

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 are grateful to these valuable comments from the reviewer. We believe that such discussion will improve our understanding the method, as well as the definition for EC, BC, brown carbon, light-absorbing carbon, char and soot.

The determination of char EC/soot EC in PM_{2.5} aerosols is an approach which may yield useful supplementary information to global and regional BC/EC studies. The basic idea of the authors is to try to lend physical meaning to data derived indirectly from a widely used (but somehow arbitrary) standard analytical protocol. The authors call the two subsets ‘char EC’ and ‘soot EC’ as if they were existing physical entities: this

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might be so but definitely not proven in the manuscript nor in previous papers. The char EC signal (I would call it ‘signal’ to indicate that it is not more than that until its physical existence is explicitly proven), depends strongly on degree of sample pyrolysis (charring) and the validity of the assumptions behind its optical corrections (which are inherently imperfect). It is well-known that a part of the water-soluble organic compounds in aerosols are very much prone to charring which cannot be compensated by the optical correction method: therefore, for example, water extract of urban or marine aerosols, as well as pure starch or cellulose do give an EC signal in the thermal-optical method (e.g. Yu et al., 2002; Schauer et al., 2003). Since biomass burning and coal combustion do give off a lot of large molecular weight soluble compounds, which may char and yield false char EC signal (artifact), one may question whether such ‘char particles’ do exist in the PM_{2.5} fraction, at least in such a large proportion compared to soot? In coal combustion aerosols it may also be possible that abundant cations such as sodium or potassium may cause premature evolution of soot carbon and again yield a false char EC (and soot EC) reading in the TOR method. Part of these uncertainties could have been greatly reduced by the authors if they have performed water extractions on another part of the filters (thus removing WSOC and cations) prior to the TOR analysis to prove that their ‘primary’ char EC/soot EC signals are indeed independent from such artifacts. Without that, I am not convinced that char EC particles do exist at such large concentrations in biomass smoke and coal burning impacted aerosols. Another possibility would have been to conduct a parallel electron microscopic study to prove that such particles are indeed so numerous in the PM_{2.5} size range. The compounds the authors call ‘char EC’ most likely belong to ‘brown carbon’ or ‘humic-like substances’, and are unlikely to bias optically based BC measurements in large cities. Part of them may be determined as ‘EC’ even in TOR measurements, as it was shown in many previous studies. An alternative option for the authors is to refrain from implying that char EC and soot EC signals correspond to existing physical entities, and restrict their discussion as such. In this case it is straightforward to state that char EC to soot EC signal is 1-45 for biomass smoke, whatever the reasons are for that. Overall,

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the manuscript present a large body of useful data but with a very one-sided focus. Its statements are not well founded and could well be misleading.

Reply: The concerns of referee 3 are similar with those proposed by the referee 2 in some points. We agree with the catalyst influence on OC/EC and char/soot determination and the comments that biomass burning and coal combustion do give off a lot of large molecular weight soluble compounds, which may char and yield false char EC signal (artifact). In practice most of the EC are operationally defined, which was suggested as "apparent EC" by Andreae and Gelencsér (2006). There are two assumptions in the TOR method: the produced char in the analysis process has the similar reflectance signal as the char in the sample, and the produced char is oxidized earlier than char in samples when O₂ was added. Char and soot in this study are also "apparent char and soot" since it is determined with the TOR method which has been mainly used for EC quantification previously. The separation between char and soot using the TOR method is based on the assumption that the TOR measured EC can reflect the real EC, since this method has been used for decades and was suggested to be the most reliable method for EC determination by Gelencsér (2004). In practice, the "apparent EC" measured by different methods are also called EC, and this is also the case for char and soot in this study. Just as there is no universally accepted EC method, even though the determination of EC has been existing for decades, we don't think that the method for char and soot separation determined by the TOR method is the "perfect" one. However, in carbonaceous aerosol studies, we think that the validity or practice may be of the most importance for methods for EC quantification, as well as char and soot quantification. Our results in this paper agree with the fact that char and soot have different behaviors in the atmosphere (Masiello, 2004), with soot being widely dispersed and char more easily being deposited, and this in turn confirms the validity of the method for the separation between char and soot. Previous studies such as char and soot in urban dust (Han et al., 2009, Atmospheric Environment; in which the water soluble matters were deleted), as well as the study on the temporal and spatial distribution of char and soot in 14 different cities (Han et al., submitted to

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Atmospheric Environment) also show that this method can also be used to indicate air pollution level.

We think that the high ratios of char to soot for coal and biomass source samples are mainly due to the very close sampling to the source location where the coal and biomass were burned. Since char consists of source particle burning residues, it is easy to be incorporated into the samples, and some large pieces were even incorporated. This may be the reason for the high char to soot ratio for these source samples. When both char and soot transport for a distance, the ratios may decrease. Our sediment core data (Y.M. Han, unpublished data; the water soluble matters were deleted in the pretreatment) in Lake Daihai showed that char to soot ratios range between 1-3 with no local human fires (which means that both come from long distance transportation), while they can reach up to 26 with local human fires. So the deposition rate is indeed an important factor influencing char to soot ratios, especially in rural areas. However in urban areas, this influence may be very small. The fact that the difference between char to soot ratios for motor vehicle exhausts and coal and biomass burning is very large suggest that such influence would not impact the source identification using their ratios in urban areas.

We also agree with the reviewer that the ions in the source samples would influence char to soot ratios. However, the presence of these ions generally decreases the activation energy of EC, leading it to be oxidized much more easily in analytic processes. Since the data of char to soot ratios for source samples is a summarization of other studies (Fig. 6), we would like to investigate some source samples using the TOR method by removing the WSOC and ions in future studies, as well as the electron microscopic study. We have checked the samples under electron microscope after char-EC (EC1) was oxidized in my previous study (Han, Ph.D thesis, 2006) and found that the majority of carbon remains are soot-like. Our previous study (Han et al., 2007, Chemosphere, 69, 569-574) showed that only soot reference materials oxidized in EC2 and EC3 steps, while char materials oxidized in EC1 step.

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Indeed, char-EC in this paper is categorized into brown carbon by many other scientists. However, I am not sure whether this is correct. Char has been defined as one kind of black carbon (BC) or EC by Goldberg (1985), and this has been identified by many other scientists such as Kuhlbusch (1997) and Masiello (2004), etc; while brown carbon is a kind of light-absorbing organic carbon (Andreae and Gelencsér, 2006). So in our opinion, char should be one kind of EC, and this part of EC occupied the big amount in previously measured EC. EC or BC are not one kind of well defined chemical component, so we suggest that it's better to use the terms char and soot to replace the previous term EC or BC as the two kinds of EC have more clear chemical and physical characteristics, as well as their optical properties. Both char and soot indeed exist as different entities, as char consists of source particle burning residues and thus have different structures, while soot consists of sub-micron particles formed at higher temperatures and is always in the form of agglomerates of 0.1-1 μm .

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