Response to Reviewer 2

This study investigates the size-resolved mixing state, absorption enhancement (E_{abs}) and single scattering albedo (SSA) of ambient aerosol at a rural site in East China. They found diurnal variability of E_{abs}, SSA and a proxy of photochemical aging (O_x). The authors suggested a three stage E_{abs} process at difference degree of atmospheric photochemical aging. Absorption enhancement is an important topic and more field measurements are needed to understand the variability of E_{abs} at different geographical locations and under different pollutant conditions. Overall, the manuscript is well written. The paper is worth publishing, but some of the points need to be explained.

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.

Authors suggest that the three stage E_{abs} process is due to collapsed semispherical to highly compact spherical morphology of BC without any morphological data. Authors should be careful to make this claim.

Done. Recent studies (China et al., 2015; He et al., 2015; Peng et al., 2016; Wu et al., 2018) on the morphology shown that aging causes dramatic changes of BC particle morphology and leads to more compact black carbon. Our speculation on the collapse concept is reasonable. However, according to the suggestion of Reviewer 1, since we did not have morphological data, we removed the emphasis on the collapse concept in the revised manuscript. We just report the solid results we have.

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.

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.

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.

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.

Why the E_{abs} was stable for O_x mixing ratio between 35 and 50 ppbv? Some of the figures (figs. 7 and 8) need expanded discussion. Authors found relatively higher E_{abs} compared to other study at similar wavelength. Authors should add some discussion on this.

Recent morphologically constrained modelling developed by Y. Wu et al. (2018) demonstrated that after full aging, the BC particles became a more compact aggregation, which leads to a stable range of E_{abs} (averaged value ~ 2.5, with a minimum value of ~ 2 and a maximum value of ~ 3.5). In this study, the observed stable E_{abs} value (2.26 ± 0.06) for O_x mixing ratios between 35 and 50 ppbv was in the range of Y. Wu et al.'s result, suggesting that BC was fully aged under this oxidation level. In addition, the calculated values of D_{shell} and k_{shell} in Fig. 8 were fairly constant in the stable stage, which means a stable contribution of the non-BC components. Fully aged BC and minor changes of non-BC components lead to a stable E_{abs} for O_x mixing ratio between 35 to 50 ppbv. The E_{abs} value reported in our work was relatively higher than others, but was still reasonable.

We added following discussion in Sect. 3.3 in the revised manuscript.

> Recent morphologically constrained modelling developed by Y. Wu et al. (2018) demonstrated that after full aging the BC particles became a more compact aggregation, which leads to a stable range of E_{abs} (averaged value ~ 2.5, with a minimum value of ~ 2 and a maximum value of ~ 3.5). Our results fall within this range and suggest that BC was fully aged under this oxidation level.

We added the following discussion for Fig. 7.

> The solid points are the observed results and color-coded with respect to the concentrations of O_x. The open circles are the single-particle Mie core-shell modeled results with an optimized BC core size of 160 nm, and color- and size-coded with respect to the imaginary part of the CRI of coating material (k_{shell}) and the diameter of coating material (D_{shell}), respectively. The color-coded plot shows the connection between E_{abs}, SSA and atmospheric

photochemistry. The modeled results are consistent with the observed results. Both SSA and E_{abs} values rise with increasing D_{shell} and k_{shell}, indicating that the coating thickness and absorption play key roles in determining SSA and E_{abs}.

We added following discussion for Fig. 8.

The fractional contribution of f_{BC}, f_{Lens}, f_{Shell} ranged from 35-49%, 35-42%, and 11-30%, respectively, with a mean value of 43±4%, 39±2%, and 18±5%. A ternary plot is shown in the supplement Fig. S14. At the first stage of Fig. 6(c), D_{shell} increased with O_x concentrations, but k_{shell} showed an obscure variation with increasing O_x mixing ratios. The rise in E_{abs} was mainly caused by the thicker coating. In the second stage, with constant E_{abs}, all the parameters (D_{shell}, k_{shell}, f_{BC}, f_{Lens}, and f_{Shell}) remained fairly constant, which suggests a stable contribution of the non-BC components. Compact aggregation of fully aged BC and minor changes of non-BC coating materials lead a stable E_{abs} for O_x mixing ratios between 35 and 50 ppbv.

References:

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.

Specific comments:

Please provide details of the detection limit of the scattering and extinction measurement. Also explain how the uncertainties in extinction, scattering and absorption coefficients were estimated.

The details of the detection limit and uncertainties of the instrument have been described in our previously published papers (Zhao et al., 2014; Xu et al., 2016; Fang et al., 2017). In this paper, we just give a brief introduction.

We added following explanation in the revised manuscript.

The details of the evaluation of the instrument have been described in our previously published paper (Zhao et al., 2014; Xu et al., 2016; Fang et al., 2017). Detection limits of each parameter were determined by using an Allan variance analysis.

The total uncertainties (summed in quadrature of each error source) in extinction, scattering, absorption coefficients, and SSA measurements were estimated to be less than 4%, 3%, 5%, and 4%, respectively.

Reference:

Fang, B., Zhao, W., Xu, X., Zhou, J., Ma, X., Wang, S., Zhang, W., Venables, D.S., and Chen, W.: Portable broadband cavity-enhanced spectrometer utilizing Kalman filtering: application to real-time, in situ monitoring of glyoxal and nitrogen dioxide, Opt. Express, 25, 26910-26922, doi:10.1364/OE.25.026910, 2017.

Xu, X., Zhao, W., Zhang, Q., Wang, S., Fang, B., Chen, W., and Gao, X.: Optical properties of atmospheric fine particles near Beijing during the HOPE-J3A campaign, Atmos. Chem. Phys., 16, 6421-6439, doi:10.5194/acp-16-6421-2016, 2016.

Zhao, W., Xu, X., Dong, M., Chen, W., Gu, X., Hu, C., Huang, Y., Gao, X., Huang, W., and Zhang, W.: Development of a cavity-enhanced aerosol albedometer, Atmos. Meas. Tech., 7, 2551-2566, doi:10.5194/amt-7-2551-2014, 2014.

Explain how the optical loss of the thermodenuded aerosol were estimated and also contribution of different uncertainties in E_{abs} measurements.

The optical loss of the TD was explained in Sec. S3 in the supplement.

We added following explanation in the revised manuscript.

> The total uncertainty in E_{abs} measurement was ~~dominated by the uncertainty in sample losses in the TD (~~about 9% (mainly contributed by uncertainties in the measurement of $b_{abs,\ ambient}$ (5%), $b_{abs,\ TD}$ (5%), and particle losses inside TD (6%)).

Authors suggested increase in SSA-TD may be due to incomplete volatilization of nonvolatile matter and generation of LV-oxygenated organic aerosol. It will be interesting to see how sca and abs response to TD at different Ox.

The scatter plots of $b_{scat,TD}$, $b_{abs,TD}$, $b_{ext,TD}$, ω_{TD}, and ambient $PM_{2.5}$ concentration versus O_x mixing ratios are shown in Fig. R1. The absorption and scattering coefficient are not intensive optical properties. The values also depended on the sample mass concentration. Very little information can be retrieved from the relationship between $b_{scat,TD}$, $b_{abs,TD}$ and O_x without the mass concentration of the heated sample.

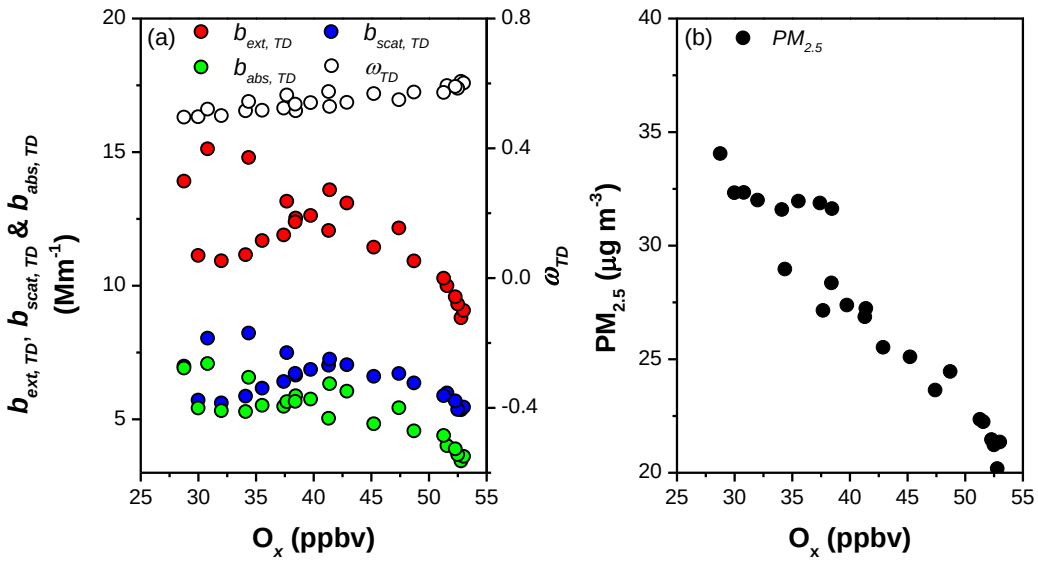

Figure R1 Scatter plots for (a) $b_{scat,TD}$, $b_{abs,TD}$, $b_{ext,TD}$ and ω_{TD} versus O_x mixing ratios of the heated sample; (b) ambient $PM_{2.5}$ concentration versus O_x mixing ratios.

Authors found average E_{abs} of 2.3 at 532 nm which is even higher than Lack et (2012) for forest fire samples (1.4 at 532 nm). Normally BC particles from forest fire are heavily coated and one would expect high E_{abs}. However, it is not clear if airmasses investigated in this study were also influenced by biomass burning? Or Authors suggest that at higher degree of photochemical aging one would expect higher E_{abs} compared to thickly coated BC from forest fire?

Recent studies suggested that the value of E_{abs} not only depends on the coating thickness, but also on the morphology of BC particles (China et al., 2013; 2015; Peng et al., 2016; Wu et al., 2018). E_{abs} value is limited to ~ 5% at the start of the aging, and increases with the collapse and encapsulation of the particle. With the ban of straw burning in China in recent years, outdoor burning of straw is now much less common. The air masses in this study were not affected by biomass burning. Higher E_{abs} value in this study was mainly caused by photochemical aging.

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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.

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.

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