Responses to comments of anonymous referees

We would like to thank the anonymous referees for reviewing our manuscript and their useful comments and suggestions. Please find below the reviewer's comments (black) and our detailed responses (blue).

Anonymous Referee #1

This study presents 14C level in carbonaceous aerosols, and inorganic ions and anhydrosugars in $PM_{2.5}$ during the spring period of 2013 in Beijing and Guangzhou. The study concludes that both primary and secondary matter from fossil sources played a key role in the blooming phase of the pollution episode. In my opinion, several critical issues need to be addressed in this study as detailed below.

1. The chemical components of PM2.5 in both Guangzhou and Beijing have evidently seasonal variations. The sources of major aerosol chemical components are expected to be highly variable with seasons, and the causes for haze formation could also be different from season to season. For example, secondary inorganic aerosols were the dominant sources in summer while biomass burning sources were in autumn/winter in Beijing (Zhang et al., 2013; Cheng et al., 2013; Du et al., 2014). Heavy haze mostly occurred in winter instead of in spring in Beijing. Why this study picked a spring period? Will the results be applicable to other seasons? Moreover, only a few data samples are presented in this study to illustrate one aerosol pollution episode during the spring period in Guangzhou and Beijing. How is the representative of the episode case in spring for these two cities?

We appreciate the reviewer's comment. We agree with the reviewer's opinion that $PM_{2.5}$ concentrations and its emission sources would vary seasonally with the highest $PM_{2.5}$ mass concentration probably appears in winter season in some years. Given this, numerous studies have been preferentially performed to investigate the chemical, physical, and microbial characteristics of $PM_{2.5}$ particles during the winter season both in Beijing and Guangzhou (*Cao et al. 2003; Sun et al. 2006; Li et al. 2013; Zhao et al. 2013; Sun et al. 2013; Cao et al. 2014; Liu et al. 2014; Quan et al. 2014; Wang et al. 2014; Zhang et al. 2014; Zhang et al. 2015; Zheng et al. 2015*).

However, the season of winter is not the only season during when severe air pollution occur. *Zhang et al. (2013)* reported that the average $PM_{2.5}$ concentrations in Beijing were 126 (39-355) $\mu g/m^3$, 138 (41-226) $\mu g/m^3$, 135 (45-251) $\mu g/m^3$, and 139 (48-355) $\mu g/m^3$, for spring, summer, autumn, and winter, respectively. Based on the results from this study, it is easily to find that $PM_{2.5}$ concentration in spring is practically the same with winter during the year of 2009-2010. In our study, the average $PM_{2.5}$ concentration in Beijing during the 2013 spring was 218 $\mu g/m^3$, which is 1.4-fold higher the winter

of 2013 (*Huang et al. 2014*) and is 8.7-fold higher health threshold (25 μg/m^3) suggested by World Health Organization (WHO). In Guangzhou, the average $PM_{2.5}$ concentration during 2013 spring is 90.6 μg/m^3, which is 1.3-fold higher the winter of 2013 (*Huang et al. 2014*) and 3.6-fold higher the WHO health threshold. Thus, in addition to winter season, more detailed studies ae urgently needed to explore the origins and formations of $PM_{2.5}$ in spring.

Furthermore, few studies regarding radiocarbon measurements nowadays were performed in Chinese cities, and most of them mainly focused on winter season. In an early study, for example, *Huang et al. (2014)* and *Zhang et al. (2015)* have already presented the radiocarbon levels of organic carbon (OC) and elemental carbon (EC) in the winter season of Beijing and Guangzhou. According to the results of *Zhang et al. (2015)*, ~50-60% of OC and 70-77% of EC were derived from the fossil-fuel related sources. These results are impacted severely by the coal combustion in Beijing due to the central heating in winter season. In spring, our results showed that 41% of OC and 67% of EC on average came from the fossil sources in Beijing, which is lower than that in winter (*Zhang et al. 2015*), evidently implying the more impacts from biomass-burning smokes on Beijing during the spring season. In addition, we further explore the radiocarbon levels of water-soluble OC and water-insoluble OC, respectively, and we found that the radiocarbon signals of water-soluble OC is significantly different from water-insoluble OC in both cities. In other words, some critical information would be lost if atmospheric scientists only analyze the radiocarbon level of OC. We also combined the measurements of biomass-burning organic tracers with an aim of studying the contributions of fossil and non-fossil sources to the secondary organic carbon (SOC).

In this study, we collected 35 $PM_{2.5}$ samples in total (21 in Beijing and 14 in Guangzhou, respectively). The sum of selected samples for radiocarbon measurements were 9 and the total radiocarbon data were 45 including OC, water-soluble OC, water-insoluble OC, EC, and total carbon. We didn't measure the radiocarbon levels of all samples we collected as the cost for radiocarbon measurements is really expensive. In fact, the radiocarbon data we presented in this study are comparable to previous and recent studies, such as *Szidat et al. (2006)* (24 data, 1 site for 1 season), *Liu et al. (2013a)* (14 data, 1 site for 1-year), *Zhang et al. (2015)* (48 data, 4 cities for 1 season), *Zong et al (2015)* (8 data, 1 site for 1 season), and *Andersson et al. (2015)* (20 data, 3 cities for 1 season). Given that radiocarbon is the most powerful tracer at present for determining the fossil and non-fossil sources and we have analyzed the radiocarbon levels of different carbon fraction of $PM_{2.5}$ samples from low to high concentrations in both cities, we think that our dataset presented in the manuscript could represent the season we studied. In addition, although this study is performed in the spring season only, the results presented in this manuscript can provide an important implication and

inspiration to the future studies regarding $PM_{2.5}$ carbonaceous aerosols and the method used in this study probably can be employed in other regions and seasons in the world in the future in order to get a better understanding of the air pollution.

2. While haze is mainly caused by aerosol pollution, they are two different definitions and should not be used interchangeably. Besides PM level, relative humidity is another key factor for haze formation. This work does not provide any information on aerosol optical properties and meteorological parameters. It only presents aerosol pollution episodes in Beijing and Guangzhou, rather than haze processes. Moreover, inorganic and organic particulate matters have different mass scattering efficiencies, it is inappropriate to conclude haze is predominantly driven by organic matter and nitrate only based on mass concentrations. The focus of the study may need to be modified based on available data and analysis conducted in the study.

Thanks for the comment. We agree that both PM level and relative humidity are key factors influencing the formation of haze pollution (atmospheric visibility < 10 km). Please see Fig. r1 below. $PM_{2.5}$ level is the most key indicator of the haze for a given range of relative humidity. In this study, the relative humidity of those selected samples for radiocarbon measurements were in the range of 20-60% in Beijing, under which the curve line in Fig. r1 is very close, implying that relative humidity played a limited role on the haze and the haze formation is practically controlled by the $PM_{2.5}$ level. As for Guangzhou samples, the relative humidity ranged from 70% to 90%, under which both humidity and $PM_{2.5}$ exert impacts on haze formation (Fig. r1). However, all these samples we selected in Guangzhou have a $PM_{2.5}$ concentration higher than 60 $\mu g/m^3$ when the humidity play a limited role on the haze formation. Thus, we think that it is reasonable to use $PM_{2.5}$ as an indicator to tracer the haze formation in this study.

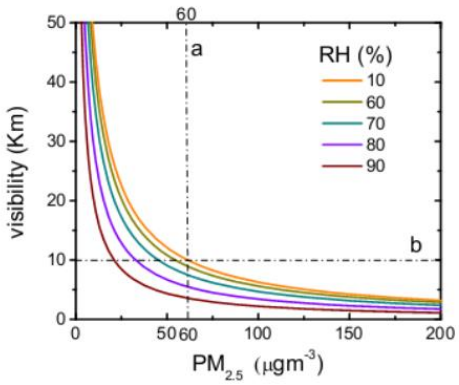

Fig. r1. A plot of atmospheric visibility versus $PM_{2.5}$ concentration at different relative humidity (*Liu et al. 2013b*)

In addition, we have presented aerosol optical depth (AOD) and meteorological

parameters in Supporting Information. Please see Fig. S1 and Fig. S2. In the 3.3 section of manuscript, we have discussed the role of relative humidity in the formation of secondary organic carbon. In this sampling campaign, we fortunately observed a dynamic process of haze formation in Guangzhou. Please see Fig. S4 and the 3.4 section of manuscript. Thus, in the Introduction section of manuscript, we said "the source dynamics of individual primary and secondary aerosols during the haze bloom-decay process in Guangzhou basing day-to-day time serials and Beijing basing low-to-high $PM_{2.5}$ concentrations were investigated as well". We agree that inorganic and organic particulate matters have different mass scattering efficiencies, while the dataset presented in this study mainly focused on the analysis of radiocarbon, organic tracers, and ions. For the haze formation process in Guangzhou, we did find that fossil-derived secondary organic matter and nitrate made a largest impact on the $PM_{2.5}$ concentrations. We seriously considered this reviewer's comments and we still think that our statements on the roles of organic matter and nitrate is reasonable in this study.

3. Page 34959, line 20. The OM is the biggest contributor to PM2.5 in Beijing and Guangzhou. However, 41~49% fraction of PM2.5 were unidentified. Such a large percentage of unknown mass fractions of PM2.5 make people wonder if the conclusions are valid. The authors are suggested to reconstruct the PM2.5 mass based on daily data. The OM conversion factors are 2.1 and 1.3 to WSOC and WSIC, respectively. However, these conversion factors are obtained from a rural site in Hungary from January to September 2000 (Kiss et al., 2002). These factors may not be suitable for application in the urban area of Beijing and Guangzhou.

Thanks for the comment. In this study, 49% and 41% of $PM_{2.5}$ in Beijing and Guangzhou were not unidentified basing on the measurement of organic carbon (OC), elemental carbon (EC), and 8 water-soluble ions, respectively. The percentage of unidentified fraction in $PM_{2.5}$ largely depends on the numbers of measured chemicals and the errors of analytical methods (*Andrews et al. 2000*). In Taiwan, ~35-40% of $PM_{2.5}$ can't be identified basing on the measurement of 10 elements, 8 water-soluble ions, OC and EC (*Chen et al. 2001*). In a recent study, after measuring the elementals, OC, EC, and water-soluble ions, *Huang et al. (2014)* found that the percentages of unidentified fraction of $PM_{2.5}$ in China were in the range of 10-36%. Relatively higher proportion of unidentified fraction in $PM_{2.5}$ probably because we didn't analyze the elementals in this study. We have made corresponding explanation in the revised manuscript.

Few studies associated with the conversion factors of WSOC and WIOC are performed simultaneously in China. While, the conversion factors used in this study are comparable to those previous studies conducted in both urban and rural sites. For example, 1.3 was employed to estimate WIOM in 3 urban and 1 rural sites in United

States (*Sun et al. 2011*). *Favez et al. (2009)* used 1.4 and 2.1 as the conversion factors for WIOC and WSOC in Paris, respectively. In Beijing, 2.1 was also used as a conversion factor to calculate the WSOM (*Chen et al. 2014*). Thus, it should be reasonable to employ 1.3 and 2.1 to calculate the WIOM and WSOM in this study, respectively. We have added these references in the revised manuscript.

4. Page 34959, the authors are suggested to provide direct evidences that the higher calcium concentration in Beijing is related with dust storm during the sampling period, as it could also come from road or/and construction fugitive dust.

Thanks for the comment. This suggestion has been employed in the revised manuscript.

5. Page 34964-34965. The growth of carbonaceous aerosols and nitrate also related to the combined influence of boundary layer height, humidity, chemical reaction and their thermodynamic properties. It would be better to provide more convincing evidence to show the growth is more related to the sources rather than the meteorological factors.

Thanks for the comment. We agree with the reviewer's point that many factors would exert impacts on the growth of carbonaceous aerosols and water-soluble ions. While, for a given city during one season, the metrological parameters would not change significantly with the exception of some special events. In the manuscript, we gave an implication that different humilities between Beijing and Guangzhou would result in their different SOC composition. In the section 3.4 of manuscript, we firstly discussed an integrated haze process in Guangzhou and a trend of low-to-high $PM_{2.5}$ in Beijing using a combined measurement of radiocarbon, organic tracers, and water-soluble ions. We also explore the potential impacts of air masses on the growths of chemical species in this section. For example, C/C_o values would change significantly when the air masses reaching Guangzhou from south region. A more detailed discussion regarding all metrological parameters, thermodynamic properties, and chemical reactions needs a modeling work which is beyond the scope of this study.

Anonymous Referee #3

This study showed the measurements of radiocarbon, anhydrosugars, and water-soluble ions in PM2.5 collected in Guangzhou and Beijing, China. The authors found that non-fossil fuel sources make a large contribution to the total carbonaceous aerosols in Chinese megacities. The authors believed that both primary and secondary species are important to the haze formation in Chinese cities. As for me, the results presented in this paper are interesting and will expand our understanding of bad air pollution. This study has a clear logic writing and completely within the scope of ACP. Therefore, I recommend its publication after the following issues are addressed.

Comments:

1. My main concern is the limited period of sampling: only about 12 samples in each site without considering the different seasons or period of years that could influence the CAs emissions and sources. More information about the experiment should be presented in the text, such as reproducibility of the experiment result.

Thanks for the comment. As for the sample numbers and the sampling season, please see our responses above (Line 63-80). In the revised manuscript, we have added the reproducibility of the measurements of WIOC, EC, WSOC, and the water-soluble ions.

2. Please add the corresponding literature to support Lev/Gal/Man is the biomass burning-specific organic tracers. Line 213: 24-hour or annual standard?

Thanks for the comment. The literature and standard has been shown in manuscript.

3. Line 245: "the EC" → "EC". In addition, I agree with you that EC suspending over urban areas are dominated by fossil-fuel combustion. What about rural region or remote areas? Does any study focused on this? I think it would be better for readers to understand this paper if the authors can cite same papers conducted in rural/remote. Readers can get a direct comparison results for radiocarbon levels in mind.

Thanks for the comment. In the manuscript, "the EC" has been replaced by "EC" and the new study regarding remote areas has been added.

4. Line 281: POC during atmospheric transportation may experience aging processes. I suggest the authors adding "gas" before "reactions".

Thanks for the comment. This suggestion has been accepted.

5. Page 34955, Line 23: Both ambient OC and EC can be produced by the combustion activities such as coal and biofuel. I am curious why their conversion factors are slightly different. Specifically, the conversion factors mentioned in this study are 1.10 and 1.06 for EC and OC, respectively. The authors should clarify this.

We would like to thank the reviewer for this comment. Atmospheric non-fossil OC is derived from biomass burning and primary biogenic emissions (solid and gas phases) while non-fossil EC only come from biomass burning. Conversion factor for biogenic emissions was obtained from the $^{14}CO_2$ level in the background locations during sampling time. However, tree age need to be considered for the conversion factor of biomass burning derived OC and EC because atmospheric $^{14}CO_2$ level are changing every year due to the nuclear bomb effect in the early of 1960s. That is why small difference exists between the conversion factors of EC and OC. We have simply mentioned this in the section of 2.3.

6. Page 34958, Line 5 – 9: To my knowledge, the ratio of biomass burning OC to

levoglucosan is highly unstable in different emission sources. One of the most possibly most important reasons, in my opinion, is the various biomass types. In particular, Guangzhou is in south China while Beijing is in north China. How the author get the corresponding ratios to calculate the primary biomass-burning OC?

Thanks for the comment. Levoglucosan (Lev) and its isomers, i.e., galactosan (Gal), and mannosan (Mann), are excellent organic tracers of biomass-burning smoke. We agree that the ratio of OC/Lev in biomass-burning smoke is largely depending on biomass types. The burnings of different biomass types would result in different ratios of Lev/Mann, Mann/Gal, and OC/Lev (*Liu et al. 2014*). Thus, in this study, we simultaneously analyzed Lev, Gal, and Mann in Guangzhou and Beijing to constrain the value of OC/Lev. Then, we found that the biomass types for burning in Beijing is different from that in Guangzhou and we got their different OC/Lev values.

References:

Andersson, A., Deng, J., Du, K., Zheng, M., Yan, C., Sköld, M. and Gustafsson, O., 2015. Regionally-varying combustion sources of the January 2013 severe haze events over eastern China. Environmental Science & Technology, 49(4), pp.2038-2043.

Andrews, E., Saxena, P., Musarra, S., Hildemann, L.M., Koutrakis, P., McMurry, P., Olmez, I. and White, W.H., 2000. Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a review of the closure between chemical and gravimetric measurements. Journal of the Air & Waste Management Association, 50(5), pp.648-664.

Cao, C., Jiang, W., Wang, B., Fang, J., Lang, J., Tian, G., Jiang, J. and Zhu, T.F., 2014. Inhalable microorganisms in Beijing's PM2.5 and PM10 pollutants during a severe smog event. Environmental Science & Technology, 48(3), pp.1499-1507.

Cao, J.J., Lee, S.C., Ho, K.F., Zhang, X.Y., Zou, S.C., Fung, K., Chow, J.C. and Watson, J.G., 2003. Characteristics of carbonaceous aerosol in Pearl River Delta Region, China during 2001 winter period. Atmospheric Environment, 37(11), pp.1451-1460.

Chen, J., Qiu, S., Shang, J., Wilfrid, O.M., Liu, X., Tian, H. and Boman, J., 2014. Impact of relative humidity and water soluble constituents of PM2.5 on visibility impairment in Beijing, China. Aerosol and Air Quality Research, 14, pp.260-268.

Chen, K.S., Lin, C.F. and Chou, Y.M., 2001. Determination of source contributions to ambient PM2.5 in Kaohsiung, Taiwan, using a receptor model. Journal of the Air & Waste Management Association, 51(4), pp.489-498.

Favez, O., Cachier, H., Sciare, J., Sarda-Estève, R. and Martinon, L., 2009. Evidence for a significant contribution of wood burning aerosols to PM 2.5 during the winter season in Paris, France. Atmospheric Environment, 43(22), pp.3640-3644.

Huang, R.J., Zhang, Y., Bozzetti, C., Ho, K.F., Cao, J.J., Han, Y., Daellenbach, K.R.,

Slowik, J.G., Platt, S.M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S.M., Bruns, E.A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., and Haddad, I.E., 2014. High secondary aerosol contribution to particulate pollution during haze events in China. Nature, 514(7521), pp.218-222.

Li, Z., Gu, X., Wang, L., Li, D., Xie, Y., Li, K., Dubovik, O., Schuster, G., Goloub, P., Zhang, Y. and Li, L., 2013. Aerosol physical and chemical properties retrieved from ground-based remote sensing measurements during heavy haze days in Beijing winter. Atmospheric Chemistry and Physics, 13(20), pp.10171-10183.

Liu, D., Li, J., Zhang, Y., Xu, Y., Liu, X., Ding, P., Shen, C., Chen, Y., Tian, C. and Zhang, G., 2013a. The use of levoglucosan and radiocarbon for source apportionment of PM2.5 carbonaceous aerosols at a background site in East China. Environmental Science & Technology, 47(18), pp.10454-10461.

Liu, X.G., Li, J., Qu, Y., Han, T., Hou, L., Gu, J., Chen, C., Yang, Y., Liu, X., Yang, T. and Zhang, Y., 2013b. Formation and evolution mechanism of regional haze: a case study in the megacity Beijing, China. Atmospheric Chemistry Physics, 13(9), pp.4501-4514.

Liu, J., Li, J., Zhang, Y., Liu, D., Ding, P., Shen, C., Shen, K., He, Q., Ding, X., Wang, X. and Chen, D., 2014. Source apportionment using radiocarbon and organic tracers for PM2. 5 carbonaceous aerosols in Guangzhou, South China: contrasting local-and regional-scale haze events. Environmental Science & Technology, 48(20), pp.12002-12011.

Quan, J., Tie, X., Zhang, Q., Liu, Q., Li, X., Gao, Y. and Zhao, D., 2014. Characteristics of heavy aerosol pollution during the 2012–2013 winter in Beijing, China. Atmospheric Environment, 88, pp.83-89.

Wang, Y., Yao, L., Wang, L., Liu, Z., Ji, D., Tang, G., Zhang, J., Sun, Y., Hu, B. and Xin, J., 2014. Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China. Science China Earth Sciences, 57(1), pp.14-25.

Sun, Y., Zhuang, G., Tang, A., Wang, Y. and An, Z., 2006. Chemical characteristics of PM2.5 and PM10 in haze-fog episodes in Beijing. Environmental Science & Technology, 40(10), pp.3148-3155.

Sun, Y.L., Wang, Z.F., Fu, P.Q., Yang, T., Jiang, Q., Dong, H.B., Li, J. and Jia, J.J., 2013. Aerosol composition, sources and processes during wintertime in Beijing, China. Atmospheric Chemistry and Physics, 13(9), pp.4577-4592.

Sun, Y., Zhang, Q., Zheng, M., Ding, X., Edgerton, E.S. and Wang, X., 2011. Characterization and source apportionment of water-soluble organic matter in atmospheric fine particles (PM2.5) with high-resolution aerosol mass spectrometry and GC–MS. Environmental Science & Technology, 45(11), pp.4854-4861.

Szidat, S., Prévôt, A.S., Sandradewi, J., Alfarra, M.R., Synal, H.A., Wacker, L. and Baltensperger, U., 2007. Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter. Geophysical Research Letters, 34(5), pp.L05820

Zhao, X.J., Zhao, P.S., Xu, J., Meng, W., Pu, W.W., Dong, F., He, D. and Shi, Q.F., 2013. Analysis of a winter regional haze event and its formation mechanism in the North China Plain. Atmospheric Chemistry and Physics, 13(11), pp.5685-5696.

Zhang, J.K., Sun, Y., Liu, Z.R., Ji, D.S., Hu, B., Liu, Q. and Wang, Y.S., 2014. Characterization of submicron aerosols during a month of serious pollution in Beijing, 2013. Atmospheric Chemistry and Physics, 14(6), pp.2887-2903.

Zhang, Y.L., Huang, R.J., El Haddad, I., Ho, K.F., Cao, J.J., Han, Y., Zotter, P., Bozzetti, C., Daellenbach, K.R., Canonaco, F., Slowik, J.G., Salazar, G., Schwikowski, M., Schnelle-Kreis, J., Abbaszade, G. Zimmermann, R., Baltensperger, U. Prévôt, A.S.H., and Szidat, S., 2015. Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode of 2013. Atmospheric Chemistry and Physics, 15(3), pp.1299-1312.

Zhang, R., Jing, J., Tao, J., Hsu, S.-C., Wang, G., Cao, J., Lee, C.S.L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z., 2013. Chemical characterization and source apportionment of $PM_{2.5}$ in Beijing: Seasonal perspective. Atmospheric Chemistry and Physics, 13(14), pp.7053-7074.

Zheng, G.J., Duan, F.K., Su, H., Ma, Y.L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D. and Pöschl, U., 2015. Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions. Atmospheric Chemistry and Physics, 15(6), pp.2969-2983.

Zong, Z., Chen, Y., Tian, C., Fang, Y., Wang, X., Huang, G., Zhang, F., Li, J. and Zhang, G., 2015. Radiocarbon-based impact assessment of open biomass burning on regional carbonaceous aerosols in North China. Science of The Total Environment, 518, pp.1-7.