Wang, J., Nie, W., Cheng, Y., Shen, Y., Chi, X., Wang, J., Huang, X., Xie, Y., Sun, P., Xu, Z., Qi, X., Su, H., and Ding, A.: Light absorption of brown carbon in eastern China based on 3-year multi-wavelength aerosol optical property observations at the SORPES station and an improved Absorption Ångstrom exponent segregation method, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-49, in review, 2018.

Replies to reviewers' comments

Overview

The authors thank the reviewers for constructive comments, they helped improving the paper. We have replied to all questions raised by the reviewer. The major changes to the paper are that the we have

- reorganized the AAE method part and revised corresponding figures
- added measurement data from single particle soot photometer (SP2) at same site to support calculation
- conducting Mie-simulation using BC size distribution and mixing state measured by SP2 to derive AAE_{BC} instead of taking a fixed typical BC core size distribution and analyzed the uncertainties of the method
- added more review on AAE segregation and BrC definition

Detailed replies to Anonymous Referee #2

General Comments The authors tried to make improvement of Aethalometer model method. However, the parameters used here, such as volume, densities and sizes of OC and EC, OM/OC ratios, and morphology and mixing state/compositions of BC particles, which are critical inputs for Mie-theory simulations, were not obtained from direct measurements, but inferred from indirect calculations based on some assumptions. Therefore, my biggest concern is about the uncertainties related to these assumptions and calculations. It would be better to add a part to notify the uncertainties and estimate the uncertainties if possible.

***Response**: Thanks for the valuable comment. To avoid the uncertainties caused by assumed BC size distribution, we reorganized our manuscript by using available BC size distribution and mixing state measured by single particle soot photometer (SP2) at the SORPES station during the study period instead of using empirical BC size distribution from previous studies. We found that our previous method is still available but we modified the method by combining SP2 data in the revision. The contribution of BrC gets larger with new parameters. Also, in the revised version we estimate the uncertainties of the calculation and update the method and result parts.*

Specific comments

1) Line 28 on page 1: It is better to defined “babs_BrC” as “light absorption coefficient of BrC”, with unit as Mm-1.

***Response**: Thanks for the suggestion. We will revise it accordingly.*

2) Line 26-27 on page 4 and line 1-6 on Page 5: There are still some brown carbon related studies conducted in China especially in north China such as in Beijing, although these studies were not based on AAE method.

***Response**: Thanks for the suggestion. We will add some relevant brown carbon studies in North China in the discussion and include these references in the revised version.*

3) Line 10 on page 6: It is still not clear, why 520 nm but not other wavelength was chosen for the following calculations.

***Response**: Thanks for the comment. As mentioned in the manuscript, the measurement wavelengths of aethalometer are 370 nm, 470 nm, 520 nm, 590 nm, 660 nm, 880 nm, and 950 nm. Measurement data at the wavelength of 880 nm is chosen because light absorption at this wavelength normally represents the BC absorption (Virkkula et al., 2015). To calculate AAE_{BC} at the wavelength range where BC is the dominant absorption component, the wavelength near 880 nm is better to be used. However, the response of 590 nm and 660 nm data may be affected by the presence of interfering materials such as hematite mineral dust and tobacco smoke (user manual of aethalometer AE-31, Hansen and Schnell, 2005). To avoid the potential impact, we use 520 nm data for the calculations. We will revise the text to further clarify this point in the revision.*

4) Line 13 on page 6: As mentioned in the manuscript, some factors might influence the accuracy of the Aethalometer measurement, such as relative humidity especially when the air was not dried prior to sampling. So is RH considered when the authors did the correction for the Aethalometer observation data?

***Response**: Thanks for the comment. We agree that relative humidity would influence the accuracy of Aethalometer measurement. In our study, RH is considered in both measurement and Aethalometer data correction processes. The impacts of RH on Aethalometer data are mainly from hygroscopic growth of scattering particles and the hydrophilic membrane under the filter. Firstly, we have added the detailed description of aerosol scattering measurement and the correction of Aethalometer data. Since the relative humidity can make influence on aerosol extinction, especially scattering, we installed an external heater prior to the measurement to prevent condensation and maintain the sample air humidity lower than 50% for the most* *of time. For data with RH higher than 50%, we did the correction for it. Detailed description is shown in the revised manuscript. Secondly, the bias of Aethalometer data caused by the hydrophilic membrane under the filter only occurs during rapid RH changes (Arnott et al., 2003). For slow RH changes, the humidification factor is compensated when calculating the attenuation change. Compared to these two factors, the direct impact of RH on light absorption is negligible (Redemann et al., 2001).*

5) Line 24 on page 6: Please add references for the laser absorbance technique for pyrolytically generated carbon correction, or at least give a brief introduction here.

***Response**: Thanks for the comment. After analyzing SP2 data, we have reorganized the method and result part as well as the corresponding figures, and OCEC data is no longer used in the Figures. Thus, the description of OCEC measurement part will be removed in the revised manuscript.*

6) Line 26-28 on page 6: Compositions and properties of fine particulate matter might be more complicated in China than other regions. However, the references Aiken et al., 2008 and Pitchford t al., 2007 were both conducted outside China several years ago. So, is it possible to cite some recent literatures especially those conducted in China? And please add a reference for density of EC (1.8 g/cm3).

***Response**: Thanks for the comment. Indeed, observation of OC/EC (Cheng et al., 2010;Cheng et al., 2011) are widely used in China. As mentioned in last response, we no longer use OC/EC data in the revised manuscript. The comparison of characteristics of BrC in Nanjing and Beijing (Yan et al., 2015;Cheng et al., 2016;Yan et al., 2017) are supplied in this study, as mentioned in the response to Comment 2).*

7) Line 8 on page 7: Please clarify the potential influence of dust, another important light absorber in the atmosphere, and explain how to exclude it.

***Response**: Thanks for the comment. Firstly, dust is abundant in coarse mode (Seinfeld and Pandis, 2006;Hu et al., 2013). The mass fraction of dust is low in $PM_{2.5}$ (Wang et al., 2017) except during dust storm episode. We used a $PM_{2.5}$ cutter on the inlet of Aethalometer to avoid the impact of coarse mode particles. Moreover, the mass absorption efficiency (MAE) of dust is around 1% of MAE of BC (Clark et al., 2016). Thus, the contribution of dust on $PM_{2.5}$ light absorption should be small. We will mentioned this point in the revised manuscript.*

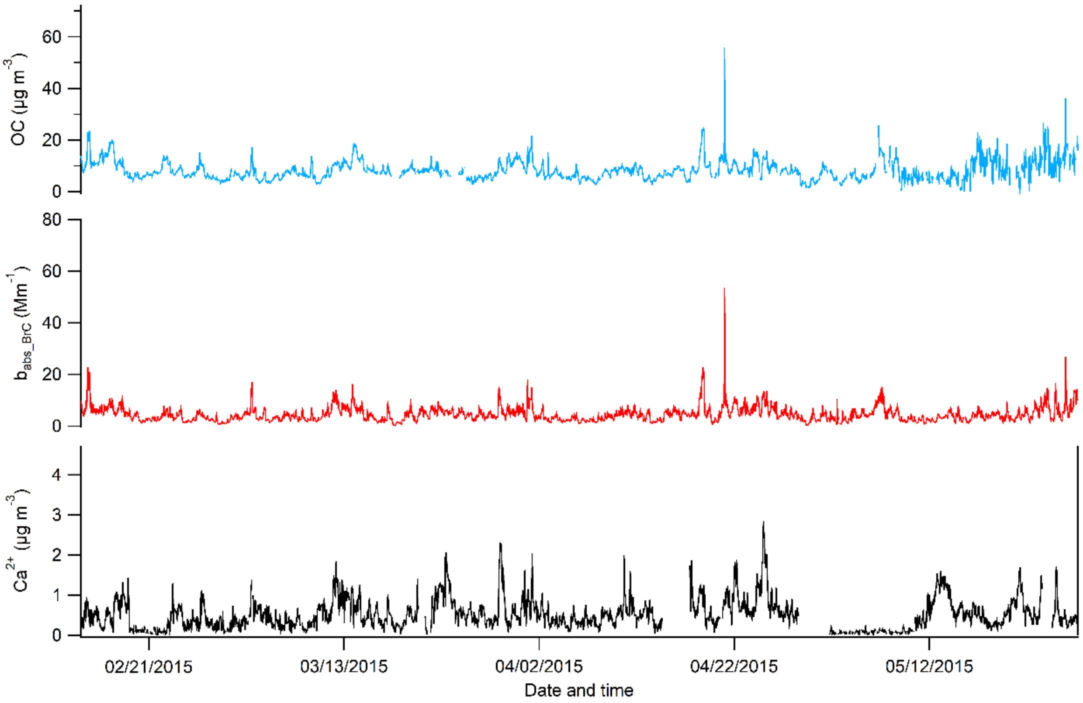

Figure 1. *Time series of the concentration of* Ca^{2+}*, a tracer to dust, OC and* b_{abs_BrC} *measured at the SORPES station. The figure shows that the calculated light absorption of BrC was less influenced by dust.*

8) Eq 2: How about the influence of other light-absorbing substances, and the coating thickness/composition of black carbon?

Response*: Thanks for the comment. As mentioned in the introduction, BC, dust, and BrC have been considered as dominant contributors to aerosol absorption. In our revised manuscript, the impact of coating thickness will be considered in both SP2 data analysis and* $AAE_{520\text{-}880}$*. We calculate* $AAE_{BC520\text{-}880}$ *and* $AAE_{BC370\text{-}520}$ *from SP2 data using core-shell Mie model. Coating thickness derived from SP2 is included in the calculation. In long-term observation,* $AAE_{520\text{-}880}$ *is calculated based on data from the Aethalometer AE31.*

9) Line 4-5 on page 8: It would be better to point out major factors which might influence the AAE values or light absorption properties of BC, before the sentence "Therefore, it is essential to firstly evaluate . . .."

Response*: Thanks for the comment. We will modify this description in the revision.*

10) Line 8 on page 10: The current display format of Figure 3 is not quite powerful for the statement of "especially in less polluted periods", as many negative values also occurred in higher polluted days, with even lower negative values.

***Response**: Thanks for the comment. Yes, this expression is not very clear here. More precise expression should be 'when light absorption of BrC is low, more negative values occur by using the assumption of AAE_{BC} = 1' (shown in Figure 4 in revised manusrcipt). We will change this sentence in the revised manuscript.*

11) The findings of this study were consistent with previous studies. It is better to refer to or compared with more previous studies. For example, some studies have also pointed out that coal combustion was one of the major sources of brown carbon in north China in winter.

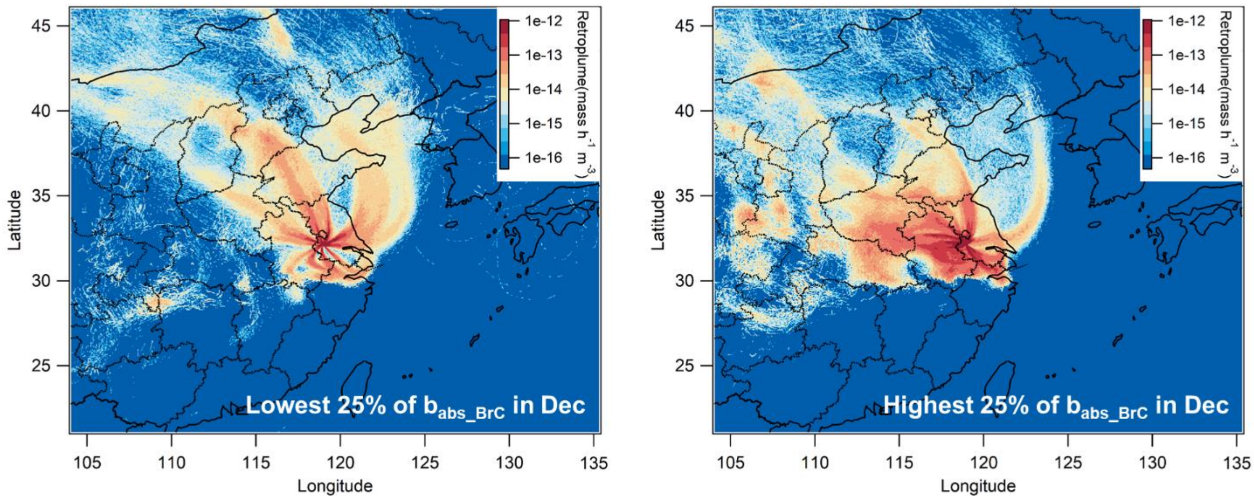

Figure 1. Averaged retroplume for air masses with highest 25% and lowest 25% of b_{abs_BrC} at the SORPES station in December. The results show that long-range transport from the North China Plain had limited influence on BrC at the station.

***Response**: Thanks for the suggestion. We compared characteristics of BrC in Nanjing and Beijing (Yan et al., 2015;Cheng et al., 2016;Yan et al., 2017). Studies conducted in Beijing have also suggested the important contribution of residential biofuel and open biomass burning on BrC in winter and summer, respectively (Yan et al., 2015;Cheng et al., 2016;Fu et al., 2013), which are consistent with our conclusions. A recent study reports that coal combustion is an important source of BrC in northern China, especially in winter (Yan et al., 2017).We will discuss these factors in the revision.*

References:

Arnott, W. P., Moosmüller, H., Sheridan, P. J., Ogren, J. A., Raspet, R., Slaton, W. V., Hand, J. L., Kreidenweis, S. M., and Collett, J. L.: Photoacoustic and filter-based ambient aerosol light absorption measurements: Instrument comparisons and the role of relative humidity, Journal of Geophysical Research: Atmospheres (1984–2012), 108, AAC 15-11, 10.1029/2002JD002165, 2003.

Cheng, Y., He, K. B., Duan, F. K., Zheng, M., Ma, Y. L., Tan, J. H., and Du, Z. Y.: Improved measurement of carbonaceous aerosol: evaluation of the sampling artifacts and inter-comparison of the thermal-optical analysis methods, Atmos. Chem. Phys. , 10, 8533-8548, 10.5194/acp-10-8533-2010, 2010.

Cheng, Y., He, K. B., Zheng, M., Duan, F. K., Du, Z. Y., Ma, Y. L., Tan, J. H., Yang, F. M., Liu, J. M., Zhang, X. L., Weber, R. J., Bergin, M. H., and Russell, A. G.: Mass absorption efficiency of elemental carbon and water-soluble organic carbon in Beijing, China, Atmos. Chem. Phys., 11, 11497-11510, 10.5194/acp-11-11497-2011, 2011.

Cheng, Y., He, K.-b., Du, Z.-y., Engling, G., Liu, J.-m., Ma, Y.-l., Zheng, M., and Weber, R. J.: The characteristics of brown carbon aerosol during winter in Beijing, Atmos. Environ. , 127, 355-364, 10.1016/j.atmosenv.2015.12.035, 2016.

Clark, C. J., Schofield, S. P., Gomez, H. L., and Davies, J. I.: An empirical determination of the dust mass absorption coefficient, κ d, using the Herschel Reference Survey, Monthly Notices of the Royal Astronomical Society, 459, 1646-1658, 2016.

Fu, X., Wang, S., Zhao, B., Xing, J., Cheng, Z., Liu, H., and Hao, J.: Emission inventory of primary pollutants and chemical speciation in 2010 for the Yangtze River Delta region, China, Atmos. Environ. , 70, 39-50, https://doi.org/10.1016/j.atmosenv.2012.12.034, 2013.

Hu, X., Ding, Z., Zhang, Y., Sun, Y., Wu, J., Chen, Y., and Lian, H.: Size distribution and source apportionment of airborne metallic elements in Nanjing, China, Aerosol Air Qual. Res, 13, 1796-1806, 2013.

Redemann, J., Russell, P. B., and Hamill, P.: Dependence of aerosol light absorption and single-scattering albedo on ambient relative humidity for sulfate aerosols with black carbon cores, Journal of Geophysical Research: Atmospheres, 106, 27485-27495, doi:10.1029/2001JD900231, 2001.

Seinfeld, J., and Pandis, S.: Atmospheric chemistry and physics. Hoboken, in, NJ: Wiley, 2006.

Virkkula, A., Chi, X., Ding, A., Shen, Y., Nie, W., Qi, X., Zheng, L., Huang, X., Xie, Y., Wang, J., Petäjä, T., and Kulmala, M.: On the interpretation of the loading correction of the aethalometer, Atmos. Meas. Tech., 8, 4415-4427, 10.5194/amt-8-4415-2015, 2015.

Wang, J., Zhao, B., Wang, S., Yang, F., Xing, J., Morawska, L., Ding, A., Kulmala, M., Kerminen, V. M., Kujansuu, J., Wang, Z., Ding, D., Zhang, X., Wang, H., Tian, M., Petaja, T., Jiang, J., and Hao, J.: Particulate matter pollution over China and the effects of control policies, Sci Total Environ, 584-585, 426-447, 10.1016/j.scitotenv.2017.01.027, 2017.

Yan, C., Zheng, M., Sullivan, A. P., Bosch, C., Desyaterik, Y., Andersson, A., Li, X., Guo, X., Zhou, T., Gustafsson, Ö., and Collett, J. L.: Chemical characteristics and light-absorbing property of water-soluble organic carbon in Beijing: Biomass burning contributions, Atmospheric Environment, 121, 4-12, https://doi.org/10.1016/j.atmosenv.2015.05.005, 2015.

Yan, C., Zheng, M., Bosch, C., Andersson, A., Desyaterik, Y., Sullivan, A. P., Collett, J. L., Zhao, B., Wang, S., He, K., and Gustafsson, O.: Important fossil source contribution to brown carbon in Beijing during winter, Sci Rep, 7, 43182, 10.1038/srep43182, 2017.