

Response to Anonymous Referee #1

We would like to thank anonymous referee #1 for the useful comments. We have responded to each specific comment in detail as well as updated the manuscript according to the suggestions, which we believe has helped to strengthen and clarify portions of the study. Comments are in blue and italics, and our responses are in black.

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.

The primary assumption behind the Angstrom matrix illustrated in Figure 1 is that three species: EC, OC and Dust, and their external mixtures are responsible for all solar absorption. Of these, Dust falls into the “coarse aerosols” category and EC and OC fall into the “fine aerosols” category (when separated by size, represented as SAE) and EC falls into the “strong absorber” category while Dust and OC fall into the “enhanced absorber at short wavelengths” category (when separated by chemistry, as represented as AAE).

Such a separation identifies three regions of the phase space corresponding to each of the absorbers, and in the context of external mixtures we can also identify the intermediate regions as their mixtures. The identification of the lower-left quadrant is somewhat speculative however, and the in-situ measurements presented here are the first step in identifying the nature of the aerosols that would inhabit this region of the phase space.

We modified the sentence where the Fig. 1 is presented:

“Figure 1 illustrates the division of the Ångström matrix with labels that represent the three aerosol absorbing species and their mixtures. The lower-left quadrant has been labeled as “coated large particles” indicating that it contains a species with $AAE < 1$ but larger in size. Lack and Cappa (2010) showed that black carbon particles with a sulfate coating might present those optical properties, and polluted dust with strong absorbers might also present the same spectral response.”

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.

High values of OC AAE have been widely documented by many field studies (Flowers et al., 2010; Gyawali et al., 2009; Moosmuller et al., 2011), typically ranging between 2.0-4.0. Similarly, field studies concentrating on dust dominated aerosols (Alfaro et al., 2004; Fialho et al. 2006; Bergstrom et al., 2007) report an AAE in the range of 2.0-3.0 indicating enhanced absorption at shorter wavelengths. In contrast, very low values of AAE (1.0 or less than 1.0) have only been reported by Bergstrom et al. (2007), Clarke et al. (2007), Roden et al. (2006) and Yang et al (2009) in measurements containing polluted urban air thought to be influenced by fossil fuel combustion. There is no evidence in the literature of strong dust or OC absorption across all wavelengths (free iron, the component most often thought to be responsible for dust related absorption has an AAE typically above 2.0), so in the model used by Bahadur et al. (2012), the only species that would be responsible for low values of AAE is black, or elemental carbon.

While Mie theory calculations indicate that BC AAE would be less than 1.0 for relatively larger particles, we do not believe this is the effect we are seeing, as the AERONET retrievals correspond to a column integrated measurement and it is unlikely that the aerosol in the entire column is dominated by large BC particles. It is more likely that the AAE<1.0 corresponds to BC particles that are internally coated by a sulfate shell, as it was shown by Lack and Cappa (2010).

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.

The reviewer is correct in pointing out that variations in the AAE can also be caused by non-absorbing coatings, as demonstrated by Gayawali et al. (2009) therefore barring further evidence the “Angstrom Matrix” of Figure 1 remains speculative. The in-situ measurements presented in this work are our first attempt to gather such evidence – and we find that indeed most particles in the EC/OC mixture contain both EC and OC markers. A complementary work that explores this phase space from a theoretical modeling perspective would also be highly useful but is beyond our current scope.

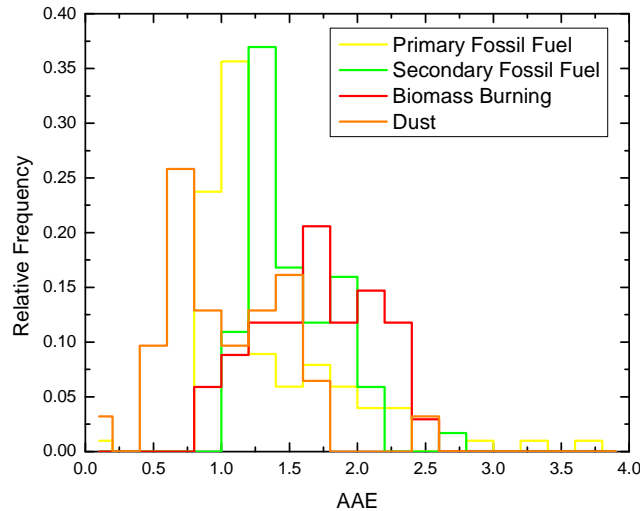
3. “OC Dominated” is misleading, as black carbon will still contribute substantially to the total absorption (especially when integrated over the entire solar spectrum) for particles in this region. Consider that AAE values for “pure” brown carbon tend to be ~5 or so. The maximum AAE in this region is 3, with most points clustering around 1.75 or so. Some simple math says that if the observed AAE = 3, the AAE_{BC} = 1 and the AAE_{OC} = 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”.

The reviewer is correct to note that in all (observed) cases containing EC, EC is likely to be the strongest absorbing agent due to its inherent nature. If we take the SSA of these species into account though, a slightly different picture is obtained. Using approximate figures of SSA of 0.40 for EC and 0.85 for OC at 440 nm, the relative AOD of EC/OC becomes 10/90 % in the first example and 34/66 % in the second example. Since the AOD is a better measure of the actual mass of OC that would be present in such a mixture, we feel that the classification is appropriate.

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).

Figure 6d is the frequency histogram result of the combination of the data show on Figs. 6a to 6c. Most of the dust points are on Fig. 6c, but they are very limited due to the availability of data out of cloud and the cut size of the A-ATOFMS (dust is in the coarse mode, and the A-ATOFMS has a cut size of 2.5 μm , i.e. it only “sees” the smaller dust particles. Figure 6d shows the frequency histogram for each

category (P-FF, S-FF, BB, Dust) but the line was smoothed just for plotting purposes. We modified the figure to avoid confusion:



The dust category is correct from the A-ATOFMS perspective but the limited data points makes it difficult to obtain a robust set of statistics for that category. In general, the in-situ spectral optical properties agree with the aerosol classification, except for the dust type due to the limited data.

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.

We reorganized the manuscript with a more classical methodology section. Now, the methodology includes the explanation of the remote sensing and in-situ measurements and there are separated sections for the results, discussion and conclusions. We think that with this new organization, the differences between studies are clearer.

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 reviewer is correct in pointing out that a full taxonomy of this phase space is not possible based simply on SAE vs. AAE considerations, as can be seen in the theoretical example constructed here. We would however counter that the phase space was divided based entirely on observations and therefore overcomes the limitations of assuming either a size distribution, refractive index, or internal structure or shape for the particles. A columnar measurement (such as those provided by AERONET) is likely to contain a mixture of several different size modes, shapes and internal mixing states, therefore a rigorous statistical analysis will provide the “most-likely” observed scenario. We do acknowledge however that the in-situ measurements presented here are our first attempt at refining and confirming the phase space division. As such measurements suffer from limitations and uncertainties as well, a comprehensive modeling study (using Mie calculations such as those shown here) would provide an ideal complement to this study but is outside our current scope.

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.

As we indicate in this work, Bahadur et al. (2012) present a simplified model where all absorbing aerosols consist of an external mixture of pure EC, OC, and dust. The divisions of the phase space developed in that paper were therefore fewer – as only regions corresponding to ‘pure’ EC, OC, and dust were constrained based on AERONET measurements. This paper describes our first attempt to refine and extend this method. So while we retain the high/low AAE/SAE combinations that correspond to the EC, OC, and dust regions, we relax their constraints somewhat and the phase space instead corresponds to events that are dominated by these species and their mixtures. The condition of $AAE > 1.50$ was retained to indicate the separation of poorly absorbing species (dust and OC), and $SAE > 1.50$ was retained to indicate combustion dominated (EC and OC) species. The phase boundaries for “large” particles ($SAE < 1.0$) and “EC dominated” particles ($AAE < 1.0$) were relaxed to the more intuitive value of 1.0.

In section 2.1, when presenting the Angström matrix we included the following clarification:

“This partition is based on a simplified division published by Bahadur et al. (2012). In the supplemental material of Bahadur et al. (2012), a threshold value of $AAE=1.5$ was found to demarcate the dust dominated region fairly well, containing 72% of all measurements in dust-dominated regions, but only 17% of measurements in fossil fuel dominated regions. Therefore, the condition of $AAE>1.5$ has been retained to delineate the aerosols that have an enhanced absorption at shorter wavelengths (i.e. dust and OC) with smaller values of AAE considered to have an influence of EC leading to more complex mixtures. Similarly, SAE of 1.5 was found to reasonably delineate the fine mode aerosols (EC and OC) with smaller values of SAE considered to have an influence of larger particles (such as dust), again leading into the mixture containing regions of the phase space. In our partition, the inclusion of mixtures changes some of the phase boundaries. Thus, the phase boundaries for large particles and “EC dominated” particles were relaxed to the more intuitive value of 1.0.”

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.

The referee is right in pointing out that different instruments might yield to differences in the optical data. However, the differences in the scatter shown in Fig. 6 are driven by the chemical composition. Only data with a dominant species are shown. This means that during the sampling period (5 minutes), 75% of the particles detected have to be of one type. Most of the data points shown during CalNex (Fig 6a) are dominated by primary fossil fuel (yellow in the figure), but the data points with no dominant species are not shown and those are scattered all over the Ångström matrix space. The same is applied to CARES in Fig. 6b but with a dominance of secondary fossil fuel (green in the figure).

On the other hand, the limitation in sampling supermicron particles during CalWater is due to the A-ATOFMS cut size (2.5 μm). The instrument cannot “see” most dust particles (coarse particles) and, adding to this, most of the time during CalWater was cloud sampling.

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.

Extracted from Table 4, what was detected by the A-ATOFMS as primary fossil fuel was classified by the Ångström matrix as OC (31.33%), EC/OC (27.71%) and OC/Dust (21.69%), i.e. the corresponding optical properties fell on those quadrants. Taking into account that the classification is based on considering that 75% of the particles detected by the A-ATOFMS are of that type, the optical properties might contain particles from other types, modifying the AAE and SAE. Similarly, on column integrated values, the contribution from other aerosol types, different from EC, yield to a higher AAE value, causing a misclassification of the primary fossil fuel source.

We modified the sentence to make it clearer:

“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. Taking into account that the classification is based on considering that 75% of the particles detected by the A-ATOFMS are of that type, the optical properties might contain particles from other types, the same way 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). This reinforces the conclusions extracted from the comparison of the overall chemistry composition for the different regions and seasons in California”

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.

What we mean with this statement is there is evidence of OC absorption. Models usually do not consider OC as an absorber and we think that it must be considered. We reworded the sentence eliminating the “primary” from the sentence to make it softer.

Other comments:

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

There are a few data points below 0 on the x-axis but we do not think that showing them improves the figure. In its current form, the x- and y-axis have the same range and we think this way the Ångström matrix looks more intuitive.

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