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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Fossil and Non-fossil Sources of Organic and Elemental Carbon Aerosols in Beijing, Shanghai and Guangzhou: Seasonal Variation of Carbon Source" *by* Di Liu et al.

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Comments from Referees Author's response Author's changes in manuscript

Comments: General comments In this work the authors collected 24-hr, PM2.5 samples in three urban centers for one month each season from October 2013 to July 2014. All samples were weighed for mass and analyzed using thermal-optical transmission for organic carbon (OC) and elemental carbon (EC). Two samples "with relatively higher and lower PM2.5 concentrations" in each season in each city were then selected for

analysis of the water soluble (WSOC) and insoluble (WIOC) organic carbon content, and these fractions were further analyzed for the radiocarbon (14C) content. Radiocarbon allows for the separation of the contributions from fossil carbon sources, e.g., coal, and biogenic carbon sources, e.g., biomass burning. The source apportionment of carbonaceous PM2.5 is an important and very challenging task. The division of the PM2.5 carbon aerosol samples into the various fractions, i.e., EC, WSOC, etc., combined with the estimation of the 14C content of each fraction, is a powerful method for assessing the contributions of major source types to the PM2.5 carbon aerosols. The authors used sound methods for filter analysis that have been used in previously pubished studies. It appears that a subset of these data or similar data have been previously published by the authors including Liu et al. (2014), EST; Liu et al. (2017a), ACP; Liu et al. (2016b) EST; and Zhang et al. (2015a), ACP, which diminishes the scientific contribution of this work. One important contribution is the examination of the variations in these carbon fractions and 14C content across the four seasons and three urban centers. However, only two 24-hr samples were analyzed in each season for each urban center. This is not enough data to assess whether the differences are due to day to day variations or represent true seasonal and urban differences. Therefore, conclusions such as "Above all, this study demonstrates that the main sources of carbonaceous aerosol in cities varied greatly across different seasons, but the carbon sources of haze and non-haze days in each season showed little difference" (see lines 266–268) are questionable. Response and RevisionsïijŽThank you for your comment. The data of this paper has not been published before. Only two samples in each city in autumn were selected for 14C analysis using two-step heating method in our lab (Liu et al, 2017, ACP), which are not same samples in this paper. The samples in this paper were analyzed for 14C using TOT methods in Switzerland. We agree to the opinions of the reviewers. This is not enough data to assess whether the differences are due to day to day variations or represent true seasonal and urban differences. Therefore, the conclusion has been changed as following: Author's changes in manuscript: Above all, this study demonstrated that the main sources of carbonaceous aerosols in cities varies

greatly among seasons. In Beijing, the seasonal variation was similar to variations in submicrometer organic aerosols measured from 2013 to 2014. (Zhang et al., 2017) Table 3 lists the 14C results from PM2.5 in three cities during 2012–2014 published in previous studies. Compared with previous studies, the seasonal variations of carbon sources in the three cities were highly consistent with previous observations conducted in different seasons.(Liu et al., 2014;Liu et al., 2017c;Liu et al., 2016;Liu et al., 2018) The carbon sources of high-PM2.5 samples and low-PM2.5 samples from each season were nearly consistent in this study (Fig. 3). Due to the limited data, these results might not reflect the true source variation over a 1-year period. For example, carbon source dynamics of carbonaceous aerosols during haze formation in Guangzhou indicated that there are significant differences in the carbon sources of high-PM2.5 samples and low-PM2.5 samples during spring and summer.(Liu et al., 2018;Liu et al., 2016) In addition, carbon sources of the high-PM2.5 samples in Guangzhou winter also differ from each other.(Liu et al., 2014) In those previous 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-PM2.5 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.

Specific Comments -Due to the number of previous publications by the authors on similar data collected at the same urban centers from 2012 to 2014, I think the introduction should contain a brief review of these results and the unique contribution of this. A table listing exactly what days were analyzed at each urban center in each publication would be valuable and aid the discussion on page 10. Response and RevisionsïijŽThank you for your suggestion. The brief review of the previous studies has been added in the introduction, and a table was also inserted. Author's changes in manuscript: 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

-Two 24-hr samples are not enough data to generate robust seasonal averages. It would be good for the authors to explore the possibility of aggregating results from this and previous studies to generate more-meaningful seasonal averages and justifiable results. Response and RevisionsïijŽThe paragraph has been changed. Author's changes in manuscript: Above all, this study demonstrated that the main sources of carbonaceous aerosols in cities varies greatly among seasons. In Beijing, the seasonal variation was similar to variations in submicrometer organic aerosols measured from 2013 to 2014. (Zhang et al., 2017) Table 3 lists the 14C results from PM2.5 in three cities during 2012–2014 published in previous studies. Compared with previous studies, the seasonal variations of carbon sources in the three cities were highly consistent with previous observations conducted in different seasons.(Liu et al., 2014;Liu et al., 2017c;Liu et al., 2016;Liu et al., 2018)

-The filter analysis methods, such as TOT, are not without issues and biases. A short discussion of the limitations and biases in all of the filter analysis methods used would aid the reader's interpretation of results. Response and RevisionsïijŽThank you for your suggestion, we have added as following. Author's changes in manuscript: 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)

-Line 101. Please provide some indication as to the importance of the OC on the filter blanks. For example, what was the fraction of OC on the blank compared to the typical

filter loading on an exposed filter? Were the filter blanks analyzed for WSOC and WIOC and the 14C fractions? If so, what were these levels relative to the exposed filters and were these data used to blank-correct the 14C data? Response and RevisionsïijŽThe description has been added. Author's changes in manuscript: 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 14C.

-Lines 136–137. "total organic matter (TOM = 1.6X OC + EC)". Note that EC is theoretically not part of TOM. I suggest this be renamed to something along the lines of total carbonaceous matter. Response and RevisionsïijŽThank you for your suggestion. TOM has been changed to TCM. Author's changes in manuscript:

-Lines 136–190. In general the manuscript was easy to understand. However, this section was poorly written, making it very difficult to understand and review. Some issues include the introduction of the terms "haze" and "haze formation" with no definition and the mixing of TOM/PM2.5 and TC/PM2.5 ratios. Is haze synonymous with PM2.5? Response and RevisionsïijŽIn this paper, we change the haze to high-PM2.5 samples, and non-haze to low-PM2.5 samples. we also changed both TOM/PM2.5 and TC/PM2.5 to TCM/PM2.5. Author's changes in manuscript:

-Lines 144–148. "Whereas in Guangzhou, the ratio of TC/PM2.5 was positively correlated with PM2.5 concentration (R2 = 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." It would seem that it is the TOM/PM2.5 ratio that defines the importance of TOM to PM2.5 (haze), not the correlation of TOM/PM2.5 to PM2.5. Response and RevisionsïijŽThank you for your suggestion, this sentence has been changed to as following: Author's changes in manuscript: On the other hand, in Guangzhou, the ratio of TCM/PM2.5 was positively correlated with the PM2.5 concentration (R2 = 0.27, p<0.05). This finding shows that the relative contributions of

carbonaceous aerosols to total fine particles increased with increasing PM2.5 concentrations in Guangzhou, implying that the role of carbonaceous aerosols in PM2.5 is greater in South China than in other parts of China.

-Lines 185–190. The conclusions drawn from Fig. 1 are not obvious and deserve some additional discussion. In addition, due to the limited number of days used in this analysis, statements such as "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" are not robust. This analysis could be done using all samples collected in each season, which would result in more-defensible conclusions Response and RevisionsïijŽThank you for your suggestion. we added the average air back trajectory of each season in Fig. 1. Author's changes in manuscript:

-Lines 215–218. As mentioned before, I question statements such as these based on the limited number of samples used in the analysis. Response and RevisionsïijŽThank you for your comments. This statement has been changed. Author's changes in manuscript:

-Line 264. "However, the carbon sources during haze and non-haze: : :" Haze and non-haze were never defined. Response and RevisionsïijŽwe change the haze to high-PM2.5 samples, and non-haze to low-PM2.5 samples.

Technical Corrections Line 60. "disintegrated" is not the proper term. Maybe use "decomposed" instead Response and RevisionsïijŽThank you for your comments. Disintegrated has been changed to decayed.

Line 162. Should "Adversely" be "Conversely"? Response and RevisionsïijŽThank you for your comments. Adversely has been changed to Conversely.

Lines 165–67. Repetitious sentences. Response and RevisionsïijŽThank you for your comments. this sentence has been changed.

Line 293. What is meant by "incensement"? Response and RevisionsïijŽThank you for

your comments. Incensement has been changed to increase.

Anonymous Referee 2 Received and published: 5 June 2018 This study compares the sources and determines the seasonal variation of carbonaceous aerosols among the three cities. The results can help to identify the carbon sources of aerosols in China. This paper is well-written and presents some the interesting data. However, more detailed explanations about the methodologies should be provide to ensure the data quality. Finally there are some technical questions that need the authors to clarify (see additional comments). Additional comments: Line 89-91: A brief introduction about the sampling instrument should be provided, e.g. brand name and model number of the hi-vol samplers; the sampling flow of the sampler etc. Response and RevisionsïijŽThank you for your comments. This description has been added. Author's changes in manuscript: 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 PM2.5 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 m3 min-1. In this study, we collected 110, 110 and 106 samples from Beijing, Shanghai and Guangzhou, respectively.

Line 106-108: Only two samples were selected in each season in each city for 14C analysis, are they good enough to represent the city? However, most of the source explanations are based on the carbon isotope data, it might lead to the bias results. Response and RevisionsïijŽThank you for your comments. Due to the expensive cost of 14C analysis, only few samples were analyzed in this study. In the revised paper, the seasonal variation was discussed combined with published data. As the response to reviewer 1, this result maybe lead to the bias results.

Line 109: The basic parameters for back trajectories analysis should be provided. Response and RevisionsïijŽThank you for your comments. The description was

added in Fig.1. Author's changes in manuscript: 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.

Line 125-190: How many samples (OCEC data) were used in this data description? Response and RevisionsïijŽThank you for your comments. Sample numbers were added in Fig. 2. Author's changes in manuscript: Beijing (BJ, total 110 samples), Shanghai (SH, total 110 samples) and Guangzhou (GZ, total 105 samples).

Line 137: If biomass burning, coal combustion and SOA formation are the major components of PM in China, I don't think 1.6 is an appropriate factor to change OC to OM. Response and RevisionsïijŽThank you for your comments. Based on the references, factors of 1.6, 1.8 and 2.0 have been using in calculation of OM. In this paper, the conservative factor of 1.6 was used to estimate the importance of carbonaceous aerosols in the haze formation. Moreover, the relationship of OM/PM2.5 and PM2.5 mass could not change when the different factor was used. So the factor of 1.6 was still used in the revised paper. Author's changes in manuscript:

Line 160-161: Any evidences can be provided that large secondary formation is one of the reasons for high concentrations of PM2.5, OC and EC in winter? Response and RevisionsïijŽThank you for your comments. I am sorry we can't provide more evidence to support this statement due to lack of other chemical components analysis and model simulation. However, many references can give the evidences. The related reference has been added in the revised paper. Author's changes in manuscript: 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)

Line 174-177; 216-247: According to the correlation results of OC and EC and OC/EC ratios in different season in Beijing and Shanghai, authors explained that the sources of carbonaceous aerosols in these two cities did not have drastic change. However, according to the results of 14C, discrete seasonal patterns were found in the three cities, e.g. “During winter, the carbon source composition of different cities were different”. How the authors interpret the conclusions from the results? Response and RevisionsïijŽThank you for your comments. I am sorry to make the reviewer misunderstand. Based on the OC/EC ratios and the correlation of OC and EC, we want to say that: the correlation between OC and EC in different seasons in Beijing and Shanghai is better, and the ratio of OC/EC is not very different in different seasons. It shows that the sources of carbonaceous aerosols in Beijing atmosphere has not changed violently in one year, and that is the same as that in Shanghai. However, there is a difference of carbon source between the two cities. This result is not in contradiction with the 14C results. We added more explications in the revised paper. Author’s changes in manuscript: 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.

Line 265-266: How the authors define haze and non-haze in this study? Which dates are hazy days in this study? Please clarify clearly. Response and RevisionsïijŽThank you for your comments. In this paper, we change the haze to high-PM2.5 samples, and non-haze to low-PM2.5 samples. Author’s changes in manuscript:

Line 277-281: Why WSOC has significant correlation with PM2.5 can indicate the importance of SOC in megacities? As WSOC is a proxy for secondary organic carbon (SOC) and biomass burning OC, biomass burning can be the dominant sources in megacities also. Response and RevisionsïijŽThank you for your comments. Based on

the references, SOC is the predominant sources of WSOC, so we added a sentence and references in the revised paper. Author’s changes in manuscript: Previous studies have indicated that SOC is the predominant component of WSOC in cities.(Huang et al., 2014;Liu et al., 2016)

Minor comments: The manuscript should be edited by a native English speaker Response and RevisionsïijŽThank you for your suggestion, parts of the paper has been edited by a native speaker before. After revised, we ask another native speaker to edit it again. The English in this document has been checked by at least two professional editors, both native speakers of English. For a certificate, please see:

http://www.textcheck.com/certificate/D5oyEM

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-295/acp-2018-295-AC1-supplement.pdf

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

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Fig. 1.