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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characteristics and the origins of the carbonaceous aerosol at a rural site of PRD in summer 2006" *by* W. W. Hu et al.

W. W. Hu et al.

minhu@pku.edu.cn

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The authors wish to thank the referees' valuable comments and feedback on our manuscript. We have endeavoured to address each of the referee's suggestion and comments. A detailed response to the comments is shown below. We welcome any further feedback that the editor and/or referees may have.

Response to referee 2#

1.The manuscript requires significant revision with respect to grammar.

Response: Sorry for the grammatical error in this paper. The manuscript has been revised by all of the co-authors to make sure there is no grammar error.

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2. Figure 2, what is the cause of the breaks in the data (especially the measurements of PM 2.5, ECOC, and WSOC that are relevant to this manuscript)? How do these breaks affect the representativeness of the sample size?

Response: There were several times of power failure during the campaign, e. g. 22 July, which caused the gap for almost all the dataset.

PM2.5: The TOEM instrument had shorter obeservation period (start later and end earlier) than the other instuments.

ECOC: For the on-line ECOC instrument, the VOC denuder filter efficience will be checked every week for 4-5 hours and also we changed the Quaze filter every 3or 4 days. All these operations on the instrument caused the missing data points on EC/OC data.

WSOC: The WSOC data was obtained by the particle-into-liquid sampler (PILS) system (Takegawa et al., 2009) combined with a total organic carbon (TOC) and IC. Two detectors (TOC and IC) were used alternatively. When the IC detector was used, the WSOC data from TOC detector was absent.

Valid hourly TEOM data accounts for about 95% of the data obtained when TEOM was used (July 10-July 25, 2006). The valid hourly OC/EC data and WSOC accounts for 90% and 40% of the whole data set (July 3-July 31, 2006). This study mainly focus on OC/EC data, which should represent the concentration characteristics of OC/EC in this region.

3. Section 3.1- The 1.01 slope of the OM/OC correlation suggests that OM=OC, which means that OM is comprised of carbon alone. By definition, OM > OC, because OM also includes elements such as oxygen, hydrogen, and nitrogen. OM/OC ratios have been documented in the literature in the range of 1.2 to 2.0 (Bae et al., 2004; Turpin and Lim, 2001). The low end of the range represents emissions with strong primary influence with the high range suggestive of oxygenated or secondary sources. The

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data shown here is not consistent with the conclusions of the manuscript, such as SOC averaged 47% of OC, which would necessitate OM/OC >1.2. Even having included high primary emission data, this result is unreasonable. The authors must explain this unexpectedly low OM/OC ratio and discuss the error in measurement.

Reponse: We have changed the Fig. 3a and Fig. 3b. (Fig. 4a and Fig. 4b in the revised paper, Fig. 1 in this response paper). Comparing the original ones, we separately showed the data points for primary emissions days and normal days. For the primary emission days, the OM/OC ratio was quite low (1.0), which means the plume was quite fresh. The following part of SOC calculation also showed neglegible levels of secondary formation. For normal days, the OM/OC ratio was 1.6, which resulted in the average 47% OC attributed to be the SOC. In the original Fig. 3a, all the data points were linear fitted in the campaign and the slope almost equals to the value in primary emission days. We think that the fit is somewhat erroneous and the linear fit weight too much to the points from the primary emission days due to the extreme high concentrations. So, we corrected the figures and also the relevant text.

Text from paper, line 184-189: "...The OM and OC concentrations showed good correlations both in primary emission days and the other days (normal days, typhoon and precipitation days) (both R2 were 0.83) in Fig. 4a. During the primary emission days, the OM/OC ratio was quite low (1.0) that was much lower than the one (1.6) in normal and typhoon and precipitation days. Previous studies show that the more aged air masses tend to have higher OM/OC ratio (Aiken et al 2008; Turpin and Lim, 2001), implying the OM and OC in the other days were more aged than that in primary emission days. ...".

4. What appears to be an error in AMS measurements of OM (discussed above) should also be discussed in the context of the other AMS measurements reported in this manuscript.

Response: This question has been answered partially in the 3rd comments. The detail

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about AMS setup, data processing and performance of AMS during the campaign could be found in Takegawa's paper (Takegawa et al., 2009). Xiao et al. (2011) further use postive matrix factorization (PMF) (Ulbrich et al., 2009) to resolve the organic aerosol factors (HOA, OOA et al.). All of the information was added in Section 2.2 in the manuscript.

5. For the purpose of validating chemical measurements, the authors should perform a mass balance on PM2.5, in which they reconstruct PM2.5 mass from the measured components and discuss the difference as a function of unmeasured species and measurement uncertainty.

Response: The Fig. 2 shows the chemical compositions of PM2.5. The Total PM2.5 was measured by the TEOM (section 2.2 in the manuscript). The OM, SO4, NO3, NH4 and Cl was measured by AMS. The EC was obtainted by on-line EC/OC instrument. The reconstructed concentrations (of different species) accounted for about 52% of total PM2.5 and other (48%) were from unmeasured components. The fractions of some aerosol species in PM2.5 were lower than the results in PRD region reported in 2002 and 2003 (Hagler et al., 2006), such as SO4 (18% in this study, 21-32% in Hagler's research) but still within a reasonable range. The lower bias of reconstructed concentration may be also due to the cut size limitation of AMS (PM1). Yu et al. (2010) reported that there was 10% difference of elemental carbon between PM1 and PM2.5. The unknown species may composite by the crustal matters, metal elements and other ions (e.g. K+, Na+, Mg2+ ...). Considering to the length of the manuscript, we intend not to include this part in the manuscript. For the quality of the species measurements, the detailed information could be found in (Xiao et al., 2011; Takegawa et al., 2009).

6. Section 3.2- Designation of three types of days- How were the "source influences" determined?

Response: "Source influences" here particularly refers to the local emssion influence happened in the 23 -25, July, 2006. To express more clearly and precisely, we changed

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the “source influences” to “emission influences”.

7. Figure 3b, it would help the viewer to visualize the data if the x and y axes were set to the same maximum value (i.e. 60 μg/m3) so that the WSOC/OC line bisects the graph.

Response: Thanks for referee’s suggestion. We changed the scale of the graph (Fig. 4b). It looks better now.

8. Abstract, Figure 4, and elsewhere, “Participation” is stated instead of “Precipitation.”

Response: Thanks. The mistakes was corrected.

9. Table 2- Mexico City T0, what is “nan”? If data are not available in the cited publication, measurements are available in other publications.

Response: We searched for the other papers published about the Mexico City T0 site and we did not find the direct OC data reported. However, the OM value at Mexico T0 site was about 17.3 μg/m3 (Aiken et al, 2009) and the OC can be calculated by equation: OC=OM/1.71 (Aiken et al., 2008), then the average OC concentration at Mexico T0 site was about 10.1 μgC/m3. The OC concentration was also added to the Table 2 of the manuscript.

10. In the text and tables, carbonaceous aerosol concentrations have units of ugC/m3, whereas in the figures they are μg m-3. Please be consistent throughout the manuscript.

Response: The unit in the graphs was changed to “μgC m-3”.

11. The authors present a different method for the determination of (OC/EC)primary that minimizes the correlation between EC and OC-secondary, rather than the two more common methods presented (1- using the OC/EC ratio when SOC is minor, or 2-OC/EC from primary emissions inventories). This approach is based on the premise that “OC-secondary and EC were totally from different sources.” However, recent stud-

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ies have suggested that SOC is a product of the photooxidation of VOC emitted from primary combustion sources, like motor vehicles (Robinson et al., 2007) and biomass burning (Aiken et al., 2008; Grieshop et al., 2009; Lee et al., 2005). Thus, it is expected that there will be some correlation between OC-secondary and EC. In presenting their new approach to estimating (OC/EC)primary, the authors should 1) address the possibility of a relationship between primary combustion sources and OC-secondary, 2) establish precedent for their selected method, and 3) compare their approach to the two more established methods for estimating this quantity.

Response:

1)We agree with referee's comments. Recent studied showed that SOC may come from the emissions of primary organic particlulate (Robinson et al., 2007; Grieshop et al., 2009). So we added these research results in our revised paper to remind readers the drawback of our method.

Line 283-285: "...It is worthy to note that the assumption of low correlation between OCsec and EC may be violated by the fact of that the SOC can be formed from primary organic particulate emissions (Robinson et al., 2007; Grieshop et al., 2009)...".

2)The source tracer ratio method is firstly introduced by Millet et al.(2005), who used VOC data as the tracer to apportion the OC sources. We mentioned that in the paper, which may be not clear. So we made some modifications to the paper.

Line 252-256: "..... The source tracer ratio method was firstly introduced by Millet et al. (2005), who applied this method to Pittsburgh EC/OC dataset. The good agreement of source tracer ratio method with other approaches has been confirmed in Zhang et al. (2005). Detailed description about source tracer ratio method can be obtained in the Millet et al. (2005)...".

3)We added one paragraph to discuss the comparison between modified EC tracer method and the two more established method. The paragraph is as following:

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Line 294-300: "...The (OC/EC)pri for the day and night in normal days were determined to be 1.57 and 1.42, respectively (Fig. 7c). The values are higher than the ratio calculated for primary emission days (1.04). It suggests that the different emission sources of OC and EC between primary emission days and normal days. However, the ratios in emission inventory both for China (1.78) and Guangdong Province (2.18) (Zhang et al., 2009) are higher than the determined (OC/EC)pri values in this study, which indicate the inventory for Guangdong Province may overestimate OC emissions or underestimate EC or BC emissions. ..."

12. The authors choose to omit OCnon-combustion as a significant source of OC. Typically, OC-non is calculated as the intercept of the OC/EC regression, which in Figure 7a is 15.1, suggesting that 15 μg/m3 of OC may be from non-combustion primary sources, which corresponds more than half of the observed OC. In light of this result, the authors need to revisit the omission of OC-non from Equation 3.

Response: The non-combustion sources was explored by the intecept of direct regression results of OC with EC. The intecept of the OC/EC regression is -0.2, which means OC from non-combustion emission was negligible in normal days. However, the large intercept of the OC/EC regression in primary emission days (Fig. 3) may come from the regional background of OC other than combustion sources. This again proved that the sources of carbonaceous aerosol between normal days and primary emission days is different.

We also made some modification to the original manuscript, line 256-261: "...OCnon is referred to the non-combustion OC from biogenic primary OC or regional OC background. The intercept of the OC/EC regression line is regarded as the OCnon. The OCnon in normal days was around -0.2, which suggested OC from non-combustion emissions was small and it does not significantly affect our results. Thus, OCnon in normal days was not considered here, which is also consistent with previous studies (Lim and Turpin, 2002; Cabada et al., 2004; Polidori et al., 2006).. ...".

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13. Also, the authors need to comment substantially on the uncertainty in the estimate of (OC/EC)primary and the resulting SOC estimates.

Response: A bootstrap analysis was applied to our dataset to calculate the uncertainty of (OC/EC)pri. After 100 times resampling of OC and EC data, the average±sdev of (OC/EC)pri is 1.57±0.13 (day) and 1.42±0.10 (night), respectively. So the uncertainty (2-Æą) of (OC/EC)pri calculated with the modified EC tracer method in this paper is about 14-16%. If necessary, we can mention the uncertainty of 14-16% in the paper.

14. Furthermore, how does (OC/EC)primary change under different conditions (i.e. typhoon, vs. local primary influence)?

Response: Since the water removal effciency between OC and EC is different, therefore, the (OC/EC)pri in typhoon and preticipation days were not calculated in the paper. So the (OC/EC)pri for normal days (day 1.57, night 1.42), and primary emission days (1.04) was mentioned in the paper.

15. How many data points are included in the EC vs. OC scatter plot (Figure 7a)?

Response: There are 25 data points in the Fig. 7a.

16. Figure 8, WSOC vs SOC, the equation shown here does not correspond to the axes on the graph.

Response: Sorry for that mistake and the mistake was corrected.

17. Figures 2 and 4 present data that was never discussed in the manuscript, such as potassium, chloride, wind speed, and UVB. If these measurements are not discussed, they should not appear in these figures.

Response: We discussed these data above in our paper, however, the text may be not very clear.

The potassium and chloride was adoptted to investigate the source of primary emission days in Section 3.2. We complemented “(Fig. 3)” (Fig. 4 in original paper) in the

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revised paper to point out where can find this data.

Text of paper, line 150-151: “To investigate the emission sources in these two days, we checked the concentrations of Cl- and K+ (Fig. 3)...”

The wind speed was used to show the strong wind in the the typoon days, and weak wind in local emission days (Section 3.1). The UVB and wind data were also metioned in the last paragraph of Section 3.4. The “Fig. 4” (Fig. 3 in the revised paper) was supplemented in the revised paper to remind the readers.

Line 311-312: “It should be noted that strong secondary formation episode happened from 19 to 21 July during the whole campaign with the enhancement of strong solar radiation and weak winds (Fig. 3)”

18. Also, a notable omission is CO data in Figure 4, as this measurement is central to the conclusions about OOA and OM sources.

Response: Thanks for referee’s suggestion. The CO timeseries has been added on Fig. 4 (Fig. 3 in the revised paper).

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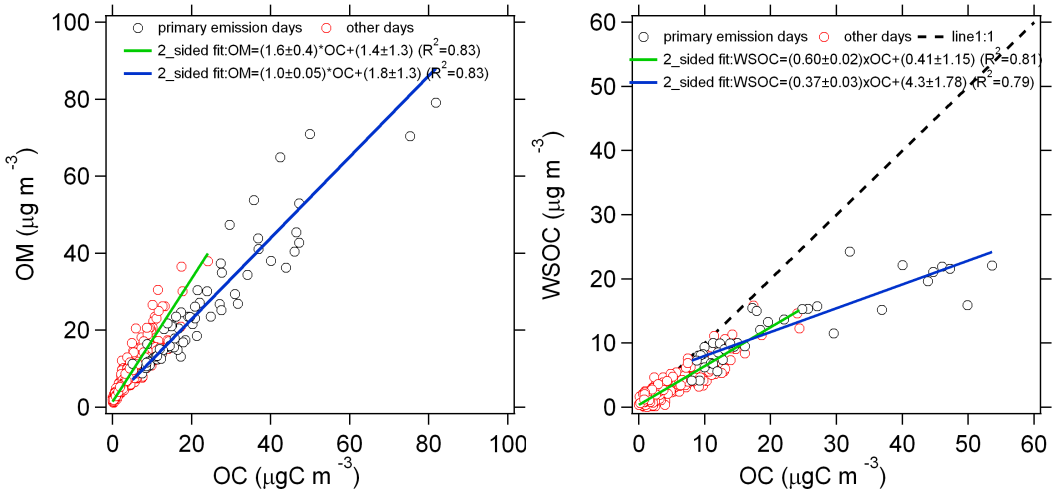

Fig. 1. The correlations of measured data between (a) OM and OC; (b) WSOC and OC.

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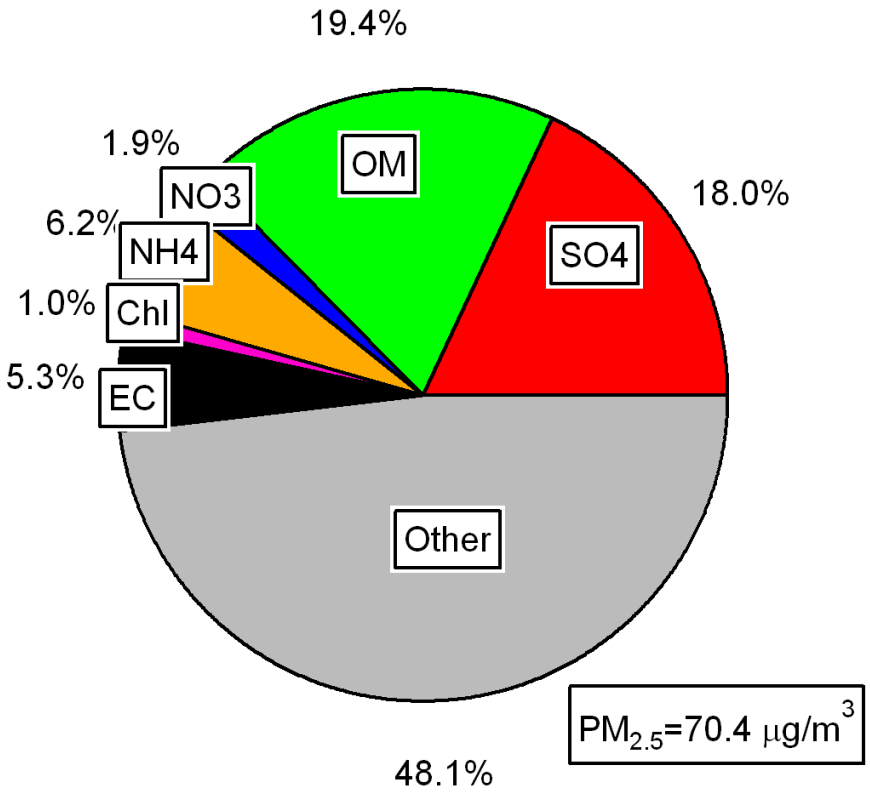

Fig. 2. The chemical composition of PM2.5 at BG site.

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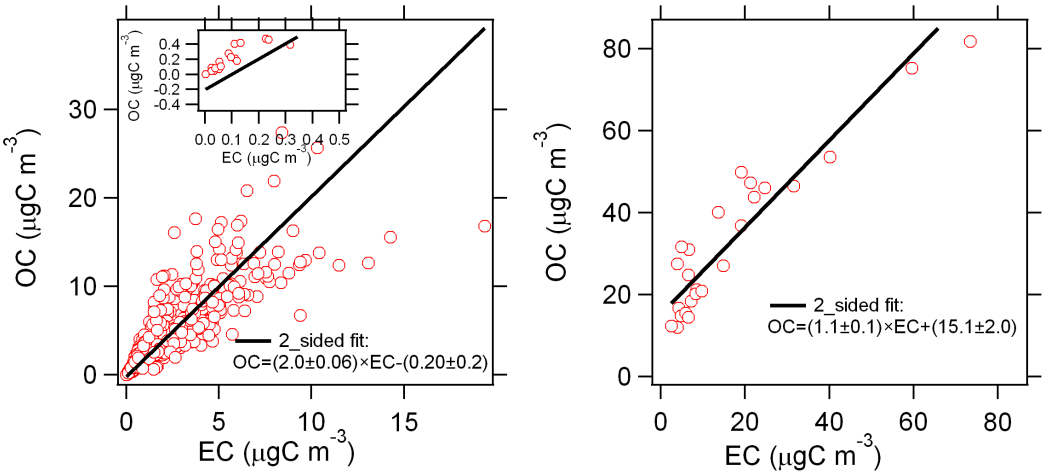

Fig. 3. The scatter plot of OC and EC in normal days and primary emission influence days.

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