

Interactive comment on “Mixing State of Refractory Black Carbon of the North China Plain Regional Aerosol Combining a Single Particle Soot Photometer and a Volatility Tandem Differential Mobility Analyzer” by Yuxuan Zhang et al.

Anonymous Referee #2

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The article by Zhang et al. retreads a lot of information already covered in Zhang et al. (AMT, 2016), with some additional analysis. Overall, I find there are potentially some interesting components of this paper that go beyond the authors previous work, but at the same time there are a number of aspects that are presented as novel insights that are either not sufficiently justified or explained, or are simply wrong. I cannot recommend this paper for publication. The authors should work to truly distinguish it from their previous work. My specific comments follow below (in chronological order, mainly).

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Consideration of the PSL's in Fig. 2 demonstrates that the observation of a wide band of refractive index values is a result of variability in particles passing through the SP2 laser and is not due to the distribution of diameters coming out of the DMA. This information can be translated into an effective uncertainty in the size of a given particle. Using the central RI value, a distribution of sizes can be constructed that would also reproduce the observed scatter. This should be considered. Very approximately, ± 0.1 in RI space = ± 20 nm in diameter space.

Page 5: I have no idea what “bones and flesh” means. This is not at all common scientific language, nor is it clear in the usage.

Eqn. 6: It is unclear where this equation comes from. It appears to be made up by the authors. Does the use of this equation have a justification? I don't see how this is physically justifiable.

I understand the idea of adjusting the RI for non-BC containing particles to match with the selected mobility diameter, as it is not unreasonable to think that the non-BC containing particles are spherical. However, I do not understand the justification for this for BC-containing (“internally mixed”) particles that are not necessarily spherical and for which the extent of sphericity is likely linked to the amount of coating material. The relationship between mobility diameter and actual particle size (characterized in some particular manner) will be dependent upon the particle shape. Thus, it is not clear how, for internally mixed particles, the tuning which the authors have done actually leads to an improvement in the estimated size. They have imparted some assumption regarding shape that has not been justified.

I do not find Fig. 3 useful. It would only be surprising if the agreement between the “optical” and “prescribed” diameters was bad, given that they have tuned the RI to make the two match. All the authors are showing is that their tuning has worked to make the $D_{optical}$ match the $D_{mobility}$. Also, this is not a validation of the “assumption of spherical BC particle[sic] in the Mie model calculation.” The authors have forced

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agreement, not demonstrated anything about sphericity. Their method says little about the method “accuracy” (P6, L16).

I find the authors’ terminology regarding “non-BC”, “internally-mixed BC” and “externally-mixed BC” confusing. There are non-BC and BC-containing particles. For BC-containing particles, there is then a distribution of relative coating amounts, with some particles having little coating (which I think the authors take to mean “externally mixed”) and some having a lot of coating (here, I think, “internally mixed”). The authors make their definition based on a “lag-time” analysis. But, the validity of such a binary framework has not been justified here. Do they find a bimodal distribution of lagtimes, thus justifying the binary framework?

Fig. 4 and Discussion: The authors assume that BC is the only component of the particles when making their fractal dimension determination. This is an assumption that must be demonstrated in some way. What if, for example, there were a 10 nm thick “coating” on the “externally mixed” BC particles? This might still have a small lag time. But, depending on the particle size, the mass contribution could be substantial (e.g. for a 100 nm BC core, a 10 nm coating corresponds to nearly 40% of the mass, assuming equal densities and spheres.) How do the authors know that the only component contributing substantially to the particle mass is BC for these particles with small lag times? What sort of uncertainty is contributed by their assumption.

P6/L19: The authors state: “For externally-mixed BC particles, a diameter is hard to define due to their irregular morphology.” This is not correct. A volume-equivalent or mass-equivalent diameter can be easily defined if the BC mass is measured and it is assumed that the particle is 100% BC (which the authors do here).

I find Fig. 5 unclear. For the mobility distributions ($dN/d\log D_p$ vs D_{pm}), is this from the measurements with the 2nd DMA? This is not stated. If so, why are the peaks so broad? The size distributions presented suggest that the authors were operating the first DMA with a very low resolution. Is that the case? If so, that would mean that the

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authors passed through particles with a broad distribution of actual mobility diameters.

P7, L3: The authors' statements regarding the density of the BC are wrong. The material density is 1.8 g/cm³ (not 1.8 g/m³, as stated). The conversion of the measured mass to a diameter requires specification of what diameter one is considering. One should absolutely use the material density if converting mass to a volume-equivalent diameter. To use a lower effective density is not correct. But, if the authors are aiming to estimate a mobility diameter from the mass, then the use of an effective density is appropriate. But, it is entirely unnecessary here since the argument is circular: the effective density is determined by comparing the selected mobility diameter with the observed volume equivalent diameter. So, conversion of the mass back to a mobility diameter is just a statement of the obvious.

P7,L9: A tandem DMA is also able to “separate aerosol particles with different charges” if the particle stream is reneutralized. The DMA + SP2 is not unique in this regard.

Fig. 6b: I find this to be unclear. Why are there so many points on the graph? There is a fixed ratio between the number of singly and doubly charged particles for each mobility diameter. Thus, there should be one point per size, as is indicated by the text on P7.

P7/L29: Again, the authors refer to the accuracy of their size determination. But, they have forced agreement. Thus, this is simply a statement that the authors have calibrated their instrument.

Fig. 7: The authors show the SP2 distribution as a sum over different particle types. However, this does not take into account the important issue that the SP2 instrument detection limit is different for scattering and incandescence. The SP2 cannot measure scattering by particles below some size. But this is not the same size below which it cannot measure incandescence. Ultimately, one cannot simply add up the size distributions from the different types of particles from the SP2 without accounting for such effects as it can give a misleading picture.

Fig. 7 and Fig. S2: The authors need to refer to their diameters using some sort of specific terminology. They are not “rBC diameters.” They are, perhaps “mobility-equivalent diameters”. The authors must be precise in their terminology. As it is, the lack of precision makes the concepts presented difficult to follow.

P8,L15: It is entirely unclear in what way specifically the “VTDMA measurement had a large uncertainty.” What is meant by “uncertainty” here? The VTDMA measurement is what it is. Also, the authors have not demonstrated an ability to measure what are predominately mostly scattering particles below 200 nm: their entire validation exercise used particles with mobility diameters ≥ 200 nm. It is not surprising that the SP2 does not measure as many purely scattering particles at smaller sizes compared to the VTDMA as it is not designed to do so. What the authors need to show is an efficiency curve, similar to that shown for BC in Fig. S1, but for scattering-only particles. Below what size does the detection efficiency fall off for scattering only particles? Also, it is unclear what the authors mean by a “significant different in BC mixing state” Between the measurements. Different in what way? What is being determined?

P8/L14-25: I find this paragraph very difficult to understand. The SP2 cannot measure small particles. I do not see how comparing the SP2 to the VTDMA in this particular way is addressing limitations of the VTDMA.

Fig. 7 vs. Fig. 8: Considering the authors’ own measurements, there is an inconsistency between these two figures. The SP2 size distributions shown in Fig. 7 suggest that the distribution is dominated by “externally-mixed BC” particles. But, Fig. 8 clearly indicates that the number is dominated by “non-BC” particles. Fig. 8 is thus more consistent with the VTDMA measurements shown in Fig. 7, which shows a substantial fraction of what might be considered “non-BC” particles (i.e. the particles that shrank a lot). Yet, the authors just spent a section arguing that the SP2 does a better job than the VTDMA. These discussions must be aligned and reconciled.

P9,L6: It is unclear how a small BC fraction necessarily indicates “long range transport.”

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This must be justified. Yes, it suggests that there is secondary processing (most likely), but why “long range transport” specifically? The authors seem to take this as a given. Why not local photochemical or nocturnal processing?

P9/L11: The authors state here that the fraction of internally-mixed particles at 200-300 nm was 38-51%. But, above, they say that these particles are only 7-10%, including externally-mixed particles. Clearly there is a discrepancy. Fig. 8 and Fig. 9 are similarly inconsistent. Perhaps they are talking about only the BC-containing particles. But this is unclear.

P9/L13: How do the authors know that the peak is from both photochemical formation and regional transport? How is the influence of regional transport identified? Why not just local production?

P9/L16: The authors compare their current results to those of Cheng et al. for Beijing. They should note that Cheng et al. also made measurements in Beijing.

Fig. 10: Much more meaningful would be a histogram of the D_p/D_c values. The justification for binning as was done here is not clear.

P9/L20: It is not at all surprising that the “internally-mixed” particles have thick coatings. This is by definition, as the authors have discriminated by the difference in lag times and thus we would fully expect that the particles should have large D_p/D_c ratios. If they did not, they would not have been identified as “internally mixed” in the first place. What is the relationship between lag time and D_p/D_c for this study? How are the authors skewing their analysis by deciding on a particular lag time cutoff?

P9/L22: The authors should comment further on the observation that D_p/D_c increases as D_p increases. (They might even make a plot. . .). Why do they think this is the case? What physical insights can be discerned?

P9/L22: The authors again point to long range transport. Why is local photochemical production of coatings not possible, especially given that there is clearly a local source

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of BC?

P9/L27: The authors cite Zhang et al., (2016b) to support their statements regarding potential for absorption enhancement. But, (i) Zhang et al simply provide calculations that say that when BC particles are coated absorption can be enhanced, which has been known for a long time since before Zhang and (ii) the Zhang results are simply calculations, and the actual magnitude of absorption enhancements in the atmosphere remains unresolved. The authors should provide a fuller discussion and not simply self-cite.

Fig. 11: This figure is fundamentally misleading. The SP2 cannot measure the size of particles via the optical method if they are too small. The lower-limit size differs for BC measurement vs. for size measurement. Thus, there is an intrinsic bias in the method that makes it appear as if the coating thicknesses of small BC particles are larger, on average, than they might be. Consider a 100 nm core. If the smallest optical diameter that can be measured is 150 nm, then the thinnest coating is 25 nm. There is no information about the concentration of 100 nm cores with $CT < 25$ nm. It may be that the decrease in coating thickness with core size, shown in Fig. 11, is valid. But, the authors must demonstrate that their measurements are not biased by differences in the lower-limit size for BC vs. for optics.

Fig. 11: The authors say that their curves follow “diffusion-controlled growth.” But, looked at another way there is absolutely no reason to think that they would obtain any other result, given their method. They size select at a given size. And they measure a core size. By definition, $D_{\text{selected}} = D_{\text{core}} + 2 \cdot CT$. Thus, there is a definite relationship between their coating thickness and D_{core} . Further, the curves shown generally follow this curve. For a 100 nm core, the “coating thickness” for a 200, 250, 300 and 350 nm selected size is 50, 75, 100 and 125 nm. These are nearly identical to what the authors obtain. In other words, their graphs show exactly what is expected based on simple algebra, with no need to invoke “diffusion-controlled growth.” Or, put another way, the results do not provide any information on the growth mechanism nor

do they demonstrate that coating thicknesses decrease with core diameter. The entire discussion regarding Fig. 10 needs to be either removed or substantially revised. And if revised, needs to move beyond the simple algebraic expectation to provide some physical insight.

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