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Patterns in atmospheric carbonaceous aerosols in China: emission estimates and observed concentrations

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Abstract

China is experiencing severe carbonaceous aerosol pollution driven mainly by large emissions resulting from intensive use of solid fuels. To gain a better understanding of the levels and trends of carbonaceous aerosol emissions and the resulting ambient concentrations at the national scale, we update an emission inventory of anthropogenic organic carbon (OC) and elemental carbon (EC) and employ existing observational studies to analyze characteristics of these aerosols including temporal, spatial, and size distributions, and the levels and shares of secondary organic carbon (SOC) in total OC. We further use ground observations to test the levels and inter-annual trends of the calculated national and provincial emissions of carbonaceous aerosols, and propose possible improvements in emission estimation for the future. The national OC emissions are estimated to have increased 29 % from 2000 (2127 Gg) to 2012 (2749 Gg) and EC by 37 % (from 1356 to 1857 Gg). The residential, industrial, and transportation sectors contributed an estimated 76 ± 2, 19 ± 2 and 5 ± 1 % of the total emissions of OC, respectively, and 52 ± 3, 32 ± 2 and 16 ± 2 % of EC. Updated emission factors based on the most recent local field measurements, particularly for biofuel stoves, lead to considerably lower emissions of OC compared to previous inventories. Compiling observational data across the country, higher concentrations of OC and EC are found in northern and inland cities, while larger OC/EC and SOC/OC ratios are found in southern cities, due to the joint effects of primary emissions and meteorology. Higher SOC/OC ratios are estimated at rural and remote sites compared to urban ones, attributed to more emissions of OC from biofuel use, more biogenic emissions of volatile organic compound (VOC) precursors to SOC, and/or transport of aged aerosols. For most sites, higher concentrations of OC, EC, and SOC are observed in colder seasons, while SOC/OC is reduced, particularly at rural and remote sites, attributed partly to weaker atmospheric oxidation and SOC formation compared to summer. Enhanced SOC formation from oxidization and anthropogenic activities like biomass combustion is judged to have crucial effects on severe haze events characterized by high particle

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concentrations. Several observational studies indicate an increasing trend in ambient OC/EC (but not in OC or EC individually) from 2000 to 2010, confirming increased atmospheric oxidation of OC across the country. Combining the results of emission estimation and observations, the improvement over prior emission inventories is indicated by inter-annual comparisons and correlation analysis. It is also indicated, however, that the estimated growth in emissions might be faster than observed growth, and that some sources with high primary OC/EC like burning of biomass are still underestimated. Further studies to determine changing emission factors over time in the residential sector and to compare to other measurements such as satellite observations are thus suggested to improve understanding of the levels and trends of primary carbonaceous aerosol emissions in China.

1 Introduction

Atmospheric carbonaceous species including organic carbon (OC) and elemental carbon (EC) are significant, sometimes dominant, components of fine particulate concentrations, accounting for 20–50 % of $PM_{2.5}$ mass in highly polluted atmospheres (Park et al., 2001). Sometimes referred to as black carbon (BC), EC mainly originates from incomplete combustion of fossil fuels and biomass. As a complex mixture of hundreds of individual compounds, OC can be both emitted directly from combustion sources (described as primary organic compounds, POC) and formed through photochemical reactions in which gaseous volatile organic compounds (VOC) are converted to pollutants in the particle phase (described as secondary organic compounds, SOC).

Because of the important roles OC and EC play in global climate, atmospheric chemistry, and environmental health (Engling and Gelencser, 2010; Mauderly and Chow, 2008), increasing attention has been paid to pollution comprised of atmospheric carbonaceous aerosols around the world, and especially in China due to its rapid economic growth and urbanization over the last 30 years. China is now estimated to have become the largest energy-consuming country, and accounted for over 50 % of global

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coal use in 2013 (BP, 2014). Severe haze events characterized by enhanced levels of airborne particulate matter (PM) and poor visibility have become a central challenge in air quality management and one of the highest profile issues in the country (Huang et al., 2014; Q. Zhang et al., 2012). Very high average concentrations of OC and EC have been found in large cities of China compared to other cities around the world, particularly in the most intensively developed areas including the Beijing–Tianjin–Hebei region (commonly called "Jing-Jin-Ji," abbreviated JJJ here) (Dan et al., 2004; Duan et al., 2005; Li and Bai, 2009; Zhang et al., 2007; P. Zhao et al., 2013; Yang et al., 2011a), the Yangtze River Delta region (YRD) (Feng et al., 2006a, b, 2013; Feng et al., 2009; Huang et al., 2013; Y. Wang et al., 2010), and the Pearl River Delta region (PRD) (Cao et al., 2003a, b, 2004; Feng et al., 2006b; H. Huang et al., 2012).

Given China's large shares of worldwide emissions and regional PM pollution, great efforts have been made for more than ten years to quantify China's emissions of carbonaceous aerosols using gradually improving bottom-up methods, from global (Bond et al., 2004, 2007), continental (Streets et al., 2003; Ohara et al., 2007; Zhang et al., 2009; Kurokawa et al., 2013) or national perspectives (Streets et al., 2001; Lei et al., 2011; Lu et al., 2011; Zhao et al., 2011; Y. Zhao et al., 2013). Limited by data access, however, previous inventory studies of China's EC and OC emissions are considered highly uncertain (Streets et al., 2003; Zhang et al., 2009), as indicated by top-down constraints through chemical transport modeling (Fu et al., 2012). Because of routine publication delays of statistics that are essential for emission inventory development, including those for energy consumption and industrial production, efforts to provide timely emission estimates sometimes rely on predicted or extrapolated activity data based on historic information or "fast-track" data that lack official validation (Streets et al., 2001; Zhang et al., 2009; Lu et al., 2011). Another important reason limiting the accuracy of current estimates is strong dependence on emission factors derived from developed countries, particularly for residential heating and cooking stoves, for which the combustion conditions can differ considerably between countries. In recent years, increasing domestic field measurements of local emission factors (EF) for EC

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and OC have been conducted, but few of these updated EFs have been applied in current estimates of emissions, which predate the much of the fieldwork. In addition, some emission sources, e.g., off-road transportation and biomass open burning, have been omitted in some inventories, making direct comparisons and evaluation of different studies difficult. With all of these various limitations, the uncertainties of China's primary carbonaceous emissions, particularly over long periods, have seldom been quantified except for in one study (Lu et al., 2011).

Aside from the trends in emissions, regional and local pollution levels of carbonaceous aerosols across the country have been drawing increased attention. Although studies of ambient concentrations of carbonaceous aerosols in China began in the 1980s, continuous observations did not begin until the mid-1990s (Cao et al., 2007). Using the methods of thermal optical reflection (TOR) or thermal optical transmission (TOT), measurements of OC and EC as airborne particles have now been conducted in urban, rural, and remote sites for typical cities and seasons. Most studies, however, focused only on a single city (except for a few including Cao et al., 2007; X. Zhang et al., 2008, 2012) or relatively short periods (except for Yang et al., 2011a). Without analyses combining results of multiple studies, pollution characteristics and trends of carbonaceous aerosols over relatively long periods remain unclear for the country. Lacking trends of ambient pollution levels, moreover, observations have seldom been linked to emission inventory studies. Thus they have contributed little to verification of estimated emissions, limiting improvement of emission estimates.

In this work, therefore, EC and OC emissions of China for 2000–2012 are estimated with a consistent framework that encompasses all anthropogenic sources: fossil fuel combustion, biofuel combustion, and biomass open burning. Newly published data from domestic field measurements are incorporated into the framework to update the emission factors, with the uncertainties carefully quantified. Based on thorough review of existing observation studies, the spatial and seasonal distributions, the long-term trends of OC and EC concentrations, and the level of SOC formation are analyzed to provide a comprehensive picture of carbonaceous aerosol pollution in China during

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a period of rapid economic development and improved pollution controls. Using available observations, the accuracy of estimated levels and trends of primary carbonaceous aerosol emissions is evaluated, and further improvement of emission inventory research is accordingly proposed.

2 Emissions of primary carbonaceous aerosols

2.1 Methods and activity data

The method to develop bottom-up emission inventories has been described in previous work (Zhao et al., 2011, 2012; Y. Zhao et al., 2013). The emission sources mainly fall into four sector categories: coal-fired power plants (CPP), industry (IND), transportation (TRA, including on-road and off-road subcategories) and the residential and commercial sectors (RES, including fossil fuel and biomass combustion subcategories). IND is further divided into cement production (CEM), iron and steel plants (ISP), other industrial boilers (OIB), and other non-combustion processes (PRO). Using Eq. (1), the EC and OC emissions are calculated by province and sector and then aggregated to the national level:

$$E_{i,j,t} = \sum_{k} \sum_{m} \sum_{n} \mathrm{AL}_{j,k,m,t} \times \mathrm{EF}_{i,j,k,m,n} \times R_{j,k,m,n,t} \quad (1)$$

where i, j, k, m, n and t stand for species (EC and OC), province, sector, fuel type, emission control technology and year, respectively; AL is the activity level, either energy consumption or industrial production; EF is the emission factor; and R is the penetration rate of emission control technology.

For small coal stoves, biofuel cook stoves and biomass open burning, $\mathrm{EF}_{\mathrm{EC}}$ and $\mathrm{EF}_{\mathrm{OC}}$ are derived from published data of local field measurements, as described in Sect. 2.2. For most other sources, $\mathrm{EF}_{\mathrm{EC}}$ and $\mathrm{EF}_{\mathrm{OC}}$ are estimated as the products of the

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$PM_{2.5}$ emission factor and the mass fraction of EC and OC for corresponding sources:

$$EF_{i,j,k,m,n} = EF_{PM,j,k,m,n} \times f_{PM_{2.5},k,m} \times (1 - \eta_{PM_{2.5},k,m,n}) \times F_{i,k,m} \quad (2)$$

where EF_{PM} is the unabated emission factor for PM; $f_{PM_{2.5}}$ is the $PM_{2.5}$ mass fraction of total PM; η is the removal efficiency of the emission control technology; and F is the EC or OC mass fraction of $PM_{2.5}$.

Activity data for 2000–2012 are compiled annually by sector from a variety of data sources. The fossil fuel consumption and industrial production are obtained at the provincial level from Chinese official energy (NBS, 2013a) and industrial economic statistics (NBS, 2013b). For some industrial sources lacking official statistics, such as brick and tile making, production data are estimated based on data from relevant industrial associations. To avoid double counting, the fuel consumption by OIB is estimated by subtracting the fuel consumed by CEM, ISP and PRO from fuel consumed by total industry (Zhao et al., 2012). In addition to coal combustion, wood combustion by industrial sector is taken from Chen et al. (2013). The annual biofuel use for residential stoves before 2008 is taken from official statistics (NBS, 2013a), and those for the following years are from unpublished data by Ministry of Agriculture, since official statistics stopped reporting the data in 2008 (Chen et al., 2013). The biomass combusted in open fields is calculated as a product of grain production, waste-to-grain ratio, and the percentage of residual material burned in the field, as described in Zhao et al. (2011, 2012).

2.2 Emission factors

Of all the sectors, the residential and commercial sector is the largest contributor of national EC and OC emissions. Parameters related with emission factors are estimated to contribute most to the uncertainties of emissions, attributed mainly to a lack of relevant local field studies (Lu et al., 2011; Y. Zhao et al., 2013). Widely used by Chinese rural families for boiling water, heating and cooking, small coal and biofuel stoves are the main emission sources of the sector. In recent years, a number of field studies

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explored EC and/or OC emission levels from those local sources (Shen et al., 2010, 2012, 2013; Wei et al., 2014). Combined with results of similar studies that were published earlier (Chen et al., 2005, 2006, 2009; Zhi et al., 2008, 2009; Y. Zhang et al., 2008; Cao et al., 2008; Li et al., 2009), EFs are shown to vary significantly among emission sources using different coal types. In this work, therefore, coal stoves are further broken down into those burning anthracite briquettes, bituminous briquettes, anthracite chunk coal, and bituminous chunk coal, and the EF for each type is determined based on corresponding field measurements. For biofuel combustion, the difference in stove design between northern and southern China is taken into account in this work, e.g., field measurements of "kangs" (traditional brick bed-stoves) which are limited to northern China, are excluded for EF analysis for southern provinces. For EFs with adequate domestic measurement data, a probability distribution is fitted using the statistical software package Crystal Ball and the Kolmogorov–Smirnov test for the goodness-of-fit ($p = 0.05$). As shown in Fig. 1, the OC EFs of crop wastes and bituminous chunk coal, and EC EF of bituminous briquettes burned in stoves pass the test and their probability distributions are presented. For EFs with insufficient observation data, and those that fail to pass the goodness-of-fit test, probability distributions must be assumed following our previous work (Zhao et al., 2011). Detailed information on EC and OC EFs by source is summarized in Table 1.

For other sectors, few studies based on EC and/or OC EF measurement have been published in recent years and the EFs summarized in Y. Zhao et al. (2013) are used in this study in most cases. For transportation, the results from on-road measurements by Huo et al. (2012), Wu et al. (2012) and Fu et al. (2013) are incorporated into the emission factor database developed by Y. Zhao et al. (2013). The $PM_{2.5}$ EF for light-duty diesel trucks meeting stage I emission standards is updated from 3.4 to 2.3 $g\,kg^{-1}$ and that for inland shipping from 1.1 to 2.2 $g\,kg^{-1}$, leading to corresponding changes of the EC and OC EFs.

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2.3 Temporal trends, spatial distribution and uncertainties of emissions

The calculated annual EC and OC emissions for 2000–2012 are presented in Fig. 2a and b, respectively. EC emissions are estimated to have increased by 37 % from 1356 Gg in 2000 to 1857 Gg in 2012, with relatively faster growth rates from 2000 to 2005 than the following years. Since 2005, improved emission control policies have resulted in reduced PM emission factors on average that partly counteracted the effects of increased activity levels. During the 2000–2012 research period, the residential sector is estimated to have accounted for 52 ± 3 % of total EC emissions as an annual average. The large contribution to total emissions is attributed mainly to generally inefficient combustion characteristics and a lack of effective emission controls in this sector. During the period, emissions from the residential sector increased by 34 %, principally due to the growth of coal consumption. The shares of the industry and transportation sectors are estimated at 32 ± 2 %, and 16 ± 2 %, respectively, while very little emissions came from power plants because of the high combustion efficiency and well-implemented particle controls. Emissions of industry and transportation increased by 39 and 47 %, much slower than the growth of activity data, namely 136 % in industrial coal consumption and 204 % in transportation oil consumption. This suggests improved emission control measures, e.g., the penetration of dust collectors with improved PM removal rates at industrial boilers, and the staged replacement of vehicles with stricter emission standards required by the national regulations.

OC emissions, shown in Fig. 2b, are estimated to have increased 29 % from 2127 Gg in 2000 to 2749 Gg in 2012, and the inter-annual trend is similar to that of EC emissions. Residential, industrial, and transportation sectors are estimated to have contributed 76 ± 2, 19 ± 2, and 5 ± 1 % to total emissions, respectively, and the emissions of those sectors grew by 30, 25, and 39 % during the research period. In particular, the share of emissions from biofuel use and biomass open burning is estimated at 58 ± 3 %. As shown in Fig. 2c, the ratios of OC to EC emissions, $(OC/EC)_{emi}$, are estimated to have declined slightly from 1.58 in 2000 to 1.52 in 2012, with higher values in southern

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China (from 1.74 to 1.68) than northern China (from 1.47 to 1.42). The regional difference in $(OC/EC)_{emi}$ can be attributed mainly to different levels of biofuel and biomass combustion, the sources with relatively high ratios of OC to EC emissions. These two sources are estimated to have contributed around 50 % to total OC emissions in north China, 66 % in the south. Moreover, some kinds of stoves that are commonly used for heating in northern China, e.g., kangs, have lower OC to EC emission ratios than cook stoves, according to recent field measurements (Shen et al., 2010, 2013).

Relative changes in emissions of total primary carbonaceous aerosols (i.e., TC, equal to OC + EC) between 2000 and 2012 are indicated by province in Fig. 3. In contrast to most provinces where growth in primary TC emissions is found, some economically-advanced provinces including Beijing in the JJJ region, Shanghai, Jiangsu, and Zhejiang in the YRD region, and Guangdong in the PRD region, are estimated to have reduced their TC emissions during the last 10 years. The emission abatement in Beijing and Shanghai is attributed mainly to reduced energy consumption in the industrial sector, while that in Zhejiang and Jiangsu to reduced solid fuel use in the residential sector. Both situations indicate gradually improving economic and energy structures in the developed areas with relatively serious air pollution, and suggest increased attention to TC emission control in less economically advanced areas in the country. Shown in Fig. 3 as well are the emission intensities (i.e., emissions per unit territorial area) of TC by province in 2012, with the shares of OC and EC also indicated. In the most densely populated provinces in eastern and central China, larger intensities are generally found in the north than the south (provinces in the far north and west such as Xinjiang, Tibet, and Inner Mongolia are sparsely populated). In the populous and industrialized eastern part of the country, the annual average emission intensity of primary TC for 2000 to 2012 is estimated at 1.30 metric tons km^{-2} ($t\,TC\,km^{-2}$) in northern provinces (Beijing, Tianjin, Hebei, Henan, Jilin, Liaoning, Shaanxi, Shandong, and Shanxi), 33 % higher than that for southern provinces (Jiangsu, Anhui, Shanghai, Zhejiang, Chongqing, Fujian, Guangdong, Guangxi, Guizhou, Hubei, Hunan, and Jiangxi) at $0.97\,t\,TC\,km^{-2}$. The differing emission levels of north and south are a primary rea-

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son for different ambient concentrations of carbonaceous aerosols, as discussed later in Sect. 3.1.

The uncertainties of emissions of EC and OC for each year are quantified with Monte-Carlo simulation as described in Zhao et al. (2011). Based on 10 000 simulations, the uncertainties of emissions, expressed as 95 % confidence intervals (CIs) around the central estimates, and the parameters most significant in determining the uncertainties, judged by their contribution to the variance, are generated by sector. As shown in Table 2, the uncertainties of EC and OC emissions for 2012 are estimated at −27 to 127 and −34 to 90 %, respectively, and no significant variation or clear inter-annual trend is found for uncertainties of emissions for other years. The uncertainties estimated in this work are smaller than previous work (Lu et al., 2011; Zhao et al., 2011; Y. Zhao et al., 2013). The decreased uncertainties mainly appear in the residential sector and can be attributed to the updated emission factors that combine the most recent results from domestic field measurements. In most cases, the parameters associated with emission factors are estimated to contribute largest to the emission uncertainties, with an exception of the industrial sector in which the coke production level is also significant. The total emissions, both for EC and OC, are most sensitive to the emission factors of small coal stoves and crop waste burning, suggesting further work on emission characteristics for those sources.

2.4 Comparison with other emission inventory studies

The comparisons of EC and OC emissions from this work and other studies are shown in Fig. 2. Note emissions of forest and savanna burning are excluded from the total emissions provided by original studies. In general, estimates of most studies are within the uncertainties evaluated in this work, with the exception of EC emissions by the Regional Emission Inventory in Asia (REAS) version 1 (REAS 1, Ohara et al., 2007). The inter-annual trends of EC emissions are in good agreement between studies, with relatively steady growth rates during 2000–2005 and then leveling off for the following years. However, our current EC estimates are hundreds of Gg higher than most others

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studies including Lei et al. (2011), Lu et al. (2011), Y. Zhao et al. (2011, 2013), Qin and Xie (2012) and REAS 2 (Kurokawa et al., 2013). The differences can be attributed to two reasons. First, some studies omitted some emission sources included here, e.g., off-road vehicles (Klimont et al., 2009; Qin and Xie, 2012; Kurokawa et al., 2013), biomass open burning (Lei et al., 2011; Kurokawa et al., 2013), and non-combustion industrial processes (Kurokawa et al., 2013). Second, emission factors for residential coal combustion used in Lu et al. (2011), Lei et al. (2011) and REAS 2 are significantly lower than ours, which based on local measurements. EC emissions from 2005 to 2010 estimated in this work are a little higher than our previous work (Y. Zhao et al., 2013), because wood combustion in industry is now included and larger emission factors for small coal and biofuel stoves are used in the current estimate. R. Wang et al. (2012) has the highest EC emission estimates among all the studies, due mainly to the higher emission factors of residential fuels used in that study.

Our estimates of OC emissions are roughly 1000 Gg lower than those of Lu et al. (2011), and 500 Gg lower than those of Zhang et al. (2009), Lei et al. (2011) and REAS 2, even though they did not include the emissions from biomass open burning, an important OC source that is estimated to contribute 400–600 Gg OC emissions per year according to Lu et al. (2011) and this work. The relatively big gaps between studies come mainly from the highly varied emission factors of residential biofuel combustion used in different inventories. The OC emission factors for biofuel employed by Lu et al. (2011), Zhang et al. (2009), Lei et al. (2011), and REAS 2 are almost twice ours. Those emission factors, however, were largely based on a review by Bond et al. (2004) with a global scope and were calculated as products of PM emission factors and mass fractions of carbonaceous species (i.e., F_{EC} and F_{OC}) from laboratory experiments, because no direct measurements of carbonaceous aerosol emission factors for cook stoves were available at that time, F_{EC} and F_{OC} for crop wastes burned in cook stoves, for example, were estimated at 0.15 and 0.57, respectively, leading to a ratio of emission factors of OC and EC of 3.8. Nevertheless, the design and combustion conditions of biofuel stoves can be differ significantly between China and western

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countries (personal communication with Y. Chen from Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, 2014). Measurements of emission factors for biofuel burned in typical Chinese cook stoves have now gradually been conducted (Cao et al., 2008; Li et al., 2009; Shen et al., 2010, 2012, 2013; Wei et al., 2014). Incorporating the results of these local studies, EF_{EC} does not differ much but the EF_{OC} to EF_{EC} ratio for crop waste burning is estimated at 2.2, i.e., 45 % lower than that suggested by Bond et al. (2004). Lower emission factors and thereby emissions of OC are thus estimated in this work compared to previous studies. Given the complexity of China's residential stoves and possible huge variation of combustion conditions, however, the representativeness and accuracy of existing measurements, and the emission inventories based on those measurements, should continue to be carefully evaluated as more observations on pollution trends of carbonaceous aerosols become available.

3 Characteristics of carbonaceous aerosols based on observations

The temporal, spatial and size distributions of ambient carbonaceous aerosols are analyzed based on available data for China. A database of OC and EC concentrations is compiled from literature on or including observation of carbonaceous aerosols over a recent 10 year period (2000–2010) in China. "Carbonaceous aerosol concentrations" refers here to those in $PM_{2.5}$, apart from discussion of size distribution in Sect. 3.4 and where otherwise specifically noted. It is also acknowledged that comparison of OC and EC concentrations in studies using different analytical methods introduces uncertainty. Given the relatively large temporal and spatial scales concerned, we believe such uncertainty would not lead to significant statistical errors in this work.

3.1 Spatial pattern of OC and EC levels

To better understand the spatial patterns of carbonaceous aerosol levels, OC and EC concentrations reported in different regions across the country with sufficient sampling

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periods (at least including both cold and warm seasons) were selected and summarized in Table S1 in the supplement. Studies with relatively short sampling periods are excluded. Geographical locations of the ground observation sites of the compiled data are illustrated in Fig. S1 in the supplement. The sites can be classified into different groups: urban/suburban sites located in/near large cities, rural sites that are more representative for regional concentrations, and remote sites that are hardly influenced by human activities and thus representative for background concentrations.

Among the selected studies, the annual means of urban ambient concentrations range from 7.1–64.8 $\mu g\,m^{-3}$ for OC and 2.2–14.3 $\mu g\,m^{-3}$ for EC, with an average of 20.2 and 6.1 $\mu g\,m^{-3}$, respectively. From fewer studies, the averages of OC and EC concentrations for suburban sites are estimated at 17.4 and 4.2 $\mu g\,m^{-3}$, respectively, lower than those for urban sites. In general, those values are much higher than those of cities in industrialized Asian countries, North America, and Europe. For example, 5.5 $\mu g\,m^{-3}$ for OC and 3.1 $\mu g\,m^{-3}$ for EC were observed at Saitama, Japan during July 2009–April 2010 (Kim et al., 2011); 2.7 $\mu g\,m^{-3}$ for OC and 1.1 $\mu g\,m^{-3}$ for EC at New York during February 2000–December 2003 (Qin et al., 2006); and 3.8 $\mu g\,m^{-3}$ for OC and 3.8 $\mu g\,m^{-3}$ for EC at Madrid during June 2009–February 2010 (Pio et al., 2011). Particularly high concentrations were found in Xi'an (64.8 $\mu g\,m^{-3}$ for OC and 14.3 $\mu g\,m^{-3}$ for EC in 2003) and Chongqing (50.9 $\mu g\,m^{-3}$ for OC and 12.3 $\mu g\,m^{-3}$ for EC in 2003), due probably to the combined contribution of coal combustion emissions and unfavorable meteorological conditions (Cao et al., 2007). However, the average carbonaceous concentrations measured by Chen et al. (2014) during May 2012–April 2013 in Chongqing (19 $\mu g\,m^{-3}$ for OC and 4.6 $\mu g\,m^{-3}$ for EC) were significantly lower than those measured by Cao et al. (2007) in 2003, presumably due to improved implementation of emission control polices. Compared with Xi'an, the relatively lower concentrations of carbonaceous aerosols in developed cities in the North China Plain (NCP) including Beijing, Tianjin, and Qingdao might result from a widespread switch from coal and biofuel to natural gas in residential use (Ge et al., 2004). As reported by P. Zhao et al. (2013), Beijing, Tianjin, Shijiazhuang, and Chengde have almost the same levels

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of OC and EC concentrations with ratios of observed OC to EC (OC/EC) of around 2.7, implying similar sources of carbonaceous aerosols and/or regional meteorological conditions. In addition, the concentrations of carbonaceous aerosols in China overall show a clear pattern, as Cao et al. (2007) investigated in 14 cities in 2003, with higher pollution levels found in northern and inland cities while lower levels found in southern and coastal ones. The difference between north and south in China results partly from (1) the larger emission intensity of primary carbonaceous aerosols in the north as described in Sect. 2.3, particularly in the heating seasons due to enhanced use of coal and biofuel in the residential sector (Lu et al., 2010); and (2) relatively favorable meteorological conditions including more frequent precipitation and less temperature inversion in the south. The effects of monsoonal rainfall could also be a reason for lower concentrations in coastal cities than inland ones.

The annual average OC and EC concentrations at rural stations range from 4.9–20.2 $\mu g\,m^{-3}$ and 0.8–4.3 $\mu g\,m^{-3}$, with the overall average concentrations at 11.9 and 2.4 $\mu g\,m^{-3}$, respectively. Most observed OC concentrations are below 16 $\mu g\,m^{-3}$ except for Jinan, a city impacted by intensive coal use. All EC concentrations are below 5 $\mu g\,m^{-3}$ and much smaller than those at the urban/suburban sites. As with the urban sites, the carbonaceous aerosol levels at rural sites are generally higher than those in other parts of the world, e.g., 1.6 $\mu g\,m^{-3}$ of OC and 0.61 $\mu g\,m^{-3}$ of EC at Egbert in Canada during August 2005–November 2007 (Yang et al., 2011b), 3.8 $\mu g\,m^{-3}$ of OC and 1.3 $\mu g\,m^{-3}$ of EC at Cape Fuguei in Taiwan during 2003–2007 (Chou et al., 2010), and 3.2 $\mu g\,m^{-3}$ of OC and 0.9 $\mu g\,m^{-3}$ of EC at West Midlands in the UK during November 2005–May 2006 (Harrison and Yin, 2008).

The annual OC and EC concentrations at remote sites range from 0.48–7.5 and 0.06–0.7 $\mu g\,m^{-3}$, respectively, much lower than those in urban, suburban, and rural sites, as expected. The background concentrations are comparable to the levels at Sonnblick in the Austrian Alps, at 0.81 $\mu g\,m^{-3}$ of OC and 0.07 $\mu g\,m^{-3}$ of EC during October–December 2002 and May–June 2003 (Gelencsér et al., 2007).

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3.2 OC/EC and SOC formation levels across the country

As noted above, ambient OC is composed of POC emitted directly and SOC formed by chemical reactions in the atmosphere. In general, an OC/EC ratio exceeding a threshold of 2 is used to indicate the presence of secondary organic aerosols (Turpin and Lim, 2001). As shown in Table S1, all of the annual mean OC/EC ratios are equal to or above 2.0, implying the prevalence of SOC across the country. In addition to annual averages, OC and EC concentrations observed across the country for relatively short sampling periods (i.e., to be seasonally representative) from available studies are compiled and included in the OC/EC analysis. Illustrated in Fig. 4a are the averages of OC/EC ratios vs. EC concentrations with standard deviations at southern (S, open symbols) and northern (N, solid symbols) remote, rural, suburban, and urban sites in China. In general, ambient EC concentrations in north are higher than those in south, but larger OC/EC ratios are found in south, particularly for remote, rural and suburban sites. The result is consistent with the spatial pattern of provincial emissions shown in Fig. 2c, with the annual means of $(OC/EC)_{emi}$ calculated at 1.67 and 1.45 for southern and northern China respectively during 2000–2012. Besides emissions, differences in the conditions for SOC formation contribute as well to the divergent ambient OC/EC ratios in the south and north, which will be discussed later in this section. While EC levels indicating pollution from primary emissions are higher at urban sites, larger ambient OC/EC ratios are found for remote and rural sites. As shown in Fig. 4b, regression analyses are conducted for seasonal OC and EC concentrations classified by functional zone (i.e., urban, suburban, rural and remote regions). Ratios of OC/EC are larger than 1.0 for all data points, and a clear difference in OC/EC is found by functional zone, with the regression slopes of seasonal mean concentrations at 2.92 for urban, 3.29 for suburban, 3.46 for rural, and 6.64 for remote sites.

The variation in OC/EC ratios by functional zone results from the joint effects of local emission characteristics and regional formation and transport of SOC. Watson et al. (2001) estimated average ratios of primary OC to EC emissions for vehicles,

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coal combustion, and biomass burning at 1.1, 2.7, and 9.0, respectively. For urban areas of economically advanced cities in the JJJ and YRD regions, vehicles make a greater contribution to total carbonaceous emissions and local sources dominate the composition of ambient carbonaceous aerosols, leading to smaller OC/EC. As can be seen in Fig. 4b, most of the seasonal OC/EC ratios lower than 2 (below the $Y = 2X$ line) were observed at urban sites. In rural areas, biomass combustion (with larger primary OC/EC emission ratio) contributes more than it does in urban areas, and the regional contribution of aged aerosols with higher SOC levels helps to elevate the ambient OC/EC. Similarly, the highest OC/EC are found for the remote or high mountain areas, attributed to the following: (1) those sites are far from anthropogenic sources, especially those with relatively high emissions of EC (e.g., vehicles), (2) the formation and regional transport of SOC has increased the contribution to OC levels compared to urban areas, (3) the influence of natural sources is significantly higher at remote sites, with enhanced production of OC but very little EC; and (4) semi-volatile organic compounds tend to be condensed to particle OC in high mountain areas due to the low temperature.

Lacking any direct analytical techniques to quantify POC or SOC concentrations, several indirect methods have been used to estimate the latter. One of the most used is the EC-tracer method due to its simplicity and data availability. The concentration of SOC can be calculated with Eq. (3):

$$\mathrm{SOC} = \mathrm{OC_{tot}} - (\mathrm{OC/EC})_{\mathrm{min}} \times \mathrm{EC} \quad (3)$$

where SOC is the secondary OC concentration; $\mathrm{OC_{tot}}$ and EC are the observed total OC and EC concentrations, respectively; and $(\mathrm{OC/EC})_{\mathrm{min}}$ is the lowest observed OC/EC ratio that is assumed to represent $(\mathrm{OC/EC})_{\mathrm{pri}}$, the ratio of primary OC and EC emissions with the contribution of SOC excluded (Castro et al., 1999).

The mass fractions of POC and SOC, estimated by individual studies in different regions across the country are shown in Fig. 5. The spatial pattern of SOC/OC levels is similar to that of OC/EC. For urban JJJ and YRD regions, POC is the main fraction

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of OC, indicating a large contribution of primary anthropogenic emissions. In contrast, higher mass fractions of SOC to OC are found in other cities, particularly those in southern China, due mainly to the favorable condition for SOC formation such as relatively high temperature and sufficient sunlight. For all sites, SOC/OC at the remote and rural sites is generally greater than those at urban sites. It thus confirms the formation and transport of SOC at a regional scale, and could partly explain the discrepancies in OC/EC by region.

It should be noted that the EC-tracer method has uncertainties. As a semi-quantitative method, the determination of $(OC/EC)_{pri}$ is arbitrary and may vary significantly depending on the observation. In urban Tianjin, for example, the estimated SOC/OC in 2008 (62 %, Gu et al., 2010) was more than twice that of 2009 (28 %, P. Zhao et al., 2013). Hu et al. (2012) modified the method by varying $(OC/EC)_{pri}$ within a defensible range to obtain a series of R^2 correlation coefficients between SOC and EC. The best $(OC/EC)_{pri}$ can then be determined as the one corresponding to the minimum R^2, or when SOC is least correlated with EC. The improved method was used to calculate the SOC concentration during the summer of 2006 in Guangzhou. The $(OC/EC)_{pri}$ from the improved method showed strong agreement with the regression slope of OC to EC in the days when the pollution was mainly influenced by local emissions, indicating that the errors from the subjectively determined OC/EC threshold can be partly reduced (Hu et al., 2012).

3.3 Seasonal variation of carbonaceous aerosol species

Seasonal variations of ambient carbonaceous aerosol levels are illustrated by region in Fig. 6. For ease of visualization, concentrations of OC, EC, and SOC for each season are normalized by dividing by the maximum seasonal concentrations, while OC/EC and SOC/OC are normalized by dividing by the maximum seasonal ratios.

For both urban and rural sites, OC and EC concentrations were generally higher in winter and lower in summer, with some exceptions. For instance, the highest concen-

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trations were found in autumn for Shanghai, probably due to the proximity of biomass combustion (Feng et al., 2009). In most cases, EC has the same seasonal pattern as OC, indicating they are of common origin and/or influenced by the same meteorological factors. On the one hand, enhanced emissions (particularly in northern China) combined with a stagnant atmosphere favor accumulation in winter and result in an increase of carbonaceous aerosol concentrations. On the other hand, the higher mixed layer and increased monsoonal precipitation in summer lead to stronger dispersion and deposition of aerosols. Similar to OC and EC, OC/EC is generally higher in spring and winter, whereas the seasonal variations in OC/EC at southern urban sites are relatively small compared to those at northern sites, reflecting less difference in emissions between cold and warm seasons in the south. Consistent seasonal patterns are found between OC/EC and carbonaceous aerosol concentrations at northern urban sites, while some inconsistencies, such as enhanced OC/EC in summer, occur in the south. It thus implies that the meteorology that favors SOC generation may play a more important role in the seasonal pattern of ambient carbonaceous aerosol levels and their ratios in south.

As a component of OC, SOC concentrations are generally higher in autumn and winter except for Beijing (Lin et al., 2009) and Akdala (Qu et al., 2009), and similar seasonal variations are found for urban and rural sites. Despite the presence of more photochemical oxidants and VOC emissions in summer, the highest SOC concentrations were observed in winter for most cities. The SOC level in winter in Shijiazhuang, for example, was notably 8 times higher than that in summer (P. Zhao et al., 2013). The stagnant conditions and low temperatures that facilitate the accumulation of air pollutants and accelerate the condensation or adsorption of VOC could be one reason for the high SOC in cold seasons (P. Zhao et al., 2013). Using a smog chamber experiment, Huang et al. (2014) confirmed that low temperature does not significantly reduce SOC formation rates from emissions of biomass burning, and large amounts of SOC could be rapidly produced, exceeding POC. During the severe haze event in January 2013, high levels of organic aerosols were found to be largely driven by SOC

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formation, estimated to be responsible for 44–71 % of total OC in four big cities across China (Huang et al., 2014).

A larger contribution of SOC to OC (SOC/OC) is found in fall and winter for most sites, while its seasonal variations are generally smaller compared to those of SOC concentrations, particularly for rural, remote, and southern urban sites. The highest SOC/OC ratios were in fact found in summer at some urban sites including Beijing (Lin et al., 2009), Nanjing (Wu et al., 2013; Li et al., 2015) and Tianjin (Gu et al., 2010, not plotted in Fig. 6), and rural or remote sites such as Longfengshan, Taiyangshan and Akdala (X. Zhang et al., 2008, 2012). Although the absolute SOC levels are higher in winter, the oxidation reactions from VOC to OC are implied to be faster in summer because of higher temperature and more abundant VOC precursors, accelerating SOC formation and thus elevating SOC/OC.

3.4 Distribution of carbonaceous species by particle size

The relationships of ambient OC, EC, and the OC/EC ratio to different particle sizes are given in Table 3. From available observations, the OC and EC mass fractions of fine particles ($PM_{2.5}$) (8.6–25.5 and 3.5–11.7 %, respectively) are larger than those of PM_{10} (4.0–20.0 and 2.8–8.3 %). The OC and EC mass in $PM_{2.5}$ respectively accounts for 51.8–86.4 and 56.7–90.9 % of that in PM_{10}, greater than the mass fractions of $PM_{2.5}$ to PM_{10} (43.0–74.4 %). This information clearly confirms that ambient OC and EC are not uniformly distributed in particles but enriched in the fine particle fraction. Larger OC/EC ratios, however, are found in PM_{10} than in $PM_{2.5}$ in most cases. Such differing distributions of OC and EC reflect the different sources of carbonaceous aerosols in the atmosphere (G. Wang et al., 2010). EC is usually associated with incomplete combustion, which releases into the atmosphere carbonaceous matter mainly in the form of submicron particles. Also enriched in fine particles, OC is nevertheless distributed over a wider range of particle sizes, because condensation processes in the atmosphere can also generate OC. In addition, particles of biogenic origin, including plant debris, pollen, and fungal spores, can accumulate in the coarse particle fraction

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(Matthias-Maser and Jaenicke, 2000). Therefore, the smaller OC/EC ratios in $PM_{2.5}$ imply a greater importance of anthropogenic sources to fine particles. The results in China are consistent with European studies, in which OC/EC in cities was higher in larger particles (Pio et al., 2011).

3.5 Characteristics of carbonaceous aerosols for typical periods

In addition to research focused on annual or seasonal averages, studies have been conducted on carbonaceous aerosol levels during high-pollution, clear, and other typical event periods. For example, at a rural site in the PRD in summer of 2006, the average OC and EC concentrations observed during days of strong influence of local emissions or of typhoons and high precipitation compared to normal days (Hu et al., 2012). Clear distinctions in pollution levels were found between periods: 28.1 $\mu g\,m^{-3}$ of OC and 11.6 $\mu g\,m^{-3}$ of EC during days of strong local emission influence; 4.0 $\mu g\,m^{-3}$ of OC and 1.8 $\mu g\,m^{-3}$ of EC during those influenced by typhoons or high precipitation; and 5.7 $\mu g\,m^{-3}$ of OC and 3.3 $\mu g\,m^{-3}$ of EC for normal days. Relatively low concentrations of carbonaceous aerosols were observed during the campaigns of the Beijing Olympics in 2008 (X. Li et al., 2012), Shanghai World Expo in 2010 (Wang et al., 2014), and Nanjing Asian Youth Games in 2013 (Yu et al., 2014), showing the effectiveness of pollution control measures on air quality for those events.

More studies have focused on heavy pollution periods, such as hazy days and biomass burning seasons. A hazy day is defined by daily average atmospheric visibility less than 10 km (Hou et al., 2011), with $PM_{2.5}$ one of the most important contributors. In this work, the seasonal averages of $PM_{2.5}$ concentrations in urban or suburban sites throughout China during 2000–2010 are compiled based on available studies, and an approximate lognormal distribution is derived for frequency of $PM_{2.5}$ levels with a data sample size of 170, as shown in Fig. 7. Around 60 % of the $PM_{2.5}$ values exceeded the national standard of 75 $\mu g\,m^{-3}$, reflecting heavy pollution throughout the country. Compared with clear periods, for example, carbonaceous aerosols as well as

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other components in $PM_{2.5}$ were greatly enhanced during local haze periods, by up to 430 % in Guangzhou (Jung et al., 2009) and about 160, 170, and 180 % for OC, EC and secondary non-organic aerosols (SNA), respectively, in Fuzhou (F. Zhang et al., 2013). As shown in Fig. 7, moreover, larger mass fractions of carbonaceous aerosols in $PM_{2.5}$ are found for periods with relatively lower $PM_{2.5}$ levels, and the fractions of OC and EC to $PM_{2.5}$ were 27 and 63 % less, respectively, at $PM_{2.5}$ concentrations of 190–380 $\mu g\,m^{-3}$ compared to those of 10–30 $\mu g\,m^{-3}$. The results indicate, on one hand, that rapid increase in other compounds like SNA contribute significantly to heavy haze events. For example, in Beijing, the fraction of particles composed of inorganic ions ($SO_4^{2-} + NO_3^- + NH_4^+$) increased as $PM_{2.5}$ levels rose during 1999–2010 (data provided by K. He of Tsinghua University, 2012). On the other hand, the sharp increase in OC/EC along with enhanced $PM_{2.5}$ levels indicates significant contribution of SOC to strong haze events. For example, Huang et al. (2011) found that hazy episodes in Harbin were closely related to the high concentrations of OC and EC, and the average OC/EC ratio on hazy days (42.2) was almost three times of that in non-haze days (14.5).

Biomass burning is another source with significant impact on ambient aerosol levels and air quality. Elevated levels of carbonaceous aerosols were usually found during the harvest season. For example, OC and EC were observed to increase by 99 and 105 %, respectively, during the biomass-burning vs. non-biomass-burning periods in Guangzhou (Zhang et al., 2010), and the analogous values for Chengdu were observed to be 148 and 51 % (Wang et al., 2013). With other methods combined, the biomass-burning share of carbonaceous aerosol enhancement has also been quantified in recent studies. Li et al. (2015), using regression analysis of particle OC and K^+ of biomass burning origin, estimated that biomass burning contributed more than half of ambient OC during the harvest season in Nanjing. Based on observations and chemical transport modeling, Cheng et al. (2014) estimated that open biomass burning contributed 37 % of $PM_{2.5}$, 70 % of OC, and 61 % of EC at five representative cities in

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the YRD region during May and June, and that a complete ban of biomass burning would reduce the human exposure level of $PM_{2.5}$ in the region 47 %.

4 Assessment of emission inventories using observations

4.1 Comparisons of inter-annual trends in ambient levels and emissions for 2000–2010

The seasonal means of OC, EC, and $PM_{2.5}$ concentrations and the ratios of OC to EC based on available observations are plotted from 2000 to 2010 in Fig. 8, to reflect the trends of carbonaceous aerosols at the national scale. Although an increasing inter-annual trend is found for estimated OC and EC emissions over the 10 years, the observed concentrations of carbonaceous aerosols did not likewise increase, and observed EC actually declined. On the one hand, the improvement of fuel combustion technologies in the residential sector and thereby the possible changes in emission factors cannot be fully captured in current emission inventory studies because of insufficient data on key parameters. This may result in overestimated growth of emissions than indicated by observed concentrations. Databases of evolving emission factors over time reflecting incremental emission control, particularly in residential combustion sources, are necessary to improve understanding of long-term emission trends in China. On the other hand, the ambient levels of carbonaceous aerosols could also be influenced by changes in meteorological factors in air quality, including wind velocity, humidity, temperature, and stability of the atmosphere (J. Wang et al., 2012). For example, divergent trends in local meteorology for the JJJ and PRD regions led to opposite trends in carbonaceous aerosol levels for the two regions (increased in JJJ but decreased in PRD) in recent years (X. Zhang et al., 2013). The estimates of emissions by region should thus be improved to incorporate detailed information on local sources, to carefully differentiate the impacts of emissions and meteorology on carbonaceous aerosol pollution at regional and local scales.

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Observations indicate increased OC/EC ratios from 2000 to 2010 at the national scale (Fig. 8), but emission inventories indicate slightly reduced ratios (from 1.58 in 2000 to 1.48 in 2010, as shown in Fig. 2c). This inconsistency might result from (1) the possible underestimate of emissions from sources with significant primary OC, e.g., biomass burning (described later in Sect. 4.2), and (2) enhanced SOC formation from increasing VOC emissions (Bo et al., 2008; Wei, 2009) and elevated atmospheric oxidation. For comparison, primary $PM_{2.5}$ emissions are estimated to have declined after 2005, due to the improved energy structure and emission controls in certain industrial sources and transportation (Y. Zhao et al., 2013), while $PM_{2.5}$ concentrations have been increasing in recent years (Fig. 8). The result emphasizes that the ambient $PM_{2.5}$ level is not only determined by primary particle emissions, and that secondary particle formation driven by emissions of precursors and enhanced atmospheric oxidation appears to be playing increasingly important roles in PM pollution across the country.

4.2 Evaluation of emission inventories based on the $(OC/EC)_{pri}$

The validity of current emission inventories of carbonaceous aerosols is evaluated through available observations of OC/EC ratios. The following criteria are used to select observational data: (1) observation sites must be located in rural or remote areas that are more representative of regional pollution from emissions, (2) the ratio of primary OC and EC, $(OC/EC)_{pri}$, must be provided or can be calculated based on the observations; and (3) the sampling period must be sufficient for evaluation of annual emissions. With these restrictions, the observational data suitable for $(OC/EC)_{pri}$ evaluation come mainly from X. Zhang et al. (2008) for 2006. As shown in Fig. 9, the value of $(OC/EC)_{pri}$ from given observational sites is indicated on the x axis, while that from the estimated emissions for the province where the site is located is shown on the y axis. The correlations of $(OC/EC)_{pri}$ between observations and emissions are then analyzed. Besides the emissions estimated in this work, other emission inventories for 2006 (Zhang et al., 2009; Kurokawa et al., 2013) and 2005 (Lei et al., 2011, as an approximation of 2006) are also included for comparison. Note that because these other

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inventories do not include emissions from open burning of biomass, we corrected their results by adding that part of emissions calculated by this work to their original totals.

As can be seen in Fig. 9, the data points based on provincial emissions estimated by this work, with a regression slope of 0.97, are in best agreement with the $Y = X$ line, while the emission ratios [$(OC/EC)_{emi}$] of the other inventories are 20–50 % higher than the observed concentration ratios. The residual sum of squares (RSS), which measures the discrepancy of the data and the linear regression model, is calculated as well for all the inventories, and the lowest RSS (and thereby random error) is found for this work, at 1.18. The comparison thus indicates improved reliability and reduced uncertainty of our inventory, resulting largely from a more detailed classification of source categories and application of emission factors from local field measurements. It should be noted that the $(OC/EC)_{pri}$ obtained from observations in Nanning is much lower than $(OC/EC)_{emi}$ for its province, Guangxi, estimated in this work (point A in Fig. 9). The deviation might result partly from the fact that the observation was actually conducted in an urban area but categorized as a rural measurement because of less intense emission activity in this relatively underdeveloped city, according to X. Zhang et al. (2008). It thus further implies the better representativeness of regional emission levels by observation at rural or remote sites. Excluding point A from the linear regressions analysis, the slope comparing the observations and emissions estimated by this work would change to 0.92, with an SSR reduced to 0.62, while those for Zhang et al. (2009), Lei et al. (2011) and REAS 2 are recalculated as 1.12, 1.27 and 1.35, with SSRs of 1.58, 1.36 and 2.60, respectively (not shown in Fig. 9).

Despite efforts to improve the emission estimation, the regression slopes comparing OC/EC from emissions in this work to observations are less than 1.0. In particular, $(OC/EC)_{pri}$ obtained from observations at two sites, Longfengshan in Heilongjiang (point B) and Taiyangshan in Hunan (point C) are clearly larger than $(OC/EC)_{emi}$ in this work, but closer to those for other inventories. This deviation thus implies a possible underestimate of emissions for sources with high OC/EC ratio, e.g., combustion of biofuel/biomass waste in agricultural areas. As mentioned in Sect. 2.4, part of the

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uncertainty comes from a lack of sufficient evaluation of the representativeness and reliability of emission factors of biofuel use from limited domestic measurements. Another important reason for the relatively low OC emission results could be possible underestimation of biomass open burning in some areas. In the bottom-up method, the amount of biomass burning in clear fields depends significantly on one parameter: the ratio of burned crop wastes to the total produced. Existing investigations of this ratio, with its spatial distribution and temporal trends across the country, are far from sufficient, and piecemeal information from local government plans on renewable energy or constant values from individual surveys (e.g., Wang and Zhang, 2008) have to be applied in emission estimation, though they likely differ significantly from facts on the ground. For example, increased ratios of crop waste recycling and utilization (which imply decreased ratios of crop wastes burned in open fields) are suggested in the government plans from 2005 to 2012 in the YRD region, where the air quality is influenced heavily by open biomass burning in harvest season. According to fire counts and intensity observed by satellite with MODIS (Moderate Resolution Imaging Spectroradiometer, https://earthdata.nasa.gov/data/near-real-time-data/firms), however, a growing trend of biomass burning is found for the region during the period (X. Huang et al., 2012; Yang et al., 2015). Moreover, relatively strong signals of fire intensity are indicated by MODIS for northeastern and south-central China, close to the observation sites of points B and C in Fig. 9, respectively, implying considerable influence of biomass burning on the ambient carbonaceous aerosol levels in those regions. To better understand the levels and trends of carbonaceous aerosol emissions in China, therefore, more observations from ground sites and satellites should be collected and incorporated into the framework of bottom-up emission estimation methods.

5 Conclusions

Due to fast growth of the economy and energy consumption, national emissions of primary carbonaceous aerosols are estimated to have increased 29 and 37 % for OC

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and EC, respectively, from 2000 to 2012. Attributed mainly to incomplete combustion of solid fuels, the residential sector is the greatest contributor to emissions, with shares of total emissions of 76±2 % for OC and 52±3 % for EC, followed by industry (19±2 % for OC and 32±2 % for EC) and transportation (5±1 % for OC and 16±2 % for EC). Higher emission intensities of carbonaceous particles but lower ratios of OC to EC emissions are estimated for northern provinces than southern ones, and this spatial pattern can be confirmed by ground observations across the country. The updated emission factors incorporating the results from the most recent local field measurements are the main reason for differences in emission estimates between our study and other inventories. In particular, the relatively low emission factors of biofuel stoves based on domestic tests lead to clearly smaller OC emissions in this work than in most other studies.

Combining available observational studies across the country, higher concentrations of carbonaceous aerosols are found for northern and inland cities while lower ones are found for southern and coastal cities. Clear concentration gradients are shown for urban, rural, and remote sites, indicating the effects of anthropogenic activities on carbonaceous PM pollution. In contrast to urban sites, especially in northern cities where primary emissions of anthropogenic origin play a more important role in ambient OC levels, larger contributions of SOC to OC are estimated at rural and remote sites, attributed to more emissions of biofuel-originated OC and biogenic VOCs, and/or transport from aged aerosols. While higher concentrations occur in cold seasons for all of the carbonaceous aerosol species (OC, EC and SOC), smaller seasonal variations are observed for SOC/OC, particularly at rural sites, implying accelerated atmospheric oxidation in summer. In urban and suburban areas, larger ratios of ambient OC to EC are observed in higher atmospheric $PM_{2.5}$ concentrations, implying the increased contribution of SOC to heavy haze pollution. As a dominant source of OC, biomass burning is confirmed to play significant roles in the carbonaceous aerosol pollution and worsened air quality during harvest seasons.

Over a relatively long-term period of 2000–2010, no significant growth is found for OC or EC concentrations but is found for OC/EC from observations, implying the en-

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hanced SOC formation across the country. The estimate of increased annual national emissions is somewhat inconsistent with relatively stable ambient levels of carbonaceous aerosols for the decade. Due to a lack of detailed information regarding emission sources, little consideration of inter-annual trends in emission factors, particularly in the residential sector, could be one of the reasons explaining the discrepancy. Through comparisons of $(OC/EC)_{pri}$ obtained from emissions and observations, the estimated emissions in this work are confirmed to better correlate with observations than other inventories, helping to validate the current work. However, the lower $(OC/EC)_{pri}$ from emissions than observations for some areas indicates that emissions of certain sources producing relatively large OC, e.g., biomass open burning, might be underestimated. More ground and satellite observations are thus encouraged, to be incorporated into the framework of bottom-up emission inventories to better understand the levels and trends of carbonaceous aerosol emissions from biomass burning.

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Table 1. EC and OC emission factors for coal and biofuel burned in small stoves ($g\,kg^{-1}$). The values in parentheses indicate the range (for uniform distribution), 95 % CI (for beta distribution), or standard deviation (SD, for lognormal distribution) of the emission factor.

	EF_{EC}		EF_{OC}	
	Value	Distribution	Value	Distribution
Anthracite briquette	0.006	Uniform (0.000–0.012)	0.20	Uniform (0.04–0.36)
Bituminous briquette	0.24	Lognormal (SD: 0.53)	5.16	Uniform (0–13.8)
Anthracite chunk coal	0.03	Uniform (0–0.04)	0.25	Uniform (0.03–0.47)
Bituminous chunk coal	3.13	Uniform (0–16.9)	4.94	Beta (0.12–14.98)
Crop wastes as biofuel	0.97	Lognormal (SD: 0.94)	2.04	Lognormal (SD: 1.09)
Firewood	0.88	Lognormal (SD: 1.15)	1.0	Lognormal (SD: 1.29)

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Table 2. Uncertainties of China's EC and OC emissions by sector and the two parameters contributing most to emission uncertainties for 2012. The emissions are expressed in Gg, with 95 % CI in parentheses. The percentages in the parentheses following parameters indicate contributions of the parameters to the variance of corresponding emission estimates. Recall from Eqs. (1) and (2) that F represents the relevant mass fraction of $PM_{2.5}$, $f_{PM_{2.5}}$ the $PM_{2.5}$ mass fraction of total PM, AL the relevant activity level, and EF the relevant emission factor.

	Power plants	Total industry	Transportation	Residential	Total
EC	6 (−67 %, 584 %) $F_{EC,\ pulverized\ boiler}$ (80.8 %) $f_{PM_{2.5},\ pulverized\ boiler}$ (5.4 %)	607 (−51 %, 142 %) $AL_{coke\ production}$ (23.1 %) $F_{EC,\ grate\ boiler}$ (17.8 %)	311 (−70 %, 73 %) $F_{EC,\ non\text{-}road\ diesel\ vehicle}$ (70.4 %) $EF_{PM_{2.5},\ rural\ machine}$ (6.3 %)	942 (−48 %, 222 %) $EF_{EC,\ small\ coal\ stove}$ (70.6 %) AL_{coal} (6.8 %)	1857 (−27 %, 127 %) $EF_{EC,\ small\ coal\ stove}$ (59.6 %) AL_{coal} (5.7 %)
OC	0 (−100 %, 2321 %) $F_{OC,\ grate\ boiler}$ (41.4 %) $f_{PM_{2.5},\ grate\ boiler}$ (25.5 %)	488 (−45 %, 179 %) $F_{OC,\ grate\ boiler}$ (20.9 %) $AL_{coke\ production}$ (20.3 %)	136 (−64 %, 93 %) $F_{OC,\ non\text{-}road\ diesel\ vehicle}$ (48.2 %) $F_{OC,\ on\text{-}road\ diesel\ vehicle}$ (23.5 %)	2125 (−52 %, 101 %) $EF_{OC,\ small\ coal\ stove}$ (42.9 %) $EF_{OC,\ biomass\ open\ burning}$ (20.5 %)	2749 (−34 %, 90 %) $EF_{OC,\ small\ coal\ stove}$ (38.9 %) $EF_{OC,\ biomass\ open\ burning}$ (18.2 %)

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Table 3. Statistical summary of OC and EC mass fractions of $PM_{2.5}$ and PM_{10}, the enrichment ratios of OC and EC in $PM_{2.5}$ and PM_{10}, the $PM_{2.5}$ mass fraction of PM_{10}, and OC/EC mass ratios in $PM_{2.5}$ and PM_{10}. (The values for Daihai refer to TSP instead of PM_{10} due to lack of PM_{10} data.)

Site	Period	$OC/PM_{2.5}$ (%)	OC/PM_{10} (%)	$OC_{PM_{2.5}}/OC_{PM_{10}}$ (%)	$EC/PM_{2.5}$ (%)	EC/PM_{10} (%)	$EC_{PM_{2.5}}/EC_{PM_{10}}$ (%)	$PM_{2.5}/PM_{10}$ (%)	$OC_{PM_{2.5}}/EC_{PM_{2.5}}$ (%)	$OC_{PM_{10}}/EC_{PM_{10}}$ (%)	Reference
Nanjing	Nov 2011	16.4	15.3	76.7	6.2	5.1	85.6	71.4	2.8	3.1	Li et al. (2015)
	Mar 2012	9.9	7.9	80.8	4.5	3.5	82.1	64.4	2.3	2.4	
	Jun 2012	9.8	8.9	81.8	4.0	3.5	85.6	74.4	2.5	2.7	
Tianjin	Jun–Jul 2007	8.6	4.3	61.0	8.7	2.9	90.9	61.4	2.0	3.0	Kong et al. (2010)
	Oct 2007	10.2	4.0	86.4	7.5	3.0	84.3	63.5	2.5	2.5	
	Jan–Feb 2008	16.9	5.4	62.2	11.7	4.1	56.7	43.0	3.2	2.9	
	Sep 2009–Feb 2010	11.7	13.2	51.8	3.5	2.8	71.7	58.4	3.7	4.7	P. Li et al. (2012)
	Jan, Apr, Jul, Oct 2008	15.1	15.1	61.4	5.3	4.4	70.1	55.9	2.9	3.4	Gu et al. (2010)
Xi'an	Fall 2003	25.5	18.0	81.8	8.0	5.7	75.0	55.6	3.3	3.2	Cao et al. (2005)
	Winter 2003	25.4	20.0	72.8	5.4	5.0	59.6	60.4	5.1	4.2	
Hong Kong	Jun–Jul 2002	18.6	15.7	84.7	8.8	8.3	78.2	70.9	1.9	1.8	Cao et al. (2004)
Guangzhou	Jun–Jul 2002	20.3	17.7	73.8	7.8	6.4	77.7	64.1	2.7	2.9	
Shenzhen	Jun–Jul 2002	15.1	13.1	71.3	8.2	6.2	80.0	62.6	1.8	2.1	
Zhuhai	Jun–Jul 2002	17.8	15.5	80.6	6.6	6.2	74.9	68.9	2.9	2.7	
Daihai	Fall 2005	24.0	18.1[a]	44.7[b]	3.6	2.4[a]	49.9[b]	33.7[b]	6.7	7.5[a]	Han et al. (2008)
	Winter 2006	24.7	13.1[a]	67.0[b]	2.8	1.4[a]	71.1[b]	35.4[b]	8.9	9.5[a]	
	Summer 2006	17.2	9.5[a]	70.2[b]	2.8	1.5[a]	69.7[b]	38.9[b]	6.2	6.2[a]	
	Spring 2007	11.3	5.6[a]	46.6[b]	2.5	1.2[a]	50.0[b]	22.9[b]	4.5	5.2[a]	

[a] Refers to that in TSP.
[b] Refers to $PM_{2.5}$/TSP.

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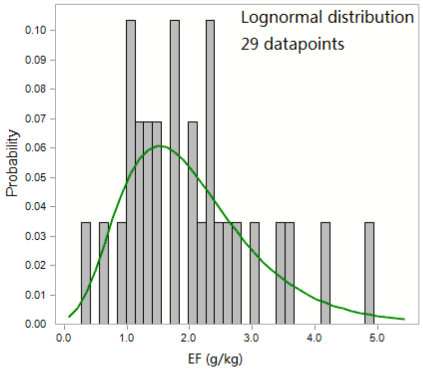
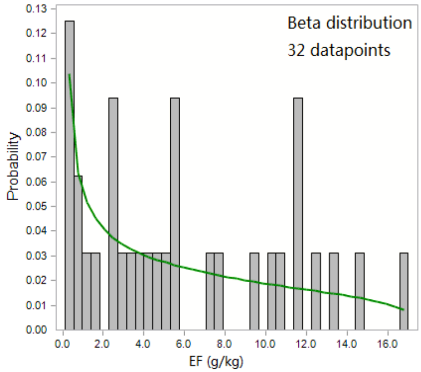
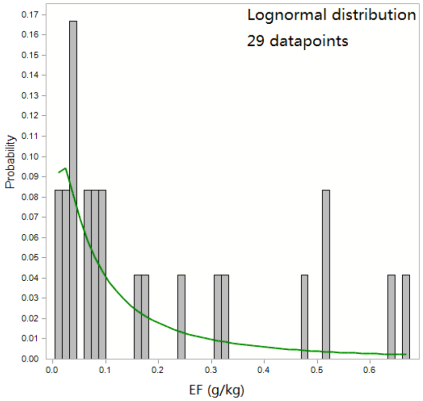


(a) OC from crop waste burning



(b) OC from bituminous chunk coal burning



(c) EC from bituminous briquette burning

Figure 1. Probability distributions of emission factors for combustion in small stoves: **(a)** OC from crop waste burning; **(b)** OC from bituminous chunk coal burning; and **(c)** EC from bituminous briquette burning.

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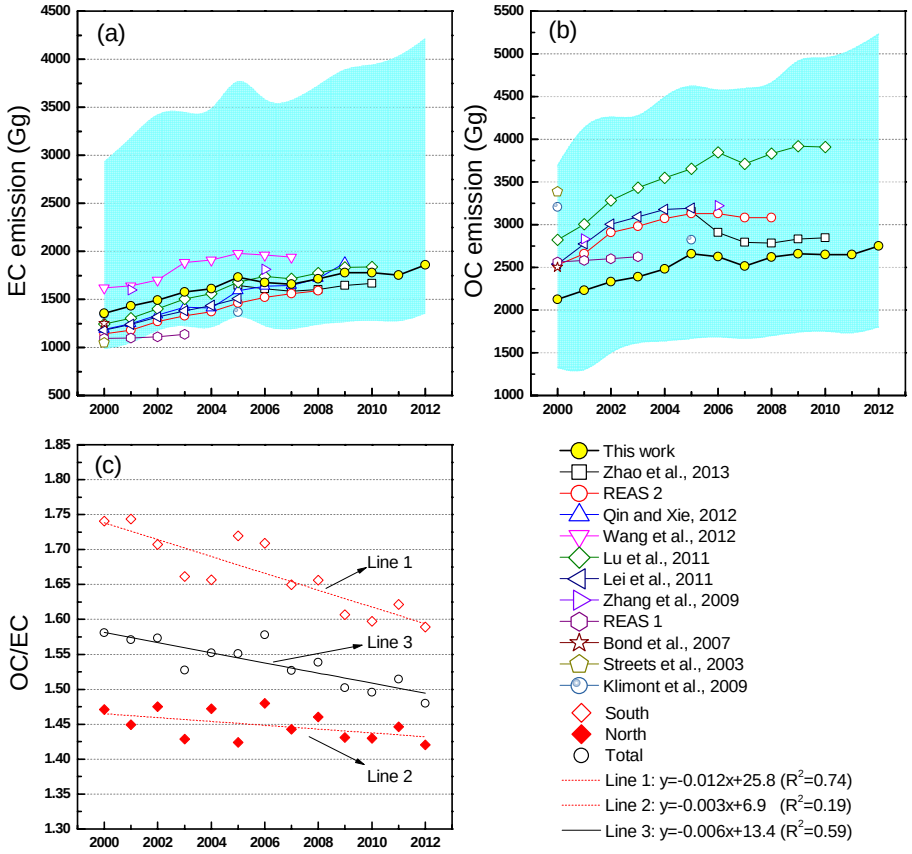

Figure 2. Inter-annual trends of **(a)** EC emissions, **(b)** OC emissions, and **(c)** ratios of OC to EC emissions ($(OC/EC)_{emi}$) for China from 2000 to 2012. The blue area indicates the 95 % CIs estimated by this work. The definition of southern and northern provinces is indicated in Fig. 3.

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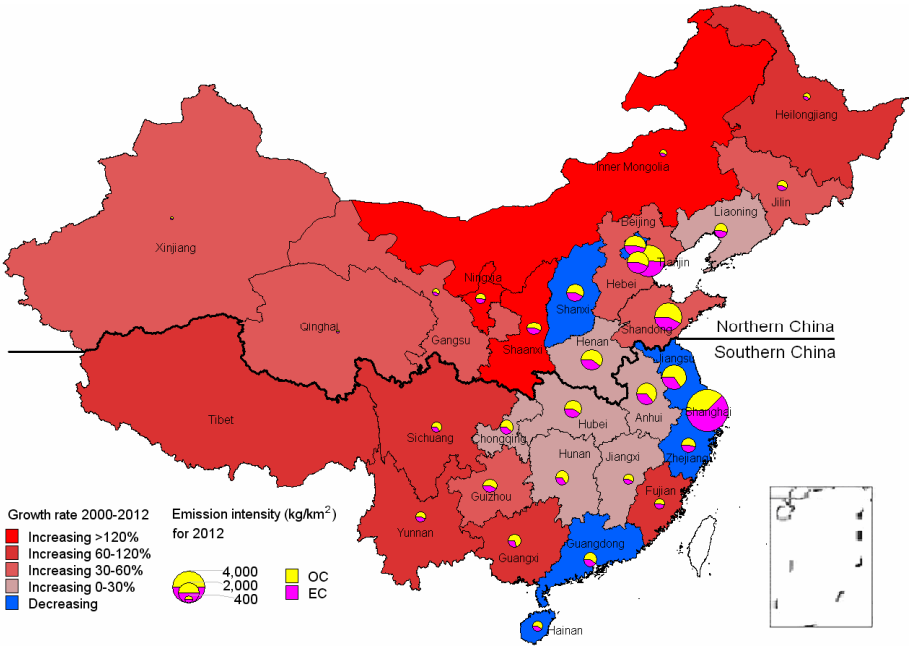

Figure 3. The provicial emission intensities of OC and EC in 2012 and relative changes of primary carbonaceous aerosol emissions (OC + EC) by province between 2000 and 2012.

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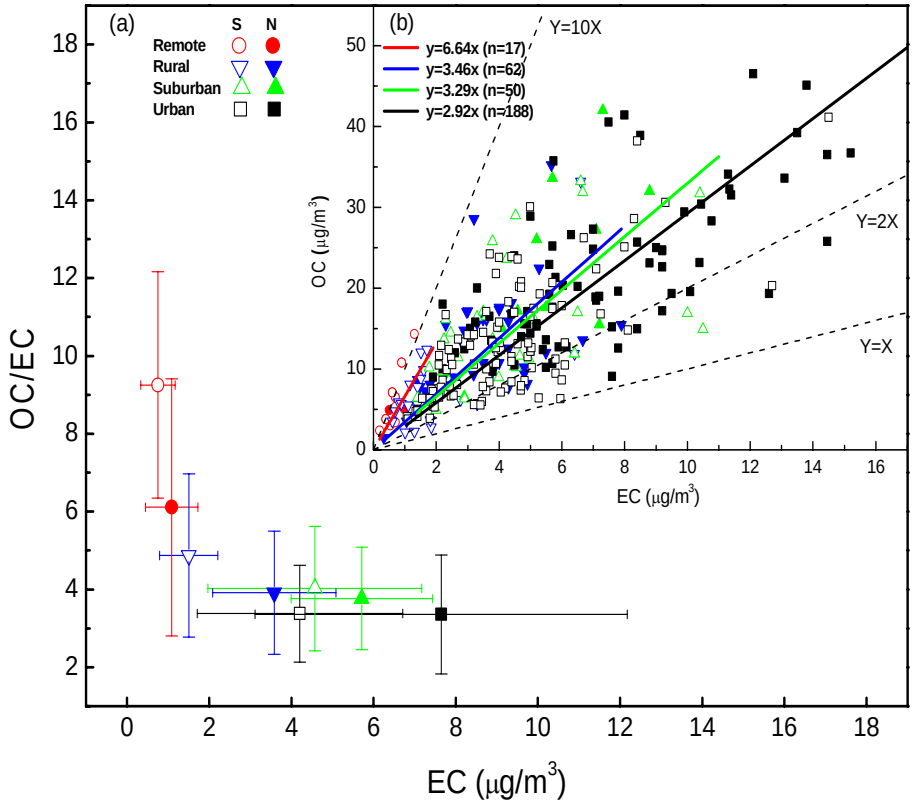

Figure 4. (a) Averaged ambient OC/EC ratios vs. EC concentrations in $PM_{2.5}$ with standard deviations from seasonal observation data at southern (S, open symbols) and northern (N, solid symbols) remote, rural, suburban, and urban sites in China; and **(b)** regressions of observed seasonal means of OC and EC concentrations in $PM_{2.5}$ for remote, rural, suburban, and urban sites in China. The lines indicating OC/EC = 1 ($Y = X$), 2 ($Y = 2X$) and 10 ($Y = 10X$) are plotted for comparison.

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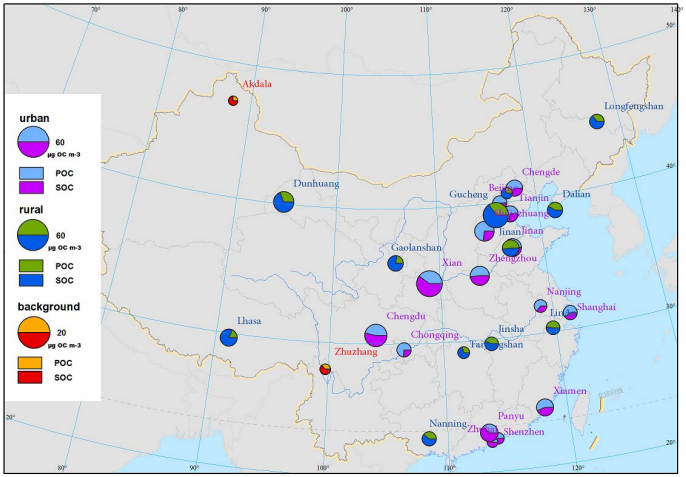

Figure 5. Annual averages of OC concentrations and mass fractions of POC and SOC to OC by region from various studies, including (1) urban sites: Beijing (Lin et al., 2009); Tianjin, Shijiazhuang, and Chengde (P. Zhao et al., 2013); Jinan (Yang et al., 2012); Guangzhou (Duan et al., 2007); Xiamen (Zhang et al., 2011); Shenzhen and Zhuhai (Cao et al., 2003a, 2004); Shanghai (Feng et al., 2009); Nanjing (Wu et al., 2013); Chongqing (Chen et al., 2014); Chengdu, Panyu, Xian, Zhengzhou, Nanning, and Dalian (X. Zhang et al., 2008); (2) rural sites: Jinan (Yang et al., 2012); Gucheng, Taiyangshan, Longfengshan, Dunhuang, LinAn, Jinsha, Lhasa, Gaolanshan, and Shangdianzi (X. Zhang et al., 2008); and (3) remote sites: Akdala and Zhuzhang (Qu et al., 2009). SOC concentrations were obtained by the EC-tracing method by using the equation: $SOC = OC_{tot} - (OC/EC)_{min} \times EC$ (Castro et al., 1999). The minimum or the lowest 5–20 % OC/EC ratios were used as the primary OC/EC ratios (Cao et al., 2007). Note the scales of piecharts indicating OC concentrations are not uniform for urban, rural, and remote sites, to ease visualization.

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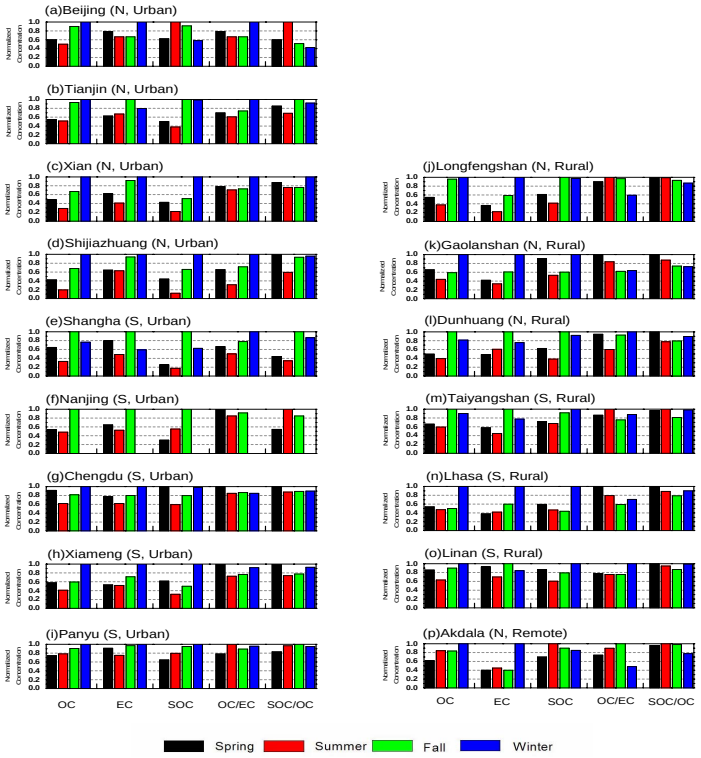

Figure 6. Seasonal variation of normalized OC, EC, SOC, OC/EC and SOC/OC in $PM_{2.5}$ (Beijing, Tianjin, Shijiazhuang, Shanghai, Nanjing, and Xiamen) or PM_{10} (other cities) by region from various studies, including (1) urban sites: Beijing (Lin et al., 2009); Tianjin and Shijiazhuang (P. Zhao et al., 2013); Shanghai (Feng et al., 2009); Nanjing (Li et al., 2015); Xiamen (F. Zhang et al., 2012); Xian, Chengdu, and Panyu (X. Zhang et al., 2008, 2012); and (2) rural/remote sites: Longfengshan, Gaolanshan, Dunhuang, Taiyangshan, Lhasa, and Linan (X. Zhang et al., 2008, 2012); Akdala (Qu et al., 2009). N and S represent northern and southern sites, respectively.

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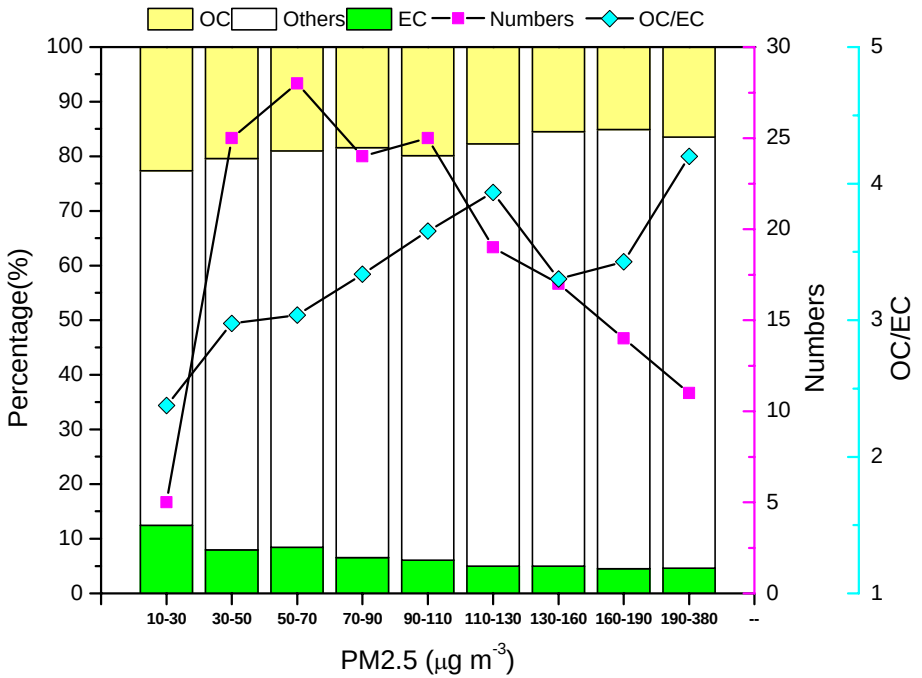

Figure 7. The carbonaceous aerosol mass fractions of ambient $PM_{2.5}$ and OC/EC ratios, classified by $PM_{2.5}$ concentration from reconstructed data measured in areas highly affected by anthropogenic sources (i.e., urban and suburban sites) in China. Numbers of data points by $PM_{2.5}$ level are also shown.

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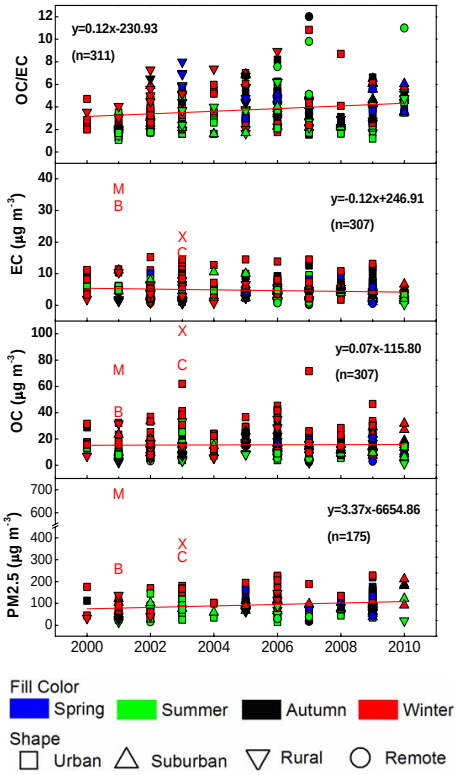

Figure 8. Inter-annual trends of concentrations of OC, EC and $PM_{2.5}$, and ratios of OC to EC from 2000 to 2010 based on ground observations from various studies. Four data points (B: Beijing; M: Miyun; X: Xian; C: Chongqing) are excluded from the linear regression analysis due to the extremely high concentrations observed during heavy haze pollution events.

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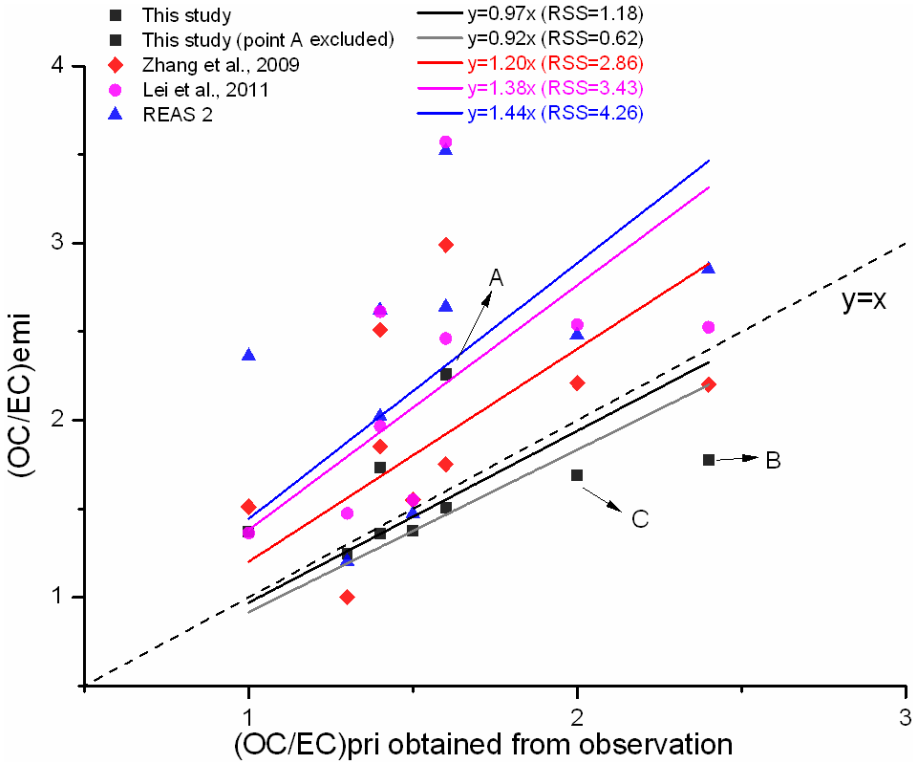

Figure 9. Correlation of $(OC/EC)_{pri}$ from ground observation (X. Zhang et al., 2008) and $(OC/EC)_{emi}$ from provincial emissions estimated by different inventory studies. Points A, B, and C represent the observations at Nanning, Longfengshan, and Jinsha, and emission results for corresponding provinces (Guangxi, Heilongjiang, and Hubei), respectively.

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