

Carbonaceous aerosols over China—review of observations, emissions, and climate forcing

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Abstract Carbonaceous aerosols have been attracting attention due to the influence on visibility, air quality, and regional climate. Statistical analyses based on concentration levels, spatial-temporal variations, correlations, and organic carbon (OC) to element carbon (EC) ratios from published data of OC and EC in particulate matter (PM_{2.5} and PM₁₀) were carried out in order to give a carbonaceous aerosol profile in China. The results showed maxima for OC of $29.5 \pm 18.2 \mu\text{g C m}^{-3}$ and for EC of $8.4 \pm 6.3 \mu\text{g C m}^{-3}$ in winter and minima for OC of $12.9 \pm 7.7 \mu\text{g C m}^{-3}$ in summer and for EC of $4.6 \pm 2.8 \mu\text{g C m}^{-3}$ in spring. In addition, OC and EC both had higher concentrations in urban than those in rural sites. Carbonaceous aerosol levels in China are about three to seven times higher compared to those in the USA and Europe. OC and EC occupied 20 ± 6 and 7 ± 3 % of PM_{2.5} mass and 17 ± 7 and 5 ± 3 % of PM₁₀ mass, respectively, implying that carbonaceous aerosols are the main component of PM, especially OC. Secondary organic carbon (SOC) was a significant portion of PM and contributed 41 ± 26 % to OC and 8 ± 6 % to PM_{2.5} mass. The OC/EC ratio was 3.63 ± 1.73 , which, along with the good correlation between OC and EC and the OC to EC slope of 2.29, signifies that coal combustion and/or

vehicular exhaust is the dominated carbonaceous aerosol source in China. These provide a primary observation-based understanding of carbonaceous aerosol pollution in China and have a great significance in improving the emission inventory and climate forcing evaluation.

Keywords Carbonaceous aerosol · Element carbon · Organic carbon · Secondary organic carbon · Emission inventory · Climate forcing

Introduction

Atmospheric particulate pollution has been an eye-catching issue in current China. Particles in the atmosphere not only play an important role on the environment and global climate but also have a health hazard as these can be absorbed into the human respiratory system and further into blood circulation through lung cells (Penner and Novakov 1996; Oberdörster et al. 2005). Carbonaceous aerosols are the main components of atmospheric particles and are composed of both light-absorbing element carbon (EC) and light-scattering organic carbon (OC) (Nunes and Pio 1993). EC, alternatively referred to as black carbon (BC) aerosol, is a product of incomplete combustion from residential coal, motor vehicle fuel, and biomass (Watson 2002). It is the mixture of graphite-like particles and optically absorbing organic matter. OC originates from primary anthropogenic sources like above combustions and from formation (secondary organic carbon, SOC) by chemical reactions in the atmosphere and represents a large variety of particulate organic compounds, including polycyclic aromatic hydrocarbons (PAHs) (Zhao et al. 2013a).

Carbonaceous aerosols have been of great concern in recent years due to their influence on regional climate, visibility,

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and air quality (Cao et al. 2004). IPCC report (Boucher et al. 2013) showed that the radiative forcing of BC and organic aerosols emitted by fossil fuel and biofuel combustion was $+0.4$ ($+0.05$ to $+0.8$) W m^{-2} and -0.12 (-0.4 to -0.1) W m^{-2} , respectively, and it was $+0.0$ (-0.2 to $+0.2$) W m^{-2} as a result of their change offset when BC and organic aerosol are emitted by biomass burning. Therefore, carbonaceous aerosols have a net warming effect on climate (Boucher et al. 2013). In addition, as the main components of atmospheric particle, OC and EC can be critical factors in the formation of severe pollution episodes, e.g., haze in East Asia, which is considered a heavily polluted region of the world, and may contribute to the highest dry extinction efficiencies among the major particulate matter ($\text{PM}_{2.5}$) species (Hou et al. 2011; Pui et al. 2014). Besides, it has been well known that PAHs in OC are carcinogenic, teratogenic, and mutagenic and may sorb on the surface of BC or small particles to enter into the lungs, even the bloodstream through the alveolar epithelium (Shrestha et al. 2010), and seriously endanger public health (Zhao et al. 2013a). Therefore, in recent years, more and more studies focused on the carbonaceous aerosols pollution (Viana et al. 2006; Harrison and Yin 2008; Yubero et al. 2014; Zhao et al. 2013b; Cao et al. 2004; Zhou et al. 2012; Sandrini et al. 2014; Srivastava et al. 2014).

China has the largest carbonaceous aerosols emissions from contained combustion in the globe with the contributions of about 24 and 30 % for OC and BC, respectively (Bond et al. 2004). Carbonaceous aerosols have been widely investigated in China since the end of last century and the number of locations keeps increasing, including urban sites in megacities (Shen et al. 2014; Xu et al. 2012), regionally representative rural sites (Zhang et al. 2005), and remote sites (Li et al. 2000; Qu et al. 2006; Tang et al. 1999). However, most of such measurements gain specific characteristics of carbonaceous aerosols at specific locations. Few measurements provide the overall profile in the whole country (Zhang et al. 2008; Cao et al. 2007). Some models (Liu et al. 2010) and emission inventories (Streets et al. 2003; Cao et al. 2006; Zhang et al. 2009a; Fu et al. 2012) may give the temporal and spatial patterns of carbonaceous aerosols across China; nevertheless, unavoidably, these results have great uncertainties due to the method itself. For example, the uncertainties of emission estimates from bottom-up inventories (95 % confidence intervals) were ± 208 % for EC and ± 258 % for OC (Zhang et al. 2009a).

In this study, we made an attempt to obtain OC and EC pollution characteristics in a nation scale in China derived from published data in the field observation. We examined the levels, spatial and seasonal variations, correlations and ratios, and sources of OC and EC. Meanwhile, the implications for the understanding of carbonaceous aerosols, including the estimation of SOC and the inventory and climate effect

of carbonaceous aerosol, were also presented. To our knowledge, this is the first time to supply the observation-based insight into the carbonaceous aerosols profile in China in a nation scale, which benefits to better understand carbonaceous aerosol pollution in the country and improve the emission inventory and climate forcing evaluation.

Database

The national-scale carbonaceous aerosols data in $\text{PM}_{2.5}$ and PM_{10} were assembled based on almost all published literatures with PM, OC, and EC concentrations in China before 2012 in the field measurement (Fig. 1). There were 252 sets of data in $\text{PM}_{2.5}$ and 128 sets in PM_{10} as compiled in Supplementary Tables S1 and S2. Data with only species without PM mass concentrations or with PM mass without any species concentrations in a set (e.g., with PM and OC without EC) were not collected. Northern (including 15 provinces, autonomous regions, and municipalities: Heilongjiang, Jilin, Liaoning, Inner Mongolia, Beijing, Tianjin, Shandong, Henan, Hebei, Shanxi, Shaanxi, Ningxia, Gansu, Qinghai, and Xinjiang) and southern China (related to the other 16 provinces, autonomous regions, and municipalities and two special administrative regions: Jiangsu, Shanghai, Anhui, Hubei, Hunan, Chongqing, Sichuan, Tibet, Yunnan, Guizhou, Guangxi, Guangdong, Jiangxi, Fujian, Zhejiang, Hainan, Hong Kong, and Macao) was divided based on the demarcation line of Qinling Mountain and its eastern extension to Huaihe River in central and eastern China as shown in Fig. 1 (Gao et al. 2011). There were 111 sets of data in 15 regions in northern China and 141 sets of data related to 18 regions in southern China for $\text{PM}_{2.5}$. For PM_{10} , there were 59 sets in 19 regions in the north and 69 sets related to 12 regions in the south.

The measurements in Supplementary Tables S1 and S2 ranged from 1999 to 2010 and covered urban, suburban, background, forest, mountain, rural, and remote areas across the nation. These data were both long-term (e.g., annual) and short-term (e.g., daily and weekly) averaged concentrations. Data based on a few measurements were not used in the review. The aerosol samples in different research groups were collected by mini-, low-, middle-, or high-volume samplers on quartz filters. The sampling artifacts had not been considered. The main analytical methods for OC and EC were thermal optical transmission (TOT) method following the National Institute for Occupational Safety and Health (NIOSH) protocol and thermal optical reflectance (TOR) method from Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol. Other analytical approaches, such as selective thermal manganese dioxide oxidation (TMO) method and thermogravimetry method, were also used. These data were processed and plotted to allow comparisons without further corrections.

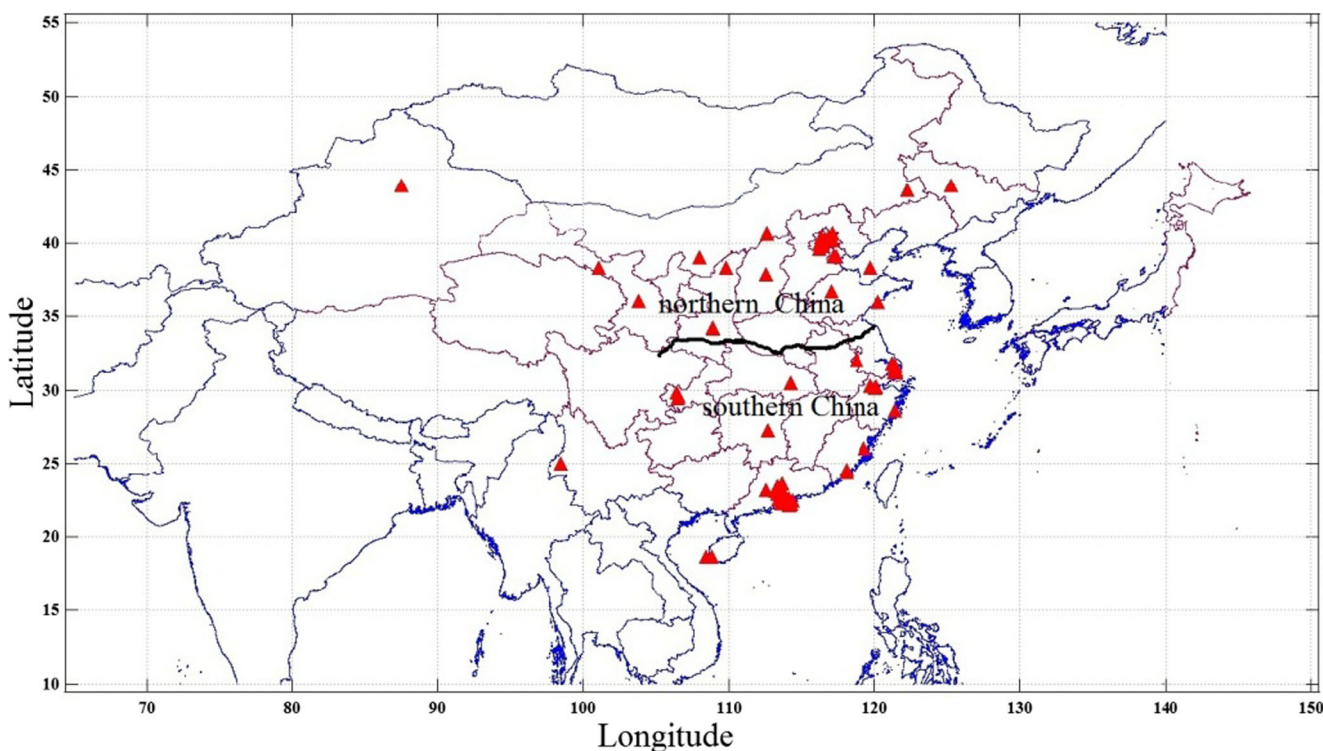


Fig. 1 The sampling sites

Results and discussion

Concentration levels of OC and EC

The concentrations of OC and EC in PM_{2.5} were from 1.5 to 102.3 μg C m⁻³ with an average of 19.6 ± 14.4 μg C m⁻³, and 0.2 to 37.0 μg C m⁻³ with an average of 6.1 ± 4.6 μg C m⁻³, respectively, in the investigation. They are nearly 3.8 and 4.2 times the OC (5.1 μg C m⁻³) and EC (1.5 μg C m⁻³) concentrations in Europe (Sillanpää et al. 2006), respectively, and 7.2 and 5.1 times the OC (2.7 μg C m⁻³) and EC (1.2 μg C m⁻³) in the USA (IMPROVE REPORT V 2011), implying a much more serious carbonaceous aerosol pollution in China. This is due to the high production and consumption of 25 % the world's total amount of coal in the country (Liu and Diamond 2005). High OC (>50 μg C m⁻³) and EC (>15 μg C m⁻³) concentrations occurred in urban in winter, such as Xi'an in northwest China (61.9 and 12.3 μg C m⁻³) (Cao et al. 2005) and Chongqing in Sichuan Basin (76.7 and 16.6 μg C m⁻³) (Cao et al. 2007). Low carbonaceous aerosol levels (<10 μg C m⁻³ for OC and <2 μg C m⁻³ for EC) were observed in forest, mountain, rural, and background sites, such as Mt. Changbai (4.9 and 0.5 μg C m⁻³) (Li et al. 2010) and Mt. Heng (3.01 and 0.54) (Zhou et al. 2012). The maximum in urban in winter was 102.3 μg C m⁻³ versus the minimum of 1.5 μg C m⁻³ in forest, mountain, rural, and background

sites for OC and the maximum was 37 μg C m⁻³ in urban in winter versus the minimum of 0.2 μg C m⁻³ in forest, mountain, rural, and background sites for EC, suggesting the huge inhomogeneity in distributions. This may be attributed to relative high emissions in winter due to heating and the more influence from the high dense population in urban against relative sparse population and less emissions in forest, mountain, rural, and background sites.

Seasonal variations of OC and EC

OC and EC in PM_{2.5} showed obvious seasonal variations with the maxima in winter, then autumn, and lower in spring and summer (Fig. 2). It is a factor of 2–3 higher in winter compared to those in spring and summer. This is probably due to the higher emissions from coal combustion for the heating in the cold season.

OC and EC had different seasonal patterns in northern and southern China (Fig. 2). Both OC and EC levels in northern China had the minima in summer, which are about one third to one half the maxima in winter. This is probably attributed to the high primary emission of coal-related aerosol as a result of the heating in winter. Low mixing height and low precipitation may be other reasons contributing to the high carbon loading in the cold season. During summer, lower carbon concentrations are associated with lower emissions and climatic conditions: monsoon from sea with little pollutant and enhanced thermal convection

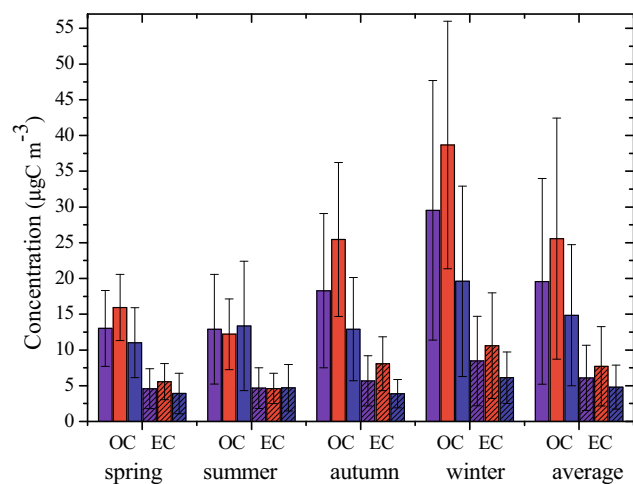


Fig. 2 Seasonal concentrations of OC and EC in PM_{2.5} in total (violet), northern (red), and southern (blue) China. Vertical bars are standard deviations

caused by monsoon, and wet deposition from frequent rainy days. In southern China, the levels of carbonaceous aerosols also varied along with seasons but showed less discrepancy among seasons compared to those in the north (Fig. 2). OC and EC concentrations were still higher in winter compared to those in the other three seasons. This is ascribed to the northeasterly monsoon, which crosses over the north and brings air pollutants to the south in winter. In addition, although there is no formal heating season in some southern cities, there are still carbonaceous emissions from space domestic heating sources due to cold weather (Cao et al. 2007). Notably, OC and EC concentrations in spring, autumn, and winter are higher in northern China than those in the south; however, both OC and EC levels in summer are comparable in the two regions.

Spatial variations of OC and EC

The areas where OC and EC were measured as shown in Supplementary Table S1 may be divided into two categories based on the density of population and sources: urban and rural sites (here, the rural sites include suburban, rural, background, mountain, and forest sites). OC and EC levels in urban were from 3.8 to 102.3 $\mu\text{g C m}^{-3}$ with an average of $21.1 \pm 15.2 \mu\text{g C m}^{-3}$, and 1.1 to 31.6 $\mu\text{g C m}^{-3}$ with an average of $6.8 \pm 4.4 \mu\text{g C m}^{-3}$, respectively, about 1.5 times those in rural sites (14.8 ± 12.0 and $4.1 \pm 5.4 \mu\text{g C m}^{-3}$) (Fig. 3), suggesting that although air quality in rural sites is being influenced more and more by emissions from urban area (Miyazaki et al. 2009; Wang et al. 2011), it is far to be consistent. In urban, OC and EC were higher in autumn and winter than those in spring and summer. While in rural sites, OC and EC showed the largest in winter and were about two times those in spring, summer, and autumn.

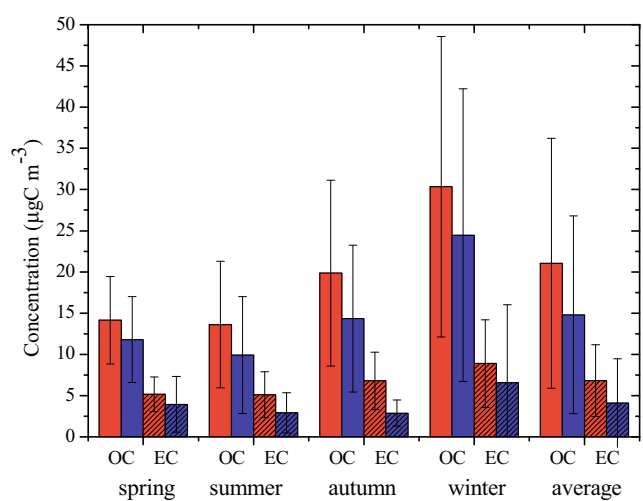


Fig. 3 The concentrations of OC and EC in four seasons and the average values in urban (red) and rural (blue) areas. Vertical bars are standard deviations

SOC evaluation

It is well known that OC may be divided into primary organic carbon (POC) and SOC. POC comes from the direct emission of combustion, and SOC is produced by the photochemical reaction of volatile organic compounds (VOCs) in the atmosphere. SOC is an important component of PM as a measure of the aged degree of aerosol, and it can change the properties of aerosols, such as hygroscopicity and optical characteristics. If OC/EC value is higher than 2, carbonaceous matter may be interpreted as containing significant quantities of SOC (Chow et al. 1993, 1996). At present, direct SOC measurements are difficult, so several indirect methodologies are applied in the evaluation of SOC formation, including EC tracer method (Cao et al. 2004, 2007; Zhang et al. 2008; Lin et al. 2009), receptor model (Yuan et al. 2006; Zhang et al. 2009b), chemical transport model (Han et al. 2008b; Fu et al. 2012), and so on (Cheng et al. 2011). Among these approaches, the EC tracer method has been widely used (Cabada et al. 2004; Duan et al. 2005; Docherty et al. 2008; Lin et al. 2009; Snyder et al. 2009) and is very suitable for this study, since it only requires ambient OC and EC concentrations (Cheng et al. 2011). According to Castro et al. (1999), the production of SOC can be calculated from the following equation:

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

where OC_{sec} is SOC, OC_{tot} is the total OC, and $(OC/EC)_{\text{min}}$ is the minimum ratio observed. The accuracy of SOC estimates is highly dependent on the accuracy of the $(OC/EC)_{\text{min}}$ ratio in representing the mixture of multiple local primary PM sources. Since the representative $(OC/EC)_{\text{min}}$ is season-dependent, here season-specific $(OC/EC)_{\text{min}}$ values were approximated using samples that had the lowest 20 % measured OC/

EC values in a given season (Lim and Turpin 2002; Yuan et al. 2006). A least squares regression of the OC and EC data in the lowest 20 % of OC/EC ratio yielded the slopes of 1.73 ($R^2=0.86$, $n=7$), 1.72 ($R^2=0.84$, $n=15$), 2.04 ($R^2=0.94$, $n=6$), and 1.71 ($R^2=0.92$, $n=16$) for spring, summer, autumn, and winter measurements, respectively (Fig. 4). The method is also applied to all data in Supplementary Table S1 to obtain the $(OC/EC)_{\min}$ in the whole country.

The results show that the concentration of estimated SOC in $PM_{2.5}$ was $8.9 \pm 10.2 \mu\text{g C m}^{-3}$ in this investigation, constituting $41 \pm 26 \%$ (0–85 %) of OC and $8 \pm 6 \%$ (0–32 %) of $PM_{2.5}$ mass, implying that SOC is a significant portion of $PM_{2.5}$ in China. This is coincident with the proportion of SOC in OC from Cao et al. (2007) (40 %) who measured EC and OC concentrations in 14 Chinese cities in January and July in 2003 and lower than the results for urban (48–62 %) and rural (53–80 %) annual surface OC over an entire year at 18 urban, rural, and background sites in the study of Zhang et al. (2008).

SOC had obvious seasonal variations with the largest concentration in winter, which is over two times those with lower levels in summer and spring. The ability of a given VOC to produce SOC during its atmospheric oxidation mainly depends on two factors: the emission rate of VOC (atmospheric abundance) and the chemical reactivity (Cao et al. 2003). In winter (0.78 Tg C/year), the VOC emissions from vegetable sources are far lower than those in summer (9.73 Tg C/year) (Yan et al. 2004), despite higher VOC emissions from anthropogenic sources in winter (7.20 Tg/year in winter vs 5.07 Tg/year in summer) (Zhang et al. 2009a); in addition, the lower temperature (−1 to 8 °C in winter vs 18 to 28 °C in summer, source: <http://www.tianqi.com/qiwen/china/>) leads to decreased photochemical activities in winter than in summer, which are unfavorable for the formation of SOC in the cold season. However, the lower temperature in winter would cause the gas–particle equilibrium shift of semivolatile organic compounds to particulate phase. In addition, the winter–summer rainfall contrast (an average of 21 mm in winter vs 124 mm in summer for the period of 1962–2013, source: <http://www.tianqi.com/qiwen/china/>) suggests that infrequent and less rainfall in winter effectively reduced the removal of aged aerosols. Moreover, lower mixing heights in winter also contribute to higher SOC concentrations. So, here it is a combined result of favorable partitioning of semivolatile SOC species in the particle phase, less wet precipitation, and lower mixing heights to compensate for the adverse factors such as less solar radiation and lower VOC emissions, and leads to more SOC formation in wintertime (Duan et al. 2005) in the country.

The average concentrations of estimated SOC in northern and southern China were 12.0 ± 12.7 and $6.5 \pm 6.8 \mu\text{g C m}^{-3}$, accounting for 43 ± 25 and $40 \pm 26 \%$ of OC, respectively (Fig. 5a, b). SOC had obvious seasonal variations in northern

China with the largest concentration in winter and the lower levels in summer and spring, which is consistent with the OC pattern in the region. In contrast, SOC concentrations in southern China were higher in winter, considering that both the ratios of SOC to OC and SOC to $PM_{2.5}$ in four seasons were comparable as shown in Fig. 5b, different from those with the significant high ratios of SOC/OC and SOC/ $PM_{2.5}$ in winter in northern China, which suggests that higher SOC concentrations in winter in the south may be due to higher $PM_{2.5}$ mass concentrations in the season ($95.0 \mu\text{g m}^{-3}$ in winter vs $64.7 \mu\text{g m}^{-3}$ in spring, $58.2 \mu\text{g m}^{-3}$ in summer, and $67.5 \mu\text{g m}^{-3}$ in autumn).

Contributions to $PM_{2.5}$ and PM_{10}

Knowledge of the relative contribution of OC and EC is important in formulating effective control measures for ambient PM. The fractions of carbonaceous aerosols in $PM_{2.5}$ were from 6 to 38 % with an average of $20 \pm 6 \%$, and 1 to 19 % with an average of $7 \pm 3 \%$ for OC and EC, respectively, in China, which are comparable to the proportions of 21 and 10 % for OC and EC in the USA (IMPROVE Report V 2011) and 25 and 7 % in Europe (Sillanpää et al. 2006). The fractions of OC in $PM_{2.5}$ were larger in winter and autumn than those in spring and summer, but the proportions of EC showed no obvious seasonal variations. Total carbon (TC), which means the sum of OC and EC, exhibited the same seasonal trend with OC (Fig. 6).

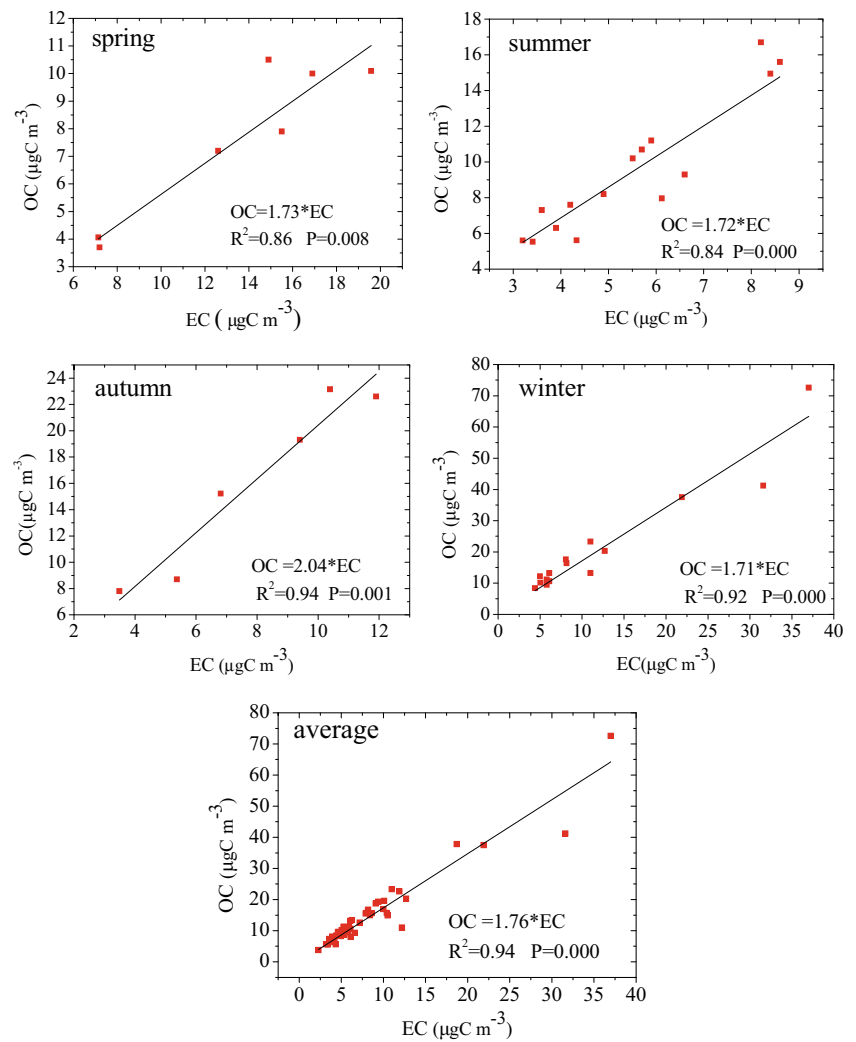
In OC, POC and SOC occupied about 12 % and about 8 % of $PM_{2.5}$ mass, respectively, suggesting that POC is a dominated part of OC. As shown in Fig. 6, POC had higher fractions in $PM_{2.5}$ in autumn and summer compared to those in spring and winter; in contrast, SOC had the highest proportion in winter than that in spring, summer, and autumn. So the higher OC fractions in autumn and winter may be attributed to the relative high POC proportion in autumn and relative high SOC proportion in winter. This means that different measures should be adopted to mitigate carbonaceous aerosol pollution in different seasons.

In comparison, in PM_{10} , the proportions of OC and EC were from 4 to 47 % with an average of $17 \pm 7 \%$, and 2 to 16 % with an average of $5 \pm 3 \%$, respectively. The seasonal patterns of the fractions of OC and EC in PM_{10} are consistent with those in fine particles.

Relationship between OC and EC

In order to explore the origin of carbonaceous aerosols in China, the relationship between OC and EC was investigated (Chow et al. 1996). The slope identifies OC associated with EC through common primary combustion sources. The intercept provides primary non-combustion and SOC. The results showed that there was a good correlation between OC and EC

Fig. 4 Scatter plots of OC versus EC for samples of the lowest 20 % (OC/EC) ratios

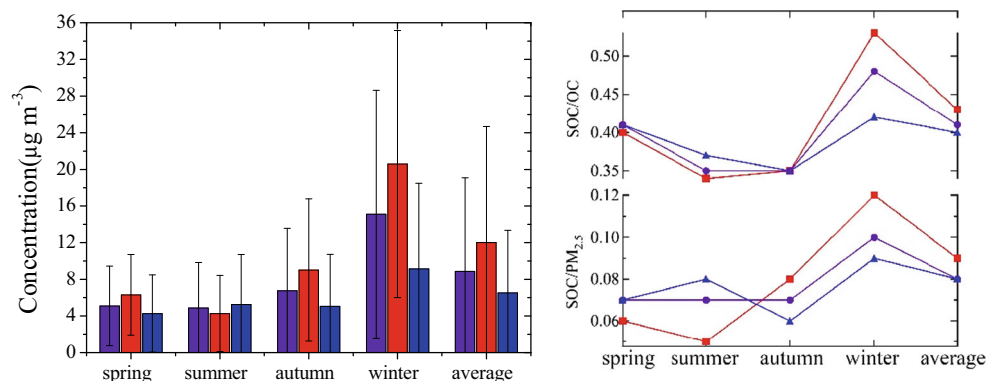


($R^2=0.53$) across China (Table 1), meaning the similar primary emission sources. The slope of 2.29 suggested that coal combustion and/or vehicular exhaust is probably the main carbonaceous aerosols source since coal and petroleum are the dominant energy sources in China with the percentages of 68 and 19 %, respectively (Zhang et al. 2012), and the

emission ratio of OC to EC is 3.31 for coal combustion and 1.54 for vehicular exhaust (Watson et al. 2001).

The correlations between OC and EC were somewhat different in different seasons. OC and EC were strongly correlated in summer and autumn, and relatively weakly correlated in spring and winter, suggesting a more changing mixture of

Fig. 5 The concentrations (a, left) and the ratios (b, right) of SOC in PM_{2.5} in China (violet), northern China (red), southern China (blue). Vertical bars (a, left) are standard deviations



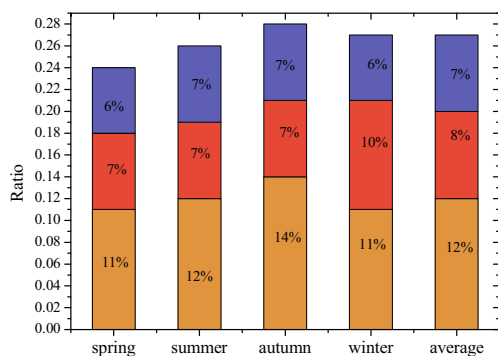


Fig. 6 The fractions of POC (orange), SOC (red), and EC (blue) in PM_{2.5} in four seasons and the average values

source contributions in the later. The wide variations in slopes with $k=1.21\text{--}2.40$ indicate their seasonal variability in OC contributions from combustion sources (coal combustion, traffic, and biomass burning) (Yang et al. 2005a, b; Feng et al. 2009). According to the source profile, such as that measured by Watson et al. (Watson et al. 2001), the OC/EC ratios for emissions from coal-fired boiler, biomass burning, and motor vehicle were 0.28–7.93 (average 3.31), 14.51, and 0.66–2.42 (average 1.54), respectively, meaning that the combustions of coal and biomass exhibited much higher OC/EC ratios than that for motor vehicle. In this study, there is the influence of intensive biomass burning in summer and autumn due to crop burning in China (Huang et al. 2012), and coal combustion in winter due to heating. So, the slopes showed summer and autumn higher, then winter and spring. The far higher intercept in winter compared to that in the other three seasons is probably due to the more SOC (see the “Spatial variations of OC and EC” section).

Variability of OC/EC ratios

Ambient OC-to-EC ratios include important information about the emission of carbonaceous aerosols. The average ratio of OC to EC in this investigation was 3.63 ± 1.73 , higher than that (2.25) in USA (IMPROVE REPORT V 2011) and comparable to that (3.52) in Europe (Sillanpää et al. 2006). The ratio is near the value (3.31) from coal combustion

Table 1 Relationship between OC and EC in PM_{2.5} in four seasons in China

		R^2	n	P
Spring	OC=1.21*EC+7.49	0.41	27	0.00
Summer	OC=2.08*EC+3.16	0.60	76	0.00
Autumn	OC=2.40*EC+4.69	0.61	28	0.00
Winter	OC=1.93* EC+12.93	0.44	74	0.00
Average	OC=2.29*EC+5.67	0.53	252	0.00

OC organic carbon, EC element carbon

reported by Watson et al. (2001), further suggesting that coal combustion is the main source of carbonaceous aerosols in China. The OC/EC ratios showed the seasonal variations with the higher values in autumn (3.84 ± 2.15) and winter (3.96 ± 1.68) than those in spring (3.57 ± 1.61) and summer (3.19 ± 1.54) due to an integrated influence of emissions, meteorological factors, and photochemical reactions. The OC/EC ratio in urban was 3.23 ± 1.37 , which is close to the result of 3.10 from Zhang et al. (2008), higher than that in urban Europe (2.69 ± 0.91) and in North America (2.94 ± 1.61) (Novakov et al. 2005), suggesting a greater proportion for coal combustion contribution in urban China than in Europe and North America considering the higher OC/EC ratio for coal combustion (3.31) than motor vehicle exhaust (1.51) (Watson et al. 2001) and dominated coal consumption in energy budget in China (68 %) (China statistical yearbook 2011). The ratios in urban showed less pronounced seasonal variation and only had a slightly higher value in winter. In rural sites, the ratio (4.72 ± 2.15) of OC/EC was higher than that in urban. This may be attributed to a larger contribution from open biomass burning in the field except the influences of regional anthropogenic sources, as these emissions are enriched in OC with a higher calculated OC/EC ratio, e.g., 14.51 in forest fire (Watson et al. 2001). The contribution of SOC formed by biogenic VOC is another possibility to lead to the higher ratio of OC/EC in rural sites (Li et al. 2010). Notably, the ratios in mountain or forest areas were especially high and might reach 4.93–12.00 (Zhou et al. 2012; Luo et al. 2010; Li et al. 2010; Han et al. 2008a; Yang et al. 2005a, b).

Implication for emission inventory and climate forcing

Implication for emission inventory

Usually, it is very difficult to get the carbonaceous aerosol levels, OC-to-EC ratio, and correlation with low uncertainties due to imperfect source statistics and large variations of emission factors which depend on fuel type and combustion practice for a sector. The comparison between the results obtained in the observation and those estimated from emission inventories benefits to improve the inventory and better understand carbonaceous aerosols pollution in China. In this study, two primary OC/EC ratios were gained across China: 2.29, which was obtained by the correlation between OC and EC (the “Relationship between OC and EC” section), and 1.76, which was determined by a least squares regression of the OC and EC data in the lowest 20 % of OC/EC ratio (the “Spatial variations of OC and EC” section). These are near the ratios from emission inventories, such as 2.17 (Fu et al. 2012), 2.18 (Lu et al. 2011), 2.73 (Cao et al. 2006), and 1.90 (Bond et al. 2004), and 1.78 (Zhang et al. 2009a), which only considered

anthropogenic sources and lacked the biomass burning emissions, and lower than the value from Streets et al. (2003) of 3.24. The OC/EC ratio of 3.63 in this study is far higher than those ratios in the inventories. This may be attributed to the scarcity of SOC formed by anthropogenic and biogenic VOCs; crop biomass burning emission, which is usually underestimated by satellite observation due to the shelter of cloud and the possible time inconsistency in the observation of satellite and the biomass burning from agriculture; and non-Chinese source and so on in these inventories, which either increase OC (SOC) or have a higher OC/EC ratio (such as biomass burning and aged transported non-Chinese source). Compared to the inventory, that the ratio of OC to EC is calculated by measured surface OC and EC concentrations in this study is a receptor method and provides the direct and true surface situation of carbonaceous aerosol pollution in China.

Implication for climate forcing

Another important implication of the result in this study is for climate forcing evaluation. Since the ratios of OC to EC determine the relative amounts of scattering and absorption, they are often used to estimate the radiative forcing caused by aerosols. The relevance of OC/EC ratios to the radiative forcing of climate by aerosols can be obtained by comparing them to those used in climate models. The average OC/EC ratio in the review is nearly 1.2–3.6 times the OC/BC ratios (1–3) obtained in the Goddard Institute for Space Studies (GISS) ModelE (Schmidt et al. 2006), which was developed by the spatial distributions of OC and BC emissions from Bond et al. (2004) for fossil fuel and biofuel sources and from Van der Werf et al. (2004) for biomass sources. Since the OC/EC ratio could influence the relative amounts of particle light scattering and absorption (Cao et al. 2007), the higher ratio of OC to EC in the review compared to that used in the climate model means that the cool effect in the climate model is probably underestimated in China.

Conclusion

Carbonaceous aerosols are the major components of ambient PM and play an important role in air quality and regional climate changes. In this investigation, the pollution of carbonaceous aerosols in China is more serious than those in USA and Europe due to the huge emissions derived from dominated coal combustion. OC and EC showed obvious seasonal variations with the maxima concentrations in winter, then autumn, and lower in summer and spring. Moreover, OC and EC were higher in urban than those in rural sites with a factor of ~1.5. Carbonaceous aerosols occupied 20 ± 6 % for OC and 7 ± 3 % for EC in $PM_{2.5}$ and 17 ± 7 and 5 ± 3 % in PM_{10} . SOC

contributed 41 ± 26 % to OC and 8 ± 6 % to $PM_{2.5}$ mass. The regression slope of 2.29 between OC and EC and the average OC to EC ratio of 3.63 ± 1.73 suggested that coal combustion and/or vehicular exhaust is the main carbonaceous aerosol source in China. These supply significant information to understand the carbonaceous aerosol pollution in China. In the comparisons with the emission inventories, the higher OC/EC ratio in the review based on surface measurement implies that the inventories had a great neglect for OC, especially SOC. Meanwhile, it also means that the cool effect in the climate model is probably underestimated in China when the spatial distributions of OC and BC emissions in the climate model come from emission inventories.

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