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Carbonaceous species in $PM_{2.5}$ at a pair of rural-urban sites in Beijing, 2005–2008

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Abstract

One-week integrated $PM_{2.5}$ samples were collected at a pair of rural (MY)-urban (TH) sites in Beijing over four years between 2005 and 2008. Weekly OC and EC in $PM_{2.5}$ were compared to investigate their respective levels and temporal patterns at the two sites, and differences in the factors contributing to them were discussed. A systematic decrease of annual mean concentration of OC and an opposite trend for EC at both sites, and the significantly lower fractions of TCM (total carbonaceous mass) in $PM_{2.5}$ mass than those measured at TH in 1999, indicate that the relative importance of carbonaceous species in $PM_{2.5}$ was probably weakened whereas that of EC in TC was steadily enhanced. Clear seasonal variations were found for both OC and EC concentrations (varying seasonally by factors of 1.35~3.0) at TH with higher weekly concentrations and fluctuations in winter and much lower values in summer and spring. The minimum seasonal urban excesses of OC (3.0 $\mu g\,m^{-3}$) and EC (1.2 $\mu g\,m^{-3}$), which were only one-ninth to one-eighth of their corresponding maxima, both occurred in 2008 summer. The noticeably more positive stable carbon isotope values ($\delta^{13}C$) of EC at TH in that summer relative to the preceding summers puts in new evidence that the contribution to carbonaceous particles from mobile sources was substantially reduced due to a concerted effort to reduce emissions from new and existing vehicles before, during and after the Summer Olympics. No consistent seasonal patterns of OC and EC concentrations without strong correlations and their high ratios (OC/EC) at the MY site reflect their complex and variable major sources and formation/production in the rural area compared to the urban area in Beijing, such as biomass burning during the harvest seasons, widely used high-polluting family stoves and small boiler for cooking and heating, and high potential formation of SOA.

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1 Introduction

The impact of air pollution in the last 50 yr has shifted from a local to global scale with the interest lately centering on small particles and more exotic organic compounds (Fenger, 2009). There has been increasing interest in specific components of fine particles (i.e. $PM_{2.5}$), especially carbonaceous species, due to their important roles playing from air pollution to climate change as well as the challenges of their proper measurements and understanding their formation mechanisms (Gelencsér, 2004; Andreae and Gelencsér, 2006; Ramanathan and Carmichael, 2008; Flanner et al., 2009). Carbonaceous aerosols, including organic and elemental carbon (OC and EC) typically constitute a significant or even dominant fraction of the total $PM_{2.5}$ mass. Both EC and OC are released from various primary emission sources and are usually concentrated in the fine size class. OC, as aggregates of hundreds of individual compounds spanning a wide range of chemical and thermodynamic properties, is also produced as secondary organic aerosol (SOA) in the atmosphere through photochemical oxidations. Renewed interest has been devoted to black (or elemental) carbon (BC), and its immediate control is believed to be a win-win choice of slowing down global warming along with improving human health (Jacobson, 2002; Ramanathan and Carmichael, 2008). It is also known that OC is a major component scattering light and cooling the atmosphere (IPCC, 2007). Therefore, studying OC to EC levels and their ratios in air column, and their changes with time will provide valuable information to constrain emission sources and atmospheric transport/transformation mechanisms as well as to assess the impact of human-induced signals on the atmospheric environment.

Studies conducted in China showed that carbonaceous aerosols maintain at high levels and are major components of $PM_{2.5}$, especially in megacities (Yang et al., 2005; Cao et al., 2007). As a rapidly developing megacity and the capital of China, Beijing has been experiencing rapid industrialization and urbanization since the 1980s. Coal has been the predominant energy with annual coal consumption at about 27–30 megatons in recent ten years. The vehicle population has kept soaring to 3.50 million in 2008 from

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2.58 million in 2005. In addition, biofuel burning around neighboring rural areas adds to the burden of high particulate levels and poor visibility, a common problem for years in the Beijing-Tianjin-Hebei Region. These emission sources together with regional-scale transport add to the complexity of understanding and reducing fine particulate pollution. On the other hand, a Master Plan for 1998–2008 was established, and during this decade the Beijing Municipal Government implemented more than 200 environmental measures in 14 stages to improve the capital's air quality (www.bjepb.gov.cn). The Beijing 2008 Olympic Games provided added incentive to accelerate the processes (UNEP, 2009). Beijing has been leading the country in phasing out leaded gasoline and low-quality coal with high sulfur and high ash, switching from coal to cleaner and more efficient energy such as natural gas or liquefied petroleum gas (LPG), and implementing stricter emission standards for vehicles and coal-fired boilers compared to state criteria. As well, heavily polluting facilities have been relocated outside Beijing. These efforts have resulted in evident improvement in air quality as compliances keep growing, but far less than expected in terms of particulate pollution control. This had been leading to additional measures to reduce emissions in targeted sectors in neighboring provinces of Tianjin, Hebei, Shanxi, Shandong, and Inner Mongolia, in order to assure air quality for the Beijing Olympic Games. Surface and satellite measurements show that the measures taken in Beijing and surrounding region during the Olympic Summer Games very likely had a noticeable effect (Cermak and Knutti, 2009; Wang et al., 2010).

The emission control and large reduction in Beijing represents a human-perturbation experiment of unprecedented scale, and provides a rare opportunity to study the impact of pollution emissions on the air quality and atmospheric chemistry (Wang et al., 2010). $PM_{2.5}$ is not currently regulated in China but there have been a number of field studies in the last decade to quantify and characterize $PM_{2.5}$ (Chan and Yao, 2008). A number of papers have also been published on the results of surface and satellite measurements during the Beijing Olympics (Wang et al., 2010). However, there is none focusing on carbonaceous aerosols based on long-term surface speciation

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measurement covering the Olympics in Beijing. In 2005, we initiated a $PM_{2.5}$ speciation measurement program at a pair of urban and rural sites in Beijing to track its trends in mass concentration and chemical composition. In this study, a simultaneous and identical speciation sampling approach was adopted to continuously collect ambient $PM_{2.5}$ at a pair of urban-rural locations. This paper will summarize the major findings for carbonaceous species in $PM_{2.5}$ from 2005 through 2008, with a focus on their temporal variations and possible sources.

2 Experimental

Beijing is located on the northern border of the Great North China Plain, with a total population of 15.8 million and an area of 16 410 km^2 (Beijing Municipal Bureau of Statistics, 2008). As the most populated city after Shanghai in China, its population is concentrated in the urbanized area (accounting only for 6% of the total area) with a maximum of 23 008 inhabitants/km^2 compared to a minimum of 366 inhabitants/km^2 in the exurb (http://www.chinapop.gov.cn). The main terrain of Beijing is plain, with surrounding mountains on three sides (Fig. 1), which traps the pollutants so they can not be easily expelled. Beijing has significant seasonal winds. From November to April, the prevailing airflow from the northwest is dry and cold, while at other times the local winds are moderate. To represent the urban influence and rural background, two sites about 70 km apart were selected. The urban site was located in the residential area inside the campus of Tsinghua University (referred to as TH, 40°19′ N, 116°19′ E); the rural site was near the Miyun Reservoir (referred to as MY, 40°29′ N, 116°47′ E), about 100 km to the northeast of city center (Fig. 1). The surrounding areas of the MY site possess abundant vegetation from agriculture and small woodlots, which help curtain soil dust but have the potential to emit biogenic hydrocarbons, precursors of ozone and SOA.

A special speciation sampler (Aerosol Dynamics Inc., Berkeley, CA) equipped with three cassettes, each with an identical flow rate of 0.4 L min^{-1}, was used to collect

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ambient $PM_{2.5}$ from the start of 2005 through the end of 2008 on a building roof about 4 m and 3 m above ground at TH and MY, respectively. A single-filter cassette accommodates a Gelman Teflon-membrane filter (47 mm, 2 µm pore size) for mass by gravimetry and then for elements, and a separate tandem-filter cassette holds a Teflon filter and a backup nylon filter for water-soluble ions by ionic chromatography (He et al., 2001). A tandem-filter cassette holds two 47-mm (in diameter) pre-fired Gelman quartz-fiber filters (#2500 QAT-UP) for carbon analysis. The sampling duration for each sample was one week. According to McDow and Huntzicker (1990) and Turpin et al. (2000), the face velocity and sampling duration are the key parameters to assess the comparability of different filters' sampling. The low face velocity adopted in the study would lead to a tendency for higher OC values, whereas the 7-day integrated sampling period appears to exacerbate the possible loss of semi-volatile organic compounds (SVOCs) from the collected particles (due to more air blown through the filter) (Yang et al., 2011a), and longer sampling periods decrease the relative importance of the positive artifacts (Turpin et al., 1994). Given these uncertain and potentially counteracting artifacts, it is uncertain to what extent the accuracy of OC measurements can be improved. A total of 192 and 191 $PM_{2.5}$ samples were collected at TH and MY during the four-year study period, respectively.

The quartz filter samples were analyzed using a thermal method instead of a thermal/optical method although a thermal-optical transmittance (TOT) carbon analyzer (Sunset Lab, Tigard, OR) was used. This thermal separation method (i.e., EnCan_Total_900) was originally developed for isotope measurements of OC and EC. The details were described by Huang et al. (2006) and Chan et al. (2010). In this method, no laser beam is used instead much longer retention times are used to ensure good baseline separations for individual carbon fractions. Three temperature stages used for separating OC, pyrolysis organic carbon (POC) + carbonate carbon (CC) and EC, are 550 °C, 870 °C and 900 °C, respectively. The first two stages are run under a pure 100% He stream, while the last stage is run under a mixed stream of 10% O_2 with 90% He. The amount of POC + CC was included in final OC mass since the CC contents

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were assumed to be negligible (based on the unpublished isotope data of a subset of the selected samples). The POC fraction released from 870 °C was found to be proportional to oxygenated OC on the filters (Chan et al., 2010). OC results are not corrected with the backup quartz filter in this study since the OC captured on it can include both positive and negative artifacts and it is hard to distinguish each other.

3 Results

The time series of weekly average concentrations of OC, EC, and total carbon (TC, i.e. OC + EC) in $PM_{2.5}$ at TH and MY sites are compared in Fig. 2. OC and EC concentrations experienced significant fluctuation from week to week at both sites. Weekly OC concentrations ranged from 4.90 to 76.9 $\mu g\,m^{-3}$ at TH and from 2.44 to 41.4 $\mu g\,m^{-3}$ at MY, while weekly EC concentrations varied from 2.37 to 51.2 $\mu g\,m^{-3}$ at TH and from 0.92 to 14.0 $\mu g\,m^{-3}$ at MY. At the TH site, the great majority of high OC and EC concentrations and their high variations were recorded in cold weather (i.e. late fall through winter), especially in December and January, while low weekly OC and EC concentrations and variations usually occurred in summer months, especially in July and August. For example, average TC concentration in July was 38% of that in December. At the MY site, high OC and EC levels and their strong variations presented discretely in different seasons with less frequencies.

Seasonal trends of OC, EC, and TC concentrations at TH and MY are diagrammed in Fig. 3. As expected, OC and EC at the TH site exhibited distinct seasonal cycle, with peak values in winter and the minima in summer or spring. OC varied seasonally by a factor of 1.4–3.0 (2.2 on average) and EC varied seasonally by a factor of 1.8–2.8 (2.0 on average). This seasonal pattern was in agreement with that observed previously at the same site (He et al., 2001; Yang et al., 2010). At the MY site, EC exhibited similar seasonal trend as that at the urban site, whereas no clear and constant seasonal trend was found for OC. Each season presented both high and low OC levels at the rural site over the four study years. As a result, the greatest seasonal gaps in OC and

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EC concentrations between TH and MY (i.e. urban excess) both tended to be in the winter of each year, while they tended to be much smaller in the summer and spring. The maximum seasonal urban excess was 27 $\mu g\,m^{-3}$ for OC and 9.2 $\mu g\,m^{-3}$ for EC. The minimum seasonal urban excess of OC (3.0 $\mu g\,m^{-3}$) and EC (1.2 $\mu g\,m^{-3}$) were only one-ninth to one-eighth of those maxima and both occurred in the summer of 2008. Despite their different levels and different seasonality, OC was the predominant contributor to TC with an average percentage of more than 70% at both TH (71%) and MY (75%).

The annual average concentrations of OC and EC at TH and the MY sites are illustrated in Fig. 4. At the urban site, average OC and TC concentrations in 2008 decreased by 13.7% and 9.9% compared to those in 2005, whereas average EC concentration leveled off. At the rural site, average OC and TC concentrations in 2008 fell 27.1% and 16.8% compared to those in 2005, whereas average EC concentration increased by 21.4%. The yearly urban excesses of OC concentration are 8.3, 13.0, 8.2, and 9.1 $\mu g\,m^{-3}$ from 2005 through 2008, and those of EC concentration are 4.3, 5.7, 6.2, and 3.6 $\mu g\,m^{-3}$. Thus, the largest urban excess of TC occurred in 2006, while the smallest one occurred in 2005 and 2008.

4 Discussion

4.1 Seasonal patterns of carbonaceous species in $PM_{2.5}$

The seasonality of carbonaceous species in $PM_{2.5}$ is influenced by the seasonal variations in their emissions/formation and meteorological factors. The peak values of OC and EC concentrations in winter at the TH site reflect the emissions resulting from space heating practices, since industrial and transportation activities are relatively constant throughout the year. In fact, more than five megatons of additional coal are used annually for the four-month heating season (Mid November through Mid March) in the urban area alone, during which coal related emissions from heating are at a maximum.

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It is noted that a considerable amount of coal was burned for this purpose in small coal fired boilers (those with an annual consumption of 20 tons or less) and family stoves (such as honeycomb briquette stoves), especially in the rural areas. As these are generally much more inefficient than large utility boilers used in district heating networks, abundant carbonaceous particles are emitted (Chen et al., 1994; Zhang et al., 2000) along with copious amounts of other gaseous pollutants such as SO_2 and NO_x (Yang et al., 2010). The stable carbon isotope values ($\delta^{13}C$) of EC in selected $PM_{2.5}$ samples collected at the TH site were noticeably more positive in winter half (−26.5‰–−24.0‰) year than those in summer half year (−27.2‰–−26.0‰) (unpublished data), also indicating that the contribution from coal combustion (with more positive $\delta^{13}C$ values, i.e. −24.0‰) was significantly enhanced with rising coal combustion.

In Fig. 5, mean surface wind flow patterns are compared between January and July, 2006, which is belonged to the winter and summer season with strikingly different TC levels as described above. Usually Beijing experiences a high number of days with thermal inversions and low mixing heights in cold season, leading to rapid accumulation of fine particles within the city since dispersion is low. On the other hand, when frequent cold fronts and strong flows from clean continental northwestern areas reach Beijing in winter (Fig. 5), the dispersion and displacement of air pollutants is strong and carbonaceous particles decline drastically. Thus the alternate thermal inversion and cold fronts result in high fluctuations of OC and EC concentrations as recorded in Fig. 2 from late fall through early spring with the prevailing winds from north and northwest. The difference of OC concentration from one week to the next reached as high as a factor of 5.9 at TH and 5.1 at MY.

The OC and EC levels and variations in summer reflect a combination of reduced coal combustion emissions and a shift in wind direction with transport patterns from south (Fig. 5) and an increase in frequency and amount of precipitation. Usually Beijing gets around three quarters of its total rainfall in summer (Yang et al., 2004). The increase in precipitation scavenges carbonaceous particles from the air, thus reducing their pollution levels. Other meteorological influences favoring lower concentrations

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of carbonaceous species in summer are higher mixing heights and higher temperatures resulted from larger surface heating, which leads to a gas–particle equilibrium shift with more SVOCs (semi-volatile organic compounds) remaining in the gas phase. Offsetting these effects, however, is that the hotter and sunnier weather is expected to enhance biogenic VOCs emissions and subsequent SOA formation, especially in the rural areas with abundant vegetation coverage (Liao et al., 2007). In this season, southerly or southeasterly winds are relatively light and are from the surface over the densely populated and industrial, coal burning cities, such as Tianjin Municipality, Shijiazhuang, and Jinan. Therefore, it is not surprising to see substantial contributions of fine carbonaceous particles and precursors from this vast region. Based on the US EPA's Models-3/CMAQ model simulation over the Beijing region, it is estimated that about 34% of $PM_{2.5}$ on average in urban Beijing during July could be attributed to these upwind outside sources (Streets et al., 2007).

In the summer of 2008, $\delta^{13}C$ values of EC at TH were noticeably more positive than those in last summer, with a difference of about one permillage. It was likely attributed to drastically reduced consumption of gasoline and diesel (with much more negative $\delta^{13}C$ values, i.e. −28.0‰), as a result of vehicular emission control to help improve air quality for the Beijing Olympic Games in 2008. From 1 July, some 300 000 heavily polluting vehicles (referred to as yellow-label vehicles) were banned from driving in the Beijing Municipality, and starting from 20 July, half of the city's vehicles were taken off the roads through the alternative day-driving scheme (Wang et al., 2010). As a result, the traffic volume and $PM_{2.5}$ concentration during the Olympic Games near a major artery, about 1.2 km away from the TH site, reduced by 21% and 46.3% compared to those in June, respectively (Kong et al., 2010). The minimum urban excess of OC and EC concentrations on a season basis occurring in 2008 summer (Fig. 3) also supports that the curtailed emissions of fine carbonaceous particles due to the special clean air campaign for 2008 Summer Olympic Games were concentrated in the urban area. These indicate that local emissions play a more important role than regional transport for contribution to fine carbonaceous particles in Beijing.

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Appreciable inter-annual variability is found as illustrated in the seasonal OC mean values for summer (Fig. 3) at the MY site, where the value for 2007 ($16 \pm 9.4\,\mu g\,m^{-3}$) was elevated to more than twice those for all other three years. With relatively lower seasonal OC levels, summer often sees spike magnitudes of weekly OC concentrations (Fig. 2). This phenomenon is likely ascribed to straw burning in the rural areas since it is popular to burn it in situ after wheat and maize harvest in rural North China. In the week between 15–22 June 2007, OC at the MY site leaped to its maximum weekly concentration ($41.4\,\mu g\,m^{-3}$), which increased more than two-fold on a week basis and even exceeded the corresponding spike value at the TH site ($39.1\,\mu g\,m^{-3}$). This likely points to biomass burning plume and implies its greater influence on OC in the rural area than that in the urban area. In fact, the air quality in Beijing during that period was deteriorated seriously by wheat straw burning, which raised great concern of local and central government as reported (http://www.chinanews.com/gn/news/2007/06-22/963012.shtml, in Chinese, last access: February 2011). The high mass ratio of OC to EC (OC/EC) in that week (as marked in a dashed circle in Fig. 6b) is also referred to the possible impact of wheat straw burning, since aerosol produced from it in Beijing was found to consist primarily of organic carbon, with OC accounting for 42% and EC accounting for only 3.7% of $PM_{2.5}$ mass (Li et al., 2009). Water soluble potassium (K^+), a tracer of biomass burning, elevated to the maximum magnitude ($7.62\,\mu g\,m^{-3}$) at the MY site in that week, putting further evidence on that. Duan et al. (2004) estimated that biomass burning contributed 43% of OC in particulate matter in urban area of Beijing during wheat harvest season. Our previous study on the radio carbon of $PM_{2.5}$ samples collected at an urban location in 1999–2000 shows that there was a significant contribution (33–50%) of modern carbon to the total carbonaceous particle burden in Beijing with larger fractions in the harvest seasons (Yang et al., 2005).

Not surprisingly given the large differences regarding to carbonaceous particles emissions related anthropogenic and natural activities between the paired urban and rural sites, there are striking difference in their OC and EC levels and variation patterns. In the urban area, about 80% of the energy consumption is concentrated, and

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the overwhelming majority of soaring population of motor vehicles in recent years (3.50 million in 2008 compared to 2.58 million in 2005) is used. The clean air campaign started in 1998 was mainly limited to the urban area (i.e. within the fifth ring road, an express highway that encircles the city in a 14 km radius from the city centre), especially for those adopted for combustion sources. This indicates that the local source emissions would significantly change for the urban site, but not that much for the rural site. Crop residue (e.g., maize residue and wheat residue), wood, and coal represent the fuel types being commonly used in rural households in north China, which emit considerably more abundant carbonaceous particles than those from coal gas/natural gas/LPG combusted in urban residential stove, depending largely on the specific fuel types and stove designs (Zhang et al., 2000). The rural area, downwind of the urban area in summer, provides favorable conditions for biogenic and anthropogenic SOA formation. This is supported by a recent finding based on modeling for the summertime OC in China that SOA concentration is high in forested areas but not in urban areas (Han et al., 2008). These may explain the complexity of temporal variations in carbonaceous species observed at the rural site, although further study is needed to explain this pattern.

4.2 Inter-annual trends of carbonaceous species in $PM_{2.5}$

The inter-annual trends in the mean values of OC and TC concentrations for the most part at both sites show a systematic decrease between 2005 and 2008 as described above, except a significant increase at TH in 2006 when OC rose by 12.7% on an annual basis. This variability reflects the significant impact that year-to-year changes in emission/formation and meteorology can have on fine carbonaceous particles in Beijing. It is noted that the annual average PM_{10} concentration, which was monitored in a monitoring network covering the whole city by Beijing Environmental Monitoring Center (www.bjepb.gov.cn), also experienced a considerable reduction (by 14.1%) over the four years, in spite of a comparable rise by 13.4% in 2006 on an annual basis as well. In contrast, those of EC concentrations exhibit a systematic elevation at both sites

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over the study years, except a sharp decline at TH in 2008 (by 20.6% on an annual basis) neutralizing the preceding growth. As EC accounts for only a small fraction (less than 0.35) of TC mass at both sites, the yearly variations in TC concentration mainly lie on OC. As a result of opposite trends of OC and EC, the fraction of EC in TC mass was enhanced whereas that of OC was weakened significantly (by 10%) as listed in Table 1.

The annual mean concentrations of OC and EC in $PM_{2.5}$ over the years 2005–2008 at the TH site decreased by 13–33% and 0–19% than those measured at the same site during 1999–2000 (Table 1), respectively. These trends reflect the complex changes in energy structure, industry activities, and emission factors resulting from technology improvement. The motor vehicle population and coal consumption amount in Beijing were 2.1 million and 30.7 million tons in 2005, increased by 120% and 16% compared to those in 1999, respectively (Beijing Municipal Bureau of Statistics, 2008). In contrast to constant soaring of vehicle population from 2005 to 2008 as listed above, coal consumption kept dropping from 30.7 million tons in 2006 to 27.5 tons by 2008, as a result of efforts made to replace coal fired boilers and family stoves with natural gas (one outcome was that the use of natural gas increased four-fold from 2000), and to replace coal heating with electrical heating. It should be noted that diesel vehicles only account for 6.6% of the total motor vehicles in Beijing, but contribute to 63% of particles exhausted from vehicle (www.bjepb.gov.cn). Although the number of vehicles in Beijing doubled between 2000 and 2008, the concentrations of CO and nitrogen dioxide (NO_2) did not increase, due to a concerted effort to reduce emissions from new and existing vehicles, including adopting clean fuels technology and new traffic planning strategies. For fine particles, a slow rise trend of the mass ratios of nitrate to sulfate in $PM_{2.5}$ at the TH site during 1999–2008 implies that the importance of vehicle emissions was likely enhanced (Yang et al., 2011b). Ongoing stable carbon measurements of individual carbon fractions in ambient $PM_{2.5}$, combined with detailed emission inventory of carbonaceous particles will provide further insight into their origins.

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Table 1 also compares average concentrations of carbonaceous species in $PM_{2.5}$ and the mass fractions of OC in TC and TCM (total carbonaceous mass, TCM = 1.4 × OC + EC for the urban sites and TCM = 1.6 × OC + EC for the rural sites) in $PM_{2.5}$ in Beijing, Shanghai, and two megacities and one rural area (i.e. Egbert) in North America, all based on long term observations. Shanghai is the largest Chinese city located in the Yangtze Delta Region in south China (see Fig. 1). Los Angels is a megacity and was of relatively high air pollution level in the United States. Toronto, the largest Canadian city, lies in south Ontario boarding on the United States. Egbert, approximately 80 km north to Toronto, is located in an agricultural and forested region without evident local anthropogenic source. After a substantial decline by 32% over the past ten years, annual mean of TC concentration at TH was still 18% higher than that measured in 1999–2000 at urban Shanghai. It was higher than that in Los Angles and Toronto by factors of 2.8 and 8.0, respectively. The value at MY was higher than that in Egbert by a factor of 6.6. The fractions of TCM in $PM_{2.5}$ mass at TH and MY in 2008 were significantly less than those measured in all other locations and that measured in Beijing before. These comparisons indicate that although the relative importance of carbonaceous species in $PM_{2.5}$ in Beijing has been weakened, they are still at much high pollution levels in both urban and rural areas, and that both local emissions and regional transportation originated mainly from anthropogenic activities likely play important roles.

4.3 OC and EC mass ratios and correlations

Since EC is ubiquitously formed through incomplete combustion of carbonaceous fuel and almost inert in the atmosphere, it is often used as a tracer of primary OC as they are typically co-emitted. OC/EC can be used to interpret the emission and transformation characteristics of carbonaceous aerosol (Gray et al., 1986; Lee and Kang, 2001; Cao et al., 2004; Yang et al., 2005). Weekly OC/EC ratios ranged from 1.2 to 5.5 with an average of 2.5 at TH, of which most lay between 2.0 and 4.0. At MY, OC/EC varied in the range from 1.0 to 8.5 with an average of 3.0. The much larger range and average

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value of OC/EC at MY reflect the more complicated sources emissions with higher OC contents relative to EC and possibly more SOA formation in the rural areas. As expected, correlations of OC and EC are clearly different between TH and the MY sites (Fig. 6). The strong correlation for all the data at the TH site implies that the majority of OC and EC were originally from the same sources and controlled by similar processes after their co-emissions. At the MY site, OC and EC were not well correlated in both warm/cold seasons, implying the contributions from different major sources, including distant and or local SOA production/formation. For the warm season at MY, OC and EC data were even more scattered with higher slope of OC/EC than those at TH, probably pointing to additional OC coming from SOA formation and/or biological origins at the rural site.

Small coal-fired boilers and domestic honeycomb briquette stoves, which have much higher OC/EC ratios (8.54 for the latter) than those from both utility boiler (2.32) and industrial boiler (2.51) (Chen et al., 1994), have been converted to cleaner energy such as natural gas or electricity in the urban area but not that much in rural residential areas. As illustrated above, the popularity to burn maize and wheat residue in situ after harvest or as biofuel for cooking and heating in the rural areas, which emit particles with high OC/EC (Zhang et al., 2000; Li et al., 2009), also favors higher abundance of OC than EC in $PM_{2.5}$ at MY. According to a late study conducted in Beijing by Li et al. (2009) , wheat residue and maize residue generate particles with very low mass ratio of EC (BC) to OC (i.e. EC/OC = 0.09, 0.10, respectively). In addition, the rural area possesses abundant vegetation to emit significant primary organic sources that are devoid of EC, such as biological material (e.g. fungal spores, vegetation detritus, endotoxins, and plant waxes), and abundant biogenic hydrocarbons in warm season. The summertime ozone is usually higher in the downwind direction of urban area, which promotes the potential for more SOA formation at MY.

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5 Conclusions

The examine of time series of weekly concentrations of OC and EC in $PM_{2.5}$ over four years from 2005 to 2008 at a pair of rural-urban locations with significant differences in their emissions/formation in Beijing provides insights into the impact of emission and meteorology on their respective levels and trends. OC and EC concentrations exhibited strong weekly variations at both sites, ranging 4.90–76.9 $\mu g\,m^{-3}$ and 2.37–51.2$\mu g\ m^{-3}$ at TH, and ranging 2.44–41.4 $\mu g\,m^{-3}$ and 0.92–14.0$\mu g\,m^{-3}$ at MY, respectively. The difference of TC concentrations between two consecutive weeks reach up to a factor of more than 5. Clear seasonal patterns were found for both OC and EC concentrations at TH with larger weekly concentrations and variations in winter, due to increased coal combustion activities for space heating and frequent alternation between thermal inversion and cold fronts. The significantly more positive $\delta^{13}C$ levels of EC at TH in winter half year than in summer half year supports the inference that the coal combustions as primary emissions play dominant roles in ambient carbonaceous particle loadings in Beijing area. No consistent seasonal patterns for OC at the MY site reflect their more complex and variable major sources emissions/formation and transport in the rural area than in the urban area, such as biomass burning during the harvest seasons, widely used family stoves and small boiler, high potential formation of SOA. The maximum weekly OC concentration at MY in 2007 July is likely attributed to the strong impact of wheat straw burning plume with high OC/EC ratios.

At the TH site, the annual average concentrations of OC and EC varied from 19.0 to 25.5 $\mu g\,m^{-3}$ and from 7.1 to 11.1$\mu g\,m^{-3}$, respectively, with a perceptible rise from 2005 to 2007 but a noticeable fall in 2008 for EC. Compared to those in 2000, they decreased by 13–33% and 0–19%, respectively, with the maximum reductions in 2008. The average TC concentrations and the fractions of TCM in $PM_{2.5}$ mass at TH and MY in 2008 were significantly decreased compared to those measured in Beijing in 1999–2000, indicating that the importance of carbonaceous species in $PM_{2.5}$ in Beijing had been weakened. OC was the predominant contributor to TC in both urban and rural

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areas in Beijing, while the relative importance of EC in TC was steadily enhanced over the study period. Nonetheless, OC and EC still kept quite high levels at both sites suggest that local emissions and regional transportation both play important roles.

The minimum seasonal urban excesses of OC (3.0 $\mu g\,m^{-3}$) and EC (1.2 $\mu g\ m^{-3}$), which were only one-ninth to one-eighth of their corresponding maxima, both occurred in 2008 summer. This suggests that the special clean air campaign for 2008 Summer Olympic Games very likely had a noticeable impact on the ambient level of carbonaceous aerosols in a local scale of Beijing area. The significant elevation of $\delta^{13}C$ values of EC at TH in 2008 summer puts in further evidence in terms of the impact of a concerted effort to reduce emissions from new and existing vehicles, including adopting new traffic planning strategies before, during and after the Summer Olympics. OC and EC were correlated well at the TH site, indicating that they were likely from common major emission sources in the urban area. Higher OC/EC ratios and much more scattered correlations at the MY site reflect the complex influences of different major sources and origins and their seasonal variations in emission and formation, including long range transport and local SOA formation in the rural area.

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Table 1. Average concentrations ($\mu g\,m^{-3}$) of carbonaceous species in $PM_{2.5}$ and the mass fractions of OC in TC and TC in $PM_{2.5}$ in Beijing and other regions.

Sampling location	Sampling period	Reference	OC	EC	OC/TC	TCM/ $PM_{2.5}$
TH, Beijing	2008	This study	19.1	8.45	0.65	0.32
MY, Beijing	2008	This study	9.96	4.52	0.69	0.33
TH, Beijing	1999.7–2000.6	He et al. (2001)	30.0	10.4	0.74	0.40
Urban, Shanghai	1999.3–2000.5	Ye et al. (2003)	16.8	6.49	0.72	0.42
Urban, Los Angeles	1995.1–1996.2	Kim et al. (2000)	5.96	3.81	0.61	0.40
Urban, Toronto	2006.10–2007.10	Yang et al. (2011a)	2.45	1.00	0.71	
Rural, Egbert	2006.1–2007.11	Yang et al. (2011a)	1.60	0.60	0.73	0.38

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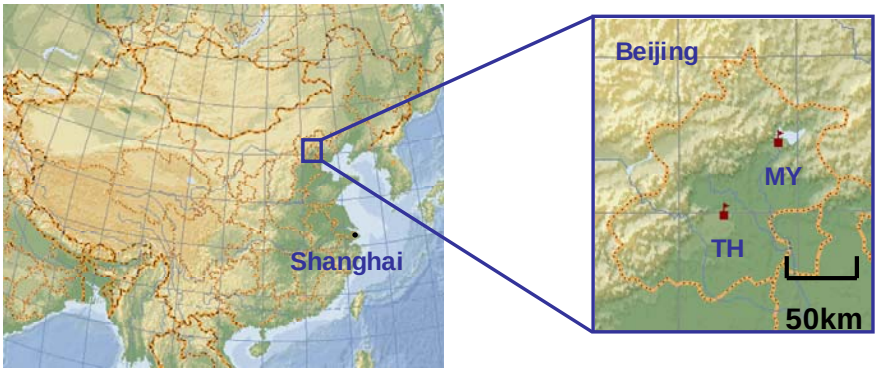

Fig. 1. Sampling sites (TH and MY) in Beijing. The location of Shanghai, the largest Chinese city is marked as well. The topography map was derived from the Microsoft® Encarta® 2009 © 1993–2008.

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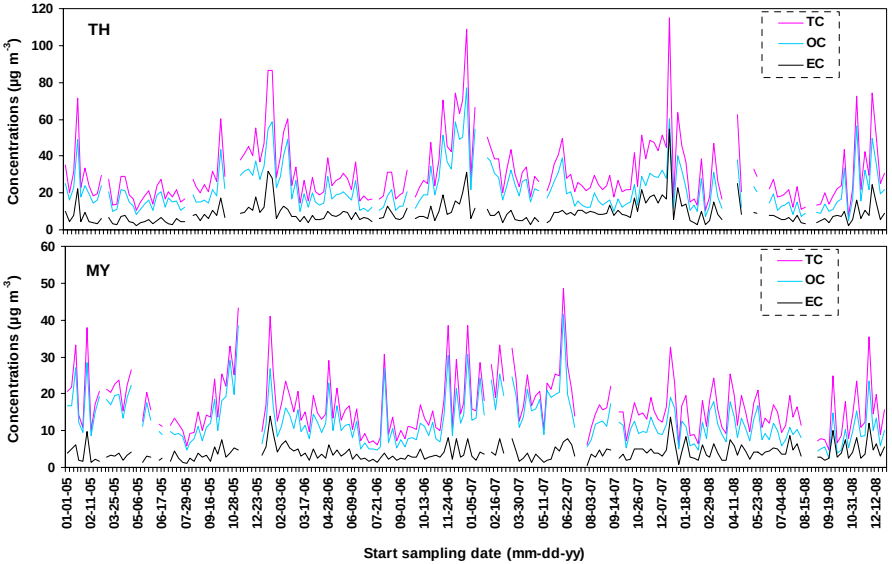

Fig. 2. Time series of weekly OC, EC, and TC concentrations at **(a)** TH and **(b)** MY.

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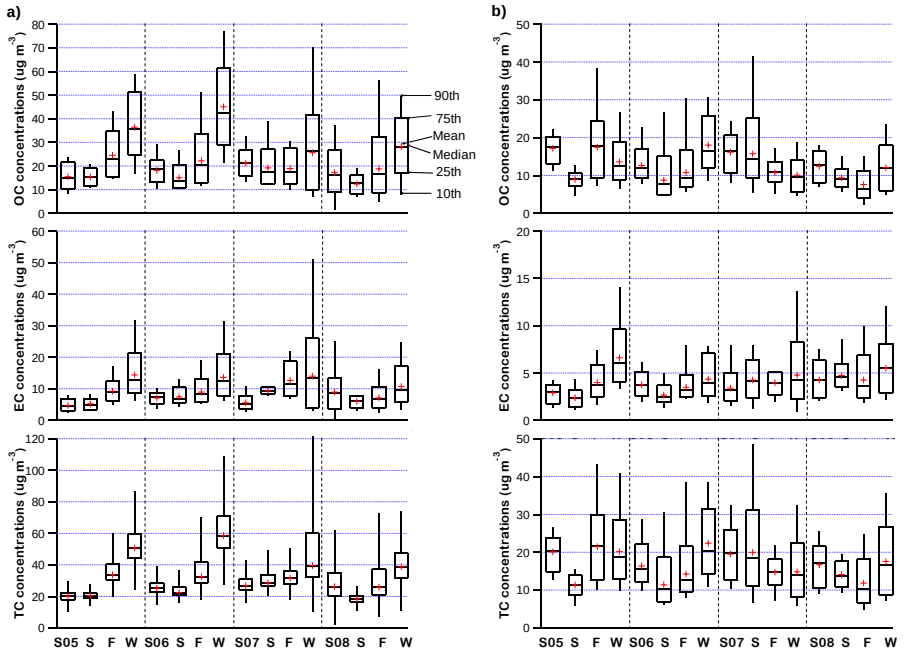

Fig. 3. Seasonal variations of OC, EC and TC concentrations in $PM_{2.5}$ during 2005–2008 at **(a)** TH and **(b)** MY. The box plots indicate the mean concentration (cross symbol) and the 10th, 25th, 75th, and 90th percentiles.

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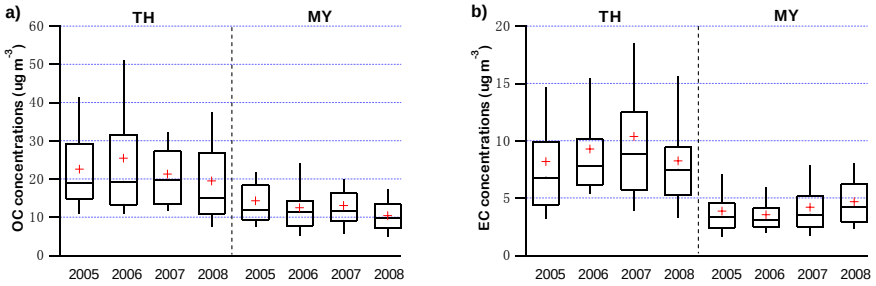

Fig. 4. Yearly variations of **(a)** OC and **(b)** EC concentrations in $PM_{2.5}$ from 2005 through 2008 at TH and MY sites. The box plots indicate the mean concentration (cross symbol) and the 10th, 25th, 50th, 75th, and 90th percentiles.

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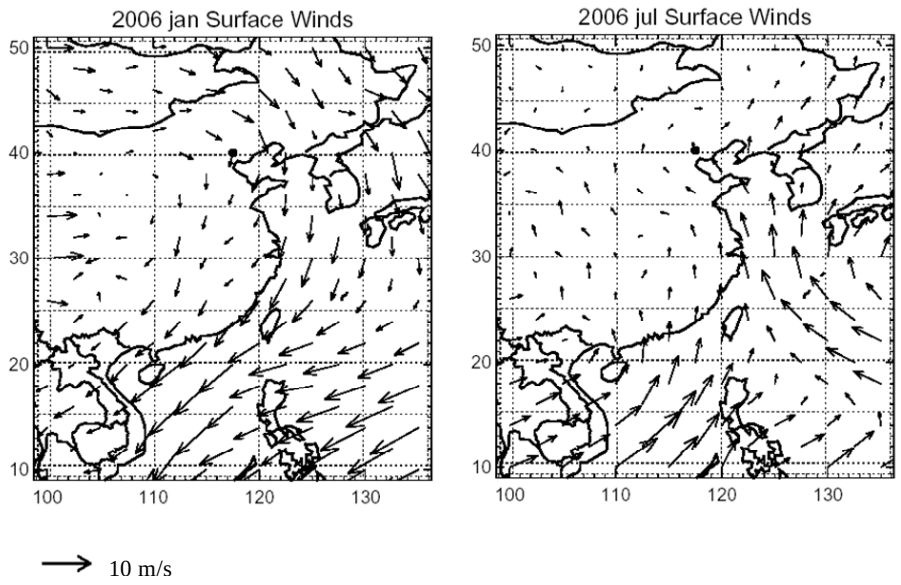

Fig. 5. Mean flow patterns at the Surface of Beijing and surrounding region in January and July of 2006. The black dot represents MY.

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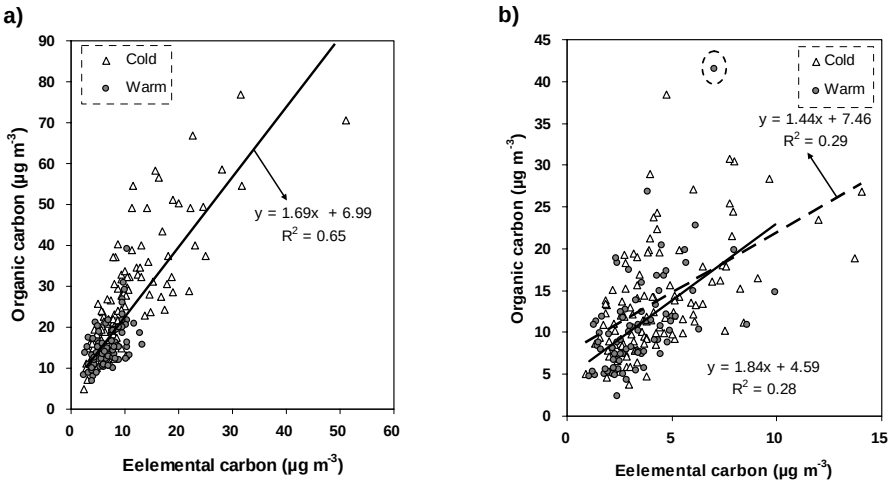

Fig. 6. Correlations of OC and EC concentrations for the study period at **(a)** TH and **(b)** MY, split by cold season (November–April) and warm season (May–October).

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