Spatial and seasonal distributions of carbonaceous aerosols over China

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[1] Simultaneous measurements of atmospheric organic and elemental carbon (OC and EC) were taken during winter and summer seasons at 2003 in 14 cities in China. Daily $PM_{2.5}$ samples were analyzed for OC and EC by the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance protocol. Average $PM_{2.5}$ OC concentrations in the 14 cities were 38.1 μg m^{-3} and 13.8 μg m^{-3} for winter and summer periods, and the corresponding EC were 9.9 μg m^{-3} and 3.6 μg m^{-3}, respectively. OC and EC concentrations had summer minima and winter maxima in all the cities. Carbonaceous matter (CM), the sum of organic matter (OM = 1.6 $\times$ OC) and EC, contributed 44.2% to $PM_{2.5}$ in winter and 38.8% in summer. OC was correlated with EC (R^2: 0.56–0.99) in winter, but correlation coefficients were lower in summer (R^2: 0.003–0.90). Using OC/EC enrichment factors, the primary OC, secondary OC and EC accounted for 47.5%, 31.7% and 20.8%, respectively, of total carbon in Chinese urban environments. More than two thirds of China's urban carbon is derived from directly emitted particles. Average OC/EC ratios ranged from 2.0 to 4.7 among 14 cities during winter and from 2.1 to 5.9 during summer. OC/EC ratios in this study were consistent with a possible cooling effect of carbonaceous aerosols over China.

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1. Introduction

[2] Aerosol has been regarded as one important factor influencing global climate, which can be compared to other climate forcing agent such as greenhouse gases, land use, solar activity, etc. [*Intergovernmental Panel on Climate Change*, 2001; *Menon*, 2004]. Carbonaceous aerosols in China have received more attention recently because of their effects on regional climate, water resources, agriculture yields, air quality, visibility reduction, and public health [*Chameides et al.*, 1999; *Menon et al.*, 2002; *Jacobson*, 2002; *Barnett et al.*, 2005]. Carbonaceous aerosols are composed of both light-absorbing black carbon (BC, or elemental carbon, EC) and light-scattering organic carbon (OC). Even though research of carbonaceous aerosol in China began in the 1980s [*Zhang and Su*, 1985], continuous observation did not start until the mid-1990s [*Tang et al.*, 1999]. Carbonaceous aerosol contributed 20–50% of aerosol in Chinese urban atmosphere from small-scale urban or regional atmosphere [*He et al.*, 2001; *Ye et al.*, 2003; *Cao et al.*, 2003, 2004, 2005; *Lee et al.*, 2006]. There is almost no study on national distribution of OC and EC in China. This paper presents a national-scale $PM_{2.5}$ (particles with aerodynamic diameters less than 2.5 microns [μm]) OC and EC measurements simultaneously in fourteen cities in China. The primary objectives of the study are to (1) characterize OC and EC in urban atmosphere, (2) examine spatial and seasonal variations of OC and EC concentrations, and (3) estimate secondary OC (SOC) contributions to total carbonaceous loading. The resulting database will provide chemical characteristics of carbonaceous particles under desert, continental and coastal environments, and will also supply information to relevant researchers in understanding

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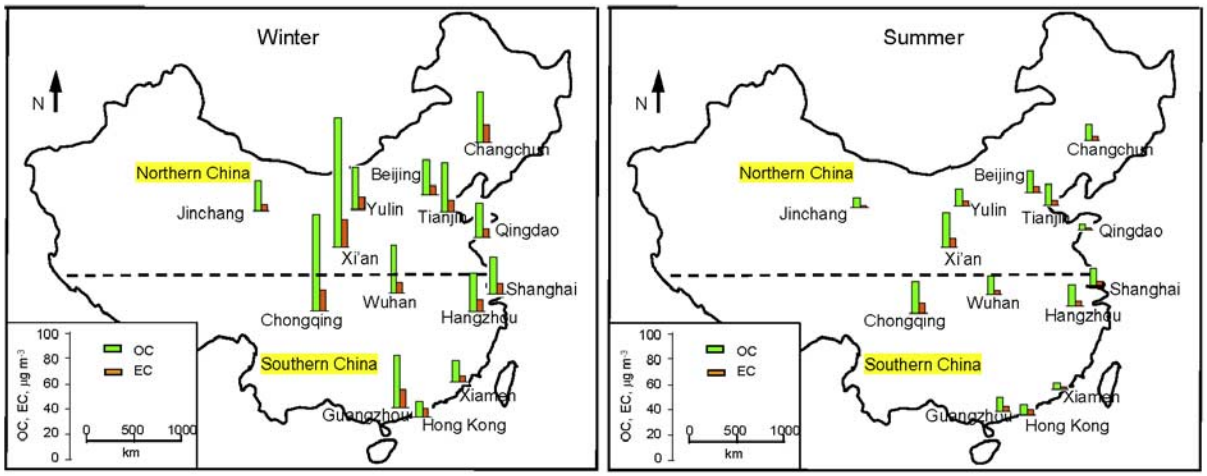

Figure 1. Location of 14 Chinese cities with summer and winter averages of $PM_{2.5}$ OC and EC indicated by bar height.

and evaluating the fine particle pollution of urban atmosphere in China, thus enriching the worldwide database of carbonaceous species in $PM_{2.5}$.

2. Sampling and Analysis

2.1. Sampling Sites and Descriptions

[3] Fourteen cities including major megacities in China were selected to represent economically developed and developing regions, which cover most of the nonmountainous urban regions in China, as shown in Figure 1. Simultaneous measurements were made during winter and summer 2003. This sampling campaign was used to obtain a snapshot of carbonaceous pollution in Chinese urban atmosphere. These cities include seven in southern China (Chongqing (CQ), Guangzhou (GZ), Hong Kong (HK), Hangzhou (HZ), Shanghai (SH), Wuhan (WH), and Xiamen (XM)) and seven in northern China (Beijing (BJ), Changchun (CC), Jinchang (JC), Qingdao (QD), Tianjin (TJ), Xi'an (XA), and Yulin (YL)) according to the natural geographic distribution of China. Detailed descriptions for the sampling network and meteorological conditions during the sampling periods are shown in Tables 1 and S1[1]. Sites were selected to represent urban-scale concentration and most were located within university or research center campus, >100 m from local sources such as major roadways.

2.2. Sample Collection

[4] In each city, 24 h aerosol sampling (0900 to 0900 local time) was performed in winter (6–20 January) and summer (3 June to 30 July) of 2003. The samples in winter were almost collected every day during the two weeks from 6 to 20 January. The samples in summer were planed to collect fourteen samples from each city to match the sample numbers in winter from 3 to 17 June. Owing to the low ambient concentrations and frequent precipitation in summer, the valid samples were less than fourteen samples in six cities (Table 2) and the sampling period was extended to 30 July. $PM_{2.5}$ samples were collected on 405 prefired (900°C, 3 h) 47 mm Whatman QM-A quartz-fiber filters, using a minivolume air sampler (Airmetrics, Eugene, OR, USA) at a flow rate of 5 L min^{-1}. The samplers were set up on rooftops at varying heights 6–20 m above the ground (Table 1), which represented the general atmosphere of each city to avoid heavy emission sources.

[5] Quartz-fiber filters were analyzed gravimetrically for mass concentrations using a Sartorius MC5 electronic microbalance with a ±1 μg sensitivity (Sartorius, Göttingen, Germany). These filters were weighed after 24-h equilibration at temperature between 2°C and 23°C and relative humidity (RH) between 35% and 45% following the US EPA methodology [*Chow and Watson*, 1998]. Each filter was weighed at least three times before and after sampling. The difference among the three repeated weighings was less than 10 μg for a blank filter and less than 20 μg for a sampled filter.

2.3. Thermal/Optical Carbon Analysis

[6] A 0.5 cm^2 punch from the filter was analyzed for eight carbon fractions following the IMPROVE (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol [*Cao et al.*, 2003; *Chow et al.*, 1993, 2004] on a DRI model 2001 carbon analyzer (Atmoslytic Inc., Calabasas, CA). This produced four OC fractions (OC1, OC2, OC3, and OC4 at 120°C, 250°C, 450°C, and 550°C, respectively, in a helium [He] atmosphere); OP (a pyrolyzed carbon fraction determined when reflected or transmitted laser light attained its original intensity after oxygen [O_2] was added to the analysis 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). IMPROVE_TOR OC is operationally defined as OC1 + OC2 + OC3 + OC4 + OP and EC is defined as EC1 + EC2 + EC3-OP [*Watson et al.*, 2005]. Interlaboratory comparisons of samples between IMPROVE_TOR protocol and the TMO (thermal manganese dioxide oxidation) approach has shown a difference of

[1]Auxiliary materials are available in the HTML. doi:10.1029/2006JD008205.

Table 1. Location and Description of Sampling Site in Each City

City Name	Code	City Description	Location	Sampling Site
Northern China				
Beijing	BJ	capital of China, developed megacity	39.9°N, 116.4°E	roof (14 m[a]) of a building at Institute of Atmospheric Physics, Chinese Academy of Sciences (CAS)
Changchun	CC	continental and developed industrial city	43.9°N, 125.3°E	roof (6 m) of a building at Jilin University
Jinchang	JC	Asian dust source region, developing city	383°N, 101.1°E	roof (10 m) of a building at Jinchang Meteorological Bureau
Qingdao	QD	developing coastal city	36°N, 120.3°E	roof (10 m) of a building at Chinese Ocean University
Tianjin	TJ	developed industrial city	39.1°N, 117.2°E	roof (20 m) of a building at Nankai University
Xi'an	XA	continental and developing industrial city	34.2°N, 108.9°E	roof (10 m) of a building at Institute of Earth Environment, CAS
Yulin	YL	continental developing city, close to a desert	38.3°N, 109.8°E	a observation tower (10 m) in Shaanxi Desert Institute
Southern China				
Chongqing	CQ	continental and developing industrial city	29.5°N, 106.5°E	roof (10 m) of the Chongqing Academy of Environmental Sciences
Guangzhou	GZ	developed industrial and commercial megacity	23.1°N, 113.2°E	roof (10 m) of a building at Zhongshan Uinversity
Hong Kong	HK	coastal and commercial city, developed city	22.2°N, 114.1°E	a monitoring site (10 m) at Hong Kong Polytechnic University
Hangzhou	HZ	developing continental city	30.2°N, 120.1°E	a substation (20 m) at Hangzhou Environmental Monitoring Station
Shanghai	SH	developed industrial and commercial megacity	31.2°N, 121.4°E	roof (8 m) of a building at Donghua University
Wuhan	WH	developed industrial and commercial city	30.5°N, 114.2°E	roof (8 m) of a building at Chinese University of Geosciences
Xiamen	XM	coastal and commercial city, developing city	24.4°N, 118.1°E	roof (8 m) of a building at Xiamen University

[a]Inlet height above ground level.

<5% for TC and <10% for OC and EC [*Fung et al.*, 2003]. Average field blanks were 1.85 and 0.53 μg m^{-3} for OC and EC, respectively.

3. Results and Discussion

3.1. Concentration Levels of OC and EC

[7] Average $PM_{2.5}$ mass, OC and EC concentrations are summarized in Table 2 and the averages of OC and EC are plotted in Figure 1. The average OC concentrations were 38.1 μg m^{-3} and 13.8 μg m^{-3} for winter and summer periods, and average EC concentrations were 9.9 μg m^{-3} and 3.6 μg m^{-3}, respectively. Winter OC and EC concentrations were as high as 169.2 μg m^{-3} and 31.2 μg m^{-3}, and as low as 3.6 μg m^{-3} and 1.0 μg m^{-3}, respectively. The corresponding summertime maximum OC and EC were 52.9 μg m^{-3} and 16.3 μg m^{-3} and minimum were 1.8 μg m^{-3} and 0.3 μg m^{-3}. These OC and EC varied by two orders of magnitude, ranging from 1.8 μg m^{-3} to 169.2 μg m^{-3} for OC and from 0.3 μg m^{-3} to 31.2 μg m^{-3} for EC. The relative standard

Table 2. Distribution of OC and EC Among 14 Cities[a]

	Winter						Summer					
	$PM_{2.5}$[b]	OC	EC	OC/EC	CM,[c] %	N[d]	$PM_{2.5}$	OC	EC	OC/EC	CM, %	N
BJ	126.5 ± 66.1	27.2 ± 15.3	7.1 ± 3.5	3.7	40.1	14	117.2 ± 48.3	17.2 ± 7.0	4.6 ± 3.0	4.4	30.1	14
CC	140.5 ± 28.6	39.2 ± 8.7	13.5 ± 2.9	2.9	54.4	14	59.6 ± 21.9	12.5 ± 5.2	2.9 ± 1.4	4.5	39.4	16
JC	105.8 ± 42.9	23.0 ± 8.4	5.0 ± 1.2	4.5	42.6	15	60.4 ± 18.2	8.1 ± 1.8	1.6 ± 0.7	5.9	25.0	8
QD	127.9 ± 58.5	26.6 ± 11.0	6.3 ± 2.4	4.3	43.7	13	30.1 ± 16.1	5.0 ± 2.9	1.4 ± 0.5	3.5	33.9	9
TJ	179.4 ± 87.8	38.9 ± 18.4	8.5 ± 3.5	4.5	41.6	16	103.2 ± 27.9	16.5 ± 4.1	3.7 ± 1.5	4.9	30.6	15
XA	375.2 ± 143.5	102.3 ± 33.0	21.6 ± 5.4	4.7	51.4	15	130.8 ± 58.5	27.3 ± 8.8	7.0 ± 2.9	4	42.7	15
YL	150.6 ± 77.3	32.5 ± 14.4	9.2 ± 4.0	3.6	44.2	14	50.5 ± 23.2	13.7 ± 9.2	3.3 ± 1.2	4.4	48.4	12
CQ	311.8 ± 114.1	76.7 ± 24.6	16.6 ± 5.4	4.7	47.9	15	116.3 ± 38.1	25.1 ± 8.2	8.0 ± 2.6	3.2	42.5	16
GZ	156.0 ± 93.6	41.1 ± 29.6	14.5 ± 9.9	2.8	47.0	14	49.1 ± 9.3	10.6 ± 2.0	3.2 ± 0.7	3.6	41.8	13
HK	64.0 ± 29.6	11.2 ± 4.8	5.8 ± 2.6	2	38.4	16	40.1 ± 14.0	7.3 ± 1.9	3.6 ± 1.0	2.1	40.6	22
HZ	168.6 ± 54.6	30.6 ± 7.7	9.3 ± 2.1	3.3	36.5	14	90.6 ± 40.8	17.1 ± 4.8	3.6 ± 1.3	5.2	37.7	16
SH	151.1 ± 94.5	28.6 ± 16.7	8.3 ± 5.4	3.9	38.4	16	52.2 ± 19.4	13.3 ± 4.6	2.9 ± 1.6	5.2	49.0	14
WH	166.6 ± 72.7	38.2 ± 15.9	8.4 ± 2.9	4.5	43.6	13	70.8 ± 21.3	14.2 ± 3.7	3.0 ± .07	4.8	38.4	13
XM	70.2 ± 32.2	16.5 ± 5.4	5.0 ± 1.4	3.3	48.6	15	25.2 ± 15.8	4.8 ± 2.4	1.4 ± 1.3	3.5	42.8	12
Ave[e]	163.9	38.1	9.9	3.8	44.2		71.2	13.8	3.6	4.2	38.8	

[a]Unit is μg m^{-3}.
[b]Values represent average ± standard deviation.
[c]CM, carbonaceous matter = 1.6*OC + EC.
[d]Numbers of samples.
[e]Ave, arithmetic average.

deviations (RSD = 100% × standard deviation/average) of OC and EC were 42% and 38% during winter, and 36% and 43% during summer, respectively. These RSD values were similar to those reported by *Novakov et al.* [2005] for OC (47%) and EC (40%) in China.

3.2. Spatial and Seasonal Variations of OC and EC

[8] EC is a product of incomplete combustion from residential coal, motor vehicle fuel, and biomass. OC originates from primary anthropogenic sources like above combustions and from formation (secondary OC) by chemical reactions in the atmosphere. OC levels were always higher than EC at all sampling sites (Figure 1). Carbon concentrations were high in some of inland cities, such as Xi'an, Chongqing, Wuhan, and Changchun; and were lower in some of coastal cities, such as Hong Kong, Xiamen, and Qingdao. Among the seven inland cites, Xi'an had the highest average OC (102.3 ± 33.0 μg m^{-3}) and EC (21.6 ± 5.4 μg m^{-3}) concentrations during winter and the highest average OC (27.3 ± 8.8 μg m^{-3}) and the second highest average EC (7.0 ± 2.9 μg m^{-3}) concentrations during summer. Xi'an experiences combined contributions from coal combustion emissions and unfavorable meteorological conditions (Table S1). There is a "heating season" from November to the following March in northern Chinese cities. The more developed cities of northern China (Beijing, Tianjin, Qingdao) have largely switched from residential coal to natural gas or central steam [*Ge et al.*, 2004], and this is reflected in lower OC and EC levels (see Table S1 for energy use). Xi'an used about 7.2 × 10^6 metric tons of standard coal equivalent (TCE), of this total coal accounted for 34.78%, oil accounted for 13.75%, electricity accounted for 43.91%, and natural gas and other clean energy sources accounted for 7.56% (Table S1). 1.5 × 10^6 TCE coal was used for winter heating, accounting for 58% of total coal burned in Xi'an. Most of the remaining coal was used for thermo power plant around Xi'an in the whole year. Monthly average wind speeds were 0.4 m s^{-1} and 0.9 m s^{-1} at Xi'an, during January and July, the lowest of all 14 cities (Table S1). Xi'an daytime mixing height averaged with 780 m during winter (Table S1), which resulted in a shallow surface inversion. Highest OC at Xi'an for both seasons may be attributed to another reason, i.e., Xi'an is a pharmacy base of China and about thirty large pharmacy factories located in Xi'an. *Jaward et al.* [2005] found that the concentration of polychlorinated biphenyls (PCBs) was highest at the same site with our observation in Xi'an compared with 32 other Chinese cities.

[9] The second highest average OC was found in Chongqing for both seasons and average EC was second highest (16.6 ± 5.4 μg m^{-3}) in winter and the highest (8.0 ± 2.6 μg m^{-3}) in summer (Table 2). Chongqing is a famous pollution industrial city with serious acid rain from coal combustion for many years, so the carbonaceous particles were also high because of the large usage of coal. The total end energy consumption was 26.9 × 10^6 TCE, which the usage of coal accounted for 65% with 17.5 × 10^6 TCE (Table S1). Although there is no formal "heating season" in Chongqing, residential coal is used when cold fronts pass through the region. Chongqing city is situated in a valley at the confluence of the Jialing and Yangtz rivers, similar to Pittsburgh, PA. It located in a basin surrounded by mountains where low wind speeds (1.3 m s^{-1} in January and 2.0 m s^{-1} in July), high relative humidity (84% in January and 81% in July), and stable atmospheric conditions (Table S1).

[10] The lowest OC averages were found in Hong Kong (11.2 ± 4.8 μg m^{-3}) during winter and in Xiamen (4.8 ± 2.4 μg m^{-3}) during summer. The lowest EC concentrations were found in Xiamen (5.0 ± 1.4 μg m^{-3}) and Jinchang (5.0 ± 1.2 μg m^{-3}) during winter, and in Xiamen (1.4 ± 1.3 μg m^{-3}) and Qingdao (1.4 ± 0.5 μg m^{-3}) during summer. Hong Kong, Xiamen, and Qingdao are located in coastal environments, where clean marine air dilutes on local and regional particulate matter accumulation. Jinchang is in a desert region (low regional background concentration) with little local industry and has the lowest population (0.2 million) of the fourteen cities (Table S1). This is reflected in its lower OC and EC levels.

[11] The concentrations of OC and EC exhibited summer minima and winter maxima in all the cities (Figure 1). Wintertime OC and EC concentrations were about two to four times those during summer. This is mainly ascribed to the primary emission of coal-related aerosol, because the measurements were taken during the "heating season" at seven northern cities. Although there is no formal "heating season" in some southern cities like Chongqing, Wuhan, Hangzhou and Shanghai, there are still carbonaceous emissions from space domestic heating sources during winter due to cold weather (around 0–10°C during the observation period, Table S1). Low mixing layer height and low precipitation amount during winter also contributed to the high carbon loading during cold season (Table S1).

[12] The ratios of winter to summer average TC concentrations among fourteen cities are: Qingdao (5.1) > Guangzhou (4.0) > Xi'an (3.6) > Xiamen (3.5) > Changchun (3.4) > Jinchang (2.9) > Chongqing (2.8) > Wuhan (2.7) > Yulin (2.5) > Shanghai (2.3) > Tianjin (2.3) > Hangzhou (1.9) > Hong Kong and Beijing (1.6). Because the ratios were mainly dependent on both pollution emission amounts and meteorological conditions in winter and summer, the ratios were not presented a simple pattern with "northern high and southern low." Northern cities like Qingdao, Xi'an, Changchun have higher winter to summer ratios (>3.0), while southern cities like Chongqing, Wuhan, Shanghai, Hangzhou, and Hong Kong has lower winter to summer ratios (<3.0). High ratios occurred in coastal Guangzhou and Xiamen, which may be attributed the influence of monsoon climate, i.e., clean summer monsoon easily alleviate urban air pollution in summer. Coastal Qingdao in northern China was influenced by "heating season" during winter and clean marine atmosphere during summer. The low winter/summer ratio in Hong Kong may be due to dominant traffic emissions year-round combined with low carbonaceous emission from clean energy sources in the city. No notable seasonal variation of OC and EC in Hong Kong was also observed by *Cao et al.* [2004]. A low winter/summer ratio in Beijing may be due to (1) less residential coal-burning in developed cities, (2) higher wind speeds and reasonable dilution in winter, and (3) photochemical conversion of VOCs to secondary OC during summer.

[13] Seasonal differences in OC and EC concentrations were tested by the one-way analysis of variance (ANOVA)

Table 3. One-Way ANOVA for OC and EC on Seasonal Variables for Each City

	OC		EC	
	F-Ratio[a]	*p*-Value[b]	*F*-Ratio	*p*-Value
BJ	3.5	0.072	2.0	0.172
CC	110.8	0.000	165.0	0.000
JC	24.3	0.000	59.7	0.000
QD	33.0	0.000	35.6	0.000
TJ	21.1	0.000	24.2	0.000
XA	72.3	0.000	86.3	0.000
YL	15.2	0.000	24.1	0.000
CQ	63.1	0.000	32.2	0.000
GZ	13.7	0.001	17.0	0.000
HK	3.6	0.075	2.4	0.135
HZ	34.1	0.000	80.8	0.000
SH	11.1	0.002	13.1	0.001
WH	29.9	0.000	46.9	0.000
XM	51.4	0.000	45.3	0.000

[a]*F*-ratio = *F* test.
[b]*p*-value = significance value for *F* test.

method, using the statistical software package SPSS v 10.0, and the results are shown in Table 3. No significant ($p > 0.05$) seasonal variabilities of OC and EC in Beijing and Hong Kong sites in *F*-ratio and *p*-value were statistically different (i.e., possibly reflecting that OC and EC source emission rates, such as vehicle exhaust, were consistent during two seasons in these two megacities). The low ratio (1.6) of winter to summer for TC is also observed in these two cities. Significant ($p < 0.05$) seasonal variabilities of OC and EC in the remaining 12 cities with high *F*-ratio and low *p*-value were statistically different. The obvious seasonal variations of OC and EC found in these sites mainly pointed to the significant differences of energy structure (such as the increasing percentage of coal consumption during ''heating season'' in northern cities) and meteorological conditions during two seasons.

3.3. Contributions to $PM_{2.5}$ Mass

[14] The 14-site average 24 h $PM_{2.5}$ mass concentrations were 163.9 $\mu g\ m^{-3}$ during winter, with the highest level (375.2 $\mu g\ m^{-3}$) found in Xi'an and the lowest (64.0 $\mu g\ m^{-3}$) found in Hong Kong. The average $PM_{2.5}$ was 71.2 $\mu g\ m^{-3}$ during summer, with the highest level (130.8 $\mu g\ m^{-3}$) in Xi'an and the lowest (25.2 $\mu g\ m^{-3}$) in Xiamen. $PM_{2.5}$ in northern cities varied by a factor of 57, ranging from 11.0 $\mu g\ m^{-3}$ (Qingdao, summer) to 629.4 $\mu g\ m^{-3}$ (Xi'an, winter). $PM_{2.5}$ in southern cities varied by a factor of 51, ranging from 9.9 $\mu g\ m^{-3}$ (Xiamen, summer) to 506.3 $\mu g\ m^{-3}$ (Chongqing, winter). In reference to the 24 h U.S. $PM_{2.5}$ standard (35 $\mu g\ m^{-3}$; China currently has no $PM_{2.5}$ national standard), ~97% and 85% of $PM_{2.5}$ mass values exceed the 24-h standard during winter and summer, respectively. Even the cleanest city experiences $PM_{2.5}$ at unhealthy levels.

[15] As shown in Table 2, carbonaceous matter (CM), which is the sum of organic matter (OM = 1.6 × OC [*Turpin and Lim*, 2001]) and EC, constituted 44.2% of $PM_{2.5}$ in winter and 38.8% in summer. The average fraction of CM in $PM_{2.5}$ in northern cities was 45.4% during winter and 35.7% during summer. While the average fraction of CM in $PM_{2.5}$ was similar in the southern cities for winter (42.9%) and summer (41.8%). Therefore carbon is a large $PM_{2.5}$ component in all cities during both summer and winter. Fugitive dust is always a major contributor to urban atmosphere in northern China [*Cao et al.*, 2005]. So it is reasonable to find that the lowest percentage (25%) of CM in $PM_{2.5}$ occurred during summer at Jinchang, a city near desert regions.

3.4. Relationship Between OC and EC

[16] Relationship of OC and EC gives some indication of the origins of carbonaceous $PM_{2.5}$ [*Chow et al.*, 1996]. As shown in Table 4, good and strong OC/EC correlations (R^2: 0.56–0.99) in winter were found in 14 cities, which suggested impacts from a combination of common source contributions (i.e., residential and commercial coal combustion, motor vehicle exhaust). OC/EC correlations (R^2: 0.003–0.90) were scattered in summer, implied a changing mixture of source contributions in these cities. The OC/EC correlations were typically larger in winter than in summer except Hong Kong, Xiamen, Changchun and Xi'an sites. The product *b*EC represents the primary OC associated with combustion sources (coal combustion, traffic). Most of *b* values (OC/EC slope) ranged from about 3.0 to 5.0 except 1.52 for Hong Kong and 2.2 for Changchun, which indicated the large contribution to carbonaceous aerosol from primary emissions in winter. The intercept *a* is interpreted as the OC background concentration originating from non-combustion sources although it can be biased by uncertainty in carbon measurement and relative large slope. From the Table 4, most of *a* values are higher in summer than in winter except for the Hong Kong, Changchun and Qingdao sites even though some negative *a* values were calculated. This possibly pointed to the high percentage of secondary OC present in the background.

3.5. Primary and Secondary Source Contributions

[17] Three indirect methodologies have been applied in the evaluation of SOC formation in the atmosphere. These include the utilization of OC/EC ratios in samples collected in condition of low photochemistry [*Strader et al.*, 1999; *Cao et al.*, 2003, 2004; *Cabada et al.*, 2004; *Chu*, 2005], the use of a source receptor model (e.g., chemical mass balance [CMB]) after speciation and identification of marker compounds [e.g., *Watson et al.*, 1984; *Strader et al.*, 1999], and

Table 4. Relationship Between OC and EC Concentrations

	Winter		Summer	
City	OC(y) = a + *b*EC(x)	R^2	OC(y) = a + *b*EC(x)	R^2
BJ	y = −3.31 + 4.31x	0.99	y = 9.56 + 1.72x	0.54
CC	y = 9.47 + 2.20x	0.56	y = 2.01 + 3.52x	0.90
JC	y = −6.04 + 5.77x	0.63	y = 7.45 + 0.42x	0.03
QD	y = −0.01 + 4.23x	0.87	y = −1.54 + 4.72x	0.78
TJ	y = −1.69 + 4.76x	0.83	y = 8.45 + 2.19x	0.64
XA	y = 1.32 + 4.67x	0.58	y = 7.42 + 2.85x	0.87
YL	y = 1.09 + 3.43x	0.90	y = 1.48 + 3.73x	0.25
CQ	y = 4.69 + 4.35x	0.91	y = 5.63 + 2.43x	0.59
GZ	y = −1.55 + 2.94x	0.96	y = 11.11 − 0.16x	0.003
HK	y = 2.40 + 1.52x	0.66	y = 1.32 + 1.68x	0.82
HZ	y = 2.94 + 2.95x	0.66	y = 10.30 + 1.88x	0.27
SH	y = 3.93 + 2.97x	0.91	y = 5.90 + 2.52x	0.72
WH	y = −2.23 + 4.81x	0.76	y = 5.61 + 2.85x	0.31
XM	y = 1.03 + 3.11x	0.63	y = 1.94 + 1.73x	0.87

Table 5. Least-Squares Regression Results for Organic (OC) and Elemental Carbon (EC) Concentrations Grouped by OC/EC Ratio

Lowest % by OC/EC	Winter, North	Number of Data	Winter, South	Number of Data	Summer, North	Number of Data	Summer, South	Number of Data
5	2.32	5	1.43	5	1.69	4	1.08	3
10	2.55	10	1.6	10	1.77	7	1.2	7
20	2.81	20	2.13	19	1.99	14	1.29	14
30	2.97	31	2.34	29	2.15	21	1.66	21
40	3.09	41	2.53	38	2.42	28	1.94	28
50	3.26	51	2.71	48	2.63	35	2.13	35

chemical transformation source models [*Strader et al.*, 1999].

[18] The measurements reported here are applicable to the OC/EC enrichment factor, the first approach. Primary OC is obtained:

$$OC_{pri} = a + bEC, \quad (1)$$

where a and b are the intercept and slope, respectively. The product bEC represents the primary OC associated with combustion sources (e.g., coal combustion, traffic). The intercept a, is considered to be the primary OC background concentration. SOC (OC_{sec}) is the difference between the measured OC and primary OC (1):

$$OC_{sec} = OC - OC_{pri} \quad (2)$$

[19] The underlying assumption of this method is that, at a certain location, there is a fixed relationship between the primary OC and EC concentrations, i.e., the OC/EC ratio (i.e., slope) and the OC background concentration (i.e., intercept) are constant during the season.

[20] Since the validity of the primary OC/EC ratio is crucial to the success of the EC tracer model (above equations), two steps are applied to search for the best estimate of this ratio [*Lim and Turpin*, 2002; *Cabada et al.*, 2004]. The first step is to subtract data points where rain and the corresponding storms cause significant changes to the OC/EC ratio [*Cabada et al.*, 2004]. These changes have a variety of causes (removal of aged particles and increased importance of the locally produced ones, preferential removal of secondary OC, etc.). These periods are excluded from the analysis to avoid unnecessary complications. The second step consists of identifying the OC and EC concentrations with lowest probability of SOC production. The most challenging point is that this approach assumes invariability in source contributions to primary particulate carbon. The abundance of OC and EC varies among sources such as coal, diesel, gasoline, and wood combustion [*Watson et al.*, 1994, 2001; *Cao et al.*, 2005]. Since the primary OC/EC ratio is location- and season-dependent [*Yuan et al.*, 2006], this analysis separates the 14 cities into northern and southern cities for winter and summer.

[21] The season-specific primary OC/EC ratios were approximated using samples that had the lowest 5–10% OC/EC ratios [*Lim and Turpin*, 2002; *Yuan et al.*, 2006]. Table 5 provides the data points and slopes of least squares regressions of OC on EC. Because the data point in the lowest 5–10% is less than 10, the OC/EC ratios may not be representative. The slopes gradually increase with inclusion of more data. The slopes in the lowest 20% OC/EC ratios would be a reasonable estimate of the primary emissions since (1) the data point is enough for a least squares regression when comparing with previous studies (26 samples in the work by *Lim and Turpin* [2002]; around 20–30 samples in the work by *Yuan et al.* [2006]) and (2) the primary OC/EC ratio is 1.29 in southern cities during summer, which is close to the summer ratio of 1.1 reported by *Cao et al.* [2004] for the Pearl River Delta Region of southern China.

[22] The fraction of SOC in total carbon (TC) is illustrated in Figure 2, based on primary OC/EC ratios of 2.81 for northern cities in winter, 2.10 for southern cities in winter, 1.99 for northern cities in summer, and 1.29 for southern cities in summer (Table 5). By this estimate, SOC accounted for 23.7% and 25.6% of TC during winter, and 36% and 41.5% of TC during summer for the northern and southern cities, respectively. It is reasonable that the lowest faction (23.7%) of SOC occurred in northern cities in winter because lower temperatures (average temperature is about −22°C to −6°C) and reduced sunlight (less photochemistry) are not favorable for SOC formation. As noted earlier, contributions from primary emissions like residential coal combustion for (from mid-November to mid-March) are expected to be higher. The highest percentage (41.5%) of SOC in southern cities during summer is consistent with high potential photochemistry and low contributions from coal combustion. On average, the POC, SOC and EC account for 47.5%, 31.7% and 20.8%, respectively, of TC for this study; that is, more than two thirds of carbonaceous particles in Chinese urban atmosphere originate from primary emission sources. The OC/EC enrichment factor is a first-order estimate with large, but correctly unquantifiable, uncertainties. These results suggest, but do not prove, that SOC could be an important $PM_{2.5}$ component that needs further study in Chinese cities.

3.6. Variability of OC/EC Ratios

[23] The OC/EC ratio influences the relative amounts of particle light scattering and absorption, and constant ratios are often assumed in radiative transfer models. For this study, average OC/EC ratios ranged from 2.0 to 4.7 during winter and from 2.1 to 5.9 during summer. Average OC to EC ratios were 3.8 during winter and 4.2 during summer, with an average of 4.0 for both seasons. A 4.0 ratio is also assumed for fossil fuels combustion emissions [*Koch*, 2001]. The OC/EC ratio as a function of EC is illustrated in Figure 3 for winter and summer. Winter OC/EC ratios ranged from 2.0–6.0 independent of EC concentrations.

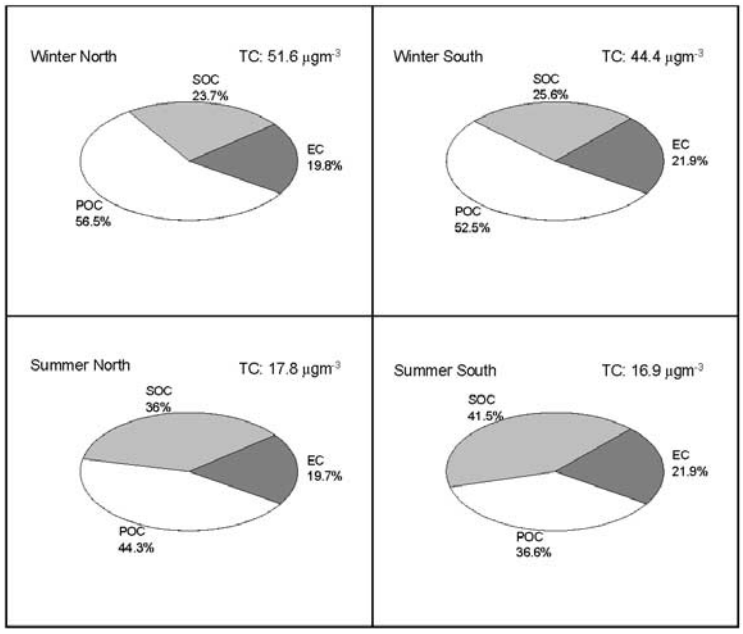

Figure 2. Relative percentage of primary and secondary sources contributed to total carbon.

However, the summer data shows that high OC/EC ratios (>6.0) are clustered at EC concentrations <2 μg m^{-3}, which were often related to the precipitation events. Other OC/EC ratios fall in the range of 2.0–6.0.

[24] Around 24% and 30% of global OC and BC emissions originate from China [*Bond et al.*, 2004]. Where coal is the major energy source. China produces and consumes 25% of the world's total coal [*Liu and Diamond*, 2005], constituting ~70% of the national energy budget. Coal will be China's dominant energy source for next 20 a owing to the abundant coal resources and a lack of petroleum and natural gas [*Aldhous*, 2005].

[25] Residential coal combustion aerosol has shown OC/EC ratios as high as 12 [*Cao et al.*, 2005]. The average OC/EC ratios from this study of 4.0 are higher than the 2.3 reported by *Novakov et al.* [2005] on the basis of published carbon concentrations from developed cities with have rising influences of motor vehicle exhaust. High OC/EC ratios may have relevance to climate effects of anthropogenic soot aerosols. *Hansen et al.* [2000] and *Jacobson* [2002] suggested that control anthropogenic BC emissions would help slow global warming. *Penner et al.* [2003] demonstrated that the cooling effect of OC that accompanies EC, together with the indirect effects of both OC and

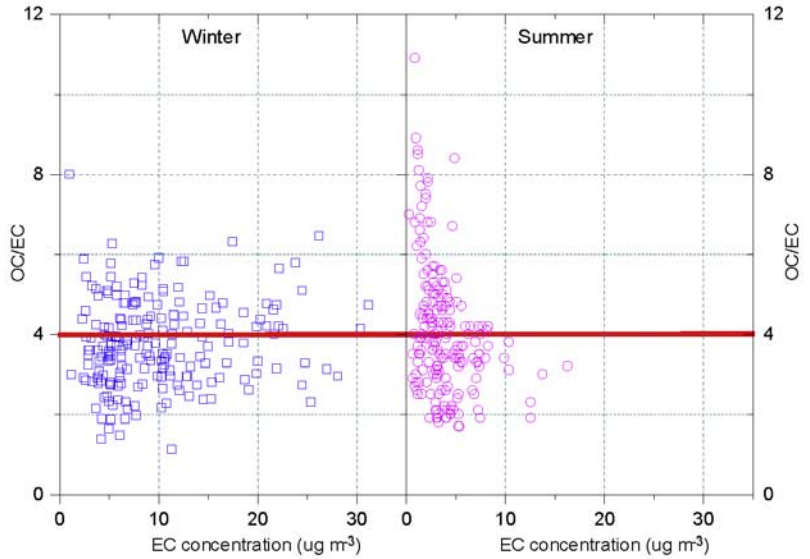

Figure 3. Distribution of OC/EC ratios versus EC concentrations in winter and summer.

EC on cloud properties, make it uncertain whether the net effect of soot (OC + EC) emission is warming or cooling. *Hansen et al.* [2005] estimated that the net effect of fossil fuel soot is warming, while biomass burning produces global cooling. So, elevated estimates for OC/EC ratios here suggest a cooling effect of carbonaceous aerosol from China.

4. Conclusion

[26] The properties and atmospheric effects of carbonaceous aerosols in China are characterized by paucity of data. This work presents a national-scale measurement of atmospheric OC and EC in fourteen selected cities. Distinct characteristics of carbonaceous aerosols in China can be summarized as follows: high levels of OC and EC, higher OC/EC ratios than elsewhere, and dominant by primary source contributions. Taking into account the important role of China's carbonaceous aerosol in global system, further work should be concentrated on their physical and chemical characterization.

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