Reply to the interactive comment from anonymous Referee #1

Thank for providing comments. We are taking the opportunity seriously to explain our study to the reviewer and potential readers who are interested in microphysical property of soot particles in mega city. We think that some understanding divergence might exist between the anonymous reviewer and us. Here, we tried our best to response all the comments one by one as follows:

General comments:

1. Pan et al. have presented measurements of a tandem AAC-DMA-(CPC/SP2) system intended for mixing state measurements of black carbon in the atmosphere. The technique is not novel, having been demonstrated earlier by Tavakoli and Olfert (2014). However, Pan et al. did not simply apply the approach of Tavakoli and Olfert. Rather, they developed alternative approaches which were not convincingly demonstrated either theoretically or experimentally, and which were fundamentally flawed. For example, Tavakoli and Olfert obtained agreement within uncertainty for their AAC-DMA-CPC density measurements of dioctyl sebacate (DOS). Pan et al. did not obtain agreement within uncertainty for PSL. They also did not obtain closure between AAC-DMA-CPC measurements and DMA-AAC-CPC measurements (even the trends differed).

Reply:

In this study, we just adopted the approach that was introduced by Tavakoli and Olfert (2014) to study the dynamic shape factor of ambient aerosols in urban environment, and we did not develop any alternative approaches. We did check the uncertainty of the AAC-DMA-CPC tandem system for the density measurement of PSL particles (results are shown in Figure 2), we found that the measured effective density of PSP particles was 1.08~1.12 g/cm^3, comparable to the nominal value (1.05 g/cm^3). Herein, an AAC was operating in constant mode to select the particles with a known aerodynamic diameter, and a DMA was operating in scanning mode to determine the and mobility diameter. Using the equation (3) – (5) and (7) in literature (Tavakoli and Olfert, 2014), the effective density was calculated. In this study, effective density of Aquadag particles (200 – 600 nm) determined by a DMA-AAC-CPC system was consistent well with previous studies (SF.1). A relatively larger effective density derived by AAC-DMA-CPC may result from complex multiple charge of irregular particles. For ambient measurement, one predominant mode of mobility diameter (~300 nm) was observed for the particles with aerodynamic diameter of 400 nm, indicating that multiple charge did not influence our conclusion. We will do more test using other particles such as soot particles produced from burner.

2. The work also misses an essential demonstration of their system using fresh (and also ideally coated) laboratory soot. The authors have interpreted all variability in soot morphology as due to atmospheric processing without measuring the initial variability in soot morphology!

Reply:

We consent to the reviewer's suggestion. We would like to perform relevant experiment. Soot particles could be flame-generated by a commercial burner (i.e. miniCAST) in the laboratory, and the dynamic shape factor could be determined and compared with the particles in ambient

environment. The main purpose of this study is to investigate the variation of dynamic shape factor of soot aerosols with known aerodynamic diameter (400 nm) at different pollution condition. The initial morphology of very freshly generated soot particles produced in the laboratory is informative for this study. In the next research, we would like to check the variability of freshly emitted soot particle in different control experiments (i.e. at different relative humidity condition).

3. The logical errors and inaccuracies I am referring to in the Introduction and Methods are egregious and do not seem to be due to English mistakes. Examples of the logical errors are (i) incorrectly defining "BC" and "rBC" in the Introduction, when these materials are the focus of this study!, (ii) using the wrong refractive index for PSL, a standard calibration material, (iii) including several inaccurate statements in the description of the SP2, the instrument on which this study relies. These are not grammatical shortcomings but are simply collections of invalid statements. Results from key studies (cited below) have been ignored. The studies which are cited are at times misinterpreted or are only cited in support of a single statement instead of influencing the authors' overall data interpretation (see the Liu et al. 2017 study discussed below).

Reply:

i), As well known, BC has been used for years as a catch-all term to describe a variety of types of carbonaceous particles (Daniel A. Lack et al., 2014), which have many different physical, optical, and chemical properties.

BC is defined as the carbonaceous component of particulate matter that absorbs all wavelengths of solar radiation (Petzold et al., 2013). Bond et al. (2013) provided a refined definition as "a distinct type of carbonaceous material that is formed primarily in flames, is directly emitted to the atmosphere, and has a unique combination of physical properties."

The carbon mass derived from laser induced incandescence (LII) is referred to as refractory black carbon (rBC) since it is derived by measuring the thermal emission of the carbon component of the particle that absorbs the laser energy (Daniel A. Lack et al., 2014). Given the inconsistencies in the aerosol literature regarding terminology, e.g., BC, soot, light-absorbing carbon, we adopted the nomenclature advocated by Schwarz et al. (2010) and widely used by the SP2 community that the Single Particle Soot Photometer measures refractory black carbon (rBC) defined operationally by its incandescence temperature (Sedlacek et al., 2012).

To avoid misunderstanding, we would like to modify the expression in line 65 – 69 to "… black carbon refers to the carbonaceous component of particulate matter that absorbs all wavelengths of solar radiation. a number of commercial instruments (i.e. aethalometer, multi-angle absorption photometer) derived a mass concentration of BC using a mass absorption coefficient. Another definition, refractory black carbon (rBC) is quantified by a single particle soot photometer on the basis of …."

References:

1) Petzold A, Ogren JA, Fiebig M, Laj P, Li S-M, Baltensperger U, Holzer-Popp T, Kinne S, Pappalardo G, Sugimoto N, Wehrli C, Wiedensohler A, Zhang X-Y (2013)

Recommendations for the interpretation of “black carbon” measurements. Atmos Chem Phys DOI: 10.5194/acpd-13-9485-2013.
2) Bond, T. C., Doherty, S., Fahey, D. W., Forster, P., Berntsen, T., DeAngelo, B., Flanner, M., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Lohmann, U., Sarofim, M., Michael, S., Schultz, M. G., Venkatamaran, C., Zhang, H., and Zender, C. S.: Bounding the role of black carbon in the climate system — A scientific assessment, Journal of Geophysical Research: Atmospheres, 118, 2013.
3) Lack, D. A., Moosmüller, H., McMeeking, G. R., Chakrabarty, R. K., and Baumgardner, D.: Characterizing elemental, equivalent black, and refractory black carbon aerosol particles: a review of techniques, their limitations and uncertainties, Analytical and bioanalytical chemistry, 406, 99-122, 10.1007/s00216-013-7402-3, 2014.
4) J. P. Schwarz , J. R. Spackman , R. S. Gao , A. E. Perring , E. Cross , T. B. Onasch , A. Ahern , W. Wrobel , P. Davidovits , J. Olfert , M. K. Dubey , C. Mazzoleni & D. W. Fahey (2010) The Detection Efficiency of the Single Particle Soot Photometer, Aerosol Science and Technology, 44:8, 612-628, DOI: 10.1080/02786826.2010.481298
5) Sedlacek, A. J., III, E. R. Lewis, L. Kleinman, J. Xu, and Q. Zhang (2012), Determination of and evidence for non- core-shell structure of particles containing black carbon using the Single-Particle Soot Photometer (SP2), Geophys. Res. Lett., 39, L06802, doi:10.1029/2012GL050905.

ii) We know that nominal refractive index of PSL particle is 1.59-0i, and we used the value for the calibration. To note that, in SP2 community, “The refractive index for the ambient data calculated with volume mixing was 1.46–1.50 (mean 1.48)” (Taylor et al., 2015). For instance, a refractive index (1.48 -0i) was used to calculated the optical size of pure scattering particles or coating matters of rBC core (Subramanian et al., 2010), and we also adopted this value. Schwarz et al., (2008) and Liu et al., (2014) used a refractive index of 1.5-0i. We will describe more clearly in the revised manuscript.

References:

1) Subramanian, R., Kok, G. L., Baumgardner, D., Clarke, A., Shinozuka, Y., Campos, T. L., Heizer, C. G., Stephens, B. B., de Foy, B., Voss, P. B., and Zaveri, R. A.: Black carbon over Mexico: the effect of atmospheric transport on mixing state, mass absorption cross-section, and BC/CO ratios, Atmospheric Chemistry and Physics, 10, 219-237, 10.5194/acp-10-219-2010, 2010.
2) Schwarz, J. P., et al. (2008), Measurement of the mixing state, mass, and optical size of individual black carbon particles in urban and biomass burning emissions, Geophys. Res. Lett., 35, L13810, doi:10.1029/2008GL033968.
3) Liu, D., Allan, J. D., Young, D. E., Coe, H., Beddows, D., Fleming, Z. L., Flynn, M. J., Gallagher, M. W., Harrison, R. M., Lee, J., Prevot, A. S. H., Taylor, J. W., Yin, J., Williams, P. I., and Zotter, P.: Size distribution, mixing state and source apportionment of black carbon aerosol in London during wintertime, Atmospheric Chemistry and Physics, 14, 10061-10084, 10.5194/acp-14-10061-2014, 2014.

iii) We would like to cite the mentioned literatures Petzold et al., (2013) , Sorensen et al., (2011) and Taylor et al., (2015) in the revised manuscript. About the paper (Liu et al., 2017), I think

our interpretation is clear and straightforward. It states that " in page 1: … black- carbon particles with a ratio greater than 3, which is typical of biomass-burning emissions, are best described assuming optical lensing leading to an absorption enhancement; In page 3: … For $M_R > 3$, we find the measured scattering cross-section is best reproduced by the core–shell model. …"

Specific comments:

1. The "shell-core ratio", S/C, the authors introduce brings confusion and no insight to the measurements. The authors define S/C as particle volume-equivalent OR mobility diameter (from the AAC-DMA) divided by mass-equivalent diameter of BC (from the SP2). First of all, this is not physically a shell-core ratio even if BC was core-shell in morphology, because even after restructuring by coatings this S/C will not be equal to 1; a compact BC aggregate is larger than a sphere.

Reply:

First of all, S/C ratio is a widely accepted definition in SP2 community to describe the coating thickness of rBC-containing particles, and it was adopted by a number of studies (i.e. Zhang et al., PNAS 2008; Shiraiwa et al., AST, 2010; Liu et al., ACP, 2014, Taylor et al, AST, 2015; Pan et al., ACP, 2017). Gao et al., (2007) introduced a Two-elemental APD in SP2 and leading-edge fitting method to estimate the "original" size of rBC-containing particles (it is termed as shell diameter). Note that, both shell diameter (D_p) and core diameter (D_c) are quantities determined by optical signals. Of course, shell diameter could also be directly selected by a DMA (Zhang et al., 2008). In general, S/C ratio is an objective indicator, and a larger S/C ratio means that rBC core is thickly coated by hosting matters. In this study, shell diameter was determined by a DMA, and volume-equivalent diameter was also calculated to support our conclusion (Figure 6). we reported that S/C ratio of rBC-containing particles (with aerodynamic diameter of 400 nm) was 2.7 +/- 0.3. DeCarlo et al., (2004) demonstrated the volume equivalent diameter is equal to the mass equivalent diameter for fresh BC aggregates, thus a fresh BC has a S/C ratio of ~1. Taylor et al., (2015) also reported that E_{sca} (the ratio of a particle's measured scattering cross-section divided by that of its uncoated core predicted by Mie theory) was close to 1 for the least chemically aged particles, supporting our viewpoint.

References:

1) M. Shiraiwa, Y. Kondo, T. Iwamoto & K. Kita (2010) Amplification of Light Absorption of Black Carbon by Organic Coating, Aerosol Science and Technology, 44:1, 46-54, DOI: 10.1080/02786820903357686.
2) Renyi Zhang, Alexei F. Khalizov, Joakim Pagels, Dan Zhang, Huaxin Xue, and Peter H. McMurry, PNAS July 29, 2008 105 (30), https://doi.org/10.1073/pnas.0804860105
4) R. S. Gao , J. P. Schwarz , K. K. Kelly , D. W. Fahey , L. A. Watts , T. L. Thompson , J. R. Spackman , J. G. Slowik , E. S. Cross , J.-H. Han , P. Davidovits , T. B. Onasch & D. R. Worsnop (2007) A Novel Method for Estimating Light- Scattering Properties of Soot Aerosols Using a Modified Single-Particle Soot Photometer, Aerosol Science and Technology, 41:2, 125-135, DOI: 10.1080/02786820601118398
5) Taylor, J., Allan, J., Liu, D., Flynn, M., Weber, R., Zhang, X., Lefer, B., Grossberg, N., Flynn, J. and Coe, H. Assessment of the sensitivity of core/shell parameters derived using

the single-particle soot photometer to density and refractive index. Atmos. Meas. Tech., Copernicus GmbH, 2015, 8 , 1701-1718
6) Decarlo, P., Slowik, J., Worsnop, D., PaulDavidovits, and Jimenez, J.: Particle Morphology and Density Characterization by Combined Mobility and Aerodynamic Diameter Measurements. Part 1: Theory, Aerosol Science & Technology, 38, 1185-1205, 2004.

2. Second, only thickly coated BC is core-shell in morphology, so this S/C cannot be used to interpret atmospheric measurements of varying coatings.

Reply:

It was well acknowledged that atmospheric processes (i.e. coagulation and condensation) evidently lead to increase in coating thickness of rBC core. The more thickly rBC core was coated, the larger S/C ratio would be. Our study reported that S/C ratio of rBC-containing particles (with aerodynamic diameter of 400 nm) was 2.7 +/- 0.3, as shown in Figure 6. It emphasized that higher fraction of rBC aggregation would lead to more irregular shape (larger χ value) of rBC-containing particles.

3. Third, a S/C of 1 does not mean that "a shell-core [optical] model could be reasonable to estimate the light enhancement effect" as stated in the abstract. This is simply wrong. There is just no physical connection between the S/C parameters and optical properties (it is possible, but absolutely not necessary). A very simple demonstration of the uselessness of this S/C is that fresh black carbon particles (no coating and no shell) will have an S/C > 1 in all cases, and even 3 for larger particles, since the shape factor χ of fresh soot is up to 3 (Sorensen, 2011). When connecting various physical parameters (mobility, mass, morphology) to predict other parameters (optical properties) it is essential to have robust constraints on the connection. Otherwise, the results are uninterpretable and only spread confusion. This is the fundamental problem here.

Reply:

The reviewer misunderstood our statement in the abstract, and the comment is confusing and misleading. What we expressed is "During heavy pollution episodes, the χ value (Not S/C ratio) of the particles was approximately 1.0, indicating that the majority of particles tended to be spherical, and a shell-core model could be reasonable to estimate the light enhancement effect." Dynamic shape factor (χ) is defined as the ratio of the actual drag on the particle to the drag on a volume-equivalent sphere. It is always larger than 1.0 for particles in irregular shape theoretically (Seinfeld and Pandis, Book, ISBN: 978-1-118-94740-1). It can be used to represent the morphology of BC-containing particle. The S/C ratio referred to the coating thickness of rBC-containing particles. χ value of normally decreased as S/C ratio increased. We hope that the reviewer can clarify the χ and S/C as well as the rBC core and rBC-containing particle. It should be emphasized that, it is impossible that fresh rBC particles has a S/C ratio larger than 3 since the volume of fresh rBC was independent with the morphology, and only the aerosols with aerodynamic diameter of 400 nm were investigated on the basis of the tandem system. As one of conclusion of this study is that thickly coated particles (high S/C ratio > 2) might not always present as spherical structure which make the core-shell Mie model overestimated its absorption enhancement.

4. The sentence on Line 62 is simply wrong. BC particles do not always contain brown carbon.

Reply:

We agree with the reviewer that "BC" do NOT contain BrC. What we want to express is that "**Soot particles**, the product of incomplete combustion of fossil and biofuel, normally consists of rBC nano-spheres but also BrC". It is our negligence during editing process. To avoid misleading. we will correct it.

5. Lines 65-68 are generally incorrect and confusing. Follow Petzold et al's (2013) definition.

Reply:

We will revise the expression as Petzold (2013): BC is defined as the carbonaceous component of particulate matter that absorbs all wavelengths of solar radiation. we adopted the terminology advocated by Schwarz et al. (2010) and widely used by the SP2 community that the Single Particle Soot Photometer measures refractory black carbon (rBC) defined operationally by its incandescence temperature (Sedlacek et al., 2012).

6. Line 86-88 the second sentence does not follow from the first, Cappa et al. (2012) did not study attachment mechanisms.

Reply:

The following sentence is cited from (Cappa et al., 2012), in which the author attributes the weak absorption enhancement of rBC-containing particles to their coating structure. "Single particle microscopy measurements from locations around the world indicate it is common to find BC inclusions at the edge of collected particles rather than deeply embedded in a "coating" material (which would be necessary to observe large absorption enhancements), which is consistent with our ambient observations."

7. Line 108 this statement is not true. χ can be less than 1.

Reply:

Dynamic shape factor (χ) is defined as the ratio of the actual drag on the particle to the drag on a volume-equivalent sphere. It is theoretically always larger than 1.0 for particles in irregular shape which have been confirmed in literatures (DeCarlo et al., 2004; Hinds, 1999) and books (Seinfeld and Pandis, ACP, ISBN: 978-1-118-94740-1). χ value of less than 1 is probably because density of particles or void structure was not properly assumed.

8. Line 135 rBC does not absorb as a black body. Line 136 rBC does not boil. Line 138 the mass-equivalent diameter is not a presumption, it is an "equivalent" diameter, like "effective density" is not a presumption.

Reply:

As mentioned, rBC is really not a black body. In SP2 community, a term of "boiling point" of the particles is normally used to describe the vaporization temperature and to distinguish incandescing non-rBC aerosols. For example, Daniel A. Lack (2014) pointed out that "The high temperature particles emit grey/blackbody radiation that can be detected and used to derive the mass of the illuminated particle or particles. At sufficient light intensities, particles are heated to their vaporization temperature (or boiling point), which for rBC is approximately 4300 K. At this point, the energy absorbed is approximately balanced by the energy lost via vaporization

and radiation." Shiraiwa et al., (2008) mentioned that "The blackbody temperature of a BC aerosol can be derived using the ratio of the LII signal intensity. BC can be distinguished from incandescing non-BC aerosols such as metal particles on the basis of the boiling points of the particles." More preciely, we will revise the expression to "…rBC continuously absorbs energy and eventually emits incandescence when it was heated to vaporization temperature of ~4000 K. … ".

References:

1) Lack, D. A., Moosmüller, H., McMeeking, G. R., Chakrabarty, R. K., and Baumgardner, D.: Characterizing elemental, equivalent black, and refractory black carbon aerosol particles: a review of techniques, their limitations and uncertainties, Analytical and bioanalytical chemistry, 406, 99-122, 10.1007/s00216-013-7402-3, 2014.
2) Shiraiwa, M., Y. Kondo, N. Moteki, N. Takegawa, L. K. Sahu, A. Takami, S. Hatakeyama, S. Yonemura, and D. R. Blake (2008), Radiative impact of mixing state of black carbon aerosol in Asian outflow, J. Geophys. Res., 113, D24210, doi:10.1029/2008JD010546.

9. Line 140 there is no connection between rBC needing more time to evaporate a coating and the delay time. This is a simple definition that should not be gotten wrong.

Reply:

Delay time, defined as "the time of the peak of the incandescence signal minus the time of the peak of the scattering signal", is widely used in SP2 community (Schwarz et al., 2006; Moteki and Kondo, 2007; Sedlacek et al., 2012 and more). As vividly displayed in Figure 2 in literature (Moteki et al., 2014), the coating matters will evaporate with temperature of particle increasing. We will revise the expression to "rBC needs more time to reach its vaporization temperature and emit incandescence due to coating."

10. Line 144 'externally mixed' is wrong.

Reply:

In SP2 data analysis, the negative value of delay time is mostly because rBC particle is attached on the surface of it hosting matters (described at length in Moteki et al., (2014)). Here we adopted "externally" to describe the non-shell-core configuration such as partially encapsulated, externally attached etc. (He et al., 2015). To avoid misleading, we will remove "externally mixed".

References:

C. He, K.N.Liou, Y. Takano, et al., (2015), Variation of the radiative properties during black carbon aging: theoretical and experimental intercomparison Atmos. Chem. Phys., 15, 11967–11980, 2015 www.atmos-chem-phys.net/15/11967/2015/ doi:10.5194/acp-15-11967-2015.

11. Line 147 why select with the AAC before the CPMA??

Reply:

A CPMA selects particles with known mass according to the balance between centrifugal force and electrostatic force. Therefore, only the charged particles could be selected by a CPMA. During calibration, we first use a DMA to select particle with known mobility size and produce charged particles. Meanwhile, a DMA-CPMA tandem system can measure the effective density of calibrating matter (i.e. Aquadag aerosol).

12. Line 161 an uncertainty of 10% is less than the 14% calibration uncertainty reported by Taylor et al. for a careful, direct, mass-based calibration (compared with the present authors' indirect, aquadag-based calibration) and I would be very surprised if this was achieved with the authors' setup considering that aquadag was used. Also explain how 20-40% variation in calibration factor becomes 10% uncertainty. Also the equivalent sphere treatment is not an ideal, it is an equivalence.

Reply:

We want to remind the reviewer that the relationship between mass to mass-equivalent diameter is $D_c \propto M^{1/3}$. The 10% uncertainty we reported is for the mass-equivalent core diameter. The 14% uncertainty in literature (Taylor et al., 2015) is uncertainty of deriving rBC mass from incandescence intensity. Taylor et al., (2015) pointed out that "The accuracy of the incandescence calibration was estimated at 14 %, corresponding to accuracy in average D_c of $^{+4.5\%}_{-4.9\%}$." In our study, the uncertainty was similar to Shiraiwa et al., (2008) and Miyakawa et al., (2016) and Taylor et al., (2015).

13. Line 166 why use RI of 1.48-0i for PSL, when this is wrong at all visible/infrared wavelengths?

Reply:

In our study, The RI of 1.59-0i is used for PSL was during calibration. For ambient particles, a RI of either 1.48-0i or 1.50-0i has been used for the ambient particles in different studies. Taylor et al., (2015) pointed out "The RI for the ambient data calculated with volume mixing was 1.46–1.50 (mean 1.48)". In this study, we adopted RI value of 1.48, and this value was also used by SP2 measurement in the Mexico city during the MIRAGE campaign (Subramanian et al., 2010). Schwarz et al., (2008) and Liu et al., (2014) used a refractive index of 1.5-0i. As a matter of fact, the results had no evident difference in shell diameter estimation.

14. Line 178 why mention chargers here, are they relevant to the AAC?

Reply:

The advantage of AAC is that it does not need a neutralizer, the transmission efficiency (~80%) is much higher than that (~20%) of differential mobility analyzer (DMA).

15. Line 219 this sentence is incorrect, this is the defining sentence for mobility diameter.

Reply: What we define is exactly the mobility diameter.

16. Line 270, was fragmentation in the AAC observed? This would be a major result. If not, then remove the statement. Figure SF1 shows no closure between AAC-DMA-CPC and DMA-AAC-CPC. This needs to be resolved.

Reply:

We consent to the comment of the reviewer. We obtained the similar effective density with (Gysel et al., 2011) by using a DMA-AAC-CPC system demonstrating the reliability of our tandem system. For PSL particle, the effective density measured by both DMA-AAC-CPC and AAC-DMA-CPC system are the same. For Aquadag aerosol (water-based colloidal graphite), the difference may result from complex multiple charge. In this study, we just studied the

aerosols with aerodynamic diameter of 400 nm in the atmosphere. The particles were mostly coated with large fraction of water-soluble compounds (such as sulfate, nitrate) and organics matter. Therefore, the multiple-charge problem did not influence our conclusion.

17. Figure SF2 shows a failed fit. The smaller peak has not been fitted. So it is not a multiple Gaussian fit.

Reply:

Multiple Gaussian fit is well performed. The peak on the left is too small to be just covered by circles markers by negligence. We will revise the figure.

18. Figure SF4: It is incorrect to keep adding multiple Gaussian curves until the residual is zero! The shape here is a Lorentzian. Use a function which describes the data. The current analysis is clearly overfitted.

Reply:

In the field of atmospheric aerosol, Gaussian and lognormal fit are usually used to describe the distribution of particles in the atmosphere. In the study, what we demonstrate in SF.4 is that Δt value was constant at ~2.6 μs with a relatively larger variability during the observation period. Fitting method make no difference. If the reviewer minds, we could revise the figure.

19. Figure 3: AMS does not measure water-soluble but non-refractory PM. The caption also fails to describe half of the points/symbols in the plot. A simple proofread was required here.

Reply:

The compounds such as sulfate and nitrate, obtained from AMS measurement, are water-soluble in PM_1. We will add more description in the caption of Figure 3.

20. Figure 4: The authors need to perform laboratory experiments in order to understand the Dmev distributions they are measuring, as noted above.

Reply:

Figure 4 clearly shows the normalized number size distribution of rBC-containing particles with aerodynamic diameter of 400 nm. Laboratory experiment is not necessary.