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Atmospheric
Chemistry
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Discussions

Interactive comment on "Relating aerosol absorption due to soot, organic carbon, and dust to emission sources determined from in-situ chemical measurements" *by* A. Cazorla et al.

Anonymous Referee #1

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Cazorla et al. aim to validate a remote sensing methodology for classification of particle types within air masses according to the location of points within the scattering Angstrom exponent (SAE) vs. absorption Angstrom exponent (AAE) phase space through comparison with in situ measurements. This is an important effort, especially as such remote sensing data are increasingly utilized to assess the importance of so-called "brown carbon" (or absorbing organic carbon) towards climate. Some of the in situ measurements support while others do not support the proposed particle type classification based solely on the intensive optical properties. I find the general idea of the study to be excellent, but I have some difficulty following the exact comparisons being made and of establishing what exactly the conclusions are (and whether the

conclusions are entirely consistent with the data as presented). It is my sense that this manuscript could benefit substantially from some reorganization to separate discussion from experimental. Further comments are below.

Major Comments:

In Figure 1, the authors divide the AAE vs. SAE space into a number of different regions of supposedly distinct particle type. However, I have a few concerns.

1. A substantial amount of data points exist with very low AAE values. The authors list these as either "coated large particles" or "EC dominated".

a. Starting with the "coated large particles", it is entirely unclear where this designation comes from and for what reason they believe that "coated large particles" as opposed to their other large particle categories (Dust, Dust/EC) would be expected to have an AAE < 1.

b. For the "EC dominated" category, it is similarly not clear why they believe that EC should have an AAE < 1 and what, in particular, would make the observation of an AAE < 1 an indicator of an "EC dominated" region. A variety of lab and in situ measurements indicate that the AAE for "pure" EC is around 1, not less than 1. This is actually stated on P3455, L6. If we even put some very approximate error bounds on this, let's say +/- 0.2 for arguments sake, then one would think that any value from 0.8-1.2 could be "EC dominated." Mie theory indicates that as the size of individual spherical BC particles increases AAE values < 1 are possible. But it is not clear from lab or in situ experiments that this is justified for EC that is produced from combustion. I know that the authors are not doing the actual AAE retrievals here, but such a large number of small («1) AAE values suggests to me larger uncertainties in the retrieved AAE than is suggested. Consider, for example, the data shown in Fig. 6 for CalNex and CARES, where data coverage is the greatest. Neither show AAE values substantially less than 1. Only the CalWater data set gives AAE values < 1, but as noted by the authors the CalWater dataset may be problematic due to the limited statistics and predominately in cloud sampling.

2. The authors seem to completely ignore the potential role of any non-OC "coating" material on the BC optical properties. Gyawali et al, for example, show that, at least theoretically, coatings of non-absorbing material on BC can modify the AAE, leading to values > 1. It is thus possible that the category the authors identify as "EC/OC mixture" could just as easily be "EC/Sulfate mixture". The point here is simply that an AAE > 1 (along with a large SAE) does not necessarily imply the presence of absorbing organics. This needs to be made clear.

3. "OC Dominated" is misleading, as black carbon will still contribute substantially to the total absorption (especially when integrated over the entire solar spectrum) for particles in this region. Consider that AAE values for "pure" brown carbon tend to be $\sim$5 or so. The maximum AAE in this region is 3, with most points clustering around 1.75 or so. Some simple math says that if the observed AAE = 3, the AAEBC = 1 and the AAEBrC = 5, then the fraction of absorption by BC at 440 nm would be 30% and at 675 nm would be 70%. And if the observed AAE = 1.75, then these percentages change to 66% (440 nm) and 91% (675 nm). Thus, this region can hardly be considered "OC Dominated". Better definitions of the regions might therefore be "EC/OC – high OC" and (for the EC/OC Mixture category) "EC/OC – low OC" The same story holds for the "OC/Dust Mix". This should really be "EC/OC/Dust Mix".

In Figure 6c, as I count it there are only 10 "Dust" points. This is not enough points to justify the very smooth frequency histogram for this aerosol category in Fig. 6d. Further, the vast majority of these "dust" points do not fall in the "Dust" region of the AAE/SAE graph. This would seem to contradict the entire premise that the AAE/SAE space provides meaningful information on sources, or alternatively indicates that either the ATOFMS categorization is no good or the absorption/scattering measurements are no good. This also fundamentally contradicts the statement on P3464, L9 that "The overall in-situ spectral properties agree with the detected chemical composition." Further, this sentence seems to contradict somewhat the discussion at the end of this page

(starting at L23).

Overall, I find the organization of the manuscript to be a bit strange, in particular the mixing of the "Methodology and Results". This mixing leads to some situations where the authors seem to discuss (or at least refer to) observations before the observational methods are ever discussed.

The authors need to provide clearer discussion of the differences in the particle size cutoffs for the various studies. This is critical to all interpretation, but gets buried in the results. I strongly suggest that the authors reorganize to have a more traditional "Methodology" section, where they introduce both the AERONET and in situ methodologies, and then go on to the results.

The division in terms of the SAE is too crude and should be refined. How have the authors decided on 1.5 as a cutoff? Below I show a graph of some simple calculations using Mie theory, where I have calculated the theoretical SAE for the 445-660 nm wavelength pair assuming (1) monodisperse particles and (2) a constant RI = 1.5 +0.0i. (Consideration of size distributions, as opposed to monodisperse particles, can be viewed simply as a weighted smoothing function.) It is clear that SAE > 1.5 is only true for particles <200 nm diameter. Larger particles give smaller SAE values. Presumably, the authors would not put the cutoff between EC/OC/Sulfate/Etc. and Dust at 200 nm. This again suggests that the classifications suggested here are only partially descriptive, and thus the names given to them should be modified accordingly. For example, it is possible to have zero dust particles in the "Dust/EC mix" category if one is dealing with particles >200 nm but still in the submicron mode.

The authors state on P3456, L20 that "Bahadur et al. (2012) provide further details on the full parameterization of the SAE-AAE phase space using a global set of aerosol measurements." However, looking at Bahudar et al., it is clear that they have fewer categories and with lines drawn in different locations than in this work. Therefore, substantially more discussion is required regarding the origin of the categorizations used here, as it is insufficient to just give a reference to Bahudar et al.

In general, the scatter in the measurements during CalNex are substantially less for a given particle type than those during CARES and CalWater. I note that these were made in different ways and on different aircraft, with CARES and CalWater using one method (nephelometer onboard the DOE G1) while CalNex used a different method (PCASP data inverted to give scattering measured onboard the CIRPAS twin otter). Do the authors think that there could be differences in data quality, in particular the sampling of supermicron particles, between the different campaigns that are causing this behavior? Or do they believe that it is simply an indication of real atmospheric variability. The apparent miscategorization of the dust particle type relative to the expected SAE/AAE phase space makes one wonder. I believe that data quality issues need to be discussed more clearly and in more detail: right now they are sort of intertwined with the discussion.

I do not understand what exactly the authors are getting at with the statement “Particles detected as a primary fossil fuel source, i.e. elemental carbon, were classified mainly as organic carbon or a mixture of organic carbon and elemental carbon or dust. This reinforces the conclusions extracted from the comparison of the overall chemistry composition for the different regions and seasons in California. The external mixing of aerosol on a column integrated value like the AOD, or its absorption and scattering components, would yield to a higher AAE value and, therefore misclassifies the EC type (primary fossil fuel source).” (P3464). Clarification would be appreciated.

P3466, L28: Concluding that some (unquantified) amount of absorption is due to “brown carbon” does not directly lead to the conclusion that “it must be a primary consideration in developing future climate mitigation policies.” The influence of brown carbon must be considered explicitly in terms of its contribution relative to black carbon. I find this statement to be an overreach.

Other comments:

Figure 1: I see no reason to limit the x-axis to a lower limit of 0. SAE values < 0 are possible.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 3451, 2013.

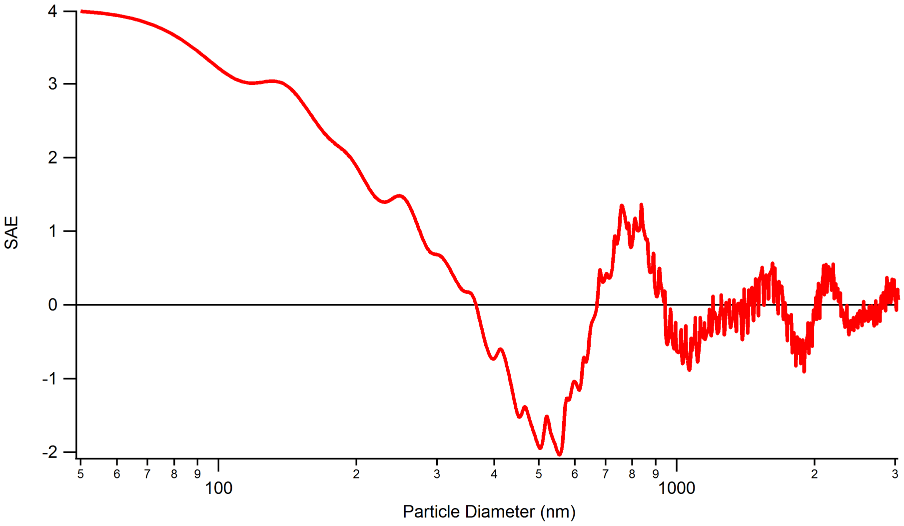

Fig. 1. Figure 1. SAE vs. monodisperse particle size