Reply to the comments of anonymous reviewer #2 on manuscript Entitled "Dynamic shape factor and mixing state of refractory black carbon particles in winter in Beijing using an AAC-DMA-SP2 tandem system"

We appreciate very much the anonymous reviewer for providing insight comments and recommendations. We will revise the manuscript carefully according to the comments. The one-to-one replies are as follows,

General comments:

1. More details need to be provided on the optical model, at a minimum the exact number of monomers, how their diameters were chosen, the index of refraction values used, etc.

Reply:

Monomer size (a) is assumed to be 0.02μm. Monomer number (N_s) is calculated by volume-equivalent radii (R_{eff}) of rBC particle, as following $N_s=(R_{eff}/a)^3$. Herein, N_s is an integer.

The refractive index of rBC particles are assumed to be 1.95-0.79i, and the refractive index of non-rBC particles are assumed to be 1.5-0i.

2. More discussion should be provided on the accuracy and precision of the chi parameter, how these accuracies and precisions are calculated/estimated, and how significant (in a statistical sense) are the differences discussed in the paper.

Reply:

We will add discussion about the uncertainty of chi parameter. As suggested in literature (Tavakoli and Olfert, 2014), the uncertainty in dynamic shape factor can be calculated as

$$\left(\frac{\varepsilon_\chi}{\chi}\right)^2=\frac{4}{9}\left(\frac{\varepsilon_{d_{mo}}}{d_{mo}}\right)^2+\frac{4}{9}\left(\frac{\varepsilon_{d_{ae}}}{d_{ae}}\right)^2+\frac{14}{9}\left(\frac{\varepsilon_{C_c}}{C_c}\right)^2+\frac{1}{9}\left(\frac{\varepsilon_{\rho_p}}{\rho_p}\right)^2$$

Where, the uncertainty of mobility diameter ($\varepsilon_{dmo}/d_{mo} \approx 3\%$), the uncertainty of aerodynamic diameter ($\varepsilon_{dae}/d_{ad} \approx 2\%$), the uncertainty of slip correction($\varepsilon_{Cc}/Cc \approx 2.1\%$), the uncertainty of density of particle ($\varepsilon_{\rho p}/\boldsymbol{\rho}_p \approx 10\ \%$), and the sum of total uncertainties is ~ 7.2%.

3. Tense consistency and grammar should be checked in the entire paper.

Reply: We will check the tense and grammar carefully in the revised manuscript.

4. The bibliography is OK, but maybe a bit biased and limited. Some additional references that might be useful (I am not suggesting the authors should cite all of them, I let them judge the relevance) to the paper discussion are added at the end of this document.

Reply: We will cite more relevant reference to support the discussion in the manuscript.

SPECIFIC COMMENTS:

Line 22: “aerosol particles” include all particles or only rBC-containing particles?

Reply: Aerosol particles here refers to all particles including both rBC-containing particles and non-rBC particles.

Lines 27-28: Maybe I am misreading this sentence, but why would condensation result in larger rBC cores? And why clean conditions would result in more coagulation processes and therefore larger particles. I would expect the opposite (more pollution should result in a higher likelihood of coagulation

and therefore larger sizes). Also – a clarification - the assertion "smaller rBC core" refers to Dmev from the SP2, correct?

Reply:

As mentioned, the "smaller rBC core" refers to D_{mev} from the SP2. In our tandem system, particles were firstly selected by AAC and thus had a fixed aerodynamic diameter. For rBC-containing particles with the same aerodynamic diameter, a smaller rBC core means a thicker coating thickness and a larger rBC core means a thin coating thickness. The coating thickness can reflect the aging degree. In pollution episodes, due to the high concentration of precursors, the rBC-containing particles were easy to undergo the coagulation and condensation processes and thus had a thicker coating and small rBC core.

Line 28: Does the chi value refer to all particle or only the rBC-containing particles?

Reply:

The chi value reported in this paper is all for all particles including rBC-containing particles and non-rBC particles.

Line 43: In general BC particles can also be mixed through (or be injected into) the upper troposphere above the PBL (for example by large fires).

Reply:

What we want to express is the strong heating effect of rBC in the PBL which may stabilize the PBL and aggregate the air pollution. However, we also agree the opinion of the reviewer and we will delete the "in the planet boundary layer (PBL)" in line 43.

Line 67: Also photoacoustic and extinction-minus-scattering techniques.

Reply:

Thanks for the advice of the reviewer, for completeness, we will add these two techniques in the revised manuscript.

Lines 68-69: The term soot is also often used in microscopy.

Reply:

We consent to the reviewer about the terminology of soot.

Line 82: To enhance clarity for a broader readership, it might be good to briefly define the "lensing effect".

Reply:

We will revised the expression according to the suggestion. "the light-absorbing capacity of rBC-containing particles will enhance significantly due to the "lensing effect" of the coatings" will change to "the light-absorbing capacity of rBC-containing particles will enhance significantly due to the "lensing effect" which means more lights will refract and interact with the rBC core due to the non-rBC coating".

Line 103: Electron or x-ray microscopy in general, not just transmission.

Reply:

We will revise the expression.

Line 108: By definition, one would think that for a spherical particle, chi should be exactly one.

Reply:

According the theoretical definition, chi should be exactly one for a spherical particle. However, in the actual measurement, the chi value is affected by the uncertainty of the instruments as well as some assumptions made in the calculation of chi. Thus, the chi value is almost but not exactly equal to 1.0 for spherical particles in the previous reported literature (Tavakoli and Olfert, 2014;Qiu et al., 2014). This sentence is from the aspect of measurement.

Line 197: Please define the setpoint Rs.

Reply:

The resolution parameter (R_s) is defined as the setpoint divided by the full width half maximum of the instrument's transfer function in the size domain.

Line 199: Consider revising "at a scanning mode"

Reply:

We will revise the expression "Then, the mode mobility size of sampled aerosol was determined using a DMA"

Line 219: "…the same as that of a spherical particle" of what size? Equation (9)

Reply:

For a non-spherical particle that is migrating at a steady velocity in an electric field, its electrical mobility is the same as that of a spherical particle of D_{mob} size.

line 239: The subscript BC here indicates BC or rBC? Also, as written the equation seems to imply that Dmob = Dve is a chi missing?

Reply:

We will replace BC with rBC in the subscript. S/C ratio was the ratio of shell diameter of rBC-containing particle to its rBC core. Here, D_{ve} is calculated using equation (7). As the reviewer mentioned, the difference between D_{ve} and D_{mob} is due to irregularity of particles that could be represented by a Chi. For We will use S/C = $D_{mob}/D_{mev,rBC}$ in the revised manuscript.

Line 296: Is this the D_{mev} of rBC particles or of any particle? This is confusing to me especially in view of the comment in lines 298 and 300. (See also one of the previous comment).

Reply:

D_{mev} is mass-equivalent diameter that only refers to the rBC particles that derived from incandescence signal by SP2. Note that, the AAC was operating at a constant mode to select the particles with aerodynamic diameter of 400 nm during the whole observation period. We found that D_{mev} during polluted period was relatively smaller than that during clean period. We suspected that freshly emitted small rBC particles cluster has more chance to be coated by non-rBC matters, especially at humid condition.

Lines 300 – 303: As mentioned above, I do not clearly understand this argument. rBC indicates the refractory part of the particle which should identify with the core of the particle, so how would the core grow due to condensation?

Reply:

Sorry for misleading. We mean that rBC core (D_{mev} < 150 nm) in polluted urban environment have more

chance to be coated by other compounds. Consequently, the size of rBC-containing particles increased to D_{ae} of 400 nm. We will revise the manuscript.

Even more confusing to me is the sentence in lines 307 - 308: how would water-soluble inorganic matter change the rBC core mass? I can understand that could change the rBC core shape to more compact, but the mass equivalent diameter should not change in the compaction process (it is just a reorganization of the monomer location).

Reply:

Yes, we agree with the reviewer that the water-soluble inorganic do not change mass of rBC core. It could lead to reconstruction of rBC monomer due to complex mixing process. During polluted period, the coating process occurs rapidly, which results in thickly coated rBC particles. We would like to revise the expression to avoid confusion.

Line 310: How large are the uncertainties on chi? Are these variations significant (in a statistical sense)? An uncertainty is mentioned in line 322 for that value of chi, but I do not recall any discussion on what that uncertainty represents and how was it estimated.

Reply:

As suggested, we will add discussion about the uncertainty of chi value. According to the estimation proposed by Tavakoli and Olfert (2014), we found that the total uncertainty was 7.2% with main contribution from variability of density of particle.

Line 312: What is an "In-BC" core?

Reply:

This term is proposed by Zhang et al., (2016). The "In-BC" means internally mixed rBC particles. The authors used on the thermo-denuder to remove the non-refractory coating of rBC-containing particle and measured the dynamic shape factor of rBC core. To avoid confusion, we will use "internally mixed rBC" in the revised manuscript.

Lines 327-329: I am not clear why coagulation would result in higher chi. To me, it makes more sense what suggested in the following sentences on diesel heavy-duty vehicle contributions (at night) and the effect of photochemical processing (during the day).

Reply:

We consent to the reviewer's comment. Previous results showed that freshely emitted rBC-containing particles from diesel-fuel engine had more irregular structure than the aged ones (Adachi et al., 2010;Wang et al., 2017). In Beijing, rBC emission from diesel-fuel engine trucks at night was much stronger because transport trucks are banned in the daytime in city area. In this study, the increase in chi value at night might be related toheavy-duty vehicle. We will revise the manuscript.

Lines 349 – 353: I don't follow the argument here. It might help some further discussion or clarification.

Reply:

We will clarify the discussion here.

Line 390: M_R indicates what? The mass ratio of core to shell?

Reply:

M_R is the mass ratio of coating to rBC core. This value is another way to quantify the coating thickness of rBC and we will specify the meaning of M_R in the text.

Line 396: Is "exponentially" meant to actually represent an analytical exponential increase, or just to mean qualitatively a large increase?

Reply:

According to the measurement, the chi value of particle with aerodynamic diameter of 400 nm increased evidently with increase of number fraction of rBC-containing particles, with suggested that rBC particle play a key role in overall morphology of particles. Here we use an exponential fitting curve to indicate the significant increase, though there were large uncertainty. Because only the particle with a fixed aerodynamic diameter was discussion, the result is informative for estimation of the optical properties.

Lines 401 – 403: Those two numbers (1.71 +/- 0.05 and 1.56 +/- 0.15) appear not to be significantly different within the uncertainties provided.

Reply:

We agree with the reviewer, and we will revise the experession.

Line 414: The authors probably meant to write "fractal" not "fractional" (?)

Reply:

Yes, we will correct the error.

Line 415: "were reported" by who?

Reply:

We referred to content in the book (Seinfeld and Pandis, Atmospheric Chemistry and Physics, Willey) will add the reference in the text.

Lines 417-418: I am not clear what the authors mean by "a faster decreasing tendency", decreasing with what?

Reply:

Sorry for misleading. what we refer is that the effective density decreases faster with D_{mob} increasing for the particles with smaller D_f. We will change the expression of this sentence.

Line 420: Just a clarification, is the effective density here referring to the entire rBC-containing particle or only to the rBC (core)?

Reply:

We refer to the rBC-containing particle.

Line 421-424: Does this refer to a result from the authors or from the literature? It is not clear to me what the authors refer to.

Reply:

To be clear, we will cite the relevant references

Line 442: “to present as aggregation: : :” should maybe be “to be present as aggregated: : :”, or “to be present as aggregation of: : :”? Or something similar. Line 436: Missing “of” in front of “climate effect”? Or alternatively, “Quantification” should maybe be “Quantifying”.

Reply:

Thanks for the advice, we will change the expression.

Line 449: Is this “simultaneity” an assumption, or an actual observation? If an observation, based on what?

Reply:

According to the observation of this study, we cannot distinguish which processes occur first. We thought that reconstruction of rBC and coating may happen simultaneously.

Line 459-460: Could the authors please elaborate a bit more on the “novel aggregate model” and provide some detail? What’s novel about? There has been a lot of published work on this topic (see some limited example in the reference below)

Reply:

We consent to the reviewer’s comments. We will remove “novel” in the text. In the aggregate model, realistic rBC particle morphologies during aging are qualified for modeling rBC optical properties dependent on the mass ratio of non-BC and BC components (M_R) or shell/core (S/C) ratio. The non-rBC/rBC mass ratio is zero (M_R=0) for indicating bare BC particles freshly emitted from incomplete combustions without mixing non-rBC materials, and their particle morphology appears as a fractal aggregated chain-like structures consisting of hundreds or thousands of spherules. The augment of non-rBC/rBC mass ratio indicates the mixing of aggregated BC monomers with larger non-BC components in the individual particles, resulting in more compact rBC structures and various mixing states. According to microphysical measurements by China et al., the single BC particles may be thinly coated (e.g. 0<M_R<=5) or partially encapsulated (e.g. 0.1<=M_R<=10), and further aging brings on compact BC aggregate heavily coated (e.g. M_R>5) with the large non-BC materials. These more realistic morphologies of BC-containing aerosols, quantitatively related to the non-BC/BC mass ratios, are applied for the modeling of their optical properties.

This sentence is modified as follow:

Herein, the morphologies of rBC-containing particles were constructed by the aggregate model (Wu et al., 2018) and their random-orientation scattering cross sections of particles was simulated on the basis of a superposition T-matric method by solves Maxwell’s equations numerically (Mackowski et al., 2011).

Line 470: What’s the reason for this diameter choice, from the literature? If so, please cite some published work. If not, please justify.

Reply:

Bond and Bergstrom (2006) reported the value of mean radii of rBC monomer (a) in the range of 0.01-0.025μm. In this study, the mean radii of rBC monomer were assumed to be 0.02μm, thus, the mean diameters of rBC monomers were 0.04 μm.

Line 473: I thought (I) indicates fresh particles and (II) indicates thinly coated, as from lines 462 – 463? Please clarify. Also, how much coating is on the thinly coated particles, and how much on the thickly coated particles in your model?

Reply:

Yes, the case I indicates the fresh particles, we will change the expression later. In fact, the what we tested was the sensitivity of different models based on the measurement properties of rBC-containing particles in this study, e.g. S/C and D_{mev}. In this study, we mainly focused on the thickly-coated rBC particles with S/C ratio = 2.7. We will revise the discussion according to your suggestion.

Line 502: “reconstruction” or “restructure”? Line 513: “was” should be “were” Line 533: “stale” should be “stable”?

Reply:

We will correct it in the revised manuscript.

Line 535: “novel” in what sense? There have been several studies (experimental as well as numerical) using similar models and mixing configurations. Lines 520-522: I am still confused by this assertion (see previous comments on this topic)

Reply:

As explained in the previous comment, and the word “novel” will be removed.

Figure 2, 4, 5 and 7: Consider using the symbol for chi as in the text instead of DSF for the plot axis title to avoid confusions.

Reply:

We will change the symbol as suggested.

Figure 4: What is the top plot, a residual plot? Please provide an axis label and explain in the caption.

Reply:

We will give detailed explanation in the caption of all figures.

Figure 5: In the caption, explain the meaning of the colored bands.

Reply:

The meaning of colored bands will be explained.