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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 sincerely thank the referee for giving valuable and critical comments. These comments, all considered and addressed, have improved the work and strengthened its findings. Please, see 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).)

1. BrC is mainly composed of aged OA

This is one of the main conclusions in this paper. The authors arrive at this conclusion based on the correlations they found between AAE and OA-to-BC ratio, and between AAE and f44. The premise that this conclusion is based on

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is that AAE is an indicator of how brown the aerosol is. This is not accurate. AAE is an indicator of the wavelength-dependence of absorption. What is more "brown" OA with MAC=2 m2/g (at 532nm) and AAE=2, or OA with MAC=0.2m2/g (at 532nm) and AAE=4? Probably the brownest OA reported in the literature is that observed by Alexander et al. (Science 321, 833-836 [2008]), and it had relatively small AAE. So, with their current analysis, the authors can only make conclusions on the wavelength-dependence of OA absorption, and not on how brown the OA is. However, even this needs further analysis to be convincing. The authors base their analysis on the AAE of the whole aerosol (including both BC and OA). The AAE of the aerosol is dictated by the relative contribution of the components (and coating effects, which we can set aside for now). The increase of AAE with increasing OA-to-BC ratio does not necessarily mean that the added OA upon aging has a larger AAE, it can simply mean that the relative contribution of BC to AAE gets smaller, so the overall AAE increases. In other words, fresh and aged OA could have similar AAE, and the increase in AAE vs OA-to-BC ratio is simply due to the decreased contribution of BC.

We agree that the conclusion **BrC is mainly composed of aged OA** is not **accurate**. In fact, we conversely concluded (and this is stressed in the revised manuscript) that: (i) *we observed the bulk nondust aerosol having the strongest spectral dependance of light absorption (AAE=2.5–6)*; (ii) AAEs of this aerosol indicate that it has brown color, but *not necessarily that it equates to brown carbon*; (iii) this aerosol with brown color is defined "brown" aerosol; (iv) *this "brown" aerosol has a secondary origin, large concentrations of organic aerosol (OA), high OA-to-BC ratios, and is dominated by accumulation mode particles*. We revised the manuscript accordingly.

In details:

(1) We modified the title: *Characteristics of brown aerosol in the urban Po Valley atmosphere*

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(2) In Sect. 4.1, we stressed that the secondary origin of the "brown" aerosol is inferred from *a strong correlation found with the droplet mode aerosol type, a submode of accumulation mode aerosol particles which is by definition secondary in origin* (formed through secondary processes in the atmosphere). This conclusion is reinforced by the correlation with f_{44}.

(3) In Sect. 4.1, we stressed that the correlation with the droplet mode aerosol *gives insights into the likely formation process of this "brown" aerosol*.

(4) In Sect. 5.3, we stressed that there are indications that *this "brown" aerosol contains aged OA*. Thus, we speculate *into aged brown OA formation processes*.

(5) In Sect. 5.1, we stressed that we did not directly measure the AAE of OA, but *the AAE of the bulk dust-free aerosol, including boh BC and OA contributions* ($AAE_{BC,OA}$). Changes in this AAE are due to changes in *relative proportions of BC and OA*. This was already illustrated in former Figure 3b of the manuscript, where AAE did not linearly decrease with decreasing f_{BC}. We added Supplementary Figure 1 showing relative contributions of OA (data color) and BC (data size) on AAE.

(6) In Sect. 5.1, we stressed that our findings indicate *patterns (not absolute values) of* AAE_{OA}, found to *increase with decreasing BC-to-OA, similarly to what observed by Saleh et al. (2014) and Lu et al. (2015)*. To this purpose, we added Supplementary figure 2 showing AAE measured (i.e., $AAE_{BC,OA}$) together with AAE used to calculate BC (AAE_{BC}) in the AAE vs BC-to-OA chart. (For this figure, please, consider the following answers to referee's comments **Comparison with Saleh et al. is not apples-to-apples...**, and **Validity of PSAP measurements and BC concentration calculations**).

2. Validity of PSAP measurements and BC concentration calculations.

Figure 4 and figure 6 show that AAE is 2 at BC-to-OA ratio of 20. This puts in question the validity of AAE retrieved from the measurements because at such

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large BC-to-OA ratio, the particles should have AAE closer to 1. The authors should address this issue to determine whether there is something wrong with the calculations or the measurements that resulted in this factor of 2 overestimation of AAE. Also, BC concentrations are largely underestimated because the calculations (section 3.1) rely on the assumption that AAE of BC is equal to 1 (which is not the case, as retrieved from the instrument in this study). Consequently, the fractions of the different components should be recalculated.

We agree that this important issue was not illustrated enough, and revised the manuscript accordingly to include: (1) PSAP measurement uncertainty (Sect.2.2), and (2) BC mass concentration calculation method and resulting uncertainty (Sect.3.1); (3) these uncertainties in relevant figures; and (4) the explanation that (Sect.4.1) the low AAE values the referee refers to, can be due to these uncertainties and relevant (low) OA values.

In details:

(1) BC was calculated from PSAP-derived absorption coefficients (σ_a), relevant uncertainties *deriving from a number of measurement artifacts.* We referenced previous works in literature which have developed correction algorithms to overcome these artifacts, and mentioned that, based on Virkkula et al. (2010)'s correction, σ_a uncertainty is $\frac{\delta(\sigma_a)}{\sigma_a}$ = 0.2.

(2) *BC mass concentration was calculated using the AAE$_{BC}$ attribution method*. This method *assumes a known value of AAE$_{BC}$ at 530-660 nm.* This value is *commonly set to 1 for externally mixed BC*. We referenced previous works in literature, in particular Lack and Langridge (2013) and references therein, which have showed this AAE$_{BC}$ to be (i) larger than 1 for BC aerosol in ambient air (including both internally and externally mixed BC); (ii) *for externally mixed BC, 1 for particles with diameter $<$ 50 mm, and 0.8–1.1 for diameters of 50-200 nm; (iii) 0.55–1.7 for internally mixed BC, depending on particle size, coating, core, wavelengths.* Based on these previous works, we

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used *AAE_{BC}=1.1, and $\frac{\delta(AAE_{BC})}{AAE_{BC}}$=0.22.* (Note that there is no **fraction of the different components** that **should be recalculated**, as no fraction due to Brown Carbon was derived.)

(3) Figure 4 was revised. Both this figure and Suppl. Fig.1, include BC and AAE uncertainties, calculated propagating these σ_a and AAE_{BC} uncertainties.

(4) We explained *the small trend of the lower AAE values toward 1.5* considering: (i) uncertainties before mentioned, and (ii) OA values ($>$0) these low AAE values are at. On one hand, Fig.1 shows that AAE values from 1 to 2 are within measurement uncertanties. On the other hand, OA values > 0 in Suppl. Fig.3 suggest that there may have been *spectrally light absorbing material that the AMS cannot detect (refractory material, or material in particles smaller than 100 nm and larger than 1 μm)* causing a bias in AAE toward values larger than 1. We referenced previous papers in literature discussing this topic. In particular, Lack et al. (2008) analyzed the "bias in filter-based aerosol light absorption measurements due to organic aerosol loading", and found that "at low OA concentrations" (similar to OA concentrations here), "where HOA was a larger fraction of the OA, PSAP-derived AAE did display a small upward trend to $\sim$ 1.5, suggesting that the HOA measured may be mildly absorbing".

P1 L15: What's the difference between brown OA and brown carbon? The referee is right for questioning this. The lack of a common definition for brown carbon causes confusion. We do believe that the scientific community should address this question.

P2 L1: What do you mean by "moderately volatile"? Also, how do you support this claim? We referred to the classification proposed by Pöschl (2003) - Figure 1 of their paper. In the revised manuscript, we referenced this work based on which *there is a gradual decrease of thermochemical refractiveness and specific optical absorption going from BC/EC graphite-like structures to non-refractive and colorless OC. Also, there is a gradual decrease in the volatility from BC (the lowest volatility), to colorless non-refractory volatile OC (the highest volatility). A broad range of coloured organic*

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compounds, with volatility in between these two extremes, have recently emerged . (These were referred to as "moderately volatile".)

P5 L12: "we fixed threshold"? please explain. We explained in the revised manuscript (Par.3.1) that *dust-free aerosol conditions were identified based on the analysis of aerosol spectral optical properties*. We referenced previous works in literature, which have used this analysis to gather information on aerosol type. Among these, Costabile et al. (2013) showed that *the aerosol dominated by dust can be unambiguously identified based on the following combination of SAE, AAE, SSA, and dSSA:* SSA_{530} *>0.85,* $SAE_{467-660}$ *<0.5 ,* $AAE_{467-660}$ *∼2,* $dSSA_{660-467}$*=0.05-0.3.* We used this method to identify cases when the aerosol was dominated by dust, and eliminate them.

P6 L24: It is not clear why this assumption is needed or whether it is valid. You need more than "mass scales with volume" to justify this assumption We agree that this assumption is not needed, and deleted lines at P6L23-28 to avoid unnecessary text.

P7 top paragraph: What are PC2 and PC4? What would be in the primary aerosol that has modes 20-100 nm and 10-40 nm? One would expect those to be BC particles.

The referee is right for noting that PC2 and PC4 are both BC primary aerosols. However, their source is different (probably, heating and traffic emissions, respectively). We revised relevant text.

In details:

(1) We added Supplementary Figure 3, to illustrate weekly diurnal cycles, and loadings of PC1-4.

(2) We clarified (P7L3-5) that *PC1, PC2, and PC4 are BC primary aerosols (all correlated to BC and* f_{BC}*). PC1 and PC4 are both sourced by traffic emissions, diurnal*

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cycles peaking at rush hours and week-days. PC1 is a fine mode aerosol component (PNSD mode peaking from 100 to 200 nm), PC4 an ultrafine aerosol component (PNSD peaking from 20 to 40 nm). PC2 is an ultrafine BC aerosol component, as PC4. Unlike PC4, however, PC2 higher scores are at night-time, and there is no weekly cycle and no peak at "rush hours": PC2 is probably sourced by heating emissions.

Section 5.1: The authors mention that they will compare results with Shinozuka et al. (2009) Russell et al. (2010), Arola et al. (2011), Saleh et al. (2014), and Lu et al. (2015) but only show comparison with Russell et al. and Saleh et al.

These comparisons (both reinforcing our findings) were missing, indeed. We revised Sect.5.1 accordingly.

In details:

(1) Shinozuka et al. (2009)'s results were added in panel a of the revised Figure 6. Relevant data for SSA bins of 0.90-0.92, 0.96-0.98 and 0.98-1.00 were indicated by grey lines.

(2) Lu et al. (2015)'s results were added by grey line in panel c of the revised Figure 6. It was indicated that y-axis of both Lu et al. (2015)'s and Saleh et al (2014)'s results refers to AAE_{OA}, while y-axis of our figure refers to AAE from both BC and OA contributions.

(3) We added that *values of AAE>3.5 are at SSA $>$ 0.98, consistent with Shinozuka et al. (2009)'s results at SSA= 0.98-1.00*. We added that *this comparison ultimately shows consistency of "brown" aerosol properties measured in situ at the ground and observed from airborne and AERONET*.

(4) Although we are consistent with Arola et al. (2011)'s findings, the comparison in Fig.6 with their work is not possible. They used absorbing OC column concentrations [mg m^{-2}] in the x-axis, whereas we show f_{OA} derived from in situ ground measurements. We therefore did not reference this work.

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Section 5.1: The AAE values in this study are much larger than Russell et al., especially at low fOA values. I believe this is due to a bias in AAE retrieval (see major comment 2). We agree that there are differences, but there is broad consistency, as well. This is more clear in the revised Figure 6, where Shinozuka et al. (2009)'s grey lines (based on the same Russell et al. (2010)'s data) reveal the strong dependence on SSA. This was less clearly indicated by Russell et al. (2010)'s black line.

Section 5.1: Comparison with Saleh et al. is not apples-to-apples. Saleh et al. reports the wavelength-dependence of the imaginary part of the refractive index of the OA only, while this study reports AAE (wavelength-dependence of the absorption coefficient) of the total aerosol (including BC). The referee is correct for mentioning this issue, which we addressed by previous comments as well. We revised the manuscript accordingly.

In details:

(1) Figure 6 was revised to show that Saleh et al. (2014)'s and Lu et al.(2015)'s curves represent AAE_{OA}.

(2) Sect.5.1 was revised to point out that *we compare, in Fig.6c, different AAE values. In our work, AAE values are due to the bulk dust-free aerosol, thus depending on both BC and OA ($AAE_{BC,OA}$). AAE values of Saleh et al. (2014) and Lu et al. (2015) (AAE_{OA}) come from the wavelength-dependence of OA alone (w_{OA}), excluding contributions from BC (AAE_{OA} values are calculated from w_{OA} based on the relation AAE=w+1, valid for small particles in the visible range). The comparison in Fig.6c is thus intended to compare patterns only, not absolute values.*

(3) The Supplementary Figure 2 was added to show AAE_{BC} together with $AAE_{BC,OA}$, in the AAE vs BC-to-OA plot. We mentioned that *this figure is intended to indicate wavelenght dependence of OA absorption, and to suggest possible AAE_{OA} patterns, increasing with decreasing BC-to-OA, similarly to what observed by Saleh et al. (2014)*

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and Lu et al. (2015).

Section 5.1: The finding that AAE in this study is twice that in Saleh et al. and Lu et al. is most probably not accurate due to overestimation of AAE in this study (see major comment 2). We agree, and revised Sect.5.1 of the manuscript to mention that *the AAE of this secondary "brown" aerosol would probably be higher than that of the fresh biomass burning OA it likely derives from* (not "twice that", but "higher than that").

Terminology: the authors go back and forth between BrC, brown, and "brown". Please be consistent. As previously mentioned, *"brown" aerosol does not necessarily equate to brown carbon.* In the revised manuscript, we stressed this and used the *"brown" aerosol* notation everywhere to indicate this aerosol type. BrC was substituted by brown carbon.

Technical corrections have all been addressed.

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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.*

Fig. 2. Revised Figure 6. *Dependence of Absorption Angstrom Exponent at 467-660 nm (AAE) on (a) organic aerosol mass fraction (f_{OA}), (b) Organic Aerosol (OA) to Black Carbon (BC) ratio (OA-to-BC), and (c) BC-to-OA ratio. Data color is Single Scattering Albedo at 530 nm. Data size is median diameter of particle surface size distributions (d_{med_S}, ranging from 50 to 300 nm). Data indicated by "*" show case study values illustrated in Fig. 5. Relevant Pearson's correlation coefficients (r) are indicated. For comparison, we show previous results: (a) by Russell et al. (2010) (black line) and Shinozuka et al. (2009) (grey lines, for the SSA bins of 0.90-0.92, 0.96-0.98 and 0.98-1.00) ; (c) by Saleh et al. (2014) (black line), and Lu et al. (2015) (grey line). Note that AAE includes contributions from both BC and OA, whereas in panel (c), Lu et al. (2015) Saleh et al. (2014)'s results refer to AAE_{OA} only.*

Fig. 3. Supplementary Figure 1. *Relative proportions of BC and OA in the AAE vs BC-to-OA relation. BC-to-OA ratio (x-axis) against Absorption Angstrom Exponent (y-axis). Data points are sized by BC mass fraction (f_{BC}), and colored by organic aerosol mass concentration (OA). Vertical and horizontal bars show uncertainties*

Fig. 4. Supplementary Figure 2. *Dependance of the Absorption Angstrom Exponent (AAE) due to organic aerosol (OA) from the BC-to-OA ratio. The AAE due to BC and OA ($AAE_{BC,OA}$) of the dust-free bulk AAE is indicated by black squares. (A subset of data is indicated with uncertainty-bars (grey lines), the interpolating curve of the whole dataset being indicated by the black curve). AAE_{BC} used to derive BC is also indicated (grey squares).*

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Fig. 5. Supplementary Figure 3. *The four principal components (PC1-PC4) of the Particle Number Size Distribution: (a-d) weekly diurnal cycles of scores (red, Week Day; green, Week End; black, all data), and (e) loadings.*

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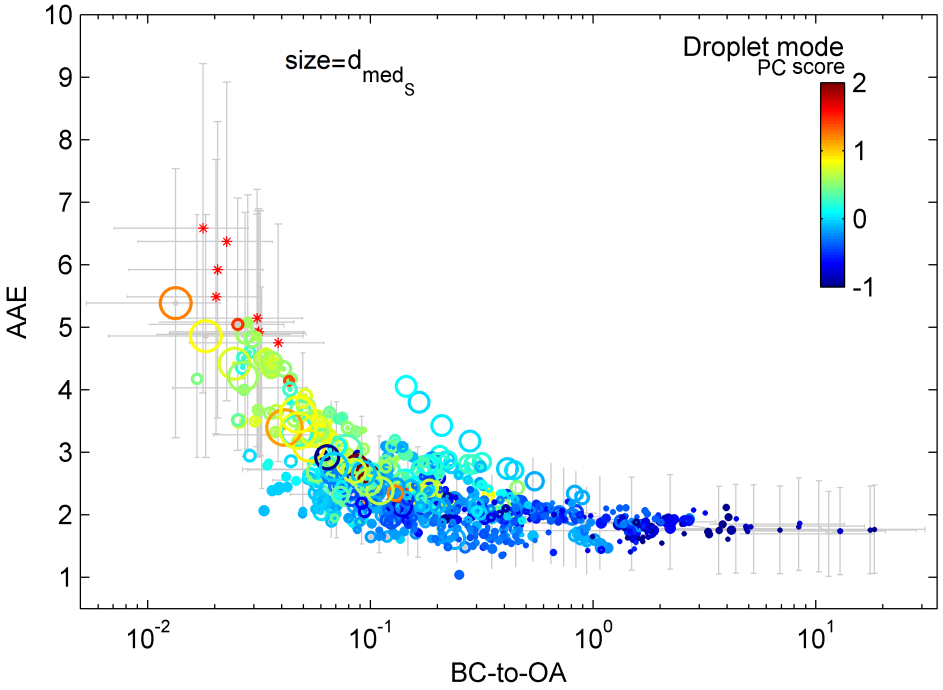

Fig. 6. Revised Figure 4.

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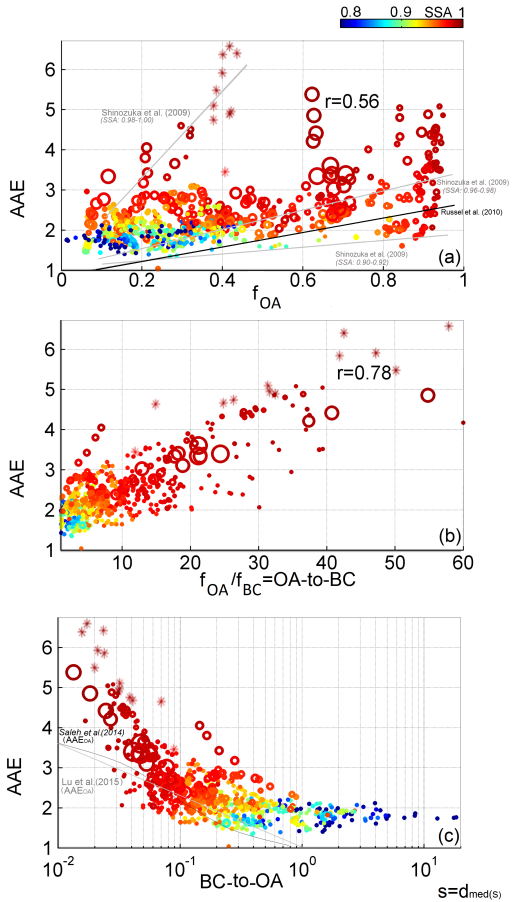

Fig. 7. Revised Figure 6.

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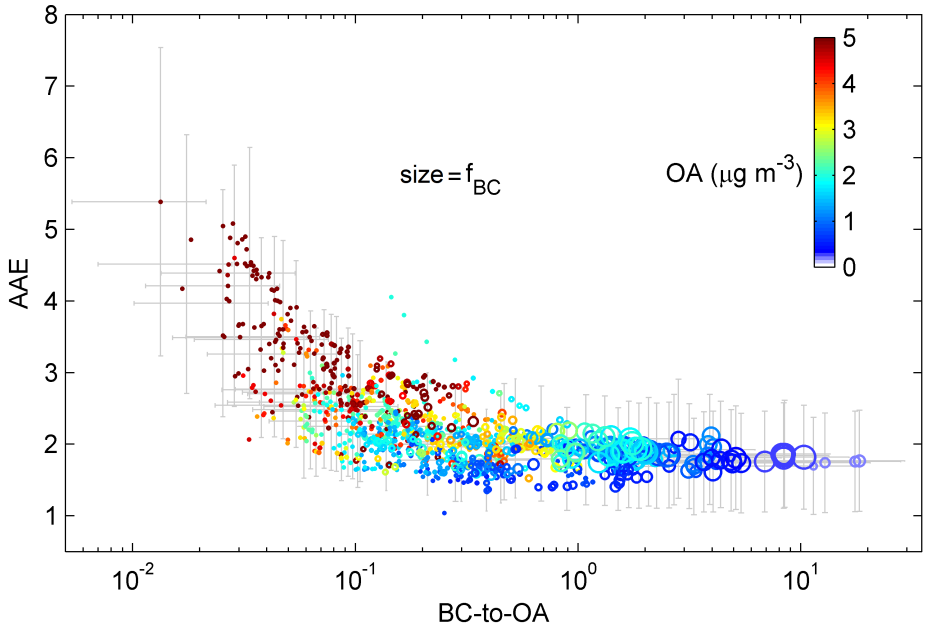

Fig. 8. Supplementary Figure 1.

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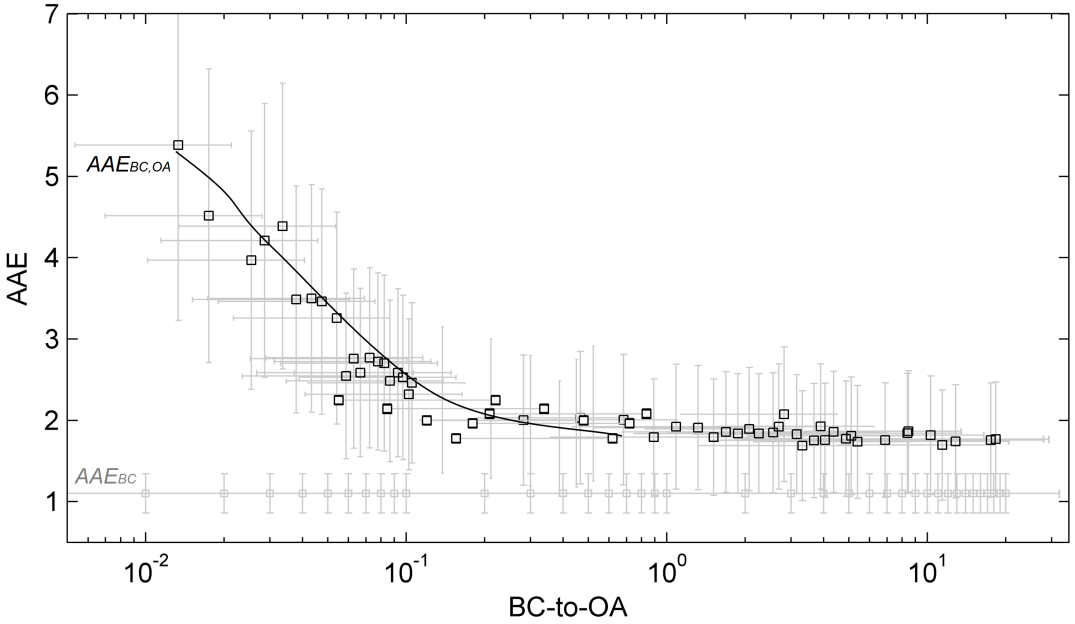

Fig. 9. Supplementary Figure 2.

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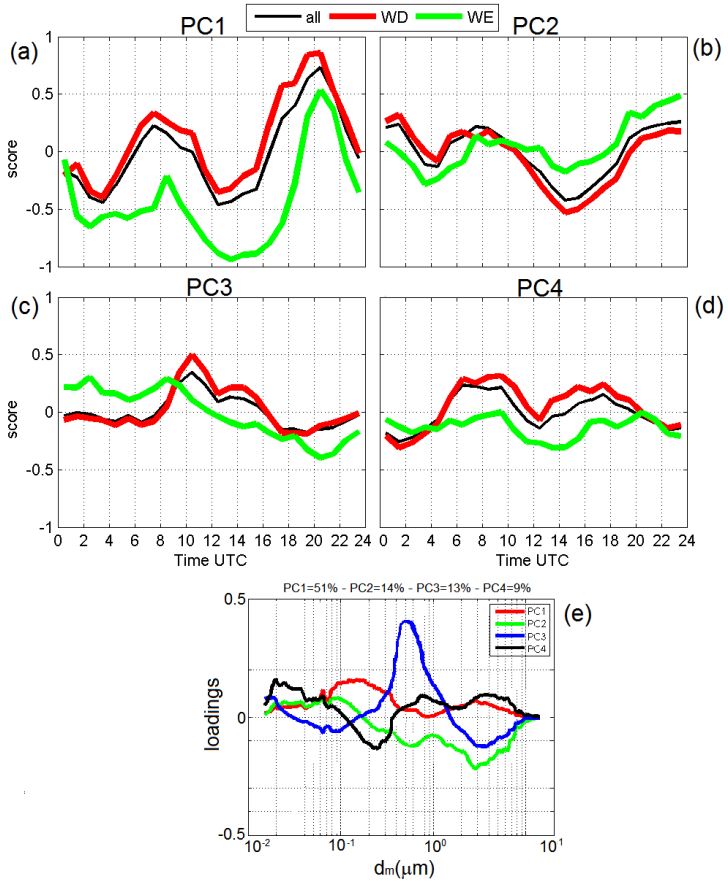

Fig. 10. Supplementary Figure 3.

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