Anonymous Referee #2:

The authors present a new measurement system for in-situ measurements of the morphology and effective density of internal mixed black carbon cores. They demonstrated the utility of this system through an intensive field study in North China in 2013, quantified the evolution of morphology and density of ambient In-BC cores during aging process and investigated the absorption enhancement of ambient In-BC aerosols taking core morphology and density into account. The material presented in the manuscript is within the scope of AMT. It includes appropriate references to previous work on this topic and the methods and results sections are, for the most part, described in adequate detail. Generally speaking, this work presents a unique new approach to improve the calculation of mixing state and optical properties of ambient In-BC particles, and these methods and observations represent sufficient new material to justify publication. Therefore I recommend this manuscript to be considered for publication in AMT after some minor revisions.

Response: We thank the referee for the positive review work and the constructive comments. The answers to the comments are given below. The comments of the referee are marked in black and the answers are marked in blue.

Major comments:

(1) The manuscript should provide more detailed description of the measurement system, including information regarding the system setup (including manufacture and model information), instrument speciation (for SP2 and VDTMA, referred to previous publications), and calibration procedures. Though thermodenuders are fairly common in the aerosol community a general reference to the technique is probably still needed here. As an AMT publication, ideally even readers unfamiliar with these instruments would be able to reproduce exactly the method used in this study from the information provided in the manuscript.

Response: We have provide more detailed description of the measurement system in section 2.1 of the revised manuscript.

“The new measurement system is developed to obtain the morphology, density, mixing state and optical properties of ambient In-BC particles, as shown in Fig. 1. The system is consisted by a VTDMA (Leibniz Institute for Tropospheric Research, Germany) and a SP2 (Droplet Measurement Technologies, United States).

As shown in Fig. 1, a SP2 instrument also measured mobility sized selected ambient particles to obtain the particle-to-particle mass of refractory BC (rBC) and scattering cross section of In-BC particle. In SP2 technique, the rBC mass in single particle is determined from its laser-induced incandescence. The SP2 uses a continuous Nd:YAG intra-cavity laser beam at 1064 nm to heat a BC-containing particle to its vaporization temperature of ~4000 K (Schwarz et al., 2006), at which detectable amounts of thermal radiation (“incandescent light”) is emitted. The intensity of the thermal radiation is linearly proportional to rBC mass (Moteki and Kondo, 2010; Baumgardner et al., 2012). Accurate calibration of SP2 is key 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.

On the other hand, SP2 technique characterizes the scattering cross section of individual In-BC particle through its scattering signal. The scattering signal was calibrated using polystyrene latex spheres (PSL). The data retrieval of scattering cross section is very challenging, because the initial scattering properties changes with evaporation of coatings for BC-containing particles. To overcome this problem, Gao et al. (2007) developed a leading-edge-only (LEO) fit method to derive the initial scattering properties of BC-containing particles. The validity of LEO fit used for ambient BC-free and BC-containing particles is checked in our study (see Fig. S1). In addition, SP2 measurement separate In-BC and Ex-BC particles by the delay time of the peaks between the incandescence and scattering signals. In our study, a delay time of 1.6 μs was chosen to discriminate between Ex-BC (< 1.6 μs) and In-BC (≥ 1.6 μs) types, based on the delay time distribution obtained from the SP2 measurements (see

Fig. S2).”

(2) It will be helpful if the measurement system section also provides more information regarding the experimental uncertainties and a comparison to those previously applied techniques.

Response: We thank the reviewer for the insightful comments. We have added two subsections in section 3.2 (p1036, line 3) to separately discuss experimental uncertainties and a comparison to those previously applied techniques.

“3.2.2 The uncertainties

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.

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 ρeff in our measurement.

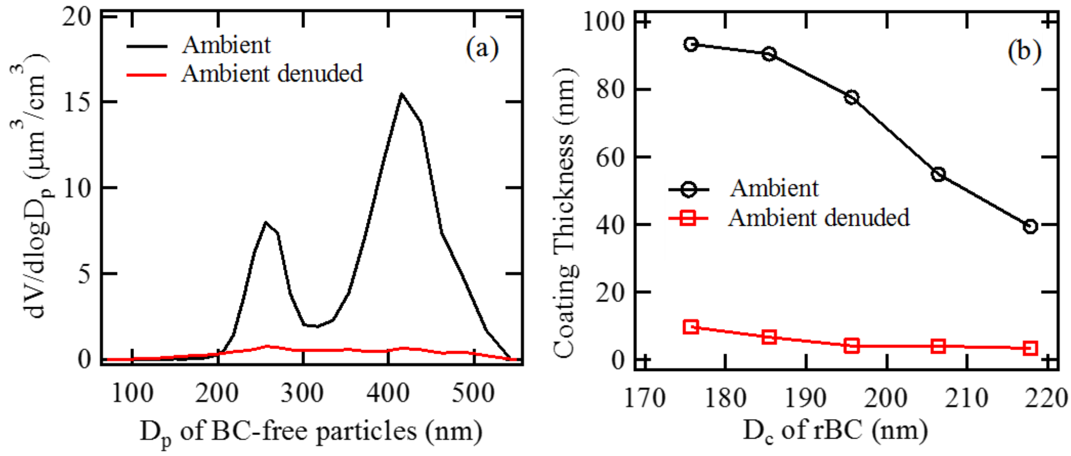

Figure S4. The removal of non-refractory component for ambient BC-free and BC-containing particles using a thermo-denuder at 300 ℃: (a) the volume size distribution of ambient BC-free particles before and after heating, (b) coating thickness of size-resolved rBC. The ambient particles was selected by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

3.2.3 Comparison of the measurement with previous laboratory studies

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

A few more points should be addressed:

(1) Page 12030 line 15-19: Authors should emphasis that at this polluted continental site, in the sub micrometer range, non-volatile fraction may consist of mainly BC. It should be mentioned here the low-volatile organic coatings may cause biases in VTDMA measurement of in-BC core diameter.

Response: We thank the reviewer for the insightful comments. We have estimated the residual of low-volatile component for ambient BC-free particles and BC coatings after the heating at 300 ℃ (Fig. S4). We have added a subsection in Sect. 3.2 (3.2.2 The uncertainties) of the revised manuscript to discuss biases in VTDMA measurement of in-BC core diameter caused by low-volatile component. Please see the answer to above comment.

(2) Page 12031 line 17-20: More detail descriptions of the Xianghe Atmospheric Observatory should be given here. Is it an urban site or polluted regional back ground site? What is the main source for BC at that site?

Response: We have improved the description of the Xianghe Atmospheric Observatory in Page 12031, line 19.

"The Xianghe site is located in the southeast of the capital Beijing (~60 km) and northwest of the megacity Tianjin (~100 km). Xianghe is a polluted regional background site which influenced by mixed regional emission sources from Jing-Jin-Ji region."

(3) Page 12034 line 20-24: One should keep in mind the diameter measured by SP2 and DMA are different.

Response: We have added the size description in page 12034, line 22.

"The In-BC core size was characterized by mass equivalent diameter from SP2 measurement and mobility diameter from VDMA measurement."

(4) Page 12035 line 11: Dp/Dc was used in this manuscript as aging indicator. More discussion should be given to support this assumption.

Response: We have given more discussion to specify the D_p/D_c as an aging indicator in page 12035, line 12.

"The aging degree in which BC was mixed with other species was quantified by the ratio between coated-particle (i.e. In-BC) and bare BC-core sizes (D_p/D_c), which would show a significant increase during aging process due to condensation of coatings (Cappa et al., 2012)."

(5) Page 12037 line 9: Long range transport? I would like suggest to replace "long range transport" with "aging process".

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

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