

Major comments:

The paper entitled “Atmospheric black carbon can exhibit enhanced light absorption at high relative humidity” addresses a topic of major importance within the aerosol sciences, i.e., the light absorption enhancement of black carbon containing particles under ambient conditions (e.g., high relative humidity). The paper presents the results of ambient measurements conducted with the aerosol albedometer (where the absorption is measured by difference of extinction and scattering) and reports significant enhancements of light absorption for coated particles under ambient humidity conditions. The subject is relevant for the scientific community and it would be proper for publication on Aerosol Chemistry and Physics. **Recently, several studies have looked at light absorption enhancement, mainly by using photo acoustic spectrometers (which make direct observation of light absorption) sometimes in conjunction with thermal denuders, which allow to remove the effect of coatings and have a direct measurement of the true absorption enhancement by referring to the absorption measured by black carbon cores. Here, the enhancement is measured as a ratio of light absorption at high and low RHs without the use of a thermal denuder (in other words, the coatings are never removed) the results are not really a measure of absorption enhancement by black carbon per se, rather this is a measurement of the response of ambient black carbon-containing particles to high humidity.** I realize that this is almost a philosophical issue, but a rather important one, in my opinion.

AUTHOR REPLY: In this experiment we have studied the effect of condensation of water into internally mixed particles presumably containing BC. By altering the RH, hygroscopic growth is caused for particles with coating materials. Thus, the water content acts as a ‘coating’ in your terminology. It is true no thermal denuder was used here to heat aerosol to high temperatures – and no attempt was made to remove organic, sulfate, or nitrate coatings from and BC particles. We argue that since water vapor is often present in much larger quantities compared to other easily condensed materials, that the effect of hygroscopic growth on absorption is important. In fact, raising the RH by slightly cooling the sample tubing is essentially opposite what occurs in a thermal denuder – but would you not argue the same reversible physical process (e.g. evaporation/condensation) is involved in both experiments?

It seems a user of a thermal denuder must be confident the heating process does not alter the sample – otherwise he/she would be comparing apples to oranges. Since it is well known that reaction rate constants increase dramatically at elevated temperatures, it seems more probable that aerosol held at high temperatures could exhibit more significant chemical or morphological changes than what would be caused by a few degree change used to raise humidity. Regardless of this point, condensing water into aerosol is simply the opposite physical process of what happens in a thermal denuder (albeit only one substance condenses). **Since water vapor is by far the most abundant easily condensed species in Earth’s atmosphere we feel the results of this paper are very important for understanding absorption enhancement (e.g. given the**

abundance of water, it is more likely optical absorption is increased by its presence in internally mixed aerosol rather than sulfate / nitrate etc...). This is indeed a different experiment that what has previously been reported in literature.

As for the photoacoustic method, it can be stated (and usually is) that photoacoustic is a direct measurement of absorption. However, recent literature reports have suggested photoacoustic methods may underestimate absorption at high humidity conditions.

see for instance : Langridge et al. "Limitations of the Photoacoustic Technique for Aerosol Absorption Measurement at High Relative Humidity." Aerosol Science and Technology Volume 47, Issue 11, 2013.

also: Kozlov et al. "Effect of relative air humidity on photoacoustic aerosol absorption measurements in the near-ground atmospheric layer." Atmospheric and Oceanic Optics, October 2011, Volume 24, Issue 5, pp 487-491, 2011.

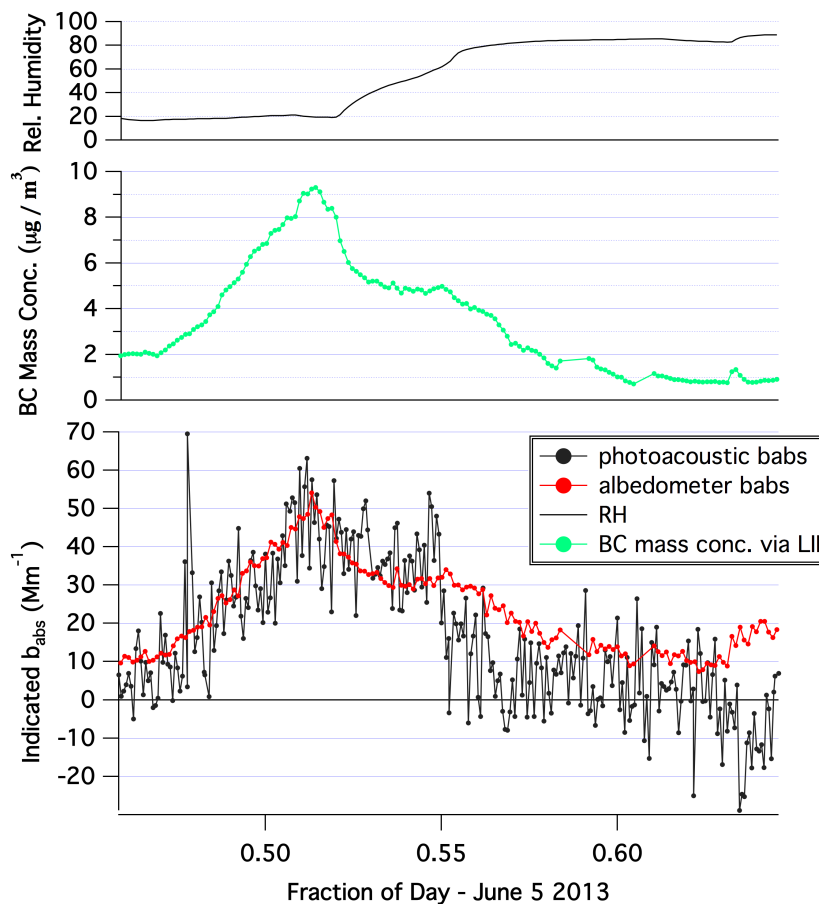


Figure 1. Comparison of photoacoustic (black) and albedometer (red) absorption data. Sample was lab generated soot ($D_p=300$ nm) internally mixed with ammonium sulfate. At approx. $x = 0.55$, the sample humidity was increased as shown in top plot. Absorption measurements agreed relatively well prior to the humidity increase. The green trace indicates BC mass concentration. As observed, photoacoustic absorbance was near zero at high RH.

We have also conducted a few experiments of this type (e.g. comparing photoacoustic with the albedometer). One result is shown at left. In this experiment we collected kerosene lamp soot, and atomized it from a solution of ammonium sulfate to assure the soot had hygroscopic sulfate internally mixed. We then size selected to 300 nm, and slowly increased sample humidity (RH as indicated in top trace). We measured the BC mass concentration

according to the method published in Wei et al. Anal. Chem. 2013, and the data is shown in middle plot (green). The lower plot reflects photoacoustic (black) and albedometer (red) absorption coefficient. Until $x = 0.54$, the red and black traces agree well with the green trace indicating BC mass. Then as the humidity is raised above 60% the red and black traces diverge. At approx. $x=0.6$, the photoacoustic trace even presents near $b_{\text{abs}} = 0$, despite an indicated BC concentration near $1 \mu\text{g} / \text{m}^3$. This also makes us wonder whether photoacoustic methods are suitable for high RH conditions. We also point out that for some very odd reason the data in the red trace from the albedometer (difference measurement) appears to be less variable or 'noisy' compared to the black photo-acoustic trace in this experiment. The exact explanation for this phenomenon is a mystery, we will let the reader speculate.

If the laboratory data shown above is converted to a plot of soot MAC vs. RH, an absorption enhancement is again observed via the albedometer (results below).

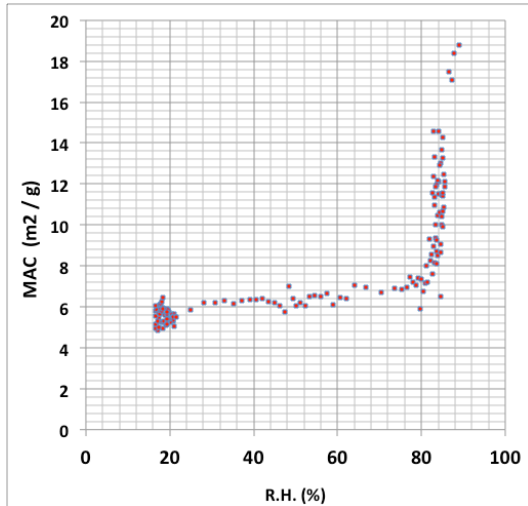


Figure 2. Data of figure 1 re-plotted to show increase in MAC as a function of RH for the lab experiment.

Now, one can certainly dry aerosol prior to measurement to avoid deleterious effects in photoacoustic spectroscopy. We advocate this procedure since the albedometer absorbance measurement (difference method) agrees well with the photoacoustic method on dry, uncoated kerosene soot aerosol as shown below in figure 3.

However, the albedometer consistently senses increased MAC for coated soot at high RH. The Wei *et al.* Anal. Chem. paper reports additional data of this type.

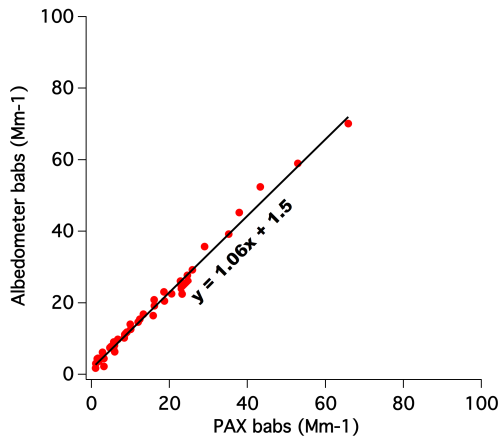


Figure 3. Comparison of photoacoustic (PAX) and albedometer absorption data for a dry kerosene soot aerosol. Good agreement is found between measurements on dry aerosol

REVIEWER COMMENTS Cont.: Beside, I see a few major issues with the study. First, the absorption is obtained by difference, and this poses the question of what kind of errors are propagated into the absorption values, especially at elevated relative humidity (RH). We know from previous studies that the absorption enhancement can be very small, and perhaps even smaller than the propagated uncertainties due to a) absorption by difference and b) measurements made at high RH. Because a full uncertainty analysis is missing from this paper, there is no way of establishing if the observations are significant.

AUTHOR RESPONSE: We did offer an uncertainty analysis in the supplement. The uncertainty is largest in regions of maximum absorption enhancement because maximum enhancement frequently was observed for presumably aged BC samples, where BC concentration and absorption was low. As presented in Fig. 1 and 3, the albedometer technique (difference method) yields results very similar to photoacoustic under low RH conditions. High RH measurements are of course more difficult since there is not a good reference method to test against. We might argue the albedometer method is the best choice for measurements at high RH. Previous studies on ambient aerosol considered dry aerosol only. From our measurements it seems the phase of the BC containing particle may be very important. See Wei et al. Anal. Chem (2013) for more details on this.

Second, the truncation correction of the scattering portion could introduce further error and increase the uncertainty. It is not clear to me what may be the effects of truncation (and truncation correction) on the results, especially because the correction should depend on RH, size and chemistry as well (i.e., refractive index).

AUTHOR RESPONSE: We agree the truncation correction is largest source of uncertainty. Correction for truncation will lower absorption coefficients reported. We feel we likely have overcorrected at high RH.

I am also very confused by what size cut was applied to the data. It seems to me that there was not impactor at all for the optical instruments, whereas we know that the SP2 - to which the authors refer for the measurement of mixing state and size - measures in the submicron range. So there is a clear disconnect here between the mass-based and optical-based methods. Furthermore, the lack of PM1 cut to the optical data makes it difficult to isolate the effect of dust and seasalt and in general of supermicron particles on the data. It is likely that supermicron particles do not contribute to the absorption, however they have large truncation, are highly hygroscopic (if seasalt is present as likely given the location) and this might propagate into even larger errors which at this point are not accountable for.

AUTHOR REPLY: Yes, no size selection was used. Houston is known to be a humid environment (i.e. significant hygroscopic growth), and we did not want to remove a significant amount of aerosol at the tubing inlet. I am not aware of a size-selective inlet for the SP2 instrument itself. However, it is true that the device measures sub

micron particles. The same could be said regarding the optical measurements though. In fact, most often the sub-micron aerosol dominates the optical effects. The devices were connected serially, so it is not as if two separate sampling lines were used. There is also no evidence that sea-salt or dust aerosol exerts any unusual optical signatures on the data.

For these reasons, I find that the results reported in this study to be inconclusive and I am not convinced that there is enough evidence to support the substantial enhancement observed in the data. Therefore, I have to suggest that the paper is rejected because the results cannot be fully verified.

AUTHOR COMMENTS: We have a proposal at NSF to obtain SP2 and continue these types of measurements. This would provide additional data and time to make improved measurements. I have no doubt this proposal will be rejected however. Perhaps you can write letter of support to program manager? In any event, this line of research will likely end. I look forward to reading other investigators papers on the topic in the near future. Maybe they will cite this ACPD work?

Minor comments

Introduction Page 29415, line 6: the MAC at 550 nm reported in Bond and Bergstrom (2006) is $7.5 \text{ m}^2\text{g}^{-1}$, and not $4\text{-}8 \text{ m}^2\text{g}^{-1}$

AUTHOR RESPONSE: This is true of Bond and Bergstrom – however figure 1 of Bond et al (JGR 2006, D20211) reports MAC computed from theory as a function of BC diameter. We see MAC is size dependent (at least in theory) and values near $5 \text{ m}^2/\text{g}$ are very reasonable. In our experience, the $7.5 \text{ m}^2/\text{g}$ value quoted seems to be subject to considerable variability. We feel it should not be treated as a natural constant.

Experimental method Pages 29416-29417: The sampling is not very well described. Were the PAX data used at all? What wavelengths were the optical measurements performed at? Also, it is not clear to me if there is a RH history (cycle) for the sample that the authors have omitted. It is not clear what the actual high and low RH values were in the instruments for the measurements. If the lowest RH was 45%, then I would not define it "dry". There is quite a bit of water at 45 % RH.

AUTHOR REPLY: Figure 1 largely summarizes the sampling. We did not use the pax data. Figure 1, 7 report 532 nm as measurement wavelength. The low end of RH varied with performance of dryer dessicant. It would be accurate to not call the sample "dry." It is likely water was not completely removed from the aerosol. As for RH history, the aerosol was subjected to ambient conditions in Houston prior to sampling.

Optical Measurements Results Page 29420, line 10 (and Figure 5): The MSC seems very low to me. What is the wavelength measurements were performed at, and what

were the particle sizes ? Page 29421, line 25 (and Figure 7): the MAC seems very low here for 532 nm and dry RH, it should be around 8 m²g⁻¹ and not half of the value.

AUTHOR REPLY: Again, we think the MAC of soot aerosol should not be considered a natural constant governed by the report of Bond and Bergstrom and can likely change. We offer no special explanation for why it's around 4-5 m²/g (as compared to 8) other than that is the value we measured.

Other studies (Cross et al., 2010) have shown that MAC for pure BC is around 8 m²g⁻¹. Have the authors tried to use the PAX measurement to compare to the albedometer-based absorption to see if MAC changes ? Or perhaps the SP2 BC mass are overestimated due to e.g., SP2 data corrections ?

AUTHOR REPLY: Experimental errors are always possible. We worked to calibrate the SP2 with size selected fullerene soot (supplement) and got good results. We did not use pax because photoacoustic spectroscopy is possibly subject to errors at high RH.

Also, from the discussion related to the figure it seems to me that enhancement is only observed at RH > 60% and only if the coating fraction is high. Are the increase in MSC and MAC with RH and coating fraction correlated ? it seems to me that there are several factor all tangled together here.

AUTHOR REPLY: This is indeed the point of the manuscript.

Page 29422, line 15-16: it seems to me that an uncertainty of 2 Mm⁻¹ in absorption by difference at high RH is a really low number.

AUTHOR REPLY: see figure 1 of this response

Mechanism of enhanced absorption How is it possible that the authors calculate a MAC of 7 m²g⁻¹ whereas the observations indicate a MAC of 4 m²g⁻¹ for "dry" particles ? Also, they indicate an increase in MAC from 7 to 15 m²g⁻¹ for "wet" and largely coated particles. This is a very large enhancement factor. At the same time the calculated and measured MAC for wet particles seem to agree, and I find this strange given that the "dry" case does not agree at all.

AUTHOR REPLY: I'll assume you are referring to the Fig 8 here. This is not measurement data, but Mie optical model results. In core-shell case, a thin water shell was placed around the BC core to obtain the 7 m²/g value. Obviously, the core-shell model employs many assumptions that may or may not be true. Difference between the Mie code modeled case and measurement data will result if reality differs from the model in any way. This is in fact very likely. We do not attempt to fit the data to the Mie core-shell or soot-on-sphere model. Instead just

reported the results and compared to the model predictions. The measurements do tend to agree best with the core-shell model but to be very honest, I am not convinced either the “core-shell” or “soot-on-sphere” model shown in Fig 8. is correct 100% of the time.

Significance and conclusions. The authors state that the measurements may have large uncertainties and that no conclusive statements can be made without knowing the chemistry of the coating fractions. I would add that even the way MAC is derived might have serious issues here.

AUTHOR REPLY: I think more experiments can certainly be done. More locations, better understanding of the chemistry of the BC containing particles, better constraints on hygroscopic growth etc... This is true of any data set. But I don't think our computation of MAC has any serious deficiency. We include an alternate approach below. This is a plot of absorption vs. BC mass concentration sensed by the SP2. The slope of this plot is the MAC. We separated data into two groups. Group 1 shown in black points is all data when $RH < 60\%$ (e.g. dryer aerosol). The second data series shown in color scale is for $RH > 80\%$ AND coat fraction > 0.65 . The color scale represents the coating fraction. The best-fit lines show the slopes differ for the two data sets. Note that many green, orange and red points (high coat fraction) appear at low rBC mass concentrations. This alternative approach to data analysis confirms MAC appears to change for coated aerosol at high RH. However, this presentation of data in this format is not optimal because of substantial differences in RH and coat state among the data series. Nonetheless, it provides confirmation MAC appears to change significantly for coated BC aerosol at high RH.

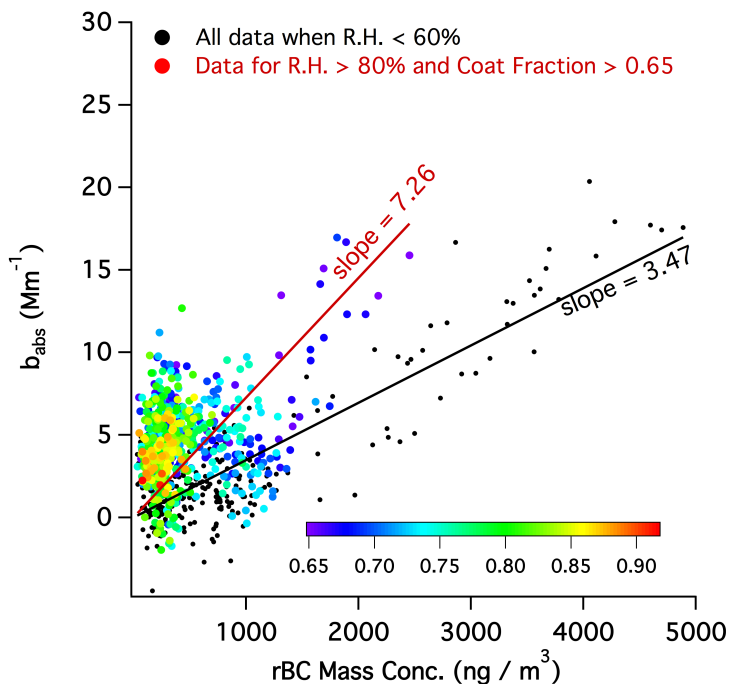


Figure 4. Plot of observed absorption coefficient for Houston dataset vs. indicated rBC mass concentration. Two data series are shown. The black points are all data when $RH < 60\%$ (dryer aerosol). The color scaled points are for data $> 80\%$ RH AND coat fraction > 0.65 . The color scale represents the coat state. The slopes of the best-fit lines differ. Since the slope represents the MAC, this provides additional evidence MAC changes at high RH for highly coated BC aerosol.