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Spatial and seasonal variations of atmospheric organic carbon and elemental carbon in Pearl River Delta Region, China

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Abstract

The concentrations of organic carbon (OC) and elemental carbon (EC) in atmospheric particles were investigated at eight sites in four cities (Hong Kong, Guangzhou, Shenzhen and Zhuhai) of the Pearl River Delta Region (PRDR), China, during winter and summer 2002. The comparison of summer and winter results was made in order to investigate spatial and seasonal variations. $PM_{2.5}$ and PM_{10} samples were collected on pre-fired quartz filters with mini-volume samplers and analyzed by the thermal optical reflectance (TOR) method following the Interagency Monitoring of PROtected Visual Environments (IMPROVE) protocol. During summer, the average OC and EC concentrations in $PM_{2.5}$ were 9.2 and 4.1 $\mu g\,m^{-3}$, while those in PM_{10} were 12.3 and 5.2 $\mu g\,m^{-3}$. Carbonaceous aerosol accounted for 38.0% of the $PM_{2.5}$ and 32.9% of the PM_{10}. The daily average OC, EC, $PM_{2.5}$ and PM_{10} concentrations in PRDR were higher in winter than in summer. The average OC/EC ratio was 2.5 for $PM_{2.5}$ and PM_{10}, suggesting the presence of secondary organic aerosols. The estimated secondary organic carbons in $PM_{2.5}$ and PM_{10} were 4.1 and 5.6 $\mu g\,m^{-3}$, respectively. The OC and EC were found to be correlated in winter (correlation coefficient $r = 0.82$) and summer ($r = 0.64$), which implied that motor vehicle sources contributed to the ambient carbonaceous particles. The distribution of eight carbon fractions in OC and EC at eight sites was first reported in ambient samples in Asia, which also indicated that motor vehicle exhaust was the dominant contributor to carbonaceous particles.

Keywords: Organic carbon; Elemental carbon; Urban aerosol; Pearl River Delta Region

1. Introduction

Atmospheric particulates are one of the main air pollutants in urban areas. Particulate matter (PM) is considered to be a health hazard since it can be absorbed into human lung tissue during breathing. Previous study has demonstrated that urban and industrial air pollution could inhibit precipitation from clouds (Rosenfeld, 2002). Therefore, much research has focused on the chemical composition of atmospheric suspended PM. Carbonaceous particles, usually classified into two categories—organic carbon (OC) and elemental carbon (EC)—are the most important constituents of the fine fraction of PM, especially in highly industrialized and urbanized areas (Nunes and Pio, 1993). OC represents a large variety of organic compounds that can be classified

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into general compound classes such as aliphatic, aromatic compounds, acids, etc. EC is actually a mixture of graphite-like particles and light-absorbing organic matter. Moreover, the surface of EC particles contains numerous adsorption sites that are capable of enhancing catalytic processes. As the result of its catalytic properties, EC may intervene in some important chemical reactions involving atmospheric sulfur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3) and other gaseous compounds (Gundel et al., 1989). Carbonaceous species in particles also play an important role in global climate change by affecting radiative forcing (Jacobson, 2001). Despite the evident significances of OC and EC in air chemistry and physics, information concerning their spatial and temporal variabilities is still quite limited.

Atmospheric OC and EC concentrations in large Chinese cities have increased in recent decades with rapid economic growth. Therefore, the OC and EC measurements become more important when considering personal exposure, local environmental effects, and effects on regional and global scales, such as radiative forcing effect. The Pearl River Delta Region (PRDR), including Hong Kong and Macao, is one of the fastest growing regions in China. It has a total land area of 42,794 km^2 with a population of over 38 million. The PRDR is situated in a transitional zone of the East Asian monsoon system, where the southwesterly summer monsoon comes from the oceans (South China Sea and tropical Pacific), while the northeasterly winter monsoon comes from Mainland China. The region has humid subtropical weather with an annual average temperature of 22°C and rainfall of 1690 mm. Astonishing growth in industrialization and urbanization in the region has resulted in the excessive release of pollutants into the air. PM levels have increased in the last few years due to the increases in motor vehicles, urban construction, heating installation and industrial combustion. Atmospheric haze is common in the region. Visible plumes from industrial stacks, diesel trucks, two-stroke motorcycles, smoke-belching cars, coal-burning, fire-places and stoves reveal many of the sources that cause regional haze (Chow et al., 2002; Watson 2002a, b). For example, the annual emissions of PM_{10}, NO_x, and SO_2 were as high as 258, 564 and 596 kt, respectively, in 1997 in PRDR (Hong Kong Environmental Protection Department, 2002). The increase in traffic is particularly compelling. The amount of motor vehicles increased from 36,000 to 584,000 from 1980 to 1996 in the urban area of Guangzhou, Guangdong Province. There are more than 2.5 million motor vehicles in the PRDR. Previous study has also observed that the traffic-related emissions contribute to airborne OC and EC (Ho et al., 2002; Cao et al., 2003).

The PRDR is one of the first regions of China to experience massive industrialization and urbanization in recent years, so a study of $PM_{2.5}$ and PM_{10} in PRDR could provide valuable and insightful information for other regions. Moreover, the findings may also be useful in the formulation of strategic air pollution control in China and other rapidly developing countries. The chemical composition of PM may vary within a broad range, according to the sources of the particles and the conditions of their dispersion. To understand anthropogenic air pollutant sources, loading, and their fate in the region, it is important to measure carbonaceous species in particles at both the polluted and background areas for different seasons and compare their characteristics. A sampling campaign was conducted in the winter, and preliminary results were presented in Cao et al. (2003). Thus, this present study, consecutive monitoring from June to July 2002 was performed at the same eight sampling sites in four cities of the region for comparison. This paper is a continuation of the previous publication (Cao et al., 2003), and the winter dataset will be included in the paper on the present discussions and conclusions. Therefore, the primary objectives of the paper are: (1) to examine spatial variations of $PM_{2.5}$, and PM_{10} carbon (OC, EC) concentrations during summer, and (2) to quantify the spatial and seasonal variations (summer versus winter) of OC and EC in $PM_{2.5}$ and PM_{10} in eight locations.

2. Methodology

2.1. PM sampling

Both the sites and sampling methodology were identical to the prior study and have been described in detail (Cao et al., 2003). In brief, eight sites were selected in the four cities including three sites in Hong Kong (The Hong Kong Polytechnic University—PU, Baptist University—BU, Hok Tusi—HT), three sites in Guangzhou (Zhongshan University—ZU, Huangpu—HP, Longgui—LG), one site in Shenzhen (Luohu—LH) and one site in Zhuhai (Xiangzhou—XZ). Among these eight sites, PU is a roadside site, BU, ZU, LH and XZ are urban sites, HP is an industrial site, HT and LG are background sites. Samples of $PM_{2.5}$ and PM_{10} were collected from June to July 2002. $PM_{2.5}$ and PM_{10} samples were collected using mini volume (mini-vol.) samplers (Airmetrics, USA), operated at flow rates of 5 $l\,min^{-1}$, equipped with 47 mm Whatman quartz microfiber filters (QM/A) (Cao et al., 2003). $PM_{2.5}$ impactor and PM_{10} impactor were installed on top of the preseparator assemblies to collect every 24 h PM samples simultaneously at eight sites.

2.2. Thermal/optical carbon analysis

The samples were analyzed for OC and EC using DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). A 0.5 cm^2

punch from the remaining half-filter was analyzed for eight carbon fractions following the IMPROVE TOR protocol (Chow et al., 1993a, 2001; Fung et al., 2002). This produced four OC fractions (OC1, OC2, OC3, and OC4 at 120°C, 250°C, 450°C, and 550°C, respectively, in a helium atmosphere), a pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen 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% oxygen/98% helium atmosphere). IMPROVE OC is operationally defined as OC1 + OC2 + OC3 + OC4 + OP and EC is defined as EC1 + EC2 + EC3-OP. An inter-laboratory comparison of IMPROVE with the DRI Model 2001 instrument with the (thermal manganese dioxide oxidation) TMO methods (done by AtmAA, Inc., in Calabasas, CA) has shown good (the difference was smaller than 5% for Total Carbon [TC] and 10% for OC and EC) (Fung et al., 2002). Twelve blank filters were also analyzed and the sample results were corrected by the average of the blank concentrations, which were 1.83 and 0.58 $\mu g\,m^{-3}$ for OC and EC, respectively. Particular quality assurance/quality control (QA/QC) procedures were described in Cao et al. (2003).

3. Results and discussion

3.1. The concentrations of OC and EC and their spatial and seasonal characterizations

The statistics for OC and EC concentrations at eight sampling sites in summer are shown in Table 1, and spatial and seasonal distributions of OC/EC are illustrated in Fig. 1. EC, which has a chemical structure similar to impure graphite, originates primarily from direct emissions of particles, predominantly during combustion. OC, from primary anthropogenic sources and from formation by chemical reactions in the atmosphere, rendered the concentrations of OC higher than EC at eight sampling sites. The average OC and EC concentrations in $PM_{2.5}$ for the PRDR were 9.2 ± 6.5 and $4.1 \pm 2.7\,\mu g\,m^{-3}$ for the summer period, respectively. The majority of carbonaceous aerosol was in the $PM_{2.5}$ fraction. Among these eight sites, average OC and EC at HP (Guangzhou) had the highest concentrations, which is attributable to the mixed contribution of high traffic flows and industrial emissions. The lowest OC and EC concentrations were found at HT (the background site in Hong Kong) because it is located upwind of the anthropogenic emission sources. In contrast, $PM_{2.5}$ OC and EC concentrations at the LG background site in Guangzhou were 5–8 times those at HT. The OC and EC concentrations at an urban site (ZU) in Guangzhou were around 1–3 times higher than those at other urban sites in the three cities (BU, LH, and XZ), implying carbonaceous pollution in Guangzhou.

OC concentrations in $PM_{2.5}$ and PM_{10} ranked in the order of Hong Kong < Zhuhai < Shenzhen < Guangzhou, but EC concentrations were in the order of Zhuhai < Hong Kong < Shenzhen < Guangzhou (Fig. 1). The average OC concentration at Guangzhou is 2 times that of Shenzhen, and 3 times that of Zhuhai and Hong Kong. Qi et al. (2000) observed similar patterns from the spatial distribution of one of the major group of OC species in PRDR. The concentrations of polycyclic aromatic hydrocarbons (PAHs) in organic

Table 1
Average of the concentrations of OC and EC at eight sites during the summer in PRDR, China[a]

City	State	OC ($\mu g\,m^{-3}$)		EC ($\mu g\,m^{-3}$)		OC/EC	
		$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}
Hong Kong	PU	6.3 ± 2.3	7.4 ± 2.9	3.9 ± 1.6	4.7 ± 2.1	1.7	1.6
	BU	5.6 ± 0.8	6.7 ± 1.1	3.2 ± 0.4	3.9 ± 0.5	1.8	1.7
	HT	3.4 ± 0.3	4.1 ± 0.6	0.7 ± 0.1	1.1 ± 0.1	4.7	3.8
	Average	5.3 ± 2.1	6.3 ± 2.5	3.2 ± 2.6	3.9 ± 2.9	1.9	1.8
Guangzhou	HP	20.0 ± 2.8	28.5 ± 5.2	7.9 ± 1.1	10.5 ± 1.9	2.5	2.7
	ZU	13.1 ± 3.9	17.8 ± 6.9	4.6 ± 1.2	5.9 ± 1.8	2.8	3.0
	LG	17.0 ± 10.6	24.7 ± 18.9	6.5 ± 2.5	8.8 ± 4.0	2.6	2.8
	Average	15.8 ± 6.4	22.2 ± 11.2	5.9 ± 2.1	7.8 ± 3.1	2.7	2.9
Shenzhen	LH	7.6 ± 4.9	10.4 ± 6.5	4.2 ± 3.1	5.0 ± 3.5	1.8	2.1
Zhuhai	XZ	5.4 ± 3.4	6.9 ± 4.3	1.9 ± 0.9	2.5 ± 1.0	2.9	2.7
PRDR	Average	9.2 ± 6.5	12.3 ± 10.1	4.1 ± 2.7	5.2 ± 3.4	2.5	2.5

[a] Values represent average ± standard deviation.

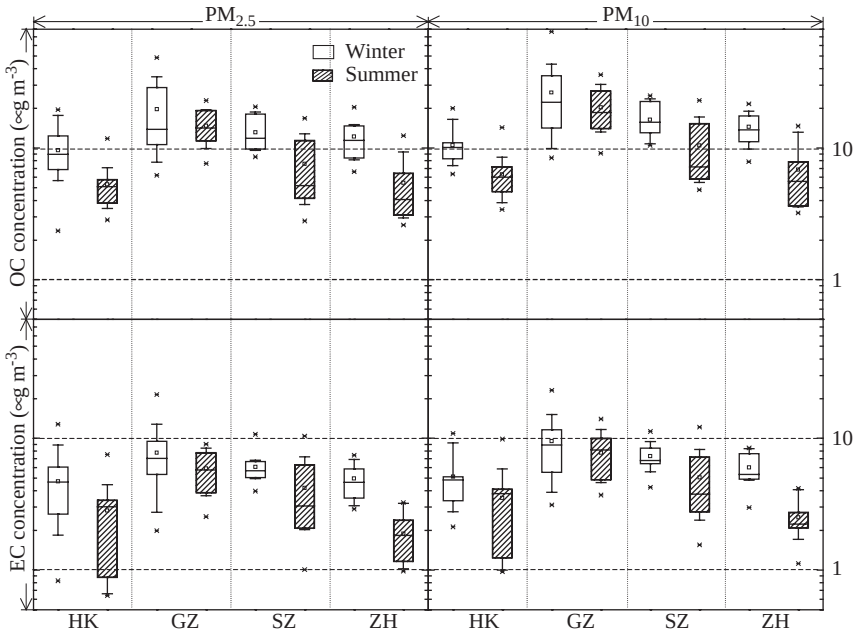

Fig. 1. Box plots of OC and EC concentrations ($\mu g\,m^{-3}$) in $PM_{2.5}$ and PM_{10} samples during winter and summer in four cities in PRDR.

aerosol at Guangzhou were 55.5 $ng\,m^{-3}$, which were twofold higher than those at Zhuhai (25.6 $ng\,m^{-3}$), threefold higher than Shenzhen (18.0 $ng\,m^{-3}$), and Hong Kong (14.8 $ng\,m^{-3}$). The population of Guangzhou is more than 15 million people, and Guangzhou is the largest light industrial production base in China, so the anthropogenic carbon-containing pollutant emissions from motor vehicle exhaust, industrial plumes, and residential cooking are highest among these four cities. Considering that the EC fraction of the aerosol mass is emitted mostly by motor vehicles sources (Watson et al., 1994), the levels of ambient EC coincided with the number of vehicles in the four cities, i.e., Zhuhai (0.2 million) < Hong Kong (0.5 million) < Shenzhen (0.7 million) < Guangzhou (1.1 million).

The concentrations of OC and EC had a summer minimum and a winter maximum at all the cities (Fig. 1). Comparing the summer results with those obtained at the same sampling sites during the winter shows that the average $PM_{2.5}$ and PM_{10} OC and EC concentrations during the winter were around 1.5 times higher than during summer in PRDR. Lower summer concentrations may be due to enhanced thermal convection during summer, which can be attributed to the influence of the Asian monsoon. The southwesterly summer monsoon brings cleaner oceanic aerosols from the oceans (South China Sea and tropical Pacific), while the northeasterly winter monsoon brings polluted air masses from Mainland China. In addition, both the increased emissions and the occurrence of stable atmospheric conditions during winter may also lead to the high carbon concentrations.

Seasonal differences in OC and EC concentrations were tested by the one-way analysis of variance (ANOVA) method, using the statistical software package SPSS v 10.0, and the results are shown in Table 2. Significant ($p<0.05$) seasonal variabilities of OC and EC at the rural HT and urban XZ sites in F-ratio and p-value were not statistically different (i.e., possibly reflecting that OC and EC source emission rates, such as vehicle exhaust, were consistent). The OC and EC levels were around 2 times those in winter higher than in summer at the background HT site. Dispersion and long-range transfer of air parcels from northeasterly polluted areas contribute to high concentrations in winter. Lower carbon concentrations at the XZ site in Zhuhai were probably because of the frequent rainy days during summer. No seasonal variations of OC and EC were found at the other six sites.

The seasonal distributions of OC and EC in this study are compared with those in other Asian cities in Fig. 2. All the OC concentrations in the winter were consistently higher than those in the summer for all the cities. Almost all the EC concentrations in the winter were higher than those in the summer, except in Seoul, South Korea. The OC and EC concentrations in PRDR were comparable to those at other Asian cities. During summer, the OC levels in these cities in decreasing order were Guangzhou (15.8 $\mu g\,m^{-3}$), Beijing (13.4 $\mu g\,m^{-3}$) (He et al., 2001), Shanghai (11.4 $\mu g\,m^{-3}$) (Ye et al.,

Table 2
One-way ANOVA for OC and EC on seasonal variables for each sampling site

	OC		EC	
	F-ratio	*p*-Value	*F*-ratio	*p*-Value
PU	2.77	0.12	2.21	0.16
BU	1.20	0.30	0.40	0.55
HT	7.87	<0.05	10.52	<0.05
HP	0.20	0.67	1.11	0.32
ZU	1.85	0.19	1.561	0.23
LG	1.10	0.33	1.232	0.30
LH	0.22	0.65	0.32	0.58
XZ	13.47	<0.05	24.42	<0.05

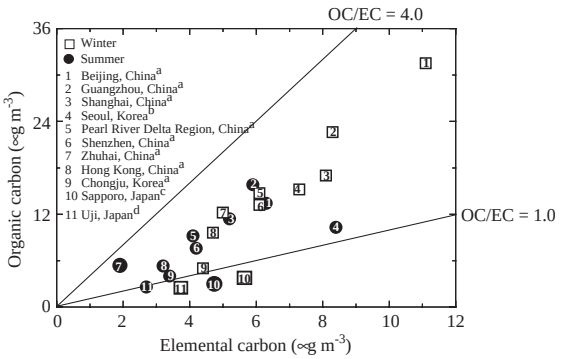

Fig. 2. Average $PM_{2.5}$ OC vs. average $PM_{2.5}$ EC in winter and summer for different urban areas in Asia. Measurement method: (a) TOR; (b) TMO; (c) Combustion method (at 300°C and 850°C); (d) Ambient Carbon Particulate Monitor (R&P, Series 5400).

2003), Seoul (10.3 μg m^{-3}) (Park et al., 2001), Shenzhen (7.6 μg m^{-3}), Zhuhai (5.4 μg m^{-3}), Hong Kong (5.3 μg m^{-3}), Chongju (4.0 μg m^{-3}) (Lee and Kang, 2001), Sapporo (3.1 μg m^{-3}) (Ohta et al., 1998), and Uji (2.6 μg m^{-3}) (Holler et al., 2002). The EC levels were in a different order: Seoul (8.4 μg m^{-3}), Beijing (6.3 μg m^{-3}), Guangzhou (5.9 μg m^{-3}), Shanghai (5.2 μg m^{-3}), Sapporo (4.7 μg m^{-3}), Shenzhen (4.2 μg m^{-3}), Chongju (3.4 μg m^{-3}), Hong Kong (3.2 μg m^{-3}), Uji (2.7 μg m^{-3}), and Zhuhai (1.9 μg m^{-3}). Compared to other cities in Asia, Guangzhou has the highest OC level and the third-highest EC level, pointing to the presence of carbonaceous pollution in the urban environment.

3.2. Contributions to $PM_{2.5}$ and PM_{10} mass

A summary of monitoring results is shown in Table 3. The average 24 h $PM_{2.5}$ mass concentrations at the eight sites were 49.1 ± 30.6 μg m^{-3} during summer, with the highest level (101.7 ± 11.4 μg m^{-3}) found at HP in Guangzhou and the lowest (15.8 ± 2.4 μg m^{-3}) found at the background HT site. Among all the sites, the $PM_{2.5}$ and PM_{10} mass concentrations in the winter were at higher levels than those in the summer. Among these four cities, Hong Kong had the lowest $PM_{2.5}$ levels for both seasons (31.0 ± 16.9 μg m^{-3} in summer and 54.5 ± 22.9 μg m^{-3} in winter), whereas Guangzhou had the highest $PM_{2.5}$ mass (78.1 ± 29.7 μg m^{-3} in summer and 105.9 ± 71.4 μg m^{-3} in winter). The average 24 h PM_{10} concentrations were 74.6 ± 51.2 μg m^{-3} in PRDR for the summer and 111.5 ± 83.5 μg m^{-3} during winter. The annual average PM_{10} concentrations for Hong Kong, Guangzhou, Shenzhen, and Zhuhai cities were 57.5, 143.2, 79.4 and 64.1 μg m^{-3}, respectively. In reference to Class 2 of the Chinese PM_{10} standard (100 μg m^{-3}), Guangzhou has particulate pollution, which is due to various emission sources, and the other 3 cities have levels obeying the legislation. The ratios of average 24 h $PM_{2.5}$ to PM_{10} concentrations varied among the eight sites, ranging from 50.3% to 83.0%, with an average of 68.7% during the summer, which is similar to that of the winter (70.4%). These results illustrated that PM tends to be present in the fine particle fraction in PRDR, with an average $PM_{2.5}$ to PM coarse ($PM_{2.5}$ minus PM_{10}) ratio of ~2.2. Therefore, to control fine particle pollution is a priority for air quality management in PRDR.

The amount of organic matter in the urban atmosphere was estimated by multiplying the amount of organic carbon by 1.6 according to Turpin and Lim (2001). Total carbonaceous aerosol (TCA) was calculated by the sum of organic matter and elemental carbon. At the eight sampling sites, TCA contributed more than one-third of the $PM_{2.5}$ and PM_{10} mass for both seasons in PRDR and accounted for an average of 38.0% of $PM_{2.5}$ mass and 32.9% of PM_{10} during the summer compared to 40.2% of $PM_{2.5}$ mass and 35.9% of PM_{10} during winter. Because the majority of carbon is in $PM_{2.5}$, the ratio of $PM_{2.5}/PM_{10}$ ranged from 0.71 to 0.85 for OC and 0.75 to 0.80 for EC (Table 4).

3.3. The relationship between OC and EC

Since EC is predominately emitted from combustion sources, it has often been used as a tracer of primary OC (Turpin and Huntzicker, 1991). The origin of carbonaceous particles can be estimated on the basis of the relationship between OC and EC. The regression between the OC and EC concentrations is shown in Fig. 3. Reasonable OC–EC correlations ($R^2 > 0.6$) of $PM_{2.5}$ and PM_{10} (the figure of PM_{10} is omitted) in PRDR were observed for summer and winter. Similar slopes of regression were found between summer and winter, implying similar emission sources (i.e., vehicle exhaust) contributing to ambient carbonaceous particles

Table 3
Ambient $PM_{2.5}$ and PM_{10} concentrations at eight sites during the summer in PRDR, China

City	Site	$PM_{2.5}$ ($\mu g\,m^{-3}$)		PM_{10} ($\mu g\,m^{-3}$)		$PM_{2.5}/PM_{10}$ (%)
		Concentration[a]	N[b]	Concentration	N	Mean
Hong Kong	PU	40.1±19.7	10	40.8±15.6	10	83.0
	BU	30.8±7.6	6	38.6±12.8	6	71.2
	HT	15.8±2.4	6	31.9±4.9	6	50.3
	Average	31±16.9	22	41.4±14.2	22	70.9
Guangzhou	HP	101.7±11.4	5	164.2±17.4	5	62.1
	ZU	66.3±18.9	10	102.7±32.5	10	65.1
	LG	78.2±46.9	5	129.5±93.5	5	64.1
	Average	78.1±29.7	20	124.7±55.5	20	64.1
Shenzhen	LH	47.1±16.7	9	75.1±23.0	9	62.6
Zhuhai	XZ	31.0±20.0	9	44.0±24.8	9	68.9
PRDR	Average	49.1±30.6	60	74.6±51.2	60	68.7

[a] Values represent average±standard deviation.
[b] Numbers of samples.

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

City	TCA (%)			OC (%)			EC (%)		
	$PM_{2.5}$	PM_{10}	$PM_{2.5}/PM_{10}$	$PM_{2.5}$	PM_{10}	$PM_{2.5}/PM_{10}$	$PM_{2.5}$	PM_{10}	$PM_{2.5}/PM_{10}$
Hong Kong	38.6±7.0	33.4±11.9	83.5±7.7	18.6±3.9	15.7±5.4	84.7±8.3	8.8±3.1	8.3±3.8	78.2±10.5
Guangzhou	40.3±5.8	35.7±4.6	74.6±8.6	20.3±2.4	17.7±2.5	73.8±8.3	7.8±2.1	6.4±1.3	77.7±11.0
Shenzhen	32.3±12.1	27.5±10.7	73.2±6.5	15.1±5.3	13.1±5.1	71.3±6.1	8.2±3.7	6.2±2.7	80.0±10.0
Zhuhai	35.1±6.5	31.0±8.0	78.7±5.3	17.8±3.3	15.5±4.1	80.6±9.0	6.6±1.6	6.2±2.0	74.9±13.7
Average	38.0±7.8	32.9±9.6	78.3±8.5	18.6±3.9	16.0±4.5	78.4±9.6	8.3±3.3	7.3±3.5	77.8±10.9

[a] Values represent average±standard deviation.

in PRDR. High OC–EC correlations ($R^2 = 0.82$) in winter, could result because the organics present were mostly primary carbon. The correlation between OC and EC ($R^2 = 0.64$) in the summer was lower than that of the winter, indicating the presence of other sources.

Particulate OC to EC ratios exceeding 2.0 have been used to identify secondary organic aerosol (SOA) formation (Chow et al., 1993b, 1996). Table 1 shows that average OC/EC ratios at the eight sites ranged from 1.6 to 4.7, with an overall average of 2.5 for $PM_{2.5}$ and PM_{10} during summer. These values are similar to the average OC/EC ratios for $PM_{2.5}$ (2.4) and for PM_{10} (2.5) in winter (Cao et al., 2003). This result validated that motor vehicles consistently contributed to OC and EC in cold and warm seasons. The OC/EC ratios were less than 2.0 at the PU and BU sites in Hong Kong for $PM_{2.5}$ and PM_{10}, indicating the influence of fresh motor vehicle exhaust. However, the OC/EC ratios were more than 3.0 at the rural HT site for both $PM_{2.5}$ and PM_{10}, suggesting the presence of SOA.

All the data of OC and EC in Chinese and Korean cities were measured using the TOR and TMO methods. Previous comparisons between TMO and TOR by Fung et al. (2002) showed good agreement in TC, OC, and EC. Fig. 2 shows that average ratios of OC/EC in the four cities fall between 1.0 and 4.0 during summer, which is consistent with the results of winter observation. Most of the ratios of OC/EC in other Asian cites also fall within the same 1.0–4.0 range, except for the results from Japanese cities (Sapporo and Uji), where OC/EC < 1.0. The OC and EC in Sapporo were measured by two-step combustion method (at 300°C and 850°C) and the OC and EC in Uji were obtained by an in-situ continuous Ambient Carbon Particulate

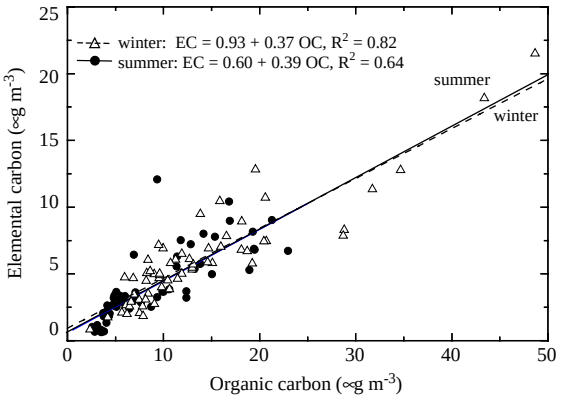

Fig. 3. Relationship between OC and EC concentration in $PM_{2.5}$ samples during winter and summer in PRDR.

Monitor (R&P, Series 5400) which separates OC and TC at 340°C and 750°C.

3.4. An estimate for the secondary organic carbon concentration

The separation and quantification of primary and secondary OC have been difficult to achieve. Because no simple, direct analytical technique is available, an indirect method was used. The minimum OC/EC ratio method was used to estimate the secondary organic carbon (OC_{sec}) formation with the following equation (Turpin and Huntzicker, 1995; Castro et al., 1999):

$$OC_{sec} = OC_{tot} - EC^{*}(OC/EC)_{min},$$

where OC_{sec} is the secondary OC (SOC), OC_{tot} is the total OC (TOC), and $(OC/EC)_{min}$ is the minimum ratio observed. The $(OC/EC)_{min}$ of 1.1 and 1.2 observed respectively, for $PM_{2.5}$ and PM_{10} were used in the calculation. Assumptions regarding the use of this procedure are discussed in detail in Castro et al. (1999).

Table 5 showed that the average SOC concentrations for $PM_{2.5}$ and PM_{10} in PRDR were 4.9 and 6.3 $\mu g\,m^{-3}$, respectively, account for 51.3% and 46.5%, respectively, of TOC. Compared with winter results (Cao et al., 2003), there is an overall trend toward lower SOC levels but with a higher percentage of SOC in the TOC at each site during the summer. Higher temperatures and more intense solar radiation during the summer months provide favorable conditions for photochemical activity and SOC production. The percentage of estimated SOC at four urban sites in the four cities ranged from 37.0% to 61.7%, which is in agreement with percentages in urban areas found in other studies (Turpin and Huntzicker, 1995; Castro et al., 1999; Lin and Tai, 2001). A higher percentage of SOC in the TOC found at the background HT site is probably due to greater residence time for atmospheric oxidation during transport and relative small contributions from local primary emission sources. A lower percentage of SOC existed at PU roadside, perhaps owing to its proximity to motor vehicle sources and the predominant fresh emissions. Considering the role of SOC in regional haze, visibility reduction, and atmospheric chemistry, further research is needed.

3.5. The characterization of eight carbon fractions at eight sites

One of the unique features of the IMPROVE TOR protocol is that it does not advance from one temperature to the next until a well-defined carbon peak has evolved (Chow et al., 1993a, 2001). Carbon abundances in each of these fractions differ by carbon source (Ellis and Novakov, 1982; Ellis et al., 1984; Watson et al., 1994). The contents of eight fractions have also been utilized in the source profile study to differentiate gasoline vehicles from diesel vehicles (Watson et al., 1994; Chow et al., 2003a) and to differentiate different geological dust (Chow et al., 2003b). The eight fractions are also included in the IMPROVE database and form the basis for calculating the OC and EC fractions for light extinction used by US EPA (US Environmental Protection Agency, 2001).

The percentages of carbon fractions collected at eight sites during the summer period were shown in Fig. 4. The average abundances of OC1, OC2, OC3, OC4, EC1-OP, EC2, EC3 and OP in TC were 4.3%, 19.9%, 17.7%, 12.6%, 15.2%, 15.4%, 2.5%, and 12.4%, respectively. Although there were substantial site-to-site variabilities, OC2, OC3, EC1-OP, and EC2 were generally the most abundant species. There was very little high-temperature (800°C) EC3 in any of these samples. Different carbon fractions have different variabilities among these eight sites. It is interesting that the greatest variability is found for EC2 in three sites with different microenvironments. The percentages of EC2 in TC decreased from 35.3% at the roadside PU site to 27.5% at the urban BU site, and to 8.2% at the background HT site in Hong Kong. Previous study has shown that EC2 is the most abundant species in the exhaust of diesel-fueled vehicles, compared with gasoline-fueled vehicles (Watson et al., 1994). The carbon profiles of the eight fractions for source-dominant samples (diesel, liquefied petroleum gas, and gasoline vehicles) in Hong Kong has also demonstrated that EC2 is the major exhaust of diesel vehicles, and accounted for about 38.2% of the TC (Chow, 2003). The compositions of eight carbon fractions at the PU site were greatly influenced by fresh diesel-fueled vehicles, which led to high EC2 abundance. The EC2 abundance at the BU site decreased due to decreasing distance from direct emissions of running vehicles. As there are very few directly anthropogenic

Table 5
Levels of possible SOC at eight sites in PRDR estimated from minimum OC/EC ratios method[a]

City	Site	Concentration ($\mu g\,m^{-3}$)		Percentage (OC_{sec}/OC, %)	
		$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}
Hong Kong	PU	2.0	1.7	32.7	24.3
	BU	2.1	2.0	37.0	29.3
	HT	2.6	2.8	76.1	67.7
	Average	2.2	2.1	45.7	37.0
Guangzhou	HP	11.3	15.8	55.6	55.1
	ZU	8.0	10.8	61.7	59.3
	LG	9.9	14.1	54.0	51.7
	Average	9.3	12.9	57.8	56.3
Shenzhen	LH	3.0	4.4	42.1	43.5
Zhuhai	XZ	3.4	3.8	59.5	51.0
Average		4.9	6.3	51.3	46.5

[a]Higher OC/EC ratios may also result from bioaerosol, fires, adsorption of organic vapors on quartz filters, and variability in composition of source emissions. Potential SOC calculated by OC/EC enrichment has a large and unquantifiable uncertainty.

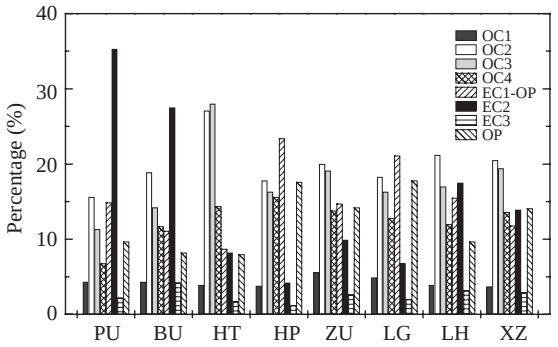

Fig. 4. Percentage of total carbon contributed by eight carbon fractions at eight sampling sites in $PM_{2.5}$ during the summer in PRDR.

emission sources around the background HT site, the long-range dispersion of pollutants resulted in the low EC2 abundance. In contrast, OC2 and OC3 abundance present in an increasing order from PU, BU, to HT. The percentages of OC2 in TC at three sites were 15.6%, 18.9%, and 27.1%, respectively, and the OC3 percentages were 11.3%, 14.2%, and 28.0%, respectively. As described above, SOC was formed during the long-range transport from emitted sources to background receptor site; thus, the increase of OC2 and OC3 abundance may be associated with SOC. This conclusion needs to be verified by further observations. The pyrolyzed carbon (OP) abundance in the TC ranges from 8.0% to 17.8% among the eight sites. Yang and Yu (2002) found that OP increases with the water-soluble organic carbon (WSOC) content, and that WSOC accounts for 13–66% of OP. Thus, substantial water-soluble polar compounds are possible expected in the PRDR atmosphere. Ho et al. (2004) found that WSOC accounted for 41.4% of the TOC in $PM_{2.5}$ and 36.3% in PM_{10} during 2001 in Hong Kong. The profiles of eight carbon fractions at eight sites in summer are quite similar to those in winter, which indicated that motor vehicles were the dominant source of carbonaceous particles in PRDR.

4. Conclusion

Carbonaceous aerosol is a major component in fine PM, which plays an important role in regional atmospheric chemistry and climate changes over China. Unfortunately, there is little carbonaceous species data available for China. This paper presents the first regional measurements of particulate OC and EC in China. $PM_{2.5}$, PM_{10}, and carbonaceous aerosol were investigated at eight ambient air quality monitoring sites in four cities (Hong Kong, Guangzhou, Shenzhen, and Zhuhai) in the PRDR during the winter and summer. PM samples were collected by mini-volume samplers on pre-fired quartz filters. The IMPROVE TOR method was used for OC and EC analyses.

Carbonaceous aerosol was averaged at one-third of the $PM_{2.5}$ and PM_{10} mass at eight sites during summer. The majority of ambient PM_{10} OC and EC were observed to be associated with $PM_{2.5}$. The estimated concentration of SOC seems to contribute significantly to the TOC due to favorable summer conditions (higher

temperatures and more intense solar radiation). Even considering differences in the analytical methods used in different studies, the concentrations of OC and EC during the summer and winter periods were comparable to those at other urban areas in East Asia. Though ambient OC and EC levels in the summer were lower than those in the winter, owing to the influence of the East Asian monsoon, OC and EC did not show notable seasonal fluctuations at six sampling sites, except for the statistically seasonal differences at the background HT and urban XZ sites. Reasonable correlations between OC and EC were found for both seasons (correlation coefficients: winter = 0.82, summer = 0.64) and the greater variabilities of EC2 (combusted at 700°C) abundance at roadside, urban, and background sites indicated that motor vehicle emissions were the major source of carbonaceous particles.

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