Manuscript number: acp-2011-532

Title: Mass absorption efficiency of elemental carbon and water-soluble organic carbon in Beijing, China

1. Comments of reviewer #1:

This manuscript describes the measurements of the mass absorption efficiency (MAE) of elemental carbon in Beijing using a thermal-optical carbon analyzer. Previous published MAE values of North America, Europe and Asia were converted to the equivalent MAE using a converting approach. Finally, water-soluble organic carbon extracted from the filter samples collected in Beijing was quantified using TOC analyzer, and the absorption spectra of the liquid extracts were also measured with a UV-Vis spectrophotometer and long-path absorption cell. Based on these data, the authors concluded: i) The daily variation of MAE in Beijing coincided with the OC abundance due to the enhancement by coating with OA (especially SOA); ii) The equivalent MAE is much lower in the regions heavily impacted by biomass burning; iii) the seasonal pattern of MAE in Beijing could be due to the difference in the precursors of SOA, of which was coupled with the previous data (Cheng et al., 2011). These experiments are potentially of interest to the ACP readership because carbonaceous aerosols exert great influence on climate by changing the energy transfer through the atmosphere, and potentially affect public health as carriers of toxic chemicals. Carbonaceous aerosol emissions in China are estimated to account for around one-fourth of global anthropogenic carbonaceous aerosols. Therefore, the study focused on MAE of carbonaceous aerosols in Beijing will appeal to a wide general readership and be of exceptional interest to the atmospheric specialist.

Major Comments:

(1) Unfortunately, however, the manuscript provides no solid evidences for these conclusions. The authors severely criticized that “the artifacts were associated with the filter-based method due to the aerosol-filter interactions shadowing of the incident light with increasing filter loading, and aerosol scattering effects.” (Page 4, in the introduction section); therefore, the main aim of this manuscript is to gain high-qualified data using a thermal-optical carbon analyzer, and to update the previously published MAE values using a converting approach in order to compare these data in different fields including North America, Europe, and Asia. However, it

seemed that the efforts of authors resulted in failure. The author also emphasized that the data may be affected by the artifacts resulting from the redistribution of liquid-like organic particles, or during the filter-based absorption measurements. The reliability of the data presented in this manuscript need to be further proved.

Our responses: We admit that filter-based measurement of light absorption (e.g., Aethalometer) is still challenged by several artifacts such as aerosol scattering effects. But the aim of this manuscript is not to develop correction factor for these artifacts, because we do not operate instruments which can measure light absorption directly on airborne particles (e.g., photoacoustic spectrometer, PAS) in this study. Instead, we want to compare the MAE values of EC measured in different regions by similar methods, and investigate the factors responsible for the discrepancy. For this purpose, we do not have to correct all of the artifacts associated with filter-based measurement of light absorption; what is really important is how to account for the discrepancy caused by the measurement of both light absorption and EC concentration.

The most important conclusion derived from the comparison of MAE values across regions is that the MAE of EC is much lower in the regions heavily impacted by biomass burning. To provide solid evidence for this conclusion, we added results from source samples in the revised manuscript. (i) Diesel exhaust samples were collected on pre-baked quartz filters using a diesel engine (China First Automobile Group Wuxi Diesel Engine Works) which is complied with the emission standard of National Standard in China (Phase Ⅲ, equivalent to the Euro Ⅲ emission standard in terms of particulate matter and gaseous pollutant emission levels). The engine was operated with the commercial-available diesel (0#); the speed and load was controlled by the Schenck DYNAS HT350 dynamometer. (ii) Biomass smoke samples were also collected. Briefly, a brick cooking stove was built in a kitchen similar to those commonly found in villages in northern China. Two crop residues (wheat and corn) and three types of wood (poplar, pine and elm) were combusted in the stove, and particles in the smokes were collected using quartz filters (without size selective inlet). The MAE of biomass smoke samples was 3.0~3.2 and 3.6~6.8 m^2/g for crop residues (wheat and corn) and wood (poplar, pine and elm) respectively whereas much higher value (8.4 m^2/g) was observed for diesel exhaust (Figure 1), providing solid evidence for the hypothesis that emissions from biomass burning would decrease the MAE of EC. **(See Line 147-159; Line 384-388; Figure 4 in the revised manuscript)**

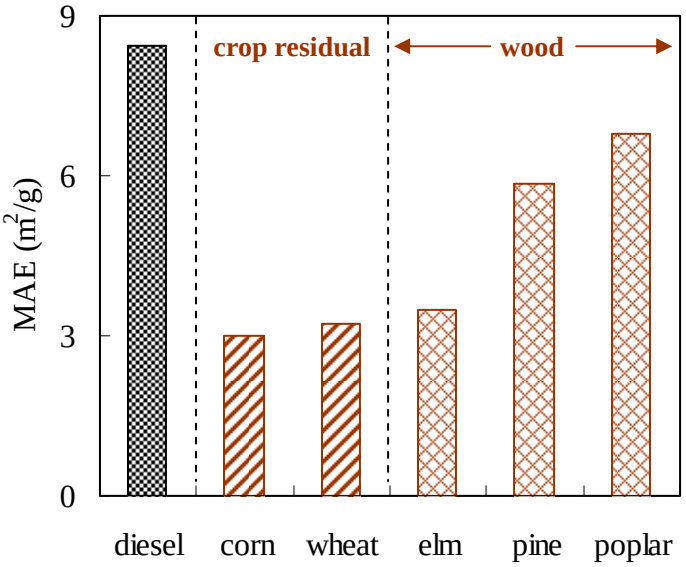

Figure 1. MAE of diesel exhaust and biomass smoke samples.

(2) Besides, the equivalent MAE of the first group and the second one were between 4-11 m^2/g and 2-9 m^2/g, respectively, as shown in Table 1; the authors thus concluded that the much lower MAE in the regions of Asia compared to North America and Europe could be due to be heavily impacted by biomass burning. Apparently, two data scopes overlapped largely, and this result was lamely inferred.

Our responses: We agree with the reviewer that MAE values of the two groups overlapped largely (Note: Group 1 includes results from North America and Europe when not impacted by biomass burning, whereas Group 2 comprises results from Asia and those measured in North America and Europe during the periods impacted by biomass burning). In the revised manuscript, frequency distribution of the MAE values of the two groups were introduced to illustrated the influence of biomass burning (Figure 2). All of the MAE values in Group 1 were above 4 m^2/g and were most frequently found in the range of 6~8 m^2/g. Comparing with Group 1, the most noticeable feature of Group 2 was that quite a few MAE values were below 4 m^2/g. For example, extremely low equivalent-MAE values, which were below 2.7 m^2/g, were found in two Indian cities (Hisar and Allahabad). Given the fact that EC in India is dominated by emissions from biomass burning, it is concluded that MAE of EC is much lower in the regions heavily impacted by biomass burning. **(See Line 359-363; and Figure 3 in the revised manuscript)**

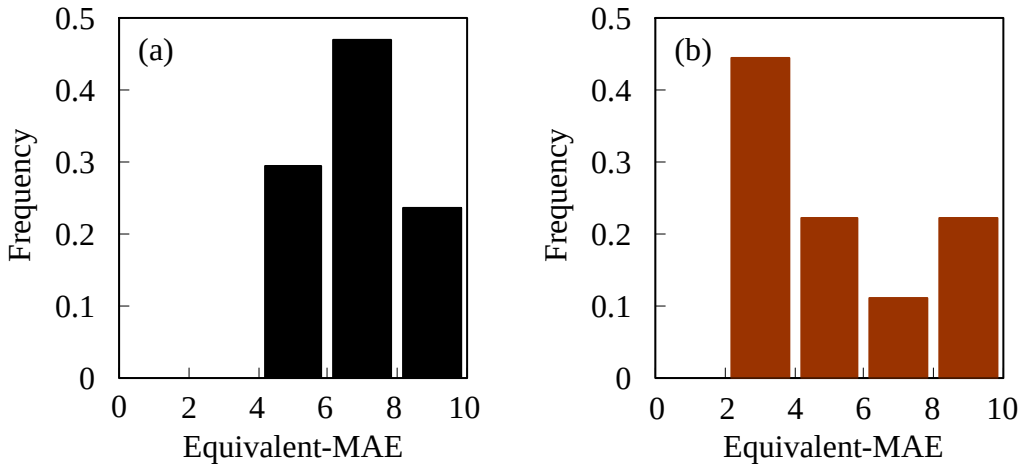

Figure 2. Frequency distribution of the average equivalent-MAE for Group 1 (a) and Group 2 (b).

In the revised manuscript, we also compared the MAE of the same location during different periods to investigate influences of biomass burning. For example, the MAE of Philadelphia, PA was only 2.4 m^2/g when heavily impacted by biomass burning (during a forest fire event), significantly lower than the result (7.1 m^2/g) when the influence of biomass burning is not important. These results strongly support the hypothesis that emissions from biomass burning would decrease the MAE of EC. **(See Line 380-383)**

(3) The manuscript was not well organized. The authors listed three sub-topics in the first section of Results and Discussion. They were "MAE" values of EC in Beijing", "Effects of the measurement methods", and "Effects of biomass burning and brown carbon". In my opinion, "Effects of the measurement methods" should be combined into the section of Experiment. The present manuscript did not meet the requirement of a scientific paper, which could be seen apparently in the Abstract, Conclusion and Implications sections. For example, the sentence of "WSOC in Beijing has been demonstrated to be strongly linked to SOA" in Abstract is not suitable; the description about the research method (line 488-492) should not be placed in the Implications section. By the way, the conclusion is so long, and it should combine the Implications section into one unit.

Our responses: We agree with most of the suggestions. In the revised manuscript, (i) the sentence of "WSOC in Beijing has been demonstrated to be strongly linked to SOA" in Abstract was removed as suggested, and the Conclusion section was revised

accordingly; (ii) the description about the research method in the Implications section was also removed as suggested; (iii) the Conclusion section was more brief; (iv) the Implication section was combined into one unit. **(See Abstract, Conclusion and Implication section)**

The sub-topic of "Effects of the measurement methods" mainly describes the development of the converting approach which can account for the discrepancy caused by measurements methods of both light absorption and EC concentration. There are substantial discussions on the converting factors between different measurement methods of both light absorption and EC concentration, including how the converting factors were derived and why using different values for different regions. We prefer to keep the sub-topic of "Effects of the measurement methods" in the section of Results and Discussion rather than the Experiment section, because the concerting approach is not a straightforward method.

Specific comments:

(4) Line 76: what is "R_{abs}" ? It is "b_{abs}"?

Our responses: R_{abs} refers to the ratio of b_{abs} measured by PSAP to that measured by the PAS. Discussions on the ratio were presented in another way to avoid misunderstanding. **(See Line 75-80)**

(5) Line 105-107: In my opinion, light-absorbing organic aerosol is tentatively named "brown carbon" and may be associated with high molecular weight humic-like substances (HULIS) from biomass burning or soil deflation. HULIS not only leads to the efficient absorption of solar radiation in the UV and visible range, but also exhibits much stronger wavelength dependence at shorter wavelengths than EC. The work by Alexander and Hoffer has proved this point. "Tar balls" and soot could be precursors of HULIS, but "Tar balls" from biomass are not the important "brown carbon".

Our responses: We agree with the reviewer that brown carbon is strongly associated with HULIS. This was included in the revised manuscript. Moreover, "tar balls" also exhibits much stronger wavelength dependence at shorter wavelengths than EC. Thus, it should also be considered as an important type of brown carbon. **(See Line 104-107)**

(6) Line 126: The map of sampling site should be shown. It will help give the readers

a direct information.

Our responses: The map of sampling site is shown intensively in our previous publications (including several recent ones such as Yang et al., Atmos. Chem. Phys., 11, 7893-7903, 2011). Thus, we only introduced the sampling site briefly in the revised manuscript. **(See Line 128-130)**

(7) Line 228-231: The corresponding literatures should be cited.

Our responses: References were added as suggested. **(See Line 241)**

(8) Line 342-380: in the section of 3.13, the data about Beijing was not involved into this discussion, which deviated from the topic of "Mass absorption efficiency of elemental carbon and water-soluble organic carbon in Beijing, China".

Our responses: We admit results from Beijing were not included apparently in this section. This section mainly focuses on the influence of biomass burning on the MAE of EC. Beijing is not a representative location heavily impacted by biomass burning, though the emission of biomass burning is higher in China compared with North America and Europe. As a result, we did not discuss results from Beijing separately.

(9) Line 414-416: The corresponding literatures should be cited.

Our responses: The conclusion that "anthropogenic volatile organic compounds (AVOCs) should be more important as the precursors of SOA during winter compared with summer" was made by this study rather than previous ones. This conclusion was based on Cheng et al. (2011, AE) who found that the contribution of SOA to OA was comparable during winter and summer in Beijing, and Wang et al. (2003, AE) who found that the emission of biogenic volatile organic compounds (BVOCs) was about 1000 times lower during winter compared with summer. To our knowledge, this conclusion has not been pointed out directly by previous literatures.

(10) Line 482: In the section of Implications, more information about radiative forcing and climate change should be discussed coupled with the present data.

Our responses: Based on the present data, we still can not estimate the contribution of brown carbon to radiative forcing and climate change. As a result, we prefer to discuss this in the Introduction section. As mentioned in the Introduction section, absorption of ultraviolet (UV) light by brown carbon is important since UV irradiance significantly affects the tropospheric ozone production and photochemistry. Moreover,

a significant fraction of brown carbon is water-soluble. Thus, dissolution of brown carbon into cloud droplets could result in homogeneous absorbing droplets that affect the overall cloud absorption, especially in the UV range, indicating that brown carbon might have important influence on climate. **(See Line 109-115)**

(11) Captions of Table and Figure were not normative. Please overwrite it.

Our responses: We have made sure that all of the captions are normative.

2. Comments of reviewer #2:

This manuscript quantifies the mass absorption efficiency (MAE) of EC in Beijing using a DRI carbon-analyzer. It suggests that MAE of EC is much lower in the regions heavily impacted by biomass burning, based on inter-comparison of MAE values across studies and regions. Moreover, absorption spectral of $PM_{2.5}$ water extracts in Beijing is also presented, and the seasonal variation of MAE of water-soluble organic carbon (WSOC) is attributed to the difference in the precursors of secondary organic aerosol (SOA). In recent years, increasing attention has been paid to the optical properties of ambient aerosol in China, especially with respect to visibility and regional haze. However, optical measurements are still very lacking, and importantly, optical properties of OC has rarely been investigated in China. Thus, this work is important and interesting. It is also a valuable contribution to our understanding about brown carbon. It should certainly be published on ACP after a few points are addressed.

Major comments:

(1) Page 24742. The equivalent MAE values quantified by this study should not be compared with the reference value suggested by Bong and Bergstrom (2006), because the measurements methods are different and the "converting factor" is unknown. As suggested by the authors, optical measurement performed by the carbon analyzer is comparable with Aethalometer. Therefore, the authors should only focus on results from carbon analyzer and Aethalometer.

Our responses: Comparison between equivalent MAE quantified by this study and the reference value suggested by Bong and Bergstrom (2006) was removed in the revised manuscript. And we have made sure that comparison of MAE values was performed only between results from carbon analyzer and Aethalometer.

(2) Figure 3 and Figure 4. The data shown in Figure 3 and Figure 4 seems exactly the same as Table 1. I do not think Figure 3 and Figure 4 provide any useful information in addition to Table1. By the way, their captions are very difficult to follow.

Our responses: Figure 3 and Figure 4 were removed in the revised manuscript. Instead, frequency distribution of the MAE values of the two groups were introduced to illustrated the influence of biomass burning. This has been explained in detail in

our response to the second major comment from Reviewer#1. **(See Figure 3 in the revised manuscript)**

(3) Page 24745. The authors discussed too much about biomass burning in Beijing. Though several representative literatures are cited, disappointedly, it only concluded than the contribution of biomass burning to Beijing aerosol is still high uncertain. These discussions should be more brief or totally removed if the authors can not provide solid evidence for the influences of biomass burning on the MAE of WSOC.

Our responses: A recent literature was added to clearly illustrate the influences of biomass burning on the MAE of WSOC. Effects of biomass burning on the MAE of WSOC could be illustrated by results from the southeastern United States. Hecobian et al. (2010) found that the MAE of WSOC (measured at 365nm using the same method as used in this study) were 0.31±0.07 m^2/g for the urban sites of the southeastern United States when the contribution of biomass burning was not important (identified by levoglucosan <50 ng/m^3, typically in the summer), whereas the MAE averaged 0.70±0.07 m^2/g when the influence of biomass burning was significant (identified by levoglucosan >50 ng/m^3, typically in the winter). On the other hand, Sun et al. (2011) compared the results from High-Resolution Time-of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and Gas Chromatography-Mass Spectrometry (GC-MS), and found that the mass spectra of WSOC collected in the southeastern United States was characterized by a less oxidized component associated with biogenic SOA and a more oxidized component associated with biomass burning. Moreover, the less oxidized component accounted for 75% of WSOC in summer while the more oxidized component accounted for 78% in winter, suggesting that WSOC in the southeastern United States is primarily contributed by SOA in summer and by biomass burning in winter. These results indicate that WSOC emitted from biomass burning is more light-absorbing compared with that formed by atmospheric reaction. **(See Line 427-442)**

Moreover, the contribution of biomass burning to Beijing aerosol is discussed more briefly. We only stated that both the ambient concentration of levoglucosan (the levoglucosan concentration was above 100 ng/m^3 all year round in Beijing; Zhang et al., 2008) and emission inventory (Bond et al., 2004) demonstrated that biomass burning emission is much higher in China compared with America, which is a likely cause of the much higher MAE value in Beijing (0.70~1.83 m^2/g) compared with the southeastern United States (0.31~0.70 m^2/g). We also clearly pointed out that biomass

burning may be also responsible for the seasonal variation of the MAE of WSOC in Beijing. **(See Line 442-453)**

Specific comments:

(4) Page 24730, what does Rabs mean?

Our responses: R_{abs} refers to the ratio of b_{abs} measured by PSAP to that measured by the PAS. Discussions on the ratio were presented in another way to avoid misunderstanding. **(See Line 75-80)**

(5) Page 24731, HULIS is another typical kind of brown carbon. It should also be included. And it is not necessary to introduce tar balls in such a detail.

Our responses: HULIS was added in the revised manuscript. And detailed introduction to tar balls was removed. **(See Line 104-107)**

(6) Page 24733, the discussion about selecting of EC method should be more brief, because it is not the focus of this study.

Our responses: Selecting of EC was presented more briefly: "The IMPROVE (the Interagency Monitoring and Protective Visual Environmental)-A temperature protocol was implemented in the present study, because it can avoid the loss of native EC in the inert mode as compared with NIOSH (National Institute for Occupational Safety and Health) or similar protocols (Cheng et al., 2010). EC was defined as the carbon evolved after the filter transmittance (monitored at 632nm) returned to its initial value in the oxidizing atmosphere (He/O_2). The transmittance charring correction was implemented because the optical attenuation (ATN) is calculated based on the transmittance signal." **(See Line 163-170)**

(7) Page 24746, the conclusion is too long. For example, seasonal variation of BVOCs should be removed.

Our responses: In the revised manuscript, detailed information in the conclusion section (e.g., the seasonal variation of BVOCs) was removed to make it briefer. **(See Conclusion section)**

(8) Figure 6, uncertainties of regression should be presented.

Our responses: Uncertainties of regression was added as suggested. **(See Figure 6)**