Response to Reviewer 1

This paper is well written and has considered many aspects in terms of absorption enhancement of BC, but it will be more convincing after addressing the following points:

We thank the reviewer for his or her thoughtful and thorough reviews. Point-by-point responses to the comments are attached below. We have made corresponding modifications/revisions based on the inputs, and these changes are marked in the revised manuscript.

The E_{abs} vs O_x and SSA vs O_x plots seem crucial, however it seems only overall hourly mean values (from the diurnal variation of entire experimental period) was used, I would say maybe making the scattering plot for all of the data points (maybe hourly average), then bin it in O_x, for each bin, giving the mean/median/percentile etc. you need to make this plot solid, also give the fitting function in the plot.

Diurnal variations in atmospheric chemistry would be influenced by underlying daily patterns in emissions, oxidation chemistry, and meteorological variables, all of which could plausibly influence both E_{abs} and O_x. Such influences could obscure values binned by O_x averages. We therefore believe diurnal averages are the most appropriate way to treat the influence of atmospheric photochemical aging on the mixing state and optical properties of BC containing particles.

We note that in gas-phase radical chemistry (Monks, 2005) and photochemical oxidation chemistry (Liu et al., 2012; Whalley et al., 2018), diurnal variation is used for modeling analysis because it reduces the influence caused by day to day variations in weather conditions and provides a clearer trend of the observed parameter.

References:

Liu, Z., Wang, Y., Gu, D., Zhao, C., Huey, L. G., Stickel, R., Liao, J., Shao, M., Zhu, T., Zeng, L., Amoroso, A., Costabile, F., Chang, C.-C., and Liu, S.-C.: Summertime photochemistry during CAREBeijing-2007: ROx budgets and O_3 formation, Atmos. Chem. Phys., 12, 7737-7752, https://doi.org/10.5194/acp-12-7737-2012, 2012.

Monks, P. S.: Gas-phase radical chemistry in the troposphere, Chem. Soc. Rev., 34, 376-395, 2005.

Whalley, L. K., Stone, D., Dunmore, R., Hamilton, J., Hopkins, J. R., Lee, J. D., Lewis, A. C., Williams, P., Kleffmann, J., Laufs, S., Woodward-Massey, R., and Heard, D. E.: Understanding in situ ozone production in the summertime through radical observations and modelling studies during the Clean air for

London project (ClearfLo), Atmos. Chem. Phys., 18, 2547-2571, https://doi.org/10.5194/acp-18-2547-2018, 2018.

It would be useful to point out O_x actually may just determine how much secondary aerosol is formed, i.e. increasing the overall ensemble of PM, then increase SSA. There may not be too much exciting to see the O_x positively correlated with SSA.

Done. We added the clarification in Section 3.3 in the revised manuscript.

> Positive correlations between ω, ω_{TD} and O_x concentrations were observed in our measurements (Fig. 6 (a) and (b)), which suggests that higher O_x actually increases the mass fraction of secondary aerosol particles and the overall ensemble of particle material and SSA. ~~The increase in SSA under higher Ox concentrations suggests a higher contribution from secondary aerosols formed during daytime photochemical processing.~~

The collapse concept is repeatedly discussed but there is no support in your work, how could you say the flat E_{abs} (even may not be flat after you put all data points in) in the medium O_x is compact soot or not? Could you somehow prove the collapse you are "guessing"? if you can't prove, it is not necessary to emphasize this at many places but just report the solid results you have.

Done. Since we do not have microscopic images to support our speculation, we removed the emphasis on the collapse concept in the revised manuscript.

What is the reason to plot ω_{TD} vs O_x? That means some of the low-volatile coating has not been removed, then you will underestimate the E_{abs}? (it has been mentioned in the text but would be good if this could be properly included)

Liu et al. (2015) report on the comparison of E_{abs} measured with two different methods: TD operating at 250 °C and MAE (mass absorption efficiency) method. They found that E_{abs} values with these two methods agreed closely, which indicated that the non- and low-volatile coating did not have a notable impact on E_{abs}'s measurement. In this work, the TD was operated at 300 °C and the low-volatile coating should not affect the measurement.

Our reported diurnal hourly average ω_{TD} ranged from 0.50 to 0.61, which is comparable with the range (0.50 - 0.60, λ = 405 nm) reported by Radney et al. (2014) for laboratory-generated soot aerosol. In Fig. 6(b), we can see that ω_{TD} increased as the increasing of the O_x concentration, which is mostly due to the morphology change during photooxidation aging (China et al., 2015). Recent results reported by Peng et al. (2016) and Y. Wu et al. (2018) show that aging causes dramatic changes of BC particle morphology and leads to more compact black carbon. As demonstrated by Radney et al. (2014) and Forestier et al. (2018), particle collapse leads to an increase

of ω. In this regard, the plot of ω_{TD} *vs* O_x can be used as an indicator for the changes of BC morphology.

We added following discussion in the revised manuscript.

> The increase in ω_{TD} resulted from incomplete vaporization of non-volatile constituents in the heating tube (Cheung et al., 2016), the generation of low-volatility oxygenated organic aerosol during photochemical aging (Paciga et al., 2016), and the changes of BC morphology (Radney et al., 2014). Summer time volatility measurement of organic aerosol in the megacity Paris shown that about 10% mass fraction remained with a TD operating at 180 ºC (Paciga et al., 2016). However, recent research demonstrated that the remaining non- and low-volatile coating has a minor impact on the absorption measurement of heated particles using TD operating at 250 °C (Liu et al., 2015). Theoretical and experiment results show that aging causes the dramatic changes of BC particle morphology (China et al., 2015; He et al., 2015; He et al., 2016; Scarnato et al., 2013; Wang et al., 2017) and leads to more compact black carbon with higher scattering cross sections (Peng et al., 2016; Y. Wu et al., 2018), which in turn results in an increase of ω_{TD} (Radney et al., 2014; Forestier et al., 2018). In this regard, the rise in ω_{TD} with increasing O_x concentration can be used as an indicator for the changes of BC morphology.

References:

China, S., Scarnato, B., Owen, R. C., Zhang, B., Ampadu, M. T., Kumar, S., Dzepina, K., Dziobak, M. P., Fialho, P., Perlinger, J. A., Hueber, J., Helmig, D., Mazzoleni, L. R., and Mazzoleni, C.: Morphology and mixing state of aged soot particles at a remote marine free troposphere site: Implications for optical properties, Geophys. Res. Lett., 42, 1243–1250, doi:10.1002/2014gl062404, 2015.

Forestieri, S. D., Helgestad, T. M., Lambe, A., Renbaum-Wolff, L., Lack, D. A., Massoli, P., Cross, E. S., Dubey, M. K., Mazzoleni, C., Olfert, J., Freedman, A., Davidovits, P., Onasch, T. B., and Cappa, C. D.: Measurement and modeling of the multi-wavelength optical properties of uncoated flame-generated soot, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2018-306, in review, 2018.

He, C., Liou, K.-N., Takano, Y., Zhang, R., Levy Zamora, M., Yang, P., Li, Q., and Leung, L. R.: Variation of the radiative properties during black carbon aging: theoretical and experimental intercomparison, Atmos. Chem. Phys., 15, 11967-11980, doi:10.5194/acp-15-11967-2015, 2015.

He, C., Takano, Y., Liou, K.-N., Yang, P., Li, Q., and Mackowski, D. W.: Intercomparison of the GOS approach, superposition T matrix method, and

laboratory measurements for black carbon optical properties during aging, J J. Quant. Spectrosc. Radiat. Transf., 184, 287–296, doi:10.1016/j.jqsrt.2016.08.004, 2016.

Liu, S., Aiken, A. C., Gorkowski, K., Dubey, M. K., Cappa, C. D., Williams, L. R., Herndon, S. C., Massoli, P., Fortner, E. C., Chhabra, P. S., Brooks, W. A., Onasch, T. B., Jayne, J. T., Worsnop, D. R., China, S., Sharma, N., Mazzoleni, C., Xu, L., Ng, N. L., Liu, D., Allan, J. D., Lee, J. D., Fleming, Z. L., Mohr, C., Zotter, P., Szidat, S., and Prevot, A. S. H.: Enhanced light absorption by mixed source black and brown carbon particles in UK winter, Nat. Commun., 6, 8435, doi:10.1038/ncomms9435, 2015.

Peng, J., Hua, M., Guo, S., Du, Z., Zheng, J., Shang, D., Zamora, M. L., Zeng, L., Shao, M., Wu, Y. S., Zheng, J., Wang, Y., Glen, C. R., Collins, D. R., Molina, M. J., and Zhang, R.: Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments, Proc. Natl. Acad. Sci. U S A, 113, 4266–4271, doi:10.1073/pnas.1602310113, 2016.

Radney, J. G., You, R., Ma, X., Conny, J. M., Zachariah, M. R., Hodges, J. T., and Zangmeister, C. D.: Dependence of Soot Optical Properties on Particle Morphology: Measurements and Model Comparisons, Environ. Sci. Technol., 48, 3169-3176, doi:10.1021/es4041804, 2014.

Scarnato, B. V., Vahidinia, S., Richard, D. T., and Kirchstetter, T. W.: Effects of internal mixing and aggregate morphology on optical properties of black carbon using a discrete dipole approximation model, Atmos. Chem. Phys., 13, 5089–5101, doi:10.5194/acp-13-5089-2013, 2013.

Wang, Y., Liu, F., He, C., Bi, L., Cheng, T., Wang, Z., Zhang, H., Zhang, X., Shi, Z., and Li, W.: Fractal dimensions and mixing structures of soot particles during atmospheric processing, Environ. Sci. Tech. Let., 4, 487–493, doi:10.1021/acs.estlett.7b00418, 2017.

Wu, Y., Cheng, T., Liu, D., Allan, J. D., Zheng, L., and Chen, H.: Light Absorption Enhancement of Black Carbon Constrained by Particle Morphology, Environ. Sci. Technol, 52, 6912–6919, doi:10.1021/acs.est.8b00636, 2018.

For your calculation at section 3, could you point out the uncertainty you have by assuming the fixed core size? But I presume you need to use a size distribution of core size? And how did you apply the coated size distribution upon core size?

Since we did not have particle size distribution information in this study, we assumed monodisperse particles in the Mie calculation. This method follows that demonstrated by Saleh et al. (2015).

We added the following discussion in the revised manuscript.

> In this work, the particle size distribution information was not available. A method based on single-particle core-shell Mie theory (Bohren and Huffman, 1983; Saleh et al., 2015) was developed to interpret the proposed three-stage

aging mechanism observed in this work. The sensitivity of this assumption is discussed in Sect. S6 in the supplement.

Reference:

Saleh, R., Marks, M., Heo, J., Adams, P. J., Donahue, N. M., and Robinson, A. L.: Contribution of brown carbon and lensing to the direct radiative effect of carbonaceous aerosols from biomass and biofuel burning emissions, J. Geophys. Res. Atmos. 120, 10285–10296, doi:10.1002/2015JD023697, 2015.

We added following discussion in the Sect. S6 in the supplement.

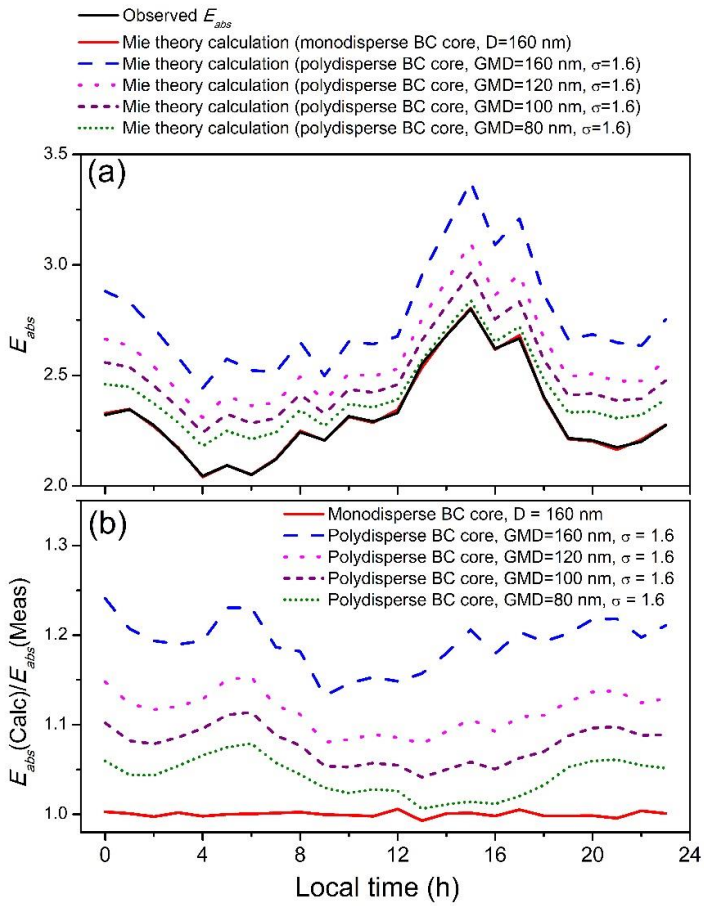

Figure S15: Comparison of the Mie theory results of E_{abs} with monodisperse BC core with 160 nm diameter and polydisperse size distributions with a geometric standard deviation of 1.6 and mode diameters of 160, 120, 100, and 80 nm, respectively. The parameters used for the calculation are the same as in Fig. 7. Polydisperse BC core sizes have larger E_{abs} values than monodisperse BC core; however, the trends of E_{abs} values are same. We use an optimization process for determining D_{core}, D_{shell}, and k_{shell}; similar trends show that monodisperse BC core can be used for the interpretation of the measurement data.

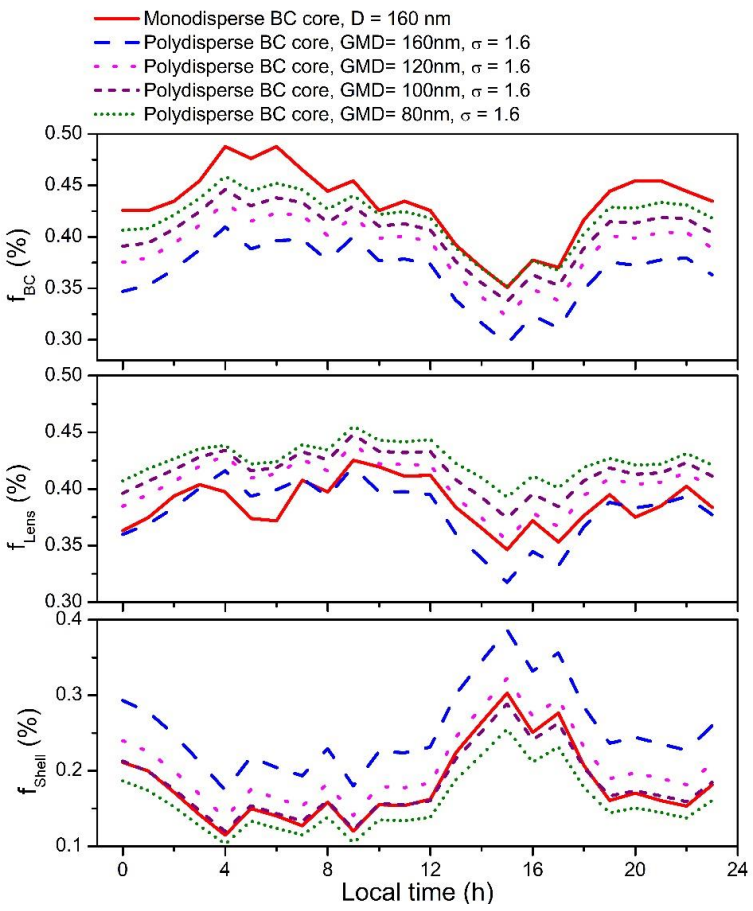

Figure S16: Fractional contribution of the lensing effect (f_{Lens}), the absorption of BC (f_{BC}) and the shell (f_{Shell}) to absorption enhancement with different BC core sizes as Fig. S15. The trends of the diurnal pattern are similar. The differences between these calculations are less than 10%.

I am still struggling to understand what is the point for section 4, your results on the E_{abs} only represent a single ground measurement with limited sources, not even open biomass burning etc. how could be recommend for global models. Also, the surface measurement cannot necessarily represent the columnar information. I would hesitate to expand your work that big given you haven't really done this job.

Done. We removed this section from the revised manuscript.