

## Answers to RC1

### General Comments:

Optical apportionment of carbonaceous aerosol is an important process in the measurement of aerosol absorption properties. This manuscript presents an improved model without initial assumptions of parameters for distinguishing the composition and sources of light-absorbing carbonaceous aerosols based on the traditional optical apportionment model used for multi-wavelength absorption coefficient detection. From a scientific perspective, this study lacks significant innovation. Additionally, the deployment and application of this improved model toolkit holds some technical value. Therefore, it is recommended to reconsider the acceptance of this study after the following issues have been well solved.

We thank the referee for her/his precious comments and suggestions. We would like to emphasize that indeed, the scope of our article is the description of a new software toolkit that implements an upgraded optical apportionment algorithm, of which we show the application and the potentiality to two case studies.

### Specific Comments:

1) The algorithm presented in this paper requires at least one additional independent measurement result (e.g., Levoglucosan), which significantly limits the application of this method. In Equations 1 and 2 within the text, each of them has four unknowns. In theory, the detection results from five wavelengths are sufficient to solve these unknowns. Why didn't the authors use the results from a multi-wavelength absorption analyzer for independent calculations?

Even if using data at 5 wavelengths to fit 4 parameters is feasible in principle, problems arise from the point of view of numerical calculation since 2 of the four parameters to be fitted are exponents and the problem cannot be reduced to a linear model. Furthermore, from a mathematical point of view, **constraining some of these parameters is necessary**, since the functional form of Eqs. (1) and (2) is the same and fitting both equations would yield the same result if no parameters are fixed.

It is noteworthy that the software toolkit presented in this paper implements the original MWAA model, whereby an apportionment of optical absorption is achieved by fixing the Absorption Ångström Exponents for BC, FF and WB to predetermined values. This analysis can be carried out **without the need of any extra measurement**.

To better emphasize this concept, we propose to modify the text as following (lines from 70 in the introduction): *"In this work we propose: 1) a toolkit that implements a revised version of the original MWAA model, as published in Massabò et al., 2015. This toolkit has been rewritten and optimized in Python and R, and is available for use by the scientific community. It has been also extended with the possibility to use an arbitrary number of spectrally resolved absorption coefficients, as long as at least 5 wavelengths are available. This model is self-consistent and can be applied to purely optical data without the need of any other information. 2) An upgrade to the original MWAA model that directly allows source and component apportionments of absorption data without the need to set any parameters before running the model. This is achieved by performing the apportionment analysis along with a correlation study with independent measurements such as chemical speciation or elemental composition. The parameters are then automatically set by the algorithm, based on the values that give the best correlation with the independent measurements. The new software toolkit presented here is written in two of the most widely used scientific programming languages, Python and R, to perform this analysis automatically. Output of the presented toolkit (MWAA\_MT) are the following quantities:  $\alpha_{FF}$ ,  $\alpha_{WB}$ ,  $\alpha_{BC}$ ,  $\alpha_{BTC}$ , and the carbonaceous masses for fossil fuels and wood burning:  $EC_{FF}/OC_{FF}$ , and  $EC_{WB}/OC_{WB}$ , respectively, where EC (OC) stands for Elemental (Organic) Carbon. Finally,*

*to demonstrate the capability of the upgraded model, we provide an example application to data published elsewhere (Bernardoni et al., 2017)."*

However, when an independent measurement is available (as an example, Levoglucosan concentration or the  $^{14}\text{C}/^{12}\text{C}$  ratio), the software toolkit allows an upgraded version of the MWAA model whereby the fit parameters are adjusted with the aim of maximising the correlation of the optical apportionment with the independent measurement. With this in mind, the additional data required to use the upgraded model allows for a more complete optical characterization of the aerosol. Furthermore, the additional measurement can be performed on a subset of the entire data, just to find the right parameters for the model that can be subsequently applied to a larger dataset and/or with different time resolution.

2) In the algorithm described in this paper,  $\alpha_{\text{BC}}$ ,  $\alpha_{\text{FF}}$ , and  $\alpha_{\text{WB}}$  remain constant over a certain period of time (such as during a field experiment), while  $\alpha_{\text{BrC}}$  varies with time. This is not reasonable. For example, in the observation example in Milan,  $\alpha_{\text{BrC}}$  clearly varies with time, while  $\alpha_{\text{WB}}$  is assumed to be a constant value in this period. This can introduce significant errors into the calculations. For example, in Figure 6, the trends of BrC and BC<sub>WB</sub> are nearly identical, while in Figure 7, there is a significant difference between them. This distinction may be a result of the algorithm rather than the environmental conditions themselves.

$\alpha_{\text{BC}}$  and  $\alpha_{\text{BrC}}$  are intrinsic properties of the respective aerosol species, while  $\alpha_{\text{FF}}$  and  $\alpha_{\text{WB}}$  are intrinsic properties of the respective aerosol sources. Since BC is a relatively well-defined and well-characterized species, it is reasonable to assume that its AAE will remain approximately constant over a measurement campaign. However, BrC is a much more variable and complex category of aerosol. Its AAE is expected to have a higher variance, even within the same measurement campaign, especially in a complex urban site like Milan where a complex mixture of different sources is expected, and strong aging processes occur. Calculating  $\alpha_{\text{BrC}}$  as proposed by the MWAA model allows to catch this variability and is, therefore, the key aspect of the model.

As for  $\alpha_{\text{FF}}$  and  $\alpha_{\text{WB}}$ , they are assumed to be constant by the original Aethalometer model (Sandradewi et al., 2008) and we have simply integrated it to our component apportionment model to reach a source-component apportionment. We agree with the reviewer that the 2-source model with constant optical properties can have higher limitations, especially in cases where there are more sources, or modification of aerosol by WB due to aging. The assumption is more accurate in a simple rural site, such as Propata, than in a busy and polluted urban site such as Milan. However, the AAE values retrieved through this method can be seen as campaign-averages that are representative of the specific sources present in that location in that season. The assumption of having a fixed  $\alpha_{\text{WB}}$  is especially robust in cases where the aerosol in the area is mainly primary and no further BrC sources/processes are expected. This means that most of the BrC is produced via WB, as is the case of Propata. In fact, in Propata,  $\alpha_{\text{BrC}}$  does not vary, and correspondingly, BrC and BC<sub>WB</sub> correlate very well. The same can't be said about Milan, where the particulate is impacted by a number of different sources, and it is heavily processed due to stagnation.

We propose to insert the following text in line 251: *"The main difference between the two sites is the correlation between  $b_{\text{abs}}^{\text{BrC}}$  and  $b_{\text{abs}}^{\text{BC,WB}}$ . In Propata (Fig. 6) the correlation is high, as can be inferred by the blue and black lines having the same time trend. This means that most of the BrC is produced via WB. On the other hand, in Milan (Fig. 7) this correlation is lower, and BrC cannot be entirely attributed to WB. In fact, in Milan the particulate is impacted by a number of different sources, and it is heavily processed due to stagnation."*

3) In Figure 3, in the left panel,  $\alpha_{\text{BC}}$  has a higher R<sup>2</sup> value around 0.93, while in the right panel,  $\alpha_{\text{WB}}$  has a higher R<sup>2</sup> value around 1.67. Why not use these two values as fitting results?

We introduced a tolerance parameter  $\Delta$  to improve the stability of the model and eliminate physically insignificant  $R^2$  fluctuations. The idea is that if the difference between the  $R^2$  for a given  $\alpha$  and the  $R^2$  for the current best  $\alpha$  is smaller than  $\Delta$ , then the variation is not considered significant and the current best  $\alpha$  value is retained. For the analysis presented in the paper,  $\Delta$  was set to 0.01 (v. lines 120-122 and Fig. 4).

In case we run the analysis with the  $\alpha_{BC}=0.93$  in Propata, the apportionment results are quite similar (differences are below 8%). However, we choose  $\alpha_{BC} = 1$  since the  $R^2$  is almost identical, and also because the  $\alpha_{BC}$  sweep analysis in Propata confirms it as the most sensible choice (please refer to the supplementary material). Similarly, if we run the analysis with  $\alpha_{WB}= 1.67$  in Milan, the apportionment results vary by up to 7%, and the correlation between  $BC_{WB}$  and  $BrC$  remains the same. On account of these consideration, we considered the changes in  $R^2$  between different  $\alpha$  values to be significant only if higher than  $\Delta = 0.01$ .

We want to emphasize that the choice of  $\Delta$  may vary depending on the characteristics of the samples under scrutiny. The user may change the resolution value ( $\Delta$ ) according to her/his scientific judgement, down to a value of 0 meaning that any  $\alpha$  value maximizing the relevant  $R^2$  will be chosen, regardless of the physical meaning of its significant digits.

4) In P6L178, the author mentioned that the Milan campaign had 20 samples, but in Figure 5, there are 25 samples. Why is that?

Thank you for your correction. We changed the text and now P6L178 reads “[...] and 25 samples from the Milan campaign (“AIN” samples).”

5) The abbreviations BC, BrC, FF, and WB should only be introduced with their full names the first time they appear, and there's no need to reintroduce them later (e.g., as in P3L90). Similarly, EC should be introduced with its full name the first time it appears.

Thank you for pointing it out. We corrected the text accordingly, in P3L90 and P3L94. Additionally, P2L77-78 now read “carbonaceous masses for fossil fuels and wood burning:  $EC_{FF}/OC_{FF}$ , and  $EC_{WB}/OC_{WB}$ , respectively, where EC (OC) stands for Elemental (Organic) Carbon.”

## REFERENCES

[1] Massabò et al., *Multi-wavelength optical determination of black and brown carbon in atmospheric aerosols*, 2015, *Atmos. Env.* 108, 1-12