

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.

Anonymous Referee #4

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General comments

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 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

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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?

My second area of concern is that potential drawbacks to the sampling method are 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.

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.

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

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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?

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.

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.

Specific comments

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.

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.

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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.

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.

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?

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?

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? 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.

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.

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

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!

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

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

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.

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

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

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.

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

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.

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.

Figure 3 should be changed to a box-and-whisker plot or something similar. Adding the

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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.

Figure 4. The caption is not a complete sentence.

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 “O₂” or “oxygen” and “He” or “helium” rather than switching between them here and in the introduction

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

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

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