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

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Abstract

Fossil fuel (FF) combustion and biomass burning are the two most important contributors to the highly polluted air in China. Given that the large territorial area of China, it is interesting to know how these two emission sources exert influences on carbonaceous particles over megacities in different regions and different seasons. Here, the radiocarbon (14C) isotopic signals are reported in Beijing, Shanghai and Guangzhou, China from 2013 to 2014. Generally, a greater contribution of non-fossil (NF) (>55%) sources were found in all cities in autumn. However, the source seasonality was different among the cities in other seasons. In winter, FF contributed the most in Beijing (64%), NF contributed the most in Guangzhou (63%), and FF contributed slightly more than NF in Shanghai (54%). In spring and summer, Beijing and Guangzhou were similar to each other with a higher contribution of FF (55% and 63%, respectively) than NF. FF had the highest contribution (71%) in Shanghai in summer. Comparison of carbon sources between haze and non-haze periods suggests that the carbon sources in each season are almost consistent. Secondary organic carbon (SOC) mainly originated from biomass burning and vehicle emissions, except in Beijing in winter when the major source was residual coal combustion.

Introduction

Fine particle ($PM_{2.5}$, aerodynamic diameters less than or equal to 2.5 μm) pollution frequently occurs at a large scale and results in the worsening of the air quality over China's megacities due to massive and intensive emissions of pollutants and unfavorable meteorological conditions. Among the aerosol pollutants, carbonaceous

aerosols, which can constitute 20-50% of aerosols in the urban atmosphere,(Cao et al., 2007;Cao et al., 2005) are of great scientific concern due to their adverse impact on air quality, visibility, climate and human health.(Highwood and Kinnersley, 2006;Mauderly and Chow, 2008;Pratsinis et al., 1984) Carbonaceous materials are operationally classified as strongly refractory and highly polymerized carbon (elemental carbon, EC) or black carbon (BC) and as weakly refractory and light polycyclic or polyacidic hydrocarbons/organic carbon (OC).(Castro et al., 1999;Pöschl, 2005) EC is exclusively of primary origin and emitted by the incomplete combustion of fossil fuels (i.e., coal and petroleum) and biomass burning (i.e., heating and woodfire). OC is a complex mixture of primary directly emitted OC particles (POC) and secondary OC (SOC) formed in situ in the atmosphere via the oxidation of gas-phase precursors. Through a recently developed method, source apportionment can be determined by measuring the radiocarbon (^{14}C) of OC and EC separately, which enables unambiguous differentiation between fossil and non-fossil sources.(Liu et al., 2013;Zong et al., 2016;Liu et al., 2016b;Liu et al., 2014;Liu et al., 2017b;Zhang et al., 2015a) This is because ^{14}C is completely disintegrated in fossil fuel sources (i.e., diesel exhaust, gasoline exhaust, and coal combustion), while non-fossil sources (i.e., biomass burning, cooking and biogenic emission) are at the contemporary radiocarbon level.(Szidat et al., 2009) Furthermore, a better understanding of carbon sources can be obtained by dividing OC into water-soluble OC and water-insoluble OC.(Liu et al., 2016b)

Beijing, Shanghai and Guangzhou are representative megacities located in different climatic regions, i.e., the Beijing-Tianjin-Hebei region, Yangtze River Delta region (YRD)

and Pearl River Delta region (PRD), that have been suffering from severe air pollution problems due to rapid industrial and transportation expansion, sharply increased demands for fossil fuel and increasing populations (Feng et al., 2015;Wei et al., 2017;Ding et al., 2017;Zhang et al., 2015a). Although source apportionments of carbonaceous aerosol have been conducted in some cities (Wei et al., 2017;Liu et al., 2014;Liu et al., 2017b;Elser et al., 2016), the results are segmented. In this study, two samples with higher and lower $PM_{2.5}$ concentrations in each season in three cities were selected for ^{14}C analysis. ^{14}C data of ambient aerosols from Beijing, Shanghai and Guangzhou are presented for the two sub-fractions of TC, OC and EC. Furthermore, OC is 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 help identify the carbon sources of aerosols in China and can support policy makers 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 in four seasons. Detailed descriptions of the sampling sites, sampling methods and protocols are given in reference (Liu et al., 2016a). 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, the 24-h integrated $PM_{2.5}$

samples were collected on pre-baked quartz-fiber filters using a high-volume sampler. In this study, we collected 110, 110 and 106 samples at Beijing, Shanghai and Guangzhou, respectively. At each sampling site and during each 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 filter samples (1.5 cm^2) were cut for analyzing organic and elemental carbon contents (OC/EC) by a thermal optical carbon analyzer (Sunset Laboratory Inc., Forest Grove, OR) with a modified NIOSH (National Institute of Occupational Safety and Health) thermal-optical transmission (TOT) protocol. Replicate samples and filter blank were conducted to determine analytical precision and background contamination. The replicate analysis of samples (n = 64) provided a good analytical precision; with relative deviation 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) as EC signal from the blank filters was undetectable. The reported OC concentrations have been subtracted for the filter blank samples.

2.3. ^{14}C Analysis of the Carbonaceous Fractions.

Radiocarbon (^{14}C) measurements in carbonaceous aerosol were used to quantitatively distinguish fossil and non-fossil sources. Two samples with relatively higher and lower $PM_{2.5}$ concentrations in each season in each city were selected for ^{14}C analysis, although only one sample was analyzed in summer in Shanghai (23 samples in total). Air mass 5-day back trajectories for all selected samples are shown in Fig. 1. The detailed method of ^{14}C measurement of different carbonaceous aerosols (i.e., TC, EC,

and water-soluble organic carbon (WSOC)) has been described elsewhere. (Zhang et al., 2012;Zhang et al., 2015a) Recently, ^{14}C measurements in aerosols collected in China were also analyzed at the University of Bern, Switzerland following this protocol.(Huang et al., 2014) In brief, ^{14}C analysis of TC was conducted at the University of Bern, Switzerland by coupling of an EA (elemental analyzer) with a MICADAS (MIni CArbon Dating System). (Szidat et al., 2014) ^{14}C analysis of EC or water-insoluble organic carbon (WIOC) was performed by coupling the MICADAS with an OC/EC analyzer (Sunset Laboratory Inc., OR, USA), where the resulting CO_2 from EC or WIOC was isolated and separated in either EC or OC step by the Swiss_4S protocol. (Agrios et al., 2015;Zhang et al., 2012) The ^{14}C analysis data results were expressed in terms of fractions of modern carbon (f_M). The f_M values of OC and WSOC were calculated by mass and isotope-mass balancing. The uncertainties of $f_{M(OC)}$, $f_{M(EC)}$, $f_{M(TC)}$ and $f_{M(WSOC)}$ were, on average, <10%, including uncertainties from ^{14}C measurements, blank correction and mass-balancing calculation.

3. Results and discussion

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

Fig. 2 shows the box-and-whisker plots for concentrations of $PM_{2.5}$, OC and EC and EC/OC ratios during the sampling campaign at the three sites. The average $PM_{2.5}$ mass concentrations at 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 $PM_{2.5}$ concentrations observed for all sites, their concentrations were generally higher in Beijing than in Shanghai and Guangzhou. This indicates a poorer air quality in north

China, which is consistent with other studies.(Cao et al., 2003;Hu et al., 2014) The average high 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 ratios of total organic matter (TOM=1.6 × OC + EC) to total fine particle mass were 20 ± 6%, 17 ± 6%, and 36 ± 8% in Beijing, Shanghai, and Guangzhou, respectively. It indicated the importance of carbonaceous aerosol in air quality, especially in Guangzhou, South China. However, carbonaceous aerosols play a different role in haze formation in each city. There are no significant correlations between the ratios of TOM/$PM_{2.5}$ and PM2.5 concentrations in Beijing and Shanghai, which implied that carbonaceous aerosols are the major component of $PM_{2.5}$ but did not play the predominant role in haze formation. Whereas in Guangzhou, the ratio of TC/$PM_{2.5}$ was positively correlated with PM2.5 concentration (R^2=0.27, $p<0.05$). This means that relative contributions of carbonaceous aerosols to total fine particles increased when the haze occurred in Guangzhou, implying the role of carbonaceous aerosols is more important in South China than those 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 at the same city during 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) and significantly higher than European urban cities like Athens, Greece (2.1 ± 1.3 μg m^{-3} and 0.54 ± 0.39 μg m^{-3}),(Paraskevopoulou et al., 2014) Elche, Spain (5.6 ± 2.8 μg m^{-3} and 1.5 ± 1.2 μg m^{-3}),(Perrone et al., 2011) other Asian urban cities like Seoul, Korea

(10.2 ± 5.5 μg m^{-3} and 4.1 ± 2.6 μg m^{-3}),(Kim et al., 2007) Yokohama, Japan (3.75 ± 1.5 μg m^{-3} and 1.94 ± 1.2 μg m^{-3}).(Khan et al., 2010)

Seasonally, the mass concentrations of $PM_{2.5}$, OC and EC were all higher in winter and lower in summer (Fig.2). During the wintertime, the high concentrations may be mainly attributed to combined and complex effects. For example, the increase emission transport of coal and biomass or biofuel combustion from local and regional scale, large secondary formation, and unfavorable metrological conditions in exacerbating the air pollution. Adversely, the low mass concentrations in summer are likely due to a significant reduction from anthropogenic source emissions (i.e. heating-related coal/biofuel), relatively high mixing layer and wet scavenging effects.

Generally, OC-EC relationship and OC/EC ratios give some indication of the origin of carbonaceous particles. Strong relationship between OC and EC might elucidate the carbonaceous particles derived from the same emission source. Lower values of the OC/EC ratio (OC/EC = 1.0-4.2) imply the sources from diesel- and gasoline-powered vehicular exhaust (Schauer et al., 2002, 1999), while higher OC/EC ratios of aerosols might source from coal combustion(Zhi et al., 2008), wood combustion (16.8-40.0) (Schauer et al., 2001), forest fires (14.5), biomass burning (7.7) (Zhang et al., 2007), and formation of SOA (Chow et al., 1993). In Beijing and Shanghai, the correlations between OC and EC (R^2 = 0.56 and 0.80, respectively) were higher than that of aerosols from Guangzhou (R^2 = 0.26). Moreover, the correlation of OC and EC and OC/EC ratios in different season in Beijing and Shanghai were almost consistent. It implied that the sources of carbonaceous aerosols in these two cities did not have drastic change and

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derived from various mixtures. In Guangzhou, higher correlations between OC and EC in autumn (R^2 = 0.71) and winter (R^2 = 0.50) and a lower correlation in spring (R^2 = 0.38) were found. However, there was no significant correlation found in summer. The average OC/EC ratios in autumn (8.6) and winter (9.6) were significantly ($p<0.01$) higher than those in spring (4.9) and summer (3.7) (Fig.2). It implied that the major sources of carbonaceous aerosols in different seasons in Guangzhou were obviously varied. The south China region is under the strong influence of anthropogenic emissions from the upwind Asian continent. The 5-days back trajectory analysis showed the seasonal variations of carbonaceous aerosol were consistent with the alteration of the winter monsoon and summer monsoon (Fig. 1). It means that the major sources of carbonaceous aerosol in autumn and winter came from inland China and from the Pearl River Delta in spring and summer. The source difference should contribute the significant seasonal difference of carbonaceous aerosols, which might be distinguished by the ^{14}C results.

3.2 ^{14}C results: fraction of modern Carbon and seasonal variation

The concentrations of different carbon species and their ratios of selected samples in 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, fossil sources annually accounted for a slightly larger contribution to TC in the three cities (average: 53±10%; range: 31-71%) than non-fossil sources (average: 47±10%; range: 29-69%), and the values in each of the three cities were similar to each other. For example, the ratio of FF:NF in Beijing, Shanghai and Guangzhou was 54:46, 53:47 and 52:48,

199 respectively. Despite the wide range of EC concentrations (Table 1), the ratios of fossil
200 EC (EC_f) to total EC in Beijing, Shanghai and Guangzhou were also comparable, with
201 averages of 73±6%, 72±6% and 74±14%, respectively, suggesting that fossil-fuel
202 combustion is the dominant contributor to EC. The high annual contribution of fossil
203 fuels to EC in the three cities was consistent with earlier reported results that used a
204 similar ^{14}C-based approach to analyze the EC in cities in China, including Beijing (i.e.,
205 79% and 82%), (Zhang et al., 2015b;Zhang et al., 2015a) Xi'an (78±3%),(Zhang et al.,
206 2015a) Shanghai (79%)(Zhang et al., 2015a) and Guangzhou (80-90%),(Liu et al., 2014)
207 and also with previous studies that have been conducted in other cities across the
208 world.(Andersson et al., 2015;Bernardoni et al., 2013;Liu et al., 2013) The average
209 contributions of fossil OC (OC_f) to OC were 50±10%, 49±9% and 45±10% in Beijing,
210 Shanghai, and Guangzhou, respectively, which were lower than the corresponding EC_f
211 contribution to EC for all samples. However, the high proportion of OC_{nf} (32%-72%)
212 also indicated that primary emissions and secondary formation from non-fossil
213 sources (i.e., biomass burning and biogenic emission) are important contributors to
214 OC in densely populated and urbanized areas of China.
215 The relative contributions of fossil and non-fossil to EC, WIOC and WSOC in each of the
216 four seasons are plotted in Fig. 3. Discrete seasonal patterns were found in the three
217 cities. Generally, the relatively higher contributions of non-fossil (54-59%) to TC were
218 found in autumn, from late October to early November. Particulate EC was
219 predominantly derived from the combustion of fossil fuels such as coal, gasoline and
220 diesel and the burning of vegetation and wood (non-fossil). In this study, the ratios of

EC that were derived primarily from biomass burning (BB) were also higher in autumn (>30%) compared to the other seasons. The 5-day back trajectory analysis revealed that air masses came from inland central China (Fig. 1). It is suggested that the burning of agricultural waste has a strong impact on air quality during this season in Beijing (Zhang et al., 2017). This result is consistent with our previous study, which indicated that NF emissions were predominant in carbonaceous aerosols in Chinese cities in this season.(Liu et al., 2017a)

During winter, the carbon source compositions of different cities were different. The percent of fossil-derived sources significantly increased in Beijing. $WIOC_f$ and EC_f were approximately 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. Beijing winter had the highest $WIOC_f/EC_f$ ratio, 2.39, in this study. This suggests that the increased emissions from fossil fuel combustion was related with the increase in coal combustion for heating purposes during the cold periods in North China (Fig. 1), which was confirmed by the aerosol mass spectrometer (AMS) measurements results performed in the same season.(Elser et al., 2016) Furthermore, based on another study, this fossil source enhancement might be attributed to residential coal combustion.(Liu et al., 2017b) In Shanghai, the contribution of fossil carbon increased approximately 11%. The $WIOC_f/EC_f$ ratio of 1.3 implied that the fossil-derived carbon sources were a mixture of coal combustion and vehicle emissions. In Guangzhou, the contribution of non-fossil sources was the highest (69%), and the ratios of EC_{BB}/EC reached 0.39 and 0.48 in the winter samples. As shown in Fig. 1, air

masses came from the north of Guangdong, Hunan and Guizhou Provinces, where a large amount of biomass, such as agricultural waste and hard wood, was burned for cooking and domestic heating during the cold and dry winter. This carbon source character is the same as the one in the regional-scale haze events reported in a previous study.(Liu et al., 2014)

In Beijing and Guangzhou, the source compositions were almost consistent in spring and summer, but the average contribution of non-fossil sources in Beijing (45±4%) was higher than that in Guangzhou (37±3%). The results of the 5-day back trajectory indicated that natural and biogenic emissions from the upwind rural and mountain area had a strong impact on the air quality of Beijing, whereas the major carbon sources in Guangzhou were from vehicle and industrial emissions in PRD. In Shanghai, the carbon source composition in spring was almost similar to that in winter, but a dramatic increase in fossil-derived carbon was observed in summer. The limited sample number in summer in Shanghai might be lead to the bias results. However, a recent study indicated that the highest number fraction of primary ship emitted particles to total particles in Shanghai urban region could reach up to 50% during the ship plume cases, and ship-plume-influenced periods usually occurred in spring and summer. (Liu et al., 2017c) The corresponding back trajectory showed that the air mass came from the East China Sea and passed through the coast of East China. In addition to pollutants from industrial and vehicle emissions, the emission contribution of fishing boat and large ship nearby to the air pollutants in Shanghai cannot be ignored. However, the carbon sources during haze and non-haze in each season were almost

consistent (Fig. 3). In addition, the air masses of haze and non-haze in each season at each site were from approximately the same direction (Fig. 1). Above all, this study demonstrates that the main sources of carbonaceous aerosols in cities varied greatly across different seasons, but the carbon sources of haze and non-haze days in each season showed little difference. Compared with previous studies, the seasonal variation in carbon sources in Beijing was similar to the variations in the submicrometer organic aerosols measured from 2013-2014 in Beijing,(Zhang et al., 2017) and variations in Shanghai and Guangzhou were consistent with the previous studies conducted in different seasons.(Liu et al., 2014;Liu et al., 2017b;Liu et al., 2016b)

3.3 Possible sources of secondary organic aerosols

Based on water solubility, OC was separated into WSOC and WIOC. EC and WIOC were approximately considered primary emissions, while WSOC was a proxy for secondary organic carbon (SOC) and biomass burning OC. (Zhang et al., 2017) In this study, WSOC accounted for 47±7%, 32±7% and 43±12% of TC and significantly positive correlated with $PM_{2.5}$ concentrations in Beijing, Shanghai and Guangzhou, respectively, which indicates the importance of SOC in megacities. Moreover, the ratios of WSOC/$PM_{2.5}$ were significantly positive correlated with $PM_{2.5}$ concentrations in Beijing (R^2=0.67, $p<0.01$) and Guangzhou (R^2=0.31, $p<0.05$), respectively, but there is no significantly correlation found in Shanghai. It is suggested that SOC is playing an important role in the haze formation in Beijing and Guangzhou.

Potential major sources of WSOC might be revealed by the plot figures. As shown in

Fig. 4A, the percent of non-fossil WSOC to TC is positively correlated with the ratio of EC_{BB}/EC. EC is exclusively of primary origin and emitted by the incomplete combustion of fossil fuels and biomass burning. The correlation indicated that the incensement of non-fossil WSOC should be contributed to the enhancements of biomass burning. In one hand, large fractions of biomass burning primary OC is water-soluble, in another hand, an increase emission of volatile organic compounds during biomass burning could lead to the incensement of non-fossil secondary organic aerosol. It suggests that BB emission has an important impact on the non-fossil SOC in China. Recently, evidence derived from a secondary organic aerosol tracer also indicated that a large nationwide increase in secondary organic aerosols during the cold period was highly associated with an increase in biomass burning emissions(Ding et al., 2017). In principle, fresh primary OC emitted from FF combustion is water-insoluble. After analyzing the differences in WSOC levels at sites with no direct influence from vehicle exhaust emissions, the previous study concluded that primary WSOC emitted directly by vehicles is very limited. (Weber et al., 2007) With regard to coal, another type of FF, only ~1% of fresh OC is water-soluble.(Park et al., 2012) Thus, primary organic carbon (POC) derived from FF combustion can reasonably be considered to be water-insoluble, and fossil WSOC is used to estimate levels of FF-derived SOC.(Weber et al., 2007) The percent of fossil WSOC to TC vs the ratio of $WIOC_f/EC_f$ is plotted in Fig. 4B. The primary sources of $WIOC_f$ and EC_f were coal combustion and emission of internal combustion engines using petroleum fuel. Generally, the $WIOC_f/EC_f$ ratio of coal combustion was higher than that of vehicle emission.(Liu et al., 2013) As shown in Fig. 4B, the

proportion of $WSOC_f$ decreased with the increase in the $WIOC_f/EC_f$ ratio in Shanghai and Guangzhou, indicating that the fossil SOC was not mainly from coal combustion sources, but rather from vehicle and ship emissions or VOCs released from industrial sources. However, this trend was different in Beijing. Excluding the winter samples, the trend in Beijing was similar to those in Shanghai and Guangzhou. However, the trend was opposite to the those in Shanghai and Guangzhou when the winter samples were included. Therefore, it is suggested that the fossil SOC in Beijing mainly came from residential coal combustion in the winter and from vehicle exhaust or industrial emissions in the other seasons.

4. Conclusion

Carbonaceous aerosols accounted for 20 ± 6%, 17 ± 6%, and 36 ± 8% of PM2.5 masses in Beijing, Shanghai, and Guangzhou, respectively. The seasonal variation of $PM_{2.5}$, OC and EC were characterized by the higher mass concentrations in winter and lower in summer. Based on ^{14}C measurements, the yearly average contribution of FF and NF to TC were almost equivalent, with FF:NF ratios of 54:46, 53:47 and 52:48 in Beijing, Shanghai and Guangzhou, respectively. FF combustion is the dominant contributor to EC (>72%), while NF contribution is a bit higher (50%-55%) than FF proportion to OC at the three sites. Generally, a greater contribution of non-fossil (>55%) sources was found in autumn in all cities. The source seasonality was different among the three cities in other seasons. In winter, FF contributed the most in Beijing (64%), NF contributed the most in Guangzhou (63%), and FF contributed slightly more than NF in Shanghai (54%). In spring and summer, Beijing and Guangzhou had similar source

compositions, with a higher contribution of FF (55% and 63%, respectively) than NF. However, FF had the highest contribution (71%) in Shanghai in summer. The carbon sources of haze and non-haze days in each season showed little difference. Secondary organic carbon (SOC) mainly originated from biomass burning and fossil oil emissions, except in winter in Beijing, when the major source was residual coal combustion.

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510 Table 1. Concentrations (μg C/m^3) of different carbon species and their ratios

511

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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514 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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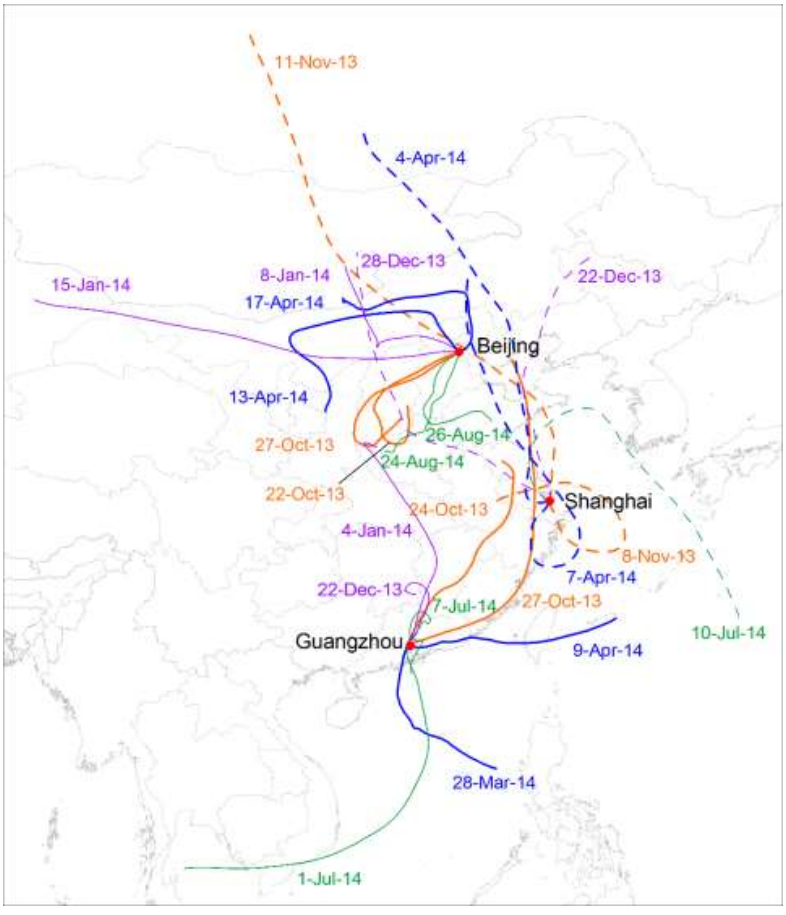

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519 Figure 1. Air mass 5-day back trajectories for all samples are modeled at 500m above

520 ground level by Air Resources Laboratory, National Oceanic and Atmospheric

521 Administration (Hybrid Single Particle Lagrangian Integrated Trajectory Model).

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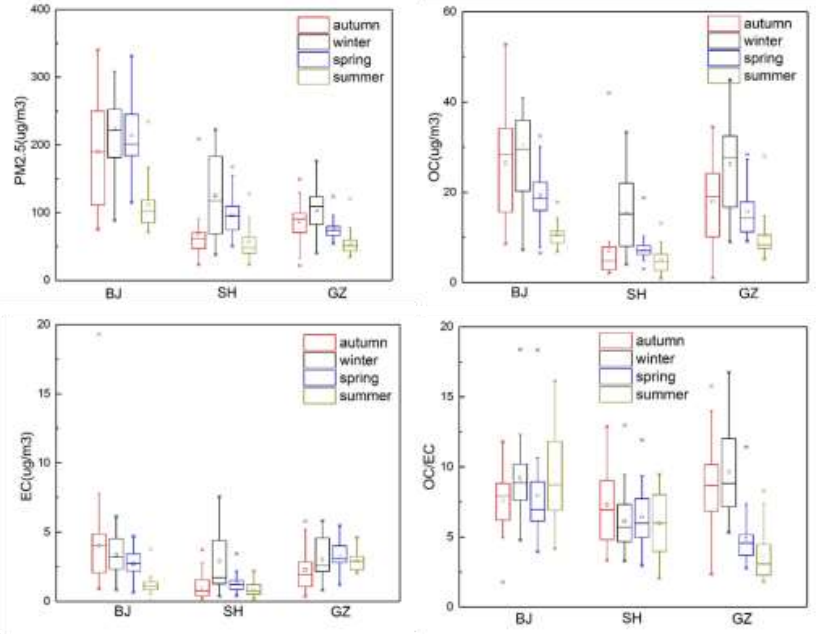

Figure 2. Box-and-whisker plots of mass concentrations of PM2.5, OC, EC and EC/OC ratios in Beijing (BJ), Shanghai (SH) and Guangzhou (GZ) during sampling periods 2013 -2014. The box represents the 25th (lower line), 50th (middle line) and 75th (top line) percentiles values, while the end of the lower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

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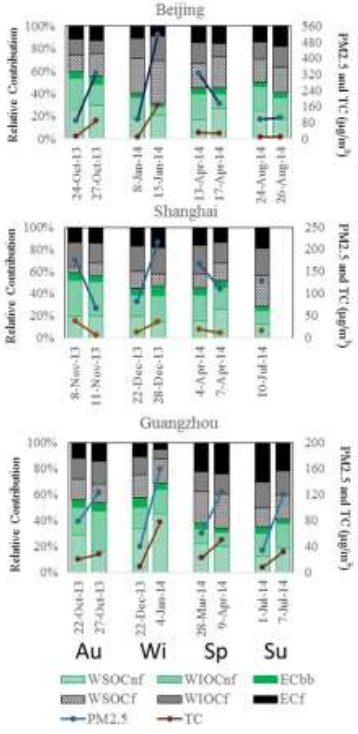

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531 Fig. 3. The relative contributions of fossil EC (EC_f), fossil water-insoluble OC ($WIOC_f$),

532 fossil water-soluble OC ($WSOC_f$), non-fossil EC (EC_{nf}), non-fossil water-insoluble OC

533 ($WIOC_{nf}$), and non-fossil water-soluble OC ($WSOC_{nf}$) to total carbon (TC) and the

534 concentrations of PM2.5 and TC in four seasons (autumn/Au, winter/Wi, spring/Sp,

535 summer/Su) in Beijing, Shanghai and Guangzhou.

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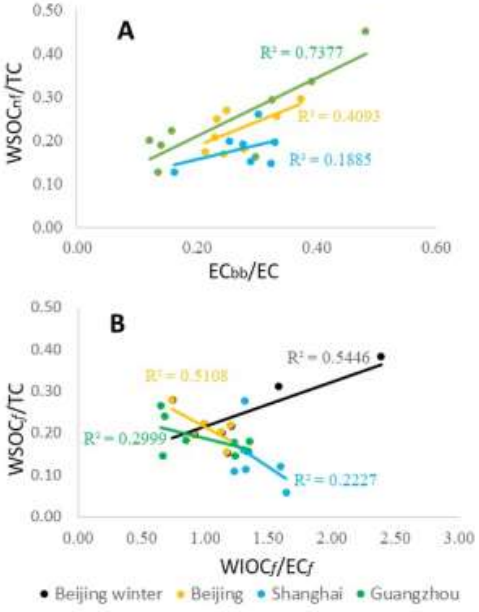

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539 Fig. 4. Correlations of WSOC*nf*/TC vs. ECbb/EC (A), and WSOC*f*/TC vs. WIOC*f*/EC*f* (B).

540 Beijing winter means all samples collected in Beijing; Beijing means winter samples

541 were excluded.

542