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# One-year record of organic and elemental carbon in fine particles in downtown Beijing and Shanghai

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## Abstract

Weekly $PM_{2.5}$ samples were collected for one year in Beijing and Shanghai and the carbonaceous species analyzed to investigate and compare their time series patterns and possible sources in the two biggest cities of China. Weekly carbonaceous concentrations varied in wide ranges with 8.6–59 $\mu g\,m^{-3}$ for OC and 1.5–25.4 $\mu g\,m^{-3}$ for EC in Beijing, and with 5.1–38.4 $\mu g\,m^{-3}$ for OC and 2.3–13.0 $\mu g\,m^{-3}$ for EC in Shanghai. The annual average concentrations of OC and EC in $PM_{2.5}$ were 23.9 and 8.8 $\mu g\,m^{-3}$ in Beijing and 14.6 and 6.10 $\mu g\,m^{-3}$ in Shanghai, respectively. Similar weekly variations of OC and EC concentrations were found for both cities with much higher concentrations in late fall through winter, probably due to enhanced emissions coupled with unfavorable meteorological conditions. The estimated SOC accounted for high portion of the total OC in both Beijing and Shanghai throughout the year, indicating SOC may be an important contributor to fine organic aerosol in these urban areas. In Beijing, the C14 analysis of limited samples suggested there was a significant contribution of modern carbon to the total fine carbonaceous particulate burden with higher fractions in the harvest seasons.

## 1. Introduction

Organic and element carbon (OC and EC) aerosol are usually concentrated in the fine size class and typically constitute a significant, sometimes dominant, fraction of the total fine particle mass, especially in urban areas (Gray et al., 1986; Shah et al., 1986; Castro et al., 1999; Andrews et al., 2000). EC is released directly from the incomplete combustion of fossil fuels and biomass while OC, an aggregate of hundreds of individual compounds spanning a wide range of chemical and thermodynamic properties, is formed by a variety of processes, including combustion and secondary organic carbon (SOC) formation. Recently, increased attention has been focused on the carbonaceous component of fine particulate matter (PM) because of the role OC and EC



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play in visibility reduction, the radiative budget of the atmosphere (Tegen et al., 1997; Malm and Day, 2000; Jacobson, 2001), and their potential to influence many heterogeneous reactions involving atmospheric aerosols and trace gases (Lary et al., 1999), and because of the suspected health effects of some of the individual OC components of known toxicity such as PAHs (Lioy and Daisey, 1986; Kunzli et al., 2000). Jacobson (2002) concludes, based on a global-model calculation, that control of fossil-fuel carbonaceous PM is possibly the most effective method of slowing global warming, along with improving human health. In the meantime, China is of great concern because its high rates of usage of coal and biofuels, which are primarily responsible for high black (element) carbon (BC) emissions (Streets et al., 2001). Menon et al. (2002) suggest that the observed trend in China over the past several decades, with increased summer floods in the south and drought in the north, may be related to increased BC aerosols,

With recent rapid industrialization and urbanization, the city-clusters have formed in the three most developed regions in China through the connection of intensive economic activities. These regions, all located in the eastern coast areas, are Pear River Delta Region (PRDR), Yangtze River Delta Region (including Shanghai, Jiangsu and Zhejiang provinces), and Beijing-Tianjin Region. Due to booming economic activities and fast increased vehicle population within the regions, high PM levels and poor visibility have become a common serious problem. According to the 1997 China Environmental Situation Report (State Environmental Protection Administration of China, 1998), Guangzhou, Beijing, and Shanghai, the center in each of these regions, are the worst for $NO_X$ pollution of all the Chinese cities with annual averages of over 100 $\mu$g $m^{-3}$, implying vehicular pollution is getting more and more serious while coal smoke pollution is still far to be under effective control. These two kinds of major sources are believed to emit abundant fine carbonaceous particles aside from biomass burning in the urban areas of China.

Cao et al. (2003) investigated the relative contribution of carbonaceous aerosol to $PM_{2.5}/PM_{10}$ and SOC production in PRDR based on ambient sampling during 2002

winter period. Their study demonstrated that carbonaceous aerosol was a significant contributor to $PM_{2.5}$ and SOC was an important component of fine organic PM with an average fraction of 42.6%. To our knowledge, there are very limited researches focusing on fine carbonaceous particles reported to date for the urban areas of the latter two regions (He et al., 2004; Dan et al., 2004), which are based on short-term measurement with the overall sampling period rarely exceeding a few weeks. We initiated a 1-year $PM_{2.5}$ monitoring program in 1999 in Beijing and Shanghai. We showed that carbonaceous and secondary ionic species (e.g., sulfate, nitrate, and ammonium) dominated the $PM_{2.5}$ in the two cities (He et al., 2001; Ye et al., 2003). This study is a part of that program with a focus on the time series of carbonaceous species, their possible sources and comparison for the two urban areas during a 1-year period. This information will provide a baseline to examine the reasons of heavy carbonaceous particulate pollution and its trends and has implications for local and regional PM control effectiveness in China.

## 2. Sampling and analysis

Beijing, the capital of China, is located at the northwestern border of the Great North China Plain at 39°48′ N latitude and 116°28′ E longitude. The main terrain of Beijing is plain, with mountain embaying in 3 directions, and on southeast, plain turns into a "dustpan" spreading forward. The area of planning district only takes 6% of the total area of Beijing, but 50% of the total population, 80% of buildings, 60% of the industrial output value and 80% of the energy consumption are concentrated here. Shanghai, a national commercial center, is situated at the mouth of the Yangtze River at 31°14′ N latitude and 121°19′ E longitude. It is bordered by the East China Sea on the east and Hangzhou Bay on the south. Population is also strongly concentrated in the inner urbanized area of Shanghai municipality. The special geographical environment and deficient city planning of Beijing make the air pollution stagnant over the urban area, which can not be easily expelled relative to that in Shanghai. The PM concentration

level in Beijing is usually about twice that in Shanghai. For example, the annual mean concentrations of the total suspended particles (TSP) in 1999 were 364 and 188 $\mu g\,m^{-3}$ in Beijing and Shanghai, respectively.

Ambient $PM_{2.5}$ sampling was conducted simultaneously at a pair of locations (Chegongzhuang and Tsinghua in Beijing and Hainan Road and Tongji in Shanghai) from July 1999 to June 2000 in Beijing and in Shanghai from March 1999 to March 2000. Chegongzhuang lies in urban area in Beijing but not Tsinghua while the two Shanghai sites both locate in urban area. Our former papers have shown impressive similarity in $PM_{2.5}$ concentration and composition for the two locations in each city of Beijing and Shanghai (He et al., 2001; Ye et al., 2003). In this study we therefore choose Chegongzhuang and Tongji sites to represent urban areas of each city for further comparative analysis since the sampling period was longer at the Tongji site than at Hainan Road (Ye et al., 2003). The sampling sites were about 3 m and 16 m above the ground in Beijing and Shanghai, respectively. Both sites were approximately 50 m from major roads. During the study period, 49 and 51 sets of samples were collected at each site in Beijing and Shanghai, respectively. More detailed introduction of the sampling locations, the ambient sampling and chemical analyses of $PM_{2.5}$, and the quality assurance employed in this study are referred to He et al. (2001) and Ye et al. (2003).

Roughly, special low flow rate samplers equipped with three cassettes for collecting $PM_{2.5}$ for speciation analysis, each at an identical flow rate of 0.4 / $min^{-1}$, were used (Aerosol Dynamics, USA). Of the three parallel sampling cassettes, a tandem-filter $PM_{2.5}$ cassette accommodates two Gelman (Ann Arbor, MI) quartz-fiber filters (#2500 QAT-UP) for carbon analysis. These filters were prefired at 900°C in air for a minimum of three hours to remove any carbon. The front quartz filter of the tandem-filter $PM_{2.5}$ cassette was analyzed for OC and EC by the thermal/optical reflectance (TOR) method at the Desert Research Institute (DRI) in Reno, NV. A subset of the backup quartz filters was also analyzed for volatilized/adsorbed carbon. It is recommended to analyze only the front quartz filter (Chow et al., 1994; US EPA/NARSTO, 1998). Therefore, the OC results reported in this paper are uncorrected, i.e. the front quartz-fiber filter only. It is

noted, however, that we analyzed the backup quartz samples once every four weeks, and the backup filter average OC concentrations were about 35% of those on the front quartz samples in our Beijing study.

## 3. Results and discussion

### 3.1. Time series of OC and EC

As shown in Fig. 1, OC and EC exhibited similar weekly variations in both Beijing and Shanghai. Weekly concentrations of OC ranged from 8.6 to 59 $\mu g\,m^{-3}$ in Beijing and from 5.1 to 38.4 $\mu g\,m^{-3}$ in Shanghai, while those of EC varied from 1.5 to 25.4 $\mu g\,m^{-3}$ in Beijing and from 2.3 to 13.0 $\mu g\,m^{-3}$ in Shanghai. OC and EC concentrations experienced more or less significant variations from week to week in both Beijing and Shanghai. The slight weekly variations and low levels of OC and EC concentrations in the summer are reasonable since the local wind is mild in this season. Strong weekly shifts and high levels of OC and EC concentrations usually occurred in the late fall through winter, probably due to much enhanced combustion source emissions coupled with frequent northerly Asian monsoon conditions.

A severe episode occurred the week of 18–25 November in Beijing, which had the maximum weekly concentrations of OC and EC for the study period. In this week, it was evident that emissions from combustion sources increased dramatically since space heating started on 15 November. Daily wind speed was less than 1.4 $m\,s^{-1}$ during the week, except on 24 November, and relative humidity was as high as 65–91% from 20 November through 23rd. This kind of meteorological condition favors trapping pollutants since dispersion is low, thereby increasing the accumulation of fine particles. In the next week, their concentrations dropped to much lower values due to snowfall and better meteorology for atmospheric dispersion. This sharp variation of meteorological conditions resulted in the OC and EC concentrations dropping by 55% and 68%, respectively, for the second of these two consecutive weeks. Due to mixed



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influences of different processes on the loadings of ambient carbonaceous species, consecutive sampling with higher resolution would be more appropriate to interpret the temporal variations of the carbonaceous species with meteorological episodes in different seasons.

As shown in Fig. 2, clear seasonal patterns in carbonaceous species were observed in the two cities. OC and EC both exhibited much higher concentrations in fall and winter and much lower concentrations in the spring and summer except that in Shanghai OC showed intermediate level in the spring. In Beijing, the average concentrations of OC and EC in the winter were 30.2 and 10.5 $\mu g\,m^{-3}$, 26% and 19% higher than their annual means, respectively. In Shanghai, the winter average concentration of OC was very close to the lowest seasonal OC value in Beijing while that of EC was intermediate between the high and low seasonal EC values in Beijing.

This seasonal variation is likely due to a combination of changes in emission rates and seasonal meteorology. Low summer concentrations can be explained in part by the fact that about three quarters of its annual precipitation (584 mm on average) in Beijing occurs in this season (Yang et al., 2004a). Shanghai also receives abundant rains in the summer with about half of its annual precipitation (1040 mm on average) falling during the May-September flood season. In the spring, the prevailing northwest wind in Beijing could cause the rapid dispersion of pollution-derived fine particles including carbonaceous particles from local emissions while increase regional and/or local soil dust (Yang et al., 2004b). Given that it was the coldest winter in the last 23 years in Beijing, the high concentrations of carbonaceous species could be due to enhanced space heating activities as well as to longer vehicle cold starts (Chow et al., 1993; Singer et al., 1999). In addition, the low temperature and frequent inversion were also likely favorable for the formation of secondary organic aerosol according to the study by Sheehan and Bowman (2001) using an absorptive-partitioning model.

### 3.2. Concentration levels of OC and EC

Descriptive statistics of the average concentrations of OC, EC, total carbon (TC, i.e. sum of OC and EC), particulate organic matter (POM), and the percentages of TC and POM in $PM_{2.5}$ for this study are summarized in Table 1. According to a very recent work by Turpin and Lim (2001), urban POM may be better estimated by multiplying the amount of OC by 1.6±0.2. The factor of 1.6 is adopted in the current study. The literature values from urban areas of Guangzhou (Cao et al., 2003), Los Angeles (Kim et al., 2000), and Chongju (Lee et al., 2001) are also included for comparison. All these studies except Guangzhou study covered a period of about one year, and adopted the same method (TOR) and analyzer (DRI products) to measure carbonaceous species, thus these results are of high comparability. Chongju is a medium sized subtropical coastal city in Korea that did not have serious atmospheric pollution problems at that time. Los Angeles is a mega city with air pollution mainly caused by vehicular emissions. Coal combustion is not a major source of PM in these two foreign cities.

The average concentrations of OC ($23.9\,\mu g\,m^{-3}$) and EC ($8.79\,\mu g\,m^{-3}$) in Beijing were 55% and 30% higher than those in Shanghai, respectively. It is noted that these concentration levels and the calculated amount and percentages of TC and POM were very close to those measured in the winter months of 2002 in Guangzhou, which had the highest $PM_{2.5}$ mass and carbonaceous concentrations among the urban areas of PRDR (Cao et al., 2003). For OC, the average concentration in Beijing was 4.8 and 4.0 times those in Los Angeles and Chongju, respectively, and 8 times the continent background value (about $3\,\mu g\,m^{-3}$) in the USA (Malm et al., 1994). The EC concentration in Beijing was a factor of 2.3 higher than in Los Angeles, approximately twice that in Chongju, and greater than that determined as the background value at Marblemount National Park in USA (Malm et al., 1994) by a factor of 22. The EC value in Shanghai was intermediate between those of Beijing and Los Angeles and Chongju while the OC value was more than 2.6-fold those of the two foreign cities. These comparisons indicate that both Beijing and Shanghai have been heavily polluted by fine carbonaceous

particles and their majorities likely originated from anthropogenic sources.

Coal is used in both honeycomb briquette stoves and industrial coal-burning boilers in Chinese cities including Beijing and Shanghai. Both of these sources emitted abundant carbonaceous particles as reported before by Chen et al. (1994) and Zhang et al. (2000), respectively. Considering the annual coal consumption was much less in Beijing than in Shanghai (26.5 and 39.6 million tons in 1999, respectively), it was expected that the emission intensities of fine carbonaceous particles were probably much higher in Beijing. Shanghai used its coal mainly in power plants and industrial sectors while Beijing consumed major its coal in winter due to residential heating (about 23% of coal was used for this purpose alone). In urban area of Beijing at that time there were many areas where crude coal was the main fuel for residents, including a significant migrant population (about 3 million in all), which tended to burn low quality honeycomb briquettes or even raw coal for heating and cooking (which were popular in residential areas with single-story houses in and around the urban area). Since the emissions from residential heating are emitted near ground level, and are likely to be higher per unit mass of coal than for boilers, their contribution to the winter levels of carbonaceous species in Beijing is likely to be significant. This is supported by the fact that the abundance of OC in $PM_{2.5}$ from a honeycomb coal stove was one order of magnitude greater than that from a utility boiler (Chen et al., 1994). In addition, it was popular to burn maize and wheat residue in situ especially in the northern rural areas. For this kind of biomass burning it was reported that over 60% was emitted as carbonaceous particulate (Watson and Chow, 2001). Another possible factor was that the SOC contribution was different between Beijing and Shanghai due to their differences in both atmospheric oxidation ability and the amount of the gaseous organic pollutants that may transform into fine particles. At last, the geographical and meteorological conditions could also be important reasons for different carbonaceous intensity in fine particles between Beijing and Shanghai as mentioned above. In the future study, an inventory and a source profile of carbonaceous particles will help explain in a quantitative way the above difference in OC and EC levels between Beijing and Shanghai.

TC was the most abundant single species of $PM_{2.5}$ in both Beijing and Shanghai. The fraction of $PM_{2.5}$ mass was highest in Shanghai (34%) and lowest in Chongju (21%). The Beijing percentage (28%) was somewhat lower than that in Los Angeles (32%) but intermediate between the highest and lowest values. POM accounted for more than 30% of $PM_{2.5}$ mass in all the listed metropolitans while in Chongju the value was as low as of 18%. OC was the predominant contributor to TC with an average percentage of more than 70% in both Beijing and Shanghai. The average EC fraction of TC in this study were much less than those (38–86%) measured in many areas worldwide including Tokyo, Nagoya, Sapporo, Uji, and some remote sites in Japan but similar to the percentages determined in Long Beach, USA and in Amsterdam, Netherlands (Hller et al., 2002). The measured concentration of EC, however, was much higher in Beijing. Because of its light-absorbing feature, the high EC level was undoubtedly one of the major factors causing visibility impairment in Beijing.

EC production is uniquely related to combustion including both fossil fuel and biomass burning while the combustion of the fossil fuel, especially of petroleum products seems to generate little non soil potassium $K_{excess}$. Therefore, Andreae (1983) suggests the mass ratio of $K_{excess}$ to EC may prove an important tracer in the source identification of pollutant aerosol. We estimate soil potassium using the mass ratio of K to Fe in Beijing and Shanghai crusts of 0.65 and 0.56, respectively (China Environmental Monitoring Center, 1990; Yang et al., 2004b). The calculated $K_{excess}$/EC ranged between 0.10–0.51 with an average of 0.23±0.08 in Beijing. This average ratio were much higher than those observed in the United States (0.025 to 0.09) and close to the lower end of the values measured on aerosols dominated by brush-fire emissions collected in Brazil (0.21 to 0.46) (Andreae, 1983), probably suggesting that biomass burning had important contribution to fine EC particles in Beijing. In Shanghai, the $K_{excess}$/EC ratio exhibited somewhat lower average with much larger deviation (0.19±0.15) than that in Beijing, probably implying that fine carbonaceous pollution in Shanghai was also significantly affected by biomass burning. This argument is supported by the work of Xu et al. (2002), who claimed that a significantly fraction of the

high OC mass in $PM_{2.5}$ ($44\,\mu g\,m^{-3}$) measured at Linan in the rural Yangtze Delta Region was likely attributed to biomass burning activities after rice harvest.

C14 analysis of a limited set of samples collected at the same site in Beijing in 2001 showed the fraction of modern carbon, which originates from modern sources such as biomass burning and restaurant emissions as opposed to the fraction that originates from fossil fuel sources such as coal or petroleum based products, ranged from 0.33 to 0.48 with an overall average of 0.40 (Table 2). These samples were collected using the same sampler employed in this study and analyzed for OC and EC at DRI using the TOR method and at the Woods Hole Oceanographic Institute (WHOI) for C14 by acceleratory mass spectrometry (Reddy et al., 2002). Given the obvious similarities in the average OC and EC concentrations (25.8 and $8.73\,\mu g\,m^{-3}$, respectively), the EC percentage of the total carbon (28%), and the total carbon percentage of the total $PM_{2.5}$ mass (27%) for these selected samples and those in this study, it is likely that modern carbon fraction determined for these samples is representative of the modern fraction for this study period as well. It is noted that the modern fraction tended to be higher in the later part of 2001(summer and autumn), likely due to intensive biomass burning - whether of agricultural residues in the field after harvest or land clearing for production of new agricultural fields. Duan et al. (2004) report that biomass burning emissions may sometimes account for 43% of OC in TSP at an urban site of Beijing during the wheat harvest season and suggest much more contribution for $PM_{2.5}$ as biomass burning is almost entirely confined in the submicrometer sized-range. These authors conclude that Beijing aerosols may be heavily influenced by different types of biomass burning all the year long with the maximum influence in June, which corresponds to the date of our highest modern carbon fraction value. Overall, it is apparent that there is a significant contribution of modern carbon to the fine carbonaceous PM burden.



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### 3.3. Relationship between OC and EC

As mentioned above, the obvious temporal coherence between OC and EC was observed for both Beijing and Shanghai samples. Further statistical analysis indicated they were strongly correlated with a correlation coefficient r=0.90 for 47 samples in Beijing and r=0.82 for 51 samples in Shanghai (Fig. 3). These co-varying patterns suggested that the ambient concentration levels of carbonaceous species were controlled by similar processes (including source emissions and atmospheric dispersion), and that OC and EC were likely attributable to their common dominant sources of combustion such as coal burning. When split seasonally, OC and EC data presented somewhat different correlations between the two cities. In Beijing, they were highly associated in all the seasons with r ranging from 0.79 to 0.94, while in Shanghai they were strongly correlated in the summer through winter (r=0.75–0.93), whereas they were not distinctly correlated in the spring. We do not have an explanation now for this difference in spring OC-EC correlations between Beijing and Shanghai, which needs to be further studied using higher resolution ambient carbonaceous PM sampling.

The mass ratio of OC to EC (OC/EC) can be used to interpret the emission and transformation characteristics of carbonaceous aerosol. As diagrammed in Fig. 1, the OC/EC ratios exhibited weekly variations and no clear seasonal trends were found in both Beijing and Shanghai for the study period. This implied that the OC/EC ratios were not sensitive to seasonal parameters such as meteorology and changing source emissions, although OC and EC concentrations were. For most of the samples, the weekly OC/EC ratios shifted between 2.0 and 4.0 in the two cities. Weekly OC/EC ranged from 1.7 to 5.8 with an average of 2.9 in Beijing, and from 1.6 to 4.3 with an average of 2.5 in Shanghai. On average, these OC/EC ratios were comparable to those measured at urban sites in the PRDR (Cao et al., 2003) but much higher than those in Chongju (Lee et al., 2001) and Los Angeles (Kim et al., 2000).

Because EC originates solely as a primary emission and is inert in the atmosphere, it is often used as a tracer of primary OC. Ambient ratios of OC/EC that are greater

than the OC/EC ratio of the primary aerosol indicate times when secondary formation occurred. An OC/EC ratio exceeding 2.0–2.2 has been used to indicate the presence of secondary organic aerosols in some studies (Gray et al., 1986; Turpin et al., 1990; Chow et al., 1996). If that was true for Beijing and Shanghai aerosol, SOC was formed during most of the study period. However, it is difficult to conclude the presence of SOC from the absolute values of OC/EC alone since OC/EC ratios are strongly source dependent and therefore quite variable (Gray et al., 1986; Watson et al., 2001; Na et al., 2004). According to a source profile measured in Beijing by Chen et al. (1994), the OC/EC ratios for emissions from honeycomb coal stove, briquette stove, utility boiler, and industrial boiler were 8.54, 1.05, 2.32, and 2.51, respectively. For different tropical biomass burning, the OC/EC was as high as 9.0 (Cachier et al., 1989). Overall, the combustions of coal and biomass exhibited much higher OC/EC ratios than that for motor vehicle (1.1) measured by Watson et al. (2001), and thereby likely important contributors to high ambient OC/EC ratios of $PM_{2.5}$ in both Beijing and Shanghai.

### 3.4. Estimation of SOC

OC consists of a complicated mixture of species from both primary and secondary sources. The fractions of organic aerosols from these two kinds of sources are not generally known although modeling efforts are proceeding. For an indirect method to evaluate the SOC concentrations, Castro et al. (1999) suggested that samples having the lowest OC/EC ratios contain almost exclusively primary carbonaceous compounds based on the consistent presence of a clear minimum ratio for OC/EC in urban and rural areas, in the winter and summer. According to these researchers, the SOC concentration can be estimated from:

$$\mathrm{SOC}=\mathrm{OC}-\mathrm{EC}\times(\mathrm{OC}/\mathrm{EC})_{min}, \quad (1)$$

where, OC the total measured OC, and$(\mathrm{OC}/\mathrm{EC})_{min}$ the minimum ambient OC/EC to represent the primary OC/EC ratio. In our study, the minimum values of OC/EC were similar with 1.68 and 1.62 in Beijing and Shanghai, respectively. These values were

close to the low end of the range of primary OC/EC values of 1.7–2.9 estimated by Turpin and Huntzicker (1995) in southern California, but much larger than the minimum OC/EC values of 1.1–1.3 determined at some urban locations in both Europe(Castro et al., 1999) and the PRDR (Cao et al., 2003).

The estimated seasonal SOC concentrations and their contributions to total OC are summarized in Fig. 4. The annual average concentrations of SOC were estimated at 9.1 $\mu g\,m^{-3}$ in Beijing and 4.7 $\mu g\,m^{-3}$ in Shanghai, accounting for 38% and 31% of the total OC mass, respectively. This high proportion indicates secondary organic material may be a significant contributor to fine organic particles throughout the year. In Beijing, SOC exhibted simialar seasonal pattern as the total OC with the highest concentrations in the winter and the lowest in the summer. In Shanghai, different from the total OC, no clear seasonal trend was found for SOC concentrations with the highest concentration and fraction both in the spring. There was only less than 10% for seasonal differences in SOC fractions in Beijing whereas those in Shanghai could be as high as close to 20%. The greatest differences in SOC concentrations and fractions between the two cities occurred in the winter, when in Beijing the OC concentration was higher by a factor of about 3 while the fraction difference was 17%. In the spring, their differences were modest.

Given that small proportions of SOC may still exist in the samples with minimum OC/EC ratios (Na et al., 2004), and that our ambient sampling was for one-week integrated periods in this study, this OC/EC method provides a lower limit for SOC content. Conversely, using the lowest value for an entire year may overestimate the SOC if the primary OC/EC ratio varies seasonally. Additional chemical characterization of the OC is needed to determine if the apparent SOC is, in fact, produced in the atmosphere, or is the result of varying impacts of different sources. In addition, there may be significant regional transport of PM within the city clusters mentioned above thereby giving a longer time for SOC to form. Additional work is ongoing to better understand the regional contribution to the Beijing and Shanghai aerosols.

## 4. Conclusions

OC and EC were at quite high levels in Beijing with annual concentration of 23.9 and 8.79 $\mu g\,m^{-3}$, 55% and 30% greater than those in Shanghai, respectively, indicating these two cities have been heavily polluted by fine carbonaceous particles and their majorities likely originate from anthropogenic sources. OC and EC exhibited both weekly and seasonal co-variation patterns in both Beijing and Shanghai. Strong weekly changes and high levels of OC and EC concentrations both occurred in late fall and winter, probably due to much enhanced combustion source emissions and low dispersion meteorology. The estimated annual average SOC concentration in Beijing was nearly twice that in Shanghai. SOC may be an important contributor to fine organic aerosol throughout the year with an average fraction of 38% and 31% to the total OC mass in Beijing and Shanghai, respectively. The C14 analysis of limited samples suggests there was a significant contribution of modern carbon to the total fine carbonaceous PM burden in Beijing with higher modern fractions in the harvest seasons. The comparative analysis of EC and excessive potassium also implies fine carbonaceous particulate pollution in both Beijing and Shanghai was strongly influenced by biomass burning throughout the year.

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**Table 1.** Statistical summary of the concentrations ($\mu g\,m^{-3}$) and percentages of carbonaceous species in $PM_{2.5}$ in Beijing, Shanghai, and other cities.

| Locations | Sampling period | OC | EC | TC | POM | $TC/PM_{2.5}$ | $POM/PM_{2.5}$ |
|---|---|---|---|---|---|---|---|
| Beijing | 1999.7–2000.6 | 23.9 | 8.79 | 32.7 | 38.2 | 28% | 33% |
| Shanghai | 1999.3–2000.3 | 14.6 | 6.10 | 20.7 | 23.4 | 34% | 38% |
| Los Angeles | 1995.1–1996.2 | 5.96 | 3.81 | 9.77 | 9.54 | 32% | 32% |
| Chongju | 1995.10–1996.8 | 4.99 | 4.44 | 9.43 | 7.98 | 21% | 18% |
| Guangzhou | 2002.1–2002.2 | 22.6 | 8.30 | 30.9 | 36.2 | 29% | 34% |

**Table 2.** Modern carbon fraction in 2001 $PM_{2.5}$ samples from Beijing.

| Season | Sample starting date | OC $\mu g\,m^{-3}$ | EC $\mu g\,m^{-3}$ | TC $\mu g\,m^{-3}$ | $PM_{2.5}$ $\mu g\,m^{-3}$ | Modern carbon fraction |
|---|---|---|---|---|---|---|
| Winter | 11 Jan. | 43.2 | 7.8 | 50.9 | 160.5 | 0.337 |
| Winter | 15 Feb. | 37 | 12 | 50 | 208.4 | 0.330 |
| Spring | 08 Mar. | 26.6 | 6.4 | 33 | 137.8 | 0.381 |
| Spring | 15 Mar.* | 16.3 | 6.6 | 22.9 | 99.2 | 0.393 |
| Summer | 14 June | 18.7 | 9.1 | 27.8 | 105.4 | 0.497 |
| Summer | 12 July, 09 Aug.* | 15.4 | 6.9 | 22.3 | 83.3 | 0.387 |
| Fall | 20 Sept., 04 Oct.* | 19.3 | 9.4 | 28.7 | 79.4 | 0.421 |
| Fall | 08 Nov. | 22.6 | 11.9 | 34.4 | 105.2 | 0.457 |

* 2-week sample



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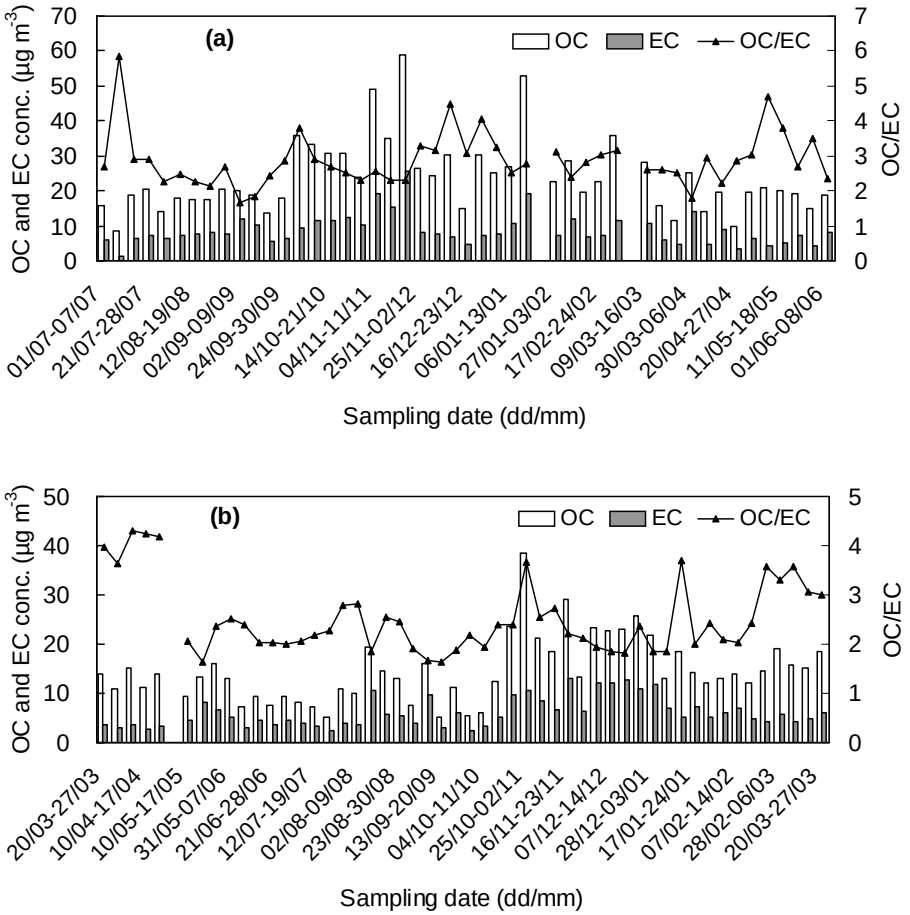


**Fig. 1.** Time series of weekly OC and EC concentrations in Beijing **(a)** and Shanghai **(b)**.



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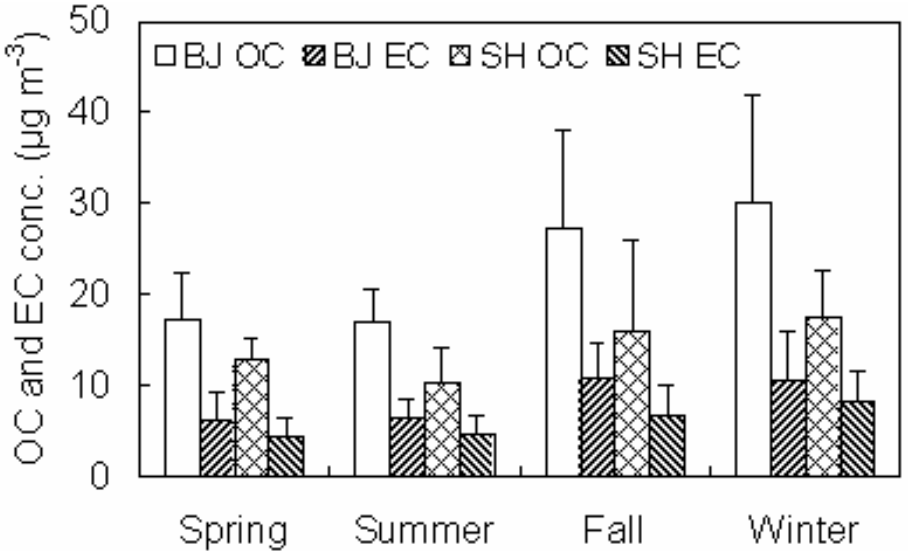


**Fig. 2.** Seasonal average concentrations of OC and EC in Beijing (BJ) and Shanghai (SH).



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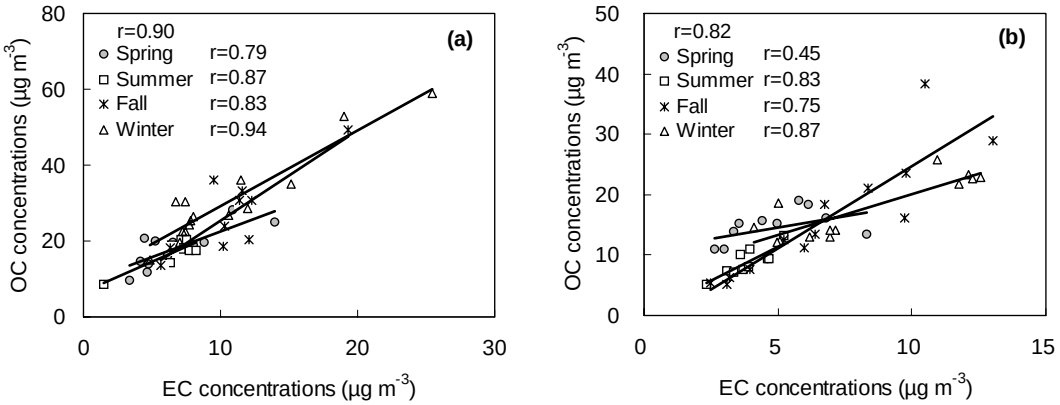


**Fig. 3.** Seasonal correlations of OC and EC concentrations in Beijing **(a)** and Shanghai **(b)**.



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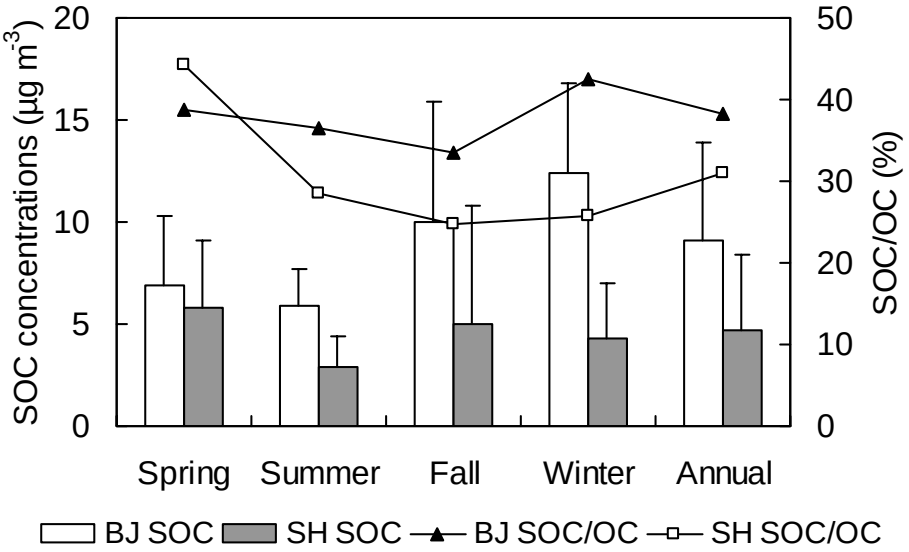


**Fig. 4.** Seasonal and annual average concentrations of estimated SOC and its fraction (%) in total OC in Beijing and Shanghai.