Atmos. Chem. Phys. Discuss., 15, C6119–C6127, 2015
www.atmos-chem-phys-discuss.net/15/C6119/2015/


Atmospheric Chemistry and Physics Discussions
Open Access

ACPD
15, C6119–C6127, 2015

Interactive Comment

# *Interactive comment on* "Variation of the radiative properties during black carbon aging: theoretical and experimental intercomparison" *by* C. He et al.

**Anonymous Referee #1**

Received and published: 21 August 2015

Review of He et al.

The authors report calculations of BC absorption, scattering and extinction using the GOS approach for a variety of different assumed particle morphologies and compare the results of their calculations to the results from one laboratory study. Like others before them, they find that the extent of agreement with the observations is highly dependent on the assumed particle morphology, with some lesser sensitivity to the assumed refractive index; the examination of morphology effects here is, perhaps, slightly more systematic than previous studies. After comparing to the laboratory experiments, they perform calculations for the LA region, using as constraints some observations of BC particle mixing state, the nuances of which are not considered in the theoretical calculations. Again, they find that assumed particle morphology matters substantially to the results, and find that the calculated direct radiative forcing depends additionally on the assumed amount of coating and the BC concentration. For the most part, I find that this work covers already well-trod territory, as this is first and foremost a computational sensitivity study of the influence of particle morphology on BC optical properties. In this regard, few new conclusions are reached, with the new-ness of this work primarily being that a computational method that had not been applied in this particular way was used, as opposed to some alternative computational method. Turning to the application of the theoretical developments to predicting atmospheric impacts in an explicitly quantitative manner, here I find that the study is a bit weak. First, I find that insufficient details are generally provided to allow one to truly understand exactly what the authors have done. Second, I find that they consider only the most simplistic aspects of the observations such that their calculations are really only a very minor extension over the laboratory-related calculations. This section is overly quantitative when really all the conclusions reached here could have been simply predicted based on the general theoretical results, i.e. the authors can easily establish the general implications of their work without having to perform what I view as highly uncertain (and less experimentally constrained than the authors believe) calculations. My specific concerns regarding these calculations can be found below. Overall, I find that the main theoretical section could be publishable, but I think that the entire "Implication for regional radiative forcing analysis" section should be removed.

Specific comments:

The authors state in the abstract that there is good agreement for extinction and absorption, but not for scattering for some of their calculations. Since Scattering = extinction – absorption, it is difficult to see how one can have good agreement for two of the three, but not the third. This should be clarified or removed. But this goes to a point that I find to be recurring throughout this manuscript: over-generalization of the results in terms of how they are presented. As one example, the authors' state in the conclusions, "Sensitivity calculations showed that variation of optical cross sections of



ACPD
15, C6119–C6127, 2015

fresh BC aggregates can be up to 60% due to the use of different BC RI, in which the scattering is most sensitive." This may be a true statement, but there is so much information hidden within regarding the differing behavior of extinction, absorption and scattering. I find that grouping these all together unnecessarily overgeneralizes. There are many statements similar to the above, and I suggest the authors revise their overall manuscript with this general concept in mind.

I have some concerns about the precision of definitions being used. The authors note in the abstract that "the resulting BC direct radiative forcing (DRF) first increases from 1.5 to 1.7 Wm-2 and subsequently decreases to 1.0Wm-2." This decrease seems to me to be attributable primarily to the material that has condensed on the BC and much less so to the BC itself. Thus, I have difficulty seeing this as truly the "BC direct radiative forcing" (further, it is technically the direct radiative effect, not forcing, as forcing requires a difference from a preindustrial reference state, see e.g. Heald et al., ACP, 2014). It is really the direct radiative effect of BC + coatings. Perhaps I am being overly pedantic, but I find it imprecise to attribute the influence of coatings to BC.

In the introduction (P19837, L12) the authors provide references to experimental studies for demonstration of changes in mixing state and hygroscopicity, but only theoretical studies when it comes to light absorption. I would suggest including experimental studies as well for light absorption.

P19837, L21: The authors reference Schnaiter et al. (2003) with regards to the statement "Recent studies confirmed that BC becomes coated by water-soluble material during atmospheric aging, including condensation of sulfate, nitrate, and organics." However, the Schnaiter study is a laboratory study and thus only demonstrates that such materials can condense on BC, not that they do upon "atmospheric ageing". Presumably the lab results translate to the atmosphere, but it would be preferable if the authors focus on studies in which this has been demonstrated in the actual atmosphere.

P19838, L7: I find the statement "Gangl et al. (2008) showed that internal BC-wax mixture amplifies BC absorption coefficient by a factor of 1.8." does not sufficiently convey the point that Gangl et al. observed a range of amplification values that depended explicitly on the amount of coating. By just stating one value, it makes it sound like this is the only value that they obtained and that it was generally true.

P19838, L13: The authors' state "The disagreement among different laboratory experiments [with respect to absorption amplification" demonstrates large uncertainties associated with BC radiative properties during aging." I find this to be too simplistic, as it implies a potentially greater variability in laboratory experiments than has actually been observed. It is known that the magnitude of the absorption enhancement depends on the (i) size of the BC particle and (ii) the amount of coating added. Each of the cited studies used different combinations of BC particle sizes and amounts of coatings, which contribute to the observed variability. The statement made by the authors seems to me to discount these experimental details to make to general of a point. I suggest that the authors reframe this to emphasize that the experimental details matter to what is observed and thus simply comparing individual numbers is not necessarily appropriate.

P19838, L15: The authors' state "Field measurements have also revealed substantial variation in BC optical properties during atmospheric aging." They then go on to give as their second and third references (Schwarz, Moffet) results from what are fundamentally computational studies that used some estimate of the amount of coating material to calculate the "expected" absorption amplification given a particular morphology and theory. These studies do not directly characterize the variations in light absorption by BC upon atmospheric ageing. This is implicit in the authors' noting that both studies used calculations to determine absorption, but I find this then conflicts with the general sentiment of the paragraph as implied by the first sentence. I suggest they are either removed or reframed more appropriately within the context of the paragraph.

P19838, L27: It is indicated that the Cappa et al. (2012) study was an "aircraft" study. This is incorrect.



ACPD
15, C6119–C6127, 2015

P19838, general: there are a variety of other recent references in which the magnitude of the absorption amplification has been assessed from field measurements that could be included here, perhaps in place of the two theoretical estimates that are mentioned.

P19839, L7: Technically, Sedlacek et al. reported evidence that particles had a non-core-shell structure. They did not actually demonstrate a morphology for these particles.

19839, L9: Adachi and Buseck report measurements from a ground site, not aircraft. To quote from their paper: “Aerosol particles were collected using three-stage impactor samplers (MPS-3, California Measurements, Inc.) placed on the roof of a building at the California Institute of Technology (Caltech), Pasadena, CA (34.138N, 118.124W).”

P19841, L20: I find the meaning of the following sentence regarding experimental uncertainties difficult to understand (especially the last part of the sentence) and suggest clarification is needed. “Khalizov et al. (2009a) showed that the experimental uncertainties associated with instrument calibration, relative humidity, and particle size measurements were within 10 %, which excludes the contribution from multiply charged particles, while the scattering measurements of freshly emitted BC aggregates were associated with high uncertainty.”

P19842, L15: The statement regarding “Babinet’s principle” could do with a reference, as this is not necessarily a widely known principle.

P19842, L27: It would be helpful if the authors stated more explicitly what they mean when they say that their approach compares “reasonably well” with other approaches.

P19843, L9: As with the abstract, I don’t fully follow how the method can be developed for extinction and absorption but not scattering as these are all related. Some clarification could be helpful.

P19846, L10 onwards: I find some of the comparisons here a bit too simplistic and could be expanded to include more detail. For example, the authors first note that the calculated extinction cross-sections are all within 20% for State I. However, this misses a visually notable aspect that the calculations tend to overestimate extinction for the smallest particles but underestimate for the largest particles. Further, visual inspection of the figure indicates that the authors seem to be talking about the central value of their calculations that they obtained, rather than the overall range. This should be clarified. Also, my understanding of their approach was not that the two values given were both bounds, but that one was their base case value and the other the lower bound. At some point it seems that the base case value turned into an "upper bound." This could be clarified.

Similarly, when they discuss absorption it would be useful if they were to mention the direction of the discrepancy, not just the percent difference. And in noting that the scattering is typically overestimated "partly because of uncertainties associated with theoretical calculations for small particles" I find that this does not fully bring out the connection between absorption, scattering and extinction.

P19846, L20: The authors incorrectly attribute the SSA values reported by Bond and Bergstrom to "atmospheric observations." This is not true. Their results shown in Table 7 are all for different individual sources and not from atmospheric observations. The authors should revise their statement accordingly.

P19847, L4: I suggest that it would be better if the authors gave specific values for extinction, absorption and scattering, not one number to cover all of these properties.

Figure 4 and General: I find the use of the term "standard" to be a bit ambiguous, as it doesn't mean the same thing for the Stage I and Stage II & III calculations. In Stage 1, standard = simple fractal aggregates (see P19843) but for Stage II & III, "standard" = "concentric core-shell". As a reader, I find the application of this single term to multiple different structures to be confusing. I suggest the authors be more specific.

P19848, L18: As with Stage I, I find that the model/measurement comparison is a bit weak with respect to details. They note "good agreement" in general (with one exception) by overlook the systematic nature of the over/under-estimates with respect to the size of the particles simulated.

P19849, L2: In discussing this “sensitivity test” the authors should also note how this change influences absorption (which is already overestimated). Is the discrepancy there also reduced, or is it exacerbated?

P19849, L6: I find the discussion here confusing. I do not see how using an RI = 1.95-0.79i can increase anything, since this is the reference case, right? At least it is the reference (“standard”) according to P19844, L5. Thus, other cases can change relative to this case, but it cannot change.

P19849, L8: I find the following statement to be an oversimplification and, at least visually, inconsistent with the results shown in Fig. 3. “We found that the effect of BC RI on extinction and absorption for coated BC particles is similar for different BC sizes, but much smaller than the case of fresh BC aggregates.”

Figure 3: it would be useful if the authors were to indicate on the “morphology” band where the “standard” values lay. Really, I think this is just the upper bound of the “RI” cases, but this could be made more explicit to help the reader understand the relationship between the “standard” Stage I calculations and the “standard” Stage II and III calculations.

Figure 7: It is somewhat unclear what the reference case (uncoated) is for each of the calculations shown. Is it the “standard”? Is it some morphology that is relevant to the particular calculation being performed, e.g. uncoated spheres for the core-shell calculations and fractal aggregates for the coated aggregates calculations? I find this to be unclear, but crucial. The “enhancements” must be considered in terms of the reference case that is used.

Figure 7: It would be helpful if the authors added horizontal lines at 1.

P19852, L6: I find the two sentences regarding the range of scattering are, as written,



ACPD
15, C6119–C6127, 2015

in conflict with each other. The range can't be 5-6 and simultaneously 3-8 or 6-15.

P19852, L12: The statement regarding the results from Cheng et al. is incorrect, or at least imprecise. Cheng et al. observed an increase in scattering, but this increase cannot be attributed solely to an "increase in BC scattering due to coating," as it was not demonstrated in that study that particle growth only occurred for BC-containing particles. In other words, particles without BC also grow and contribute to scattering. The statement should be revised to reflect what was actually reported.

Field measurements comparison/prediction: Overall, I find that the description of how the model was developed is insufficient to really allow one to understand what was done. First, the provenance of the data is not entirely clear since the authors refer to the Calnex website as the source of the data, but give Metcalf et al. (2012) as the key reference. If I look on the CalNex website, the data from Metcalf et al. are not available. The specific origin of the data should be clarified. Secondarily, I have concerns that the authors do not fully understand the nature of the data they are using. For example, it seems that the authors have used some constant "mean coating thickness" that they, presumably, applied across all particle sizes. However, if one looks at the Metcalf et al. paper it is clear that the coating thickness is explicitly BC size-dependent. Not to mention that the definition of "mean coating thickness" is, by itself, ambiguous and dependent upon particular instrumental biases with respect to detectable particles. By using a constant coating thickness across all particle sizes, the authors calculations diverge from the actual observations (which show thicker coatings on smaller particles), which in my mind makes this a bit more like a simple sensitivity study of the influence of coating thickness on particle optical properties. While perhaps useful, such calculations are should not necessarily be viewed as something more directly applicable to the atmosphere. (I also have questions about the absolute number shown in Figure 7, since in Metcalf et al. (Fig. 9) they have a "mean coating thickness" of ~160 nm reported in the outflow range, not 80 nm as is indicated in Fig. 7.) My concerns are similar for how the authors treat "coating fraction". How was "coating fraction" dealt



ACPD

15, C6119–C6127, 2015

with? How was this property interpreted from a model perspective? Did some particles have no coating and some have some thick coating? Was a binary distribution applied? The experimental dichotomy is not no coating and lots of coating. It is “thin” and “thick” as defined based on some observable (lag time). The authors need to state how they interpreted this specifically. Overall, I find there are too many details that are lacking here that are really important if this study is to not just be a theoretical sensitivity study but a predictive study that is directly relatable to the atmosphere. Ultimately, I find that the conclusions obtained from the “regional forcing analysis” add little to the theoretical discussion that was already provided: assumed morphology matters. I suggest that this section is removed and replaced with a more general “implications” section.

P19850, L25: The authors conclude this section stating: “Thus, in order to produce reliable and accurate estimates of BC radiative forcing in climate models, the development of a realistic BC coating morphology parameterization appears to be essential.” Although I do not disagree with the general sentiment, the authors might point out that right now such a development is really data limited. Consider that their own calculations here show that morphology can matter, but at the same time they find that the simple “core-shell” model does well in comparison with laboratory observations. This would almost imply the opposite: that despite the variability in the calculations, the simplest morphology ‘works’ and thus consideration of morphology in more detail may not actually help.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 19835, 2015.