Response to reviewer #1

General comments

The study by Ueda et al. addresses the effect of coatings on the absorptive properties of atmospheric black carbon particles, which is important in evaluating their radiative impacts. The authors conducted a field campaign at Noto Peninsula, Japan, a site that frequently receives pollutants transported from mainland China. A variety of instruments, including PASS-3, SP2,SMPS, and TEM were employed to measure the physical, chemical, optical, and morphology of aerosols. NOx and NOy were also measured to assist photochemical age determination. The main conclusion is that coatings on black carbon particles can enhance the absorption by uncoated black carbon by ~22%. This observation adds to the limited database on field measurements of the lensing effect of black carbon. The measurement and discussion are generally sound but a number of details need to be added or explained, most importantly the charring of aerosols in the thermodenuder and its impact on the absorption enhancement measurements. I recommend publication of this manuscript after the following concerns are addressed.

(reply)

We appreciate the valuable comments from the reviewer. We have considered the comments carefully and replies are described below.

Specific comments

1. Abstract, L13, the absorption enhancement is 22-23%. This is not a range. I suggest to report either 22% or 23%. The same comment applies to the Eabs of 1.22 – 1.23 in the conclusion. In addition, please either use percentage or absolute numbers to be consistent throughout the text.

(reply)

We have corrected the descriptions on the average absorption enhancement value throughout the text in the revised manuscript.

2. Please use "thermodenuder" instead of "heater" throughout the text to be consistent with literature in this field.

(reply)

We have replaced the "heater" with "thermodenuder".

3. Abstract, L21-22, it is a bit surprising that most of the coatings on black carbon are sulfates,

given that organic materials dominate the aerosol mass (Table 2). The measurement period is after the intense coal burning season in northern China, so it is expected that the coatings are dominated by organics.

(reply)

Yes, coating materials should include not only sulfate but also organics. In the EDS analysis, the quantitative detection of C atoms is difficult due to the large background signal from C-coated collodion film. Therefore, there is a possibility that the number of C-rich particles is actually higher than that counted, as described in section 2.3. We have revised the sentence as follows.

(original)

"The majority of the soot in all samples was found as mixed particles with spherical sulfate or as clusters of sulfate spherules. For samples showing high enhancement (>1.30) of BC light absorption, TEM showed that the internally mixed soot-containing particles tended to have a more spherical shape and to be thickly-coated."

(revised)

"The majority of the soot in all samples was found as mixed particles with sulfate-containing spherules or as clusters of such spherules. For samples showing high enhancement (>1.30) of BC light absorption, TEM showed that the internally mixed soot-containing particles tended to have a more spherical shape and to be embedded into the sulfate."

4. P25093, "Models often estimate Eabs assuming a core-shell…" Many models simply apply a constant Eabs value rather than estimating Eabs.

(reply)

We have revised the sentence according to the comment.

(original)

"Models often estimate E_{abs} assuming a core-shell (the BC core and coating materials) shaped spherical particle (Bond et al., 2006; Ma et al., 2012)"

(revised)

"Models often apply a constant E_{abs} value or estimate E_{abs} assuming a core-shell (the BC core and coating materials) shaped spherical particle (Bond et al., 2013 and references therein)"

5. P25093, the last paragraph. What are the values reported from these previous Eabs measurements? These values should be summarize here. In addition, two recent studies that address Eabs via field measurements are missing and should be added to the summary: "Healy, R. M., et al.

(2015), Light-absorbing properties of ambient black carbon and brown carbon from fossil fuel and biomass burning sources, J. Geophys. Res. Atmos., 120, 6619–6633, doi:10.1002/2015JD023382" and "Liu, S. et al. Enhanced light absorption by mixed source black and brown carbon particles in UK winter. Nat. Commun. 6:8435 doi: 10.1038/ncomms9435 (2015)."

(reply)

We have added the values of the enhancement of light absorption due to coating and these new literatures in the revised manuscript.

6. P25093-25094, "However, these studies were conducted … has been reported." The Liu et al. study mentioned above was conducted at a rural site and measured aged air masses. That study also combines optical and morphology measurements. Therefore the author's statements need to be removed or changed.

(reply)

We have revised these sentences in the revised manuscript as follows.

(original)

"However, these studies were conducted in or around urban areas; therefore, the contribution of the lensing effect in a well-aged air mass remains unclear. In addition, to our knowledge, no direct comparison of the observed lensing effect with the particle morphology of individual BC-containing particles has been reported."

(revised)

"However, there have been very few observational studies reported the contributions of lensing effect and their relation with morphology of individual BC-containing particles in a well-aged air mass."

We have also added the following sentences in the discussion section of the revised manuscript.

"Very recently, Liu et al. (2015) reported the average E_{abs}(781 nm) of 1.4 for BC particles emitted from fossil fuel and residential burning sources in winter at a rural site, Detling (45 km away from London) in UK. The average E_{abs}(781 nm) value obtained in the present study is slightly lower than the value reported by Liu et al. (2015)."

7. P25094, the second paragraph is not discussing absorption enhancement and is not closely related to the paragraphs before and after, this paragraph should be moved forward where the concept of black carbon is introduced.

(reply)

According to the comment, this paragraph has been moved forward in the revised manuscript.

8. P25095, the CE of 0.3 is very low compared to the typical CE of 0.5. It says the CE was derived by comparing the mass concentration of the ACSM data with filter data, but how the filter sample was collected is not clear, e.g., what is the duration of the sample collection, what is the size cut of the filter measurements, was the filter weighed to get the mass concentration. In addition, the ACSM does not measure refractory components, while the weight of the filter is a sum of all materials on the filter. This could result in a low CE.

(reply)

The filter samples were collected using a 9-stage Andersen sampler (model AN-200, Tokyo Dylec corp.) with a flow rate of 28.3 L/min. Sampling duration was 1 week per sample. The mass concentration was not obtained by weighing the filter. Instead, the filters were extracted and water soluble inorganic components were analyzed by ion chromatography. Ammonium and sulfate concentrations were integrated for the smallest 3 stages (including backup filter) to obtain the PM1.1 fraction. The CE was tuned so that the ACSM derived ammonium and sulfate match the filter based analysis. We have added the information in the revised manuscript.

9. Related to the question above, the CE can also be derived by comparing ACSM with SMPS measurements. Since the SMPS data are available, this approach should be tested and may result in a different CE.

(reply)

According the comment, the volume concentrations of NR components have been calculated using the ACSM data and were compared to volume concentrations estimated using the SMPS data. The volume concentrations estimated from SMPS data are found to be about 1.7 times larger than those calculated from ACSM data. While different size-cut profiles of the ACSM, Andersen sampler, and SMPS may have affect the result, measurement uncertainty of SMPS may also contribute to the difference. It should be noted that selection of the CE value itself does not affect the discussion in this study. We have added the information in the revised manuscript.

10. P25096, more details about the thermodenuder should be added, e.g., what are the dimensions of the denuder? What is the residence time of particles in the denuder? These are important features as a short residence time will result in incomplete removal of the coating materials on BC.

(reply)

The same type of TDs used in a previous study (Guo et al., 2014; Nakayama et al., 2014) was used in this study. The TD consists of a stainless tube (outer and inner diameters: 12.7and 10.2 mm, respectively; length: 600 mm) and electronic jacket heaters (Heater Engineer, P-series). Flow rates through the TD was 1.28 lpm, and the residence time for the sample aerosols in the TD was estimated to be 2.3 s, on the assumption of plug flow conditions (at 20°C). We have added the information in the revised manuscript.

11. P25097, it is surprising that there is no particle loss in the thermodenuder as the ratio is not significantly different than 1. This is inconsistent with many previous studies, e.g., the Cappa et al. 2012 paper cited in the manuscript and the references therein. Could this be due to the generation of brown carbon in the thermodenuder? This could be a critical problem as it affects the calculation of Eabs.

(reply)

The ratios of mass concentration of rBC measured by the SP2 without heating to that after heating (1.08 and 1.03 at 300 °C and 400 °C, respectively, on average) include contributions of both loss and formation of rBC in the TD. Considering the estimated particle loss in our TD, ~17% and ~20% at 300 °C and 400 °C, respectively (Guo et al. 2014), our results suggest that non-negligible amount of rBC (10-20% of ambient rBC) were formed in the TD, possibly due to charring by heating. In the present study, the E_{abs} values were estimated by taken these effects into account, assuming that light absorbing property of ambient rBC is same with that of rBC generated in the TD and detected by the SP2, using the equation,

$$E_{\mathrm{abs}}(\lambda,\ T) = \frac{b_{\mathrm{abs}}(\lambda, 25\ ^{\circ}\mathrm{C})/b_{\mathrm{abs}}(\lambda, T)}{m_{\mathrm{rBC}}(25\ ^{\circ}\mathrm{C})/m_{\mathrm{rBC}}(T)}\ ,$$

where λ and T were measurement wavelength and TD temperature, respectively. If mass absorption cross section at 781 nm for rBC generated in the TD would be different by 50% with that for ambient rBC, the lensing effect could be underestimated or overestimated by 0.05-0.10, The information and equation to calculate E_{abs} have been added in the revised manuscript (sections 2.2 and 3.1).

12. P25097, L1, references are needed after "scattering signal".

(reply)

A reference (Moteki and Kondo. 2007) has been added in the revised manuscript.

13. P25097, was a NO2 scrubber installed upstream of the PASS-3 instrument? If not, NO2 could influence the absorption measurement at 405 nm and also the Eabs calculation at 405 nm. This needs to be examined as it may influence the hypothesis of brown carbon formation in the thermodenuder.

(reply)

The influence of light absorption of NO_2 has been evaluated based on the estimation using transmittance of NO_2 through filter and inlet tube as well as mixing ratio of NO_2, and confirmed to be small (<0.05 Mm^{-1} at 405 nm and <0.04 Mm^{-1} at 532 nm). The effects have been taken into account for the determination of b_{abs} in the revised manuscript. The information has been added.

14. P25097, the detection limit of the PASS-3 measurements. Are the data reported as 3-h averages, e.g., the data presented in Fig. 2? If not, the detection limit should be calculated using data with the same time resolution as the real measurements.

(reply)

Yes, we used 3-h averages data in Fig. 2 and Fig. 3. This explanation has been added in caption of Fig. 2.

15. P25097, "Using babs values after the above ratios," it is not clear what this sentence means. In addition, how was the particle loss accounted for?

(reply)

As described in the reply for the comment 11, contributions of both loss and formation of rBC in TD were taken into account. We have corrected the sentence and added the equation to estimate E_{abs} in the revised manuscript.

16. P25099, L11, "a prior test". What test is it? When was the test? More information is needed here.

(reply)

The description was not correct. We used spectra for non-particle areas measured between each sample analysis as background spectra. This sentence has been revised as follows.

(original)

"In this classification, a spectrum larger than two times the standard deviation of the background spectra measured in a prior test was used as the detectable spectrum of the particles to eliminate

background noise effects”

(revised)

“In this classification, a spectrum larger than two times the standard deviation of the background spectra, which are spectra for non-particle areas measured between each sample analysis, was used as the detectable spectrum of the particles to eliminate background noise effects.”

17. P25100, “the Eabs values at all wavelengths are expected to be greater than 1.0”. This is not true given the sequential bypass and thermodenuder measurements in this study. Values smaller than 1.0 are likely due to the atmospheric variability the BC concentration.

(reply)

As commented by the reviewer, we cannot rule out the possible contributions of the temporal variation of BC concentration to the variation in E_{abs} values, while the observed wavelength dependence of E_{abs} values cannot be explained by the temporal variation of BC concentration. We have removed this sentence in the revised manuscript.

18. P25100, L17, “This can be explained by the increase of absorbing materials by heating.” The formation of brown carbon in thermodenuder is interesting, is there any literature on this topic? Later it says in P25112 that the formation of brown carbon is “probably due to the condensation of non-volatile organic.” Under the 300 – 400 C condition in the thermodenuder, how can condensation occur?

(reply)

Thank you for the valuable comment. While several literatures reported the charring of organic carbon by heating as described in section 2.2, to our knowledge, there is no report on the formation of brownish materials by heating. Although the formation process of brownish materials by heating is unclear, the brownish materials may not be generated by condensation but by incomplete charring process. We have revised the sentence in P25112 as follows.

(original)

“Therefore, the spherical, carbon-rich particles might be formed by heating, probably due to the condensation of non-volatile organic compounds within the particles, and could be brown in colour.”

(revised)

“Therefore, the spherical, carbon-rich particles might be formed by heating, probably due to the incomplete charring of organic compounds, and could be brown in colour.”

19. Charring in the thermodenuder could produce elemental carbon, how can formation of elemental carbon be excluded? This could affect the calculation of Eabs at 781 nm, and could also be related to the observation that the Eabs at 781 nm is independent on NOx to NOy ratio.

(reply)

As described in the reply for the comment 11, contributions of both loss and formation of rBC in TD were taken into account for the estimation of E_{abs}. Discussion on the possible contributions of for the formation of rBC by heating has been added in section 3.1 in the revised manuscript.

20. P25101, L11, "north and west of the site." There is a significant fraction of air mass coming from northeast section of the site.

(reply)

We have removed the sentences in the revised manuscript.

21. P25101, L25, the location of Shanghai should be added to the figure as it is the origin of air masses.

(reply)

The location of Shanghai was already shown in Fig. 3a.

22. P25103, L1-2, the photochemical age can be directly calculated using NOx and NOy.

(reply)

Quantitative estimation of the photochemical age has been removed according to the Referee #2's comments.

23. P25104, L14, "a mechanical issue", it is not clear what issue results in the inability to calculate BC coating thickness.

(reply)

Mechanical issue is that one of detectors in the SP2 did not work well. This detector can measure the scattering light signal to estimate the absolute position of particles in the laser beam, we called "split detector", which is important information to conduct the fitting to estimate the BC coating thickness. Therefore, we could not obtain the BC coating thickness, unfortunately. We have added the information.

24. P25105-25111, section 3.3.2 and 3.3.3. There is a vast amount of information in these two sections (6.5 pages). While the information is useful to understand the aerosol properties, much is not related to the absorptive properties of BC, which is the theme of this paper. I think these two sections can be substantially shortened, or some information and related figures can be moved to SI information so that the main text is more succinct.

(reply)

According to the reviewer's comments, some information, one table, and one figure in section 3.3.2 and 3.3.3 were moved to supplemental materials (S2-S4).

25. Fig 1 e-f, the green and blue traces cannot be differentiated visually. Please make separate panels.

(reply)

We have remade the figure, according to the comment.

Technical corrections

1. Abstract, L14, change "under high absorption coefficient conditions" to "under high absorption coefficient periods"

2. Abstract, L18, remove "coefficient"

3. P25092, L12, change "defined operationally" to "operationally defined"

4. P25093, change "noncoated" to "uncoated"

5. P25093, L22, change "estimated" to "measured"

6. P25094, L18, change "absorbing" to "absorption"

7. P25094, L19, remove "suspended in air"

8. P25098, L5, remove "a"

(reply)

According to the reviewer's comments, we revised above all technical corrections.