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 different 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:
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 $E_{\text{abs}}$ values rise with increasing $D_{\text{shell}}$ and $k_{\text{shell}}$, indicating that the coating thickness and absorption play key roles in determining SSA and $E_{\text{abs}}$.

We added following discussion for Fig. 8.

The fractional contribution of $f_{\text{BC}}$, $f_{\text{Lens}}$, $f_{\text{Shell}}$ 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), $D_{\text{shell}}$ increased with $O_x$ concentrations, but $k_{\text{shell}}$ showed an obscure variation with increasing $O_x$ mixing ratios. The rise in $E_{\text{abs}}$ was mainly caused by the thicker coating. In the second stage, with constant $E_{\text{abs}}$, all the parameters ($D_{\text{shell}}$, $k_{\text{shell}}$, $f_{\text{BC}}$, $f_{\text{Lens}}$, and $f_{\text{Shell}}$) 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 $E_{\text{abs}}$ for $O_x$ mixing ratios between 35 and 50 ppbv.

References:


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:

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 \( scat \) and \( abs \) response to TD at different \( Ox \).

The scatter plots of \( b_{scat,TD}, b_{abs,TD}, b_{ext,TD}, \omega_{TD} \), and ambient PM\(_{2.5}\) concentration versus \( Ox \) 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 \( Ox \) without the mass concentration of the heated sample.
Authors found average $E_{abs}$ of 2.3 at 532 nm which is even higher than Lack et al. (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.
