

Review of "Time-resolved measurements of black carbon light absorption enhancement in urban and near-urban locations of Southern Ontario, Canada" by Chan et al.

The paper by Chan et al. discusses measurements of light absorption, black carbon mass and non-refractory aerosol mass in various regions in Canada. It is my opinion that this paper should be rejected for the following reasons: (1) the analysis is fundamentally flawed and premised on extremely poor assumptions (2) the paper is difficult to follow, (3) the figures/tables are poorly conceived and do not always seem to show what the authors purport to show. These will be discussed further below, in both general and specific terms. In order to be publishable, it is my opinion that the manuscript will require a fundamental reworking that is well beyond the scope of a typical revision.

(1) The analysis is fundamentally flawed: The authors appear to be confusing what should be considered an *intensive* property (the actual absorption enhancement) with what is an extensive property (their  $\Delta B_{\text{abs}}$ ). Furthermore, they go on to compare this extensive property,  $\Delta B_{\text{abs}}$ , with another extensive property,  $\Delta M$ , which is purportedly the "coating mass." The absorption enhancement, when properly defined as an intensive parameter, depends on the *relative* amount of coating material compared to the black carbon mass (see e.g. Bond and Bergstrom, 2006). Furthermore, the authors assume that even their poorly defined  $\Delta B_{\text{abs}}$  should have a linear relationship with  $\Delta M$ . Mie theory is, however, an extremely non-linear theory and thus there is no reason whatsoever to think that even properly defined intensive parameters should exhibit a linear relationship.

To make clear what I mean when I say that  $\Delta B_{\text{abs}}$  and  $\Delta M$  are poorly defined and used, consider the difference between two particle ensembles wherein  $\Delta M$  (as they have defined it) is equal to  $10 \mu\text{g}/\text{m}^3$  in both cases, but in one case  $B_{\text{abs}} = 15 \text{ Mm}^{-1}$  while in the second  $B_{\text{abs}} = 1 \text{ Mm}^{-1}$ . In the first case, the actual coating thickness would be small because the amount of black carbon is large (and thus the  $10 \mu\text{g}/\text{m}^3$  is distributed among many particles) while in the second case the coatings would be quite thick. In general (although certainly not always, given the surprises Mie theory brings), thicker coatings equal greater enhancements. Let's say that in the first case, the enhancement is 10% of the uncoated particle but in the second case it is 50%. Then, as they have defined it,  $\Delta B_{\text{abs}} = 1.5 \text{ Mm}^{-1}$  in the first case and  $0.5 \text{ Mm}^{-1}$  in the second. The "enhancement"  $B_{\text{abs}}$  would appear to be larger in the first case, even though the *actual* enhancement is smaller.

Also, implicit in the analysis is the assumption that the particles are completely internally mixed with respect to BC and coating mass. However, no justification is given for this assumption based on observations. In fact, I would argue that their observations speak against this. For example, the single scatter albedo (SSA) values measured at the various sites are across the board quite low (0.79, 0.42, 0.68 and 0.68 for the sites listed in Table 1 in order). This suggests a preponderance of fresh emissions, perhaps not surprising given the sites of the measurements close to emissions sources (particularly at the Ottawa street canyon site where  $\text{SSA} = 0.42$ ). Thus, very little time for coatings to form will have passed, which suggests that much of the non-refractory mass was in "old" particles while a preponderance of BC was in "new" particles. If true, this suggests a highly non-uniform system, with some heavily coated and some thinly coated particles. Thus, the thermogravimetric measurements, in particular, may not provide a correct measure of what the authors suggest they have measured, namely

the absorption enhancement. This is an unavoidable aspect of any field study attempting to get at this effect, and thus is not a reason by itself to reject the paper, but it certainly must be dealt with in a much clearer way by the authors.

(2) The paper is difficult to follow: Although there are a number of points to be made here, I will limit my discussion to a few. For one, the authors have chosen to use an unconventional relationship, the PAS absorption-to-LII volume ratio, to describe the influence of coatings on the total absorption. The authors should focus their discussion using a term much more common in the atmospheric literature, the mass (or specific) absorption coefficient. The introduction of this term, as to a more commonly used one, makes the discussion unnecessarily complicated.

(3) The figures/tables are poorly conceived and do not always seem to show what the authors purport to show: Here are a few examples: (Figure 2) The AMS particle mass measurements are presented in a manner that makes them appear fake. Clear differences in total mass from one on/off cycle to the next are observed (indicating atmospheric variability) but the values within a given on/off period are shown as perfectly constant. I assume that what is actually being shown is the average value during each on/off period, only that it is shown as multiple points within each period instead of as a single point. However, if my assumption is incorrect and this is the real data, then the authors must address why the particle mass is so constant within a given on/off period, but differs from one period to the next. (Table 1) The values listed for the AMS are confusing. What is meant by “%”? Should these add up to 100%? They don’t. Actual mass values would be much more useful than whatever this % value is. Also, there are no values in bold (which are supposedly the mean values). (Figure 4) The caption for panel d is very confusing. What do the authors mean “at different stages in a thermodenuder experiment?” This does not appear to be what the panel shows.

In addition to these points, further specific comments follow below.

Page 19942-10: A reference to Schnaiter et al., *JGR* (2005) is warranted.

Page 19944-6: A reference to the work by the NOAA group (Schwarz, Gao, Fahey et al.) is clearly warranted.

Methods: The authors need to report the total flow rate and overall residence time through the thermodenuder (and also use consistent spelling throughout the manuscript). Just knowing that this is a Dekati thermodenuder does not help the reader to understand how specifically it was operated, although I will assume that the entire 16.7 lpm were passed through.

Methods: Detection limits and uncertainties should be reported for all instruments, including (and especially) the DMT PA.

Methods: The atmospheric community is becoming somewhat familiar with the LII technique for determining BC mass concentrations. However, the method used to estimate the primary particle size (PPS) is not as well known and therefore I suggest much more detail be given regarding this method. For

example, how exactly is the heat loss rate determined? What are the uncertainties associated with the PPS method? I feel that this is necessary given that two of the references are to conference proceedings and one is to a thesis.

Methods: To what extent are the authors able to conclude as to the internal vs. external mixing nature of the sampled particles? Neither the PAS or AMS cannot provide this information. Can the LII instrument give some guidance in this regard?

Page 19944-15: I do not see where Murphy (2009) came to the conclusion presented.

P.19953-11: The atmospheric community is much more familiar with mass absorption coefficients than the "PA:LII Ratio." I strongly encourage the authors to reframe their entire discussion in terms of the MAC instead of this ratio (I believe the authors refer to this as the specific attenuation coefficient).

P. 19953-13: The utility or physical meaning of the "normalized" PA:LII ratio is entirely unclear.

Page 19953-25: The authors state that "The light scattering and signal enhancement generally, but not always followed the same site to site pattern as the particle coating mass. The most obvious case is the Bscat values for the Windsor data which are small despite of the largest amount of particle coating mass present on the particles." If this is true, where is this data in Figure 4b? There should be points at high mass/low scattering, but there are none.

Figure 2: It would be helpful if the authors presented a denuder on/off time series behind the measurements (particularly in panels b and c) to emphasize which periods are on/off.

Figure 2/P. 19950-7: This figure does not really show a time series of the "total particle coating mass", but actually a time series of the refractory particle mass, both after passing the particles through the thermodenuder and through the bypass line. To state that this is the particle coating mass suggests that the authors have specific knowledge about the mixing state of the particles.

Figure 2c: The SVF results presented in this figure is more important than the authors acknowledge. This figure appears to indicate that particle losses through the thermodenuder relative to the bypass are extremely small. This is crucial to the authors interpretation, and should be explicitly mentioned. However, at the same token, I am a bit surprised that there is no particle losses through the thermodenuder. Have the authors validated this in the laboratory?

P. 19950-21: I see no point or justification in using a cubic spline to estimate values "when the sample was following the alternate flow path." Since the AMS, PA and LII measurements are all in-phase w.r.t. the thermodenuder on/off cycles, there is no reason to look at these "alternate" values. These points should be removed, and if they are included in any of the other figures they should likewise be removed.

P. 19951-3: I do not see how either assumption 1 or 2 are justified or needed. The measured signal enhancement does not depend on these assumptions. However, the *interpretation* of the signal enhancement does depend on assumptions.

P. 19951-8: I do not understand how the use of the median as opposed to the mean serves to “minimize the impact caused by occasional fluctuations in the time-dependent data,” especially since, at most, 5 points could be included in any of the averages/medians (assuming everything was timed perfectly, which Figure 2 seems to indicate was not the case).

P. 19955: The discussion presented here is wrong. The authors are using extensive properties where they should be using intensive properties. The differences between the different “regions” cannot be interpreted in the manner presented here. For example, the decrease in going from “region II” to “region III” is not support for collapse of the BC fractal structure. It could just as easily be a changing balance between fresh and aged (e.g. background) particles. (As an aside, the terminology “regions” is confusing.)

P. 19957-4: The discussion in this paragraph makes no sense. The logic being employed is circular. One can't use SAC values derived here from PA/LII measurements to estimate mass from PA measurements alone. These are not separable.

Section 4.3.1: Only a general discussion is given here. This discussion should be put in the context of the actual observations. Related to this, the observations do not seem to follow from the discussion. Why, for example, are the Toronto PPS values so small? This is supposedly “aged” and should contain collapsed BC, at least relative to e.g. the Ottawa sites.

Section 4.3.2: The authors' discussion makes it seem as if they are doing something beyond simply calculating the SAC from their measurements. They are not.

P. 19960-8: The PA:LII ratio is equivalent to the intensive property the SAC. By “normalizing” to the “particle coating mass”, the authors are taking this intensive property and turning it back into an extensive property, which actually has exactly the opposite effect of what the authors were attempting to do.

P. 19960-25: The statement here is false. See above comment.

P. 19963-9: The PA measurements here were made at 781 nm. Absorption by “brown carbon” at this wavelength is very likely to be extremely small (indistinguishable from zero). Thus, this discussion is out of place.

P. 19964-20: To the extent that Rayleigh-Debye-Gans theory can be used to accurately describe absorption by fractal BC particles, this discussion does not hold. RDG says that the total absorption by a fractal particle is just the sum of the absorption by the individual spherules. The mass absorption coefficient for an individual BC spherule is relatively constant for spherules smaller than ca. 100 nm. Thus, if we distribute the same total mass per particle amongst some number of different sized spherules comprising that particle, the total per particle absorption (according to RDG) does not differ by much, and certainly is not thought to vary by the extremely large factors observed here. This is because as the size of the primary spherule decreases, the number of spherules per particle increases in

an offsetting manner. Furthermore, the authors appear to be implying that the particles observed in Toronto were 'fresher' than those in Ottawa. This does not seem justifiable given the site locations.

Figure 3: It would be helpful to color the appropriate axis red to make it more quickly apparent which trace corresponds to which axis.

Figure 3: The figure caption/figure is confusing. The axis label is "total particle mass loading" but the text refers to this as particle coating mass. Which is correct? And does the total particle mass include the black carbon (e.g. refractory material) mass? Also, I presume the values shown are corrected for particle number losses.

Figure 4: The caption for panel d is very confusing. What do the authors mean "at different stages in a thermodenuder experiment?" This does not appear to be what the panel shows.

Figures General: I assume that higher quality figures will be included upon revision? Some of the labels/points did not transfer well to pdf.