Atmos. Chem. Phys. Discuss., 13, C6823–C6828, 2013
www.atmos-chem-phys-discuss.net/13/C6823/2013/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Size-resolved measurements of brown carbon and estimates of their contribution to ambient fine particle light absorption based on water and methanol extracts" *by* J. Liu et al.

R. Holzinger (Editor)

r.holzinger@uu.nl

Received and published: 12 September 2013

Dear Authors,

I received a late report from Referee #3 (copied below). Please consider their comments in the revised version of the manuscript.

Sincerely,

Rupert Holzinger

Comments Anonymous Referee #3:

This is a nice paper looking at light absorption by water and methanol extracts of collected filter samples. The authors aim to utilize the size-dependent collection to understand how absorption varies as a function of size and, in particular, estimate particulate absorption from these particles based on Mie theory, which requires particle size. I think that this paper will be publishable, but ask that the authors first address the questions/comments below (given in mostly chronological order, not order of importance).

Line 23: The reference to Gyawali is a bit premature as that reference is (a) only a discussion paper and (b) did not do a sufficient uncertainty analysis in the presented data to justify their conclusions (although this may change in the revised version. . .but currently only the discussion paper is available). There are presumably better references (such as some of the authors own work). Further, the authors seem to say the same thing twice in this paragraph, i.e. the first sentence is redundant with the 2nd and 3rd, so the issue can be alleviated by simply deleting the first sentence.

Line 11: "Exponentially"? Then why do we parameterize as a power law (i.e. the Angstrom relationship)?

Line 4: In addition to noting that there were 6 complete samples collected, this is a good place to note that 2 were from JST, three from YRK and only one from RS.

Table 1 lists the EC as "optical". If it is "optical", then it is actually BC, not EC that was measured. Also, this listing as the EC as "optical" seems somewhat inconsistent with the discussion on p18239 where it is stated that OC and EC were determined using the NIOSH protocol, which I understand to measure EC via the thermal method, not BC via the optical method. I also think that, given that a unique temperature split point was not determined for each sample, that non-standard uncertainties apply. The uncertainty in EC (and OC) are determined based on "blank variability" and uncertainties in flow rate. This would not capture any uncertainties due to variations in the split point, which might occur for the different samples. Thus, these uncertainties are undoubtedly lower limits. It would be useful if a more robust uncertainty estimate could be provided.

In general, how were samples treated between collection and analysis? How long did they sit out at room temperature?

It is stated on L5, p 18239 that two blanks were included. The uncertainties in the OC/EC and brown carbon absorption and WSOC are apparently derived primarily from “blank variability (1 sigma)”. If only 2 blanks were run, how is a 1 sigma value determined and how robust could it possibly be?

P18242, L20: How was single scatter albedo estimated?

P18242, L22: It would be really nice to see that the size distributions measured by Carrico (2003) were similar to those measured during this study, as this will affect the scattering/mass relationship. If the particle size is not the same, then the relationship will not be the same and the scattering will be under/over estimated. How accurate do they believe this estimate to be? Similarly, I do not understand how it is appropriate to use a scattering Angstrom exponent of 1.4 that derives from a study that measured particles around Asia from a plane. The Angstrom exponent depends on the size distribution. A value of 1.4 implies something specific about the size distribution. Is this value consistent with the particle size during this study? How would the results be changed if they assumed a value of 2 (smaller particles)? Or 0 (bigger particles)?

Also, it is not made particularly clear that the absorption at 670 nm comes from the MAAP. Or at least I assume it comes from the MAAP in determining the SSA, otherwise this would be a problem of circularity. So if the absorption used to determine the SSA comes from the MAAP, then how are the Aeth data corrected at the YRK site (since the MAAP was only deployed at the JST site)? This is not clear. Further, although JST is an urban site, the derived SSA values seem low to me. Can these be justified based on previous measurements? Could this, perhaps, indicate a limitation of the Angstrom scattering coefficient used or the scattering/mass relationship used?

Fig. 1: What sort of fit was done? A strict linear fit is not appropriate as there is uncertainty in the x-axis as well as the y. An ODR (or equivalent) fit is more appropriate.

P. 18243, L18: The authors state that complex refractive indices can be obtained from the solution data. However, they only present results for the imaginary part of the complex refractive index. (The complex refractive index includes both the real and imaginary parts). This should be restated.

P18241/L11: The authors state that the system was cleaned and then baseline zeroed using mill-Q water. They indicate that this was done for both the on and offline systems. I assume that for the methanol extracts the system was actually zeroed using methanol, not water and that this is just not stated? This needs to be stated or, if the system was always zeroed on water, the impacts on the methanol extract measurements needs to be discussed.

Fig. 2: How important is the forcing the intercept to zero?

P18247/L1: The RS OC is not greater than all of the YRK OC measurements. I also do not understand why it would be “expected” that the OC would be larger at the RS site than the other sites since the road the measurements were made by had limited truck traffic and, in general, the OC/EC for this site is larger than I would expect for very fresh gasoline-vehicle emissions.

Section 3.3.1: The authors cite Bond and Bergstrom (listed actually as Bond and Bertram) as the source for their EC refractive indices for use in Mie theory calculations. However, if they read this paper closely they will realize that it is well known that spherical particle Mie theory calculations using this refractive index will substantially underestimate the MAC (see Fig. 9 in B&B). Given this, it is somewhat surprising that the agreement between the calculated and observed “BC” absorption is so good. At the same time, though, I am still somewhat confused as to how exactly the “EC” was determined. Is this thermal EC or optical EC? Table 1 suggests optical EC, in which case some MAC must have been applied to determine the EC concentration. What MAC was used to derive optical EC and how does this compare with the calculated MAC? The authors are also doing calculations assuming spherical particles in the limit where the spherical particle assumption may not apply. In fact, the assumption of an AAE = 1 is inconsistent with their calculations: an AAE = 1 for BC only comes about from consideration of absorption by very small particles (less than ~50 nm or so). Above this, the AAE deviates from 1. Further, the calculated MAC falls off dramatically with particle size above some critical (wavelength-dependent) size. This does not happen if absorption is governed by the spherules that make up BC as opposed to the entire particle. Note that all of this will impact the BrC/BC comparison in section 3.3.5 because the particular behavior of BC comes about because it is so strongly absorbing; more weakly absorbing species show different behavior.

Section 3.3.4: I must admit that I don't really follow this section. If I understand this correctly, the k values used in the calculations come from analysis of the water/MeOH extracts, which are then used to calculate the absorption by the water/MeOH extracts. This, to me, seems like a circular argument and I am in fact somewhat surprised that the level of agreement is not better in Fig. 5. I believe that some clarification regarding the potential circularity of the analysis at this point is needed. At the same time, I do sort of understand that the authors are making the point that particles can absorb more than the equivalent solution. Another way to state this is simply that the imaginary refractive index is a more descriptive metric than the MAC in that it is independent of particle shape/size.

Section 3.3.5: IF the authors were to add the calculated EC and calculated MeOH BrC absorption together at the different wavelengths, and then were to calculate an AAE based on this combination, what would one obtain? A value that makes sense in the context of the Aeth measurements? I ask because the Aeth AAE seems quite small if BrC really is contributing 30-40% of the total absorption at 350 nm at at least one of the sites. Also, what is the AAE for the calculated EC absorption? I ask because the calculations seem to be done using relatively "large" BC particles, which should

give very low AAE values (much lower than 1). For example, 500 nm diameter BC particles would give an AAE closer to -0.3 than to 1. To the extent that the calculated EC absorption is dominated by where the mass is (large particles) I am having some difficulty understanding why the calculated EC absorption visually looks as if there is an AAE close to 1…unless smaller particles were used in the calculations. Perhaps I am just missing something in how the calculations are being done or in what exactly is being shown in Fig. 6?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 18233, 2013.