

## ***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.***

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We thank the reviewer for his critical and valuable comments and suggestions at helping us to improve our manuscript.

General comments 1. The manuscript presents carbonaceous aerosol measurements collected for one year in Xi’an, China and makes a case for using char-EC/soot-EC ratios as a marker for different combustion sources rather than OC/EC ratios. My principal concern with the manuscript echoes the comments of the other reviewers: the method relies on the operationally defined TOR protocol to distinguish between char-EC and soot-EC, particularly the impact POC may have on their analysis. The

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manuscript relies on one previously published study by the same lead author to show that soot and char are differentiated accurately by the TOR method. I’d like to see a better case laid out that shows that other factors (POC determination, presence of inorganics, etc.) are not responsible for any differences in when EC is measured (e.g., EC1, EC2, EC3), given it is the bedrock of the analysis. The manuscript provides very little discussion of the sources of error that result from incorrect identification of POC. Little information is provided to allow the reader to gauge the importance of the POC correction, such as the relative abundance of POC compared to char-EC. Of course, I would not expect the authors to make the case favouring one POC correction approach to another, but I would expect to see at least some discussion of the impacts of picking one method over another on their results. For example, if the actual POC is twice as large as the measured values, what impact does this have on char-EC/soot-EC ratios?

Reply: We have to say that there are still some factors (POC determination, presence of inorganics, etc.) influencing EC, as well as char and soot determination. These factors have been investigated by many other scientists and have been proposed for more than a decade. Different factors influencing EC quantification exist in different EC methods. This may be one of the reasons that to date there is still no universally accepted method for EC quantification. However, different methods have been practiced long term. The thermal optical method has been suggested to be the most reliable method for aerosol EC quantification (Gelencsér, 2004) because it uses laser light to detect the charring of OC. The char and soot quantification using the TOR method is based on the assumption of the reliability of the TOR-EC quantification. Comparison between different methods has shown that the discrepancy for the same sample using the different methods reaches up to 500 times (e.g. Schmidt et al., 2001; Hammes et al., 2007), which has been associated with the different parts of EC measured with different methods. The TOT and TOR methods also have very different EC results and the TOR EC is generally higher than the TOT EC. However, we are still unsure of which method is better for the accuracy of EC (or POC) determination. Thus, we suggest that knowing what we are measuring is of the most importance for EC determination. Then

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the accuracy of a method can be precisely assessed. This is why we try to assign the physical entities for different kinds of EC and differentiate between char and soot. To date definitions for different parts of EC have been used in different fields (e.g. Goldberg, 1985; Jones et al., 1997; Kuhlbusch, 1997; Masiello, 2004; Andreae and Gelencsér, 2006), though there are still some gaps for the different parts of EC from different scientists. In general, soot is acknowledged as part of EC (despite some scientists who acknowledge that soot alone is EC) and has its own physical entity. However, the burning residues (defined as char in this paper) are more complicated. There is no clear-cut line between char and some organic carbon such as the humic-like materials. Char is an impure form of graphitic carbon obtained as residues when carbonaceous material is partially burned or heated, with limited access of air. In aerosol studies this part of EC was suggested as brown carbon or some light-absorbing organic carbon by some scientists (e.g. Andreae and Gelencsér, 2006). But this part of EC existed in most of the previously measured EC. The confusion in the definition of this part of EC may result in the difference between TOT and TOR methods. This also has an influence on the POC determination. Indeed, the POC determination is an important factor influencing not only EC concentrations but also char-EC concentrations. The amount of charring depends on many factors, such as the nature of OC, the amount of oxygenated compounds (the supply of oxygen), heating temperature and heating periods. Generally, samples from biomass and coal combustion show higher POC than samples from motor vehicle exhausts. The POC determination depends on the two assumptions: (1) POC and native EC have the same light attenuation coefficient, and (2) POC evolves before the native EC in the oxidizing atmosphere. Although the two assumptions are somewhat arbitrary, the monitoring of the charring itself is still a nice point in the thermal optical method (Gelencsér, 2004). Thus, it is difficult to determine the correction of the POC determination and is hard to say which method is better for POC determination. This depends, in part, on the definition of char. We would like to discuss this point in our revised paper.

2. My second area of concern is that potential drawbacks to the sampling method are  
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not discussed. Gas-phase species have been repeatedly shown to adsorb on quartz filters and/or volatilize from sampled particles, causing biases in OC measurements. The adsorbed gases can be prone to pyrolysis in the TOR analysis, leading to errors in EC measurements depending on the ability of the optical methods to correctly identify the POC. The manuscript should at least discuss the possibility that their results may be biased by these artifacts, and ideally show that the determination of char-EC and soot-EC are not affected by gas-phase sampling artifacts.

Reply: We agree with the reviewer that the gas-phase species adsorbed on quartz filters (positive artifact to particulate organic carbon) and/or volatilized from sampled particles (negative artifact to particulate organic carbon) is an important factor of OC measurement. This point has been discussed by many other scientists (e.g. Turpin et al., 2000; Kirchstetter et al., 2001; Subramanian, 2004; Olson and Norris, 2005; Cheng et al., 2009). For example, Subramanian's study (2004) on a hill in an urban park next to Carnegie Mellon University campus in Pittsburgh, Pennsylvania showed that "With a bare quartz filter sampling for 24 h at 16.7 lpm (face velocity of 29 cm/s), an almost constant positive artifact of 0.5  $\mu\text{g-C}/\text{m}^3$  is found, irrespective of the season.", and that "The negative artifact due to volatilization of the organic particulate matter from the denuded quartz filter is on average 6.3% (SD 6.2%) of the ambient POC". This means that if there is such a similar influence in Xi'an from the sampling artifacts the integrated effects may be very low for OC measurement since Xi'an has much higher OC and EC concentrations (36.4 and 8.4  $\mu\text{g m}^{-3}$ , respectively, on average). The absorbed gases are indeed prone to pyrolysis. However, the pyrolysis can be monitored by the laser light in the analytic process and can be returned to OC. There may be some biases existing in this process. Since far high EC and char amounts exist in the atmosphere in Xi'an, the influence by gas-phase sampling artifacts on EC and char-EC measurement may be small in our study. The charring is mainly monitored in EC1 step and has similar characteristics to the native chars, so the sampling artifact would have little influence on soot-EC determination.

3. The authors correctly point out that OC concentrations can vary depending on SOA production, thus making the OC/EC ratio less useful as a tracer for combustion. They have not shown, however that SOA production does not affect char-EC determination in the analysis, nor have they shown that char-EC is chemically stable with transport away from source. Can it partition to the gas-phase with dilution? The recent Carnegie Mellon papers have found a substantial amount of POA can partition to the gas-phase with dilution. For these reasons I am not sure that they have made as good a case as they think they have for using the char-EC/soot-EC ratio as a combustion tracer.

Reply: EC, including char and soot, is chemically inert, which has been proposed by Goldberg, (1985) for decades. Soil and sediment studies have found clear evidence of millennial turnover of char (Masiello and Druffel, 1998; Middelburg et al., 1999). Recently, Hammes et al's study (2008) demonstrated that char turnover in the soil is 293 years. Lipsky and Robinson's study (2006) shows that EC emission measured by the TOT method cannot be affected by dilution. Since char also is a kind of EC and is included in TOT measured EC, this means that there would be little effect from the partitioning to the gas-phase with dilution for char. As for whether SOA production affects char-EC determination in the analysis, SOA is also organic carbon and it has similar effects in the EC analysis process (such as the influence on POC determination). Thus if we acknowledge the two assumptions mentioned above for POC determination, the SOA influence on char-EC determination might be negligible.

4. I would also be curious about what the authors think regarding the substantial size differences between soot and char that they themselves point out. If char is indeed only found between 1-100 um and soot in the sub-micron mode, wouldn't it be easier to simply use the ratio of super-micron EC to sub-micron EC to examine relationships between soot and char?

Reply: This comes from our clerical error. We want to state that soot is mainly in sub-micron mode, while char is mainly in the micron mode. There is no clear-cut distinction in size differences between char and soot. Char is also composed of some sub-micron

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particles. Generally char is an impure form of graphitic carbon obtained as residues when carbonaceous material is partially burned or heated, with limited access of air.

5. Please be consistent with significant figures. If replicates showed 10% order errors than I doubt the mean concentrations can be reported with two significant figures. I do not mean to pick on the authors on issues that have complicated this field for some years. I feel the work presented is a valuable contribution to a difficult field, but would really like to see more attention paid to defending the analysis method than is currently provided. I think the authors are perhaps too confident that their approach is best and, as another reviewer pointed out, present things a little one-sidedly. I think the community would be well served if they provided a bit more of a defense of their approach as I and the other reviewers have suggested.

Reply: Thanks for this suggestion. The two significant figures are consistent with the precision of the carbon analyzer. We agree with the reviewer that this paper contribute to a difficult field, and more studies are needed for methods for EC quantification, as well as the differentiation between char and soot. However, it is still very important to give the physical entities to different parts of EC.

6. Finally, there are numerous grammatical errors in the text and it would benefit greatly by a thorough proof-reading to catch all of these. I have only noted a few.

Reply: Thank you for this suggestion and thanks for your help. We will do this in the revised paper.

#### 7. Specific comments

7.1. Page 13273, line 20: the Kirchstetter et al. 2004 paper attributed light absorption due to colored organics, or brown carbon. I think there is a slight difference in how the terms are used by the authors of the manuscript and Kirchstetter et al. (2004), but perhaps I am wrong.

Reply: This comes from the promiscuous use of different terms. Most of the brown

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carbons used by different researchers are similar with the definition from Andreae and Gelencsér (2006). They defined char as brown carbon, a kind of light-absorbing organic carbon. However, in our opinion, char is indeed a kind of EC, which has been identified by many scientists (Goldberg, 1985; Jones et al., 1997; Kuhlbusch, 1997; Masiello, 2004), and this part of EC exists in most previously measured EC using different methods.

7.2. Page 13723, lines 25-28: wording of the sentence is awkward. Did Gelencser find TOR to be the most reliable EC measurement method, or that it was best for differentiating between char and soot? I believe the authors are trying to say that Han et al. (2007a) differentiated between char and soot using TOR, a commonly applied method for measuring EC content of carbonaceous aerosol (Gelencser, 2004). Did they use the IMPROVE protocol, or IMPROVE\_A protocol? If so one of the Chow et al. papers should be cited.

Reply: Gelencsér (2004) suggested the thermal optical method to be the most reliable method for carbonaceous aerosol studies. We want to say that Han et al. (2007a) differentiated between char and soot using TOR, a commonly applied method for measuring EC content of carbonaceous aerosol. In addition, we want to say that the thermal optical method, including the TOR method, is suggested by Gelencsér (2004) to be the most reliable method for carbonaceous aerosol studies. In this study the IMPROVE protocol was used. The reference Chow et al. (1993) was cited. This sentence was changed to "Recently, Han et al. (2007a) differentiate between char and soot using the thermal optical reflectance (TOR) method, a commonly applied method for measuring EC content of carbonaceous aerosol (Chow et al., 1993). The thermal optical method has been suggested to be the most reliable method for carbonaceous aerosol studies (Gelencsér, 2004)."

7.3. Page 13724, lines 1-2: where do the definitions of EC1, EC2, and EC3 come from? The authors should state that they are specific stages in the EC evolution portion of the IMPROVE protocol before using the terms rather than in the methods section.

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Reply: This sentence "In the TOR method following the IMPROVE (Interagency Monitoring of Protected Visual Environments) protocol, carbon on filter substrates was made to evolve through programmed, progressive heating in a controlled atmosphere, making available eight separate carbon fractions — four OC, one pyrolyzed organic carbon and three EC." was added before the terms.

7.4. Page 13274, line 20: the mean temperature and annual rainfall should be single numbers, not ranges. Are the numbers reported the mean high and low temperatures? Inter-quartile range? +/- one standard deviation range? Please cite the source of the reported values.

Reply: The ranges represent the variation of the annual mean temperature and annual rainfall from 1950. The source of the reported values ([http://www.xawb.com/gb/city/2006-02/17/content\\_661171.htm](http://www.xawb.com/gb/city/2006-02/17/content_661171.htm)) was cited.

7.5. Page 13275, lines 13-14: where the samples conditioned at constant relative humidity prior to the measurements? If not, can the authors estimate the uncertainty in the measurements associated with water uptake by the sampled particles?

Reply: That was done in our lab (Aerosol Environment Division, the Institute of Earth Environment, Chinese Academy of Sciences). Each filter was weighed twice before and after sampling using an electronic microbalance with 1  $\mu\text{g}$  sensitivity (MC5; Sartorius, Goettingen, Germany) in a temperature and relative humidity controlled environment (35-45% RH at 20-23°C). The filters were equilibrated for 24 h before gravimetric analysis. The precision of mass measurements before and after sampling based on replicate weighing are lower than 15  $\mu\text{g}$  per filter; filters were reweighed if the difference between the replicate weighing was out of that range.

7.6. Page 13276, lines 2-4: please provide more information about the filter blanks. Where these collected periodically through the study? How many blanks? What was the standard deviation about the mean?

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Reply: Filter blanks were collected every month. The systemic sampling has been conducted from Sep. 13, 2003 and will be done for the next several years. Twelve blanks were collected in 2004 and were used for carbon analysis in this study. The average concentrations of filter blanks were  $1.56 \pm 1.01$ ,  $0.42 \pm 0.28$ ,  $0.32 \pm 0.24$ , and  $0.10 \pm 0.04 \mu\text{g m}^{-3}$  for OC, EC, char-EC, and soot-EC, respectively.

7.7. Page 13726, lines 20-23: "EC rank highly in Xi'an" What does this mean? Does Xi'an have the highest EC concentrations of previously reported measurements in Chinese cities? Or is EC relatively more important in Xi'an compared to other aerosol species?

Reply: This sentence was changed to "Comparing EC concentrations in Xi'an with those of other Chinese cities reported in previous studies (e.g. He et al., 2001; Cao et al., 2003, 2007; Ye et al., 2003; Yu et al., 2004; Duan et al., 2007) 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)."

7.8. Also, why not compare the measurements of char-EC in this study to Han et al. (2009) as is done for soot-EC later in the paragraph.

Reply: We think that the comparison of EC can represent the differences of char-EC since char-EC is well correlated with EC in different Chinese cities. The carbon concentrations of the 14 different cities comes from only short period sampling (concentrated sampling for  $\sim 20$  days in summer and winter, respectively), which may bias the real carbon concentrations. This has also been discussed in that paper. Since char-EC is well correlated with EC, the comparison of char-EC from these previously reported EC from long term sampling may be much more accurate.

7.9. Page 13276, lines 23 – Page 13277, line 3: It is not clear that these concentrations are for Xi'an. Please report standard deviations. Without reported standard deviations it is difficult for the reader to evaluate the comparisons to the other cities. The phrase "was close to" doesn't mean anything without some kind of context.

C3799

Reply: The standard deviations have been presented in Table 1. Also, we added them for all reported average concentrations for different components. The last sentence was changed to "In contrast to the great differences of EC in different Chinese cities (Cao et al., 2007), the average soot-EC concentration in Xi'an was close to that ( $1.24 \pm 1.06 \mu\text{g m}^{-3}$ ) from 14 Chinese cities (Han et al., submitted), which confirms the similarity in soot-EC values across China."

7.10. Page 13277, line 21-23: Report standard deviations. Are the differences in the seasonal averages statistically significant?

Reply: The standard deviations were added for all reported average concentrations in the paper. Indeed, the differences in the seasonal averages are statistically significant.

7.11. Page 13277, lines 23-26: Since wet-scavenging is the primary removal mechanism for soot it is not surprising that neglecting it results in a longer soot lifetime!

Reply: "If the influence of wet scavenging (see Sect. 4.4) is neglected, the seasonal variations in soot-EC concentrations may be even smaller" was deleted.

7.12. Page 13278, lines 26-27: I think the others mean the "relatively limited sources" is really the "relatively limited range of sources"

Reply: Sure, corrected.

7.13. Page 13279, lines 8-24: This paragraph should be in the introduction.

Reply: We will do some modification in our revised paper.

7.14. Page 13281, line 7: Remove the word "obviously" as it is not obvious to me that the higher ratios are due to coal consumption, just likely.

Reply: Corrected.

7.15. Page 13281, line 8: What was used to determine there was biomass burning on June 8 and 9?

C3800

Reply: It was recorded in our sampling record, and this can also be found from the report of the local newspaper.

7.16. Page 13281, lines 17-20: Another “obviously”. There is very little supporting evidence in the manuscript to show the seasonal variations in fuel usage.

Reply: The “obviously” was deleted. In Xi’an the residential coal consumption mainly occurs in winter. The 2004 data showed that the residential coal consumption was 0.9 Tg, which can be assumed to be mainly consumed in winter. This point was incorporated into the text.

7.17. Page 13281, line 25: The authors themselves note that “higher temperature in summer would produce more SOA”, so how can they then say that “temperature itself should not affect carbon concentrations”. Temperature will also affect partitioning of semi-volatile material, including carbonaceous species.

Reply: We agree with the reviewer. We made the corrections. “That temperature showed negative correlations with the mass and carbon concentrations (Table 2) may be associated with the different usage of fuel consumption in different seasons in Xi’an. In addition, temperature varies with mixing height in Xi’an, which would also influence carbon concentrations. For example, in winter, especially in cold weather, more coal is used for heating in Xi’an, which would result in higher emissions. Meanwhile low temperatures would lead to a lower mixing height, reducing particulate dispersion and thus enhancing local pollutant levels. The daily minimum temperature showed relatively stronger correlations with carbon concentrations and char-EC/soot-EC ratio than the daily maximum temperature, which may be attributed to increased coal combustion during cold periods. Furthermore, temperature may influence carbon, especially OC concentrations through the formation of SOA (Turpin and Huntzicker, 1991; Cabada et al., 2004) and the partitioning of semi-volatile material (Lipsky and Robinson, 2006; Robinson et al., 2007) ”.

7.18. Page 13282, line 1: Is there fuel consumption data to back this up?

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Reply: In Xi’an there are little data on the usage of the coal consumption for heating. However, the 2004 data showed that the residential coal consumption was 0.9 Tg, which can be assumed to be mainly consumed in winter.

7.19. Page 13282, line 7: This should be the first paragraph of section 4.4, as the previous paragraph does not discuss precipitation. Change “Rain and snow were thought” to “rain and snow are”. In fact, it is probably best to change all of the “rain and snow” references to “precipitation” unless the authors are making some distinction between removal processes by rain and snow.

Reply: Corrected.

7.20. Page 13283, line 23-25. This statement needs to be supported by some information regarding the relative importance of motor-vehicle and biomass/coal combustion emissions on EC concentrations. If there is substantially more char-EC than soot-EC than the difference in light absorption efficiency may be nullified by the substantially greater char-EC mass concentrations.

Reply: we agree with the reviewer. However, we think that the reducing of the same amount of carbon from motor vehicle emissions may have a greater impact on the mitigation of the present warming trends than the reduction of biomass burning and coal combustion. We modified this sentence to “Thus, efforts to reduce motor vehicle emissions, if in the same amount, may have a greater impact on the mitigation of the present warming trends than the reduction of biomass burning and coal combustion.”

7.21. Figure 3 should be changed to a box-and-whisker plot or something similar. Adding the standard deviation to the average values is a little mis-leading in that it exaggerates the patterns in the data in that larger means will generally have larger absolute standard deviations.

Reply:

7.22. Figure 4. The caption is not a complete sentence.

C3802

Reply: The word “strong” was deleted.

8. Technical corrections

Page 13273, line 5: change “risk” to “risks”

Page 13274, line 12: omit “micrometers”

Page 13274, lines 13-14: awkward wording

Page 13275, line 1-2: omit “L per minute”

Page 13275, lines 19-23: should be consistent in either using “O<sub>2</sub>” or “oxygen” and “He” or “helium” rather than switching between them here and in the introduction

Page 13276, lines 14-15: “35” appears twice.

Corrected.

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