Fossil and Non-fossil Fuel Sources of Organic and Elemental Carbon Aerosols in Beijing, Shanghai and Guangzhou: Seasonal Carbon-source Variation

Di Liu[1], Matthias Vonwiller[2], Jun Li[*1], Junwen Liu[3], Sönke Szidat[2], Yanlin Zhang[4], Chongguo Tian[5], Yinjun Chen[6], Zhineng Cheng[1], Guangcai Zhong[1], Pingqing Fu[7], Gan Zhang[1]

[1]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China

[2]Department of Chemistry and Biochemistry & Oeschger Centre for Climate Change Research, University of Bern, Berne, 3012, Switzerland

[3]Institute for Environmental and Climate Research, Jinan University, Guangzhou, 511443, China

[4]Yale-NUIST Center on Atmospheric Environment, International Joint Laboratory on Climate and Environment Change (ILCEC), Nanjing University of Information Science and Technology, Nanjing 210044, China

[5]Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

[6]State Key Laboratory of Pollution Control and Resources Reuse, Key Laboratory of Cities' Mitigation and Adaptation to Climate Change, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

[7] Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China

*To whom correspondence may be addressed:

Dr. Jun Li; Email: junli@gig.ac.cn; Tel.: +86-20-85291508; Fax: +86-20-85290706

Abstract

Fossil fuel (FF) combustion and non-fossil fuel (NF) emissions (such as biomass burning) are the two most important contributors to the high air pollution in China. Within the large territorial area of China, these two emission sources may exert different influences on the carbonaceous particles sampled in megacities among regions and seasons. Here, the radiocarbon isotopic signals in Beijing, Shanghai and Guangzhou, China from 2013 to 2014 are reported. Generally, a greater contribution of NF (>55%) sources was found in all cities during autumn. However, source seasonality differed among cities during the other seasons. During winter, FF contributed to the majority of pollution in Beijing (64%), NF contributed to the majority in Guangzhou (63%), and FF contributed slightly more than NF in Shanghai (54%). During spring and summer, Beijing and Guangzhou showed similar patterns, with higher contributions from FF (55% and 63%, respectively) than NF. FF made the greatest contribution (71%) in Shanghai during summer. Secondary organic carbon originated mainly from biomass burning and vehicle emissions, except in Beijing during winter, when the major source was residual coal combustion.

Introduction

Large-scale pollution of fine particles (aerodynamic diameter ≤ 2.5 μm; $PM_{2.5}$) occurs frequently, impacting air quality in the megacities of China due to massive and intensive pollutant emissions combined with unfavorable meteorological conditions. Among aerosol pollutants, carbonaceous aerosols, which can constitute 20–50% of aerosols in the urban atmosphere,(Cao et al., 2007) are of great concern due to their

adverse impacts on air quality, visibility, human health and climate.(Highwood and Kinnersley, 2006;Mauderly and Chow, 2008;Pratsinis et al., 1984) Carbonaceous materials are operationally classified as strongly refractory, highly polymerized carbon (elemental carbon, EC) and black carbon (BC) or weakly refractory, light polycyclic or polyacidic hydrocarbon (organic carbon, OC).(Castro et al., 1999;Pöschl, 2005) EC originates exclusively from primary sources and is emitted during incomplete combustion of fossil fuels (FFs; i.e., coal and petroleum) and biomass burning (BB; i.e., heating and wood fires). OC is a complex mixture of primary (directly emitted) OC (POC) and secondary OC (SOC) particles formed in situ in the atmosphere via oxidation of gas-phase precursors. Using a recently developed method, source apportionment can be determined by measuring the radiocarbon (^{14}C) content of OC and EC separately, which enables unambiguous differentiation between FF and non-FF (NF) sources.(Liu et al., 2013;Zong et al., 2016;Liu et al., 2016;Liu et al., 2014;Liu et al., 2017c;Zhang et al., 2015a) This differentiation is possible because ^{14}C is completely decayed in FF sources (i.e., diesel exhaust, gasoline exhaust and coal combustion), whereas NF sources (i.e., BB, cooking and biogenic emissions) exhibit contemporary ^{14}C levels.(Szidat et al., 2009) Even more precise ^{14}C-based source apportionment can be obtained by dividing OC into water-soluble OC and water-insoluble OC.(Liu et al., 2016)

Beijing, Shanghai and Guangzhou are representative megacities located in different climatic regions (the Beijing–Tianjin–Hebei region, Yangtze River Delta region and Pearl River Delta region, respectively) that suffer from severe air pollution due to

rapid expansion of industry and transportation, sharply increasing the population and thus the demand for FFs.(Feng et al., 2015;Wei et al., 2017;Ding et al., 2017;Zhang et al., 2015a;Ling et al., 2011) Although source apportionment of carbonaceous aerosols has been conducted in some cities,(Wei et al., 2017;Liu et al., 2014;Liu et al., 2017c;Elser et al., 2016;Liu et al., 2018) the results are segmented and generally pertain to haze events during winter. In our previous research, several independent case studies were conducted in Guangzhou. For example, during winter (Nov. 29, 2012 to Jan. 19, 2013), higher contributions of FF sources to EC (80–90%) were observed for haze samples that were substantially impacted by local emissions, and lower contributions of FF to EC (60–70%) were found for haze particles impacted by regional transport.(Liu et al., 2014) During Spring (Mar. 15 to Apr. 15 2013), NF sources majorly contributed to total carbonaceous aerosols (46 ± 5%).(Liu et al., 2016) During summer (June 25, 2013 to July 15, 2013), 87% of EC and 53% of OC in $PM_{2.5}$ were derived from FF sources on a typical summer day, but these values dropped significantly with invasion of NF-enriched air masses from rural and suburban areas.(Liu et al., 2018) During autumn (Oct. 15 2013 to Nov. 15 2013), NF was the predominant source of total carbon (TC; average = 65 ± 7%).(Liu et al., 2017a) In this study, a $PM_{2.5}$ sampling campaign was conducted simultaneously in three cities over 1 year, and two samples with relatively high and low $PM_{2.5}$ concentrations during each season in the three cities were selected for ^{14}C analysis. ^{14}C data of ambient aerosols from Beijing, Shanghai and Guangzhou are presented for these two sub-fractions in terms of TC, OC and EC. Furthermore, OC was divided into

water-insoluble OC and water-soluble OC. A comparison of the sources and seasonal variation of carbonaceous aerosols among the three cities was conducted. The results can help identify the carbon sources of aerosols in China and support policymakers in developing appropriate air-quality management initiatives for particulate matter pollution.

2. Methods and experiments

2.1 Aerosol sampling

$PM_{2.5}$ samples were collected in Beijing, Shanghai and Guangzhou during the four seasons. Detailed descriptions of the sampling sites, sampling methods and protocols have been described previously.(Liu et al., 2017a) Briefly, four sampling periods were selected to represent the four seasons: autumn (October 16 to November 15, 2013), winter (December 20, 2013 to January 20, 2014), spring (March 20 to April 20, 2014), and summer (June 20 to July 20, 2014). During each season, 24-h integrated $PM_{2.5}$ samples were collected on pre-heated (450 °C for 5 h) quartz fiber filters (8 × 10 in; Whatman, UK or PALL, USA) using a high-volume sampler (Shanghai Xintuo) at a flow rate of 0.3 m^3 min^{-1}. In this study, we collected 110, 110 and 106 samples from Beijing, Shanghai and Guangzhou, respectively. At each sampling site and season, one field blank sample was collected and analyzed. All samples were stored at −20 °C until analysis.

2.2. Thermal–optical carbon analysis

Portions of the filter samples (1.5 cm^2) were cut for analysis of the OC and EC contents (OC/EC) using a thermal–optical carbon analyzer (Sunset Laboratory Inc.,

Forest Grove, OR, USA) following a modified National Institute of Occupational Safety and Health (NIOSH) thermal–optical transmission protocol. NIOSH thermal–optical transmission and the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal–optical reflectance are two common thermal–optical methods. Due to differences in charring correction and the temperature program, the NIOSH-defined EC concentration was slightly lower than that defined by IMPROVE, although the TC concentrations measured by the two methods were comparable.(Cheng et al., 2011) Replicate samples and a filter blank were conducted to determine the analytical precision and identify background contamination. Analysis of replicate samples (n = 64) provided good analytical precision, with relative deviations of 4.5%, 8.6% and 4.5% for OC, EC and TC, respectively. The average field blank concentration of OC was 1.47 ± 0.17 μg cm^{-2} (1 σ, n = 12), and that of EC was undetectable. The lowest OC value observed on a filter was ~10 μg cm^{-2} before subtraction of the blank value. The reported OC concentrations were adjusted by subtraction of the values of the filter blanks. Field blanks were not analyzed for OC and EC ^{14}C.

2.3. ^{14}C analysis of the carbonaceous fractions

^{14}C was measured in carbonaceous aerosols to distinguish FF and NF sources quantitatively. Two samples with relatively high and low $PM_{2.5}$ concentrations collected in each season and city were selected for ^{14}C analysis, although only one sample was analyzed during summer in Shanghai (23 samples total). The 3-day air mass back trajectories for all selected samples are shown in Fig. 1. The detailed

method of ^{14}C measurement in various carbonaceous aerosols (i.e., TC, EC and water-soluble OC (WSOC)) has been described elsewhere.(Zhang et al., 2012;Zhang et al., 2015a) Recently, ^{14}C measurements in aerosols collected in China were analyzed following this protocol.(Huang et al., 2014) Briefly, the ^{14}C content of TC was analyzed through coupling of an elemental analyzer with a MIni CArbon Dating System (MICADAS) at the University of Bern, Switzerland.(Szidat et al., 2014) ^{14}C analysis of EC and water-insoluble OC (WIOC) were carried out through online coupling of the MICADAS with a Sunset Lab OC/EC analyzer, and the CO_2 resulting from EC or WIOC was separated during either the EC or OC step of the Swiss_4S protocol.(Agrios et al., 2015;Zhang et al., 2012) The ^{14}C analysis results were expressed as fractions of modern carbon (f_M). The f_M values for OC were not measured directly but were deduced through subtraction of TC and EC based on mass balancing. Similarly, the f_M values of WSOC were further calculated via mass balancing through subtraction of OC and WIOC. The average uncertainties of f_M values for OC, EC, TC and WSOC were <10%, including uncertainties from ^{14}C measurements, blank correction and mass-balance calculations.

3. Results and discussion

3.1 Seasonal variation and concentrations of $PM_{2.5}$, OC and EC

Fig. 2 shows box-and-whisker plots for the concentrations of $PM_{2.5}$, OC and EC and EC/OC ratios during the sampling campaign at all three sites. The average $PM_{2.5}$ mass concentrations in Beijing, Shanghai and Guangzhou were 182 ± 78.3 μg m^{-3}, 88.6 ± 49.4 μg m^{-3} and 80.4 ± 30.7 μg m^{-3}, respectively. Despite large variations in the $PM_{2.5}$

levels observed at all sites, concentrations were generally higher in Beijing than in Shanghai or Guangzhou. This result indicates poorer air quality in northern China, which is consistent with previous studies.(Hu et al., 2014)

On average, the highest concentrations of OC and EC in $PM_{2.5}$ were observed in Beijing (21.1 ± 13.9 μg m^{-3} and 2.8 ± 2.2 μg m^{-3}), followed by Guangzhou (17.3 ± 9.6 μg m^{-3} and 2.9 ± 1.3 μg m^{-3}) and Shanghai (9.0 ± 7.6 μg m^{-3} and 1.6 ± 1.5 μg m^{-3}). The percentages of TC matter (TCM = 1.6 × OC + EC) to total fine particle mass were 20 ± 6%, 17 ± 6% and 36 ± 8% in Beijing, Shanghai and Guangzhou, respectively, indicating the importance of carbonaceous aerosols in air quality, especially in Guangzhou, South China. However, no significant correlations were found between the ratio of TCM/$PM_{2.5}$ and $PM_{2.5}$ concentration in Beijing and Shanghai, indicating that carbonaceous aerosols are the major component of $PM_{2.5}$ but did not play a predominant role when $PM_{2.5}$ concentrations were higher. On the other hand, in Guangzhou, the ratio of TCM/$PM_{2.5}$ was positively correlated with the $PM_{2.5}$ concentration (R^2 = 0.27, $p<0.05$). This finding shows that the relative contributions of carbonaceous aerosols to total fine particles increased with increasing $PM_{2.5}$ concentrations in Guangzhou, implying that the role of carbonaceous aerosols in $PM_{2.5}$ is greater in South China than in other parts of China. The average concentrations of OC and EC in Beijing, Shanghai and Guangzhou in this study were similar to those reported in the same respective cities in 2013 (OC: 38.6 μg m^{-3}; EC: 5.83 μg m^{-3} in Beijing; 10.9 μg m^{-3} and 3.03 μg m^{-3} in Shanghai; 14.4 μg m^{-3} and 3.87 μg m^{-3} in Guangzhou)(Zhang et al., 2016) but were significantly higher than those in

European urban cities such as Athens, Greece (2.1 ± 1.3 μg m^{-3} and 0.54 ± 0.39 μg m^{-3})(Paraskevopoulou et al., 2014) and Elche, Spain (5.6 ± 2.8 μg m^{-3} and 1.5 ± 1.2 μg m^{-3})(Perrone et al., 2011) and in other Asian urban cities such as Seoul, Korea (10.2 ± 5.5 μg m^{-3} and 4.1 ± 2.6 μg m^{-3})(Kim et al., 2007) and Yokohama, Japan (3.75 ± 1.5 μg m^{-3} and 1.94 ± 1.2 μg m^{-3}).(Khan et al., 2010)

The seasonal variations of $PM_{2.5}$, OC and EC were characterized by mass concentrations that were higher during winter and lower during summer (Fig. 2). The high winter concentrations can be attributed mainly to a combination of complex effects, such as increasing emissions from local and regional coal and biomass or biofuel combustion and the associated secondary formation processes, as well as unfavorable metrological conditions for pollution dispersal.(Huang et al., 2014) Conversely, the low mass concentrations during summer are likely due to a sharp decrease in anthropogenic source emissions (i.e., heating-related coal and biofuel burning), relatively high wet-scavenging effects and a high mixing layer. (Zhang et al., 2017)

Generally, the relationship between OC and EC can give some indication of the origin of carbonaceous particles. A strong relationship between OC and EC might indicate that the carbonaceous particles are derived from the same emission source. Lower OC/EC ratios (1.0–4.2) imply sources from diesel- and gasoline-powered vehicular exhaust,(Schauer et al., 2002, 1999) whereas aerosols with higher OC/EC ratios might originate from coal combustion,(Zhi et al., 2008) wood combustion (16.8–40.0),(Schauer et al., 2001) forest fires (14.5), BB (7.7),(Zhang et al., 2007) or

formation of SOC.(Chow et al., 1993) The correlations between OC and EC (R^2 = 0.56 and 0.80, respectively) were higher in Beijing and Shanghai than in Guangzhou (R^2 = 0.26). Moreover, the correlations of OC with EC and the OC/EC ratio during different seasons in Beijing and Shanghai were generally consistent. This consistency implies that the sources of the carbonaceous aerosols in Beijing did not change drastically, and that these aerosols were derived from various mixtures. This characteristic was also observed in Shanghai, although the sources of the carbonaceous aerosols differed between the two cities. In Guangzhou, higher correlations between OC and EC during autumn (R^2 = 0.71) and winter (R^2 = 0.50) were found, with a lower correlation during spring (R^2 = 0.38) and no significant correlation during summer. The average OC/EC ratios were significantly ($p < 0.01$) higher during autumn (8.6) and winter (9.6) than spring (4.9) and summer (3.7) (Fig. 2). This finding suggests that the major sources of carbonaceous aerosols differed markedly during different seasons in Guangzhou. The south China region is strongly influenced by anthropogenic emissions from the upwind Asian continent. Analysis of 3-day back trajectories showed that seasonal variations of carbonaceous aerosols were consistent with alteration of the winter and summer monsoons (Fig. 1b); therefore, the major sources of carbonaceous aerosols originated from inland China during autumn and winter but from the Pearl River Delta during spring and summer. This difference in sources likely contributes to the significant seasonal differences in carbonaceous aerosols, which may be elucidated by the ^{14}C results.

3.2 ^{14}C results: f_M and seasonal variation

The concentrations of different carbon species and their ratios in selected samples from three cities are listed in Table 1, and the proportion (%) of FF sources in various carbon fractions of the corresponding samples are shown in Table 2. Overall, FF sources accounted for slightly greater contributions to TC in the three cities annually (average: 53 ± 10%; range: 31–71%) than those of NF sources (average: 47 ± 10%; range: 29–69%), and the values in all three cities were similar. For example, the FF:NF ratios in Beijing, Shanghai and Guangzhou were 54:46, 53:47 and 52:48, respectively. Despite the wide range of EC concentrations (Table 1), the ratios of fossil EC (EC_f) to total EC in Beijing, Shanghai and Guangzhou were comparable, with averages of 73 ± 6%, 72 ± 6% and 74 ± 14%, respectively, suggesting that FF combustion is the dominant contributor to EC. The high annual contribution of FFs to EC in the three cities was consistent with previously reports based on a similar ^{14}C-based approach for analyzing EC in cities in China, including Beijing (79% and 82%),(Zhang et al., 2015b;Zhang et al., 2015a) Xi'an (78 ± 3%),(Zhang et al., 2015a) Shanghai (79%)(Zhang et al., 2015a) and Guangzhou (80–90%),(Liu et al., 2014) as well as previous studies conducted in other cities around the world.(Andersson et al., 2015;Bernardoni et al., 2013;Liu et al., 2013) The average contributions of fossil OC (OC_f) to OC were 50 ± 10%, 49 ± 9% and 45 ± 10% in Beijing, Shanghai, and Guangzhou, respectively, which were lower than the corresponding EC_f contributions in all samples. The high proportion of OC_{nf} (32–72%) indicated that primary emissions and secondary formation from NF sources (i.e., BB and biogenic emissions) are important contributors to OC in densely populated urbanized areas of China.

The relative contributions of FF and NF sources to EC, WIOC and WSOC in each of the four seasons are plotted in Fig. 3. Distinct seasonal patterns were found in the three cities. Generally, relatively high contributions of NF sources (54–59%) to TC were found during autumn (late October to early November). Particulate EC was predominantly derived from the combustion of FFs such as coal, gasoline and diesel and burning of vegetation and wood (NF sources). In this study, the proportion of EC derived primarily from BB was also higher during autumn (>30%) than during the other seasons. Three-day back trajectory analysis revealed air masses that arrived from inland central China (Fig. 1). Burning of agricultural waste has been suggested to have a strong impact on air quality during this season in Beijing.(Zhang et al., 2017) That result is consistent with our previous study, which indicated that NF emissions were predominant in carbonaceous aerosols in Chinese cities during this season.(Liu et al., 2017a)

During winter, the carbon source compositions of the cities differed. The percentage of FF-derived sources was increased significantly in Beijing. $WIOC_f$ and EC_f were generally considered to be primary emissions from coal combustion and vehicle exhaust. Generally, the $WIOC_f/EC_f$ ratios of coal combustion were higher than those of vehicle emissions. The highest $WIOC_f/EC_f$ ratio in this study, 2.39, was obtained in Beijing during winter; this suggests that the increase in the FF-derived contribution was associated with increasing emissions from coal combustion for heating purposes during the cold season in North China (Fig. 1a), which was confirmed by the aerosol mass spectrometer measurements obtained during the same season.(Elser et al.,

2016) Based on another study, this FF source enhancement might be attributed to residential coal combustion.(Liu et al., 2017c) In Shanghai, the contribution of fossil carbon increased approximately 11%. The $WIOC_f/EC_f$ ratio of 1.3 indicated that the FF-derived carbon source was a mixture of coal combustion and vehicle emissions. In Guangzhou, the contribution of NF sources was the highest (69%), and the EC_{BB}/EC ratio reached 0.39 and 0.48 in winter samples. As shown in Fig. 1, air masses arrived from the north of Guangdong, Hunan and Guizhou Provinces, where a large amount of biomass, including agricultural waste and hard wood, was burned for cooking and domestic heating during the cold, dry winter. This carbon source characterization matches that reported for regional-scale haze events in a previous study.(Liu et al., 2014)

In Beijing and Guangzhou, the source compositions were generally consistent during spring and summer, but the average contribution of NF sources in Beijing (45 ± 4%) was higher than that in Guangzhou (37 ± 3%). The results of 3-day back trajectory analysis indicated that natural and biogenic emissions from upwind rural and mountainous areas strongly impacted the air quality in Beijing, whereas the major carbon sources in Guangzhou were from vehicle and industrial emissions in the Pearl River Delta region. In Shanghai, the carbon source composition during spring was most similar to that during winter, but a dramatic increase in FF-derived carbon was observed during summer. The limited sample numbers during summer in Shanghai might have led to biased results. On the other hand, a recent study indicated that the greatest ratio of primary ship-emitted particles to total particles in the Shanghai

288 urban region could reach 50% during ship plume cases, which usually occur during
289 spring and summer. (Liu et al., 2017b) The corresponding back trajectory showed
290 that the air mass came from the East China Sea and passed over the eastern coast of
291 China. In addition to pollutants from industrial and vehicle emissions, the
292 contribution of emissions from fishing boats and large ships near the air-sampling
293 site in Shanghai cannot be ignored.
294 Above all, this study demonstrated that the main sources of carbonaceous aerosols
295 in cities varies greatly among seasons. In Beijing, the seasonal variation was similar to
296 variations in submicrometer organic aerosols measured from 2013 to 2014. (Zhang et
297 al., 2017) Table 3 lists the ^{14}C results from $PM_{2.5}$ in three cities during 2012–2014
298 published in previous studies. Compared with previous studies, the seasonal
299 variations of carbon sources in the three cities were highly consistent with previous
300 observations conducted in different seasons.(Liu et al., 2014;Liu et al., 2017c;Liu et al.,
301 2016;Liu et al., 2018) The carbon sources of high-$PM_{2.5}$ samples and low-$PM_{2.5}$
302 samples from each season were nearly consistent in this study (Fig. 3). Due to the
303 limited data, these results might not reflect the true source variation over a 1-year
304 period. For example, carbon source dynamics of carbonaceous aerosols during haze
305 formation in Guangzhou indicated that there are significant differences in the carbon
306 sources of high-$PM_{2.5}$ samples and low-$PM_{2.5}$ samples during spring and summer.(Liu
307 et al., 2018;Liu et al., 2016) In addition, carbon sources of the high-$PM_{2.5}$ samples in
308 Guangzhou winter also differ from each other.(Liu et al., 2014) In those previous
309 studies, variation of the carbon source of atmospheric aerosols is often affected by

changes in meteorological conditions, such as wind direction and speed. In this study, the air masses of the high- and low-$PM_{2.5}$ samples during each season and at each site originated from approximately the same direction (Fig. 1), following the average wind direction of this season. Thus, the results of this study may reflect regional pollution characteristic during different seasons in each city.

3.3 Possible sources of secondary organic aerosols

Based on water solubility, OC was separated into WSOC and WIOC. EC and WIOC were generally considered primary emissions, whereas WSOC was a proxy for secondary OC (SOC) and BB OC.(Zhang et al., 2017) Previous studies have indicated that SOC is the predominant component of WSOC in cities.(Huang et al., 2014;Liu et al., 2016) In this study, WSOC accounted for 47 ± 7%, 32 ± 7% and 43 ± 12% of TC in Beijing, Shanghai and Guangzhou, respectively, and was significantly positively correlated with $PM_{2.5}$ concentrations, showing the importance of WSOC in megacities. Moreover, the WSOC/$PM_{2.5}$ ratio was significantly positive correlated with the $PM_{2.5}$ concentration in Beijing (R^2 = 0.67, $p<0.01$) and Guangzhou (R^2 = 0.31, $p<0.05$), but no significant correlation was found in Shanghai. This finding suggests that SOC plays an important role in high-$PM_{2.5}$ events in Beijing and Guangzhou.

The potential major sources of WSOC may be revealed by plotting our data. As shown in Fig. 4A, the percentage of non-fossil WSOC to TC was positively correlated with the ratio of EC_{BB}/EC. EC is exclusively of primary origin and is emitted from incomplete combustion of FFs and BB. This correlation indicates that the increase in non-fossil WSOC is likely due to enhanced BB. On one hand, a large fraction of the POC from BB

is water soluble; on the other hand, increased emission of volatile organic compounds during BB could lead to an increase in NF secondary organic aerosols. This suggests that BB emissions have an important impact on non-fossil SOC in China. Recently, evidence from a secondary organic aerosol tracer indicated that a large nationwide increase in secondary organic aerosols during the cold season was highly associated with an increase in BB emissions(Ding et al., 2017). In principle, fresh POC emitted from FF combustion is water insoluble. A previous study evaluated the differences in WSOC levels at sites with no direct influence from vehicle exhaust emissions and concluded that very little primary WSOC is emitted directly from vehicles.(Weber et al., 2007) Regarding another type of FF, only ~1% of coal-sourced fresh OC is water soluble.(Park et al., 2012) Thus, POC derived from FF combustion can reasonably be considered water insoluble, and fossil WSOC is used to estimate the levels of FF-derived SOC.(Weber et al., 2007) The fossil WSOC/TC ratio versus the $WIOC_f/EC_f$ ratio is plotted in Fig. 4B. The primary sources of $WIOC_f$ and EC_f were coal combustion and emissions from internal combustion engines fueled by petroleum. Generally, the $WIOC_f/EC_f$ ratio from coal combustion was higher than that from vehicle emissions.(Liu et al., 2013) As shown in Fig. 4B, the proportion of $WSOC_f$ decreased with increasing $WIOC_f/EC_f$ ratios in Shanghai and Guangzhou, indicating that fossil SOC did not originate mainly from coal combustion sources, but rather from vehicle and ship emissions or violate organic compounds (VOCs) released from industrial sources. However, the trend differed in Beijing. Excluding winter samples, the pattern in Beijing was similar to those in Shanghai and Guangzhou, but the trend

354 shifted to the opposite of those in Shanghai and Guangzhou when the winter
355 samples were included. These results suggest that the fossil SOC in Beijing is sourced
356 mainly from residential coal combustion during winter and from vehicle exhaust or
357 industrial emissions during other seasons.

358 **4. Conclusion**

359 Carbonaceous aerosols accounted for 20 ± 6%, 17 ± 6% and 36 ± 8% of the mass of
360 $PM_{2.5}$ in Beijing, Shanghai and Guangzhou, respectively. The seasonal variation of
361 $PM_{2.5}$, OC and EC were characterized by mass concentrations that were higher during
362 winter and lower during summer. Based on ^{14}C measurements, the yearly average
363 contributions of FF and NF to TC were almost equal, with FF:NF ratios of 54:46, 53:47
364 and 52:48 in Beijing, Shanghai and Guangzhou, respectively. FF combustion is the
365 dominant contributor to EC (>72%), whereas NF contributes to a slightly higher
366 proportion of OC (50–55%) than does FF at the three sites. Generally, a greater
367 contribution of NF (>55%) sources was found during autumn in all cities. The source
368 seasonality differed among the three cities during the other seasons. During winter,
369 FF contributed more in Beijing (64%), NF in Guangzhou (63%) and FF in Shanghai
370 (54%). During spring and summer, Beijing and Guangzhou had similar source
371 compositions, with higher contributions from FF (55% and 63%, respectively) than NF.
372 However, FF had the highest contribution (71%) in Shanghai during summer. SOC
373 originated mainly from BB and FF oil emissions, except during winter in Beijing, when
374 the major source was residual coal combustion.
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543 Table 1. Concentrations (μg C/m^3) of different carbon species and their ratios

Site	PM2.5	WSOC	WIOC	EC	OC	TC	OC/EC	TC/PM2.5
Beijing								
24-Oct-13	89.1	5.23	5.28	2.23	10.5	12.7	4.71	0.14
27-Oct-13	326	43.8	26.9	18.2	70.7	89.0	3.88	0.27
8-Jan-14	97.0	3.61	2.60	1.12	6.21	7.33	5.56	0.08
15-Jan-14	518	98.3	48.9	19.7	147	167	7.49	0.32
13-Apr-14	326	11.4	12.2	5.92	23.6	29.5	3.98	0.09
17-Apr-14	176	14.1	6.28	5.39	20.4	25.7	3.78	0.15
24-Aug-14	96.0	4.40	3.60	1.77	8.00	9.77	4.52	0.10
26-Aug-14	103	3.71	3.48	2.20	7.19	9.39	3.28	0.09
Shanghai								
8-Nov-13	176	9.56	20.6	7.49	30.1	37.6	4.02	0.21
11-Nov-13	67.2	1.88	2.56	1.02	4.44	5.46	4.37	0.08
22-Dec-13	81.8	4.16	5.07	2.82	9.23	12.1	3.27	0.15
28-Dec-13	216	9.51	17.2	9.73	26.7	36.4	2.75	0.17
4-Apr-14	168	5.37	9.77	4.59	15.1	19.7	3.30	0.12
7-Apr-14	110	4.63	4.19	2.20	8.81	11.0	4.00	0.10
10-Jul-14	128	6.25	5.72	3.49	12.0	15.5	3.43	0.12
Guangzhou								
22-Oct-13	79.3	9.09	7.41	3.62	16.5	20.1	4.56	0.25
27-Oct-13	124	8.79	14.0	5.80	22.8	28.6	3.93	0.23
22-Dec-13	40.1	4.90	2.92	1.73	7.83	9.56	4.51	0.24
4-Jan-14	159	48.9	20.4	8.04	69.2	77.3	8.61	0.49
28-Mar-14	61.0	10.3	6.06	5.98	16.4	22.3	2.74	0.37
9-Apr-14	124	23.3	13.2	13.5	36.4	50.0	2.69	0.40
1-Jul-14	34.5	2.07	2.90	2.70	4.97	7.66	1.84	0.22
7-Jul-14	120	11.7	11.8	8.09	23.5	31.6	2.90	0.26

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547 Table 2. Relative contribution of fossil fuel sources to different carbon fractions

Site/Time	WSOC	WIOC	EC	OC	TC
Beijing					
24-Oct-13	0.37	0.33	0.67	0.35	0.41
27-Oct-13	0.40	0.39	0.63	0.39	0.44
8-Jan-14	0.63	0.49	0.72	0.57	0.60
15-Jan-14	0.65	0.74	0.77	0.68	0.69
13-Apr-14	0.56	0.44	0.75	0.50	0.55
17-Apr-14	0.51	0.48	0.75	0.50	0.55
24-Aug-14	0.45	0.43	0.77	0.44	0.50
26-Aug-14	0.56	0.49	0.79	0.53	0.59
Shanghai					
8-Nov-13	0.23	0.40	0.67	0.35	0.41
11-Nov-13	0.37	0.36	0.75	0.37	0.44
22-Dec-13	0.45	0.54	0.72	0.50	0.55
28-Dec-13	0.44	0.50	0.68	0.48	0.53
4-Apr-14	0.44	0.53	0.71	0.50	0.55
7-Apr-14	0.38	0.48	0.70	0.43	0.48
10-Jul-14	0.69	0.67	0.84	0.68	0.71
Guangzhou					
22-Oct-13	0.35	0.44	0.67	0.39	0.44
27-Oct-13	0.47	0.36	0.70	0.40	0.46
22-Dec-13	0.35	0.44	0.61	0.38	0.42
4-Jan-14	0.29	0.28	0.52	0.28	0.31
28-Mar-14	0.52	0.57	0.84	0.54	0.62
9-Apr-14	0.57	0.59	0.88	0.58	0.66
1-Jul-14	0.54	0.53	0.86	0.54	0.65
7-Jul-14	0.49	0.50	0.86	0.50	0.59

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551 Table 3. Fossil fuel fraction of TC and EC in $PM_{2.5}$ during 2012-2014 in three cities

Site/Time	Beijing		Shanghai		Guangzhou		Ref
	TC	EC	TC	EC	TC	EC	
Jan-2013(H)		74%		68%		68%	(Andersson et al., 2015)
Jan-13(L)	49%		43%		22%		(Huang et al., 2014)
Jan-13(H)	60%		46%		36%		
Jan-13(H)					53%	86%	(Liu et al., 2014)
Jan-13(H)					36%	66%	
Jan-13(L)					40%	66%	
Jan-13 (H)				69%			(Wei et al., 2017)
Mar- Apr, 2013(A)	44%	67%			54%	80%	(Liu et al., 2016)
Jul-13(H)					32%	76%	(Liu et al., 2018)
Jul-13(L)					60%	86%	
Oct-Nov-13(H)	37%	51%	33%	67%	29%	51%	(Liu et al., 2017a)
Oct-Nov-13(L)	30%	49%	29%	44%	41%	76%	

552 Note. H means higher $PM_{2.5}$ concentration, L means lower $PM_{2.5}$, A means average

553 levels.

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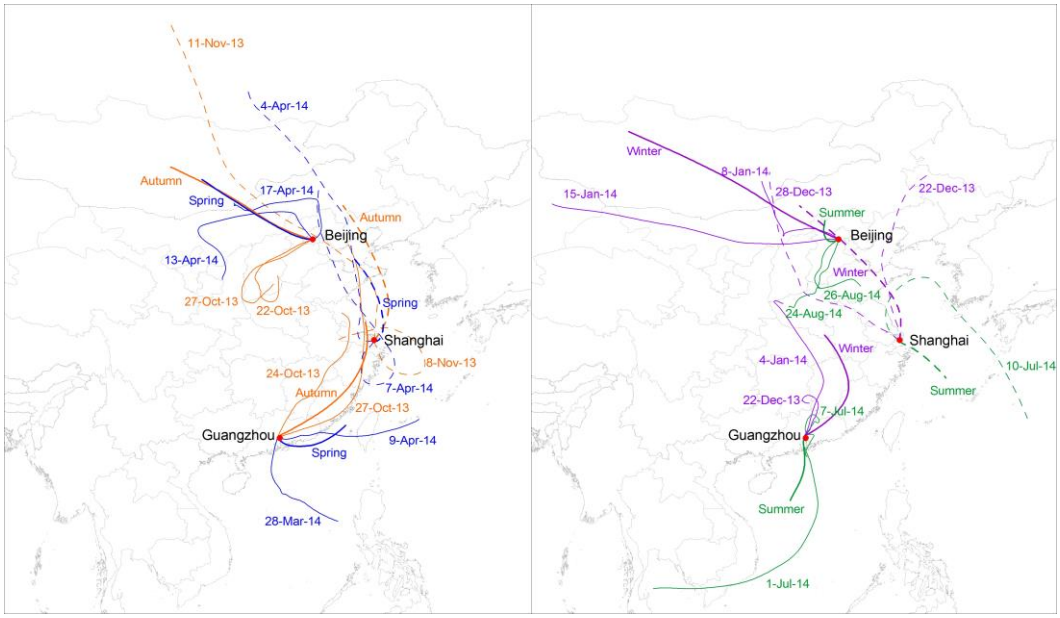

Figure 1. Air mass 3-day back trajectories at 6 h intervals for all samples are modeled at 500m above ground level by Air Resources Laboratory, National Oceanic and Atmospheric Administration (http://ready.arl.noaa.gov/HYSPLIT.php). Autumn, Winter, Spring and Summer mean the average 3-day back trajectories of all samples collected during each season.

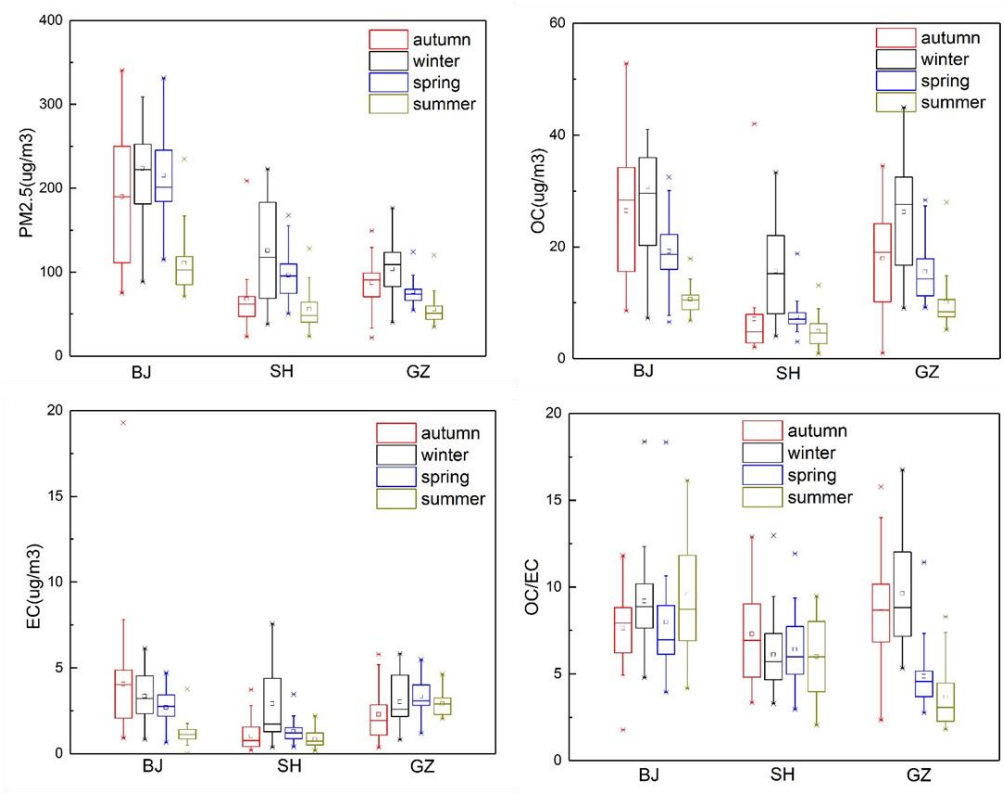

Figure 2. Box-and-whisker plots of mass concentrations of PM2.5, OC, EC and EC/OC ratios in Beijing (BJ, total 110 samples), Shanghai (SH, total 110 samples) and Guangzhou (GZ, total 105 samples) during sampling periods 2013 -2014. The box represents the 25th (lower line), 50th (middle line) and 75th (top line) percentiles values, while the end of the lower and upper vertical line represents the 10th and 90th percentile values, respectively.

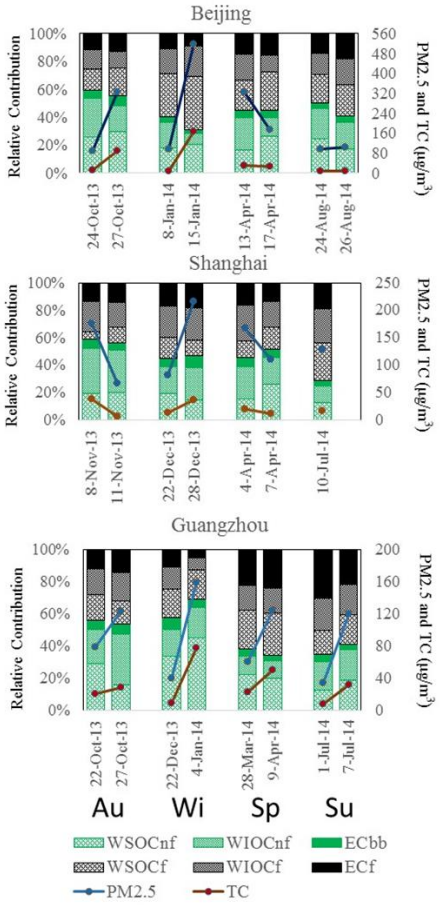

Fig. 3. The relative contributions of fossil EC (EC_f), fossil water-insoluble OC ($WIOC_f$), fossil water-soluble OC ($WSOC_f$), non-fossil EC (EC_{nf}), non-fossil water-insoluble OC ($WIOC_{nf}$), and non-fossil water-soluble OC ($WSOC_{nf}$) to total carbon (TC) and the concentrations of PM2.5 and TC in four seasons (autumn/Au, winter/Wi, spring/Sp, summer/Su) in Beijing, Shanghai and Guangzhou.

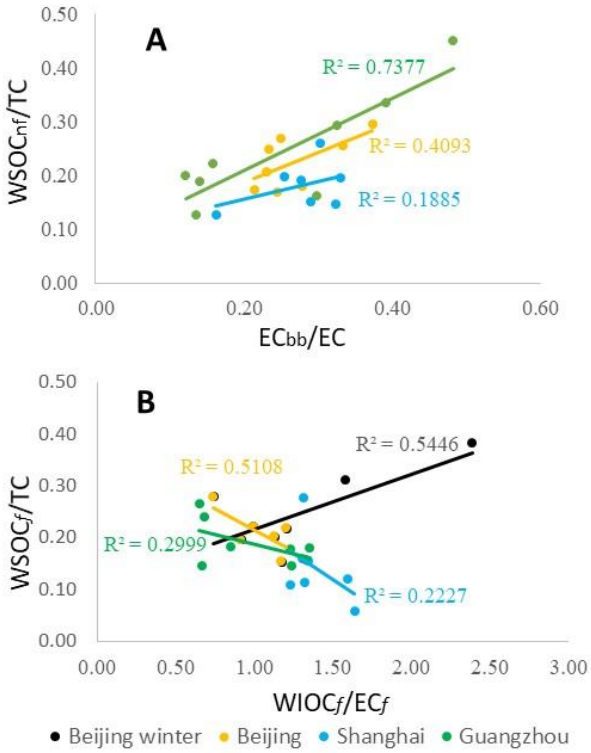

Fig. 4. Correlations of WSOC*nf*/TC vs. ECbb/EC (A), and WSOC*f*/TC vs. WIOC*f*/EC*f* (B). Beijing winter means all samples collected in Beijing; Beijing means winter samples were excluded.