

Manuscript number: acp-2011-70

Title: Optical properties of elemental carbon and water-soluble organic carbon in Beijing, China

Many thanks to the anonymous referees for their valuable comments and suggestions on our submitted paper. We have considered the points raised and revised our manuscript accordingly. In the revised manuscript, the discussion about coating, which invites the most significant challenge, was removed; the method that using the carbon analyzer to quantify the MAC of EC was more carefully evaluated; substantial information, including a paragraph, two figures and a supplement, were added to make the readers more easily understand the “equivalent MAC”; influence of brown carbon on the MAC of EC was more carefully assessed; a new section was included to illustrate the implications of the present study. We are now detailing our responses and the changes that we have made.

### **1. Comments of reviewer #1:**

The manuscript by Cheng et al. attempts to use observations of light absorption, made using a filter-based Aethelometer method, and elemental carbon concentrations, made using a thermal-optical method, to assess how coatings influence the light absorption by EC particles. They also use extracts of WSOC to determine absorption properties of the WSOC. Finally, they attempt to take disparate measurements of absorption and [EC] (reported as the mass absorption coefficient), correct them all to a common basis, and make comparisons between MAC values determined in different regions.

My assessment is that this paper should be rejected. Firstly, it is extremely difficult to follow what they are comparing to what when it comes to the MAC values for EC because so many corrections have been applied AND they have a tendency to intermix discussion of uncorrected and corrected MAC values. Secondly, and most importantly, there are some fundamental mis-understandings related to aerosol optical properties and their measurement, which will be detailed below.

**(1)** The authors appear to be conflating intensive and extensive properties. The influence of coatings on MAC is an intensive property, whereas absolute concentrations are extensive properties. It only makes sense to plot e.g. the MAC vs.

sulfate if one knows for certain that the [EC] is constant while sulfate varies (thus changing the coating thickness). Here, the requirement to turn correlation into causation has not been met. The authors should look at the recent review of “Time-resolved measurements of black carbon light absorption enhancement in urban and near-urban locations of Southern Ontario, Canada” by “Anonymous Referee #2”, available at <http://www.atmos-chemphys-discuss.net/10/19939/2010/acpd-10-19939-2010-discussion.html>.

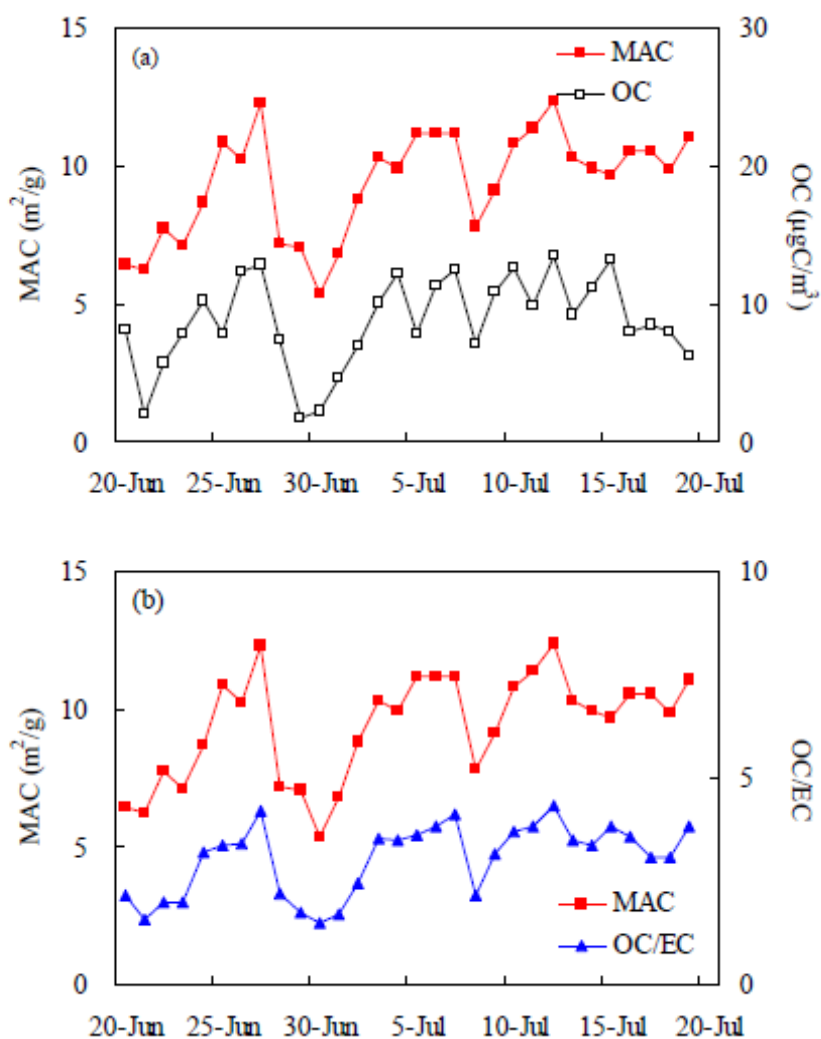
(2) Absorption enhancements don't just shut-off at high coating thicknesses. There is a continuum. If the authors want to argue that the low vs. high sulfate dependence is a result of Mie theory and is “consistent with Bond et al. (2006)”, then they need to provide supporting calculations. However, they can't do this because they don't know the fundamental size of their BC particles. Core size has a direct impact on the potential magnitude of the absorption enhancement.

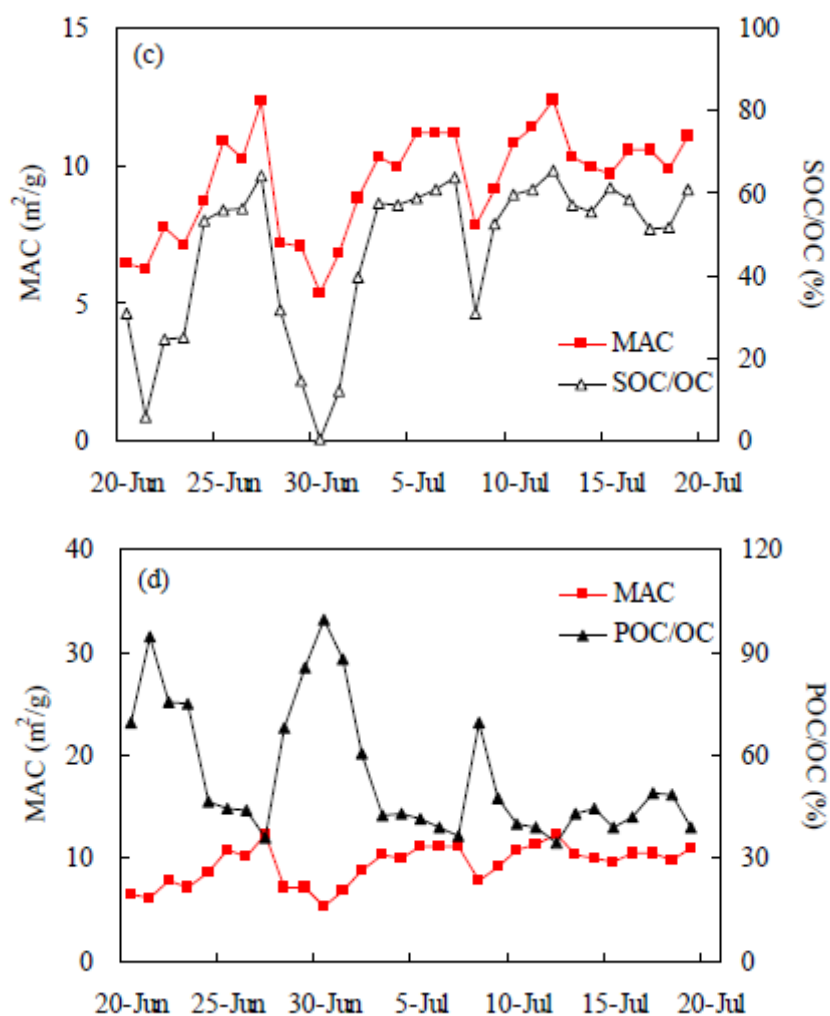
(3) Have the authors read Lack et al. (2008) and Cappa et al. (2008)? These are not cited, yet should be, as these works call into question much of the presented analysis related to MACs for EC. Essentially, these works suggest and show that filter based methods are (very likely) incapable of determining absorption enhancements due to inherent biases in filter based methods. The authors should pay particular attention to Figure 4a and 4b in Lack et al. (2008) and how they relate to Figure 3 here. Granted, the Lack et al. and Cappa et al. results were done using a PSAP, not an Aethelometer, but the issues discussed are general to all filter based absorption measurements. In light of these works, the authors need to convince the reader (and reviewer) that their methods are not similarly biased. This will not be an easy task and, in my estimation, will ultimately preclude any analysis of the type presented here.

**Our response:** The first three comments are about our discussion on coating. We agree with the reviewer that we can not absolutely attribute the observed variation of MAC to the influence of coating with OA/sulphate, because artifacts resulting from the redistribution of liquid-like organic particles during the filter-based absorption measurements maybe also responsible for the observed variation. As a result, we removed all of the discussion on coating in the revised manuscript.

We also agree with the reviewer that it only makes sense to plot the MAC vs. sulphate (or OA) if one knows for certain that the EC is constant while sulphate (or

OA) varies (thus changing the coating thickness). In the revised manuscript, we plotted the MAC vs. the sampling date to illustrate its daily variation; and we only stated that “the daily pattern of MAC seemed to coincide with the OC abundance, especially the OC to EC ratio (Figure 1 (a) ~ (b))”. Based on the SOC and POC concentrations predicted by the EC-tracer method (Cheng et al., 2011), we also found that the daily pattern of MAC coincided well with that of SOC to OC ratio, whereas no correlation between MAC and POC to OC ratio was seen (Figure 1 (c) ~ (d)). Finally, it was hypothesized that the agreement between the daily pattern of MAC and OC abundance may be caused by the artifacts resulting from the redistribution of liquid-like organic particles during the filter-based absorption measurements (Cappa et al., 2008; Lack et al., 2008), which include (1) a physical change in the shape of the liquid-like organic particles (presumably oxidized) as they deposit and then coat the filter fibers, and (2) the possible coating of pre-existing absorbing particles with the liquid-like organic particles during sampling.





**Figure 1.** Daily variation of MAC in Beijing during summer. The OC concentration (a), the OC to EC ratio (b), the percentage of SOC in OC (c), and the percentage of POC in OC (d) are also shown for comparison.

(4) Why are the authors even presenting uncorrected MAC values? This is confusing/misleading, making the apparent MAC values seem much larger than they actually are. As the authors state, “the unrealistically high values of MAC in Table 1 are mainly due to the artifacts associated with the “filter-based” methods...” If this is true, then these results are meaningless and should not be presented in a table unless the “corrected” values are given right in a column next to them. In other words, Equation 3 should have as part of it a correction for the absorption. Certainly, the uncorrected MAC values should not be presented in the abstract!

**Our response:** Only corrected MAC values were presented throughout the revised manuscript. The correction procedure was described in the Method section (Section 2.2.1):

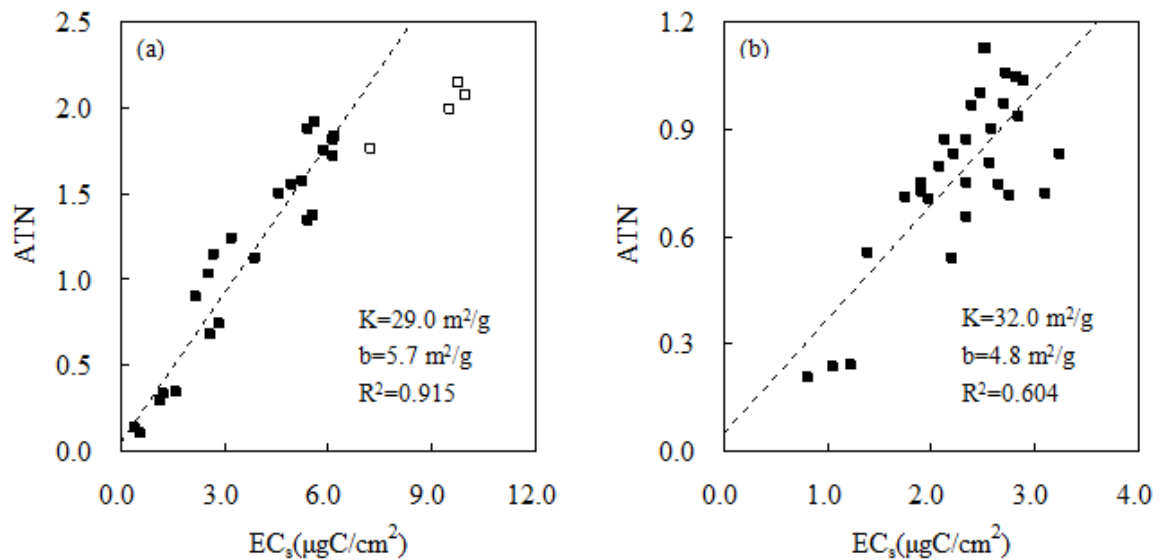
Uncorrected MAC is calculated as:

$$\text{MAC}(\text{m}^2/\text{g}) = \frac{b_{\text{abs}}}{\text{EC}} = \frac{\text{ATN} \times A}{\text{EC} \times V} = \frac{\text{ATN}}{\text{EC}_s} \times 10^2 \quad (1)$$

where  $\text{EC}_s$  ( $\mu\text{gC}/\text{cm}^2$ ) is the filter loading of EC. Among the artifacts associated with the filter-based measurement of absorption, the multiple scattering effects have been typically corrected by an empirical correction factor,  $C$ . In the present study, MAC calculated by Equation (1) was divided by a value of  $C=3.6$ , as suggested by Weingartner et al. (2003) for the internally mixed aerosol:

$$\text{MAC}_{\text{corrected}}(\text{m}^2/\text{g}) = \frac{\text{MAC}}{3.6} = \frac{\text{ATN}}{\text{EC}_s} \times 10^2 \times \frac{1}{3.6} \quad (2)$$

All the MAC values presented in the present study have been corrected for the multiple scattering effects using Equation (2). Another artifact associated with the filter-based method is the shadowing effect, which could partially be identified by the dependence of ATN on EC loading ( $\text{EC}_s$ ). As shown in Figure 2, during the winter, ATN and  $\text{EC}_s$  correlated well ( $R^2=0.915$ ) with a slope of  $29.0 \text{ m}^2/\text{g}$  and an intercept of  $5.7 \text{ m}^2/\text{g}$  when the  $\text{EC}_s$  was below  $7 \mu\text{gC}/\text{cm}^2$ , whereas the linearity did not extend for  $\text{EC}_s$  exceeding  $7 \mu\text{gC}/\text{cm}^2$  indicating the presence of shadowing effect. During the summer,  $\text{EC}_s$  was much lower (below  $4 \mu\text{gC}/\text{cm}^2$ ), and the shadowing effect was not identified. As a result, winter samples with  $\text{EC}_s$  exceeding  $7 \mu\text{gC}/\text{cm}^2$  were not included when calculating the MAC value by Equation (2).



**Figure 2.** Dependence of light attenuation measured at 632nm (ATN) on the EC loading ( $\text{EC}_s$ )

during winter (a) and summer (b) respectively. Linear regression results are shown with K as the slope and b as the intercept. Data points with  $EC_s$  exceeding  $7\mu\text{gC}/\text{cm}^2$ , as shown by the open squares, indicated presence of the shadowing effect.

(5) It might be that the authors have been able to “correct” for differences in [EC] between different TO protocols, but they give no discussion of how different studies may/may not have accounted for biases in the absorption measurements used to determine the MAC. Note that some of the studies listed in Table 1 used an Aethelometer (as in this study), but others apparently derived absorption from the TOT measurement itself. No discussion at all was given as to how these TOT absorbances should/could be corrected. In other words, although the authors may have been able to make the [EC] from different studies “equivalent”, they have in no way made the absorptions “equivalent”, thus invalidating their global analysis of variability in MACs.

**Our response:** With respect to the absorption measurements performed by the carbon analyzer and Aethalometer, we mainly focused on the measurement wavelength in our converting approach. In fact, the determination of ATN in the carbon analyzer is similar to that used in the Aethalometer, which simultaneously measures light passing through a loaded and a particle-free reference quartz filter. Moreover, the equivalence between ATN retrieved from the carbon analyzer and that measured by the Aethalometer (when both the particle loading and the measurement wavelength were the same) has been demonstrated (Ram and Sarin, 2009). The discussion above indicates “ATN retrieved from the carbon analyzer can be used to determine the absorption coefficient ( $b_{\text{abs}}$ ) of the loaded aerosol by the same approach as used in the Aethalometer, which is calculated as:  $b_{\text{abs}}(\text{Mm}^{-1}) = \text{ATN} \times \frac{A}{V}$ , where A is the filter area with particle loading ( $\text{mm}^2$ ) and V is the volume of air sampled ( $\text{m}^3$ )”. Moreover, this is also the reason why we compared MAC values quantified by the carbon analyzer with those based on Aethalometer rather than those based on other optical equipments such as PSAP and MAAP.

(6) There are large enough differences in the sources of biomass burning aerosol between the seasons to make the contention that the difference in the MAC for WSOC between the seasons arises from differences in anthropogenic vs. biogenic SOA

untenable.

**Our response:** We attributed the observed seasonal pattern of the MAC of WSOC to the difference in the precursors of SOA, because WSOC in Beijing has been demonstrated to be strongly linked to SOA.

In a previous study based on the same samples as used in the present one, we found that WSOC correlated well ( $R^2=0.84\sim 0.94$ ) with the secondary organic aerosol (SOA) predicted by the EC-tracer method, indicating a substantial fraction of WSOC is SOA in Beijing; moreover, we found the estimated SOA accounted for about 40 and 50% of organic aerosol (OA, measured by the denuded quartz filter) during winter and summer respectively, suggesting considerable SOA production despite the low temperature in winter. Importantly, the emission of biogenic volatile organic compounds (BVOCs) in Beijing showed a distinct seasonal pattern such that the emission of biogenic volatile organic compounds (BVOCs) in Beijing was approximately 1000 times lower during winter compared with summer (Wang et al., 2003), indicating anthropogenic volatile organic compounds (AVOCs) should be more important as the precursors of SOA during winter compared with summer. As a result, it was hypothesized that the difference in the precursors of SOA is a most likely cause of the discrepancy in the MAC of WSOC during winter and summer.

We agree with the reviewer that the influence of biomass burning might also contribute to the observed seasonal pattern of the MAC of WSOC. However, the biomass burning contribution and its seasonal pattern is still highly uncertain for the Beijing region. For example, if using the levoglucosan to OC ratio as an indicator of the biomass burning contribution, results from He et al. (2006) and Zhang et al. (2008) indicated the biomass burning contribution was comparable during winter and summer, whereas results from Wang et al. (2009) indicated the biomass burning contribution was larger in winter comparing with summer. As a result, we do not conclude whether the contribution of biomass burning contributes to the seasonal variation of MAC of WSOC in Beijing.

(7) Section 3.1: Two fundamental over-(mis-) interpretations here. (1) The authors cannot simultaneously argue for such a large MAC while suggesting that the MAC can be determined from a linear fit to ATN vs. [EC]. The coating thickness may vary for each point, making the single point MAC very different from the average. Further, it is not unreasonable to think that [EC] may be correlated with coating thickness (more emissions = greater potential for coatings). Are the authors arguing that the

coating thickness is always the same? (2) Just because there is an intercept close to zero does not indicate that EC was the major light-absorbing component, as stated. It is entirely possible (in fact, probable) that [EC] is correlated with brown carbon, and thus as [EC]  $\rightarrow$  0, so would [brown carbon].

**Our response:** The MAC value was quantified by Equation (2) described above for each sample in the revised manuscript. The dependence of ATN on EC loading was only used to identify the shadowing effect. Moreover, the discussion about the intercept of linear regression between ATN and EC loading was removed.

(8) Section 3.2 (1): Although I see some value in converting different thermal EC measurements to a common basis, what is really needed (if the authors are to truly be quantitative with regards to their MAC results) is a way to put the measurements on an absolute basis. Simply referencing one (potentially wrong) measurement to another (potentially wrong) measurement does not make either correct. By converting measurements to “equivalent” MAC values, are the authors implicitly arguing that the method they used is the best, i.e. most accurate? This would seem to be their argument, since they go on to do quantitative analysis, but they do not state this. Additionally, the variability about any of the conversion factors is so large that such conversion has significant uncertainty. This is partially reflected in the range of values given in Table 1 for “equivalent” MAC values, but it is not clear why only some values have an upper and lower bound while others have only an upper bound.

**Our response:** We agree with the reviewer about the benefits and importance of standardized methods for the EC concentration. However, it is still impossible at present that all of the investigators perform the OC and EC analysis using a same method; this is also the reason why we developed the converting approach that accounts for the influence of measurement methods on the MAC of EC. Evaluation of the thermal-optical methods has long been investigated; however, this topic still invites lively debate up to now. Based on our previous studies on the thermal-optical method (Cheng et al., 2010, 2011), we do think that the method used in the present study (IMPROVE-A temperature protocol with transmittance charring correction) is more reliable. We explained the reasons in detail in the revised manuscript. Briefly, the IMPROVE-A temperature protocol was implemented to avoid the premature evolution of light-absorbing carbon (including both native EC and pyrolyzed OC); the transmittance correction was used because we have demonstrated that the SOA



concentrations predicted based on the transmittance-defined OC and EC values were more reliable.

We admit that the variability of the converting factors for the temperature protocol and charring correction method is a little large, which should be due to the complex influences of the aerosol composition and sources. The relative large variability also indicates the benefits and importance of standardized methods for the EC concentration.

To make the readers more easily understand how the “equivalent MAC” values were calculated, **(i)** we added a new paragraph describing the whole converting approach and the range/value of each factor: After incorporating the EC method conversion and the wavelength measurement correction, the whole converting approach to calculate the “equivalent MAC” from reported values is:

$$\text{equivalent MAC} = \text{MAC}_\lambda \times \frac{f_{\text{charring}}}{f_{\text{protocol}}} \times \left( \frac{\lambda}{632} \right)^A \quad (3)$$

$f_{\text{charring}}$  is the converting factor of charring correction method.  $f_{\text{charring}} = 1.3 \sim 1.8$  for the reported MAC in which EC was determined by the IMPROVE (or IMPROVE-A) temperature protocol with reflectance correction.  $f_{\text{protocol}}$  is the converting factor of temperature protocol. With respect to the reported MAC in which EC was determined by the NIOSH temperature protocol with transmittance correction,  $f_{\text{protocol}} = 1.2 \sim 1.5$  if the reported MAC was measured in North America or Europe (including that measured during the heating or wood burning season), whereas  $f_{\text{protocol}} \geq 1.5$  if the reported MAC was measured in Asia.  $\lambda$  is the wavelength at which the reported MAC is measured.  $A$  is the Ångström exponent.  $A = 2$  if the reported MAC was measured during the period or in the region that impacted by biomass burning; in other cases, it is assumed that  $A = 1$ . **(ii)** We also added a table in the Supporting Information that illustrating the detailed procedure of calculating the “equivalent MAC” for each location (Table 1).

**Table 1.** The detailed procedure of calculating the “equivalent MAC” for each location.

Sampling site	Methods of $b_{\text{abs}}$	Methods of EC	Reported MAC	Converting factors used in Equation (11) <sup>a</sup>				Equivalent MAC		
				$f_{\text{charring}}$	$f_{\text{protocol}}$	$\lambda$	A	Range of the whole converting factor <sup>b</sup>	Lower	Upper
<i>Group 1</i>										
Philadelphia, PA	Aethalometer	NIOSH (TOT)	16.6	1	1.2~1.5	880	1	0.93~1.16	15.4	19.3
Riverside, CA	Aethalometer	IMPROVE (TOR)	4.4	1.3~1.8	1	880	1	1.81~2.51	7.9	11.0
New York	Aethalometer	NIOSH (TOT)	9.2	1	1.2~1.5	880	1	0.93~1.16	8.6	10.7
Chicago, IL	Aethalometer	IMPROVE (TOR)	4.0	1.3~1.8	1	880	1	1.81~2.51	7.3	10.1
Phoenix, AZ	Aethalometer	IMPROVE (TOR)	3.8	1.3~1.8	1	880	1	1.81~2.51	6.8	9.4
Bakersfield, CA	Aethalometer	IMPROVE (TOR)	3.3	1.3~1.8	1	880	1	1.81~2.51	6.0	8.3
Dallas, TX	Aethalometer	IMPROVE (TOR)	3.3	1.3~1.8	1	880	1	1.81~2.51	5.9	8.2
Philadelphia, PA	Aethalometer	IMPROVE (TOR)	3.3	1.3~1.8	1	880	1	1.81~2.51	5.9	8.2
Uniontown, PA	Aethalometer	IMPROVE (TOR)	5.0	1.3~1.8	1	530	1	1.09~1.51	5.5	7.6
New York	Aethalometer	NIOSH (TOT)	6.4	1	1.2~1.5	880	1	0.93~1.16	6.0	7.5
Evans, Canada	Aethalometer	MSC (TOT)	2.6	(1.3~1.8) × 1.09	1	880	1	1.97~2.73	5.2	7.2
Scotland, UK	Aethalometer	NIOSH (TOT)	6.1	1	1.2~1.5	880	1	0.93~1.16	5.7	7.1
Atlanta, GA	Aethalometer	NIOSH (TOT)	5.7	1	1.2~1.5	880	1	0.93~1.16	5.3	6.6
Toronto, Canada	Aethalometer	NIOSH (TOT)	5.5	1	1.2~1.5	880	1	0.93~1.16	5.1	6.4
Durham, NC	Aethalometer	NIOSH (TOT)	5.4	1	1.2~1.5	880	1	0.93~1.16	5.0	6.3
Egbert, Canada	Aethalometer	IMPROVE (TOR)	2.4	1.3~1.8	1	880	1	1.81~2.51	4.4	6.1
Riverside, CA	Aethalometer	NIOSH (TOT)	5.1	1	1.2~1.5	880	1	0.93~1.16	4.8	6.0
Palmerston, Canada	Aethalometer	MSC (TOT)	2.1	(1.3~1.8) × 1.09	1	880	1	1.97~2.73	4.1	5.7

*Group 2*

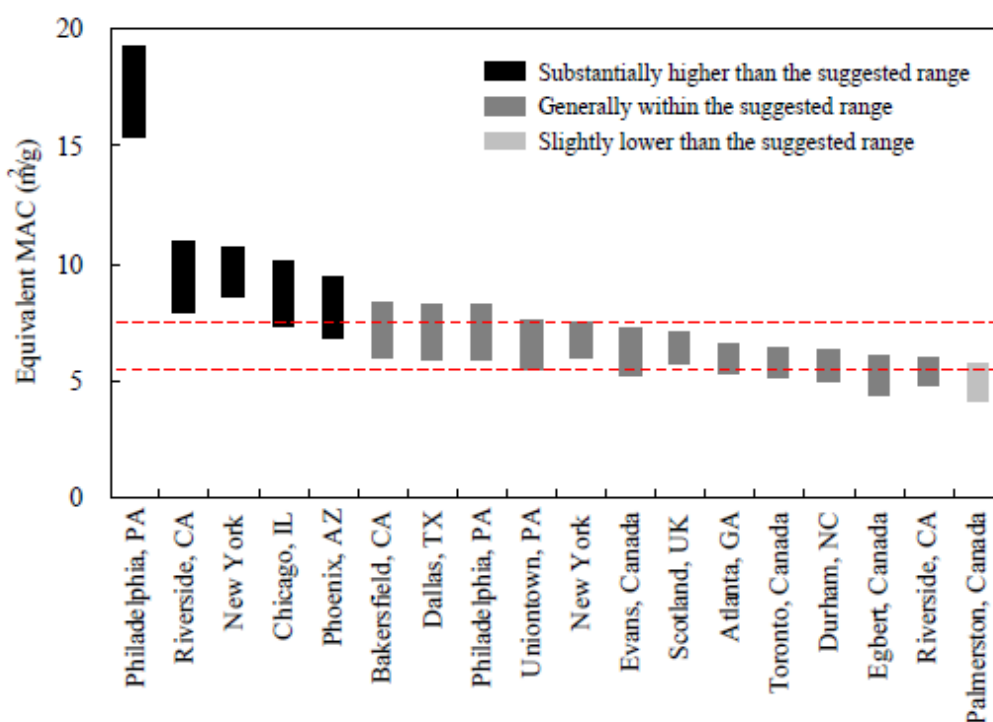
Beijing, China	DRI analyzer	IMPROVE-A (TOT)	9.4	—	—	—	—	—	—	—
Beijing, China	DRI analyzer	IMPROVE-A (TOT)	8.5	—	—	—	—	—	—	—
Lahore, Pakistan	Aethalometer	NIOSH (TOT)	5.8	1	$\geq 1.5$	880	2	$\leq 1.29$	n.a.	7.5
Lycksele, Sweden	Aethalometer	NIOSH (TOT)	3.7	1	1.2~1.5	880	2	1.29~1.62	4.8	6.0
Manora Peak, India	Sunset analyzer	NIOSH (TOT)	6.9	1	$\geq 1.5$	678	2	$\leq 0.77$	n.a.	5.3
Mt. Abu, India	Sunset analyzer	NIOSH (TOT)	4.6	1	$\geq 1.5$	678	2	$\leq 0.77$	n.a.	3.5
Hisar, India	Sunset analyzer	NIOSH (TOT)	3.6	1	$\geq 1.5$	678	2	$\leq 0.77$	n.a.	2.7
Allahabad, India	Sunset analyzer	NIOSH (TOT)	3.1	1	$\geq 1.5$	678	2	$\leq 0.77$	n.a.	2.4
Philadelphia, PA	Aethalometer	NIOSH (TOT)	1.6	1	1.2~1.5	880	2	1.29~1.62	2.1	2.6

Note:

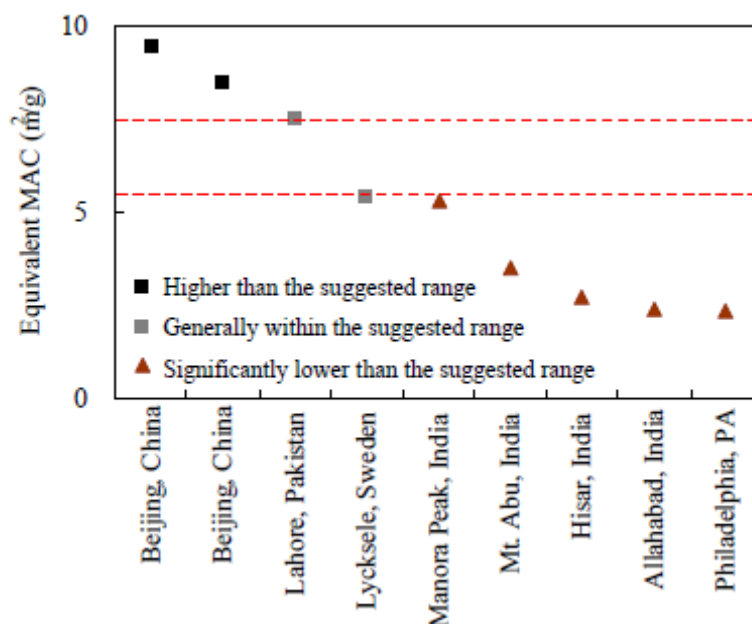
<sup>a</sup> The whole converting approach (Equation 3) is: equivalent  $MAC = MAC_{\lambda} \times \frac{f_{\text{charring}}}{f_{\text{protocol}}} \times \left( \frac{\lambda}{632} \right)^A$ .

<sup>b</sup> The whole converting factor indicates  $\frac{f_{\text{charring}}}{f_{\text{protocol}}} \times \left( \frac{\lambda}{632} \right)^A$  in Equation 3.

(iii) We added two figures presenting the “equivalent MAC” values. In the revised manuscript, the “equivalent MAC” values shown in Table 1 were classified into two groups. The first group includes most of the results from North America and Europe, in which the “equivalent MAC” values were between 4~11 m<sup>2</sup>/g except an extremely high value (15~19 m<sup>2</sup>/g) measured in Philadelphia, PA during severe sulphate haze episodes occurred in the summer of 2002 (Figure 3). The second group comprises results from Asia and those measured in North America and Europe during the periods impacted by biomass burning; in this group, the “equivalent MAC” were between 2~9 m<sup>2</sup>/g (Figure 4). Comparing with the first group, the most noticeable feature of the second group was that several “equivalent MAC” values were significantly lower than that of uncoated elemental carbon suggested by Bond and Bergstrom (2006), such as those measured in four Indian cities and measured in Philadelphia, PA during a Canadian forest fire event (Figure 4). The much lower “equivalent MAC” values were attributed to the influence of brown carbon.



**Figure 3.** The “equivalent MAC” of the first group in Table 1. The boundary of the box closest to zero indicates the lower estimate of the “equivalent MAC”, whereas the boundary farthest from zero indicates the upper estimate. The red dashed line indicates the range (5.5~7.5 m<sup>2</sup>/g) suggested by Bond and Bergstrom (2006).



**Figure 4.** The “equivalent MAC” of the second group in Table 1. The values shown for Beijing, China were quantified by the present study (the summer result is shown first, followed by the winter result); and the “equivalent MAC” was the same as the un-converted value. The values shown for Lycksele, Sweden and Philadelphia, PA were average of the lower and upper estimate of the “equivalent MAC”, whereas the values shown for Lahore, Pakistan and the four Indian sites were the upper estimate. The red dashed line indicates the range (5.5~7.5 m<sup>2</sup>/g) suggested by Bond and Bergstrom (2006).

(9) Section 3.2 (2): The authors discuss how brown carbon is important in their region of measurement. Yet they adjust everything to 632 nm (which is seemingly randomly chosen) using an Angstrom exponent of 1. I don’t see how this is self-consistent.

**Our response:** We adjusted the Ångström exponent (A) used in the converting approach. Then the MAC measured at a given wavelength (MAC<sub>λ</sub>) was converted to that measured at 632 nm (MAC<sub>632</sub>) by the following equation:

$$MAC_{632} = MAC_{\lambda} \times \left( \frac{\lambda}{632} \right)^A \quad (4)$$

Kirchstetter et al (2004) found that light absorption by the motor vehicle aerosols (roadway and tunnel samples) exhibited relatively weak wavelength dependence such that absorption varied approximately as  $\lambda^{-1}$ , whereas the biomass smoke aerosols (produced by wood and savanna burning) had much stronger wavelength dependence, approximately  $\lambda^{-2}$ . Schnaiter et al (2003) also suggested a value of 1.056 for the Ångström exponent of diesel soot. Comparably, results quantified by the electron energy-loss spectrum in the transmission electron microscope showed that the

Ångström exponent of ambient soot and “tar balls” (a typical type of brown carbon) was about 1 and 1.5 respectively (Alexander et al., 2008). When performing the wavelength correction by Equation (4), a value of Ångström exponent=2 was used in the present study if the reported MAC was measured during the period or in the region that impacted by biomass burning; in other cases, we assumed the Ångström exponent was 1.

(10) Table 1: Although I am not convinced that the “charring” and “temperature” protocol corrections are likely to give robust results, the authors should nonetheless include the exact values used for each location in Table 1 so that the reader can understand exactly what correction has been done. From the text alone it is a bit confusing.

**Our response:** As mentioned above, we added a table in the Supporting Information that illustrating the detailed procedure of calculating the “equivalent MAC” for each location.

(11) Equation 12: “f” is not defined. Further, the “f” values that are referenced come from an entirely different study and are almost definitely going to differ depending on the type of aerosol being sampled. Thus, they are not applicable to this study. The authors should be able to use the same methods as Sandradewi et al. (2008) to determine their own “f” values. Further, the R(ATN) factor depends on the current ATN, which is not a constant (as implied) and depends on how long the system has been operating and what the current loading is. That the authors give  $C \times R(ATN)$  as a constant suggests a fundamental mis-understanding of how the correction is supposed to work.

**Our response:** As mentioned in our reply to comment (4), we have adjusted the procedure correcting the artifacts associated with filter-based measurement of absorption. Briefly, the multiple scattering effects were corrected by an empirical correction factor of 3.6; and the shadowing effect was avoided based on the dependence of ATN on EC loading. The R(ATN) factor (which was used to correct the shadowing effect) was not included in the adjusted procedure, because we can not determine our own f factors using a carbon analyzer.

(12) P. 6236, Line 1: I do not see why it matters whether the OC is POC or SOC. The only thing that should matter is how much OC is internally mixed with the EC.

**Our response:** This comment was about our interpretation when discussing the influence of coating on the MAC of EC. As mentioned in our reply to comment (1) ~ (3), all of the discussion about coating were removed in the revised manuscript.

(13) P. 6236, Line 7: The relationship between MAC and OC/EC does NOT provide “important information about the extent of secondary organic aerosol (SOA) production.” See point 3 above. Also, there is no Figure 3b in Cheng et al., 2011. Do the authors mean to refer to their own figure in this manuscript?

**Our response:** This comment was also about our interpretation when discussing the influence of coating on the MAC values. In fact, what we want to say is “the OC to EC ratio provides important information about the extent of secondary organic aerosol (SOA) production”. This misunderstanding was avoided in the revised manuscript.

(14) P. 6237, Line 6: The authors state, without proof “the presence of brown carbon would not significantly influence the value of ATN, which is usually measured at wavelengths greater than 500nm.” Brown carbon may indeed absorb at wavelengths above 500 nm. When they say “greater than”, what do they mean? 501 nm? 900 nm? It matters. Also, the authors misunderstand the (potential) impact of brown carbon on the MAC. If brown carbon is not measured as EC, then any absorption at all by brown carbon for a fixed amount of EC will increase the MAC, not decrease it, unless of course brown carbon is identified as EC in the TO method. But if this is the case, then the EC measurement should not be used for this analysis in the first place.

**Our response:** We re-wrote this part according to the comment. First, we clearly stated that a substantial fraction of brown carbon would be classified as EC: “Reisinger et al. (2008) and Wonaschütz et al. (2009) found that thermal-optical method significantly overestimated EC concentration when the contribution of brown carbon was important, indicating a substantial fraction of brown carbon was classified as EC”. Second, we clearly stated that brown carbon is less absorbing comparing with native EC: “On the other hand, brown carbon is less absorbing comparing with native EC. For example, the MAC of “tar balls” (a typical type of brown carbon) and soot was estimated to be 3.6~4.1 and 4.3~4.8 m<sup>2</sup>/g respectively (Alexander et al., 2008)”. Finally, we suggested that brown carbon is expected to decrease the value of MAC, and pointed out that this hypothesis was further supported by results from Philadelphia, PA such that the “equivalent MAC” was only 2.1~2.6 when heavily impacted by biomass burning (Jeong et al., 2004).

(15) I believe that in Equation 3, it should be delta ATN, not ATN.

**Our response:** We have checked the equation, and confirmed that it should be ATN rather than delta ATN.



## 2. Comments of reviewer #2:

Optical properties of elemental carbon and water-soluble organic carbon in Beijing, China by Cheng et al. provides an estimate of mass absorption cross section (MAC) of elemental carbon sampled in Beijing. Their approach is to divide the absorption coefficient by the mass, both derived from filter-based measurements.

I recommend rejection, for the lack of proper evaluation of the uncertainty in their absorption measurement. Light absorption by atmospheric particles is notoriously difficult to measure. Filter based instruments are typically confronted by two factors – changes in physical properties upon deposition and interference of light scattering. Efforts have been made over more than a decade to confine these effects (Bond et al., 1999; Lack et al. 2008; Virkkula 2010). These studies all find that the effects are significant and require adjustment of the obtained data. The present study neglects all these efforts. It employs a DRI Model 2001 thermal/optical carbon analyzer (Atmosphytic Inc., Calabasasa, CA), an instrument not tested in the previous studies listed above. The present study does not include, or refer to, an evaluation of the performance of this instrument.

In Section 3.2 the authors develop an approach “to account for the discrepancy caused by measurements methods of both ATN and ECs”. However, the two factors I raised above are not addressed. “transmittance correction” mentioned in Section 3.2 (2) Wavelength measurement correction may be meant to address the scattering interference, one of the two factors. If so, this mention should have been accompanied by a proper explanation and/or reference, in a subsection separate from that of wavelength adjustment.

I encourage the authors to carefully assess the quality of the measured absorption coefficient, before discussing its ratio to the particle mass.

**Our response:** We revised the section (2.2.1) which introduces the method that is used to quantify the MAC of EC. We added new results and discussion about the evaluation of our method. Following are the changes that we have made:

(1) We added the ATN values of blank filters (averaging  $0.00 \pm 0.01$ ,  $N=30$ ), which demonstrates that the ATN of loaded filter could approximately be attributed to the presence of light-absorbing carbon (the mineral dust is far less absorbing, Yang et al., 2009).

(2) We added results that could demonstrate the precision of our absorption measurement: “ATN calculated agreed well between duplicate analyses with a slope of 0.99 ( $R^2=0.984$ ,  $N=28$ ; intercept was set as zero)”.

(3) We added discussion about the equivalence between optical measurements performed by the carbon analyzer and Aethalometer (when both the particle loading and the measurement wavelength were the same): “The determination of ATN is similar to that used in the Aethalometer, which simultaneously measures light passing through a loaded and a particle-free reference quartz filter. Moreover, the equivalence between ATN retrieved from the carbon analyzer and that measured by the Aethalometer, when both the particle loading and the measurement wavelength were the same, has been demonstrated (Ram and Sarin, 2009).” The added discussion indicates “ATN retrieved from the carbon analyzer can be used to determine the absorption coefficient ( $b_{\text{abs}}$ ) of the loaded aerosol by the same approach as used in the Aethalometer, which is calculated as:  $b_{\text{abs}}(\text{Mm}^{-1}) = \text{ATN} \times \frac{A}{V}$ , where A is the filter area with particle loading ( $\text{mm}^2$ ) and V is the volume of air sampled ( $\text{m}^3$ )”. Moreover, the added discussion is also the reason why we compared MAC values quantified by the carbon analyzer with those based on Aethalometer rather than those based on other optical equipments such as PSAP and MAAP.

(4) We added the approach that is used for correcting the multiple scattering effects: “Among the artifacts associated with the “filter-based” measurement of absorption, the multiple scattering effects have been typically corrected by an empirical correction factor, C. In the present study, MAC was divided by a value of  $C=3.6$ , as suggested by Weingartner et al. (2003) for the internally mixed aerosol”. We also clearly stated that “All the MAC values reported in the present study have been corrected for the multiple scattering effects”.

(5) We added the approach that is used for avoiding the shadowing effect: “Another artifact associated with the filter-based method is the shadowing effect, which could partially be identified by the dependence of ATN on EC loading ( $\text{EC}_s$ )”, “during the winter, ATN and  $\text{EC}_s$  correlated well ( $R^2=0.915$ ) with a slope of  $29.0 \text{ m}^2/\text{g}$  and an

intercept of  $5.7 \text{ m}^2/\text{g}$  when the  $\text{EC}_s$  was below  $7 \text{ }\mu\text{gC}/\text{cm}^2$ , whereas the linearity did not extend for  $\text{EC}_s$  exceeding  $7 \text{ }\mu\text{gC}/\text{cm}^2$  indicating the presence of shadowing effect. During the summer,  $\text{EC}_s$  was much lower (below  $4 \text{ }\mu\text{gC}/\text{cm}^2$ ), and the shadowing effect was not identified. As a result, winter samples with  $\text{EC}_s$  exceeding  $7 \text{ }\mu\text{gC}/\text{cm}^2$  were not included when calculating the MAC values”.

(6) We also added the evaluation of our measurement of EC. We mainly focused on the reasons why the current temperature protocol and charring correction method were used. Briefly, the IMPROVE-A temperature protocol was implemented to avoid the premature evolution of light-absorbing carbon (including both native EC and pyrolyzed OC); the transmittance correction was used because we have demonstrated that the SOA concentrations predicted based on the transmittance-defined OC and EC values were more reliable.

### 3. Comments of reviewer #3:

The manuscript by Cheng et al. reports mass absorption cross-sections for elemental carbon and optical properties of water-soluble organic carbon for data collected in Beijing, China. The authors compare their data with those from other filter-based studies. The issues with filter-based EC measurements are addressed, but the biases with filter-based absorption measurements are not. Lack et al., *Aerosol Science and Technology*, 2008 and Cappa et al., *Aerosol Science and Technology*, 2008 should be referenced and utilized. A thorough description of the absorption measurement and the quality of that measurement should also be discussed. An uncertainty analysis should be included for all measurements. The manuscript also makes some statements that need more clarification and/or support in order to make their conclusions. For these reasons, I am recommending rejection.

(1) Throughout the paper, mass absorption cross-section (MAC), efficiency, and coefficient are all used. I urge the authors to choose one and be consistent throughout.

**Our response:** MAC was used throughout the revised manuscript.

(2) The statements about SOA dominating the OC need to be backed up more with other data and/or intercomparisons.

**Our response:** This comment was about our interpretation when discussing the influence of coating on the MAC values. As mentioned in our response to comment (1) ~ (3) of reviewer #1, the all of the discussion about coating were removed in the revised manuscript.

(3) Only corrected MAC's should be reported. The details of the corrections should be included in the experimental section, but the uncorrected data should not be included in the final tables. Comparisons to other studies should be done using the most standardized method as the reference.

**Our response:** As mentioned in our response to comment (4) of reviewer #1, only corrected MAC values were presented throughout the revised manuscript, and the correction procedure was described in detail in the Method section (Section 2.2.1).

To make the readers more easily understand how the “equivalent MAC” values were calculated when comparing our results to other studies, we added a new paragraph describing the whole converting approach and the range/value of each

factor, and a table in the Supporting Information that illustrating the detailed procedure of calculating the “equivalent MAC” for each location. We also added two figures presenting the “equivalent MAC” values.

(4) The statement about an absorption enhancement by a sulfate coating needs more data to support this statement, e.g., comparison to periods when EC is constant, in order to determine that a correlation between higher EC and sulfate is not the cause of the increased MAC. Further support for coating statements, OC or sulfate, should be supported with data from the denuded vs non-denuded samples if possible.

**Our response:** This comment was also about our interpretation when discussing the influence of coating on the MAC values, which was removed in the revised manuscript.

(5) The details of the high and low bounds for the equivalent MAC’s should be described in more detail in the experimental section.

**Our response:** As mentioned above, we added a new paragraph describing the whole converting approach and the range/value of each factor, a table in the Supporting Information that illustrating the detailed procedure of calculating the “equivalent MAC” for each location.

(6) It is not clear in the method of analysis whether brown carbon is separated from the EC in the absorption measurement, therefore, it is not clear how the data will be biased in the presence of biomass burning. An assessment of brown carbon should also be more carefully addressed, taking into account such findings as were reported in Alexander et al., Science, 2008.

**Our response:** We re-wrote the discussion about how the MAC of EC would be influenced by brown carbon, after considering both this comment and comment (14) of reviewer #1. First, we clearly stated that a substantial fraction of brown carbon would be classified as EC: “Reisinger et al. (2008) and Wonaschütz et al. (2009) found that thermal-optical method significantly overestimated EC concentration when the contribution of brown carbon was important, indicating a substantial fraction of brown carbon was classified as EC”. Second, we clearly stated that brown carbon is less absorbing comparing with native EC: “On the other hand, brown carbon is less absorbing comparing with native EC. For example, the MAC of “tar balls” (a typical type of brown carbon) and soot was estimated to be 3.6~4.1 and 4.3~4.8 m<sup>2</sup>/g

respectively (Alexander et al., 2008)”. Finally, we suggested that brown carbon is expected to decrease the value of MAC, and pointed out that this hypothesis was further supported by results from Philadelphia, PA such that the “equivalent MAC” was only 2.1~2.6 when heavily impacted by biomass burning (Jeong et al., 2004).

(7) Finally, there should also be a discussion comparing filter-based measurements with direct measurements, e.g. Cross et al., ACP, 2009 and Flowers et al., ACP, 2010, and an attempt to clarify the biases and increased uncertainties of purely filter based MAC measurements.

**Our response:** The comparison between direct and filter-based measurements was included in the Introduction section: “results from downtown Toronto showed that the MAC calculated based on Aethalometer was about 2.4 times the value based on photoacoustic spectrometer (PAS) which can measure light absorption directly on airborne particles (Knox et al., 2009). In addition, during the 2006 Texas Air Quality Study/ Gulf of Mexico Atmospheric Composition and Climate Study, it was found that the ratio of  $b_{\text{abs}}$  measured by the Particle Soot Absorption Photometer (PSAP, also a filter-based method) to that measured by the PAS,  $R_{\text{abs}}$ , depended on the abundance of organic aerosol (OA) such that  $R_{\text{abs}}$  increased by about 8% for every  $1 \mu\text{g}/\text{m}^3$  increase in OA; and  $R_{\text{abs}}$  was estimated to be 1.12, 1.40 and 1.69 for rural, urban and heavily polluted regions respectively; moreover,  $R_{\text{abs}}$  was found to correlate more strongly with the OA to BC ratio rather than just OA (Lack et al., 2008). A companion laboratory study also indicated that  $R_{\text{abs}}$  increased with the OA to BC ratio (Cappa et al., 2008).”

That is all of our responses to the comments from referees. We appreciate referees very much for their constructive comments.

Sincerely yours,

Cheng Yuan, and He Ke-bin

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