Response to Reviewer 3

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.

This study presents a short period in-situ measurement of black carbon in Shanghai urban area. Both Single Particle Aerosol Mass Spectrometer (SPAMS) and Particle Soot Photometer (SP2) were employed to get comprehensive information of BC- containing particles, including the number size distribution of BC-containing particles and BC cores, chemical composition of BC-containing particles, and the core-size and coating thickness of BC-containing particles. The combination of SPAMS and SP2 pro- vides a perfect tool to investigate the aging process of BC particles in the atmosphere. This study is probably the first one conducting such a measurement in heavy polluted megacities in China. Although there is not detailed discussion on the aging of BC particles from different sources, it provides some interesting results about the mixing state of BC in heavy polluted atmosphere. I therefore recommend the final publication of this study on ACP.

Specific comments:

1) Abstract: The abstract should be condensed. It is not necessary to list all the numbers like the PM concentrations in the first paragraph and the number fraction of the 7 groups in the second paragraph.

Response: We shortened the abstract by removing some detailed experimental data, including the PM concentration, BC size distribution and number fractions of different particle types. The observations of the fast growth rate of BC particles and the resulting thick coating were highlighted in the revised abstract.

2) Introduction: I suggest the author to better motivate the study. Some similar studies in other big cities are listed in the 5th paragraph of section 1. What information is still missing or not clear? What may this study contribute to our knowledge?

Response: We rewrote the last paragraph of introduction and added the following paragraph to stress the motivation of this study.

"All of the studies mentioned above relied on either an SP2 instrument or a single particle mass spectrometer to characterize BC particles. Combining these two methods would provide the chemical and physical prosperities of individual BC particles simultaneously and greatly enhance our understanding of their sources and evolution processes. Furthermore, most previous SP2 studies focused on the BC particles during relatively clean days. Quantitative analysis on the mixing state of BC particles during heavy pollution episodes is still lacking."

3) Sect. 2.1.3: To derive the optical diameter of a particle, did you assume a core-shell particle structure in the Mie calculation? As mentioned in this paragraph, an effective negative coating thickness will be yielded if small amount of BC stays on the surface of a big particle. I think in atmosphere, the structure of most BC-containing particles is neither ideally core-shell nor BC staying on surface, but something in between (e.g. BC coated with other species but not at the center). Do you have any estimate about the possible influence of this effect on the ACT yielded with your method?

Response: The SP2 data analysis was based on the LEO-fit method. In this method, a concentric core-shell structure of BC-containing particles was assumed. In ambient atmosphere, China et al. (2013) quantified the morphology of BC particles and classified them into four categories: ~ 50 % were embedded (heavily coated), ~34 % were partly coated, ~12 % had inclusions and ~4 % were bare. We believed that during the heavily air pollution period, the heavily coated BC-containing should account for much more than 50%. The ACT in the manuscript did not present the precise coating thickness of BC-containing in the atmosphere, but displayed the aging degree of BC-containing particles. Moteki et al. (2014) combined the LEO-fit and lag-time methods to identify the morphological types of BC-containing particles. However, this was beyond the scope of this manuscript.

4) Sect. 3.2 para. 2: These comparisons are not necessary. I think it does not make too much sense to compare your 5-day measurement during extreme pollution episode with other results with might be yielded in different seasons, pollution situations, and types of site. Such a comparison may give the audience a wrong impression.

Response: The cited works were all measured by SP2. So far, there are limited SP2 measurement all over the world. We do think that a comparison is justified even though different environments are compared.

5) Sect. 3.3: Some of the groups (e.g. KBC and NaKBC) have similar mass spectra and are attributed to similar sources, and are not really distinguished in the follow sections. Please consider reducing the number of groups. Or keep the classification as it is in this section, and combine some of them in the later discussion (fig. 4 and 5).

Response: We accepted the suggestion and carefully rechecked the classification process.

For BBBC particles, we combined ART-2a and ion-marker methods to validate the classification. We have done lab study and field measurement on the chemistry of biomass burning (mostly crop straw burning in China) BC-containing particles (Huo et al., 2015). Briefly, except for black carbon fragment ions (C_n^+ and C_n^-) in both positive and negative ion mass spectra, +39 (K^+), -26 (CN^-), -42 (CNO^-) were used as the most important tracers for BBBC particles here. Given the extremely high detection sensitivity of potassium (due to the high ionization cross-section of potassium at 266 nm) in SPAMS, we defined that +39 (K^+) as the marker must have the peak area more than 1000. Meanwhile, the peak area of +56 (CaO^+/Fe^+) and -76 (SiO_3^-) must be less than 50 because paucity of Si, Ca and Fe is the major characterization of biomass burning particles differing from coal burning particles. Because the K-rich nature of biomass material, +113 (K_2Cl^+) or +213 ($K_3SO_4^+$) were constantly observed in the mass spectra of biomass burning particles by ATOFMS, then here were alternatively selected as markers for BBBC particles instead of +39 (K^+). Lastly, -71 ($C_3H_3O_2^-$), as a significant fragment of levoglucosan, was a marker to confirm our classification. We have applied these ion markers when regrouping the ART-2a results.

We reclassified the NaKBC particles by running ART-2a. We found that more than 88% particles in this group could be re-assigned to either BBBC or KBC patterns. The rest could be assigned to pure BC, BCOC-NOx or BCOC-SOx. Therefore, we eliminated the NaKBC group, and added these particles into the other BC groups according to the mass patterns.

Water-soluble K^+ in ambient aerosol measured by an online analyzer for Monitoring Aerosols and Gases (MARGA, ADI 2080, Netherlands) was used to compare with the SPAMS biomass burning particles. K^+ mass concentration by MARGA agreed well with

BBBC particles number (R^2=0.64), which confirmed our classification. We added the operation of MARGA in the experimental. We added the following figure as Fig. S6.

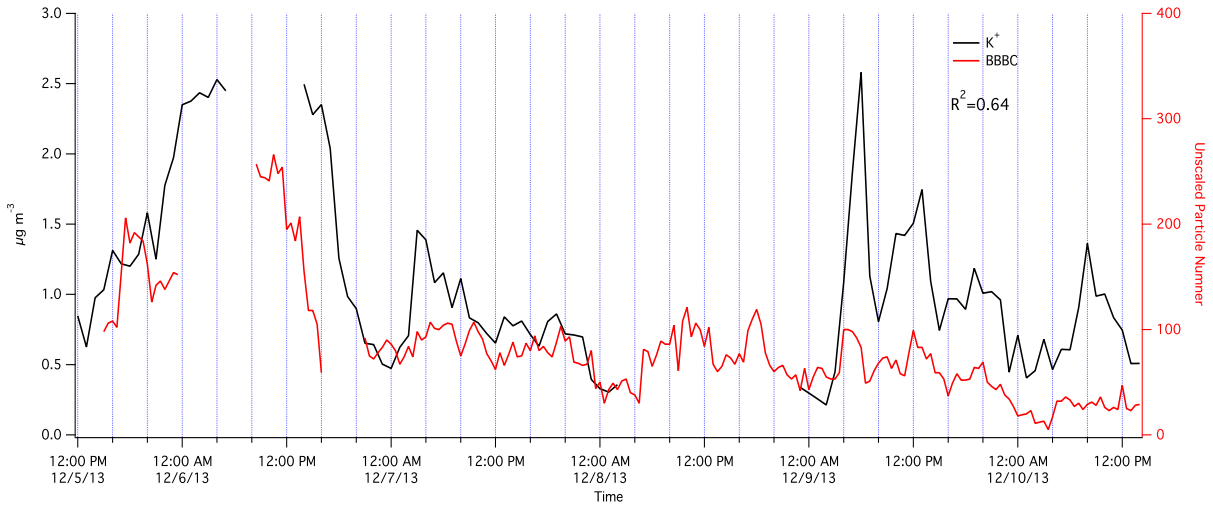

Figure S6. Temporal variations of K+ mass concentration in particles (measured with MARGA) and biomass burning BC-containing particles (measured with SPAMS).

The newly obtained KBC group exhibited pronounced diurnal variation, with two major peaks during early morning (4:00- 7:00 LT) and night hours (20:00- 22:00 LT). In the manuscript, we assigned the KBC to the diesel truck emission. Shanghai municipal government regulates that the heavily loaded diesel trucks cannot go into downtown area from 7:00 - 20:00. The diurnal variation of KBC consisted with the traffic flow of diesel trucks and confirmed our assignment. We added this part of discussion in the revised manuscript. We added the following figure as Fig. S7.

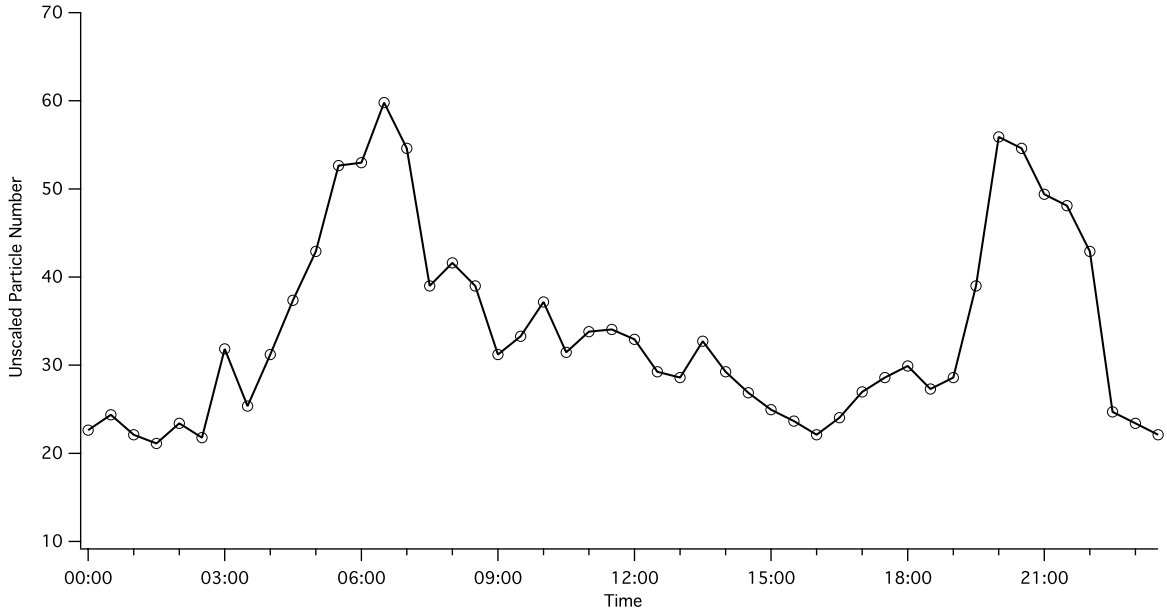

Figure S7. Diurnal variation of KBC particles measured with SPAMS.

NOx can be used as a tracer of local traffic emission in urban. Likely, the mass concentration of NOx should positively correlate to the particles emitted from vehicles (i.e. KBC, BCOC-NOx and BCOC-SOx). In this study, the NOx concentration agreed well with the sum of

KBC, BCOC-NOx and BCOC-SOx particles numbers (R^2=0.65). We added this part of discussion in the revised manuscript. We added the following figure as Fig. S8.

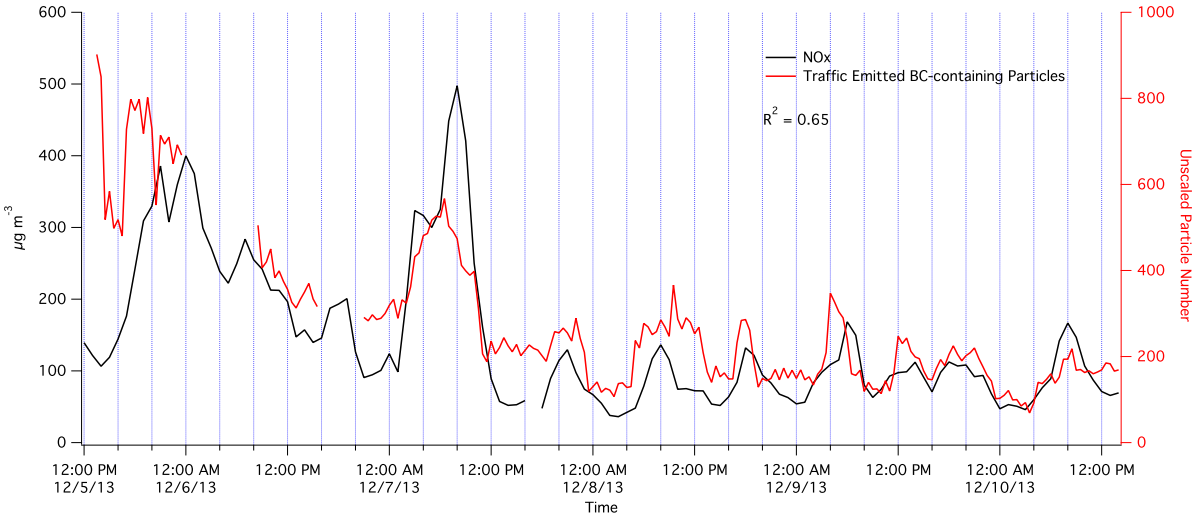

Figure S8. Temporal variation of NOx mass concentration and traffic-emitted BC-containing particles measured with SPAMS.

Moreover, to show more details of the mass spectra patterns, we moved Fig. 3 to supplementary as Fig. S5 and enlarged each mass spectrum.

6) Sect. 3.4.2: The author mentioned that BCOC-NOx particles are much older and are supposed to have larger size (P35396L19). But in Fig. 5B we can see the ratio of BCOC-NOx particle number to BCOC-SOx particle number is even higher in condensation mode. Do you have any explanation on this?

Response: In this work, particles detected by SPAMS were mostly aged including the condensation mode particles. The higher BCOC-NOx number fraction in condensation mode is because of the less fractions of KBC and BBBC particles in this mode. In droplet mode, all the KBC and BBBC particles presented strong nitrate signals. To avoid any confusion, we deleted this statement and rephrased the discussion in the revised manuscript.

7) Sect. 3.4.2: Fig. 6 only shows the information of traffic-emitted BC-containing particles. I think it is not enough to support the conclusion of "Reductions in the emissions of gaseous precursors, such as NO2 in the urban area, are critical for remediation of the severe urban haze pollution in China.".

Response: In this work, traffic-emitted BC-containing particle was taken as an example to see the ageing process of primary particles. To make our conclusion more convincing, in the revised manuscript, we included the MARGA data on PM_1 to illustrate the important contribution of nitrate to the PM concentration. Please also see the following paragraph and figure we added in the manuscript and supplementary.

"Variations of the major chemical species in the vehicle-emitted BC-containing particles (selected by SPAMS) were also analyzed. The relative peak areas of nitrate -63 (NO_3^-) and organic carbon (i.e., +27 ($C_2H_3^+$), +43 (CH_3CO^+)) showed a relatively high level during 16:00 LT on 5 December- 13:00 LT on 6 December (Fig. 6(b)). Guo et al. (2014) observed that gaseous emissions of volatile organic compounds, nitrogen oxides from urban transportation

and sulfur dioxide from region industry were responsible for large secondary particle matter formation in Beijing. Fig. S10 shows the mass concentrations of SO_2, NO_2, the mass ratio of NO_2/SO_2, MARGA-measured mass concentrations of particulate sulfate and nitrate, and the mass ratio of NO_3^-/SO_4^{2-} in PM_1 during the whole sampling period. The average mass ratios of NO_2/SO_2 in gas phase and NO_3^-/SO_4^{2-} in particles phase were 2.8 and 1.4 respectively. During the heavy air pollution episode (12:00 LT, 5 December 2013 – 13:00 LT, 6 December 2013), both NO_2 and particulate nitrate increased dramatically along with the traffic emitted BC particle growth (as shown Fig. 6), while SO_2 and sulfate remained at a relatively low level. Apparently, the gas to particle conversion of NO_2 to nitrate played a more important role in the particle growth during this pollution episode. In the previous field studies (Huebert et al., 1988;Yao et al., 2002), the high mass ratio of NO_3^-/SO_4^{2-} (>1.0) was regarded as a sign of dominant traffic emission. Wang et al. (2015) found that the high mass ratio of NO_2/SO_2 resulting from traffic emissions was a major reason in triggering the heavy haze in Shanghai. In this work, the evaluation of BC-containing particles also suggested that high concentrations of NO_2 and possibly volatile organics and their transformations play a vital role for particle growth and the increase of PM loading in urban area especially during a heavy pollution episode. Reductions in the emissions of gaseous precursors are critical for remediation of the severe urban haze pollution in China."

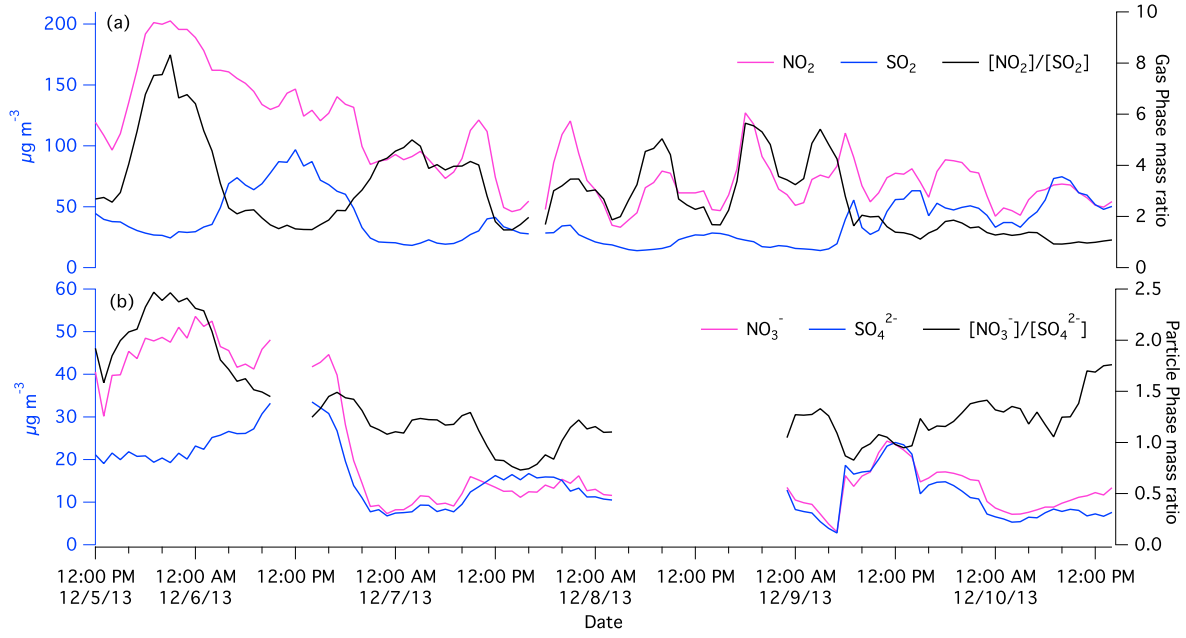

Figure S10. (a) Temporal variations of the NO_2 and SO_2 mass concentration in the atmosphere and mass ration of NO_2/SO_2 with 60 min resolution. (b) Temporal variation of NO_3^- and SO_4^{2-} mass concentration in particles and mass ratio of NO_3^-/SO_4^{2-} with 60 min resolution.

8) P35387L4: it is better to use rBC here and after for SP2 measurement

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.

9) P35385L26: absorption cross section

Response: Fixed.

10) P35390L17: please give the information of manufactory of SPAMS

Response: The SPAMS in the manuscript was developed by Hexin Analytical Instrument Co., Ltd., Guangdong, China. We added this information to the experimental section.

11) P35391L12: please give the full name of Dva

Response: We added the full name of D_{va} (vacuum aerodynamic diameter) in the revised manuscript.

12) P35396L13: I would not say BBBC particles dominate the droplet mode if they take less than 30% number.

Response: We changed "dominant" to "higher".

13) P35398L26: I did not see any "significant incensement". Maybe use "a relatively high level" instead.

Response: Fixed.

14) Figures: it is better to use the same style of unit as in the text, e.g. ugm-3 instead of ug/m3.

Response: Fixed.

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

Sincerely,

Xin Yang

Literature:

China, S., Mazzoleni, C., Gorkowski, K., Aiken, A. C., and Dubey, M. K.: Morphology and mixing state of individual freshly emitted wildfire carbonaceous particles, Nature communications, 4, 2013.

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Huebert, B., Mingxing, W., and Weixiu, L.: Atmospheric nitrate, sulfate, ammonium and calcium concentrations in China, Tellus B, 40, 1988.

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Moteki, N., Kondo, Y., and Adachi, K.: Identification by single‐particle soot photometer of black carbon particles attached to other particles: Laboratory experiments and ground observations in Tokyo, Journal of Geophysical Research: Atmospheres, 2014.
Wang, Q., Zhuang, G., Huang, K., Liu, T., Deng, C., Xu, J., Lin, Y., Guo, Z., Chen, Y., Fu, Q., Fu, J. S., and Chen, J.: Probing the severe haze pollution in three typical regions of China: Characteristics, sources and regional impacts, Atmos. Environ., 120, 76-88, http://dx.doi.org/10.1016/j.atmosenv.2015.08.076, 2015.
Yao, X., Chan, C. K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K., and Ye, B.: The water-soluble ionic composition of PM2.5 in Shanghai and Beijing, China, Atmos. Environ., 36, 4223-4234, http://dx.doi.org/10.1016/S1352-2310(02)00342-4, 2002.