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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characteristics of an aged organic "brown" aerosol in the urban Po Valley atmosphere" *by* F. Costabile et al.

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We would like to thank the referee for his constructive and precious comments. These comments have all been considered and addressed, and have significantly improved upon the work. Please, see our detailed author's responses below.

(In Bold, comments from the Referee; plain text is used for author's answers ; in Italic, the new text added in the revised manuscript, including page and line numbers (Px,Lx-x).)

The concept of measurement uncertainty has not been addressed at all in the manuscript. This needs to be added throughout - especially for the measurements that are central to the analyses: AAE and OA/BC ratio (or BC-to-OA ratio, as in Fig. 4). Similarly, the QA/QC procedures and standards need to be dis-

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cussed and defended. E.g., all data with $\sigma_a < 1$ Mm^{-1} and $\sigma_s < 10$ Mm-1 were removed : why were these the limits imposed? How much data were discarded?

We revised the manuscript to address: (1) uncertainties of optical variables in Sect.2.2; (2) uncertainty of OA in Sect.2.3; (3) uncertainty of BC in Sect.3.1; (4) the resulting uncertainties in the AAE vs BC-to-OA relation in Sect.4.1 (Figure 4 was revised); (5) QA/QC procedures and standards in Sect.2. We referenced previous papers in literature these uncertainties were based on.

In details:

(1) *The uncertainty of the scattering coefficient* $\frac{\delta(\sigma_s)}{\sigma_s}$ *= 0.02, and that of the absorption coefficient* $\frac{\delta(\sigma_a)}{\sigma_a}$ *= 0.2*.

(2) *The uncertainty of the AMS-derived OA* $\frac{\delta(OA)}{OA}$ *= 0.2.*

(3) The uncertainty of BC was calculated by propagating $\frac{\delta(\sigma_a)}{\sigma_a}$, together with the uncertainty deriving from the AAE$_{BC}$ attribution method used to calculate BC. In this method, we set AAE$_{BC}$ =1.1, and $\frac{\delta(AAE_{BC})}{AAE_{BC}}$=0.22.

(4) Uncertainties of AAE and BC-to-OA were calculated propagating these values. Figure 4 of the manuscript was revised to include these uncertainties.

(5) We mentioned that *outlier/low values can significantly influence data statistics*. We hence checked carefully values of: (i) $\sigma_a < 1$ Mm^{-1} and > 50 Mm^{-1}, as *PSAP sensitivity <1 Mm^{-1} in the measurement range 0-50 Mm^{-1}; (ii)* $\sigma_s < 10$ *Mm^{-1} and* > 1000 *Mm^{-1}, as nephelometer lower detectable limit= 0.3 Mm^{-1}, with calibration tolerance of* $\pm$ *4 Mm^{-1}, in the measurement range 0-2000 Mm^{-1}.* These values are set by instrument manufacturers. *A few data (124 records having* σ_a *<1 Mm^{-1}, less than 20 records with* σ_s *<10 Mm^{-1}, and some points with* σ_s *>700 Mm^{-1}) were discarded, as they were considered dubious values, comparing to data variability during the field* (illustrated in Supplementary Figure 1).

In Section 3, what is meant by "The dataset consisted of 11211 records (5764 in fall, and 5447 in winter), including 2551 records (covering 40 days of measurements) with no missing value, and 1087 records (150 in fall, and 937 in winter) of cleaned data after data analysis."? Does this mean only 10% of the measurements were ultimately included in this analysis?

The referee is right for noting that there was an error. Text was corrected as it follows:

Dataset consisted of 3211 records (1764 in fall, and 1447 in winter). The statistical analysis was done on a subset of these data with no empty field (2551 records, covering 40 days of measurements). These data were then cleaned, and a final dataset of 1487 records (550 in fall, and 937 in winter) was ultimately included in the statistical analysis. The longer dataset was, however, used in the analysis to evaluate single cases (e.g., the case-study).

Section 3.2 : what constituted an acceptable merge of the SMPS and APS size distributions? What was considered unacceptable? How many measurements were eliminated using the smoothing procedure and visual inspection?

The referee correctly mentions an issue that was addressed in the revised version (Sect.3.2, P5L24-25).

In details:

$PNSD_{fitted}$ replaced $PNSD_{APS}$ and $PNSD_{SMPS}$ when their relative difference (d_r, Eq.1):

$$d_r = \frac{|PNSD_{SMPS} - PNSD_{APS}|}{max[PNSD_{SMPS}, PNSD_{APS}]} \quad (1)$$

was larger than 0.1 cm^{-3}. This procedure was considered acceptable if: (i) the minimum mean squared error between $PNSD_{fitted}$ and $PNSD_{APS}$ was less than 1%; (ii) correlation coefficients between $PNSD_{fitted}$ and $PNSD_{SMPS}$, and between $PNSD_{fitted}$

and PNSD$_{APS}$ were larger than 0.8. A number of 98 records did not verify these conditions, and were checked by visual inspection: 94 of them were discarded, and 4 accepted.

Section 4.1 and Figures 2-4: discussion is needed to explain the physical meaning of the PC score and the factor loading numbers. We agree with the referee, and added this in the revised manuscript.

In details:

Coefficients of PC$_k$ represent the relative weight (in terms of correlation) of original variables (i.e.,time series of dN/dlog(d$_p$)) in PC$_k$. Factor loadings of PC$_k$ represent these coefficients scaled by the variance explained by PC$_k$ ($\varkappa_k$) . Loadings of PC$_k$ thus represent the relative weight of the dN/dlog(d$_p$) variables in PC$_k$ re-scaled by $\varkappa_k$. Factor scores of PC$_k$ are the transformed variables corresponding to a particular data point in the dN/dlog(d$_p$) time series. Factor scores thus represent PC$_k$ values corresponding to each particular data point of the dN/dlog(d$_p$) time series.

Section 4.1 : what does the following sentence mean? "BC mass concentration was assumed to increase mostly with increasing concentration of larger BC particles"? Section 4.1 ? what does the following sentence mean? "Higher fBC values coupled to lower BC mass concentration were, therefore, interpreted as indicators of ultrafine BC particles, and vice versa."

Both referees (and editor, as well) indicated that this sentence is both unclear and not necessary. To avoid unnecessary text, we decided to delete it (P6L23-28).

Figure 1: it is not clear why the present results from the Po Valley are compared to results from Leipzig made 7-8 years ago? We revised the manuscript (Sect.4.1) to clarify that: (1) this comparison aims at reinforcing *the interpretation that the aerosol type represented by PC3* is the droplet mode aerosol; and (2) the correlation found between the droplet mode aerosol and the "brown" aerosol *demostrates that the "brown"*

aerosol is secondary in origin (the droplet mode is secondary in origin), and gives insights into its likely formation process.

In details:

(1) To our knowledge, results from Leipzig are *the only work in literature showing a similar aerosol principal component to compare with*. The statistical methodology of the two works is the same, but datasets are very different, in time and space. Results from Leipzig were *based on five different statistical analysis based on different datasets* (two year data at eight concurrent measurement sites were available to create these five different dataset to be analaysed). *Results were correlated to meteorological and air quality data.* Our work here was based on a shorter time period, and one measurement site. We do believe that results from Leipzig are statistically strong. These identified clearly the *PC representing the droplet mode aerosol*, which shows *broad similarities with PC3* obtained in our work. *This allows to deduce with a reasonable statistical accuracy that PC3 does represent the droplet mode aerosol.*

The authors have missed some other relevant work that also shows associations between ambient SOA and BrC - see for example X. Zhang et al. (2011; 2013).

The referee is right for mentioning that these are important works, both supporting our findings. In fact, we referenced the work by Zhang et al. (2013) in the former manuscript (P2L12, P10L13-15). In the revised manuscript, we referenced these works more explicitly.

In details:

(1) In Sect.1 (P2L12-13), we indicated that *secondary organic aerosol (SOA) formed in the atmosphere contributes to the light absorbing carbon, as well (Moise et al., 2015), but only a few works have analysed secondary brown carbon associated to SOA (Zhang et al., 2013, 2011), and Saleh et al.(2013).*

(2) In Sect.5.3 (P10L13-15), we mentioned that *the composition found for this "brown"*

aerosol (high OA, nitrates being a likely component), its formation process (involving aqueous phase reactions), and AAEs values, are all coherent with previous studies, which showed increased light absorption towards UV for SOA particles (Jacobson, 1999; Lee et al., 2013; Song et al., 2013; Zhang et al., 2013; Powelson et al., 2014; Lin et al., 2014; Laskin et al., 2015), and sources, composition, and AAE of light-absorbing soluble organic aerosol in urban areas (Zhang et al., 2013, 2011) .

Section 5.2 and Figure 7: although the "paradigm" discussed here may have been developed in a prior paper, it is not something I think most readers will be familiar with (this reviewer was not). Provide the necessary explanation and context to interpret the present results. We agree with the comment. In the revised manuscript, we added in Sect.5.2: (1) the context (including references to previous relevant works which have analysed the topic); (2) additional explanations to interpret results (including the revised Figure 7), and (3) Table 2 summarising these results (in particular, k_{530}, which is compared to relevant values of bulk aged OA in literature).

In details:

(1) We indicated that *cluster analysis of aerosol spectral optical properties is becoming more and more used to infer information on aerosol type from optical data.* We mentioned that *Costabile et al. (2013) assessed spectral optical properties of key aerosol populations through Mie theory: soot, biomass burning, two types of organics, dust and marine particles were simulated through a sectional approach where each of these aerosol types was given a monomodal PNSD and a set of three refractive indices (RIs) in the visible range. Relevant Angstrom Exponents of extinction, scattering, and absorption (EAE, SAE, AAE), SSA and its spectral variation (dSSA) were calculated. It was proved that these aerosol types separately cluster within a "paradigm" where SAE is on the y-axis, dSSA times AAE is on the x-axis, and SSA is on the z-axis.*

(2) We indicated that *experimental data of the "brown" aerosol do cluster in this paradigm* (Fig. 7), and that *the cluster of "brown" aerosol data is separated from all*

other simulated aerosol types, except that named "large organics". Data of "large organics" and "brown" aerosol do overlap, indicating that they may represent the same aerosol type. In fact, microphysical properties of the aerosol type named "large organics" were simulated to be same as those of the droplet mode aerosol (i.e., PNSD peaking in the "large" accumulation mode, 300-800 nm size range). Spectral optical properties of this "large organics" aerosol type were simulated by RIs of spectrally absorbing organic material in the visible region: these RIs, given the broad similarities in Fig.7, can be assumed to be those of the "brown" aerosol.

(3) We added Table 2 summarizing these results, and pointed that *this comparison ultimately allows to infer spectral optical properties of "brown" aerosol* (in particular, k_{530}, compared to relevant values recently reviewed by Lu et al. (2015)).

- Section 5.2, lines 28-34: perhaps this is in line with the above comment, but I was completely confused by this entire passage. This text has been changed (see previous comment).

- In my opinion, Figure 8 does not much at all to the paper ? I would recommend removing it. We agree with the referee that this figure is not needed. However, it may be useful to connect results from different aerosol communities. As well, it reinforce findings. We would therefore prefer to keep it.

- Section 6: the findings do not "prove" the formation of BrC in the atmosphere. We agree with the referee, and revised the text (P6L22-23) to mention that *findings show that there is "brown" aerosol in the atmosphere*.

- Pg. 7, line 21-22: "The dependence on the nitrate mass fraction (fNO3 , Fig.3d) is not obvious, as high AAE values and droplet mode scores are observed for both fNO3 <0.05 and fNO3 '0.25." This does not seem consistent with the discussion of nitrate's importance in the abstract or in Section 6. The referee is right and we modified text accordingly, indicating (P1L4-5), that *findings show that "brown" aerosol... contains large concentrations of organic aerosol (OA) in droplet mode parti-*

cles and that *Nitrate is an additional likely component.*

Technical corrections have been addessed.

References

Zhang, X., Y.-H. Lin, J. D. Surratt, and R. J. Weber: Sources, composition and absorption angström exponent of light-absorbing organic components in aerosol extracts from the Los Angeles Basin, Environ. Sci. Technol., 47(8), 3685-3693, 2013.

Zhang, X., Lin, Y. H., Surratt, J. D., Zotter, P., Prévˆt, A. S., Weber, R. J.:. Light?absorbing soluble organic aerosol in Los Angeles and Atlanta: A contrast in secondary organic aerosol. Geophys. Res. Lett., 38(21), 2011.

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Fig. 1. Revised Figure 4. *Relation between "brown" aerosol and Black Carbon (BC) to Organic Aerosol (OA) ratio (BC-to-OA). Absorption Angstrom Exponent at 467-660 nm (AAE) is plotted against BC-to-OA. Data color is the score of the droplet mode PC extracted by the statistical analysis. Data size is the median diameter of the particle surface size distribution ($d_{med(S)}$). Data indicated by "*" show case-study values illustrated in Fig.5. Grey bars indicate measurement uncertainty, added to a subset of data only.*

Fig. 2. Revised Figure 7. *Optical signature of the "brown aerosol" as indicated by the paradigm proposed by Costabile et al. (2013). Absorption Angstrom Exponent at 467-660 nm (AAE) times spectral variation of Single Scattering Albedo from 660 to 467 nm (dSSA = SSA_{660} - SSA_{467}) is plotted against Scattering Angstrom Exponent at 467-660 nm (SAE). Experimental data of the droplet mode obtained in this work (representing the "brown" aerosol) are compared with key aerosol types obtained through Mie simulations. Data color is SSA at 520 nm. Relevant AAE values for key aerosol types are indicated as mean$\pm$standard deviation.*

Fig. 3. Supplementary Figure. *Spectral optical properties during the two measurement fields: y-axis shows data of scattering and absorption coefficients, colored by the Scattering Angstrom Exponent (SAE), and Absorption Angstrom Exponent (AAE), respectively.*

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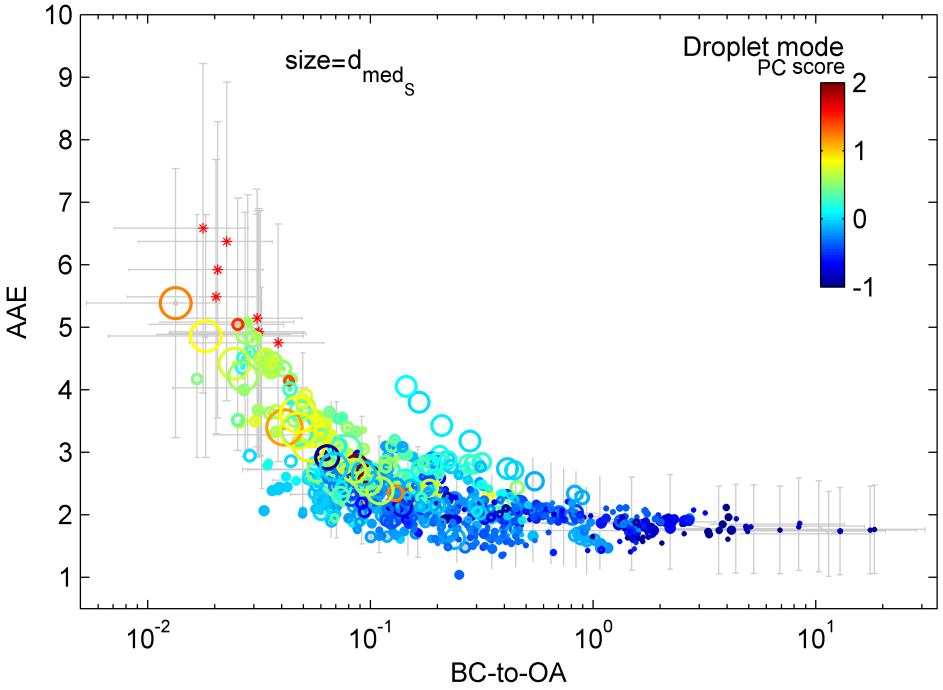

Fig. 4. Revised Figure 4.

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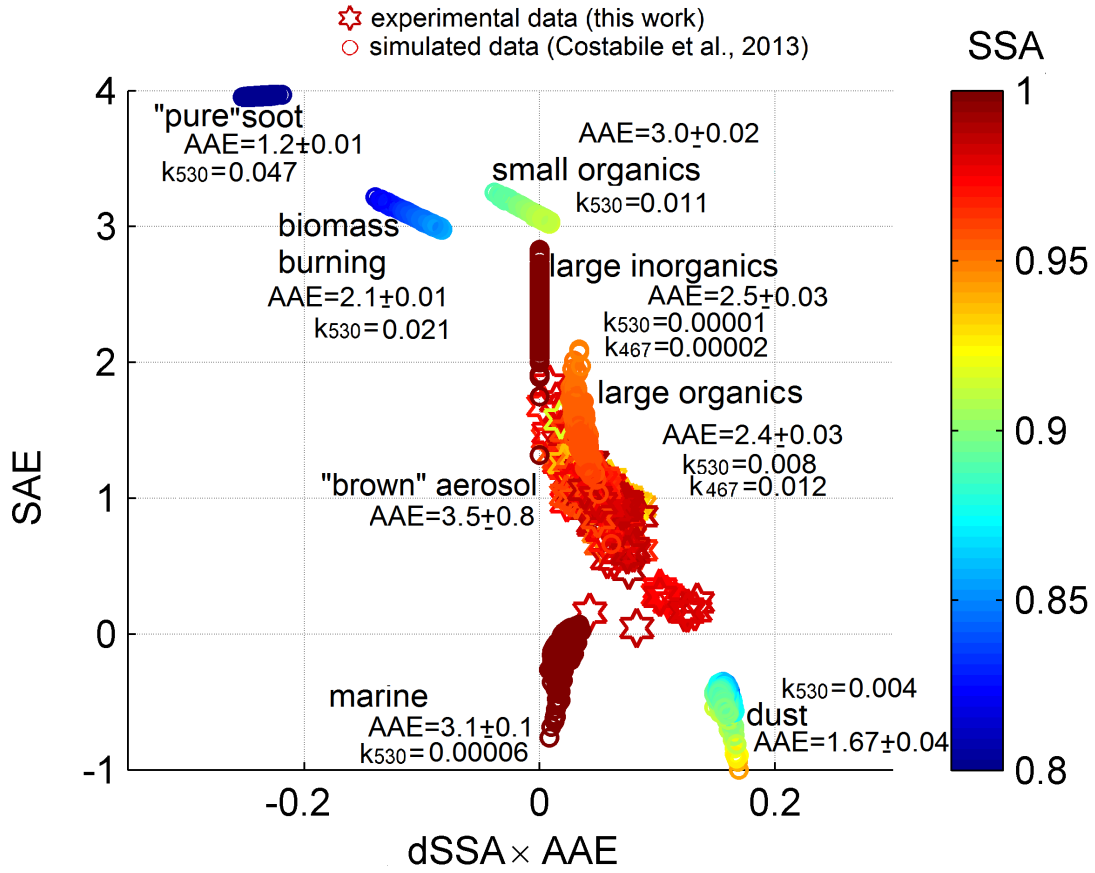

Fig. 5. Revised Figure 7.

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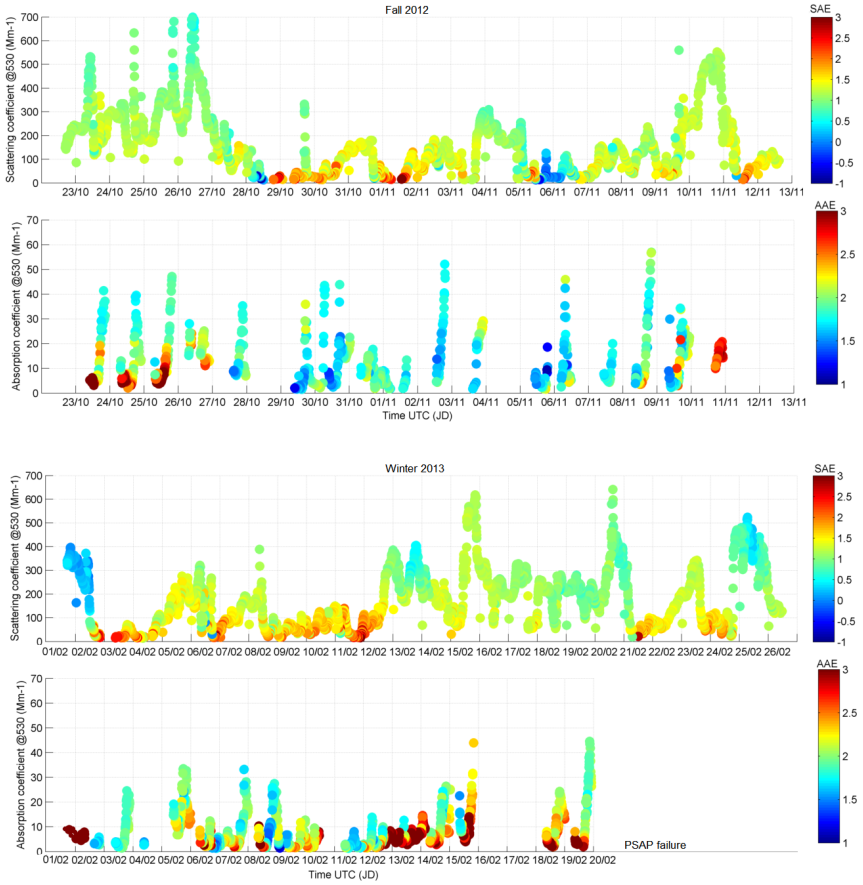

Fig. 6. Supplementary Figure 1.

Table 1. Spectral optical properties of the "brown" aerosol in the visible range: AAE, SSA, and SAE (expressed as mean±standard deviation and variation range [minimum- maximum value]), and real and imaginary part (k_λ) of the complex refractive index (RI [λ]).

$AAE_{467-660}$	SSA_{530}	$SAE_{467-660}$	RI_λ real part	RI_λ k_λ	[λ]
3.5±0.8 [2.5-6]	0.97±0.01 [0.92-0.99]	0.8±0.3 [0-2]	1.460	$1.2 \cdot 10^{-2}$	[467nm]
			1.454	$8 \cdot 10^{-3}$	[530nm]
			1.512	$7.5 \cdot 10^{-3}$	[660nm]

Fig. 7. Table 2.

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