

***Interactive comment on* “Size distributions of elemental carbon in a coastal urban atmosphere in South China: characteristics, evolution processes, and implications for the mixing state” by Xiao-Feng Huang and Jian Zhen Yu**

Xiao-Feng Huang and Jian Zhen Yu

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We thank both reviewers for their comments. Our responses to the review comments are listed below.

Anonymous Referee 2

(Received and published: 9 September 2007)

Reviewer: The paper presents the evaluation of the mass size-distribution of EC concentrations in a megacity in Southern China. While the topics could be in itself interesting, there are several major shortcomings in the approach the authors take.

Response:

Below is our point-by-point rebuttal.

Reviewer:

1) The authors, for technical reasons, do not apply the optical corrections in defining the OC/EC split in their adapted NIOSH method. Although they claim that this does not introduce error to the relative distribution of EC, this is not proven in the paper and presumably it is not true. Many studies have revealed that charring is a very significant process in thermo-optical measurements. It has also been shown that the tendency for charring increases markedly with increasing share of heteroatoms (increasing degree of oxidation that occurs upon atmospheric ageing). It is therefore very likely that while freshly emitted soot nanoparticles are not prone to charring, aged oxygenated soot particles and secondary organic aerosol (which are in the accumulation mode) show very high charring efficiency. Thus, contrary to the statements of the authors the uncorrected mass size-distribution measurements should not be reliable even in relative terms!

Response:

Having done some work on effects of OC charring on EC and OC determination (e.g., Yu et al., 2002, Yang and Yu, 2002), we are aware of and agree with the reviewer that charring could be a significant process during thermal analysis of carbonaceous aerosols. In this work, we opted not to apply any charring correction schemes in the determination of EC and OC because of lack of a better alternative as stated in our manuscript. Below is a detailed explanation.

The very nature of non-uniform deposition in impactor samples makes the optical charring correction scheme not operative, since the laser beam could pass through aerosol deposit or through blank filter space in between aerosol deposits depending on the position of the filter location in the analyzer. Let us consider two hypothetical scenarios

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of the laser beam position relative to aerosol deposits. In scenario 1, the laser beam path passes through a portion of filter fully covered by an aerosol deposit and EC1 is the corresponding EC determined using the optical charring correction scheme. In scenario 2, the laser beam path passes through a portion of the impactor substrate partially covered by aerosol deposit and partially being blank substrate and EC2 is the corresponding EC determined using the optical charring correction scheme. One can see that the initial laser transmittance in scenario 2 would be higher than that in scenario 1 because of the lesser amount of aerosol deposit in the light path. Consequently, the EC/OC split point, at which the laser transmittance returns to the initial reading, would be later in the analysis in scenario 2 than in scenario 1. This leads to a smaller EC2 than EC1 by an unknown percentage. (A figure to illustrate these two scenarios can be viewed at <http://landsea.ust.hk/~chjيانyu/figs.pdf>.)

Despite the problem with applying optical charring scheme to non-uniform aerosol deposit, Jaffrezo et al (2005) nevertheless determined EC and OC in impactor samples using the automatic split time offered by an optical EC/OC analyzer. They found that EC in impactor samples determined this way was only 76% of EC in collocated filter-based samples, in which the aerosol deposition was uniform. Similar results (71%) were obtained by ten Brink et al (2004). A much lower value (25%) was reported in the work by Viidanoja et al (2002). Summarizing their own work and similar work in the literature, Jaffrezo et al concluded that the difference in EC between filter and impactor samples was unexplained and deserves additional research. Our analysis of the problem described in the previous paragraph offers an explanation why the impactor-based EC, if determined using the optical charring correction scheme, was consistently lower than EC determined in filter-based samples. With the non-uniform impactor samples, it is more often than not that the laser beam would pass through a portion of the impactor substrate not fully covered by aerosol deposit (i.e., scenario 2).

The data by Viidanoja et al [2002], ten Brink et al [2004], and Jaffrezo et al [2005] clearly demonstrates that the use of optical charring correction in the impactor sam-

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ples is not a better alternative. At the same time, Viidanoja et al showed that EC in impactor samples determined with no charring correction compared much better with the filter-based EC measurements and with BC measured by an aethalometer, both with deviation less than 30%. With their data, Viidanoja et al concluded that the lack of charring correction for their impactor samplers did not cause significant errors in the OC/EC split.

If one surveys studies in the literature reporting size distributions of aerosol EC and OC, majority of the studies have adopted the no-charring correction approach. For examples, the studies by Chen et al. [1997], Kerminen et al. [1997], Plewka et al. [2004], Gnauk et al. [2005], Cheng et al. [2006] used various forms of a two-step thermographic method to obtain EC and OC by a conventional carbon analyzer, which does not have an optical feature for charring correction. In their two-step thermographic methods, OC is operationally defined as C that evolves from collection substrates in an inert atmosphere (e.g., N₂, Ar, or He) at a fixed temperature (typically in the range of 340-590°C); EC is defined as the residue C after the previous step and is typically determined by analyzing the residue samples in an oxidative atmosphere (e.g., O₂). The studies by Ma et al. [2004], Zielinska et al. [2004], and Cabada et al [2004] used an aerosol carbon analyzer with either filter reflectance or transmittance feature for charring correction. For the same reason as we have cited, EC in these three studies was defined to be C that evolved in the O₂/He stage (without making charring correction).

While we acknowledge the uncertainty in EC concentration measurements with the no charring approach, we argue that the size bin of the EC modal peak is insensitive to whether charring correction is applied or not. Figure 1 in the manuscript shows that the different split times, which in essence correspond to scenarios of no charring correction and charring correction, had no influence on the size distribution pattern. That is, regardless of the OC/EC split position, EC always shows a dominant fine mode in the same size bin. To better demonstrate this point, we now produce in Figure R3 (can

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be viewed at <http://landsea.ust.hk/~chjianyu/figs.pdf>) the normalized size distribution curves (normalized against the sum amount of the 10 stages) with EC obtained at the three different split times. Figure R3 clearly shows the size distribution patterns of EC obtained with different split times (i.e., with and without charring correction) were very similar.

In the above analysis, we have investigated the charring correction on the EC modal peak position by assuming charring correction at an EC/OC split time fixed for samples of all size bins. We agree that the fraction of charring OC may vary with the stages, but this variation is likely small between samples of adjacent stages due to similar chemical compositions (Figure R4, available at <http://landsea.ust.hk/~chjianyu/figs.pdf>). It is clear from Figure R4 that the chemical compositions of the three stages (0.32-0.56 μm , 0.32-0.56 μm and 1.0-1.8 μm) that define the EC modal peak in the accumulation size range are similar.

After all things considered, we conclude that the identification of the EC peaking in the size bin of 0.56-1.0 μm is not affected by whether charring correction scheme is applied or not. The subsequent discussion on the evolution processes of EC, which is the main focus of this manuscript, therefore has a valid starting point.

References:

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Reviewer:

2) The calculation scheme that the authors present in their paper is basically a reproduction of well-known mechanism that leads to bifurcation of the accumulation mode. The existence of condensation mode and droplet mode is now widely known, but the authors avoid these terms throughout their paper, except on page 10755 where they also give reference for them.

Response:

If we have left readers the impression of avoiding the terms "droplet mode" and "condensation mode", it is not our intention to do so. Neither do we intend to report the bifurcation of the accumulation mode (of the overall aerosol mass) as a new finding. The new finding we report here is the observation of EC peaking in the droplet mode in the ambient air in a location in South China. The shift of EC particles from the condensation mode to the droplet mode has significance in quantifying aerosol's role in radiative balance since the light absorption efficiency of EC is a function of particle size and the mixing state. It is therefore meaningful to understand the evolution processes for condensation mode EC to grow into the droplet mode. Processes leading to the droplet mode sulfate, as observed and reported for locations in California, U.S. have been investigated and known to the atmospheric science community to arise from the in-cloud processes [Meng and Seinfeld, 1994]. However, the droplet mode EC has not been explained in the literature. It is one of our objectives to explain such a droplet mode EC mode. Our calculations based on meteorological conditions and gas/ aerosol

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chemical characteristics typical of our observation site in South China confirmed that in-cloud formation of sulfate is the only mechanism leading to the growth of EC particles from $<0.5 \mu\text{m}$ to $0.7 \mu\text{m}$ or larger. Our results revealed that cloud processing of primary EC particles could enhance light absorbing capacities through mixing EC and sulfate, which needs to be considered in modeling aerosol optical properties in this region. Our work is not just a reproduction of well-known mechanism that leads to bifurcation of the accumulation mode.

Reviewer:

3) For the estimate of the mixing state of EC the authors rely solely on a relative shift in the mass size distribution of EC. Apart from the experimental concerns discussed above the authors simply fail to consider the fact that near the sources a significant fraction of freshly emitted soot nanoparticles rapidly attach to available surfaces by dry deposition, thus severely distorting the relative mass distribution towards larger particle sizes away from the sources. Therefore the authors' approach for calculating the degree of mixing is simply not valid.

Response:

We disagree with the reviewer's statement that the relative mass distribution would be severely distorted towards larger particle sizes by way of dry deposition when the freshly emitted EC particles move away from emission sources. We think the "dry deposition" process referred by the reviewer is the same as the more commonly called "coagulation" process. The nature of coagulation dictates that while coagulation is an effective mechanism in depleting the small particles (such as nanoparticles) but it does not cause significant particle growth in the accumulation mode size range [Kerminen and Wexler, 1995; Seinfeld and Pandis, 1998]. In another words, the mass size distribution of EC in the accumulation and coarse modes is little affected by coagulation process near the emission source. This point has been discussed in details in section 3.2.2 in our manuscript.

In our manuscript, we focus on the shift of EC mass size distribution in the accumulation mode and limit our estimate to the fraction of internally mixed EC particles due to cloud processing. There is no theoretical basis that the depletion of small nucleation mode particles due to coagulation would impact such estimates.

References:

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Seinfeld, J. H. and Pandis, S. N.: *Atmospheric chemistry and physics: from air pollution to climate change*, John Wiley, New York, 1998.

Anonymous Referee 1

Received and published: 17 September 2007

Reviewer:

1. MOUDI normally uses Al foil as the impaction substrate which does not adsorb organic compounds. How does substituting quartz for Al change the size cut for the stages? The spacing between the stages becomes narrower due to increase in the thickness of quartz filter over Al foil. This in turn affects the aerodynamics of the particles and thus the size cuts. Changes in the impaction efficiency can also affect the amount collected at each stage, thus altering the mass distribution by size.

Response:

Considering the thickness of quartz fiber, we have used special quartz fiber spacers of 0.05 inch in thickness (MSP Corp.) to compensate the reduced space between two adjacent impact plates. As a result, the spaces between the impactor stages have been maintained the same as those with Al foil as the collection substrates. This information was given in our previous paper reporting other results from these MOUDI samples

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[Huang et al., 2006]. In the revised manuscript, we will explicitly report this detail.

Reference:

Huang, X.-F., Yu, J. Z., He, L.-Y. and Yuan, Z.: Water-soluble organic carbon and oxalate in aerosols at a coastal urban site in China: Size distribution characteristics, sources, and formation mechanisms, *J. Geophys. Res.*, 111, D22212, doi: 10.1029/2006JD007408, 2006

Reviewer:

2. Without pyrolysis correction, how does one account for the pyrolytic EC from the adsorbed organic gases in the quartz filter? The fraction of adsorbed organic compounds (hence the apparent EC) may vary with the stages and may not be always a constant proportion or amount of the OC on each stage. So this can skew the observed (apparent) amount of EC on each stage and hence the size distribution.

Response:

This comment is in essence the same as Comment 1 from Referee 2. Please see our response to Comment 1 from Referee 2.

Reviewer:

3. While the paper showed similar distribution regardless of run time used for the OC/EC split, the accuracy of the size fraction may be in error due to (1) and (2).

Response:

Comments (1) and (2) have been addressed above. Our data analysis shows that the identification of EC peaking in the size bin of 0.56-1.0 μm is not affected by EC/OC split point. The subsequent discussion on the evolution processes of EC, which is the main focus of this manuscript, therefore has a valid starting point.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 7, 10743, 2007.