Response to comments on "Undersizing of Aged African Biomass Burning Aerosol by an Ultra High Sensitivity Aerosol Spectrometer" by Richard Moore

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October 6, 2021

We'd like to thank Richard Moore for his review. It was particularly interesting to see his figure showing results similar to ours for Aquadag and fullerene soot, and his recommendation that calibrations be performed with partcles whose refractive index is close to that found in the deployment is wise. However, the pattern seen in the field calibration with aged smoke is clearly more dramatic than that seen in our data or that presented in the comment.

We contend that Mie scattering cannot explain our data and that heating in the laser is a plausible explanation. Dr. Moore's comment suggests that the real problem is that the UHSAS does not respond properly to Mie scattering and that refractive indices near 1.52 are simply sized poorly. (He does not propose that scattering from those particles might deviate significantly from Mie behavior.) For relatively large particles, where Mie wiggles hit, it is quite likely that given the uncertainties in refractive index, precise diameters, non-sphericity, and perhaps the actual (as opposed to specified) optical geometry of the UHSAS, the Mie calculations might be far off, as indeed they are in the lab calibrations. But for spherical particles with diameter much smaller than the wavelength, it is hard to see how the UHSAS could respond in a way that differs much from calculations. That leaves either particle geometry or changes in particle sizing due to heating as the likely causes.

Comments from Richard Moore

1. *The main peak undersizing of 0-15% (depending on size) is largely consistent with the difference in UHSAS size response between PSL particles and size-classified ammonium sulfate particles, and that the finding reported in the second bullet point above is due to differences in refractive index between the PSL calibration standard and aged, biomass burning aerosols.*

   But the pattern is different, with the BB particle undersizing much more strongly related to diameter. I see no indication that the $(NH_4)_2SO_4$ behavior deviates significantly from that predicted by Mie scattering (though it's hard to tell from a log-log plot). Note that when you plotted our data, the line actually crosses your 2020 data. As you'll see in the revised version of the paper, the volatility changes very little with diameter, suggesting that composition (and hence refractive index) is not a strong function of particle size. I'm also a bit curious what shape $(NH_4)_2SO_4$ particles have.

2. *Can the dual peaks between 100-180 nm be attributed to a stitching error in the transition region between the G3 to G2 gain stages, where the smaller 'anomalous' peak is from the G3 detector? While such a stitching error would not bias the polydisperse size distribution (or indeed even be noticeable in many cases), it may give rise to extra peaks when looking at monodisperse aerosols near the gain stage transition point. What was the G3 gain stage saturation diameter for this instrument during the ORACLES campaigns as well as the subsequent tests?*

   No, it's not a stitching error. Those tend to be very sharp and distinctive, while the anomalous peaks are of a breadth comparable to the other peaks (there is no smoothing applied in the figure). In addition, while stitching errors occur at fixed diameters (for a given calibration file) the anomalous particles show up at different diameters for different mobility diameters.

3. *Differences between Mie theory and the actual instrument performance may be substantial between 600-1000 nm as indicated by Figure 3, which may explain the poor performance of the extrapolated correction. The difference between NaCl (refractive index of 1.53+0i) and PSLs is particularly noticeable and seems to exhibit 20% undersizing between 600-1000 nm.*

   Yes, once the particles are large enough that Mie wiggles start to appear, theory and data seem to part company. The question is whether that is due to the particles not behaving like ideal Mie spheres or the instrument not responding to scattering as predicted. Certainly part of it is the former: particles aren't spheres and the refractive indexes aren't known perfectly. Some of it may be the latter: perhaps the optical angles aren't as well defined as hoped or the jet isn't through the center of the beam or there's a size-dependent defect in focusing the beam.

4. *Along the lines of my Point 1 and the authors' caution in the final bullet above, it's not clear to me that aged biomass burning particles or other atmospherically-relevant absorbing aerosols far from emissions sources are meaningfully different from non-absorbing aerosols in terms of UHSAS sizing. Instead, these results motivate the need to calibrate the UHSAS with particles of atmospherically- relevant refractive index instead of PSLs.*

   I emphatically agree, of course, since that's exactly what we were trying to do with the in-flight tests. The surprise was the extent of the undersizing, particularly for the anomalous particles. But for particles below 300 nm, much smaller than the 1054 nm laser, Mie calculations ought to be reliable!

   Part of the purpose of our lab work prior to deployment was to bracket the refractive indices we might see in the field, with higher (PSL) and lower (H_2SO_4) as well as something in the middle (NaCl).

I'd suggest that the authors compare their biomass burning curve from Figure 6 to the NaCl curve from Figures 2-3 rather than relying only on Mie Theory calculations as in Figure 7 to rule out the refractive index explanation.

As you requested, that is shown in Fig 1, including the airborne data from the plume and the NaCl data from the plume, along with the fit to the NaCl data using the same mathematical form, but extending the fit to 500 nm. The results are admittedly somewhat ambiguous, but the slope of the plume data is clearly steeper than the NaCl.

But it makes little sense to concentrate solely on the NaCl, when the other non-absorbing materials behaved quite differently. The H_2SO_4 is the only material we tested that is almost certainly spherical, and the UHSAS slightly oversized it until well into the Mie wiggles. The refractive index is not perfectly known, since it attracts water very effectively and also lab air typically has elevated NO_3, so there could have been a small fraction of NH_3HSO_4. Up to around 500 nm the Na_2SO_4 particles are very close (within 3%) to that predicted by the Mie calculations, even though the particles are not likely to be spherical and the refractive index used was for 589 nm, not the 1054 nm of the UHSAS laser.

The issue cannot simply be that the refractive index of NaCl is lower than that of PSL, since both sulfate particles have even lower refractive indices. The most obvious explanation is non-sphericity, even though it is true that the literature suggests it's not a really big factor. Perhaps the nebulizer we used in the lab or the drying rates were so different that the dynamic shape factor from Zieger et al. (2017) is optimistic and the resulting particles have significantly less mass. Of course if the mis-sizing of NaCl is due to non-sphericity, it suggests that perhaps the plume particles were strongly aspherical too. That seems unlikely for non-rBC particles since they are a product of vapor deposition to nucleation mode particles.

In any case, it would clearly be valuable to do a series of calibrations with definitely spherical particles having a variety of refractive indices to test whether the UHSAS does respond as predicted by Mie theory. It looks like you have been doing that, given the plot with numerous organics. Might my Mie code for scattering into UHSAS optics be of use?

That the 'anomalous' particle size curve lines up so well with that for fullerene soot seems like more than a coincidence and would seem to imply the existence of a small, externally-mixed aerosol population in this aged biomass burning plume.

Yes, it might, but that conflicts with the SP2 data, which showed thick coatings. Given the new heating calculations, it is inevitable that particles with even a small amount of rBC will get sufficiently hot to evaporate coatings, so the anomalous particles need not be made primarily of rBC.
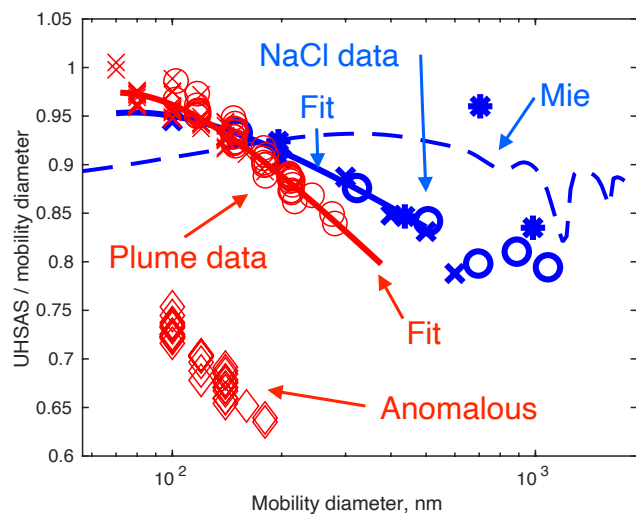
Figure 1: UHSAS sizing of NaCl in the lab tests and of plume particles in flight. The solid blue curve is a fit of the same form as used for the smoke plume particles. The dashed blue line is the Mie calculation for spherical particles with the refractive index of NaCl after correcting for the DMA mis-sizing due to non-sphericity (Zieger et al. 2017).

References

Zieger, P., O. Väisänen, J. C. Corbin, D. G. Partridge, S. Bastelberger, M. Mousavi-Fard, B. Rosati, M. Gysel, U. K. Krieger, C. Leck, A. Nenes, I. Riipinen, A. Virtanen, and M. E. Salter (2017). "Revising the hygroscopicity of inorganic sea salt particles". 8.1, p. 15883. DOI: 10.1038/ncomms15883.