

Interactive comment on “Dynamic shape factor and mixing state of refractory black carbon particles in winter in Beijing using an AAC-DMA-SP2 tandem system” by Xiaole Pan et al.

Anonymous Referee #1

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1 Review of Pan et al. ACP 2019

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 exam-

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ple, 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). 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!

These approaches, in addition to a plethora of simple logical errors and inaccuracies in the Introductions and Methods of the paper, lead to a very unconvincing manuscript which I am obliged to recommend for rejection from ACP.

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). For completeness I will now describe some of these errors in addition to many more.

1.1 Incorrect shell-core ratio concept

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

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

1.2 Comments to Introduction

There are various incorrect statements in the Introduction which are completely incorrect and either lack citations or have misinterpreted the citations. The authors need to take care not to introduce inaccuracies into the literature.

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

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

Line 72 is wrong, it is not a reasonable estimate, as was proven in Liu et al. (2017) [authors' own reference].

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Line 76 "particulate" not "particles"

Line 77 there is no "etc." to this list.

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

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

Line 117 cite previous studies.

1.3 Comments to Methods

There are many incorrect statements in the Methods section which call into question the authors' data interpretation.

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.

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.

Line 144 'externally mixed' is wrong.

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

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

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sphere treatment is not an ideal, it is an equivalence.

Line 166 why use RI of 1.48-0i for PSL, when this is wrong at all visible/infrared wavelengths? (e.g. Sultanova et al., 2009).

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

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

Line 257 is not understandable.

1.4 Comments to Results

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.

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

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.

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.

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

I have provided comments up to Section 3.2 and will not provide comments beyond.

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The basis of the work is fundamentally flawed, so a discussion or detailed criticism of the subsequent modelling and interpretation of the work would not be worthwhile.

Based on these severe errors and shortcomings this manuscript is not suitable for publication in *Atmos. Chem. Phys.*

2 References

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