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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Source apportionment of fine organic aerosols in Beijing" *by* Q. Wang et al.

Q. Wang et al.

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Letter of Responses Response to reviewer #1 (Acpd-9-S2231)

General comments: 1. This manuscript deals with the study of the composition of PM2.5 organic aerosol in the Beijing urban area during summer and winter campaigns. Organic aerosol composition evaluation was achieved through measurement of OC and EC and of specific organic tracers by GC/MS analysis. Several of these tracer compounds are specific of particular emission sources and can be used in the source apportionment of the aerosol. The authors employed CMB to apportion the sources of organic matter and of total PM2.5 mass. CMB has advantages in source apportionment studies when the number of samples analyzed is reduced, such it is usually the case of GC/MS organic tracer analysis. The method has however the limitation of not accounting with the formation of secondary aerosol mass and variability in source composition in space and time. The authors tried to improve the quality of CMB predictions by mostly using source profiles of local and regional origin. The fact that we

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they were dealing with urban aerosols of a large and polluted metropolis where the primary emissions are huge may reduce the interferences of secondary aerosol transformation and formation. However the lone utilization of organic profiles to calculate not only the organic aerosol load but also the contribution to total PM2.5 mass (including inorganic material) may introduce important errors in the estimations. Analysis of inorganic aerosol composition would be quite helpful to help in consolidating the estimations of source contributions. In my opinion the authors should invest some effort more in discussing the limitations and imprecisions of the methodology.

Response: We agree with the evaluation on the CMB methodology. The organic tracers for CMB were used in our work due to 2 facts: one is the higher mass loading of organics in PM2.5, and the other one is that the organics serve as better fingerprints to identify sources. Therefore it is acceptable to do source apportionment of fine particles with the data of organics from both ambient air and sources. It could be better of the information of combine the organic and inorganic species were used in source apportionment model. However the source profiles with them compiled together were not available, and we suspect that the CMB performance would not improve as we expected because of the not-as-good capacity of inorganic species to trace sources in Beijing. The understanding of SOA is very important, and the lack of directly measured profiles for SOA will add more uncertainties to our CMB results. Comparing with measured results, the CMB can only explain less than 70% ambient OC, we attributed the facts largely to the contribution of SOA. As we are not able to quantify the uncertainty of the CMB calculation, the discussion was added in the last part of the conclusion section.

2. The information provided in the paper in relation to the CMB process is limited (a table with the profile compositions of all the sources used in CMB would be helpful). However the CMB outcome is reasonable and comparable with the results of other source apportionment studies performed in this urban area region. Especially interesting is the capability of the CMB to infer the important contribution of food cooking to the

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urban organic aerosol load. I therefore recommend publication of the manuscript after some corrections.

Response: Thanks for the encouragement of the reviewer. As the full list of the source profiles will be a very table, we intend to present a profiles for the fitting species we used for the CMB model run, and the table will still be a quite big one.

Specific comments:

1.Page 9043, line 3 - Use <August 2005> instead of <August 2006>.

Response: Accepted and changed. 2.Page 9046, line 24 - Use <1.13> instead of <1.31>.

Response: Accepted and changed.

3.Page 9047, line 17 - Use <NIOSH> instead of <NOISH>.

Response: Accepted and changed.

4.Page 9047, lines 18-20 - In the sentence <Quartz filters ...were combined> it is not clearly explained if the combination was done separately for day and night or if day and night time samples were combined together. Anyway, the daytime and nighttime separated collection of aerosols did not seem to be used in any further study and discussion of the aerosol characterization.

Response: In the paper, the sentence is: “The quartz filters from several consecutive days were combined to meet the limits of detection for speciated organic compounds”. So we did not separate daytime samples from nighttime samples.

5.Page 9050, line 18 - The sentence <...in winter were 0.3-1.3-fold higher than in summer> does not give any clear information about higher pollution levels in winter. On the contrary, the average of the interval 0.3-1.3 (0.8) indicates lower values in winter. So rephrase the sentence to be in agreement with your conclusions (or change the conclusions!).

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Response: Accepted. The average OC and EC concentrations, as well as PM2.5 concentrations in winter, were 1.3–2.3 times those in summer, which may have been due to larger amounts of emission and more unfavorable dispersion conditions in winter. The sentences here and in the conclusion section were modified accordingly.

6.Page 9053, lines 5-6 - From Figure 5 it is not possible to confirm the <strong odd carbon number preference>. There was some preference which in winter was weak. Perhaps the calculation of CPI could better quantify this observation.

Response: In fact, a strong odd carbon number preference was observed for higher n-alkanes (≥C27) in both summer and winter, indicating their origin from biogenic sources. Value of CPI (carbon predominance index) is 1.8, 2.0 and 1.7 in Summer I, Summer II and winter, respectively.

7.Page 9054, lines 24-26 - Hopanoids (C30 mainly) are also known to be present in certain higher plants (e.g. ferns). In the case of lignite combustion the dominant hopanoids are C30 (Oros and Simoneit, (2000), Fuel, 79, 515.

Response: Yes, The sentence was modified to be “Hopanes are a series of pentacyclic triterpenoids, which are considered as organic tracers for fossil fuel combustion. Their fingerprint distribution could even indicate the maturity of fossil fuels and their emissions (Oros and Simoneit, 2000; Zhang et al., 2008). For example, almost all the Chinese coal combustion (except industrial bituminite) emitted HP29 as a dominant compound, while the predominant hopane in vehicle exhausts was HP30 (Zhang et al., 2008).”

Although the origin of hopanoid hydrocarbons may be from certain high plants such as ferns, the original structures of hopanoids gradually transformed into more stable thermodynamic structures during geological periods, i.e., Hopanes with the structure of 17(H),21 (H) are immature, 17 (H),21 (H) are moderately mature and 17 (H),21 (H) are fully mature Therefore, the fingerprint distributions of hopanoid isomers can be indictors of maturities of fossil

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fuel (Zhang et al., 2008).

8.Page 9055, lines 10-11 - Add references to the sentence.

Response: accepted. The reference (Ravindra et al., 2008) was added.

9.Page 9056, lines7-8 - Clarify in the sentence, when did the <Levo/EC increased markedly>.

Response: Accepted. The correspond text was modified to be “Ambient ratios of Levo/EC in summer were similar to those of cooking emissions, and some were slightly higher than those of other sources, except biomass burning, indicating the influence of biomass burning to some degree in summer. Those ambient ratios also increased markedly in winter and approached those of wood burning, indicating a strong impact of biomass burning.”

10.Page 9058, line 24 - Substitute the value <2.8%> by <8.2%>. This is the value tat can be calculated from the reference Zhang et al (2007) (8.2=4.52*0.546). Taking into account that 8.2 is bigger than 5.9, I have difficulties in understanding the sentence that follows <Given that all levoglucosan was emitted from wood burning and the use of a method similar to that described by Wang et al. (2007), ...>. Please correct or clarify.

Response: This is a very important issue need to be clarified. For the POM speciation analysis, we use for long the mixture standards from US EPA, which is actually prepared by J Schauer. He informed us that the concentrations of levoglucosan in the standard were 5 times higher than the real value after Zhang et al. (2007) was published. In this manuscript, we changed all the levoglucosan data (including source profiles and ambient samples) according to the real levo concentrations in the standards Also the value is a weighted average instead of arithmetic average. So it is around 2.8%.

11.Page 9060, lines 24-26 - Please clarify the reasoning related with this sentence.

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Which is the amount of coal combustion that is used at home heating by comparison with industrial utilization? If home heating emits at much higher rates than industrial burning why where the results of PMF much higher? Why, in CMB was not the industrial burning of coal taken into account?

Response: Coal combustion contributions in PMF may include both residential and industrial coal combustion. In our work, we only adopt source profile of residential coal combustion to do source apportionment. Therefore, contribution of industrial coal combustion may not be included. Due to the collinearity, industrial coal combustion and residential coal combustion could be not used at the same time in CMB. The reason why we choose residential coal combustion rather than industrial coal combustion is stated in the paper: “Of the various usages of coal, residential coal burning can have much more adverse effects due to its higher emission factors and lower emission altitude; i.e., the average emission factors are 43.7% for OC and 9% for EC in PM2.5 emitted from residential coal burning, and about 8% for OC and 1.5% for EC in PM2.5 emitted from industrial coal burning (Zhang, 2006).” There may be possible that results from CMB also include industrial coal combustion due to the similarity in emissions from these two sources. However, we use the ratio of OC/PM2.5 for residential coal combustion to obtain the coal contribution to PM2.5 from the coal contribution to OC. Since the ratio of OC/PM2.5 for residential coal combustion is much higher than the one of industrial coal combustion, their contributions to PM2.5 can still be underestimated

12.Page 9061, lines 6-8 - Present an explanation for the variability on relative contribution of diesel and gasoline vehicles between summer and winter.

Response: This is a very interesting comment. Actually we do not have an answer for sure to this point. Maybe it’s due to uncertainties in CMB, or annual decrease of diesel vehicle exhaust or annual increase of gasoline vehicle exhaust instead of seasonal trends. So I modified the sentences as followings: “The CMB results showed that the contributions of vehicle exhaust accounted for 13–20%

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of ambient OC and 8–12% of ambient PM2.5. There seems to be a noticeable decrease in the contributions of both gasoline vehicles and diesel vehicles from summer in 2005 to summer in 2006. This may be attributed to the implementation of new standard for emissions from vehicles in Beijing late in 2005 (equivalent to the European emission standards for vehicles Ⅲ, Ⅳ) (http://news.163.com/05/1226/13/25TCSDNI0001124T.html). The relative contributions from gasoline vehicles are somewhat higher than those of diesel vehicles during the campaigns.”

13.Page 9061, lines 11-13 - This sentence is not convincing. Was road dust composition taken into account in CMB? If not, the ratio of organics to PM2.5 in road dust should be completely different from car emission profiles.

Response: Road dust is not considered in CMB because the collinearity between source profiles of road dust and vehicle emissions. It’s true that OC accounts for much less percents of PM2.5 in road dust than in vehicle emissions. However, tracers used here in CMB are just organic compounds and EC normalized by TC (total carbonaceous compounds). So the ratio of OC/PM2.5 does not help distinguish road dust from vehicle exhausts. Meanwhile, because road dust is partly from the deposition of vehicle exhaust, composition of organic compounds in road dust is similar to the one in vehicle exhaust (We have also done the comparison among these source profiles of organic compounds).

14.Page 9068, Table 2 - Please reduce the number of significant digits in the Table.

Response: Accepted. The number of significant digits for annual average travel distance, vehicle number, emission factor and weighting factor in the revised table 2.

15.Page 9073, Figure 2 - This figure does not add much more information to the paper and can be removed.

Response: This figure was actually added according to the comments during the ACPD

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reviewing, we leave this decision to the editor, and will keep the figure or delete it at the decision of the editor.

16.Page 9080, Figure9 - Change colour or form of points referred to wood burning and straw burning. Both are diamonds with similar reddish colours.

Response: Accepted, and changed.

Response to Reviewer #2 (Acpd-9-S2289) General comments: In this manuscript the authors report the results of chemical analyses of PM 2.5 aerosol carried out with GC-MS. A number of organic tracers characteristic for particular sources were quantified and CMB was applied to apportion the sources of organic aerosol. An advantage of the manuscript is that source profiles were taken from local studies. The paper is well organized and in most parts clearly presented.

Response: Thanks for the encouragement.

Specific comments: 1.Page 9044: In the abstract the authors write “Particulate organic matter” in the ambient samples was quantified by gas chromatography/mass pectrometry; It turns out later that only 3-6% of organic matter was recovered by GC-MS and thus POM was not quantified. Replace “particulate organic matter” with e.g “individual organic compounds”

and 2.Similarly on Page 9047 line 19 “The rest of the quartz fiber filter was then extracted and analyzed using an Agilent GC-MS system (6890 plus GC-5973N MSD) to determine the concentrations of POM”; DCM/methanol extracts only a fraction of POM and 3-6% of organic matter was recovered by GC-MS.

Response: We understand this argument. Actually the mass concentration of organic matters, and the chemical speciation were all measured in this study. To avoid the confusion, we modified the two places by replacing particulate organic matters with the chemical compositions of particulate organic matters (or POM).

3.Page 9047 line 17 Change NOISH into NIOSH

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Response: Sorry for this mistake. It's accepted and changed.

4.Page 9046 The description of the three sampling campaigns is detailed enough in the text, therefore Table 1 is unnecessary.

Response: Accepted.

5.In table 2 and 3 the wording for weighting factor is not consistent (weight factor, weighting factor, weight value). Furthermore, the sum of weighting factors in Table 3 equals 1 but it is more than 1 in Table 2. What is the explanation for that?

Response: Accepted. And in the revised version, we used the weighting factor only. In the original table 3 (table 2 in the revised version), we treat gasoline vehicles and diesel vehicles separately. So the sum of the weighting factors for gasoline vehicles and diesel vehicles were 1, respectively. In fact, we can have weighting factors for all kinds of vehicles summing up to 1. But in this case, we try to differentiate gasoline vehicle exhaust from diesel vehicle exhaust. So we calculate them separately.

6.Also in table 2 the annual average travel distance (49736 km) seems to be very high. What is the source for this value?

Response: This value is mainly from the work by Song and Xie (Development of vehicular emission inventory in China. Environmental Science, 2006, Vol. 27, No.6) and paper by Hu et. al. (A detailed list for exhaust in development models of automobile technology in China. Journal of WUT (Information & Management Engineering), 2002, Vol. 24, No.2). In their paper, annual average travel distance for motorcycles are 1.2*104 km, for small gasoline passenger cars are 5*104 km, for medium/large gasoline passenger cars are 4*104 km, for light duty trucks are 4*104 km, and medium/heavy trucks are 3*104 km. We further calculate annual average travel distance of light-duty and heavy-duty vehicles based on the ratio of trucks versus passenger cars.

7.I think the fraction of organic matter explained by the CMB is an important number when talking about source apportionment. In this study this value was 64%+-15% but

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it is not mentioned in the conclusion (neither in the abstract). Also the lack of ability of the CMB to deal with secondary aerosol formation should be mentioned.

Response: Fully agree. We add these points in the conclusion section, with also the discussion on the secondary organic aerosols.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 9043, 2009.