

## ***Interactive comment on “Different characteristics of char and soot in the atmosphere and their ratio as an indicator for source identification in Xi’an, China” by Y. M. Han et al.***

**Y. M. Han et al.**

yongming@ieecas.cn

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We sincerely appreciate the positive and valuable comments from the reviewer for helping us to improve the quality of our paper. Following the suggestions of the reviewer, we have performed the required improvements in the manuscript.

1. General comments There are numerous aspects about this manuscript that are very well done, i.e. the authors have done a thorough study, on an important topic in a critical geographical region. The paper is well written, concise, and creative and with some minor revisions is of merit for publication. My two primary questions about this paper are in regard to the role of OP in these determinations and the generalization

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that the Char-EC/Soot-EC ratio is a better indicator of source than OC/EC. However, I believe that these issues can be adequately addressed by the authors.

Reply: Thank you for your comments.

2. Specific comments While the authors discuss the possibility that SOA formation interferes with the determination of OC/EC, it is unclear what uncertainty arises due to pyrolyzed organic carbon (OP in the manuscript). While in Fig. 6, there are clearly cases when the Char-EC/Soot-EC ratio may be a better indicator than OC/EC, it is clear that there are just as many cases when it is not. One of the primary points of the manuscript is that because it is not influenced by SOA formation, the Char-EC/Soot-EC ratio is a better indicator of source than OC/EC. However, from this manuscript alone, it is unclear if I would draw this conclusion. Is the claim that the Char-EC/Soot-EC ratio is a better indicator of source than OC/EC dependent upon the relative contributions of Char-EC and Soot-EC. In this particular study, the influence of traffic (Soot-EC source) is relatively low compared to Char-EC (coal and biomass sources). Is it possible that the Char-EC/Soot-EC ratio is only better when Soot-EC is a relatively small contribution such as the present study? Ultimately, both the OC/EC ratio and the Char-EC/Soot-EC ratio are a function of OP (equations given in words in text). Mathematically propagating the uncertainty in OP would provide some insight into the limitations of each of these methods. As the uncertainty in OP may be a function of how large the OP contribution is, examining this over a range of OP's could provide clarity on which method works better under high char conditions and which under low char conditions. It isn't obvious that the uncertainty due to SOA is always greater than that due to OP.

Reply: The concern of the reviewer regarding the methodology of OC and EC is a critical point for all OC/EC studies. However, to date there is no universally accepted method for EC determination. In thermal-involved methods, the key point is to determine the split point of OC and EC, that is, the POC determination (OP has changed to POC in the ACPD manuscript) in thermal optical (TO) method. Many studies have pointed out the existing problems of the POC determination, however, no studies have

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really solved this problem. In our view, this may be a pseudo-proposition if no limited conditions exist. We think that the diversity of EC's physical and chemical characteristics would cause POC to vary in different conditions. This is also a point that merits the differentiation between char and soot. Generally, soot particles have similar structures, while char particles, as source material burning residues, vary greatly depending on their sources. Perhaps the reason that most of the different thermal involved methods gave similar EC results for soot reference materials may be associated with the similar structure of soot. There are both TOR and TOT methods to quantify OC/EC in TO method. Both of them are involved in POC determination. Originally, TOT method was designed for vehicle pollution, while TOR was designed for ambient environmental pollution. Thus TOT may mainly focus on the soot determination (although TOT is not only for soot-EC determination and its determined EC also contains some of char), while TOR also considers char in the atmosphere. The TOT and TOR methods also give similar EC results for soot reference materials. If there no differentiation between char and soot in EC method, simply talking about the split of OC and EC in TO method is not meaningful because some researchers in aerosol study suggest that only soot is EC, while char is categorized under brown carbon, which was thought to be organic light-absorbing carbon. However if we agree with this definition, then EC determined in majority of previous studies would be too large to reflect soot-EC alone. When discussing the split of OC and EC, therefore, the definition of OC and EC is of particular importance. For ambient environment the TOR method seems more likely to reflect char in the atmosphere.

As for the influence of POC determination on OC/EC ratio and char-EC/soot-EC ratio, we agree with the reviewer that this indeed exists for all studies since POC's determination is operationally defined. It assumes that the produced char in the sample analysis process has the similar reflectance signal as the char in the sample, and the produced char is oxidized earlier than char in the sample when O<sub>2</sub> enters. The assumption seems authoritative. However, to date it seems there are no better methods for POC determination, and for TOR method the assumption of the earlier oxidization

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of the produced char seems good since it produces in low heating temperature (up to 550 °C) in the inert atmosphere.

The conclusion that the char-EC/Soot-EC ratio is a better indicator of source than OC/EC is based mainly on two factors. The first one is that OC/EC is influenced by SOA, which was put forward by many studies and some of SOA can account for more than 50% in TC. However, char-EC and soot-EC, as primary particles, are not impacted in their transportation process. Another one comes from our study that shows that in summer Xi'an has much high OC/EC ratios, which, apparently, are not from source contributions since motor traffic has higher contribution in summer than other seasons. The high OC/EC in summer thus can only be attributed to the SOA. In contrast, char-EC/soot-EC demonstrated high in winter and low in summer, which is in good agreement with the fuel consumption in Xi'an. The special point occurring in June 7-8 when there is biomass burning for clean agriculture also confirms the use of char-EC/soot-EC for source identification. Of course, the meteorological influences such as the wet precipitation on char-EC/soot-EC ratios also exist, which was discussed in the text. Very detailed analyses of char-EC/soot-EC ratio are impossible in this study because at present there is no such detailed data, including the variation of hourly char and soot data and the corresponding meteorological data.

We don't think that char-EC/soot-EC ratio as source indicator is dependent on the relative contribution of char and soot, and this conclusion is not only suitable for the relatively low soot contributions (traffic), but also for high soot contributions (biomass). The source profile in Fig. 6 showed that the motor traffic has very low char-EC/soot-EC. In some tunnel studies it is also the case. In fact, source samples from motor vehicle exhaust from Cao et al. (2006) and Chow et al. (2004) in Fig. 6 come from a ground-based source-dominated method, and can be seen as ambient samples with soot-dominated sources.

We concur with the reviewer that "examining over a range of POC could provide clarity on which method works better under high char conditions and which under low char

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conditions". Indeed motor vehicle samples have much lower POC than other sources. POC influence mainly on char-EC concentrations and low POC should lead to high char-EC if there is similar EC1, and thus to high char-EC/soot-EC ratio. However, in fact, motor vehicle samples have low POC and low char-EC/soot-EC, such as samples in summer. This is opposite to the OC/EC ratio, which suggests that high POC would lead to low EC and thus to high OC/EC ratio.

3. Lines 200-203 While the text says that the strong correlation between EC and Char-EC in Figure 2 is consistent with that observed in 14 other cities, the data that support that conclusion are provided elsewhere. Yet the correlation of EC and Char-EC is one of the primary conclusions of this manuscript. From the data presented in this paper it isn't obvious that this strong correlation doesn't arise due to the dominance of biomass burn as a source.

Reply: Sure, the strong correlation between EC and char-EC also exists for data of all 14 cities, which has only 9-22 samples for each city in each season. However, the correlation from a whole year observation with daily, monthly and seasonal variation is still unknown. Here we focus on whether it also shows strong correlation between char-EC and EC for a whole year data. The biomass burning may be some influence on the relationship between char-EC and EC. However, in summer when the biomass burning influence is at a minimum scale in Xi'an, the correlation between char-EC and EC is still very strong ( $R^2 = 0.969$ ). When the biomass burning data (which occurs on June 7-8) were deleted, the correlation between char-EC and EC is a little better ( $R^2 = 0.971$ ). This may suggest that source contribution is the main factor influencing the correlation between EC and char-EC. The summer data from the 14 cities also show very strong correlation between char-EC and EC ( $R^2 = 0.958$ ), just a little lower than that in winter ( $R^2 = 0.976$ ).

4. L230. The claim that char-EC/soot-EC has distinctive values from primary emissions is not clearly substantiated in Figure 6. In Fig. 6, this ratio, assuming the y axis should be Char-EC/Soot-EC (not Coal Char-EC/Soot-EC), varies from 1 to as high as 30 or

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65 for coal, and from 1 to 45 for biomass burning. These ranges do not imply that this ratio is a good indicator of emissions source as claimed in the manuscript.

Reply: Yes, the claim seems to be unclearly substantiated between coal and biomass burning in Figure 6. However, the distinctive values are much clearer between motor vehicle sources and coal and biomass source. Since all those source data are from other previous studies, more detailed studies pointing to the char-EC/soot-EC ratio from different sources are needed.

5. In the three sections, lines 33-35, 320-324 and 337-341 it is difficult to read these and see how they fit together (I have re-read them at least 4 times). In one section it says that Soot-EC is primarily affected by wet precipitation, and in another section it emphasizes its global dispersion. As written, it seems contradictory.

Reply: Thank you very much for this point. In the paper we want to emphasize the regional to global dispersion of soot, however, the wet scavenging influence can not be overlooked for soot deposition. Thus, we modify the tone of the wet scavenging influence on soot deposition. It is changed to "Soot-EC concentrations showed coupling with the snow and rain precipitation, with the highest in spring (March and April), and the lowest in summer (Figs. 2, 3, and 7). This pattern may suggest that soot, as a regionally-to-globally dispersed particle, is also affected by wet precipitation."

6. Technical corrections Line 61 change to Soot is composed of submicron particles of grape-like clusters formed : : :

Reply: Corrected.

Line 62-63 change to Char retains the morphology of the source material (current sentence doesn't make sense)

Reply: Corrected.

line 63-64 provide reference

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Reply: Reference "(Masiello, 2004)" is added.

line 70 "estimated to differentiate" doesn't make sense, suggest changing to either attempted to differentiate between or differentiated between

Reply: Corrected to "differentiated between"

Line 86-87 This sentence doesn't make sense-check grammar.

Reply: It is changed to "In addition, the ratio of char to soot is tested as means of source identification for carbonaceous aerosols."

Line 122-125 unclear provide more detail

Reply: Sentences below are added. "At the same time, a pyrolyzed organic carbon fraction (POC) was produced as a result of heating processes in the first inert atmosphere, which decreases reflected light. When oxygen was added the POC was oxidized and reflected light again increased. The POC was determined when a reflected laser light attained its original value after O<sub>2</sub> was added."

Line 150-151 "indicated EC rank highly in Xi'an" and "that char-EC rank highly". This use of rank doesn't make sense.

Reply: We change it to "indicates that EC is very high in Xi'an, and this may also imply that char-EC is high since char-EC is well correlated with EC in different Chinese cities (Han et al., submitted)."

Line 294 an effective indicator

Reply: Corrected.

Line 320 should invasion be inversion

Reply: The "invasion" may be correct.

Line 350-351 English unclear

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Reply: It is changed to "This confirms the regional to global dispersion of soot particles, while char is dispersed at the local to regional scale."

Figure 3. Fonts are much too small to read. Is it possible to put propagated error bars on the data points? As the X axis is identical in every graph-it could be used once. Soot EC appears larger than the other sub graphs.

Reply: This point also has been put forward by another referee and that was corrected in the ACPD manuscript. The error bars were also added.

Figure 6. Should the word coal be deleted from the Y axis label? As the text comments that the char-EC/Soot-EC ratio depends upon the type of coal, if these are known for the data points, perhaps they could be indicated by filled and unfilled squares for bituminous and anthracite coal. Given the size of the figure, symbols could be larger, as well as the Font sizes.

Reply: I have checked the figure last time in the technical correction process and the corrected points, including the word "coal" in the Y axis label, the symbols, and the Font sizes, has been presented in the ACPD manuscript. We don't differentiate between bituminous and anthracite coal in the figure because the data of coal combustion are from several references, most of which do not differentiate between the two, only the data from Liu et al. (2006) differentiate between bituminous and anthracite coal.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13271, 2009.

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