong Kong to PRD region. In addition, both increases of the emissions and occurrence of stable atmospheric conditions in winter can lead to the raised carbon concentrations (see next section). Prevailing northeasterly winds travel across industrial southern China before reaching Hong Kong in winter. The increases of pollutant concentrations were thus more significant in PU and HT than in ZQ and GZ during the sampling period. This phenomenon explains why the poorest air quality in Hong Kong is typically observed in winter, under the combined influences of local emissions and polluted air mass transportation from South China.

The OC to EC ratio has been used to infer the origin of carbonaceous particles (Chow et al., 1993; Turpin and Huntzicker, 1995). The average OC/EC ratios at regional-scale sites were *ca.* 2–4 times higher than those found at the PU roadside site, which showed little variation between summer and winter. The low OC/EC ratio at PU was primarily due to the high EC emissions from automobiles. Higher OC/EC ratios at the regional-scale sites suggest that the transportation of older aerosol as well as SOA were significant. However, OC/EC ratios observed were generally lower than previous studies in PRD (Cao et al., 2003; Ho et al., 2006; Duan et al., 2007) and some overseas urban studies (Viana et al., 2007; Sullivan et al., 2004; Weber et al., 2007). The relatively high concentration of EC observed in this study maybe due to increased primary emissions and specific meteorological conditions during sampling period. Since the OC/EC ratio depends upon the method

and analysis temperature program used, the comparison between our result and those from other studies should be done very carefully.

The correlation coefficients between OC and EC concentrations at the four sampling sites are shown in Table 3. A strong relationship between OC and EC was observed for the samples collected at GZ ($r=0.90$, $p<0.01$), ZQ ($r=0.85$, $p<0.01$) and HT ($r=0.92$, $p<0.01$), further suggesting that the carbonaceous particles were likely attributed to the same pollution sources. However, moderate OC–EC correlation at PU ($r=0.35$, $p<0.05$) indicates that their dominant sources were from different origins.

3.2. Spatial and seasonal distribution of WSOC

The concentrations of WSOC ranged from 0.16 to 9.44 $\mu g\ m^{-3}$, with an average of $2.1\pm1.7\ \mu g\ m^{-3}$ in the PRD region (Table 2). Among the four sampling sites, the average WSOC at ZQ had the highest concentrations, while the lowest was found at HT. The trend is consistent with the OC concentrations in $PM_{2.5}$. Huang et al. (2006) suggested that potential sources of the WSOC in fine particles include both primary and secondary sources, often being associated with polar organic compounds (e.g., dicarboxylic acids) correlated with SOA formation (Grosjean et al., 1978; Rogge et al., 1993).

Fig. 2 clearly shows seasonal variations of the WSOC concentration in $PM_{2.5}$. Again, the WSOC was ~1.8–2.9 times higher in autumn/winter than in spring/summer. The lower WSOC level in summer is understandably explained by clean marine air masses advected from the South China Sea and the washing effect of frequent rainfall in the PRD region. In winter, transformation and transportation of the secondary pollutants from south China were dominant. The most significant influence of these effects can be seen at the downwind site of HT, where local emission sources were very limited. Here, the average WSOC concentration of 2.1 $\mu g\ m^{-3}$ in winter was double that in summer.

The water-soluble fraction of total OC provides valuable clues to the composition and chemical process of organic aerosols (Miyazaki et al., 2007). WSOC/OC ratios can be used as an indicator for the secondary organic aerosol (SOA) formation because most of the SOA are soluble in water (Kondo et al., 2007; Weber et al., 2007). In the samples collected at the four sampling sites, the WSOC/OC ratio was on average of 0.30, ranging from 0.11 to 0.67. The differences in the WSOC/OC ratios (Table 4) indicate that the chemical compositions and characteristics of OC greatly varied between the sites. Therefore, an increase in WSOC/OC ratios suggests the aging, chemically processed aerosols and/or possible contribution from the SOA. The primary emissions or/and secondary formation (e.g., gas to particle conversion and photochemical oxidation) were dominant in the PRD area during the sampling periods. The highest WSOC/OC ratio was seen at ZQ with an average of 0.41, suggesting that the OC was more oxidized in the atmosphere at the semi-rural site. Primary OC is mostly water-insoluble (Miyazaki et al., 2006) so the lowest WSOC/OC was found at the roadside site PU. Conversely, secondary OC formation predominated during the transport of pollutants to ZQ and GZ. This caused the WSOC fraction to have a higher contribution in OC at ZQ and GZ than that at PU and HT. We compared the WSOC/OC ratios with other worldwide cities (Table 5). The ratio at ZQ was comparable to urban background sites in Europe (Barcelona and Ghent) and other rural/sub-urban areas in China. The results provide clear evidence that the WSOC is an important component of OC in China.

Seasonal variations of WSOC/OC ratios can also be seen in Table 2. The ratios were higher in autumn/winter than in spring/summer. However, the seasonal variation was again absent from PU, where a strong but relatively constant vehicular emission source influences the roadside site throughout the year. We also found that the WSOC/OC ratios tended to increase while the WSOC concentrations were elevated, indicating that WSOC typically dominates the increase of OC in $PM_{2.5}$, especially in autumn/winter. Sullivan et al. (2004) reported that the WSOC/OC ratios of 0.61–0.64 in summer and 0.31 in autumn at an urban site increase under high photochemical activity conditions in summer. In this study, the WSOC/OC ratio increased in autumn, when the photochemical reactions are the most active in the PRD region. This can be attributed to aging and atmospheric processing of the organic compounds during their transportation, or to formation of SOA. In the PRD region, lower ozone (O_3) concentrations are generally observed in summer, while high O_3 levels occur in autumn due to the unique meteorological conditions (Zheng et al., 2010). In autumn, the high frequency of surface high pressure ridges and tropical cyclones, as well as the occurrence of a sea–land breeze from the estuary of the Pearl River lead to reduced wind speeds that favor the formation and build-up of O_3. The O_3 concentrations are thus elevated in the fall season (Fan et al., 2008). In hot summers, the prevailing south or south-west monsoon brings clean oceanic air

Table 3
Correlation coefficients between OC and EC, and SOC and WSOC.

Species	Correlations	GZ	ZQ	PU	HT
OC–EC	Pearson correlation (r)	0.90[a]	0.85[a]	0.35 [b]	0.92[a]
	Sig. (2-tailed) (p)	0.000 ($p<0.01$)	0.000 ($p<0.01$)	0.012 ($p<0.05$)	0.000 ($p<0.01$)
	Number of samples	52	52	52	52
SOC–WSOC	Pearson correlation(r)	0.57[a]	0.74[a]	-	0.84[a]
	Sig. (2-tailed) (p)	0.000 ($p<0.01$)	0.000 ($p<0.01$)	-	0.000 ($p<0.01$)
	Number of samples	52	52	-	52

[a] Correlation is significant at the 0.01 level (2-tailed).
[b] Correlation is significant at the 0.05 level (2-tailed).

Table 4
Average WSOC/OC ratios in the PRD region in the four seasons.

Seasons	Sampling sites			
	GZ	ZQ	PU	HT
Spring	24%	35%	22%	23%
Summer	27%	39%	18%	27%
Autumn	38%	49%	26%	34%
Winter	28%	43%	20%	34%
Annual average	28%	41%	21%	29%

Table 5
Comparisons of OC, EC, WSOC and WSOC/OC ratio with other cities from other studies.

Nation/region	City	Site	Site type	Sampling period	n	OC	EC	WSOC	WSOC/OC	Reference
PRD region, China	Guangzhou	GZ	Urban	2006–2007 (winter)	13	8.53	4.81	2.39	0.28	This study
				2006–2007 (summer)	13	5.97	3.46	1.60	0.27	
				Annual average	52	7.07	4.01	2.03	0.28	
	Zhaoqing	ZQ	Semi-rural	2006–2007 (winter)	13	10.2	4.55	4.00	0.43	
				2006–2007 (summer)	13	6.31	2.91	2.43	0.39	
				Annual average	52	8.15	3.82	3.26	0.41	
	Hong Kong	PU	Roadside	2006–2007 (winter)	13	11.6	13.7	2.53	0.20	
				2006–2007 (summer)	13	6.53	15.3	1.19	0.18	
				Annual average	52	7.94	13.45	1.79	0.21	
		HT	Background	2006–2007 (winter)	13	6.23	2.78	2.13	0.34	
				2006–2007 (summer)	13	2.20	1.01	0.66	0.27	
				Annual average	52	4.1	1.79	1.31	0.29	
	Hong Kong	PU	Roadside	2000–2001(winter)	26	11.2	6.4	3.5	0.31	Ho et al., 2006
				2000–2001(summer)	10	10.2	5.9	2.1	0.21	
				Annual average	36	10.7	6.15	2.8	0.26	
		KT	Mixing	2000–2001(winter)	22	8.8	4.8	3.4	0.39	
				2000–2001(summer)	22	5.9	4.5	2.1	0.36	
				Annual average	44	7.4	4.7	2.8	0.37	
		HT	Background	2000–2001(winter)	10	5.5	1.4	2.8	0.51	
				2000–2001 (summer)	10	1.5	0.4	1.0	0.67	
				Annual average	20	3.5	0.9	1.9	0.54	
	Guangzhou	WS	Urban	2004 (summer)		17.5	5.7		3.1	Duan et al., 2007
				2005 (winter)		23.9	4.4		5.0	
		LW	Urban	2004 (summer)		17.5	5.1		3.5	
				2005 (winter)		23.8	4.0		5.8	
	Hong Kong	YL	Urban	2004 (summer)		11.3	4.3		2.6	
				2005 (winter)		13.4	2.3		6.4	
		TW	Urban	2004 (summer)		11.7	4.5		2.7	
				2005 (winter)		11.4	2.6		4.9	
		HT	Background	2004 (summer)		5.6	1.4		3.8	
				2005 (winter)		5.9	0.8		7.2	
	Hong Kong	HT	Background	2000–2001	50	4.2	1.7			So et al., 2007
				2004–2005	50	4.3	2.1			
		TW	Mixing	2000–2001	50	8.7	5.4			
				2004–2005	50	7.4	6.0			
		MK	Roadside	2000–2001	50	16.7	20.2			
				2004–2005	50	11.9	13.7			
	Guangzhou	LG	Sub-urban	2003 (summer)	7	11.9	6.4	5.1	0.43	Feng et al., 2006
				2002 (winter)	7	33.2	6.6	9.6	0.29	
				Annual average	14	22.6	6.5	7.4	0.36	
		TH	Mixing	2003 (summer)	7	10.5	6.1	4.6	0.44	
				2002 (winter)	7	26.2	6.7	7.5	0.29	
				Annual average	14	18.4	6.4	6.1	0.36	
Beijing-Tianjin-Tangshan Region, China	Beijing	AES	Sub-urban	2002 (summer)	7	17.6	5.5	5.5	0.31	Feng et al., 2006
				2002 (winter)	7	33.6	5.7	7.5	0.22	
				Annual average	14	25.6	5.6	6.5	0.27	
		PKU	Mixing	2002 (summer)	7	17.6	5.7	5.7	0.32	
				2002 (winter)	7	25.2	5.7	6.6	0.26	
				Annual average	14	21.4	5.7	6.2	0.29	
	Beijing	BNU	Traffic	2002–2003(summer)	20	11.5	5.2		0.16	Sun et al., 2004
				2002–2003(winter)	20	33.2	11		0.38	
				Annual average	40	22.4	8.1		0.27	
		CS	Industrial	2002–2003(summer)	22	9.3	6.6		0.15	
				2002–2003(winter)	20	36.3	9.8		0.49	
				Annual average	42	22.8	8.2		0.32	
		YH	Residential	2002–2003(summer)	21	11.2	5.9		0.13	
				2002–2003(winter)	20	37.5	21.9		0.38	
				Annual average	41	24.4	13.9		0.25	
Yangtze River Delta, China	Shanghai	SHO		2003 (summer)	7	4.9	2.1	2.2	0.45	Feng et al., 2006
				2002 (winter)	7	16.5	3.6	6.7	0.41	
				Annual average	14	10.7	2.9	4.5	0.43	
		FDU		2003 (summer)	7	3.9	1.8	1.5	0.38	
				2002 (winter)	7	15.8	4.0	5.9	0.37	
				Annual average	14	9.9	2.9	3.7	0.38	
Netherlands	Amsterdam			2005 (summer)	30	3.9	1.9	1.0	0.26	Viana et al., 2007
				2006 (winter)	30	6.7	1.7	1.9	0.28	
Spain	Barcelona			2004 (summer)	30	3.6	1.5	1.6	0.44	
				2004 (winter)	30	6.9	2.6	2.1	0.30	
Belgium	Ghent			2004 (summer)	30	2.7	0.8	1.0	0.37	
				2005 (winter)	30	5.4	1.2	2.3	0.43	

and rainy conditions alleviate the pollutant levels, resulting in decreases of O_3 concentration. Such O_3 variations can affect the SOA formation as well as the WSOC fraction in OC.

3.3. Relationship between WSOC and other components

WSOC can be produced in the atmosphere by photochemical chain reactions of primary emitted organic pollutants as well as their oxidation products (Kawamura et al., 1996; Kawamura and Sakaguchi, 1999); however, their formation mechanisms are poorly understood. The correlation coefficients of WSOC with other species were examined for the samples collected at the four sites. Fig. 3 shows that the WSOC had a positive correlation with EC (used as an inert tracer of incomplete combustion) at GZ, ZQ, and HT ($p<0.01$). Fuel combustion as well as biomass burning is the main sources of EC. The strong correlation between EC and WSOC was a result of the conversion of hydrocarbons in OC, which are WSOC precursors and mainly produced by combustion processes in the local or regional areas. Moreover, higher correlations were observed in winter than in summer (except in ZQ) suggesting that as with the OC, primary combustion emissions contributed significantly to the abundance of the WSOC observed in winter than in summer. The low EC/WSOC correlation at PU (highly trafficked site) indicates that most of WSOC concentrations are not driven by local primary vehicular emissions but they probably have a dominant regional origin.

The relative percentages of WSOC, water-insoluble OC (WIOC = OC–WSOC), and EC in TC are presented in the ternary diagrams (Fig. 4). The percentages of WSOC in TC were similar at GZ (8–37%) and HT (7–38%) while the PU showed the smallest WSOC contribution (3%–18%). In contrast, the samples collected at ZQ had the largest WSOC fraction in TC (7–51%), indicating that WSOC was the primary component of TC at ZQ. The results are consistent with the notion that regional-scale sites are mostly impacted by the aged aerosols. Salma et al. (2001) showed that the mass fraction of WSOC increased from a tunnel to a background area. Meanwhile, the EC concentration was reduced during transport to the background site because of air dilution. This explains why larger fractions of the WSOC in OC were found at ZQ and HT and why the WSOC only accounted for about one quarter of OC at PU. Moreover, the ratio of WSOC to EC can be used as an indicator for aerosol age. The average WSOC/EC ratios at the urban GZ site were 0.22–1.20, which were within the range reported in our previous study in the PRD region (Ho et al., 2006). The average WSOC/EC ratios at PU ranged from 0.04 to 0.32, which were close to the ratio (0.32) measured at a high-traffic roadside site in Paris, France (Ruellan and Cachier, 2000). However, the average WSOC/EC ratios at ZQ were higher than those at the other three sites (0.25–2.07), showing that the aerosols were older in the semi-rural site.

Meteorological parameters, such as wind speed, wind direction and weather patterns, can influence the levels of particulate air pollution at a receptor site. However, in this study, poor correlations were observed between WSOC and meteorological parameters (e.g.: wind spend, temperature and relative humidity), suggesting that the local meteorological parameters could not be a factor in determining the levels of WSOC measured during both in summer and winter.

3.4. Estimation of secondary organic aerosols formation

In order to understand the nature of the WSOC in the samples collected in the PRD region, the secondary organic

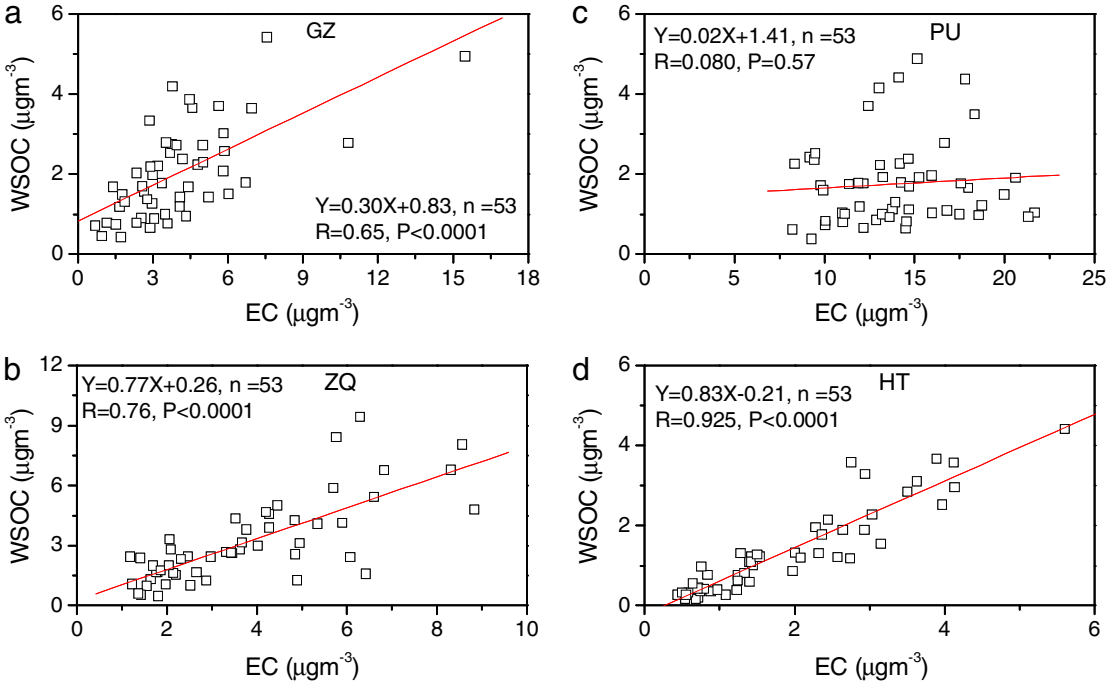

Fig. 3. Correlation plots between WSOC and EC in the PRD region (a: GZ; b: ZQ; c: PU; d: HT).

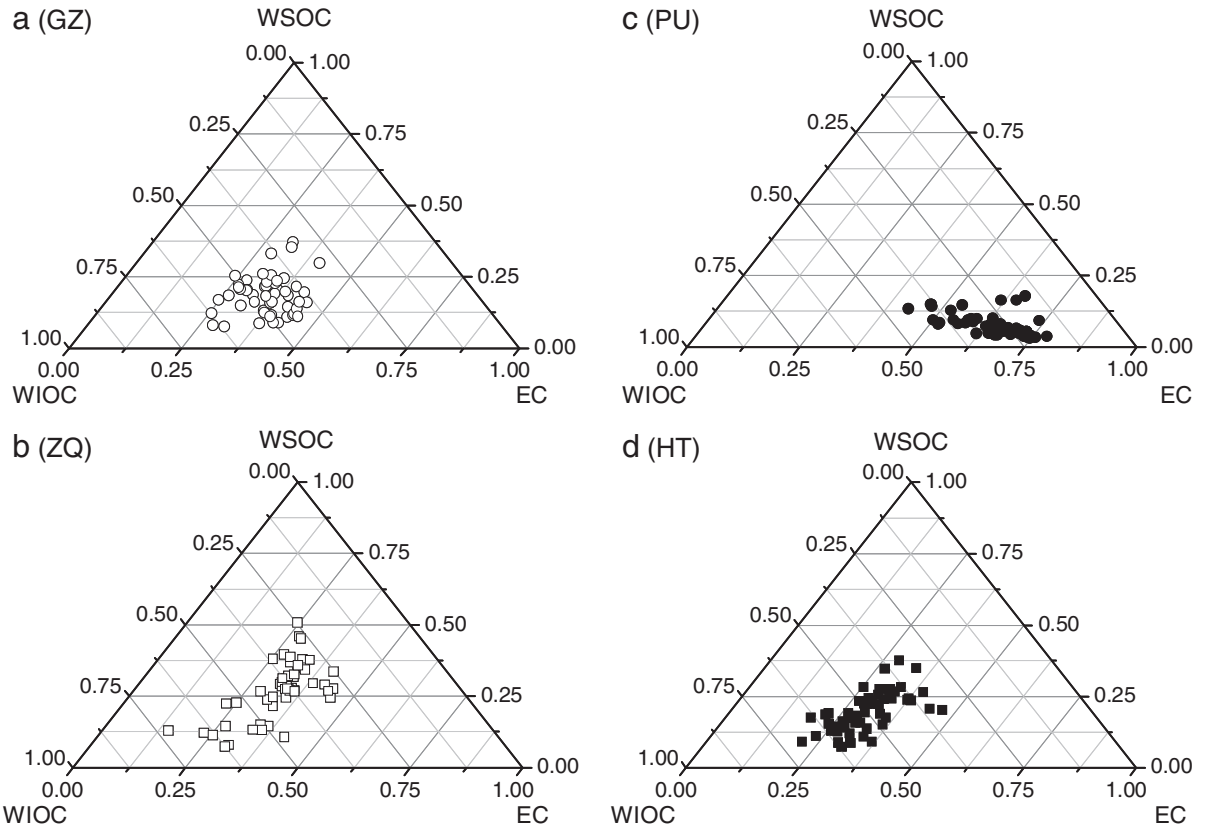

Fig. 4. Ternary diagrams showing correlation between EC, WSOC and WIOC in the PRD region (a: GZ; b: ZQ; c: PU; d: HT).

carbon (SOC) formation was estimated with the EC-tracer method and compared with the observed WSOC concentrations, based on the following equation (Cao et al., 2003):

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

where OC_{tot} is the total OC (TOC) and $(OC/EC)_{min}$ is the minimum observed value of the ratio. Particulate OC/EC ratios exceeding 2.0 were used to identify significant SOA formation. In this study, the average OC/EC ratios were 2.0, 2.2, 0.6 and 2.4 at GZ, ZQ, PU and HT, respectively. The average OC/EC ratio at PU was much lower than 2.0, suggesting that primary vehicle exhaust is the dominant source for carbonaceous aerosols at the roadside area. Moreover, HT is affected by meteorological condition and long-range transported aerosol significantly, it is not proper to calculate the contribution of SOA employing the equation (Duan et al., 2007). Estimates of SOC were thus only made for the sites GZ, ZQ and HT. Following the assumptions adopted and discussed in Castro et al. (1999), the SOC concentrations and their contributions in OC are given in Table 6. Average annual SOC concentrations in $PM_{2.5}$ were estimated as 2.2 and 3.5 μg m^{-3} at GZ and ZQ, comprising 33.5% and 42.8% of the corresponding OC concentrations, respectively. The results indicate that SOC formation is significant in the PRD region.

Seasonal variations of the SOC concentrations and SOC/OC ratios were found (Table 6). The concentrations of SOA in autumn/winter were generally higher than in spring/summer. It is likely that the high SOC concentrations in autumn/winter are due to the regional long-range transport of pollutants from southern China when the air mass mainly came from the north. Lower SOC concentrations were found in spring/summer because the polluted emission sources were diluted by marine air masses transported from the South China Sea. The contributions of SOC in OC in summer were similar to those in autumn/winter, being consistent with enhanced secondary pollutant production during warmer weather with high photochemical activity. Good correlations were obtained between the WSOC and the estimated SOC ($r = 0.57$ in GZ and $r = 0.64$ in ZQ) (Table 3). The results suggest that the WSOC and the SOA have the same origin in the PRD region. The primary insoluble organics were oxidized during the

Table 6
OC/EC ratio, estimated SOC and its contribution to OC in the PRD region in the four seasons.

Season	GZ			ZQ		
	OC/EC	SOC (μg m^{-3})	SOC/OC	OC/EC	SOC (μg m^{-3})	SOC /OC
Spring	1.8	1.6	29.7%	2.0	2.1	34.3%
Summer	2.0	1.8	32.4%	2.2	2.5	44.3%
Autumn	2.0	2.9	38.0%	2.2	4.5	43.5%
Winter	2.0	2.7	34.5%	2.3	4.6	45.3%
Annual average	2.0	2.2	33.5%	2.2	3.5	42.8%

photochemical oxidation and carried active functional groups that increase their water solubility.

4. Summary and conclusions

This work presents regional-scale measurements of atmospheric OC, EC and WSOC at four sites in the PRD region. The OC concentrations in $PM_{2.5}$ ranked in the ascending order HT<GZ<PU≈ZQ while the EC concentrations ranked in the order HT<ZQ≈GZ<PU.

The study of WSOC is one method for investigating SOA as the production of secondary organic aerosol (SOA), via the photochemical oxidation of precursor organic compounds, leads to the formation of water-soluble organic compounds. The highest average WSOC concentration was measured at the semi-rural ZQ site, while the lowest was measured at the background location HT. The percentages of WSOC in TC were similar at GZ (8–37%) and HT (7–38%) while PU showed the smallest WSOC contribution (3–18%). The samples collected at ZQ had the largest WSOC fraction in TC (7–51%). The results are consistent with the notion that regional-scale sites are mostly impacted by older aerosols. Good correlations were obtained between WSOC and the estimated SOC ($r = 0.57$ in GZ, $r = 0.64$ in ZQ and $r = 0.84$ in HT), which further suggest that WSOC can be used as an indicator for SOA in the PRD region. The primary insoluble organics were oxidized during photochemical oxidation and formed active functional groups that increase their water solubility. In comparison to other worldwide cities, the WSOC/OC ratio at ZQ was comparable to urban background sites in Europe (Barcelona and Ghent) and other rural/sub-urban areas in China. The results provide clear evidence that the WSOC is an important component of OC in China.

Moreover, average annual SOC concentrations in $PM_{2.5}$ were estimated to be 34% and 43% of the corresponding OC concentrations at the regional sites of GZ and ZQ, respectively. This indicates that SOC formation is significant in the PRD region.

Acknowledgements

This study is in part supported by the Chinese Academy of Sciences (KZCX2-YW-BR-10), and supported by an open fund of the State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, CAS (SKLLQG0808 and SKLLQG0902).

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