Response to Reviewer 1

We sincerely thank the reviewer for the valuable comments and suggestions. Below we list our point-by-point replies to the comments and the descriptions of the changes we made in the revised manuscript.

1. *The manuscript presents a short collection of data from two single-particle instruments measured during a pollution episode in Shanghai, China. A single particle soot photometer (SP2) measured refractory black carbon (rBC) number and mass distributions as well as optical size. A single particle aerosol mass spectrometer (SPAMS) measured mass spectra of individual particles in parallel. Together the instruments provided information on the abundance and composition of BC-containing particles. To my knowledge this is the first direct comparison and analysis of single-particle data from the two approaches, and while the manuscript does not exploit the advantages of the two techniques as much as might be possible, it still represents a valuable contribution and presents information from a unique and important region (Chinese megacities). I recommend it for publication in ACP once the following comments have been addressed:*

General comments

2. *There are a few places where I think more could be done with the co-located single particle instruments. For example, was there much consistency in results between SPAMS "mixed" particle clusters and SP-derived coating thickness?*

Response: We discussed the correlation between the particle mixing state revealed by SPAMS and the SP2-derived coating thickness in Section 3.4.2. In the revised manuscript, we have added a more detailed discussion in this section, including some new data from online ion chromatograph measurements (MARGA) and the observation of gas to particle conversion to support the consistency between the two instruments. Please also see our response to the Question 11 of Reviewer 2.

3. *In addition, more details should be provided on the comparisons between the two instruments:*

+ were the number concentrations calculated for the same diameter range for both instruments?

Response: The particles number of particles detected by SPAMS (or ATOFMS) is not quantitative (labeled as unscaled particle number in the manuscript) because of the unknown sampling efficiency (including total transmission efficiency and size-dependent sampling efficiency). The strength of this instrument is to characterize the chemical composition at a single particle level and determine the number fractions of different particle types. Besides, SPAMS detects the vacuum aerodynamic diameter in the size range of 200 - 2000 nm while SP2 detects the optical diameter of BC-containing particles in the size range of ~170 to 800 nm. Without the information of each particle's morphology and density, we couldn't convert the two different diameters precisely. It is hard to do any further quantitative comparison between the two instruments beyond the time-resolved correlation as presented in Fig. S4 and Fig. S5. In this work, we paid more attention to the mixing state and its evolution of BC-containing particles revealed by the two instruments rather than the mass or number concentrations of BC particles.

4. *+ was the reduced detection efficiency (about half) for the SPAMS accounted for in the comparison?*

Response: In this experiment, we obtained 385 683 particles with mass spectra, accounting for 56% of the total sized particles. We had no chemical information of the rest 44% particles and they were not included in the comparison.

5. *+ what is considered "internally mixed" for both instruments? Were all rBC particles measured by the SP2 included, or only those with a coating thickness above some value. If so, why?*

Response: For SPAMS, we could tell BC particles are internally mixed or pure through the mass spectral patterns. Internally mixed BC particles present not only signals of carbon cluster ions (C^-_n and C^+_n) in both positive and negative ion mass spectra, but also signal of secondary species like sulfate or nitrate.

For SP2, the internally mixed BC particles are those with a certain coating thicknesses. The internally mixed BC particles have both scattering (related to optical diameter) and incandescence (related to BC core diameter) signals. In the SP2 measurement, particles with optical diameter above ~170 nm and BC core diameter above 70nm can be observed. This is due to the scattering and incandescence detector sensitivity. Therefore, we miss some internally mixed BC particles with small core and thin coating thickness.

6. *Related point: I am not aware of any studies that directly compare single-particle MS results to a co-located SP2, so think the scatter plot in the supplementary material is worth including in the main paper. If there are some recent papers comparing SP2 to single-particle MS suggest including a short comparison of the results here to those.*

Response: We moved Fig. S4 from supplementary material to the main text as Fig. 3. We haven't found any published data comparing SP2 to single particles MS.

7. *35384 – 6: The term "refractory black carbon (rBC)" should be used when presenting any results specifically from the SP2. Recommend changing text here and throughout the manuscript. The distinction will also help distinguish results from the mass spectrometer versus SP2.*

Response: We accepted this suggestion. We used refractory black carbon (rBC) when presenting results from the SP2 and used black carbon (BC) when presenting results from the SPAMS throughout this manuscript. Both terms were explained in the introduction.

8. *35384 – 9: Add "in diameter" after 60-400 nm (assuming results are reported as diameters).*

Response: Done

9. *35387 – 28: It might be beneficial to add a small note to clarify that the "SPAMS" here is NOT the same as the SP-AMS (Soot Particle-AMS), which shares the laser system of the SP2 and therefore might lead to a little confusion.*

Response: Reviewer 2 also suggested that some related SP-AMS works should be cited. We added the following paragraph in the introduction to cite 6 SP-AMS works and also clarified the SPAMS was different from SP-AMS in the fourth paragraph of introduction.

"Recently, a soot particle aerosol mass spectrometer (SP-AMS) was developed to characterize rBC and non-refractory particulate matter simultaneously (Cross et al., 2010;Onasch et al., 2012;Corbin et al., 2014). SP-AMS was previously used to quantify rBC mass concentration, mixing state and chemical composition in urban environment and biomass burning influenced air (Lee et al., 2015b;Lee et al., 2015a;Willis et al., 2015)."

10. *35389 – 14/15: Change "laser power" to "laser current". Note that a constant laser current does not necessarily mean a constant cavity laser power. Ideally PSL could be used to verify the laser power before and after the study period, however considering the data are reported for a five-day period I do not think this is especially important in this case.*

Response: We changed "laser power" to "laser current" here. We used the 220 nm PSL to detect the laser power before and after the sampling period. The nearest equivalent scattering signal verified the constant cavity laser power.

11. *36390 – 7: suggest changing/adding ". . .was calculated as (Dp-Dc)/2, which assumes a concentric core-shell morphology."*

Response: Done

12. *35390 – 17: Is the SPAMS a laboratory-built instrument or the commercial instrument available from Livermore Instruments (SPAMS 3.0). Please specify here in addition to citing the reference.*

Response: The SPAMS is a commercial instrument developed by Hexin Analytical Instrument Co., Ltd., Guangdong, China. We added this information in the manuscript when first introducing SPAMS.

13. *35391 – 8: Are the final number concentrations corrected for this factor when comparing to SP2? Please clarify.*

Response: Please see the responses to comments 2 & 3.

14. *35391 – 28: Please state if there was a sizecut (cyclone, impactor) used on the main inlet, or if the instruments sampled all transmitted particles (with their response limited by upper size limit of the instruments).*

Response: We used a $PM_{2.5}$ cyclone on the main inlet. We added this information to the experimental section.

15. *35392 – 1: Suggest renaming this section because it focuses more on the trace gas measurements then meteorology. Also, according to the caption for Figure 1 data were*

taken from the Hongkou Station. This information should be provided in the main text as well.

Response: We renamed the section title as: Overview of the meteorology and air quality.

We also added the information of Hongkou Station in Section 3.1.

16. *35392 – 25: The data shown in Figure 2 are study averages? Please state.*

Response: This distribution was over the entire study period. We stated this in the first sentence of section 3.2.

17. *33393 – 8: All comparisons are to SP2-measured values, correct? Should be stated if so.*

Response: Yes. We added the following sentence here to clarify this point: "All of the values quoted above were based on SP2 measurement." We also added similar statements in several other parts of the manuscript for clarity.

18. *35396 – 5: Should be stressed here that the results discussed here are from the LEO-fitting of SP2 data and not BC cores but the total, mixed diameter particle.*

Response: Yes, the results here are the entire diameter (D_p) of BC-containing particles. We changed "D_p" to "the entire diameter (D_p)" here.

19. *35396 – 12: The paragraphs in this section move back and forth between SP2 and SPAMS data, so it would be a little more clear to state when SPAMS data is being discussed and when we are back to SP2 data.*

Response: The logic flow of Section 3.4.2 was: Firstly, we showed the similarity (two-mode distribution) between SP2 and SPAMS measured size distributions. Then we used the size-resolved chemical information from SPAMS to support the BC core vs. ACT data from SP2. The comparison of the two measurements back and forth are inevitable here. Separating the two set of data in discussion would cut the logic flow.

20. *35397 – 4: The condensation and droplet modes are defined in terms of vacuum aerodynamic diameter in the manuscript, but I did not see what value was used to distinguish the modes for the SP2. I assume to make the two plots shown in Figure 5c the data was split for some mixed particle diameter. It would be useful to show that as a line on both figures, because by definition you cannot have any particles above it for the condensation mode or below for the droplet mode. It would be good to shade this region of Figure 5c either black or weight since it is an invalid data region for both plots. Finally, it is not stated if this analysis was performed for all particles measured during the study or only during specific time periods.*

Response: Thank you for this suggestion. We used the minimum value between the two peaks in Fig. 5(a) (black line) and its corresponding Dp (320 nm) as the separation of the condensation mode and droplet mode. We added this separation line in Fig. 5(c) to separate the condensation mode particles (left side) and the droplet mode particles (right side).

This analysis was performed for all the particles during the study. We clarified this point in the first sentence of section 3.4.2.

21. *35397 – 26: This is a nice example of using both instruments to better understand what is happening, though there should be some care in treating the correlation as direct evidence (how well do the large, thickly coated particles correlate with other BC particle categories identified by the SPAMS?). I do think the figure (S5) should be moved out of supplementary material into the main text. Also, the text discusses the number fraction of BC from biomass burning, but not mass fraction (which could be estimated from the SP2 data). A 20% contribution (or higher, for mass) from biomass burning seems high for an urban region, but can the authors discuss more. Do they expect significant residential burning near their site?*

Response: Those larger core (80–130 nm) with thicker coating (120–300 nm) particles showed a poor correlation (R^2<0.24) with SPAMS detected traffic emitted BC-containing particles.

We moved Figure S4 from supplementary material to the main text. Since the information in Figure S5 and S4 were similar, we decided to keep Figure S5 in the supplementary section.

There is no significant residential burning near the sampling site. However, around Shanghai, there are some rural areas where people burn the crop residues as daily household fuel. We constantly observed high number fraction (15-20%) biomass burning particles in Shanghai especially during and right after harvest seasons (Yang et al., 2009;Fu et al., 2015).

22. *35397 – 13: Do either of these studies report PM? Values in Shanghai were probably much higher than in the other locations mentioned, so you might have much more rapid mixing with BC acquiring thicker coatings faster.*

Response: The studies we cited here did not report PM mass concentrations. Laborde et al. (2013) reported that number concentration was around 10^3-10^4 particle cm^{-3}. We agreed that the extremely high PM concentration could contribute to the rapid mixing of BC in this study.

23. *35398 – 16: There should be a note here that the choice of BC core diameter (60-80 nm) means that you will only obtain optical sizing for the most thickly coated particles due to the scattering detector sensitivity (minimum optical diameter of about 170 nm). Do the larger BC cores display a similar rapid coating behavior?*

Response: We agree with this comment. The SP2 only obtained optical size more than 170 nm, so the observed RCT of BC-containing particles grew from 2 to 9 in this period, as shown in Fig. 6a. We might miss the initial growth of some small BC particles, but we could still capture most part of the fast growth of traffic emitted BC-containing particles. In response to this suggestion, we added the following note: "Note that we could only obtain optical sizing information from sufficiently coated particles because of the SP2 obtained minimal detectable optical diameter of ~170 nm."

The larger BC cores were composed of both biomass burning BC particles and some traffic emitted BC particles. The biomass burning particles were already deeply aged when reaching the sampling site. The overall growth trend of larger BC core particles was not obvious.

24. 35398 – 26: "incensement"?

Response: We changed to "a relatively high level".

25. Figure 4: Please add label for color scale including units (dN/dlogDp)? Caption for (b) states the red lines shows number concentration but axis label gives particle number.

Response: In the original manuscript, the color scale presented the number concentration with a 10nm resolution. In the revised manuscript, we redrew Fig. 4(a) using dN/dlogDp as the color scale. Since we moved Fig. S4 to the main text, we deleted the red lines in the revised Fig. 4(a & b). We also corrected the figure caption accordingly.

26. Figure 6: Information for color scale should be provided.

Response: Done.

Again, we thank you very much for your effort and contribution!

Sincerely,

Xin Yang

Literature:

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