Anonymous Referee #1:

1. Summary

The manuscript presents a method for inferring the effective density and particle morphology of atmospheric black carbon cores. Extensive optical modelling work is then developed to investigate the enhancement of light absorption as a function of the coating thickness and core density. This is an interesting idea and worth pursuing. The paper is well organized but it needs a grammar revision and rephrasing. Although the theoretical calculations are well explained, the characteristics and advantages of the measuring system (LII technique), compared to previous work, are poorly described. A comparison of the presented setup with more traditional techniques (DMA-APM) would have given more reliability to the absolute values showed here. The relative contribution of BC core density and morphology to absorption enhancement, compared to lensing effect is not stated. The application of the results presented here, especially the core density of black carbon, will be of major interest in radiative forcing modelling. However the manuscript needs rewriting, possible instrumental biases needs to be addressed and comparisons with more traditional technique are required. I do not recommend the publication of the manuscript under its current form.

Response: We would like to thank the referee for the valuable comments. Listed below are our responses to the comments and the corresponding changes made to the revised manuscript. The comments of the referee are marked in black and the answers are marked in blue.

2. Major comments

(1) I suggest the author to read the paper of Petzold et al. of 2013 (DOI: 10.5194/acp-13-8365-2013) and consider a change in the nomenclature following Petzold's recommendations.

Response: In the manuscript, we have changed some nomenclatures following Petzold's recommendations (Petzold et al., 2013). Refractory black carbon (rBC) was

used instead of BC for measurements derived from SP2. Mixed particles containing a BC fraction was termed BC-containing particles instead of BC particles.

(2) In the methods and data section the author should mention the work of Gysel et al. (2011). In this work is explained that DMA-SP2 is a trustful technique to measure BC effective density. On the other side, Gysel et al. (2011) specifies that: "DMA-SP2 system can be used for fast effective density measurements of pure BC particles if an accurate calibration of the SP2 has been done using a APM". The author should specify which particle-selection approach have been used for the SP2 calibration.

Response: We have included a citation to Gysel et al. (2011) and specified the particle-selection approach for the SP2 calibration in the methods and data section (p12031, line 3).

"Accurate calibration of SP2 is crucial in the measurement of effective density of BC particles by the DMA-SP2 system (Gysel et al. 2011). Such calibrations require the knowledge of mobility size-mass relationship (i.e., effective density) of calibration BC particles (Gysel et al. 2011). In our study, we used Aquadag with size-resolved effective densities for the purpose of calibration. The calibration curve was fitted by recording the incandescence signal peak height for Aquadag particles of known mass."

(3) In this work two instruments based on different principles are compared. Comparability of optical diameter (SP2) and mobility diameter (DMA) of BC-free and BC-containing particles must be mentioned or provided in the supplementary. Especially because the scattering cross section measured by SP2 is a key factor in Dp calculation.

Response: We have added a paragraph and a figure (see Fig. S2) in the supplementary to discuss the comparability of optical diameter (SP2) and mobility diameter (DMA) of BC-free and BC-containing particles:

"For ambient BC-free and BC-containing particles, the optical diameters at peaks of number size distribution derived from SP2 measurement were chosen to compare

with the prescribed mobility size (through DMA), as shown in Fig. S2. The difference between optical size and mobility size was 3% and 0.3% for ambient BC-free particles and BC-containing particles, respectively. The excellent coherence demonstrated the validity of LEO method for ambient measurements."

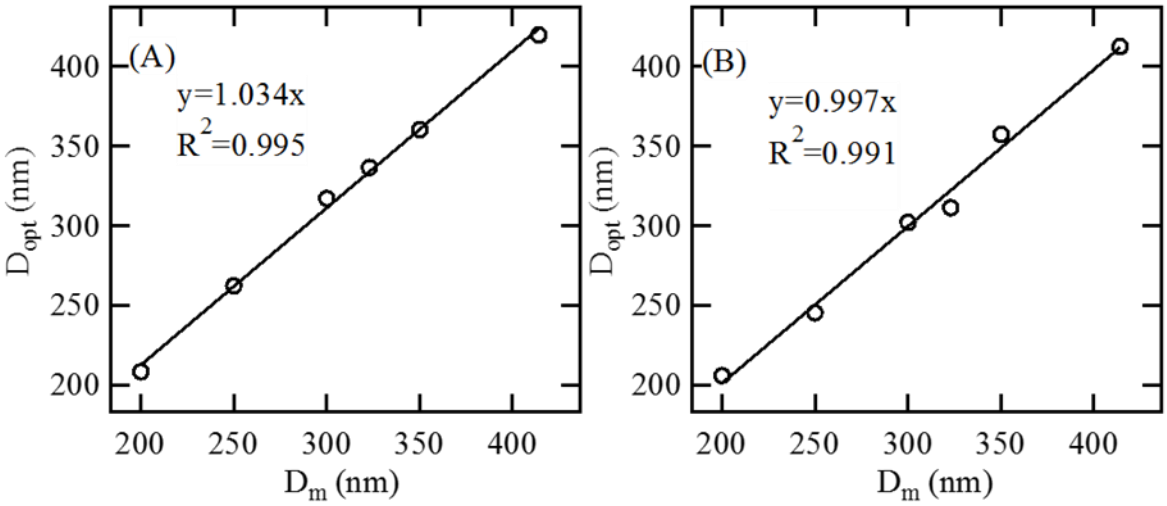

Figure S1. Mobility size vs. optical size for ambient BC-free particles (A) and BC-containing particles (B) observed in Xianghe site.

(4) My further concern is about the accuracy of your system compared to previous reference techniques used for effective density observation. I would have added an aerosol particle mass analyzer in parallel to SP2 and DMA2. Assuming that the thermo-denuder is 100% efficient in removing the non-refractory components, the effective density could be calculated from both SP2 and APM mass, giving more strength to your results. At the actual status, the accuracy of the technique is easily questionable because no comparison with a reference technique is presented.

Response: We fully agree that our results could be strengthen if we compare our method with previous reference techniques to assess the accuracy of our system. However, we don't have an APM so far. In the future work, we will test the idea of the referee with other partner in future studies. The accuracy of effective density measurements relies on the accuracy of DMA in measuring particle size and the accuracy of SP2 in measuring the particle mass. Since APM has been used in the determination of the mass-size relation of Aquadaq, SP2 calibrated with Aquadaq is expected to produce equivalent mass information as an APM. In addition, we find that

in the measurement of ambient particles, the efficiency of thermos-denuder is 90-95% rather than 100%, making it more difficult in the data interpretation of the APM method.

In order to assess our measurement of In-BC cores in the atmosphere, we have added a subsection entitled “Comparison of the measurement with previous laboratory studies” in section 3.2 (p1036, line 12).

“Laboratory measurements are widely used to measure morphology and density of In-BC cores. The In-BC particles were generated when the flame soot particles was exposed to vapor (e.g., sulfuric acid), then vaporized the coatings using a thermal-denuder (e.g. 200 ℃) to obtained bared In-BC cores. The morphology and density of In-BC cores were then derived from combining measurements of particle mass and mobility size. The main difference between this work and previous reference techniques was the measurements of the mass of In-BC cores (SP2 in this work and APM or AMS in other studies).

Here we compared our results with laboratory measurements reported in the literature (Table 2). For the In-BC cores with D_m of 150-200 nm and D_{me} of 100-160 nm that was studied in our work, the observed χ and ρ_{eff} were in the ranged from 1.4-2.0 and 0.5-0.9 g/cm^3 respectively. These ranges generally agree well with the previously reported ranges of In-BC cores generated in laboratory, indicating that the values of χ and ρ_{eff} observed in our study are reasonable. Therefore, our measurement method was valid for the determinations of morphology and density of In-BC cores.”

Table 2. Comparison of VTDMA-SP2 measurement s and laboratory measurement techniques for determining the morphology and density of In-BC cores

Methods	Mass measurement	Core	Coatings	D_m (nm)	D_{me} (nm)	χ	ρ_{eff} (g cm^{-3})	Reference
VTDMA-SP2	SP2	rBC	Non-BC	150-200	100-160	1.4-2.0	0.5-0.9	This study
VTDMA-APM	APM	Soot	Sulfuric acid (1.4×10^{10} cm^{-3})	150-210		1.7-1.9	0.5-0.7	Pagels et al., 2009
VTDMA-APM	APM	Soot	Sulfuric acid (2.5×10^{9} cm^{-3})	150-210			0.2-0.5	Pagels et al., 2009
VTDMA-APM	APM	Soot	Succinic acid	150-200		2.4-3.0	0.2-0.4	Xue et al., 2009b
VTDMA-APM	APM	Soot	Glutaric acid	150-240		1.8-2.0	0.6-1.0	Xue et al., 2009b
VTDMA-AMS	AMS	Soot	Oleic acid		120-160	1.3-2.5		Slowik et al., 2007
VTDMA-AMS	AMS	Soot	Anthracene	135-225	120-180	1.2-1.5		Slowik et al., 2007

(5) The features of the SP2 are not fully exploited, especially the coating thickness. There is a specific reason for this?

Response: The purpose of this study is to develop a new method to measure the morphology and effective density of In-BC cores in the atmosphere and investigate their effect on absorption enhancement. In this work, we have used the shell/core ratio (Dp/Dc) to represent the mixing state of BC particles instead of coating thickness.

(6) The efficiency of the thermal removal mechanism of non-refractory component is a critical point, but in this work is poorly investigated. Inefficiency in coating removal will positively bias the Cs and then the Dp, and possibly lead to an underestimation of the In-BC effective density, due to overestimation of In-BC core diameter determined

with DMA2. Presence of BC-free particles after denuding would consistently affect the size distributions showed in figure 2. The SP2 is a useful tool to estimate the removal of non-refractory component and BC-free particulate after the heating stage. See attached figure. Coating removal may be estimated with LEO-fit approach.

Response: We thank the reviewer for the insightful comments. We have estimated the removal of non-refractory component for ambient BC-free and BC-containing particles after the heating at 300 ℃ (see below figure). We have added a subsection in section 3.2 (p1036, line 3) to discuss the uncertainties of our measurement to determine the morphology and effective density of In-BC cores.

"It should be noted that presence of non-refractory component after thermo-denuder (a part of VTDMA) could induce biases in measured mobility size of In-BC cores. For example, inefficiency in coating removal would cause an overestimate of mobility size, leading to overestimates of χ and underestimates of ρ_{eff}. The removal of non-refractory component for ambient BC-free and BC-containing particles using a thermo-denuder at 300 ℃ was determined by SP2 (Fig. S4). In general, the first peak position of volume size distribution of residual particles from VTDMA measurement (Fig. 2 red lines) was dominated by In-BC cores and residual coatings, and the residual BC-free particles had a little influence. The efficiency of coating removal using a thermo-denuder in our measurement was about 95% (volume fraction).

Fig. 3 also presented the relationships between χ, ρ_{eff} and D_p/D_c ratio when we considered the effect of residual coatings on volume size distribution in VTDMA measurement. It is found that presence of ~5% residual coatings can lead to ~10% uncertainties in average χ (~1.2) and ρ_{eff} (1.2 g cm^{-3}) calculation. In addition, the uncertainties increased with aging process due to more accumulation of non-volatile coatings, indicated that the present of residual coatings mainly influenced the calculation of χ and ρ_{eff} of In-BC cores with smaller size. However, the relationships between χ, ρ_{eff} and D_p/D_c are still valid."

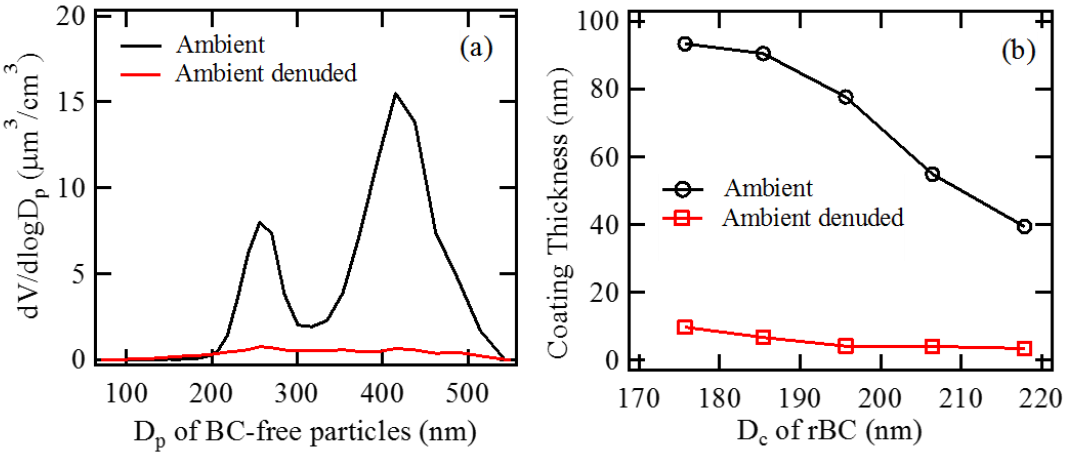

Figure S4. The removal of non-refractory component for ambient BC-free and BC-containing particles using a thermo-denuder at 300 ℃: (a) the volume size distribution of ambient BC-free particles before and after heating, (b) coating thickness of size-resolved rBC. The ambient particles was selected by the DMA1 prescribed 250 nm.

(7) The author assumes that during the coating evaporation the morphology of BC core does not change, this possibility is never mentioned. Did the author consider such process and what would be the effects on the final conclusions?

Response: We agree that if the morphology of In-BC cores was changed due to coating evaporation during heating, it would lead to a bias in our measurement. It's very difficult to validate our assumptions that during the coating evaporation the morphology of BC core does not change. In the Section 3.2.2 of the revised manuscript, we have discussed the possible effects: "On the other hand, the changes in the morphology of In-BC cores caused by coating evaporation during heating would also lead to a bias in measured mobility size from VTDMA measurement. If the In-BC cores became less compact caused by coating evaporation during heating, the mobility diameter of In-BC core determined with DMA2 would be overestimated, leading to an overestimate of χ and an underestimate of ρ_{eff} in our measurement."

(8) All the past works on absorption enhancement due to internal mixing of BC with other non-absorbing materials were focused on the lensing effect. The latter is never mentioned here, the reader has the impression that density and morphology of BC core lead the absorption enhancement. It would be interesting to specify the relative

contribution of the density to absorption compared to the lensing effect. Figure 5 and 6 might be merged in a scatterplot composed by shell:core ratio as horizontal axes and enhancement as vertical axes. In this way it would be easier to visualize the enhancement due to lensing effect and the relative impact of density in one plot.

Response: Thanks for the constructive comments. In the Sect. 3.3.2 of the revised manuscript, we have added a paragraph to specify the relative contribution of the density to absorption enhancement compared to the lensing effect. A new figure (Fig. 7) was added to present the impact of effective density and lensing effect on absorption enhancement.

"Fig. 7 shows the changes of absorption enhancement (E_{ab}) at 550 nm wavelength with shell/core ratios (D_p/D_c) for size-resolved ambient In-BC particles (250 nm) with different core densities. The light absorption enhancement (E_{ab}) of In-BC particles has been investigated based on the theory of lensing effect (Fuller et al. 1999; Moffet et al. 2009; Lack and Cappa 2010), in which the coatings act as a lens and focuses more photons onto BC core. As shown in Fig.7, the E_{ab} of In-BC particles significantly increased when shell/core ratio increasing, demonstrated the lensing effect of coatings. On the other hand, significant increases in E_{ab} with core density at a given shell/core ratio provide strong evidence that the light absorption could be enhanced when the BC core became compact with large density. Most likely, the contribution of core density to light absorption enhancement could be attribute to the changes in refractive index of In-BC core (RI_c), as following Eq. (8). Compared with lensing effect, the relative contribution of core density to absorption enhancement could be up to ~20% when the core density increased from 1.0 g cm^{-3} to 1.8 g cm^{-3} for In-BC particles with ~3 shell/core ratio. More significant contribution of core density on E_{ab} was found when the shell/core ratio increased for size-resolved In-BC particles, because the increase of E_{ab} caused by lensing effect became weaker with more coatings. In summary, the light absorption enhancement of In-BC particles during aging process was also impacted by changes in core density in addition to lensing effects."

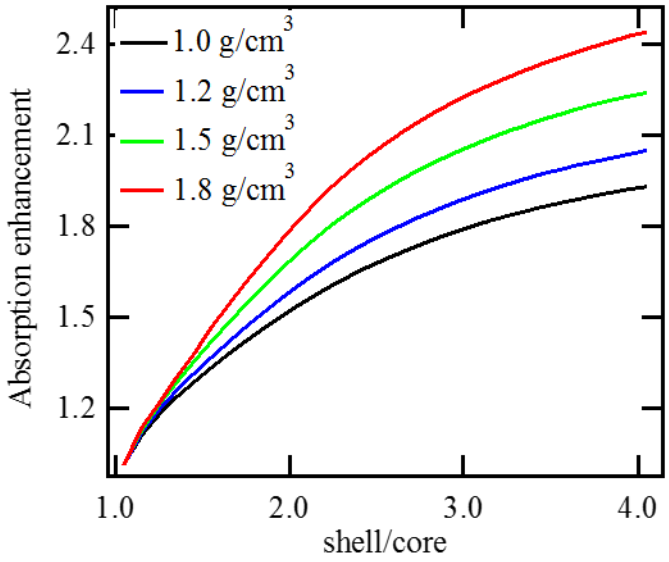

Figure 7. Changes of absorption enhancement (E_{ab}) at 550 nm wavelength with shell/core ratios (D_p/D_c) for size-resolved ambient In-BC particles (250 nm) with different core densities.

(9) Even if the coating is assumed to do not absorb light (imaginary part of refractive index = 0), the wavelength at which the absorption enhancement is estimated should be showed.

Response: We calculated the absorption enhancement at 550 nm wavelength using Mie mode. In the Sect. 2.2 and Sect. 3.3.2 of the revised manuscript, we have mentioned the wavelength (550 nm). .

(10) I raise a provocative question. Here you just assume that the difference in dp/dc is due only to aging. It was observed in the past how emission source might change the optical properties of BC (Sandradevi et al., 2008). Is it possible that you are simply measuring two distinct BC types, like traffic and biomass burning emitted BC?

Response: We are aware that it will be meaningful to investigate the morphology and density of distinct BC types, like traffic and biomass burning emitted BC. However, in the campaign site, Xianghe, is a polluted regional background site which influenced by mixed regional emission sources from Jing-Jin-Ji region. It is difficult to distinguish different BC emissions from Xianghe site. In future study, we will try to measure distinct BC types using our system in a specific period or site.

(11) Care must be used with climatology statements; I would avoid the term "long

range transport" because the author is not able to justify the origin of the particles.

Response: Thanks. The statement has been corrected in the revised manuscript.

3. Specific points

(1) The grammatical, lexical and logical errors are ignored here, since a rewriting is needed.

Response: The revised manuscript has been copyediting by native language speaker to avoid grammatical errors.

(2) P. 12030 L 5: please specify the manufacturer and possible customizations of the two main instruments.

Response: The system is consisted by a VTDMA (Leibniz Institute for Tropospheric Research, Germany) and a SP2 (Droplet Measurement Technologies, United States). We have clarified this in the Sect. 2.1 of the revised manuscript.

(3) P. 12030, L 23 - P 12031, L16: I strongly suggest improving the technical description of the SP2 functioning principles. The subchapter is definitely confused and confusing.

Response: We have improved the technical description of the SP2 functioning principles in section 2.1 of the revised manuscript.

(4) P. 12031 L 1: the vaporization or boiling temperature is usually expressed in K. Please add a reference. L 7-10: Were the standard aquadag particles been selected in function of their size (DMA) or mass (APM) during the calibration? Which kind of neutralizer have been used, corona discharger or Kr-source during calibration and atmospheric measurements? L15-16: You proved the validity of the LEO approach only for BC-free particle, where there is no evaporation in the laser beam. The author should show (in the supplementary) that LEO fit was working properly also for BC-containing particles.

Response: Thanks. We have expressed the vaporization temperature in K, and have added a reference to Schwarz et al. (2006). We selected the size-resolved standard

Aquadag particles by DMA during the SP2 calibration. The neutralizer with Kr-source was used during calibration and atmospheric measurements. In the supplementary (see Fig. S2), we have added the results of LEO fit for BC-containing particles and also demonstrated its validity. We also revised the technical description of the SP2 functioning principles in section 2.1.

(5) P. 12033 L 11: I disagree with the author; in the paper of Cappa et al. (2012) BC density is never mentioned. L 8-20 Both Dp and Dc can be optically measured by the SP2 using the LEO fit. Despite the paper is focusing on aging and coating, a coating thickness derived with the SP2 is never showed. Why?

Response: Cappa et al. (2012) mentioned BC density in the supplementary of their paper (S1.2.6): "ρ_x is the species density, assumed to be 1.8 g cm^{-3} for BC."

The purpose of this study is to develop a new method to measure the morphology and effective density of In-BC cores in the atmosphere and investigate their effect on absorption enhancement. In this work, we have used the shell/core ratio (D_p/D_c) to represent the mixing state of BC particles instead of coating thickness.

(6) P. 12034 L 16-19. Unclear. I suggest showing in a table the observed values for each case.

Response: We have added a table to list peak position of volume size distribution for each case (see below).

Table 1. The mobility size ($D_{c,m}$) and mass equivalent diameter ($D_{c,me}$) of In-BC cores at peak positions of size distribution (Fig. 2) from VTDMA and SP2 measurement for size-resolved In-BC particles at 200-350 nm ($D_{p,m}$)

$D_{p,m}$ (nm)	200	250	300	350
$D_{c,m}$ (nm)	154	165	190	201
$D_{c,me}$ (nm)	102	123	145	161

(7) P. 12035 L 9-10: in the SP2 community, what you call here "volume equivalent diameter" is commonly called "mass equivalent diameter".

Response: We have changed "volume equivalent diameter" into "mass equivalent

diameter" in the manuscript.

(8) P. 12036 L 13: I would avoid using symbols or specific abbreviations as subchapter title L 20-21: In your system particles are selected by a first DMA, then measured by VTDMA and SP2. SP2 does not select particles since is a destructive technique, at least for BC-containing particles.

Response: The subchapter title of "D_p/D_c" has been changed into the "Mixing state".

We did not use the SP2 to select particles, because it is a destructive technique as the referee pointed out. In our study, SP2 measured all particles (BC-free and BC-containing particles) that selected by DMA1. During SP2 data process, however, we only chose a few of data points by adding filtering on the measured data set. In the revised manuscript, we have added the following sentence to make the statement more clear: "we only chose the data populations that characterized single-charged particles around the first peak to investigate the shell/core ratios and absorption enhancement of In-BC particles."

(9) Fig. 2 One is mass equivalent diameter (SP2) and the other is the electrical mobility diameter (DMA). This should be specified in the label. How the peaks of both SP2 and DMA were determined, which fit was used? Specify here or in the text.

Response: We have added the size description in the label of Fig. 2: "The In-BC core size was characterized by mass equivalent diameter from SP2 measurement and mobility diameter from VDMA measurement."

In our study, Gaussian fit was used to determine the peaks of both SP2 and DMA.

References:

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