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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Identification of key aerosol populations through their size and composition resolved spectral scattering and absorption" *by* F. Costabile et al.

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(Itemized Italic text refers to the referee's comments, while authors reply (AR) indicates the answer to referee's comment. Each AR is followed by the corresponding new text of the revised manuscript, labeled by NTRM. Here, quoted text refers to the old version of the manuscript, while bold quoted text is new text added to the revised manuscript.)

We thank the referee # 3 for the very interesting review. All observations have been fully addressed as detailed below.

- *This manuscript by Costabile et al., "Identification of key aerosol populations*

through their size and composition resolved spectral scattering and absorption", analyzed absorption and scattering measurements and proposed a scheme to optically classify aerosols. This is an interesting approach, and in my mind, the manuscript could be published after a rather substantial revision to improve, strengthen and clarify several points that are suggested below.

General comments:

- *The authors proposed a "paradigm" to classify the aerosols, but no reasoning was given to support (theoretically) this particular choice, other than that it "revealed some relations" (block 17510, line 10, where it is discussed first time). Also, since similar classifications have been proposed before (with slightly different variables in y- and xaxis), it is important to discuss (to give theoretical justifications) those aspects of this scheme that gives now a more detailed picture about the dominating aerosol types, if compared to the previous methods.*

AR: The theoretical choice underling the paradigm is better described in the revised manuscript. In particular, reasons for the clearer separation provided by the proposed paradigm with respect to previous classifications are discussed. These include: (1) the inverse correlation between SAE and dSSA resulting from their common dependence on particle size; (2) the inverse correlation between AAE and dSSA resulting from their common dependence on particle composition; (3) the dependence of SSA on particle size in addition to particle composition, which translates into a SSA decrease for ultrafine particles regardless of their composition (in the ultrafine particle size range, scattering decreases faster than absorption with particle diameter); (4) the dependence of SAE on particle composition in addition to particle size; (5) the fact that separating SAE from AAE (instead of combining them in EAE) helps in separating particle size from particle composition effects.

NTRM: New text added at the very beginning of the Section 3 (sect.Results) :

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"An aerosol population can be considered as a set of particles being "homogeneous" with respect to their sizes and composition (and shape and mixing state). The variation of this "homogeneity" translates into a different spectral variation of aerosol scattering and absorption, SAE (or EAE) and AAE varying with varying particle size and composition. In this work, our aim is to find proper combination of the intensive parameters SAE, AAE, SSA and dSSA by which key aerosol populations can be optically separated. Similar classifications have been proposed before (cf. Introduction section). Some of those classifications (e.g.,Russell et al (2010)) were based on AAE vs EAE plots. The advantage of using EAE is that it takes contemporarily into account SAE and AAE; but this is also a disadvantage as EAE fails in separating particle size effects (mainly linked to SAE) from particle composition effects (mainly linked to AAE). To make this separation more evident (i.e., to separate particle size from particle composition effects on the spectral variables) SAE was used instead of EAE.

The SAE vs AAE relation was first experimentally analysed (Sect.3.1). Since SAE represents the scattering spectral variation, and AAE represents the absorption spectral variation, one might expect their combination to correlate to the SSA spectral variation (SSA being a mathematical combination of scattering and absorption). To investigate the way SAE and AAE shall correlate to dSSA (the SSA spectral variation) we combined the relevant experimental data, and found significant inverse correlation between SAE and dSSA, and between SAE and dSSA·AAE (Fig.1). Those behaviors observed on experimental data were reproduced by numerical simulations (Sect.3.2), thus providing a theoretical support to the observations. A classification scheme (hereafter referred to as "paradigm") resulted. The relevance of the paradigm is discussed in the Discussion section (sect.4.1) based on both experimental results (Fig.1) and numerical simulations (Fig.3)."

Text added in the Experimental results section (Sect.3.1) in the block 17510, lines 9-13:

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"**By analysing the $SAE_{467--660}$ vs $AAE_{467--660}$ experimental data we found inverse correlations between $SAE_{467--660}$ and $dSSA_{660--467}$=SSA_{660}-SSA_{467}, i.e. the spectral variability of the SSA, .** Figure 1 shows the observed data (more than 15500 data points) as **either EAE (y-axis, upper panels) or SAE (y-axis, lower panels) versus either AAE, dSSA, and dSSA·AAE(x axis). As previously discussed, SAE vs dSSA·AAE data (R^2=-0.66) correlate more than SAE vs AAE data (R^2=-0.07). As well, SAE vs dSSA·AAE (lower panels, R^2=-0.66) correlate better than EAE vs dSSA·AAE (upper panels, R^2=-0.58).** Data are color coded by SSA530..."

Text modified in the discussion section, block 17514, lines 9-11:

"By combining the experimental results (Fig. 2) and the numerical simulations (Fig. 3) it is possible to explain the effects of key aerosol populations on the bulk intensive optical properties. **Reasons for the clearer separation provided by the proposed paradigm with respect to previous classifications are detailed below. First, the inverse correlation between SAE and dSSA resulting from their common dependence on particle size. Second, the inverse correlation between AAE and dSSA resulting from their common dependence on particle composition. Third, the dependence of SSA on particle size in addition to particle composition, which translates into a SSA decrease for ultrafine particles regardless of their composition (in the ultrafine particle size range, scattering decreases faster than absorption with particle diameter). Then, the dependence of SAE on particle composition in addition to particle size. Lastly, the fact that separating SAE from AAE (instead of combining them in EAE) helps in separating particle size from particle composition effects.**

This is shown in Fig.4 **where SAE vs dSSA·AAE relation is separately plot for all identified aerosol populations. Figure S1 is same as Fig.4 but for the fact that it also shows relations between SAE (y-axis) and either AAE or dSSA (x axis).**"

Text modified in the discussion section, block 17514, line 23 ("The resulting graph

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mirrors the experimentally observed graph in Fig. 1"):

"**The variables this "paradigm" is built on come out by the experimental data analysis (Sect.3.1), their relevant relations being theorized by the numerical simulations (Sect.3.2). Numerical results (Fig.3) both confirmed the inverse relation experimentally found between SAE and dSSA (Fig.1) and explained its variation with particle size and composition. dSSA is larger for large absorbing particles (CDM) as well as for small absorbing particles (STM), both of them (STM and CDM) having low SAE.**" (Please note that, as suggested by the other reviewer, we have made clearer some acronyms: the former AM (Aitken mode) has been substituted by AKM, the former SM (soot mode) by STM, the former MM (Marine mode) by CMM (coarse marine mode), and the former DM (dust mode) by CDM (coarse dust mode).) "**Contrarily, dSSA approaches zero for accumulation mode particles for which SAE is large. This finding fits in previous studies on dSSA, which (being a sort of SSA Angstrom exponent) has been shown to depend on both particle size and composition (Bergstrom 1973; Ackerman and Toon, 1981; Kaufman et al. 2001; Dubovik et al.2002; Bergstrom et al., 2002; Russell et al.,2010; cf. Introduction section). In addition, the simulation results (Fig.3) evidence that ultrafine particles can be identified by low SSA thus regardless of their absorption properties (i.e., AKM in addition to STM). The SSA information added (as color) in the plot thus enhances the identification of both black carbon, and UFPs.**

Our paradigm is based on the observation that (cf.Sect.3) a combination of SAE and AAE shall correlate to dSSA, SAE being the scattering spectral variation (depending mainly on size), AAE being the absorption spectral variation (mainly depending on particle composition), and dSSA being the spectral variation of a combination of scattering and absorption (the SSA, depending on both particle size and composition). Therefore, the simpler SAE vs dSSA relation (Fig.1 and Fig.S1) is partly incomplete: it fails in completely separating aerosols with similar particle sizes and different composition. By way of evidence, one might

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note that the SAE vs dSSA plot is ineffective in separating aerosols with same particle diameters from 80 to 300 nm (typically classified as "urban pollution") , but different composition: they are here represented by SOM and BBM (and by some AKM, LIM and LOM). Both SOM and BBM have (Fig.3) dSSA approaching zero, and similar SAE (and similar SSA, as well).

Contrarily, the paradigm built on dSSA·AAE as x-axis (instead of dSSA only) is more complete: the inverse relation between AAE and dSSA (simulated in Fig.3, and based on the fact that both parameters vary with varying aerosol composition) is effective in separating aerosols with similar SAE. This is the case of urban pollution aerosols, for which dSSA approaches zero: AAE is sufficiently large and largely varies with aerosol type to zoom in variations with particle composition (required to separate BBM from SOM)."

- *It is absolutely necessary to show SAE467-660 (or EAE as suggested by the other reviewer) vs. AAE467-660 and vs. dSSA also separately; at least in the review response, but probably also in the revised manuscript. Those kind of relationships have been plotted before, so then the reader could better see and appreciate the novelty of your approach. These could be included in one three-panel plot, similar to the Figure 1 but with different x-axes: first showing AAE in x-axis (a-panel), then dSSA in x-axis (b-panel), and finally AAE*dSSA (your current Figure 1) in c-panel.*

AR: This is an interesting suggestion entirely addressed in the revised version. To show relevant differences between our paradigm and the version suggested, we have extended the former fig.1 and added a supplementary figure S1). The new figure 1 now includes EAE and SAE in the y axis, and AAE, dSSA and dSSA·AAE in the x axis based on experimental data. The other figure, added as supplementary material (fig.S1) shows the corresponding numerical simulations. Both figures are arranged as

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a three panel plot showing SAE (and EAE as suggested by the other reviewer) vs AAE and vs dSSA separately, in addition to SAE vs dSSA·AAE.

- *You have Cimel instrument in your site too. There are very little level2 inversion data, due to the AOD threshold: the single scattering albedo and absorption optical depth are considered having too high uncertainty below AOD of 0.4 at 440nm. Apparently you considered all the measurements, regardless of the aerosol loading. Do you consider there is a similar aerosol loading dependent uncertainty in your measurements (that could affect your analysis, although you have now ignored that)? Please discuss this issue also in the revised manuscript.*

AR: Thank you for this comment. Actually, we did not ignore the aerosol loading effect, but we missed to mention it in the former text. Now we specify that raw measurements were carefully analyzed to correct for possible errors, and that after all corrections, very low values of scattering and absorption coefficients ($<$10 and $<$1 Mm^{-1}, respectively) were excluded.

NTRM: Text modified accordingly in the Experimental section (block 17509, line 15):

"**Even if the accuracy of both PSAP and nephelometer was sufficiently large - after all corrections discussed - we excluded very low values of scattering and absorption coefficients ($<$10 and $<$1 Mm^{-1}, respectively). Outliers values were also excluded (respectively, $>$700 and $>$130 Mm^{-1} for scattering and absorption coefficients.**"

- *Since there are not much level2 AERONET data, I took level15 and applied all the same criteria than in level2 except for the AOD threshold (e.g. sky-error and sza limits) and plotted Rome data according to your paradigm. Clearly the strongest density of data are centered at SAE440-670 of around 1.7 and at AAE440-670*dSSA(670-440) of around -0.025, so best matching the region*

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of AM in your plot. On the other hand, only very little data are in positive x-axis side, where you, on the other hand, have the majority. What do you think is the reason why your surface in-situ data are VERY different, in this regard, to Cimel measurements in the same site? The manuscript would be strengthened, if you would discuss this also there.

AR: This is an enthralling comment carefully addressed in the revised manuscript. We believe that the paradigm has a general validity, that is that the underling relations between SAE, AAE, SSA and dSSA are valid regardless the fact that they are calculated on surface in situ or AERONET data. However, the paradigm was tailored on surface in situ aerosol types, representative of dry, 24-hours, all-weather aerosols in close proximity of combustion emissions. Other aerosol measurement techniques as the remote sensing photometric ones, on the contrary, refer to the columnar aerosol burden, and to ambient (i.e., hydrated), clear sky conditions. Those elements are probably at the basis of the differences found between our plot and the ones based on AERONET data (a relevant figure is added here as Figure AC3), in which, as the referee, we applied to AERONET level 1.5 all the level 2 criteria except for the AOD threshold).

A comprehensive analysis of those elements is beyond the scope of this paper, and it is actually the topic of investigation for a follow-up study. At the moment, we can only speculate on the following. Among the others, we believe aerosol hydration to be a major factor for the differences found between in situ and Cimel measurements. Aerosol hydration can particularly be relevant for particles from 80 to 300 nm, typically being carbonaceous aerosols, the so-called "urban aerosols", here represented by SOM, BBM, and part of the AKM aerosol populations.

The simulation (Fig.3 of the manuscript) suggests those "urban aerosols" to have dSSA approaching zero, and SSA decreasing with decreasing AAE (the lower the AAE, the lower the SSA). Accordingly, surface in-situ measurements (plot SAE vs AAE, new fig.1) show everywhere (also for dSSA approaching zero) either low AAE and low SSA,

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or large AAE and large SSA (i.e., AAE<2 and SSA<0.9). Contrarily, the SAE vs AAE plot filled in by Cimel data (Fig.AC3 here) shows several cases having contemporarily low AAE (<2) and large SSA (>0.9).

"Urban aerosols" (80 to 300 nm urban aerosol particles) are likely to contain water soluble particles. By changing the particle refractive index, aerosol hydration can cause the SSA vs AAE relation to change. This could explain the reason why for in-situ dried observations the lower the AAE the lower the SSA, whereas for Cimel hydrated observations there is not such a relation. As well, by changing the particle size distribution, aerosol hydration can cause a variation of the corresponding dSSA. This shall give reason for the diameter changes of "urban aerosols" as seen by dried in situ observation or hydrated Cimel observations: the increase in particle diameter due to the particle hydration can cause dSSA to shift from positive to negative values. This difference may be relevant in the 80-300 nm particle size region where very small variation of particle sizes can cause dSSA to change its sign (from positive to negative, and viceversa). Accordingly, the paradigm will show a "strongest density of data" for dSSA either negative or positive.

NTRM: Text added at the very end of the Discussion section (new text added at block 17522, line 8):

"**Lastly, it should be noted that the paradigm (Fig.1) has been filled in by surface in-situ aerosol data. When attempting a comparison between the paradigm filled in by similar surface measurements and data measured by remote sensing techniques (e.g., columnar aerosol data from AERONET), some differences can occur. Differences can be due to several factors. (1) Surface in-situ datasets generally include 24-hours (day and night, all sky conditions) measurements with 1 to 5 minute resolution. (2) The contribution of local emissions, particularly soot particles (here referred to as STM) to the bulk aerosol is expected to be larger in in-situ data: STM can be very abundant at the surface and can often dominate surface in-situ aerosol data, contrarily to columnar observations (being ex-**

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tremely diluted over columnar aerosols observations, STM can be less evident in the case of AERONET data, soot particles rarely dominating columnar aerosol observations).” This turns the majority of data to be in the positive x-axis side for surface in-situ paradigms in fig.1, contrarily to what observed by AERONET (Fig.AC3 here). “**(3) Differences can be due to the way in-situ measurements “observe” aerosols: in-situ instruments measure dried aerosols while AERONET observes, on the contrary, aerosols as they are in the atmosphere (i.e.,hydrated aerosols), aerosol hydration being effective in changing both particle refractive index and size distribution.**”

Specific comments:

- *Block 17509, line 20. You mentioned having used Lidar data and meteorological variables in the data interpretation. How they were used?*

AR: Both data were used in case of doubtful situations. Lidar data were used to gain some conclusions concerning coarse aerosols, such as to be sure that there was no dust advection in case of low SAE and large soot particle concentrations. Meteorological data were used to interpret some temporal paths, such as influence of rain on intensive aerosol parameters. This is now specified in the text.

NTRM: Text added at Block 17509, line 23: “**Both data were used in case of doubtful situations. Lidar data were used to gain some conclusions concerning coarse aerosols, such as to be sure that there was no dust advection in case of low SAE and large soot particle concentrations. Meteorological data were used to interpret some temporal paths, such as influence of rain on intensive aerosol parameters..**”

- *Block 17512, lines 14-16. Please specify which reference was used for each type. For instance, please give the the reference explicitly for SM (imaginary part*

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of 0.047, which sounds relatively high), so that the reader can go and find the source for this particular choice. And similarly for all the types. Perhaps this could be done by a citation in the Table 2 for each row.

AR: The referee is right: although relevant references were mentioned in the former manuscript, there is not a single reference for every single aerosol type. This was mentioned in the manuscript (block 17512 lines 14-21). In fact, previously published refractive indices did not completely fit our atmospheric measurements and numerical simulations.

For instance, for the mentioned case of soot, the refractive index is based on Lack and Cappa (2010). In any case, the given value is well within the range indicated by Bond and Bergstrom (2006) review (imaginary part of LAC ranging from 0.01 to 1.0), and below the value recently used for soot by Arola et al. [*Arola, A., Schuster, G., Myhre, G., Kazadzis, S., Dey, S., and Tripathi, S. N.: Inferring absorbing organic carbon content from AERONET data, Atmos. Chem. Phys., 11, 215-225, 2011*] analyzing AERONET data (1.95-i·0.79).

More in general, the way refractive indices were selected is as follows. In case of highly absorbing aerosol types (STM and BBM), the black/brown carbon content was simulated by refractive indices derived from Bond and Bergstrom (2006), the variability of light absorbing particles with particle core/shell/diameter being simulated according to Lack and Cappa (2010). (The imaginary refractive indices for STM is deduced by Fig.9 of Lack and Cappa (2010).) In case of aerosol types composed by both OC and sulfates (AKM, SOM, LOM, and partly CMM), the OC versus sulfates content was simulated by values and spectral variability of refractive indices derived from the results of Flowers et al.(2010). In case of inorganic aerosol types (LIM, CMM), refractive indices were based on well-established literature (e.g., Dubovik et al.(2002); Seinfeld and Pandis (2006)), variability of the real refractive index with particle diameters being simulated according to the results of Cai et al., 2011. In case of coarse dust (CDM),

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refractive indices came from well-established literature (e.g., Kaufman et al., 2001 and Dubovik et al., 2002), doubt cases (e.g., many dust refractive indices given in Dubovik et al.(2002)) being solved by fitting simulations to experimental observation.

A list summarizing references according which refractive indices of each aerosol population were deduced from is:

- AKM: Flowers et al., 2010; Bond and Bergstrom, 2006;
- STM: Lack and Cappa, 2010; Bond and Bergstrom, 2006;
- SOM: Flowers et al., 2010; Bond and Bergstrom, 2006;
- BBM: Dubovik et al., 2002; Bond and Bergstrom, 2006;
- LIM: Seinfeld and Pandis, 2006; variability with D according to Cai et al., 2011;
- LOM: Flowers et al., 2010 ; variability with D according to Cai et al., 2011;
- CMM: Seinfeld and Pandis, 2006; Flowers et al., 2010;
- CDM: Kaufman et al., 2001; Dubovik et al., 2002.

All these references were already included in the former manuscript reference list. We would prefer to avoid including this list in table 2, since in most of the cases refractive indices are based on more than one reference.

- *Block 17513, line 3, "size-dependent m". Do you mean type-dependent here?*

AR: Yes, right. Changed.

- *Block 17523, line 11, what do you mean by "STRICT agreement" (that the point number 8, for instance, is precisely where it "should be")?*

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AR: Strict was intended for compliant, in the sense that it demands that relations concerning the paradigm are respected. To avoid misunderstanding the text at Block 17523, line 11 is changed by:

"The work finally presented a comparison between the proposed aerosol classification scheme and observations taken during previous field campaigns, the comparison showing **that relations concerning the paradigm have a general validity** .

- *Figure 5. How exactly did you locate the data from the previous studies into this figure? If I look at Dubovik et al 2002 and their Figure 1, for instance, I see that dSSA is negative for ALL the sites except for the sites in the "desert dust" category. So why is the number 6 (Mexico City) in the positive x-axis? Or data for ICARTT, which has also negative dSSA; why is it exactly at zero in x-axis? Just to give two examples.*

AR: The referee is right: there was a typing error in the two mentioned cases. The corresponding figure has been changed, the two points being now located for dSSA$<$0 in the new Fig.5 of the manuscript (Fig.4 here).

In general, due to the lack of complete data (EAE, SAE, AAE, SSA, dSSA), some points in Fig.5 of the manuscript (Fig.4 here) were located by extrapolating values from the plots (not from the data), some point were located by deducing data from available ones, some points were mediated from a range of possible values.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 17503, 2012.

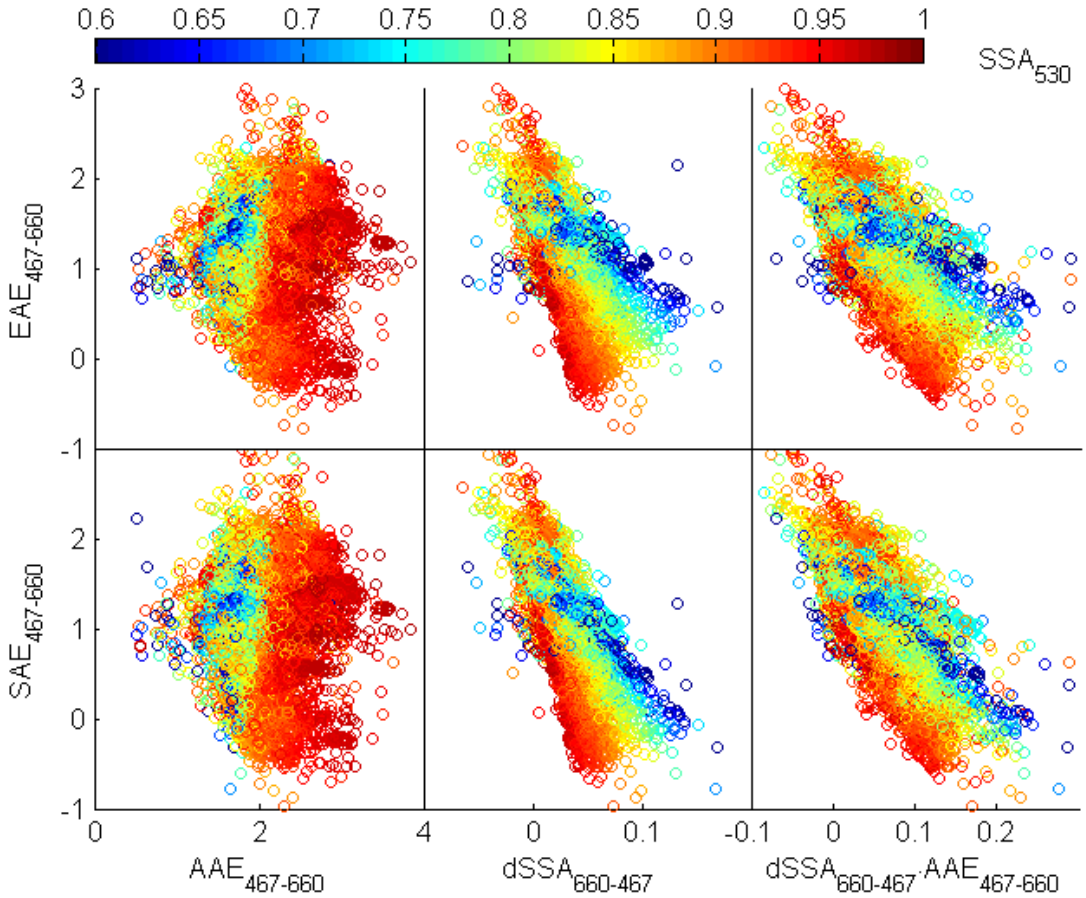

Fig. 1. New Figure 1: "Inverse linear relation observed between EAE and SAE (y-axis) and AAE, dSSA, and dSSA.AAE (x-axis). The slope varies with varying SSA (color code)."

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Interactive Comment

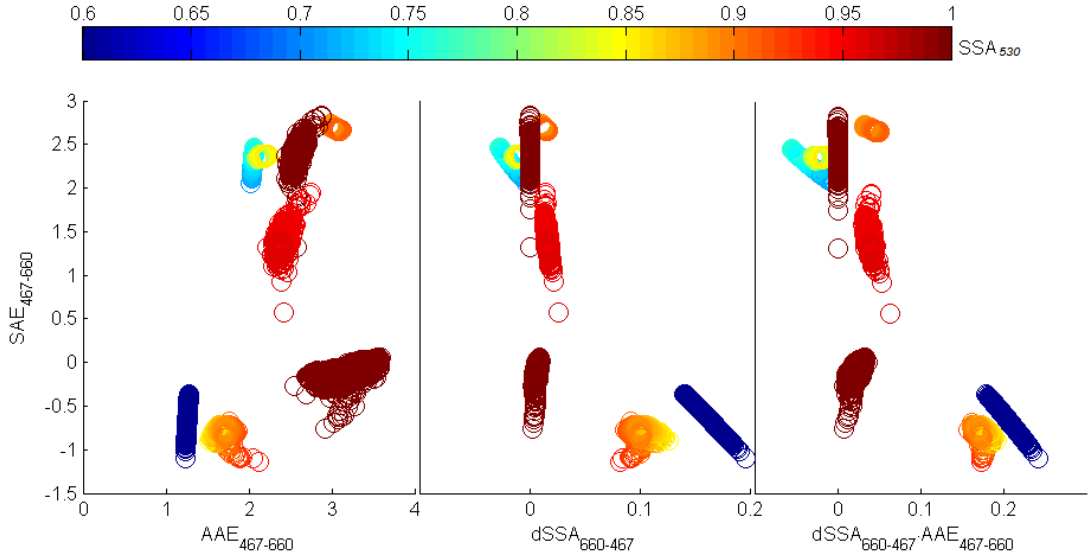

Fig. 2. Supplementary Figure S1:“ Results of the numerical simulations illustrating the “paradigm” proposed. The figure is same as the lower panels of Fig.1, but shows the relevant numerical simulations”

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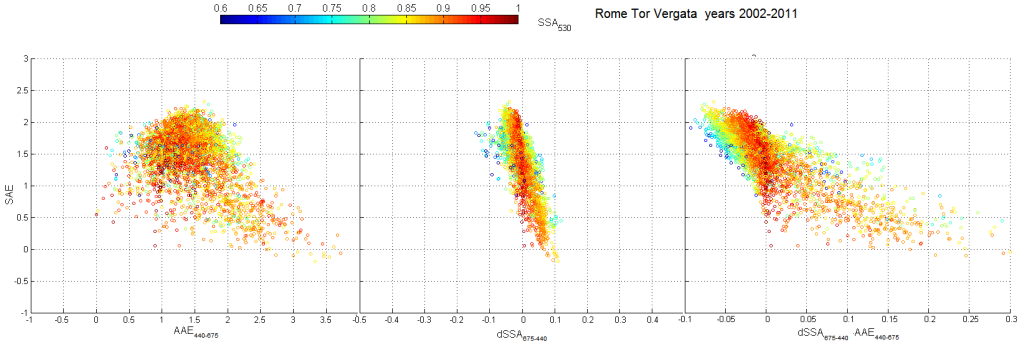

Fig. 3. Figure AC3:"Same as Fig.1 but using ten years of AERONET data in Rome (2002-2011). Note that we applied to AERONET level 1.5 all the level 2 criteria except for the AOD threshold

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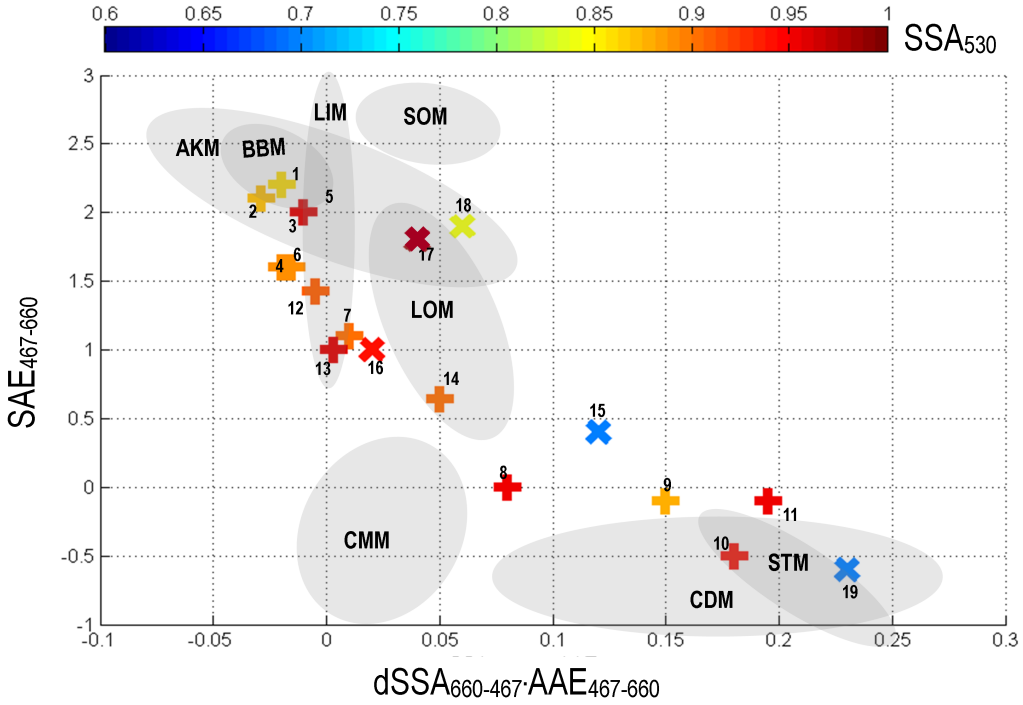

Fig. 4. New Figure 5: "Comparison between the aerosol classification paradigm proposed and observations taken during previous field campaigns."

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