Atmos. Chem. Phys., 11, 7893–7903, 2011
www.atmos-chem-phys.net/11/7893/2011/
doi:10.5194/acp-11-7893-2011

Atmospheric Chemistry and Physics

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

F. Yang[1,2], L. Huang[2], F. Duan[3], W. Zhang[2], K. He[3], Y. Ma[3], J. R. Brook[2], J. Tan[1], Q. Zhao[3], and Y. Cheng[3]

[1]Key Laboratory of Computational Geodynamics, College of Earth Science, Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[2]Atmospheric Science and Technology Directorate/Science and Technology Branch, Environment Canada, Toronto, ON M3H 5T4, Canada
[3]School of Environment, Tsinghua University, Beijing 100084, China

Received: 3 March 2011 – Published in Atmos. Chem. Phys. Discuss.: 14 March 2011
Revised: 28 July 2011 – Accepted: 29 July 2011 – Published: 4 August 2011

Abstract. One-week integrated $PM_{2.5}$ samples were collected over four years (2005–2008) at a pair of sites, one rural and one urban site, in the area of Beijing, China. Weekly organic and elemental carbon (OC and EC) concentrations from these samples were measured to investigate their atmospheric concentrations, temporal variation patterns and the factors influencing these aspects. A slightly systematic decrease in annual mean concentration of OC and an opposite trend for EC at both sites was observed. Since OC accounted for about 70 % of total carbon (TC, i.e. OC + EC) the total carbonaceous mass experienced a slight decline on a yearly basis over the study period. Its fraction of $PM_{2.5}$ mass at the urban site in 2008 was significantly lower than observed 10 years earlier (1999), indicating that the relative importance of carbonaceous species in $PM_{2.5}$ has decreased. In urban Beijing clear seasonal variations (by factors of $1.35 \sim 3.0$) were shown in both OC and EC 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 ($1.3\,\mu g\,m^{-3}$) occurred in the summer of 2008, which were only one-ninth and one-seventh of their corresponding maximum values, respectively. This reduction in the urban-difference, coupled with more positive stable carbon isotope values of EC at the urban site in that summer relative to the preceding summers, supports that the special clean air campaign for the 2008 Summer Olympic Games very likely had noticeable impact on the ambient concentrations of carbonaceous aerosols in the Beijing area, particularly on the local urban scale. Less consistent seasonal patterns in OC and EC, their scattered correlation, and higher mass ratios of OC to EC (OC/EC) at the rural site indicate more complex and variable major sources regarding aerosol formation in the rural area. These emission sources include biomass burning during the harvest seasons, widely used high-polluting family stoves and small boilers for cooking and heating with high OC/EC ratios, and a greater relative quantity of secondary organic aerosols.

Correspondence to: K. He
(hekb@tsinghua.edu.cn)

1 Introduction

The impact of air pollution in the last 50 years has shifted from being mostly a local issue to being recognized as both a local and global issue, and a common sense to address air pollution and climate change in an integrated way is reached. Recent interest has centered on fine particle ($PM_{2.5}$) and its chemical species, particularly carbonaceous fractions (Fenger, 2009), since they act as both air pollutants and climate agents and represent the complexity of aerosols regarding their proper quantification, and scientific understanding of their atmospheric formation and evolution mechanisms (Gelencsér, 2004; Andreae and Gelencsér, 2006; Ramanathan and Carmichael, 2008; Flanner et al., 2009). Carbonaceous species, which include 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 carbon (BC), often equally referred as EC, since the immediate

control of BC emission 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 in scattering light and cooling the atmosphere (IPCC, 2007). Therefore, studying OC and EC levels and tracking their changes with time provide valuable information for constraining their emission sources, understanding their atmospheric transport/transformation mechanisms as well as assessing the impact of human activity on the atmospheric environment.

Studies conducted in China show that carbonaceous aerosols occur at high levels and are major components of $PM_{2.5}$, especially in megacities (Cao et al., 2004, 2007; Yang et al., 2005, 2011a; Ho et al., 2006). Beijing – the capital of China – has been experiencing rapid industrialization and urbanization since the 1980s and becomes one of the largest megacities. Coal has been the predominant energy source with annual coal consumption at about 27–30 megatons over the past decade. Meanwhile the vehicle population has kept soaring with one million increments over only four years from 2005 to 2008. In addition, biofuel burning around neighboring rural areas adds more to the burden of high particulate levels and poor visibility – traditionally a common problem in the Beijing-Tianjin-Hebei Region. The change of emission sources coupled with the regional-scale transport patterns made the understanding and controlling fine particulate pollution more complex.

To improve air quality in the capital area 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 (www.bjepb.gov.cn). To host the 2008 Olympic Games successfully provided an added incentive and measures to accelerate the processes (UNEP, 2009). Beijing has subsequently, been leading the country in phasing out leaded gasoline and low-quality coal with high sulfur and high ash contents, 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. In addition, heavily polluting industrial facilities have been relocated outside of Beijing. These efforts resulted in an evident improvement in air quality, but less than what was expected in terms of particulate pollution control. This led to additional measures to reduce emissions in targeted sectors in neighboring provinces of Tianjin, Hebei, Shanxi, Shandong, and Inner Mongolia, in order to assure good air quality for the Beijing Olympic Games. Consequently, surface and satellite measurements showed that the measures taken in Beijing and surrounding regions during the Olympic Summer Games likely had a noticeable effect on emission reduction and air quality improvement (Cermak and Knutti 2009; UNEP, 2009; Wang et al., 2010a, b).

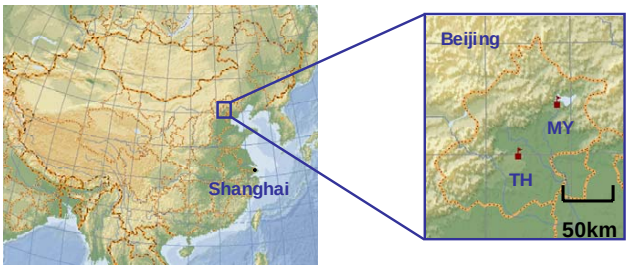

Fig. 1. Sampling sites (TH and MY) in Beijing. The location of Shanghai – the largest Chinese city – is also marked. The topographical map was derived from the Microsoft Encarta 2009© 1993–2008.

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., 2010b). Although $PM_{2.5}$ is not currently regulated in China, there have been a number of field studies in the last decade to quantify and characterize fine particulate matter (Chan and Yao, 2008). A number of papers have also been published on the results during the Beijing Olympics (Wang et al., 2010b). However, there are none focusing on carbonaceous aerosols based on long-term surface measurements for a period covering the Olympic period. In 2005, we initiated a $PM_{2.5}$ speciation measurement program at a pair of rural/urban sites in the Beijing area to track the $PM_{2.5}$ trends in mass concentration and chemical composition. This paper will summarize some preliminary findings for the carbonaceous species in $PM_{2.5}$ from 2005 through 2008, with a focus on their temporal variations and the possible mechanisms influencing the trends will also be explored.

2 Experimental

2.1 Study locations and description

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 16410 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 city's landmass) 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), thus the pollutants can not be easily expelled. Beijing lies in the warm temperate zone and has typical continental monsoon climate with four distinct seasons. From November–April, the prevailing airflow from the northwest is dry and cold, while at other times the local winds are moderate and mostly from the south and southeast.

To explore the urban influence on carbonaceous $PM_{2.5}$ and its rural background, a pair of rural/urban sites that are about 70 km apart were selected (Fig. 1). The urban site is located in the semi-residential area inside the campus of TsingHua University (here referred to as TH, 40°19′ N, 116°19′ E), about 12 km northwest of the city center. Our previous studies (He et al., 2001) showed that it is representative of an urban area because of a strong impact by a mixture of emission sources due to rapid urbanization in and around this area. The rural site is near the MiYun Reservoir (here referred to as MY, 40°29′ N, 116°47′ E), about 90 km northeast of the city center and there are no obvious anthropogenic emission sources within 5 km. The surrounding areas of this 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.

2.2 Sample collection

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 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 OC and EC measurement. The sampling duration for each sample was one week. A total of 192 and 191 $PM_{2.5}$ samples were collected at TH and MY during the four-year study period, respectively.

Sampling for OC is an ongoing challenge. According to McDow and Huntzicker (1990) and Turpin et al. (2000), the face velocity and sampling duration are the key parameters to consider in sampling for OC. The low face velocity adopted in this study is expected to lead to a tendency for higher OC values, whereas the 7-day integrated sampling period appears exacerbating the possible loss of semi-volatile organic compounds (SVOCs) from the collected particles (due to more air blown through the filter) (Yang et al., 2011b). Therefore, the longer sampling periods decrease the relative importance of the positive artifacts (Turpin et al., 1994). While these uncertain and potentially counteracting artifacts lead to uncertainty in the OC measurements, a consistent sampling approach was used at both sites allowing for direct comparison of differences.

2.3 Sample analysis

All the quartz filter samples were analyzed on a Sunset instrument (http://www.sunlab.com) at Environment Canada's Toronto lab, using a thermal method (i.e., EnCan_Total_900) originally developed for isotope measurements of OC and EC (Huang et al., 2006; Chan et al., 2010). Although a Sunset instrument was used, no laser beam is applied in this method, instead long residence times at each temperature stage are optimized to ensure good baseline separation for individual carbon fractions. This is a modified NIOSH (National Institute of Occupational Safety and Health) protocol (Chow et al., 2001). Three temperature stages used for separating OC, pyrolized 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 the final OC mass since the CC content was found 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), suggesting that it is not EC despite from a high temperature step.

This method is potentially applicable for samples with high carbonaceous loadings and has been included in an international comparison activity for BC measurements as one of thermal/optical methods (Hammes et al., 2007). Nonetheless it should be aware of that the approach to determine the absolute OC-EC split point is still method dependent. But it is important to note that the same method has been applied to this study at the same lab. It should be also mentioned that OC results are not corrected with the backup quartz filter in this study, since the OC captured on it include both positive and negative artifacts and it is not possible to distinguish between them (Yang et al., 2005; Cheng et al., 2009). In order to have a better idea for the data comparability between this method and other two widely used thermal-optical methods (i.e., IMPROVE and NIOSH), a reference material – RM 8785 – produced by the US National Institute of Standards and Technology (NIST) (https://www-s.nist.gov/srmors/view_detail.cfm?srm=8785) was measured in the lab during 2006-2009 when the ambient samples were analyzed. As shown in Table 1, the results by EnCan_Total_900 are comparable to those by the other two methods, particularly for OC/EC and EC/TC ratios.

3 Results

The time series of weekly average concentrations of OC, EC, and TC at the TH and MY sites are compared in Fig. 2. OC and EC experienced significant fluctuation from week to week at both sites. Weekly OC concentrations ranged from 4.9 to 76.9 µg m^{-3} at TH and from 2.44 to 41.4 µg m^{-3}

Table 1. Comparison results of OC and EC measurements in NIST RM 8785 between three methods.

Method	N	TC ($g\,g^{-1}$)		EC ($g\,g^{-1}$)		OC ($g\,g^{-1}$)		EC/TC		OC/EC	
		Ave.	2 s.e.	Ave.	2 s.e.	Ave.	2 s.e.	Ave.	2 s.e.	Ave.	2 s.e.
IMPROVE[a]	40	0.223	0.057	0.111	0.035	0.112	0.022	0.490	0.050	1.009	0.375
STN-NIOSH[b]	40	0.236	0.030	0.067	0.008	0.169	0.024	0.279	0.023	2.522	0.468
EnCan_Total_900[c]	116	0.302	0.009	0.110	0.004	0.188	0.007	0.365	0.011	1.704	0.092

RM 8785: NIST reference material for air particulate matter on filter media (https://www-s.nist.gov/srmors/view_detail.cfm?srm=8785); s.e.: standard error.
[a] used by Desert Research Institute, US on DRI/OGC TOR & DRI Model 2001 TOR, analyzed before July 2005.
[b] used by NIST Lab on an "Original TOT" and Sunset Laboratory Inc. on a "new version of TOT", analyzed before July 2005.
[c] used by Environment Canada's CRD_Lab in Toronto on a Sunset lab new version of TOT, analyzed during 2006–2009.

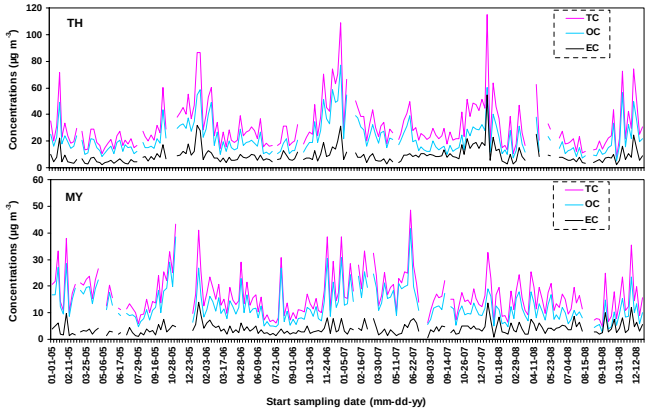

Fig. 2. Time series of weekly OC, EC, and TC concentrations at TH and MY.

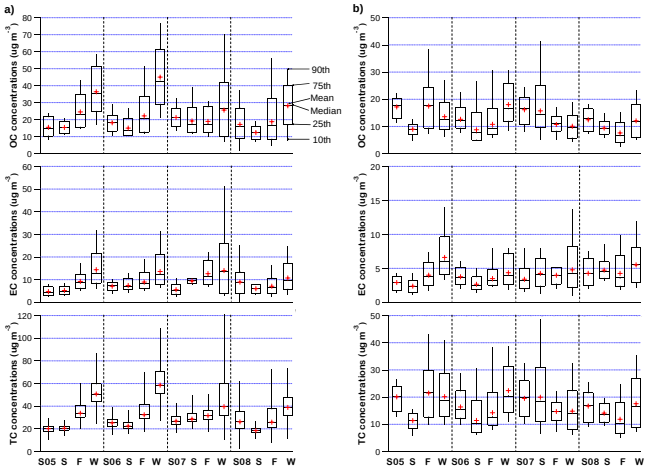

Fig. 3. Seasonal variations of OC, EC and TC concentrations in $PM_{2.5}$ during 2005–2008 at **(a)** TH and **(b)** MY. The box plots indicate the mean concentration (cross symbol) and the 10th, 25th, 50th, 75th, and 90th percentiles.

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 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.

Season to season changes in OC, EC, and TC concentration at both sites are highlighted in Fig. 3. At TH, 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 is in agreement with that observed during 1999–2000 and 2001–2003 at the same site (He et al., 2001; Yang et al., 2010). At the MY site, EC exhibited similar seasonal changes whereas there was no clear seasonal trend for OC over the four study years. As a result, the greatest urban-rural differences in both OC and EC concentrations (i.e. urban excess) tended to be in the winter of each year, while they tended to be 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 (1.3 $\mu g\,m^{-3}$) were one-ninth and one-seventh of their maximum values respectively, 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 the TH and 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 concentrations from the first to the last year were similar. At the rural site, average OC and TC concentrations in 2008 fell 27.1 % and 16.8 % respectively compared to those in 2005, whereas the average EC concentration increased by 21.4 %. The annual average urban excesses for OC concentration were 8.3, 13.0, 8.2, and 9.1 $\mu g\,m^{-3}$ from 2005 through 2008, and those for EC concentration were 4.3, 5.7, 6.2, and 3.6 $\mu g\,m^{-3}$, respectively. The largest urban excess of TC occurred in 2006, while the smallest urban-rural difference appeared in 2005 and 2008.

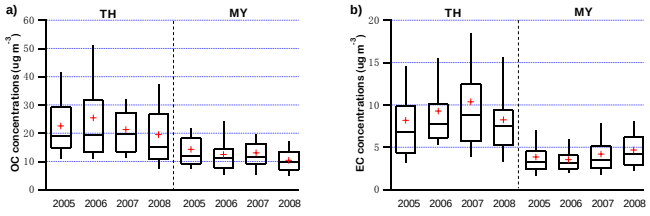

Fig. 4. Yearly variations of **(a)** OC and **(b)** EC concentrations in $PM_{2.5}$ from 2005 through 2008 at TH and MY sites. The box plots indicate the mean concentration (cross symbol) and the 10th, 25th, 50th, 75th, and 90th percentiles.

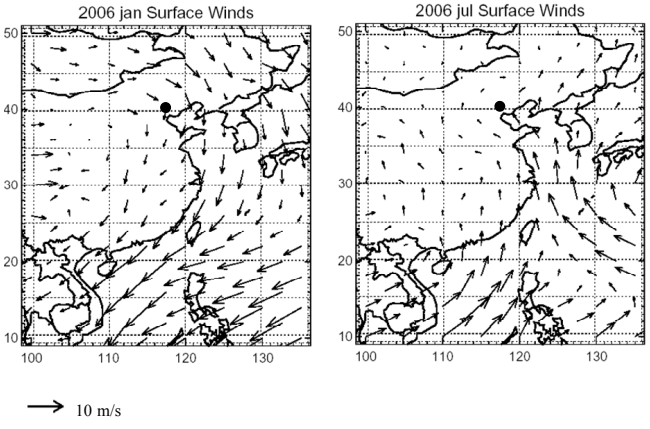

Fig. 5. Mean wind flow patterns at the surface over eastern Asia in January and July of 2006. The black dot represents the location of MY.

4 Discussion

4.1 Seasonal patterns of carbonaceous species

The seasonality of carbonaceous species in $PM_{2.5}$ is influenced by seasonal variations in their emissions and formation, as well as by meteorological factors. The peak values of OC and EC concentration in winter at the TH site are likely attributed mainly to emissions resulting from commercial/residential heating using coal as the fuel. In fact, more than five additional megatons of coal are used during the four-month heating season (Mid November through Mid March) in the urban area alone (http://www.bjepb.gov.cn), resulting in the maximum coal-related emissions during this time of year. It is noted that a considerable amount of the coal burned for this purpose occurs in small 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 CO, SO_2 and NO_2 (Yang et al., 2010).

According to Huang et al. (2010), it is also observed that the stable carbon isotope values ($\delta^{13}C$) of EC at the TH site were noticeably more positive (-26.0 ‰ to -24.0 ‰) during cold season (November to March) than those (-27.2 ‰ to -26.0 ‰) during warm season (May to October), supporting that there was considerable increase in the contribution from coal combustion (with $\delta^{13}C$ values of $\sim -24 \pm 1$ ‰) in cold season due to the soaring usages of coal. A 2003 study by Cao et al. (2011) also found significant differences of winter vs. summer in $\delta^{13}C$ values ($\sim$1–3 ‰) for OC and EC in seven northern Chinese cities including Beijing, and ascribed the elevated levels in January compared to June/July to the stronger impact by coal combustion. In addition to enhanced coal-fired heating emissions in winter, vehicular cold starts also significantly increase emissions of carbonaceous particles and precursors (Singer et al., 1999). Lower temperatures also lead to a gas-particle equilibrium shift with more SVOCs appearing in the particle phase in winter.

In Fig. 5 mean surface wind flow patterns in Beijing and surrounding area are compared between January and July 2006. The large difference in predominant wind fields adds additional constraint on the seasonal patterns of carbonaceous aerosol levels, as described above. Usually Beijing experiences a higher number of days with thermal inversions and low mixing heights in cold seasons, which lead to relatively rapid accumulation of fine particles within the city since dispersion is low but emission is high (Jia et al., 2008). On the other hand, when frequent cold fronts and strong flows from clean continental northwestern areas reach Beijing in cold season (Fig. 5) the dispersion and displacement of air pollutants are strong and the carbonaceous particles decline drastically. Thus, this alternation between thermal inversions and cold fronts results in large fluctuations in OC and EC from late fall through early spring under 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 during this time of year.

The OC and EC levels and variations in summer reflect a combination of reduced heating-related coal combustion and a shift in wind direction with transport patterns from the south to North (Fig. 5). An increase in the frequency and amount of precipitation also has an influence due to increased scavenging of particles. Usually Beijing gets around three quarters of its total annual precipitation in the summer (Yang et al., 2004). Other meteorological influences favoring lower concentrations of carbonaceous particles in summer are higher mixing heights and higher temperatures, the latter of which results in a shift in the gas-particle equilibrium with more SVOCs remaining in the gas phase. Offsetting these effects, however, is that the hotter and sunnier weather is expected to enhance biogenic VOC emissions and subsequent SOA formation, especially in the rural areas where there is abundant vegetation coverage (Liao et al., 2007). During summer season, southerly or southeasterly winds are relatively light and are from the surface over the densely

populated and industrialized 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 was estimated that about an average of 34 % of $PM_{2.5}$ in urban Beijing during July could be attributed to these upwind sources (Streets et al., 2007). It should be noticed that the formations of SOA do not totally offset the general season trend in OC concentrations.

It is known that from the 1 July 2008, about 300 000 heavily polluting vehicles (referred to as yellow-label vehicles) were banned from driving in the Beijing Municipality, and then starting from the 20 July, half of the city's vehicles were taken off the roads through the alternative day-driving scheme (Wang et al., 2010b). As a result, the traffic volume and vehicular exhaust decreased significantly (Wang et al., 2010a; Zhou et al., 2010). For example, during the Olympic Games the traffic volume and average $PM_{2.5}$ concentration near a major road – 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 lower urban excess of TC, reduced from 8.6 $\mu g\,m^{-3}$ in the previous summer to 4.3 $\mu g\,m^{-3}$ (Fig. 3), implies that the curtailed emissions of fine carbonaceous particles were concentrated in the urban area and thus had their greatest benefit in that area. The more positive $\delta^{13}C$ values in EC observed during the summer of 2008 at TH compared to the two preceding summers (Huang et al., 2010) also reflect a decrease in relative contribution from gasoline and diesel emissions. These substantial differences in urban excess and $\delta^{13}C$ values imply that the special clean air campaign for the 2008 Summer Olympic Games had a noticeable impact on the ambient level of carbonaceous aerosols on a local scale of the Beijing area. Furthermore, these changes together with the different seasonal patterns of rural/urban OC and EC suggest that local emissions likely play a primary role in contribution to high fine carbonaceous loadings in urban Beijing.

Appreciable inter-annual variability was found in the seasonal mean of OC at the MY site (Fig. 3), where the value for 2007 ($16 \pm 9.4\,\mu g\,m^{-3}$) was more than twice of those from the other three years. Although with relatively lower seasonal means in OC concentration during summer, spikes are often shown in weekly OC values (Fig. 2). This phenomenon is likely ascribed mainly to biomass burning since it is popular to burn straw after wheat and maize harvest in rural areas of northern China. Take the week between 15–22 June 2007 for an example, OC at the MY site leaped to its maximum weekly concentration (41.4 $\mu g\,m^{-3}$), which was more than two-fold of an normal weekly value and even exceeded the corresponding spike value at the TH site (39.1 $\mu g\,m^{-3}$). These suggest the influences from a biomass burning plume with a greater impact on the rural area than that in the urban area. In fact, the air quality in Beijing during that period deteriorated seriously as a result of wheat straw burning and raised great concern from local and central government (http://www.chinanews.com/gn/news/2007/06-22/963012.shtml). The OC/EC ratio in that week (as marked in a dashed circle in Fig. 6b) is also suggestive of possible impact from wheat straw burning, since aerosols produced from biomass burning in Beijing were of high primary OC content. According to Li et al. (2009), OC and EC account for 42 % and only 3.7 % of $PM_{2.5}$ mass from wheat straw burning, respectively. Water soluble potassium (K^+), a tracer of biomass burning, elevated to the maximum magnitude (7.62 $\mu g\,m^{-3}$) at the MY site during that week, providing further evidence supporting the inference. Duan et al. (2004) estimated that biomass burning contributed 43 % of OC in particulate matter for the urban areas of Beijing during the wheat harvest season. Our previous study on the radiocarbon dating of $PM_{2.5}$ samples collected at an urban location in 1999–2000 also showed 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).

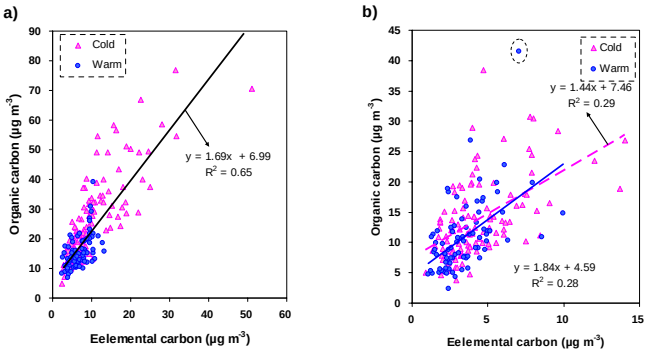

Fig. 6. Correlations of OC and EC concentrations for the study period at **(a)** TH and **(b)** MY, split by the cold season (November–April) and warm season (May–October).

Not surprisingly, given the large differences in carbonaceous particle emissions (anthropogenic vs. natural activities) between the urban and rural sites, there are striking difference in their OC and EC levels and variability. It is in the urban area that about 80 % of the region's energy consumption is concentrated along with an overwhelming majority of the soaring number of motor vehicles in recent years (3.50 million in 2008 vs. 2.58 million in 2005). The clean air campaign started in 1998 and was mainly limited to combustion sources in the urban area (i.e. within the fifth ring road – an express highway that encircles the city at a 14 km radius from the city centre). This suggests that the impact of local source emissions would change significantly 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 the coal gas/natural gas/LPG combusted in the urban residential stoves. In addition, stove

design also has impacts on particle emissions (Zhang et al., 2000). The rural area, which is downwind of the urban area in summer is in a favorable location to experience the enhanced impact of SOA formation from both biogenic and anthropogenic precursors with the accumulation of oxidants to drive the process (Wang et al., 2009). This is supported by a recent finding, based on model results for the summertime OC in China, that SOA concentration is high in forested areas compared to that in urban areas (Han et al., 2008). These may further explain the complexity of temporal variations in carbonaceous species observed at the rural site, although further study would help to explain the overall patterns discussed in this section.

4.2 Inter-annual trends of carbonaceous species

The inter-annual trends in the mean values of OC and TC for the most part at both sites show a systematic decrease between 2005 and 2008, as described above. The exception is a significant increase at TH in 2006 when annual OC rose by 12.7 %. This variability reflects that year-to-year changes in emission/formation and meteorology can have significant impact on fine carbonaceous particles in Beijing. It is noted that the annual average PM_{10} concentration, which was measured by the 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. In contrast, the inter-annual changes in EC concentrations exhibit a systematic increase at both sites over the study years, except a sharp decline (by 20.6 %) at TH in 2008 neutralizing the preceding growth. As EC accounts for only a small fraction of TC mass at both sites, the yearly variations in TC are mainly due to changes in OC. A result of the opposite trends for OC and EC is that the fraction of EC in TC mass was enhanced over the years, whereas that of OC was weakened significantly (by 10 %) as listed in Table 2.

At the TH site the annual mean concentrations of OC and EC over the years 2005–2008 decreased by 13–33 % and 0–19 %, respectively, compared to those measured at the same site during 1999–2000 (Table 2). These trends reflect the complex changes in energy structure, industrial activities, and emission factors resulting from technology improvements over the 10-year span (Lei et al., 2011). In 2005, the motor vehicle population and coal consumption quantity in Beijing increased by 120 % and 16 % compared to those in 1999, respectively (Beijing Municipal Bureau of Statistics, 2008). In contrast to the consistent soaring of vehicles on the roads from 2005 to 2008, coal consumption continued to drop by ∼10 %, from 30.7 million tons in 2005 to 27.5 tons by 2008. This was a result of efforts made to replace coal fired boilers and family stoves with natural gas (as one outcome, the use of natural gas in 2008 was increased by four-fold from that in 2000) and to replace coal-fired heating systems with electrical ones. Although the number of vehicles in Beijing doubled between 2000 and 2008, the concentrations of CO and NO_2 did not increase due to a concerted effort to reduce emissions from new and existing vehicles, including adopting clean fuel technology and new traffic planning strategies. Nonetheless, a slow rise in 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 for fine particles likely increased (Yang et al., 2011a). Ongoing stable carbon measurements of individual carbon fractions in ambient $PM_{2.5}$ combined with detailed emission inventories for carbonaceous particles would provide further constraints on the relative energy structure changes over the period.

Table 2 also compares average concentrations of carbonaceous species in $PM_{2.5}$ and the mass fractions of OC in TC and in total carbonaceous mass (TCM, TCM = $1.4 \times OC + EC$ for the urban sites and TCM = $1.6 \times OC + EC$ for the rural sites) in Beijing, Shanghai, and two other 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 east China (see Fig. 1). Los Angeles is the largest city situated in the east part of Pacific Ocean and with relatively high air pollution levels among the cities in North America. Toronto, the largest Canadian city, lies in east North America bordering on the United States. Egbert, approximately 80 km north to Toronto, is located in an agricultural and forested region with few local anthropogenic sources. After a substantial decline by 32 % over the past ten years, the annual mean TC concentration at TH was still 18 % higher than that measured in 1999–2000 at the urban Shanghai location. It was higher than that in Los Angeles 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 noticeably lower than those observed at the above locations, and lower than those measured at the urban Beijing site during 1999–2000. It is indicated that although the relative importance of carbonaceous species in $PM_{2.5}$ in urban Beijing had been weakened, they were still at much higher pollution levels in both urban and surrounding rural areas and their reductions are mainly attributed to the control of local anthropogenic emissions.

4.3 OC and EC mass ratios and correlations

Since EC is only formed through incomplete combustion of carbonaceous fuel and mostly inert in the atmosphere it is often used as a tracer of primary OC as they are typically co-emitted. OC/EC can thus be used to gain some insights regarding the emission and transformation characteristics of carbonaceous aerosol (Gray et al., 1986; Lee and Kang, 2001; Cao et al., 2004). 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 larger range and

Table 2. Average concentrations ($\mu g\,m^{-3}$) of carbonaceous species in $PM_{2.5}$ and the mass fractions of OC in TC and TCM in $PM_{2.5}$ in Beijing and other selected regions.

Sampling location	Sampling period	OC	EC	OC/TC	TCM/ $PM_{2.5}$	OC&EC method	Reference
TH, Beijing	2008	19.1	8.45	0.69	0.32	EnCan_Total_900	This study
MY, Beijing	2008	9.96	4.52	0.69	0.33	EnCan_Total_900	This study
TH, Beijing	Jul 1999–Jun 2000	30.0	10.4	0.74	0.40	TOR	He et al. (2001)
Urban, Shanghai	Mar 1999–May 2000	16.8	6.49	0.72	0.42	TOR	Ye et al. (2003)
Urban, Los Angeles	Jan 1995–Feb 1996	5.96	3.81	0.61	0.40		Kim et al. (2000)
Urban, Toronto	Oct 2006–Oct 2007	2.45	1.00	0.71		EnCan_Total_900	Yang et al. (2011b)
Rural, Egbert	Jan 2006–Nov 2007	1.60	0.60	0.73	0.38	EnCan_Total_900	Yang et al. (2011b)

higher average values of OC/EC at MY suggest that there was a different mix of sources with more complicated temporal variations compared to TH. Not surprisingly, correlations of OC and EC are also different between the TH and the MY sites (Fig. 6). The correlation for all the data at the TH site was relatively strong ($R^2 = 0.65$) implying that the OC and EC tend to be mainly from the same primary sources and are controlled by similar processes after being emitted. At the MY site, however, OC and EC were not as well correlated ($R^2 = 0.29$) in both warm and cold seasons, implying contributions from different major sources, including distant and or local SOA production/formation. For warm seasons at MY OC and EC was even more scattered with a higher OC/EC ratio compared to cold seasons and also compared to that at TH year-round. This suggests that some of the additional OC at MY, leading to a larger ratio and weaker OC-EC correlation, was likely due mainly to SOA formation.

It is known that 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 the utility boiler (2.32) and the industrial boiler (2.51) (Chen et al., 1994), have been converted to those using cleaner energy, such as natural gas or electricity in the urban area, but not as much in the rural residential areas. This difference likely also explains some of the larger OC/EC ratio at MY compared to TH, especially in winter. The practice of burning maize and wheat residue after harvest or as biofuel for cooking and heating in the rural areas, which was mentioned above, may also explain the larger ratio at MY during some weeks. This is because this form of combustion emits particles with a high OC/EC (Zhang et al., 2000; Li et al., 2009). For example, according to a recent study conducted in Beijing by Li et al. (2009), wheat residue and maize residue generate particles with a low mass ratio of EC to OC (i.e. EC/OC = 0.09, 0.10, respectively). In addition, the rural area possesses abundant vegetation potentially releasing significant primary organic matter devoid of EC, such as biological material (e.g. fungal spores, vegetation detritus, endotoxin, and plant waxes), as well as emitting biogenic hydrocarbons in warm season. Given that the summertime ozone is usually higher, particularly in the downwind direction of the urban area (Wang et al., 2009), the potential for these biogenic hydrocarbons to lead to more SOA at MY compared to TH is relatively high.

5 Conclusions

The time series of weekly concentrations of OC and EC in $PM_{2.5}$ from 2005 to 2008 at a rural and urban site in the Beijing area have been examined together with the information on energy usages and transport patterns, providing insight into the impact of emissions and meteorology on their respective levels and trends in the region. OC and EC exhibited strong weekly variations at both sites, ranging from 4.90–76.9 $\mu g\,m^{-3}$ and 2.37–51.2 $\mu g\,m^{-3}$ at TH, and ranging from 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 could be large with a factor of more than 5 at both sites. Clear seasonal patterns were found for both OC and EC at TH with larger weekly concentrations and variations in winter, due to increased coal combustion for heating and frequent alternations between thermal inversion and cleaner post cold front situations. It is likely that coal combustions play dominant roles in the ambient levels of carbonaceous particle in urban Beijing, which are supported by the more positive $\delta^{13}C$ observation in EC at TH during cold seasons in comparison with that during warm seasons. The seasonal pattern in OC at the MY site was less consistent compared to TH, reflecting a more complex and variable situation. The relative impacts from different major sources emissions, formation processes and/or regional transport are different in the rural area north of Beijing compared to the urban area. Relatively local biomass burning during the harvest seasons, widely used family stoves and small boilers and a higher potential for significant formation of SOA locally and upwind all play a role in this rural site. For example, the maximum weekly OC concentration at MY in 2007 July was attributed to a large impact from a wheat straw burning plume due to high OC/EC ratios and such impacts were much less apparent at TH.

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 2005–2007 but a noticeable fall in 2008. However, compared to the levels in 2000, there was a decrease by 13–33 % for OC and 0–19 % for EC on a yearly basis, 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 lower compared to those measured in Beijing 10 years earlier, indicating that the importance of carbonaceous species in $PM_{2.5}$ in Beijing has been diminished. Nonetheless, OC and EC still reserved quite high levels at both rural/urban sites, in comparison with those from other cities in China and around the world. OC was the predominant contributor to TC in both urban and rural Beijing. Interestingly, the relative importance of EC in TC has steadily increased over the study period, particularly at the rural location. The reason for this observation requires further research.

The minimum seasonal urban excesses of OC (3.0 $\mu g\,m^{-3}$) and EC (1.3 $\mu g\,m^{-3}$), which were only one-ninth and one-seventh of their corresponding maximum ones respectively, both occurred in the summer of 2008. This suggests that the special clean air campaign for 2008 Summer Olympic Games, including new traffic planning strategies before, during and after the Summer Olympics, very likely had an impact on the ambient level of carbonaceous aerosols on a local scale over the Beijing area (also supported by more positive $\delta^{13}C$ observations during the period relative to the two preceding summers). OC and EC were reasonably well-correlated at the TH site, indicating that both were most often from common major emission sources in the urban area. High OC/EC ratios and their weaker correlation at the MY site reflects the complex influence of different major sources and processes at this rural location north of Beijing. These include biomass burning, variations in upwind origin of the $PM_{2.5}$ and formation of SOA, all of which vary differently by season.

Acknowledgements. We thank Yu Lei, Yingtao Jia, Hui Liu, Siwen Wang, Zhenyu Du, Kai Liu, and Jinlu Dong for their contributions to the filed work, and Yuxuan Wang for providing the mean flow patterns at the surface of Beijing area. All the OC-EC measurements and Fumo Yang's work during 2006–2007 were funded by Environment Canada OPP3a1f_U046 and the Program of Energy Research and Development Program (NRCan, Canada) through Natural Sciences and Engineering Research Council of Canada's visiting fellowship program. This study was also funded by the National Natural Science Foundation of China (NSFC) projects (41075093 and 40675079), National Basic Research Program (2010CB951803) and the National Science Fund for Distinguished Young Scholars of NSFC (20625722) and supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (XMXX280732).

Edited by: X. Tie

References

Andreae, M. O. and Gelencsér, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, Atmos. Chem. Phys., 6, 3131–3148, doi:10.5194/acp-6-3131-2006, 2006.

Beijing Municipal Bureau of Statistics: Beijing statistical Yearbook, available at: http://www.bjstats.gov.cn/tjnj/2008-tjnj (last access: February 2011), 2008 (in Chinese).

Cao, J., Lee, S. C., Ho, K. F., Zou, S. C., Fung, K., Fung, K., Li, Y., Watson, J. G., and Chow, J. C.,: Spatial and seasonal variations of atmospheric organic carbon and elemental carbon in Pearl River Delta Region, China, Atmos. Environ., 38, 4447–4456, 2004.

Cao, J. J., Lee, S. C., Chow, J. C., Watson , J. G., Ho, K. F., Zhang, R. J., Jin, Z. D., Shen, Z. X., Chen, G. C., Kang, Y. M., Zou, S. C., Zhang, L. Z., Qi, S. H., Dai, M. H., Cheng, Y., and Hu, K.: Spatial and seasonal distributions of carbonaceous aerosols over China, J. Geophys. Res., 112, D22S11, doi:10.1029/2006JD008205, 2007.

Cao, J.-J., Chow, J. C., Tao, J., Lee, S.-C., Watson, J. G., Ho, K.-f., Wang, G.-H., Zhu, C.-S., and Han, Y.-M.: Stable carbon isotopes in aerosols from Chinese cities: Influence of fossil fuels, Atmos. Environ., 45, 1359–1363, 2011.

Cermak, J. and Knutti, R.: Beijing Olympics as an aerosol field experiment, Geophys. Res. Lett., 36, L10806, doi:10.1029/2009GL038572, 2009.

Chan., C. K. and Yao, X. H.: Air pollution in mega cities in China, Atmos. Environ., 42, 1–42, 2008.

Chan, T. W., Huang, L., Leaitch, W. R., Sharma, S., Brook, J. R., Slowik, J. G., Abbatt, J. P. D., Brickell, P. C., Liggio, J., Li, S.-M., and Moosmüller, H.: Observations of OM/OC and specific attenuation coefficients (SAC) in ambient fine PM at a rural site in central Ontario, Canada, Atmos. Chem. Phys., 10, 2393–2411, doi:10.5194/acp-10-2393-2010, 2010.

Chen, Z., Ge, S., and Zhang, J.: Measurement and analysis for atmospheric aerosol particulates in Beijing, Res. Environ. Sci., 7(3), 1–9, 1994 (in Chinese).

Cheng, Y., He, K. B., Duan, F. K., Zheng, M., Ma, Y. L., and Tan, J. H.: Measurement of semivolatile carbonaceous aerosols and its implications: A review, Environ. Int., 35, 674–681, 2009.

Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., and Merrifield, T.: Comparison of IMPROVE and NIOSH carbon measurements, Aerosol Sci. Technol. 34, 23–34 , 2001.

Duan, F., Liu, X., Yu, T., and Cachier, H.: Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing, Atmos. Environ., 38, 1275–1282, 2004.

Fenger, J.: Air pollution in the last 50 years – From local to global, Atmos. Environ., 43, 13–22, 2009.

Flanner, M. G., Zender, C. S., Hess, P. G., Mahowald, N. M., Painter, T. H., Ramanathan, V., and Rasch, P. J.: Springtime warming and reduced snow cover from carbonaceous particles, Atmos. Chem. Phys., 9, 2481–2497, doi:10.5194/acp-9-2481-2009, 2009.

Gelencsér, A.: Carbonaceous Aerosol, Dordrecht, The Netherlands: Springer, 2004.

Gray, H. A., Cass, G. R., Huntzicker, J. J., Heyerdahl, E. K., and Rau., J. A.: Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles, Environ. Sci. Technol., 20, 580–582, 1986.

Hammes, K., Schmidt, M. W. I., Smernik, R. J., Currie, L. A. R., Ball, W. P., Nguyen, T. H., Louchouarn, P., Houel, S., Gustafsson, Ö., Elmquist, M., Cornelissen, G., Skjemstad, J. O., Masiello, C. A., Song, J., Peng, P., Mitra, S., Dunn, J. C., Hatcher, P. G., Hockaday, W. C., Smith, D. M., Hartkopf-Fröder, C., Böhmer, A., Lüer, B., Huebert, B. J., Amelung, W., Brodowski, S., Huang, L., Zhang, W., Gschwend, P. M., Flores-Cervantes, D. X., Largeau, C., Rouzaud, J.-N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F. J., Gonzalez-Perez, J. A., de la Rosa, J. M., Manning, D. A. C., López-Capél, E., and Ding, L.: Comparison of black carbon quantification methods using reference materials from soil, water, sediment and the atmosphere, and implications for the global carbon cycle, Global Biogeochem. Cy., 21, GB3016, doi:10.1029/2006GB002914, 2007.

Han, Z., Zhang R., Wang Q., Wang W., Cao J., and Xu, J.: Regional modeling of organic aerosols over China in summertime, J. Geophys. Res., 113, D11202, doi:10.1029/2007JD009436, 2008.

He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C. K., Cadle, S., Chan, T., and Mulawa, P.: The characteristics of $PM_{2.5}$ in Beijing, China, Atmos. Environ., 35, 4959–4970, 2001.

Huang, L., Brook, J. R., Zhang, W., Li, S. M., Graham, L., Ernst, D., Chivulescu, A., and Lu, G.: Stable isotope measurements of carbon fractions (OC/EC) in airborne particulate: A new dimension for source Characterization & apportionment, Atmos. Environ., 40, 2690–2705, 2006.

Huang, L., Lee, Y.-S., Chivulescu, A., Zhang, W., Ernst, D., Sharma, S., Worthy, D., Ernst, M., Brook, J., Leaitch, R., Chan, E., Tans, P., Sweeney, C., White, J., Vaughn, B., Yang, F., and He, K.: $^{13}C/^{12}C$ isotopic constraints on inter-continental transport of fossil fuel CO_2 & BC aerosols, NOAA ESRL Global Monitoring Annual Conference, 17–19 May, Boulder, Colorado, USA, available at: http://www.esrl.noaa.gov/gmd/annualconference/previous/2010/pdfs/6-LinHuang.pdf (last access: May 2011), 2010.

Ho, K. F., Lee, S. C., Cao, J. J., Chow, Judith C., Watson, John G., and Chan, C. K.: Seasonal variations and mass closure analysis of particulate matter in Hong Kong, Sci. Total Environ., 355, 276–287, 2006.

IPCC: Climate Change 2007: The physical science basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press, 160–168, 2007.

Jacobson, M. Z.: Control of fossil-fuel particulate black carbon and organic matter, possibly the most effective method of slowing global warming, J. Geophys. Res., 107(D19), 4410, doi:10.1029/2001JD001376, 2002.

Jia, Y. T., Rahn, K. A., He, K. B., Wen, T. X., and Wang, Y. S.: A novel technique for quantifying the regional component of urban aerosol solely from its sawtooth cycles, J. Geophys. Res., 113, D21309, doi:10.1029/2008JD010389, 2008.

Kim, B. M., Teffera, S., and Zeldin, M. D.: Characterization of $PM_{2.5}$ and PM_{10} in the South Coast Air Basin of Southern California: part 1-Spatial variations, J. Air Waste Manage., 50, 2034–2044, 2000.

Kong, Q., Wu, Y., Yang, L., Du, H., Zhou, Y., and Fu, L.: Characteristics and intake dose of gaseous pollutants near a major Beijing road during the 29th Olympic Games, Acta Sci. Circumst., 30(2), 281–286, 2010 (in Chinese).

Lee, H. S. and Kang, B.-W.: Chemical characteristics of principal $PM_{2.5}$ species in Chongju, South Korea, Atmos. Environ., 35, 739–746, 2001.

Lei, Y., Zhang, Q., He, K. B., and Streets, D. G.: Primary anthropogenic aerosol emission trends for China, 1990-2005, Atmos. Chem. Phys., 11, 931–954, doi:10.5194/acp-11-931-2011, 2011.

Li, X. H., Wang, S. X., Duan, L., Hao, J. M., and Nie, Y.: Carbonaceous aerosol emissions from household biofuel combustion in China, Environ. Sci. Technol., 43, 6076–6081, 2009.

Liao, H., Henze, D. K., Seinfeld, J. H., Wu, S., and Mickley, L. J.: Biogenic secondary organic aerosol over the United States: Comparison of climatological simulations with observations, J. Geophys. Res., 112, D06201, doi:10.1029/2006JD007813, 2007.

McDow, S. R. and Huntzicker, J. J.: Vapor adsorption artefact in the sampling of organic aerosol: face velocity effects, Atmos. Environ., 24A, 2563–2571, 1990.

Ramanathan, V. and Carmichael, G.: Global and regional climate changes due to black carbon, Nat. Geosci., 221–227, 2008.

Singer, B. C., Kirchstetter, T. W., Harley, R. A., Kendall, G. R., and Hesson, J. M.: A fuel-based approach to estimating motor vehicle cold-start emissions, J. Air Waste Manage., 49, 125–135, 1999.

Streets, D. G., Fu, J. S., Jang, C. J., Hao, J., He, K., Tang, X., Zhang, Y., Wang, Z., Zhang, Q., Wang, L., Wang, B., and Yu, C.: Air quality during the 2008 Beijing Olympic Games, Atmos. Environ., 41, 480–492, 2007.

Turpin, B. J., Huntzicker, J. J., and Hering, S. V.: Investigation of organic aerosol sampling artefacts in the Los Angeles basin, Atmos. Environ., 28, 3061–3071, 1994.

Turpin, B. J., Saxena, P. ,and Andrews, E.: Measuring and simulating particulate organics in the atmosphere: problems and prospects, Atmos. Environ., 34, 2983–3013, 2000.

UNEP, United Nations Environmental Programme: Independent Environmental Assessment Beijing 2008 Plympic Games, Nairobi, Kenya, 2009, available at: http://www.unep.org/pdf/BEIJING_REPORT_COMPLETE.pdf, (last access: February 2011), 2009.

Wang, Y., Hao, J., McElroy, M. B., Munger, J. W., Ma, H., Chen, D., and Nielsen, C. P.: Ozone air quality during the 2008 Beijing Olympics: effectiveness of emission restrictions, Atmos. Chem. Phys., 9, 5237–5251, doi:10.5194/acp-9-5237-2009, 2009.

Wang, S. X., Zhao, M., Xing, J.,Wu, Y., Zhou, Y., Lei, Y., He, K. B., Fu, L. X., and Hao, J. M.: Quantifying the Air Pollutants Emission Reduction during the 2008 Olympic Games in Beijing, Environ. Sci. Technol., 44(7), 2490–2496, 2010a.

Wang, T., Nie, W., Gao, J., Xue, L. K., Gao, X. M., Wang, X. F., Qiu, J., Poon, C. N., Meinardi, S., Blake, D., Wang, S. L., Ding, A. J., Chai, F. H., Zhang, Q. Z., and Wang, W. X.: Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact, Atmos. Chem. Phys., 10, 7603–7615, doi:10.5194/acp-10-7603-2010, 2010b.

Yang, F., He, K., Ma, Y., Zhang, Q., Cadle, S., Chan, T., and Mulawa, P.: Characterization of mass balance of $PM_{2.5}$ chemical speciation in Beijing, Environ. Chem., 23(3), 326–333, 2004 (in Chinese).

Yang, F., He, K., Ye, B., Chen, X., Cha, L., Cadle, S. H., Chan, T., and Mulawa, P. A.: One-year record of organic and elemental carbon in fine particles in downtown Beijing and Shanghai, At-

mos. Chem. Phys., 5, 1449–1457, doi:10.5194/acp-5-1449-2005, 2005.

Yang, F., Brook, J., He, K., Duan, F., and Ma, Y.: Temporal variability in fine carbonaceous aerosol over two years in two megacities: Beijing and Toronto, Adv. Atmos. Sci., 27(3), 705–714, doi:10.1007/s00376-009-9103-6 , 2010.

Yang, F., Tan, J., Zhao, Q., Du, Z., He, K., Ma, Y., Duan, F., Chen, G., and Zhao, Q.: Characteristics of $PM_{2.5}$ speciation in representative megacities and across China, Atmos. Chem. Phys., 11, 5207–5219, doi:10.5194/acp-11-5207-2011, 2011a.

Yang, F., Huang, L., Sharma, S., Brook, J. R., Zhang, W., Li, S.-M., and Tan, J.: Two-year observations of fine carbonaceous particles in variable sampling intervals, Atmos. Environ., 45, 2418–2426, 2011b.

Ye, B. M., Ji, X. L., Yang, H. Z., Yao, X. H., Chan, C. K., Cadle, S. H., Chan, T., and Mulawa, P. A.: Concentration and chemical composition of $PM_{2.5}$ in Shanghai for a 1-year period, Atmos. Environ., 37(4), 499–510, 2003.

Zhang, J., Smith, K. R., Ma, Y., Jiang, F., Qi, W., Liu, P., Kahlil, M. A. K., Rasmussen, R. A., and Thornelow, S. A.: Greenhouse gases and other airborne pollutants from household stoves in China: a database for emission factors, Atmos. Environ., 34: 4537–4549, 2000.

Zhou, Y., Wu, Y., Yang, L., Fu, L., He, K., Wang, S., Hao, J., Chen, J., and Li, C.: The impact of transportation control measures on emission reductions during the 2008 Olympic Games in Beijing, China, Atmos. Environ., 44, 285–293, 2010.