

## ***Interactive comment on “Variability in the mass absorption cross-section of black carbon (BC) aerosols is driven by BC internal mixing state at a central European background site (Melpitz, Germany) in winter” by Jinfeng Yuan et al.***

**Anonymous Referee #2**

Received and published: 2 April 2020

The authors report on measurements of the relationship between absorption by black carbon and the extent to which the BC particles are coated. Overall, I find this is a nice addition to the existing literature on this topic, and the results appear to be of high quality. I have a number of comments that I think the authors should address before this is accepted for publication. I would ask that they pay particular attention to the comments regarding Fig. 8 as there are a number of aspects that I find unclear about the data presented in this figure.

L40: The authors might more accurately state that when BC is freshly emitted it “may

C1

be” separated from other species. Some combustion processes emit BC already internally mixed with some other components (e.g. organics). Also, in the next sentence I suggest it would be more precise to say that “particles” coagulate (not “species”).

L47: I’m not certain that Mie theory deals with “refraction” of light, as the authors state. “Refraction” is more of a geometric optics concept.

L70: The authors might note that the results of Qiu et al. (2012) are outliers among the now numerous lab experiments that indicate notable enhancements occur for size-selected BC.

L80: It seems a bit of a stretch to me to simply state that the SP-AMS is not quantitative owing to variability in detection efficiency, with citing only of the Taylor et al. (2015) paper. This effect has been noted by others in papers that focused on this issue (Willis et al., 2014) and others have used this knowledge to account for the variability in the detection efficiency (e.g., Collier et al., 2018). (I’ll also note that Taylor et al. show the SP-AMS/SP2 BC ratio versus the absolute concentration of inorganic species measured by the SP-AMS, not versus the coating-to-BC ratio as implied by the authors use of the term “mixing state” here.) I suggest the authors temper the statement here a bit to indicate that quantification is challenging and care must be taken to account for changes in detection efficiency that might occur as the coating state of the BC changes. Also, it would be useful if the authors would clarify whether they are using “absolute” here to mean the absolute concentrations or the absolute coating thickness. I believe they mean the latter, based on the discussion in the next paragraph. However, this seems to contradict, somewhat, the authors statement that the SP-AMS does well with the coating-to-core ratio, which is the primary determinant of the coating thickness (if one translates from a mass ratio to a coating amount).

L87: Given the citation of the Taylor et al. (2015) paper above, it seems appropriate that the authors here might acknowledge some of the challenges in extracting absolute measures of the coating thickness that result from having to make particular assump-

C2

tions regarding the BC material properties. (This does come up later, briefly.) Additionally, the SP2 interpretation method inherently assumes spheres yet the particles may not be spherical (as the authors note above), which will affect the accuracy of the method; it seems this should be noted. Also, the authors cite here Laborde et al. (2012a) as justification for “quantitative” coating thickness determination. It is unclear where in that paper coating thickness determination is shown to be quantitative; the paper seems to actually be quite qualitative in terms of coatings. As such, I suggest this reference be clarified, removed, or replaced with a more appropriate reference.

L115: Is it quite correct to state that the MAC is compared to the “BC particle mixing state?” Coating thickness is not exactly mixing state. At minimum, the authors should clarify that they mean “internal mixing state” per their discussion earlier. But I suggest that rather than using “mixing state” here and “infer[ring]” mixing state from coating thickness they just state that they compare with mean coating thickness for particles in a particular size range from the SP2. I feel that the use of the term “mixing state” here serves to confuse rather than clarify, at least for me. The same I find true when the authors state that they determine “mixing state” by thermodenuding. I suggest just stating what specifically was measured, for example (L120) that the authors aim to infer a causal relationship between the lensing effect and the “coating amount” rather than “mixing state.”

L192: The authors note that the SP2 “missing mass correction” will be detailed in a separate paper that is not available for review at this time. Therefore, I suggest that the authors provide at least a short summary of the correction method. For example, was a single campaign average value applied, or did the authors determine a missing mass correction based on three hour averages (as this is their averaging time for the various measurements)? If the latter, noting min/max values (as percents) would seem appropriate. It seems to me that the latter is more appropriate. Certainly, based on the mean values given the missing mass correction details should have small effect, but they should nonetheless be noted here.

C3

SP2 coating determination: While the details provided here are most certainly important, the authors could probably move most of these details to the supplemental and then note more succinctly in the main text the method used and the key uncertainties.

L211: It is unclear to me how Fig. S1 shows that optical diameters are within “a few percent” of the mobility diameters. Are the authors making this statement based on some general similarity in shape? Also, in Fig. S1 I find it unclear whether the red curve is the sum of the blue and the black, as it should be based on the definitions provided. If it is the sum, this means that the entirety of the blue curve is not shown. The authors might consider visual ways to clarify.

The minimum detectable coating thickness seems to come from Fig. S3b. I suggest that the authors report the +/- 10% and the 10th and 90th percentile bounds as diameter equivalent. I think the +/- 10% line is nominally 10 nm and the 10th/90th percentile is 30 nm.

L305: A minor issue, but the authors might clarify whether the AAE values here are the concurrently measured 3-h averages.

L308: It would be helpful if the authors clarify how a 31% bias translates to a scaling factor of 1.44. Why not 1.31?

Fig. 2: Visually, it appears that the difference between the 1:1 line and the scaled measurements is largest at intermediate absorption values. It would be useful if the authors were to consider the percent difference as a function of absolute absorption, and comment on how this might (or might not) impact their conclusions here.

L322: Since the losses are size dependent, and since coating-to-BC ratios are likely size dependent as is the SP2 detection efficiency, the authors might instead state that the losses likely introduced minimal bias, rather than stating categorically that they introduced no bias.

L323: The shapes of the particles may have changed upon denuding. Might this impact

C4

the determination of coating thickness, as the method assumes spherical particles (even for the BC)?

L416: It is not clear to me how Fig. 2 indicates the lower limit of quantification for the PAX. It just shows the relationship between the PAX and MAAP. The limit of quantification typically comes from consideration of the instrument noise when sampling zero particles over the time period of the instrument zeros.

L438: It would be helpful if the authors could clarify why they are not considering emissions from biomass combustion, which tend to also produce larger BC cores, instead focusing on coal as the major BC source.

L468: Do the results here change if the authors instead use the median values (rather than the mean)? Or, what if the authors use a geometric average rather than an arithmetic average. The former is typically more appropriate for distributions that are bounded on one side. Here, the coating thickness cannot be  $<0$  nm (within error), and thus the distributions are inherently non-Gaussian but instead more log normal. (Also, Fig. S7 reports the medians. It would be good to see things reported in a common way.)

Fig. 6: Given that the authors use the standard error of the mean to show their uncertainties here, it would be helpful if they would report the typical instrumental averaging times so that the reader can know how many points go into the 3-h averages. (In other words, are these averages of 1s data? 1 min? 10 min?)

Fig. 6b: Given that the denuded particles appear to still have coatings, I suggest that it would be helpful to show also a composite plot with the ambient particles versus their coating thickness and the denuded particles versus their coating thickness so that the continuity between these can be seen.

L497: It is not accurate to state that “all” the denuded MAC values fall in the stated range. There are some points that are outside this range. “Most” of the denuded MAC

C5

values fall in the stated range.

L549: Biomass burning emissions also exhibit a wide range of AAE values. Thus, it is not clear why apportionment is appropriate in the biomass burning assumption above but not for coal. It is also not clear why the biomass burning method would provide an “upper limit estimate” for the contributions. How is it specifically known that this is an upper limit?

L 562: I suggest it would be useful for the authors to calculate and report the  $R^2$  value when the two clear outlier points are excluded. These correspond to the short period when the BC source was quite different. The  $R^2$  in this case would definitely be  $>0.01$ , although still not as large as the relationship with the coating thickness shown previously. Also, I find it a little awkward to note that variability in the BC diameter over the range 150 nm to 250 nm is a “narrow range” but the coating thicknesses, that only varied from  $\sim 40$ -60 nm is not “narrow.” Also, visually there appears some correlation between the BC diameter and the coating thickness from Fig. 5 (excluding the short plume). Finally, from the size distributions shown in Fig. S5, it would seem that any missing mass correction would be larger for period 2 than for period 3 than for period 1. To what extent might uncertainty in the missing mass correction contribute to the relationships shown? The distributions are close to log-normal, but not quite and thus use of a single mode fit might underestimate the correction that is necessary.

L567: The authors might note that this is the theoretical result of Mie theory, which might not be fully applicable to fractal-like particles for which absorption by the individual spherules might dominate.

L578: I would suggest the authors go a bit further and argue that it is very likely that the coating amounts differed, as no attempt was made in that study to ensure that the particles had the same amount of coating.

Fig. 8 and origin of Ueda et al. (2016) data: The authors show results from Ueda et al. (2016) in this figure. In their caption they note that the points shown might differ

C6

from those shown in Cappa et al. (2019). However, in looking at Cappa et al. (2019) the Ueda et al. data are not included. As such, it is unclear where these data come from. Looking at the Ueda et al. (2016) paper directly, there is no indication that values of  $R_{\text{coat-BC}}$  are available in a general sense. At best, it would seem that up to four data points might be included, corresponding to the periods A-D in Ueda et al. (2016). It looks like the authors used the mean volume fraction of soot for particles in varying size ranges and with varying number of particles analyzed (per Ueda et al., Table 3) to calculate the volume fractions. For one of these periods (C), only 6 particles were analyzed, calling into question the statistical significance of any volume fraction. As for the Eabs values, did the authors use the 400 degC results reported? Or did they calculate an estimated Eabs based on the reported [BC] and absorption at 781 nm? I suspect the former, but it might be noted that if one assumes a constant MAC for uncoated BC and calculates an Eabs from the reported measurements, the thus derived Eabs does not match with the value derived from heating to 400 degC in terms of their apparent dependence on the coating volume fraction.

Fig. 8b: It is unclear whether the x-axis is really the total NRPM-to-BC ratio for all studies shown. For some of the studies, the x-axis values in panel b appear the same as in panel a, which cannot be the case unless all NRPM is internally mixed with BC. But for other studies the relationship differs. Additionally, it is also not clear for the current measurements that the x-axis is correct. Looking at Fig. 2, the BC fraction ranges from about 0.04 to 0.22, excluding the short plume. The NRPM/BC ratio should just be  $(1-\text{BCfraction})/\text{BCfraction}$ , and so should range from approximately 3.5 to 24. But the data shown in Fig. 8b only range from 2-4 for the current study. I suggest that clarification is needed. Perhaps I am just misunderstanding the relationship between the  $R_{\text{coat-BC}}$  and  $M_{\text{total}}/M_{\text{BC}}$  as used here. Or misunderstanding what the authors mean in the figure caption when they note that the  $M_{\text{total}}/M_{\text{BC}}$  is a “free parameter.” Free in what way? (As a minor note, inclusion of ticks between 1 and 2 on the y-axis would be helpful to the reader.)

C7

L638: I suggest it would be helpful for the authors to be more explicit about the SP-AMS here. The introduction section does not indicate that the coating-to-core ratio from the SP-AMS should depend strongly on the coating amount but instead notes that absolute quantification of concentrations depends on the coating amount. How does a change in the collection efficiency affect the ratio, rather than the absolute values? Also, they might note that the laboratory studies that have looked at this effect find that above a coating-to-core ratio of  $\sim 3$  that the collection efficiency is effectively constant, and some of the studies shown do have coating-to-core ratios this large.

L640: This is a really great point, that I suggest the authors re-emphasize specifically in their conclusions.

In their discussion of physical explanations for the differences between studies, the authors might note that some of the studies are more likely to be impacted by local sources and some by particles that have undergone long-range transport. The latter might tend to homogenize the population, which could affect the observable absorption enhancement.

L681: The sentence beginning “The enhancement. . .” does not seem to be a complete sentence.

L691: It is not overly clear to me how “such effects” might be obscured here. What do the authors mean when they indicate “a more quantitative assessment?” Do they mean calculated across the entire size distribution?

#### References

Collier, S., Williams, L. R., Onasch, T. B., Cappa, C. D., Zhang, X., Russell, L. M., Chen, C.-L., Sanchez, K. J., Worsnop, D. R., and Zhang, Q.: Influence of emissions and aqueous processing on particles containing black carbon in a polluted urban environment: Insights from a soot particle – aerosol mass spectrometer, *Journal of Geophysical Research-Atmospheres*, 123, 6648-6666, <https://doi.org/10.1002/2017JD027851>,

C8

2018. Taylor, J. W., Allan, J. D., Liu, D., Flynn, M., Weber, R., Zhang, X., Lefer, B. L., 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.*, 8, 1701-1718, <https://doi.org/10.5194/amt-8-1701-2015>, 2015. Willis, M. D., Lee, A. K. Y., Onasch, T. B., Fortner, E. C., Williams, L. R., Lambe, A. T., Worsnop, D. R., and Abbatt, J. P. D.: Collection efficiency of the soot-particle aerosol mass spectrometer (SP-AMS) for internally mixed particulate black carbon, *Atmospheric Measurement Techniques*, 7, 4507-4516, <https://doi.org/10.5194/amt-7-4507-2014>, 2014.

---

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2020-41>, 2020.