**Responses to Reviewer's Comments to**

Zhang et al., *"Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode in 2013"*

We thank the reviewers for their comments on our paper. To guide the review process we have copied the reviewer comments in black color font. Our responses are in blue font. We have responded to all the referee comments and done the modifications accordingly.

Anonymous Referee #1

General comments:

This manuscript describes radiocarbon source apportionment of organic aerosols during winter-time smog episodes in China. Air quality is a big concern in Chinese cities and especially the sources and formation mechanisms of organic aerosol are still un-certain. Using radiocarbon for source apportionment of organic aerosols is a very useful method, because, unlike tracer ratios, the 14C signature of the sources is not changed by chemical transformations in the atmosphere.

The methods and results are described clearly. The results are very relevant, showing that winter haze episodes do not necessarily result from an increase of specific fossil or non-fossil sources, but from an accumulation of pollutants accompanied by strong formation of secondary organic aerosol.

Given these results, the manuscript could be made significantly stronger, if the authors would additionally investigate meteorological conditions and air mass histories and their potential role in the pollution episodes. If the conditions could be identified that favor the accumulation of pollutant and secondary organic aerosol formation, this would give important insight into the pollution episodes.

However, the presented results are sufficiently interesting and important to be published and therefore I recommend acceptance with minor revisions, detailed below.

Reply: We thank the reviewer for the nice summary of our paper and the positive comments. In the following we will respond to each comment listed below separately. The primary objective is to study fossil versus non-fossil contribution to both the OC and EC during the moderately polluted days and heavily polluted days. As a result, we did not include intensive discussion on how meteorological conditions affect PM and SOA formation in current study. Actually, this kind of studies has already been reported in several other studies (Wehner et al., 2008; Zhang et al., 2014). In the revised MS, we add following sentence in Sec 3.1: "The higher PM2.5 mass, OC and EC observed during the polluted period was characterized by low wind speed but not significantly sensitive by the temperature and relative humidity." Concerning air mass back trajectory, we did not find any significant dependence between PM2.5 (OC, EC) and air mass

origins (see the response and Figure R2 below). Therefore, we decided not include air mass back trajectory analysis in this study.

Specific comments:

p26264, line 10ff: Is the uncertainty for fm(OC) based on the reproducibility of the sunset OC/EC measurements and the uncertainties of the fraction modern? If, yes, please state so explicitly. In principle the uncertainty of EC-OC determination is much larger than the reproducibility derived from using one particular protocol. Inter-laboratory comparisons using different protocols for EC-OC determination show much larger uncertainties, on the order of 30% for EC. Please discuss this and estimate a resulting uncertainty for fm(OC).

Reply: the uncertainty for fm(OC) (8%) was obtained from an error propagation and include all the individual uncertainties of the fM(TC) (2%), fM(EC) (5%), TC (8%)and EC (25%). The sentence is changed as "The uncertainty of $f_M$(OC) estimated by this approach is on average 8% obtained from an error propagation and include all the individual uncertainties of the $f_M$(TC) (2%), $f_M$(EC) (5%), TC (8%) and EC (25%)." We would also like to emphasize that the variability of EC concentrations between different protocols is substantially reduced, if water-extracted filters are used (see Zhang et al., 2012 in MS).

p26272, line 7: What are the uncertainties given here (standard deviation, standard error of the mean, propagated experimental uncertainties)?

Reply: it is standard deviation. The sentence is changed as "OCf contributions (mean± standard deviation) to total OC were 37 ±3 %…"

p26272, line 11: You mean the variability between different cities? Because within each city the fraction of OCf in OC still seems relatively constant

Reply: yes. The sentence is changed as "The large variability of the fraction of OCf to total OC among the different cities…"

p26273, line 11: Please give a reference for the lev-to-K ratio in hardwood burning.

Reply: the reference is now added.

p26273, line 25: Please note that in the corresponding figure, OCother,nf is called OCbio

Reply: the figure is now changed.

p26273, line 27ff: In this sentence it is already assumed that OCother,nf is mainly secondary aerosol. This is discussed in more detail later. Please state this more clearly here, or maybe already on page 26267, line 5ff.

Reply: The sentences are changed as "Despite a large spread of $OC_{sec,f}$ and $OC_{other,\ nf}$, the data conclusively shows that both contributions were always larger on the heavily than on the moderately polluted days, highlighting the importance of fossil-derived SOC formation and other non-fossil emissions excluding primary biomass burning sources. The increased $OC_{other,nf}$ is likely

due to enhanced SOC formation from biomass burning and other non-fossil sources (see Sec. 3.3)."

p26274, line 22ff: Here you state very generally that SOC from non-fossil sources is mainly from biomass burning. However, this need not necessarily be true for SH and GZ, where temperatures during this time period are well above 0 degrees.

Reply: yes, the biogenic SOC could not be excluded for SH and GZ. The sentence is changed as "The dominating contribution of $OC_{other, nf}$ is likely due to the increase of SOC formation from non-fossil sources mainly from biomass-burning emissions, although biogenic-derived SOC could not be excluded for SH and GZ where temperatures during the sampling period are above 0 degrees. "

p26275, line 9: Do you mean here the fossil contribution to primary aerosol?

Reply: "fossil contribution" here means "fossil contribution to TC" which is now clarified.

P26276, line 10: Given that Huang et al., 2014 reached similar conclusions for total PM2.5, I think comparing the results and conclusions between these two studies, should go further than just comparison of the source apportionment methods. Please compare the results of this study to Huang et al., 2014 in more detail.

Reply: the primary objective of our study is to investigate sources and formation mechanisms of fine carbonaceous aerosols. The comparison between this study and Huang et al., 2014 is to evaluate the LHS model performance used in this study (see Sec2.5). We believe that both studies have already given sufficient but different information, so further comparison between 2 studies is not necessary.

P26276, line 25: A slope of 1.13 is usually not called a 13% offset. More often, the intercept of the regression line is called 'offset'. In general, it is better not to force the regression line through 0, because the intercept also contains information. Please change this.

Reply: The term "offset" was changed to "deviation" in the text. As the intercept is statistically insignificant (see below in Fig. R1), we remained the figure as it was and added the sentence to the caption: "Note that the intercepts are insignificant for all three cases."

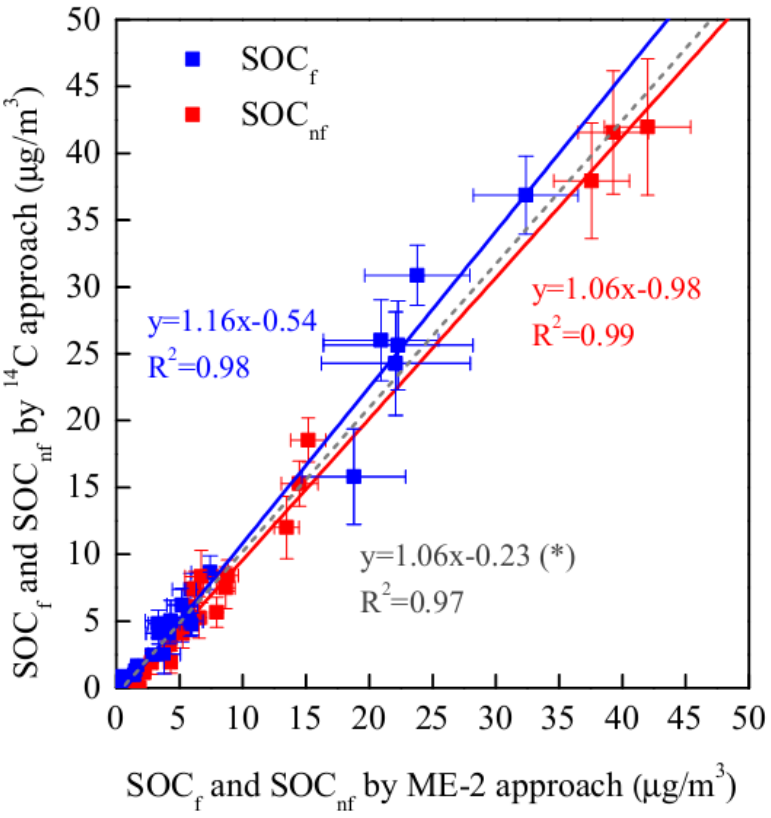


Figure R1: Figure 7 with intercepts for the three cases. All of which are statistically insignificant so that we omit to show them in the manuscript.

Figure 5: The labeling in this Figure is much too small. I had to use 400% magnification to read the subscripts. Maybe using on general legend for all the figures (e.g. on the top) would be a solution:

Reply: the figure is now changed according to the reviewer's comment.

Anonymous Referee #2

This paper describes a source apportionment of the carbonaceous component of 24h samples of PM2.5 collected in four major cities in China in January 2013, when total PM2.5 concentrations reached very high levels (up to 100s g m-3). The source apportionment is principally based on the proportion fossil/non-fossil carbon in the TC, and in the OC and EC fractions, as determined from accelerator mass spectrometry (AMS) measurements of the amount of the radiocarbon isotope, 14C, in the carbon. These data were supplemented by measurements of the levoglucosan, mannosan and water-soluble K+ concentrations in the PM2.5 which provide additional information for the source apportionment of biomass burning.

Both the analytical and data-interpretation methodologies for this study follow very closely that of a number of previous studies, particularly in Europe, undertaking similar source apportionment

of the carbonaceous aerosol. This has the advantage of use of methodology that has already been through the peer-reviewed literature. The novelty here is its application to PM2.5 samples in very large Chinese cities that have experienced PM2.5 levels up to an order of magnitude greater than in many European urban locations. Poor air quality in China is clearly a major cause for concern and it is important for all, particularly policy-makers, to have insight into the constituent components and sources of the PM2.5.

Key results from this study include the finding of substantial non-fossil contribution to OC (in common with similar studies globally) and the inference that a substantial fraction of this non-fossil OC is primary rather than secondary in nature. The authors also compared their source apportionments between the most heavily-polluted days and moderately polluted days and noted that despite the increase in absolute masses the proportion of secondary was even slightly higher.

The paper describes thorough experimental procedures and appropriate data analysis methodologies. The writing is generally fluent, although occasional grammar and comma punctuation usage requires amendments. I have a couple of points regarding scientific interpretation, and the remaining points are largely concerned with presentation. I recommend this paper as suitable for publication in ACP following attention to these issues and any other relevant issues raised by other reviewers.

Reply: we thank the reviewer for the nice summary of our paper and the positive comments. In the following we will respond to each comment listed below separately.

(1) The authors could likely gain some greater insight into the origin of their various carbon fractions by undertaking an air-mass back-trajectory investigation for the days of their samples, particularly through a comparison of the high-pollution vs. moderate-pollution days.

Reply: the carbon faction is not dependent on air mass origins. The air mass back trajectory analysis (see Figure R2 below) shows the prevailing air masses are generally from the north during our measurement period which has already been reported by Huang et al. (2014). As a result, it is not included in the current study.

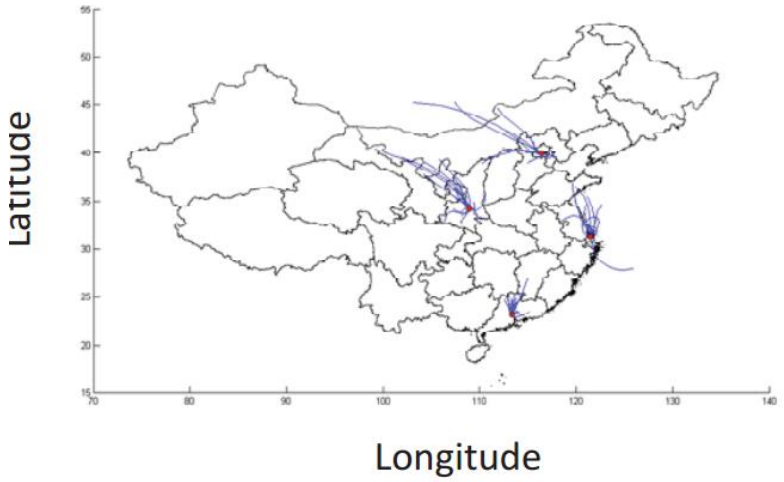

Figure R2: Air mass back trajectories of air arriving the measurement sites on each measurement day, calculated using the NOAA HYSPLIT model (Huang et al., 2014)

(2) The description and nomenclature of the divisors used in Equations (3) and (5) was not immediately clear to me, i.e. the terms fM(bb) and fM(nf) in the two equations respectively. I interpret these terms as being the values used to correct the fM(EC) and fM(OC) values to yield a fraction contemporary carbon in EC and OC, rather than the fraction modern carbon in EC and OC. In my opinion, the terminology fM(bb), and the phrase "a 14C reference value for biomass burning" do not make it clear that the reference value is the percent modern in EC emitted from burning contemporary carbon-containing fuel. Likewise, for lack of clarity in Equation (5). The application of these terms does not become clearer until the text in point #1 on P26267.

Reply: To make the Equation (3) clearer, the sentence is changed as "ECbb is calculated from the EC mass concentration, fM(EC) and a reference value of biomass-burning EC (i.e. fraction of modern in EC emitted from biomass burning sources, fM(bb))". To make the Equation (5) clearer, the sentence is changed as "Analogously, OC is divided into two sub-fractions, OC from fossil fuel (OCf) and non-fossil emissions (OCnf). To account for the thermonuclear weapon tests of the late 1950s and early 1960s, $OC_{nf}$ is calculated from the OC mass concentration, $f_M(OC)$ and a $^{14}C$ reference value of non-fossil emissions (i.e. fraction of modern in OC emitted from non-fossil sources, $f_M(nf)$)."

Technical corrections:

Abstract: State the collection duration of each PM2.5 sample (24 h).

Reply: it is added.

Abstract: State the number of samples analysed for 14C, i.e. the number of sample values that underpin the mean and standard deviation of source apportionment pro-portions presented in the abstract.

Reply: it is added.

P26259, L6: Rephrase end of the sentence as ":::was conducted at the four major cities of Xian, Beijing, Shanghai and Guangzhou." (The fact that the study was conducted in several large cities in China has already been stated in the previous sentence.)

Reply: it is corrected.

P26259, L7. Delete "An effective" and start the sentence directly as "Statistical analysis of:::" Remove the words "An effective" from in front of similar phrasing elsewhere in the paper where the Latin Hypercube technique is mentioned; it is a redundant adjective.

Reply: it is corrected.

P26259, L11: Rewrite as "across all sites."

Reply: this is corrected.

P26259, L19: Delete “rather”.

Reply: this is corrected.

P26260, L1: Delete both the two commas.

Reply: this is corrected.

P26261, L9: Delete comma.

Reply: this is corrected.

P2621, L22: Please provide a quantitative indication of what is meant by “extremely high concentrations of PM2.5”

Reply: It is changed as “During January 2013, the severe problem of air pollution in China became a worldwide concern, as extremely high concentrations of 24-h PM2.5 (i.e. often >100 $\mu m/m^3$) were reported in several large cities affecting ~1.3 million $km^2$ and ~800 million people.”

P26263, L4: “Six filters were selected:::”

Reply: this is corrected.

P26265, L12: Sort out the formatting of the citation in this sentence.

Reply: this is corrected.

P26267, L21: Insert “for” to read “To correct for the:::”

Reply: this is corrected.

P26271, L16: Correct the sentence containing the phrase “:::with an equally enhancement:::” which doesn’t make grammatical sense.

Reply: the sentence is changed as “This finding suggests that the increase of $EC_f$ and $EC_{bb}$ emissions in the three cities on the heavily polluted days is likely due to an equal enhancement of fossil fuel and biomass-burning combustion emissions and the accumulation of these particulate pollutants.”

P26272, L13: Should this read the “ratio of ECf to OCf”?

Reply: this is corrected.

P26273, L6: Insert comma after “marker”

Reply: this is corrected.

P26273, L7: Insert comma after “)”

Reply: this is corrected.

P26277, LL6&&: Provide a definition here of the two acronyms MPD and HPD.

Reply: the sentences are changed as: "Furthermore, it decreases the $OC_{sec,f}$-to-$OC_{pri,f}$ ratio of Beijing from 2.7 and 5.9 to 1.2 and 2.9 for the moderately and heavily polluted days, respectively. As a consequence, these values become better comparable with those of the other cities, but still underline the importance of secondary aerosol formation during the heavily polluted days."

P26295: Delete the word "below" from the last line of the caption of Figure 6.

Reply: this is corrected.

Supplementary information, caption to Table S1: Should read "The sampling dates for the:::."

Reply: this is corrected.

Anonymous Referee #3

The manuscript presents comprehensive and well-established methodology to reveal the sources of fine carbonaceous aerosols in China under conditions of heavy pollution episodes. The approach taken by the authors is not particularly innovative, it is put together from previous works, many of which are linked to the authors themselves. Nevertheless, it is worth publication since it deals with pollution levels not frequently encountered in other parts of the world, and applies methods that are adequate, up-to-date and well-proven in similar studies. However, I have two major points that need to be addressed before publication in ACP

Reply: we thank the reviewer for the nice summary of our paper and the positive comments. In the following we will respond to each comment listed below separately.

1) On Page 26266, as part of their own innovation, the authors introduce a p factor that is intended to split OC/EC primary emission factor between coal combustion and vehicular emission. p is simply defined as a percentage of coal combustion within total fossil fuel emission in China. Since the focus of this study is exclusively fine particulates, and coal combustion and tailpipe emission is well-known to produce fundamentally different size distributions, the use of this overly simplified p factor cannot be justified. This should either be omitted or estimated on the basis of relevant studies that take into account the size-resolved emission factors from both coal combustion and vehicular emission.

Reply: we agreed that the size distribution may differ in particles emitted from coal and tailpipe emission. However, it should be noted that the size of particles emitted from coal and tailpipe are mostly smaller than 2.5 μm (the particle size used in this study) (Huang et al., 2006; Zhang et al., 2012). As a result, the size distribution would not affect our results if we did not study fossil and non-fossil carbon in size-resolved particles (i.e. from 0.056 μm to 10 μm). In fact, a very large range of p (0-0.7) instead of simply p value was used in the study. In addition, when increasing the p value (i.e. from 0.35 to 0.70 for central p value) for Beijing, we found ECf, ECbb, OCbb and OCother, nf are independent of the choice of the p value (see Table S2 and Fig. S1), although the contribution of SOCf was decreased, but still underlining the importance of fossil-derived

SOC. Moreover, the comparison of our study and Huang et al (2014) confirmed that our source apportionment model and input parameters were justified.

2) My other major concern is related to the assumption that OCsecondary becomes relatively more important in times of high levels of air pollutions. This issue is dis-cussed in details in many previous source apportionment papers, and is partly related to nomenclature. Can we consider enhanced particle-phase partitioning (condensation) of semi-volatile organic compounds at colder temperatures simply as an increase in secondary organic aerosol (SOA)? Traditional perception of SOA generally implies some photochemical transformations prior to aerosol partitioning, which may not be the case here, at least not for the entire mass increment that is declared to be OC-secondary. In my opinion, part of this apparent SOA is not SOA if we strictly follow the definitions of atmospheric chemistry. However, the methodology applied by the authors does not allow distinction to be made between simple condensation and photochemical transformations. Thus, at least a critical discussion of the issue needs to be added to the manuscript.

Reply: we agree that the condensation of semi-volatile organic compounds at colder temperatures may contribute to the explained SOA in source apportionment study. However, this contribution is very small compared to the real SOA enhancement because the temperatures during the heavily polluted days were not significant lower than those found on other days. So we do not believe that the increased SOA measured by our model is due to condensation of semi-volatile organic compounds. The condensation of semi-volatile organic aerosol generally may contribute with some extent to the measured SOA in winter but the increased SOA between the moderately and heavily polluted days is largely due to enhanced SOA formation. To make it clearer, the statement is added in Sec 3.3.1 "It should be also noted that the condensation of semi-volatile organic aerosols generally may contribute to some extent to the measured SOA in winter due to the colder temperature in the northern sites such as Beijing and Xian. However, the increased SOA between the MPD and HPD measured by the current method is mostly if not exclusively due to enhanced SOA formation since the temperatures during the moderately and heavily polluted days were not significantly different."

References:


Huang, X. F., Yu, J. Z., He, L. Y., and Hu, M.: Size distribution characteristics of elemental carbon emitted from Chinese vehicles: results of a tunnel study and atmospheric implications, Environ. Sci. Technol., 40, 5355-5360, 2006.

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