Response to Reviewers' comments on "Variation of the radiative properties during black carbon aging: theoretical and experimental intercomparison" by He et al.

Dr. Manabu Shiraiwa
Editor, *Atmospheric Chemistry and Physics*

Dear Dr. Shiraiwa,

We are submitting a revised manuscript (#acp-2015-425) for your consideration of publication in *Atmospheric Chemistry and Physics.* We have carefully studied the reviewers' comments and carried out revisions accordingly. Below is a point-by-point response to the reviewers' comments. We have also provided a copy of track-change manuscript and a clean copy of the revised manuscript.

Thank you for your consideration of this submission. We hope you find our responses adequately address the reviewers' comments and the revisions acceptable. We would greatly appreciate it if you could get back to us with your decision at your earliest convenience.

Sincerely,

Cenlin He
Dept. of Atmospheric and Oceanic Sciences
University of California, Los Angeles (UCLA)
Los Angeles, CA 90095, USA

Point-by-Point Responses to Reviewers' Comments

Reviewer #1

"…. 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."

Response: We thank the reviewer for constructive comments and suggestions. We have provided itemized responses to the following specific comments. Particularly, in response to the comments on Section "Implication for regional radiative forcing analysis", we have removed the entire section and replaced it with a more general "Atmospheric implications" section (see the response to Reviewer #1, Comment #30).

Specific Comments:

1. *"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 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."*

Response: We thank the reviewer for this constructive comment. In the Abstract, we have removed the statement for scattering ("but overestimate the scattering cross sections … as

well as laboratory scattering measurements.") to avoid confusion and rewritten the statement for extinction and absorption in Lines 23-26 (of track-change manuscript) as follows:

"Theoretical calculations are consistent with measurements in extinction and absorption cross sections for fresh BC aggregates with different BC sizes (i.e., mobility diameters of 155, 245, and 320 nm), with differences of ≤ 25%."

Corresponding to this revision, we also rephrased the sentence in Lines 335-337 (Sect. 3.1) as follows:

"Although the calculated scattering cross sections at Stage I are consistently overestimated for different BC sizes compared with measurements, the absolute discrepancies are small."

For the over-generalization of our statements in the entire manuscript, we have made corresponding modifications to make them more specific (see also the responses to the following comments). In response to the over-generalization example given by the reviewer, we have revised the sentences as follows:

Lines 351-355:

"Because of using the BC RIs of 1.95 – 0.79*i* (upper bound) and 1.75 - 0.63*i* (lower bound), the extinction and absorption cross sections of fresh BC aggregates can vary by 25-40% and 20-30%, respectively, while the scattering cross section ranges from 50% to 65% with a higher sensitivity for larger BC sizes."

Lines 34-39 ("Abstract"):

"We find that the absorption and scattering cross sections of fresh BC aggregates vary by 20-40% and 50-65%, respectively, due to the use of upper (1.95 – 0.79*i*) and lower (1.75 – 0.63*i*) bounds of BC refractive index, while the variations are <20% in absorption and <50% in scattering in the case of coated BC particles."

Lines 584-587 ("Conclusions"):

"Sensitivity calculations showed that variation of the extinction and absorption cross sections of fresh BC aggregates is 20-40% due to the use of upper and lower bounds of BC RIs, while variation of the scattering cross section ranges from 50% to 65% with a higher sensitivity for larger BC sizes."

2. *"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."*

Response: We agree that the "direct radiative effects" is more precise than "direct radiative forcing" and have changed "radiative forcing" to "radiative effects" throughout the text. Additionally, following reviewer's suggestions in the general comment, we have removed the entire Sect. 4 on specific calculations of regional radiative effect and replaced it with a more general "Atmospheric implications" section (see also the response to Reviewer #1, comment #30). We have also removed corresponding sentences in the Abstract (Lines 44-49).

3. *"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."*

Response: Thank you. We have included Shiraiwa et al. (2010) and Qiu et al. (2012) in Lines 61-62 as experimental study references for light absorption:
"… and light absorption (Jacobson, 2001; Shiraiwa et al., 2010; Qiu et al., 2012; Scarnato et al., 2013)."

4. *"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."*

Response: Following the suggestion, we have replaced Schnaiter et al. (2003) with Shiraiwa et al. (2007) regarding evidence for the BC coating during aging based on field observations (Line 70).

5. *"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."*

Response: In response, we have revised the statement about Gangl et al. (2008) in Lines 81-82 as follows:
"Gangl et al. (2008) showed that the internal BC-wax mixture amplifies BC absorption coefficient by 10–90%, depending on the amount of coating."

6. *"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."*

Response: Following the reviewer's suggestion, we have reframed the paragraph (Lines 80-96) to emphasize the importance of experimental details (e.g., coating thickness and particle size) which result in a large variation in BC absorption enhancement among different studies:

"A number of laboratory experiments have been conducted to investigate the effects of atmospheric aging on BC radiative properties. Gangl et al. (2008) showed that the internal BC-wax mixture amplifies BC absorption coefficient by 10–90%, depending on the amount of coating. Shiraiwa et al. (2010) found that BC absorption enhancement due to organic coating varies significantly for various BC sizes and coating thickness, with up to a factor of 2 enhancement for thick coatings. Under different experimental conditions, relatively small increases (~30%) in BC absorption have also been observed for BC coated by sulfuric acid (Zhang et al., 2008) and some organics (Saathoff et al. 2003). Furthermore, Xue et al. (2009) and Qiu et al. (2012) showed a less than 20% increase in BC absorption for organic coating, which depends on organic species and coating thickness. Thus, the resulting large variation among different experimental studies indicates that the aging effects on BC radiative properties strongly depend on coating material and thickness as well as BC particle size. It is clear, therefore, that experimental details are critically important in making meaningful and appropriate comparisons among various experimental studies involving BC absorption enhancement associated with coating."

7. *"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."

Response: Following the reviewer's suggestion, we have removed two references (Schwarz et al. (2008) and Moffet and Prather (2009)) in Lines 102-107 and added another two references that directly assess absorption amplification in field measurements in Lines 107-110 (see the response to Reviewer #1, comment #9).

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

Response: We thank the reviewer for pointing this out. The *in situ* observations in Cappa et al. (2012) are based on both aircraft and ground measurements. We have revised this sentence in Lines 112-113 as follows:
"Cappa et al. (2012) reported that the observed BC absorption increased only by 6% due to internal mixing based on direct *in situ* measurements over California."

9. *"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."*

Response: We have removed the original two references on theoretical estimates (see the response to Reviewer #1, comment #7) and added two references on field measurements in Lines 107-110 as follows:
"Based on direct measurements at a suburban site in Japan, Naoe et al. (2009) showed that coating increases BC absorption by a factor of 1.1-1.4 with a larger increase for thicker coatings. Knox et al. (2009) found an absorption enhancement of up to 45% due to BC coating based on measurements in downtown Toronto."

10. *"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."*

Response: We agree with the reviewer and have removed this reference in Lines 123-124.

11. *"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)'."*

Response: We thank the reviewer for pointing this out. We have revised the statement about Adachi and Buseck (2013) in Lines 124-126 as follows:
"Based on ground-based measurements during the California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign, Adachi and Buseck (2013) further observed …"

12. *"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'."*

Response: To clarify, we have revised the sentence in Lines 192-199 as follows:
"Khalizov et al. (2009a) showed that uncertainty in measured optical cross sections of coated BC particles is within 10%, which primarily represents uncertainty in relative humidity, particle size, number density, and instrument calibration. This uncertainty, however, does not include the contribution from multiply charged particles. For freshly emitted BC aggregates, measured scattering cross sections involve relatively large uncertainties."

13. *"P19842, L15: The statement regarding "Babinet's principle" could do with a reference, as this is not necessarily a widely known principle."*

Response: Thank you. We have added a reference (Born and Wolf, 1999) for Babinet's principle in Line 217.

14. *"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."*

Response:. We have revised the statement in Line 227 as follows:
"… the GOS approach compares reasonably well (differences < 20%) with the Finite Difference Time Domain (FDTD) method …"

15. *"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."*

Response: To clarify, we have revised the statement in Lines 236-238 as follows:
"… the GOS approach has been developed specifically for optical cross sections (i.e., extinction, absorption, and scattering) and the asymmetry factor."

16. *"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."*

Response: We thank the reviewer for this comment. We have included a more detailed discussion in Lines 327-333 as follows:
"For comparison with experimental measurements, theoretical results with BC RI of 1.95 – 0.79*i* (i.e., standard simulation) are used unless stated otherwise. The calculated extinction cross sections are consistent (differences ≤ 20%) with measurements for fresh BC aggregates at Stage I with different sizes (i.e., D_{BC} = 155, 245, and 320 nm). However, theoretical calculations tend to overestimate and underestimate extinction for the smallest and largest BC aggregates, respectively."
To clarify and to be consistent throughout the manuscript, we have removed the comparison using mean values of theoretical results with upper and lower bounds of BC refractive index (RI). Our standard (base) case is using BC RI of 1.95-0.79*i*, which is the upper bound recommended by Bond and Bergstrom (2006). The RI of 1.75-0.63*i* is the lower bound. We have revised the text and figures accordingly (see the response to Reviewer #1, comment #23).

17. *"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."*

Response: In response, we have revised the statement about absorption and scattering in Lines 333-340 as follows:
"The discrepancies between theoretical and measured BC absorption cross sections at Stage I increase from 7% (overestimate) to -15% (underestimate) as BC size becomes

larger (Fig. 3). Although the calculated scattering cross sections at Stage I are consistently overestimated for different BC sizes compared with measurements, the absolute discrepancies are small. This overestimate is partly because of the uncertainty associated with extinction and absorption calculations for small particles, where theoretical results overestimate (underestimate) extinction cross sections more (less) than absorption cross sections for D_{BC} of 155 nm (D_{BC} of 245 and 320 nm)."

18. *"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."*

Response: Thank you. We have revised the statement in Lines 343-345 as follows:
"We note that the calculated SSA (~0.16) of BC aggregates at Stage I is within the range of 0.15-0.3 measured for BC from different combustion sources (Bond and Bergstrom, 2006) …"

19. *"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."*

Response: We have included specific values for extinction, absorption, and scattering in Lines 351-355 as follows:
"Because of using the BC RIs of 1.95 – 0.79*i* (upper bound) and 1.75 - 0.63*i* (lower bound), the extinction and absorption cross sections of fresh BC aggregates can vary by 25-40% and 20-30%, respectively, while the scattering cross section ranges from 50% to 65% with a higher sensitivity for larger BC sizes."

20. *"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."*

Response: In order to be more specific, we have revised the name "standard" in the x-axis of Figure 4 (see the revised Figure 4), the figure caption, and the text accordingly as follows:
Line 363: "… BC aggregate cross sections determined from standard calculations (i.e., fractal aggregates with a D_f of 2.1 and D_p of 15 nm; see Sect. 2.4) at Stage I."
Lines 946-951 (Figure caption): "Figure 4 … Results for four BC structures are shown, including BC aggregates in standard calculations (circles) with a fractal dimension (D_f) of 2.1 and a primary spherule diameter (D_p) of 15 nm, BC aggregates with D_f of 2.5

(triangles; versus 2.1 in standard calculations), BC aggregates with a D_p of 20 nm (squares; versus 15 nm in standard calculations), and a single mass-equivalent BC sphere (crosses; versus fractal aggregate in standard calculations)."

21. *"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."*

Response: We have included a more detailed discussion in Lines 396-404 as follows:
"The calculated optical cross sections (i.e., extinction, absorption, and scattering) of coated BC at Stages II and III are in general agreements (differences ≤ 30%) with laboratory measurements, because of the observed efficient structure compaction during aging in laboratory experiments (Zhang et al., 2008). However, theoretical calculations tend to overestimate extinction and absorption for D_{BC} of 155 and 245 nm at both Stages II and III, while the extinction and absorption for the largest particle (D_{BC} of 320 nm) is underestimated at Stage II. The calculated scattering cross sections are overestimated for the smallest BC size (D_{BC} of 155 nm) at Stage II, but tend to be underestimated for larger BC sizes at Stage III, particularly for D_{BC} of 320 nm."

22. *"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?"*

Response: Although the discrepancy in scattering is largely reduced, the discrepancy in absorption is exacerbated by replacing H_2O with H_2SO_4 in the coating material for D_{BC} of 320 nm at Stage III. We have included additional discussions on absorption changes in Lines 415-418 as follows:
"A sensitivity calculation shows that replacing H_2O by H_2SO_4 in the coating material reduces scattering discrepancy to 10% for D_{BC} of 320 nm at Stage III, since H_2SO_4 is more reflective than H_2O, but increases overestimate in BC absorption from 17% to 25%."

23. *"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."*

Response: Yes, our standard (reference) case is using RI = 1.95-0.79*i*, which has been stated in the methodology part (Sect. 2.4). In the original manuscript (as the reviewer pointed out in P19849, L6), we stated "using BC RI of 1.95-0.79*i* increases …", because

we compared the result using RI of 1.95-0.79*i* with the mean value by using RIs of 1.95-0.79*i* and 1.75-0.63*i*. To clarify and to be consistent throughout the manuscript, we have removed the comparison using the mean value and kept the RI of 1.95-0.79*i* as the standard (reference) case. We have revised the text in the track-change manuscript as follows:

Lines 327-329: "For comparison with experimental measurements, theoretical results with the BC RI of 1.95 – 0.79*i* (i.e., standard simulation) are used unless stated otherwise."

Lines 350-351: We removed "while using a BC RI of 1.95 - 0.79*i* reduces underestimates in the calculated BC absorption which dominates the extinction at Stage I."

Lines 394-395: "Theoretical results with the BC RI of 1.95 – 0.79*i* are used for comparison with experimental measurements unless stated otherwise."

Lines 420-425: "Theoretical calculations show that using BC RI of 1.75 – 0.63*i* decreases extinction and absorption cross sections of coated BC particles by 10-17% at Stage II and by 5-15% at Stage III for different BC sizes, which, however, is smaller compared with the decrease for fresh BC aggregates (20-40%). The scattering cross sections of coated BC particles decrease by up to 50% due to the use of smaller BC RI for different BC sizes and aging stages."

To be consistent, we have removed red crosses (the symbol showing the mean value by using RI of 1.95-0.79*i* and 1.75-0.63*i*) in Figure 3 (see the revised Figure 3). The figure caption has also been revised accordingly (Lines 935-939).

24. *"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'."*

Response: To be more specific and clearer, we have revised the statement in Lines 420-425 as follows:

"Theoretical calculations show that using BC RI of 1.75 – 0.63*i* decreases extinction and absorption cross sections of coated BC particles by 10-17% at Stage II and by 5-15% at Stage III for different BC sizes, which, however, is smaller compared with the decrease for fresh BC aggregates (20-40%). The scattering cross sections of coated BC particles decrease by up to 50% due to the use of smaller BC RI for different BC sizes and aging stages."

25. *"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."*

Response: We have added symbols (green squares) in Figure 3 to indicate "standard" values from our standard calculations at each aging stage for different BC sizes (see the revised Figure 3). We have also revised the figure caption accordingly (Lines 935-939).

26. *"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."*

Response: We thank the reviewer for this comment. In Figure 7, we used the freshly emitted BC aggregates measured in laboratory experiments as the reference case for the enhancement calculation. Thus, the enhancement factor is computed as the ratio of calculated absorption (or scattering) cross sections of coated BC particles (Stage II or III) to measured cross sections of fresh BC aggregates (Stage I). The reference case is the same for the calculation of all six BC coating structures shown in Figure 7. The reason for using the measured, instead of calculated, cross sections of fresh BC aggregates as the reference values is to avoid introducing the bias from theoretical calculations to reference values. Otherwise, the enhancement factor could be affected by the bias from calculated cross sections of fresh BC aggregates. To clarify, we have revised the caption of Figure 7 (Lines 971-975) as follows:
"Figure 7. … The reference case for enhancement calculation is the fresh BC aggregate measured in laboratory experiments, which is used for all six BC coating morphology cases. Thus, the enhancement is computed as the ratio of calculated absorption/scattering cross sections of coated BC particles to observed values of fresh BC aggregates. …"

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

Response: Horizontal dashed lines indicating a value of 1.0 have been added in the revised Figure 7. We have also revised the figure caption accordingly (Line 976).

28. *"P19852, L6: I find the two sentences regarding the range of scattering are, as written, in conflict with each other. The range can't be 5-6 and simultaneously 3-8 or 6-15."*

Response: The range "a factor of 5-6" refers to the measured scattering enhancement from laboratory experiments, but the range "a factor of 3-8" or "a factor of 6-15" refers to the scattering enhancement based on theoretical calculations for different BC sizes with different coating morphology. To clarify, we have revised the statement in Lines 502-507

as follows:
"The measured scattering cross sections from laboratory experiments for different BC sizes increase by a factor of 5-6 from Stage I to II and a factor of 11-13 from Stage I to III. Theoretical calculations show that the increase in scattering cross sections from Stage I to II varies from a factor of 3 to 8 for D_{BC} of 245 and 320 nm depending on coating morphology, while both the magnitude and variation of enhancement are much larger for D_{BC} of 155 nm ranging from a factor of 6 to 15."

29. *"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."*

Response: To quote the original text from the abstract of Cheng et al. (2009):
"The coating enhancement in σ_{ap} (absorption coefficient) and σ_{sp} (scattering coefficient) of the coated soot can reach up to a factor of 8–10 within several hours owing to the secondary processing during daytime. It was contributed not only by the increased thickness of coating shell, but also the transition of soot from externally mixed to coated one."
According to this, we have revised the statement regarding Cheng et al. (2009) in Lines 508-510 as follows:
"Cheng et al. (2009) observed that the increase in BC scattering, due to both the increased amount of coating and the transition of uncoated to coated BC, can reach up to a factor of 8-10 within several hours' aging at a polluted site in northeastern China, …"

30. *"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 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.****"*

Response: We thank the reviewer for this comment. Following the reviewer's suggestion, we have removed the entire Sect. 4 "Implication for regional radiative forcing analysis" and replaced with a more general "Atmospheric implications" section in Lines 515-536 as follows:

"Our theoretical calculations have shown that BC absorption and scattering are highly sensitive to coating morphology and the amount of coating at different aging stages. This suggests that the change of BC coating states (e.g., coating thickness, morphology, and composition) during aging process in the real atmosphere could substantially affect BC radiative properties and thus its climatic effects. Metcalf et al. (2012) observed that the mean BC coating thickness increases from ~95 nm over urban areas within boundary layers to ~150 nm in its downwind regions and ~190 nm in the free troposphere, with a factor of two higher number fractions of thickly coated BC in the free troposphere and downwind regions than near the source. Such large variations in BC coating thickness and number fraction of thickly coated BC during aging have also been observed over the tropics from the ground to high altitudes (Schwarz et al., 2008), implying a strong dependence of BC coating state on aging condition and timescale that BC particles have experienced. Furthermore, atmospheric observations also suggest large variability in the composition of coating materials (Moteki et al. 2007; Metcalf et al., 2012) and coating morphology (China et al., 2013; 2015) during BC aging under different atmospheric conditions. Thus, better characterizations of BC coating mass, composition, and morphology during aging are critically important to accurately estimate BC radiative effects.

However, many global models tend to use fixed BC optical properties or simplified

core-shell models for the computation of BC radiative effects (Bond et al., 2013), which may not be representative and sufficiently accurate in view of various BC coating states in the real atmosphere. This study suggests that a reliable estimate of BC radiative effects in climate models would require the representation of a dynamic BC aging process with realistic coating structures, especially for regional analysis with highly heterogeneous atmospheric conditions."

We have also revised the "Abstract", "Introduction", "Methods", and "Conclusion" sections to reflect the preceding revisions:

Lines 44-49 (Abstract): Sentences have been removed.

Lines 49-51 (Abstract):

"This study suggests that an accurate estimate of BC radiative effects requires the incorporation of a dynamic BC aging process that accounts for realistic morphology in climate models."

Lines 145-147 (Introduction): We removed the sentence "We further apply the aging model to the CalNex 2010 field campaign to evaluate the evolution of BC DRF over southern California by coupling with a radiative transfer model (RTM) for analysis."

Lines 295-321 (Methods): We removed Sect. 2.5 ("Application to field measurements").

Lines 575-576 (Conclusions):

"Finally, we discussed atmospheric implications of our results in the assessment of BC radiative effects."

Lines 619-624 (Conclusions):

"Our theoretical calculations suggested that the evolution of BC coating states (e.g., coating thickness, morphology, and composition) during aging in the real atmosphere could exert significant impacts on BC radiative properties and thus its climatic effects, particularly over regions with high heterogeneity. Therefore, to accurately estimate BC radiative effects requires the incorporation of a dynamic BC aging process accounting for realistic coating structures in climate models."

31. *"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."*

Response: We thank the reviewer for these comments. Accordingly, we have added a statement to point out that the development of realistic BC coating morphology

parameterization is currently data-limited in Lines 467-470 as follows:
"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, which, however, could be a challenging task in view of limited observations available at the present time."

Our results using the core-shell model is in a general agreement with laboratory measurements, because of the efficient structure compaction observed in laboratory settings. The statement "general agreement" is only applicable to the core-shell model assumed for this specific laboratory study. However, the real atmosphere is much more complex than controlled laboratory settings, which could result in larger variations in BC coating morphology (e.g., Adachi et al., 2010; China et al., 2013, 2015). Our study showed a strong dependence of BC optical properties on coating morphology, suggesting that accurate estimates of BC radiative effects in climate models require a better characterization of coating morphology in view of various irregular coating structures based on atmospheric observations. We have included the corresponding discussions on the "Atmospheric implications" section (see also the response to Reviewer #1, comment #30).

Reviewer #2

"The authors theoretically investigate the effects of morphology on optical properties of black carbon using the GOS approximation and compare the theoretical results with laboratory experiments. After that, the developed optical model was implemented to the radiative transfer simulation for evaluating the evolution of direct radiative forcing of BC with aging. Overall, this paper is well written and I recommend its publication in ACP, provided the following comments/questions are taken into account in revision."

Response: We thank the reviewer for kind words. We have provided itemized responses to the following comments.

General Comments:

1. *"Although the observed shape of internally-mixed compounds with BC (e.g., sulfate, organics) is usually dissimilar to composite of spheres (e.g., Fig.5 of Adachi et al. 2010), they are simply represented by a cluster/composite of spheres or core-shell spheres throughout this work. I hardly imagine physical processes (i.e., condensation, coagulation, cloud processing) that can produce "closed-cell" and "open-cell" structures (Fig.1) in the atmosphere. It seems to me that use of these two morphological models is too artificial and only of theoretical interest. It is more plausible to adopt nonspherical morphological models (e.g., "thinly-coated" or "partial thin-coating")*

without restriction to cluster/composite of spheres, instead of unrealistic "closed-cell" and "open-cell"."

Response: We thank the reviewer for this comment. To clarify, the "closed-cell" model shown in Figure 1 is to mimic the observed structure presented in Strawa et al. (1999), while the "open-cell" model is to mimic the structure generated in the laboratory by Stratmann et al. (2010). Thus, "closed-cell" and "open-cell" structures are physical models to approximately represent actual observations. We have included discussions on the limitation of using "closed-cell" and "open-cell" structures in the following:
Lines 157-159:
"In this study, six typical BC coating structures (Fig. 1) have been considered for Stages II and III to approximately represent observations in the real atmosphere or laboratory, …"
Lines 170-173:
"We wish to note that the six coating structures used in this study, including closed-cell and open-cell structures, are theoretical models and as such, they may not completely capture detailed BC coating structures from aircraft and ground-based observations."

We also agree with the reviewer that the nonspherical morphology models (e.g., partial thin-coating) without restriction to composite of spheres are more realistic, which, however, could be much more complex in terms of representing the structure with geometric parameters compared with primary spherules used in the present study. This will be investigated in our future work. We have added discussions on the limitation of assuming composite of spheres in Lines 289-292 as follows:
"We note that assuming a cluster of spheres for the above-mentioned coating structures may not be sufficiently realistic and that nonspherical morphology models without restrictions to composite of spheres appear to be more plausible (Adachi et al., 2010), a challenging subject to be investigated in future work."

2. *"If the authors restrict the model particles to clusters/composites of spheres, why don't you use numerically-exact superposition T-matrix method (e.g., MSTM code developed by Mackowski) instead of the GOS approximation. MSTM version 3 can be applied to any internal and external composites of spheres without surface cut, encompassing all morphological models assumed in this paper. The authors need to explain the advantages of GOS compared to MSTM (or DDA or FDTD) under the ranges of size parameter and refractive index considered in this work."*

Response: The main reason that we used the GOS approach is that it is computationally efficient and sufficiently accurate for the simulations involved in this manuscript. Validation of GOS has been reported by Takano et al. (2013). In particular, we showed that the GOS and superposition T-matrix results are both close to the observed specific absorption of BC aggregates for the size range used in the present work. Also, in Liou et

al. (2011), we compared GOS results for specific absorption with superposition T-matrix results published in Liu et al. (2008) and demonstrated close comparison for the mass absorption coefficient measured by Sheridan et al. (2005). Furthermore, we respectfully submit that the comparison between GOS and experimental results conducted in this study constitutes a significant verification of the GOS approach. Also, GOS does not pose a limit on the number of spherical monomers of an aggregate from the perspective of practical light scattering computations. Some numerical methods such as DDA and FDTD require a substantial amount of computational resources and are not practical for moderate and large size parameters. Because the GOS approach is quite accurate, using either GOS or MSTM will not alter the major findings presented in this study. We have incorporated additional discussions in the track-change manuscript to reflect the above-mentioned points:

Lines 242-245:

"Takano et al. (2013) showed that the coupled GOS-RGD and superposition T-matrix results are both close to the observed specific absorption of BC aggregates for the range of size parameter considered in the present study."

Lines 268-269:

"The comparison between GOS and experimental results in this study provides an additional dimension of validation/cross-check of the GOS approach."

Specific Comments:

1. *"P.19842, L.25∼ 'Liou et al. (2010, 2011) and Takano et al. (2013) demonstrated that the single scattering properties of aerosols with different sizes and shapes determined from the GOS approach compare reasonably well with those determined from the Finite Difference Time Domain (FDTD) method (Yang and Liou, 1996) and DDA (Draine and Flatau, 1994) for column and plate ice crystals, the superposition T-matrix method (Mackowski and Mishchenko, 1996) for fractal aggregates, and the Lorenz–Mie model (Toon and Ackerman, 1981) for a concentric core-shell shape.' In these referred papers, I could not find any results supporting the accuracy of GOS for BC-containing particles with morphologies "off-center core-shell", "closed-cell aggregate", "partially encapsulated", "open-cell aggregate", and "externally attached", by mean of comparison with numerically-exact techniques (e.g., superposition T-matrix). The authors need to show results (or refer specific part of some publications) supporting the accuracy of GOS/RDG approach for all the morphologies assumed here, because it seems difficult to quantify the error of GOS/RDG approximation without comparisons with some numerically-exact solver of Maxwell equation."*

Response: Please see the Responses to general comment #2. In addition, we would like to point out that every light-scattering approach has its limitation, including the superposition T-matrix methods. Moreover, the GOS approach has been cross-validated with both observations and T-matrix/DDA/FDTD (Liou et al., 2011; Takano et al., 2013)

for various particle structures as stated in the text (Lines 225-231), which shows the accuracy and capability of GOS in dealing with different BC coating structures to certain extent. Lastly, we submit that the current comparison of GOS results with laboratory measurements for extinction, absorption, and scattering cross sections provides an additional dimension of validation/cross-check of the GOS approach. In response to the reviewer comments, we have incorporated additional discussions to reflect the preceding points (see also the response to general comment #2).

2. *"P.19843, L3~ 'Moreover, compared with other numerical methods, the GOS approach can be applied to a wider range of particle sizes, shapes, and coating morphology with a high computational efficiency, including very large particles (e.g., ~100–1000 μm snowflakes) and complex multiple inclusions of aerosols within irregular snow grains (Liou et al., 2014; He et al., 2014), in which the FDTD, DDA, and T-matrix methods have not been able to apply.' As far as I read the references cited in this paper, the accuracy of GOS has been investigated only limited number of particle shapes: sphere, core-shell sphere, hexagonal ice-crystals, and aggregate of spheres. The authors need to show (or refer) the direct evidences on the accuracy of GOS in other shapes considering in this work. Computational efficiency seems to be of secondary importance at least for the purpose of this paper."*

Response: Thank you. Please see the Responses to general comment #2 and specific comment #1.

3. *"P.19843, L13~ 'To supplement GOS, we have developed the Rayleigh–Gan–Debye (RGD) approximation coupled with GOS for very small particles, which has been cross-validated with the superposition T-matrix method (Takano et al., 2013). The combined GOS/RGD approach can be applied to size parameters covering 0.1 to 1000.' Please clarify which of GOS and RGD was assumed in each theoretical calculation in this paper."*

Response: We thank the reviewer for this comment. To clarify, we have included the following statement in Lines 246-248:
"In the present study, the coupled GOS-RGD approach is used for fresh BC aggregates (Stage I), while the GOS approach without RGD coupling is used for coated BC particles (Stages II and III)."