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Atmospheric Measurement Techniques Discussions

Interactive comment on "Undersizing of Aged African Biomass Burning Aerosol by an Ultra High Sensitivity Aerosol Spectrometer" *by* Steven G. Howell et al.

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The manuscript amt-2020-416 by Howell et al. presents a systematic investigation into the reasons that an infrared-laser optical particle sizer, the UHSAS, could have reported optical particle diameters (Dopt) at m=1.572+0i smaller than mobility particle diameters (Dmob) during an aircraft study of biomass-burning plumes. This is essentially an attempt at closure between Dopt and Dmob for particles of potentially complex morphology and refractive index, and is a difficult enough task even without considering particle evaporation in the UHSAS.

The authors support the interpretation of their field data using laboratory experiments,

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Mie-theory (spherical-particle) calculations, and particle-heating calculations. The interpretation is presented as a series of hypotheses which are eliminated one by one, which is a particularly clear approach. The main conclusions are that the UHSAS measures (1) Dopt $\approx$ Dmob for non-absorbing spheres, (2) Dopt $\approx$ 0.9*Dmob for the measured brown carbon, and (3) Dopt $\leq$ 0.7*Dmob for anomalously low scatterers (black carbon or tarballs). The authors attribute Conclusion (2) to partial evaporation and therefore propose (4) an empirical correction to force Dopt' = 1*Dmob for their brown carbon samples.

Overall, the work is of excellent quality and contributes substantially to the understanding of IR laser particle sizers (UHSAS) as well as including some conclusions applicable to the single particle soot photometer (SP2). I have some major concerns, but these can be practically addressed by adding a few calibration particle types. So I will request that these experiments are included in a revised manuscript.

Major comments

Briefly, my two major concerns are (i) an alternative hypothesis for the field data is internal mixing of soot and organic matter (OM), and (ii) the UHSAS has a similar laser intensity than the SP2. The second concern implies that tarballs should evaporate in the UHSAS (in support of this work's conclusions), rBC should be vapourized and not detected (in apparent contradiction of the laboratory work), and particle heating is much larger than currently calculated, at least for soot.

These two concerns are fleshed out in the following comments, which address the manuscript more directly.

1. The evaporation hypothesis has not been unambiguously shown from the laboratory experiments. The authors have not measured absorbing spheres to demon-

strate evaporation. It would be relatively simple for the authors to reproduce the experiments of Sedlacek et al. (2018), using nigrosin. This would let the authors clearly demonstrate what the hypothesized evaporation effects would look like in the UHSAS. Ideally, different laser powers would be used (by varying the pump laser power). Because evaporation in the UHSAS is a strong claim, it should be supported by this direct demonstration.

2. The laboratory experiments have not shown the response of the UHSAS to realistic soot with a DLCA morphology. This morphology plays a major role in the light scattering properties of atmospheric black carbon (Sorensen et al., 2018). Light scattering by fractal soot aggregates is significantly lower than that of equivalent spheres due to its morphology alone (Mishchenko, 2009's Figure 12). Atmospheric black carbon either has DLCA morphology or is compacted from DLCA by coatings. The fullerene soot sample may at best represent compacted DLCA soot, which is adequate but could be much improved by a simple experiment with a kerosene flame or similar.

3. The calibration experiments are also missing a non-absorbing, non-spherical case, which would help to explain whether absorption is really important here, or just morphology. Silica or titania aggregates could be used (Schmoll et al., 2009) and would ideally be generated as DLCA aggregates (Eggersdorfer and Pratsinis, 2013) for comparison with soot. The authors may avoid this suggestion by including both soot and absorbing spheres, however.

4. In the scattering calculations corresponding to the calibrations, the authors should follow the literature to use the relatively simple RDGFA approach (Sorensen et al., 2018) rather than an effective medium approach in approximating soot properties. The combustion literature has long used the RDGFA approach to obtain reasonable results for soot and to show that soot scatters very little light at similar wavelengths (Liu et al., 2019). With the addition of an

absorbing spherical particle type, a DLCA soot sample, and optionally a non-absorbing DLCA aggregate, the authors' work would represent a comprehensive study of the UHSAS response. So, these first 4 comments would not only close an important gap in the reasoning here but provide valuable reference data for others.

5. I have requested a direct demonstration of the evaporation hypothesis because I can propose an alternative hypothesis which the authors have not discussed: internal mixing of soot with non-absorbing or slightly absorbing material. Internal mixing is almost inevitable for plumes as old as those studied here (2 days to 2 weeks, Line 309). The authors' laboratory data shows that black-carbon surrogates scatter much less than predicted by equivalent spheres (as expected and noted in the previous comment). It can be expected that coated black carbon would behave somewhere in between soot and non-absorbing spheres, as suggested by previous work (Mikhailov et al., 2006). This does not univocally imply a continuous range of UHSAS signals in Figure 7, because particle breakup due to laser heating (Moteki and Kondo, 2007) could cause two UHSAS modes: either coatings evaporate and give a smaller signal, or they fragment and give a larger signal. The field data (authors' Figure 7) can therefore be explained simply as a mixture of soot, organic matter (OM), and soot+OM particles:

   (a) The soot particles are the anomalous low scatterers with Dmob> 100nm, as expected for DLCA aggregates.

   (b) The OM particles are the smallest particles (circles and squares with Dmob< 100nm).

   (c) The soot+OM particles are the larger particles (circles and squares with Dmob> 100nm).

   (d) The ratio of Dopt/Dmob (y axis of Figure 7) may decrease with increasing Dmob because larger soot particles have larger shape factors (Sorensen,

2011), or because larger soot particles have larger internal coupling parameters (Sorensen et al., 2018), or both. I made a rough calculation of the latter effect and it appears to be smaller than the former.

A second internal-mixing hypothesis replaces soot with tarballs above.

The current laboratory experiments on soot surrogates (Aquadag and fullerene soot) actually support this internal-mixing hypothesis more than the brown-carbon evaporation hypothesis. These surrogates anyway probably scatter more light than soot since their structure is more compact, and since Aquadag is made up of larger graphite flakes. The authors may perhaps consider my alternative as a sub-set of their evaporation hypothesis, or disprove it using their thermal denuder data.

6. In the context of the previous comments, I question the value of a "correction" to the UHSAS. If the surpising signals represent real physical phenomena, and the UHSAS is working correctly, why "correct" the data? Section 3.2 could instead follow the tone of Section 3.1, and focus on the prediction of the UHSAS response from fundamental particle properties. Since the particle properties are not known exactly, the properties (morphology effects on scattering, morphology effects on Dmob, refractive index and – if justified – evaporated volume fraction) required to explain the observations can be discussed. If the authors' answer is that a correction is valuable to predict volumetric size distributions and total light scattering, then please modify the manuscript to emphasize this.

7. The manuscript has cited relevant SP2 work but there are a few points where the SP2 literature should be used to constrain the UHSAS predictions.

   (a) The intensity of the SP2 laser has been reported as 1.7E+05 W cm^{-2}, 6.5E+05 W cm^{-2}, and 4.05E+05 W cm-2 by Schwarz et al., 2006, Moteki and Kondo 2007, and Bambha and Michelsen 2015, respectively. Cai et al.

(2008) reported the UHSAS laser intensity as 5.1E+05 W m-2. These are all similar to the 5.1E+09 W m^{-2} (5.1E+05 W cm^{-2}) reported here. The SP2 and UHSAS wavelengths are about the same.

So, the behaviour of a given particle in the SP2 can be extrapolated to the UHSAS. (While thinking about this I consulted Figure 1 of Corbin and Gysel-Beer 2019, which shows the behaviour of various particle types in the SP2 laser.) Any particles which vapourize (or carbonize) in the SP2 must vapourize in the UHSAS. Therefore, Equation 1 and Figure 4 cannot be correct. The SP2 routinely observes soot particles down to about 80 nm from their incandescence at $>$3000 K, yet Equation 1 apparently predicts only 1000 K at steady state for 100 nm soot. Moreover, this size is an overestimation for aggregate particles like fullerene soot. The assumptions behind Equation 1 must be flawed, at least for non-spherical particles. Bambha and Michelsen (2015) performed more detailed calculations than Cai et al. (2008); probably too detailed for this manuscript. So it becomes even more important to perform UHSAS calibration experiments with DLCA soot.

(b) Sedlacek et al. (2018) showed that nigrosin (brown carbon / tarball surrogate) absorbs the SP2 laser. Corbin and Gysel-Beer (2019) reported SP2 time-resolve scattering cross-sections for the evaporation of tar brown carbon (TB) from heavy-fuel oil that was similar to Alexander et al. (2008)'s tarballs Their scattering cross-sections for TB actually look very similar to the "anomalous" particles reported here. In contrast, their scattering cross-sections for rBC actually show that the rBC evaporates before reaching the centre of the laser.

So, how can the UHSAS see rBC? Presumably, the software uses the peak signal for all particles. This would correspond to the peak laser intensity for non-evaporating particles, but would occur before the peak for evaporating particles. This difference in incident laser intensity would result in an undersizing of evaporating particles, in addition to their actual change in volume.

(I have presumed that the software uses the peak signal because the SP2 would have to do the same if it did not have a “split” detector.) This is an important issue which will be implicitly addressed by the addition of soot particles in the calibrations.

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Minor comments

While reading the manuscript carefully a number of minor comments arose, which I list here.

1. I appreciated the original structure of the introduction, but please add a short goals paragraph at the end. Please also consider moving parts of Section 1.3 to Methods.

2. Please add an Appendix section where the prediction of nephelometer signals from UHSAS signals is explicitly described. I can imagine what was done but it should be spelt out.

3. In Section 1.2 of the introduction, the authors' use of light-absorbing carbon (LAC) terminology could be refined. The section should cite Petzold et al. (2013) in its first paragraph, which is a review of the topics discussed there.

   In the next paragraph, change boiling to incandescence (line 79) since rBC actually sublimates.

   Please reword the statement that BC is a hypothetical material that includes graphitic soot nanospheres and amorphous C, citing either the definitions given by Petzold et al. (2013), Bond and Bergstrom (2006). The word hypothetical suggests that soot is not of a consistent composition, which may mislead readers (Michelsen et al. 2020).

   Please also reconsider the statement that quantitatively connecting the amount of carbon with the light absorption of LAC remains a challenge. The issue is not that connecting the two is challenging, but that the range of light-absorbing compounds formed by carbon is vast. These LAC compounds include brC, black carbon, and amorphous carbon in tarballs (a recent summary is given in Corbin et al., 2019). When the authors mention amorphous C, are they referring to

the degree of graphitization (Michelsen et al., 2020) of the sample? The term amorphous C is often used for a specific carbon material, rather than amorphous domains within soot. Please reword to clarify.

4. Please add a short description of the UHSAS to Methods. How are particle focussed into the beam, at what flow rate, etc.

5. Please mention the particle counter after the DMA in Methods. Of course, a DMA by itself does not provide size distributions, so I assume a CPC was used. Similarly, at line 126, please clarify that it is not the DMA but the CPC which cannot tell the difference between charges (especially important since this work uses a UHSAS to tell the difference).

6. Line 147 mentions an empirical correction to a valve – please clarify if this correction was applied to CPC, UHSAS, or both. Please consider adding a graph to the supplement and/or stating here the magnitude of the correction.

7. Line 151 and surrounding, please mention what RH the sample would have had without dessication or what the maximum dewpoint would have been (I assume it is very low given the altitude).

8. Line 161 please briefly mention the reason why the fraction is trivial, especially since the detector is missing from Figure 1. I am assuming that the reason is the small collection angle of the detector optics.

9. Figure 2 please change soot to ambient soot with a citation to Moteki et al (2010) in the legend. I originally misunderstood it as fullerene soot. Please also change graphite to graphite sphere (or similar) for clarity, since Aquadag is also graphite.

10. Line 180 please provide a citation for this description of fullerene soot. Please change to the RDG approximation here.

11. Line 191 “poor statistics”... how exactly was the statistical analysis done? Was the mode or median of the distributions used?

12. Line 192 please change “than expected” to “than predicted for equivalent spheres” or similar.

13. Table 1, what is “amorphous C” here? I did not see this term used by Moteki et al. 2010. They did use the term “non-graphitic” to describe samples with a lower degree of graphitization. I suggest omitting this entirely as the optical properties of soot (one row above) will be similar. This comment relates to my general comment on LAC terminology above.

14. Table 1, please indicate either how these values were extrapolated from measurements at other wavelengths, or the measurement wavelength if they were not.

15. Table 1, please change ’variable’ to the values used in order to convey more precise information.

16. Line 124, I do not agree that Gysel et al. (2011) concluded that Aquadag particles are 13% unknown composition after denuding at 450 degrees C, and I do not see the statement in that work. These particles would be 100% rBC by definition, but may have a different SP2 response to other forms of rBC. In other words, this statement is illogical since the SP2 is calibrated to the total mass of denuded particles. Perhaps the authors are referring here to the EC content of Aquadag; this excludes oxygen and other atoms, so is smaller than rBC mass.

17. Figure 6 should not show the extrapolation if the discussion describes it as “completely inappropriate”, please harmonize.

18. Line 250 please change “kernel function” to “transfer function” according to convention.

19. Line 303 please report the wavelengths which the AAE was calculated from.

20. Throughout the manuscript, error bars were generally missing and not discussed, please add them or an overall comment.

21. Line 204 please mention $1/e^2$ as the measure of beam diameter (if correct).

22. Line 382 much lower temperatures than 400 C, are enough to evaporate most coatings. e.g. https://doi.org/10.1016/j.jhazmat.2011.12.061

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