A point-by-point response to the reviewer

General Comments:

Chen et al. conducted ambient measurements in Beijing in summer and winter from which they calculated size-dependent volatility shrinkage factors (VSF) and mixing states of urban aerosols and compared the volatility properties in different seasons. The measurements were conducted with the use of a VTDMA of which size-selected aerosols ranging from 40-nm to 300-nm were heated up to 300℃. The non-volatile particles that remained in the particle phase upon heating up to 300℃ were assumed to be black carbon (BC) in the analysis. Although volatility analysis of ambient aerosols has been intensively studied in general, this manuscript presents measurement results in different seasons in north China. The dataset presented in the manuscript is overall comprehensive but could be more thorough when interpreting the results.

Re: We are grateful to the reviewer for your insightful comments, all of which have been considered carefully during the revision (a point-by-point response to the reviewer as follows). The result has been carefully analyzed accordingly to the reviewer's suggestions and other comments have also been addressed.

Specific Comments:

1. I have similar concerns about the major assumption of attributing the non-volatile composition in urban aerosols to be BC in your analysis, as already detailed by another referee. Please consider providing more information, such as chemical composition data, or data from other instruments, if available, to support your assumption, which is critical to your analyses and discussions thereafter.

Re: It is possible that there may be some other non-volatile compounds in submicron aerosols will not evaporate even at 300 °C. To investigate the composition of the refractory component and verify whether they consist mainly of BC, we quantify the mass concentration of these non-volatile material and correlate it with the measured BC mass concentrations by AE33, which are shown in Fig. R1. The calculated non-volatile particle mass concentration and the measured BC concentration correlated well, with slope of 1.02. The mass fraction of non-volatile compounds except BC was further evaluated, which accounted for ~1.8 %. Consequently, at 300 °C, contribution of non-volatile materials except BC is expected to be quite negligible (< 5 %). This result suggests that BC can explain almost the non-volatile mass fraction in this study. In addition, we compared the mean VSF measured at 200 and 300 °C, results show that the VSF values varied greatly under different heating temperatures especially for large particles (Fig. R2), hence some studies (Xu et al., 2016; Cappa & Jimenez, 2010) obtained considerable non-volatile OA at 250 °C may differ from the fractions at 300 °C.

Actually, the composition of these non-volatile residuals may vary spatially and temporally (Poulain et al., 2014). For example, black carbon is considered a major non-

volatile component in sub-μm PM in many studies (e.g., Pöschl, 2005; Frey et al., 2008; Birmili et al., 2009; Birmili et al., 2010). Frey et al. (2008) have demonstrated a good agreement between the mass concentration of BC and the mass concentration of non-volatile particles upon heating at 300 °C in the VTDMA; Birmili et al. (2009) found linear relationships between the BC mass concentrations and the non-volatile volume concentrations for five different atmospheric measurement sites; Birmili et al. (2010) found the non-volatile aerosol material had a clear correlation with BC aerosols in polluted areas. Generally, BC constitutes a major part of the non-volatile mass concentration.

The reliability of retrieved Ex-BC is also verified by comparison with SPAMS data, see Fig. R3, both the overall temporal variations and proportion for Ex-BC particles measured by SPAMS and calculated from VTDMA using the retrieved method are consistent, confirming our method are reliable for retrieving mixing state of BC in the study periods. Some discussions and evidences about this issue have been included in the revised paper, see **Lines 122-132** and **Lines 172-177**, as follows:

"The detailed correlations between mass concentration of non-volatile particles estimated from VTDMA and BC measured by AE-33 in this study are shown in Fig. S2. The total mass concentration of non-volatile particles was determined from the measured particle number size distributions after heating by assuming particle density of 1.6 g cm^{-3} (Häkkinen et al., 2012; Poulain et al., 2014). The calculated non-volatile particle mass concentration distributed on both sides of the line 1:1. We further evaluated the mass fraction of non-volatile compounds except BC, which accounted for ~1.8 %. This result suggests that BC can explain almost of the non-volatile mass fraction in this study. In addition, we compared the mean VSF measured at 200 and 300 ℃, results show that the VSF values varied greatly under different heating temperatures especially for large particles (Fig. S3), hence some studies (Xu et al., 2016; Cappa & Jimenez, 2010) obtained considerable non-volatile OA at 250 °C may differ from the fractions at 300 °C."

"The retrieval result, which has been compared with the measurements by single particle aerosol mass spectrometer (SPAMS) in the Fig. S5 and in the previous study (Chen et al., 2020), both the overall temporal variations and proportion for BC-containing and Ex-BC particles measured by SPAMS and calculated from VTDMA using the retrieved method are consistent, confirming this method is reliable for deriving the mixing state of BC."

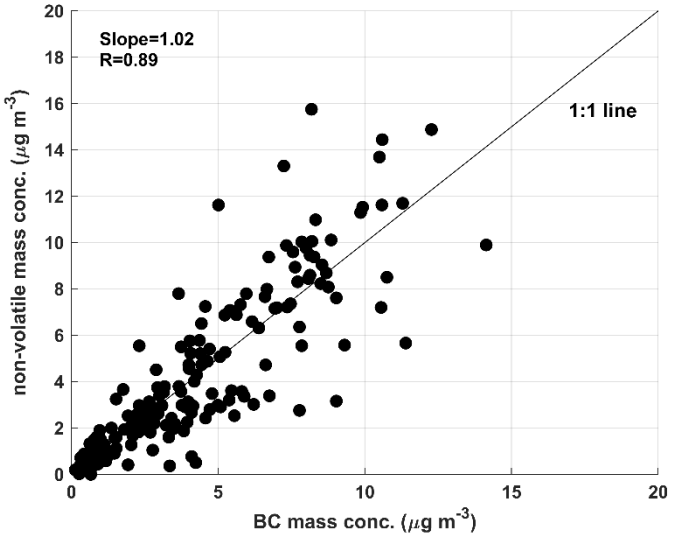

Figure R1. Black carbon (BC) mass concentration measured by AE-33 vs. the non-volatile mass concentration estimated from the VTDMA for winter 2019 periods. Estimation of the non-volatile mass concentration was made assuming a density of 1.6 g cm^{-3}.

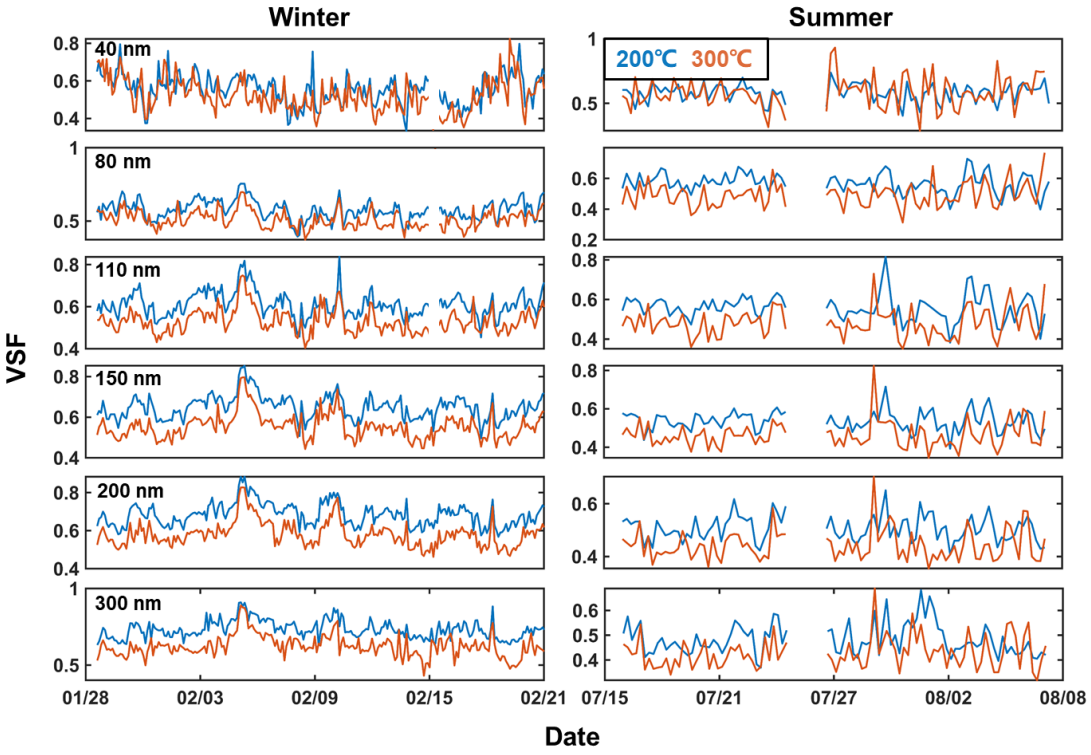

Figure R2. The mean volatility shrink factor (VSF) of all measured size particles after heating at 200 (blue line) and 300 °C (red line) during the winter and summer periods.

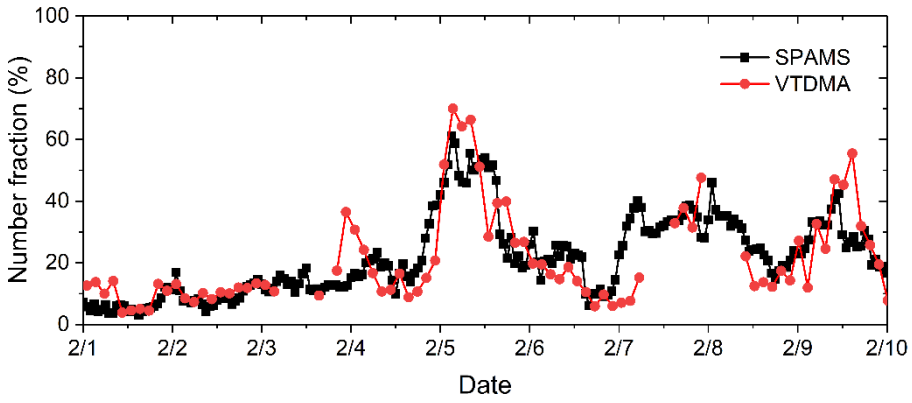

Figure R3. Time series of number fraction of Ex-BC particles measured by SPAMS (in black) and calculated from VTDMA (in red), the 200 nm particles from VTDMA are chosen.

2. Since the manuscript aims to characterize the volatility properties of urban aerosols and tries to link the properties to the source, formation and growth, the authors may consider adding more materials to enrich the discussion, such as air masses origins information and their effect on the aerosols' volatility and mixing states.

Re: According to the reviewer's suggestion, we have added the air masses origins information during the two sampling periods (Fig. R4), and some discussions about their effect on the aerosols' volatility and mixing state have been included in the revised paper, see **Lines 302-327**, as follows:

"Fig. 7 presents the 72-h back trajectories arriving at the sampling site during the two periods from 00:00 to 23:00 LT calculated applying the TrajStat software (Wang et al., 2009) (Fig. 7a), and the mean VSF (VSF_{mean}) of the corresponding cluster during the winter and summer periods (Fig. 7b). In the winter, the air masses were categorized into five clusters and mainly from the north. The short northwest clusters (C2 and C3) were predominant, contributing of ~76.7%, which associated with the high $PM_{2.5}$ concentrations (Wang et al., 2015). The VSF_{mean} difference of small particle size between different clusters is greater than that of large size, implying the source impacts greatly on the volatility of small particles. The VSF_{mean} of C5 was higher, indicating that particles experienced long-range transport from the northwestern region of Siberia, with high aging degree and low volatility. In the summer, the air masses were classified into six clusters and coming from almost all directions, the short south clusters (C1 and C3) were prevailing, comprising ~50%. There were slight differences of VSF_{mean} among different clusters. In general, The VSF_{mean} of all clusters in the summer (~0.47) was lower than that in the winter (~0.55), especially for large particles. This would be attributed to that in winter, particles from the northern region of urban Beijing experienced a longer aging process during the transportation, the highly internally-mixed particles are with more non-volatile compounds, leading to a higher VSF_{mean}. Lin et al (2009) reported that the important coal mining and power generation region and numerous metallurgical works are located in western Beijing (Shanxi and a small part of southwestern Inner Mongolia), thus, $PM_{2.5}$ and precursors such as SO_2 and NO_x can be brought down into the downwind regions with northwest cluster, hence higher

VSF_{mean} in the winter were associated with northwest trajectories. However, the seasonal transported contribution of Beijing was the lowest in summer (Wang et al., 2015), so the lower VSF_{mean} of particles emitted from local sources further indicated that Non-BC particles were dominant in the summer periods."

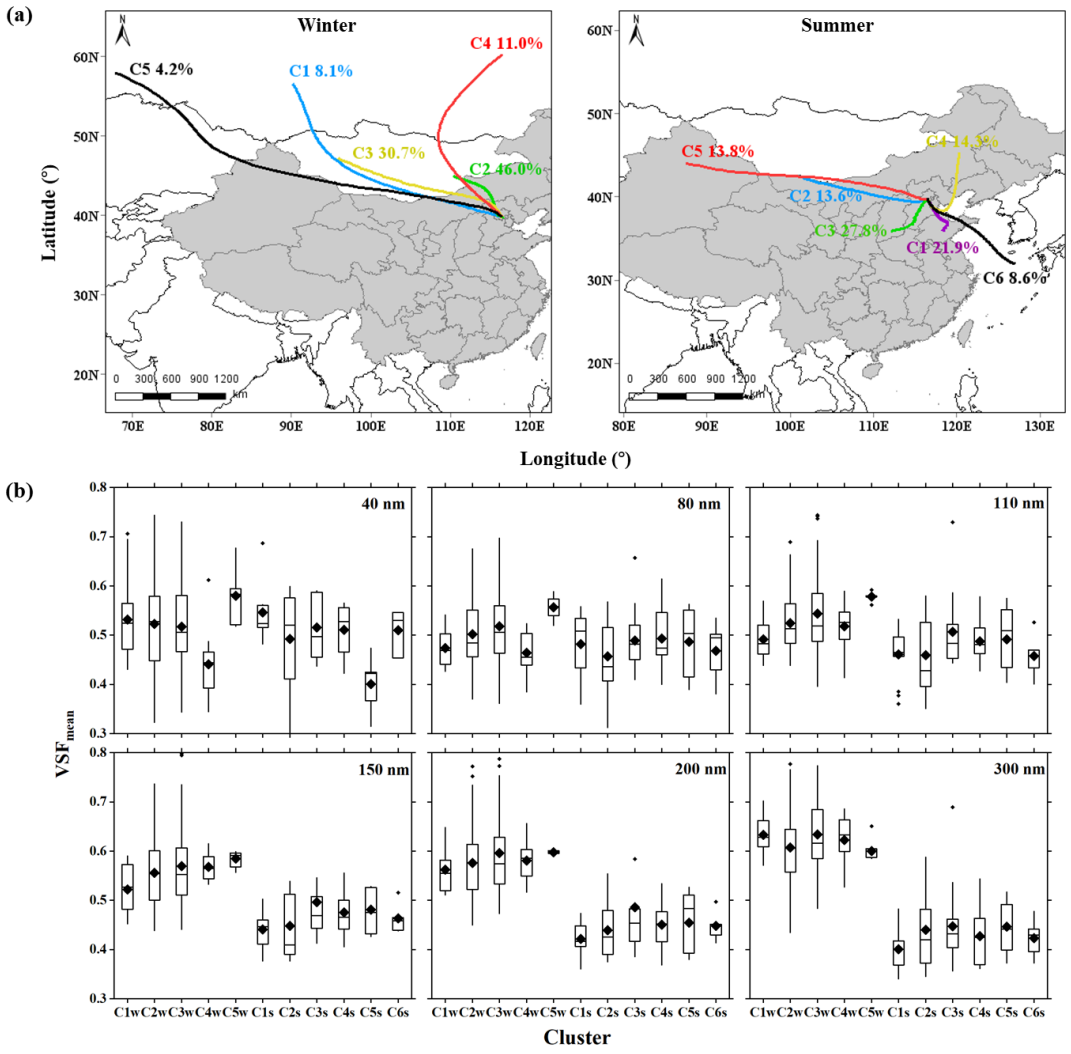

Figure R4. (a) The 72-h back trajectories arriving at Nanjiao site during the winter (left) and summer (right) periods. C1-C6 represent Cluster 1-Cluster 6 respectively. The percentages present the relative occurrences. **(b)** Box diagram for the mean volatility shrink factor (VSF_{mean}) of all selected diameter particles (40-300 nm) from different clusters during the winter and summer periods. The horizontal line in the block diagram represents the median, the diamond represents the mean, the upper and lower borders represent the 25th and 75th percentiles, and the upper and lower borders of the dotted vertical line represent the 10th and 90th percentiles.

3. It is frequently mentioned throughout Section 3 about the impact of new particle formation (NPF) and the growth on the volatility properties of aerosols. Please consider providing more details, such as the number of NPF events in summer and winter, respectively, to give a clearer picture and support to your analysis. Furthermore,

although NPF events occurred less frequently in winter, did it have similar impact on aerosols' volatility as that in summer?

Re: The NPF events took place frequently during the sampling periods of summer, with about 10 NPF events occurred (see Fig. R5). The time series of the aerosol particle number size distribution measured by the SMPS during the campaign have been added to the supplement (Fig. S7). Fig. R5 shows that almost no NPF events occurred during the campaign. Some statements have been included in the revised text of **Lines 235-240**, as follows:

"Fig. 4g displays the mean diurnal variations of PNSDs in the summer. During the summer sampling periods, new particle formation (NPF) events took place frequently, with 10 NPF events occurred (Fig. S7). The NPF events almost all started at around 10:00 LT. After the starting of NPF, the volatile mode in VSF-PDF was obviously enhanced, corresponding to significant decreases of the mean VSF values. This suggests that the more volatile chemical components were formed in the nucleation and growth processes."

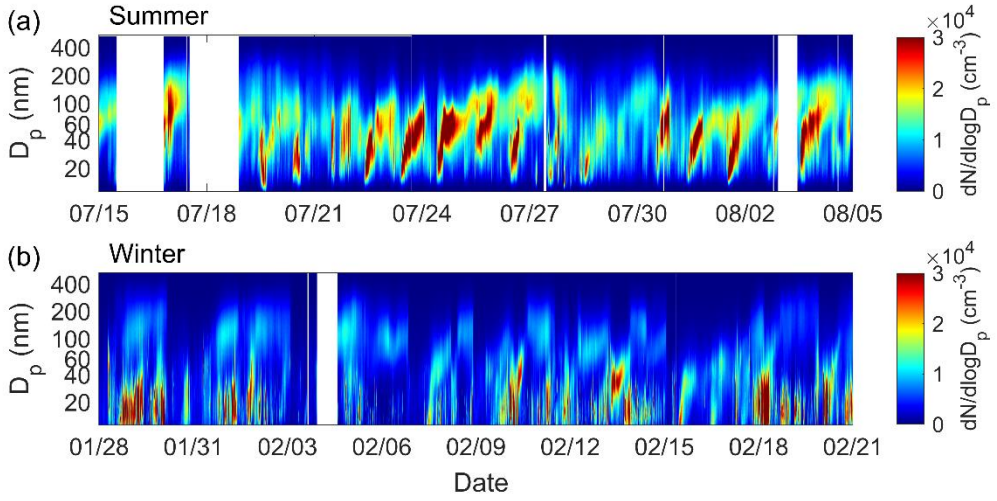

Figure R5. Time series of the aerosol particle number size distribution measured by the SMPS during the **(a)** summer and **(b)** winter periods.

4. In line 178 – 181, the authors mention that the distributions of VSF for 150-nm particles were generally unimodal in both summer and winter. However, from Fig. 2(e), it seems that 150-nm particles were generally bi-modal with a non-volatile mode and a high-volatile mode in winter.

Re: Thanks for the comments. The description has been revised in **Lines 192-196**, as follows:

"For the 150-nm particles, the distributions were generally unimodal, with VSF of about 0.3-0.6 in the winter, but were almost bimodal with a non-volatile mode and a high-volatile mode in the summer, indicating the mixing and aging of the primary particles during growth to larger sizes during the winter sampling periods."

5. Section 3.3 compares the diurnal variation of particles volatility between summer and winter based on the mean VSF and VSF probability distribution function (VSF-PDF) as illustrated on Fig. 4, yet I was lost from line 229 to 236 when the number fraction of the low-volatile mode is discussed. Is the discussion still based on Fig. 4 or other figures in the manuscript?

Re: Yes, the discussion is still based on Fig. 4c-f. Actually, the less-volatile mode for both 40- and 150-nm particles was more significant during the summer. A statement has been included in the revised text, see **Lines 255-256**, as follows:

"In addition, the number fraction of the LV mode for both 40- and 150-nm particles is much lower during the winter (Figs. 4c-f)."

6. Fig. 5(a) presents the time series of the number concentrations of Non-BC, In-BC and Ex-BC 150-nm particles in summer and winter. While this work shall be the same as that presented in their previous publication (Chen et al., 2020), the number concentration of 150-nm particles in this manuscript seems to be different from that on Fig. 5(a) in Chen et al. (2020). The scale also looks different from that of other sizes as shown in Fig. S4 in the Supplement.

Re: Thank you for your careful check. Per your comments, we checked the data and found some are incorrect that used in Fig. 5(a) in this manuscript. We have updated the figure, as follows (see Figs. R6 and R7):

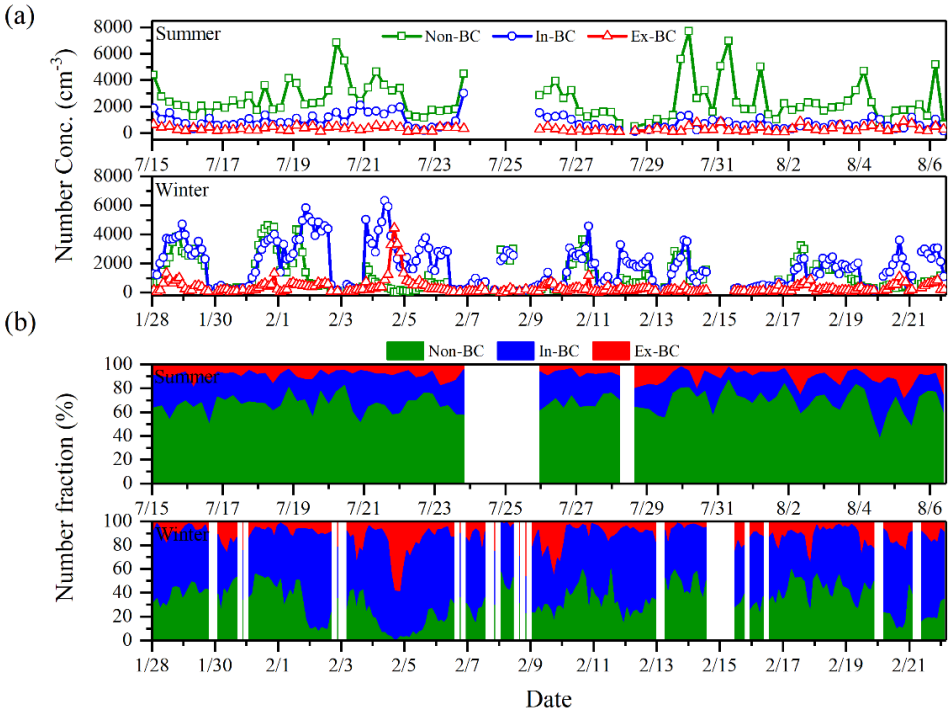

Figure R6. Summer (top) and winter (bottom) time series of **(a)** number concentrations and **(b)** number fractions of Non-BC (in green), In-BC (in blue), and Ex-BC (in red) 150-nm particles.

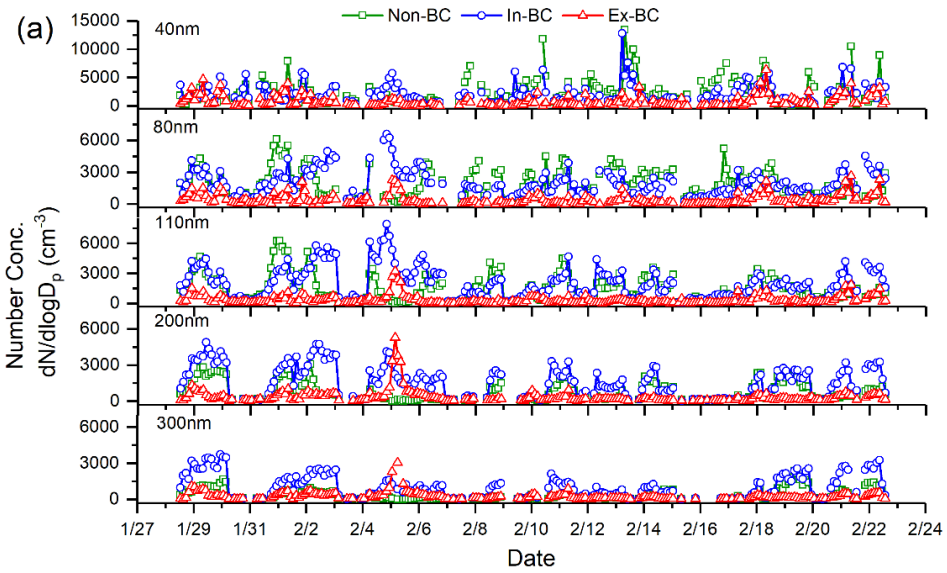

Figure R7. Temporal variation of number concentrations of Non-BC (in green), In-BC (in blue), and Ex-BC (in red) in the range of 40-300 nm particles during the winter periods.

7. In line 285 – 288, the authors state: "non-BC concentration / fraction in winter exhibits a daily minimum and nightly maximum". It is not clear to me whether this observation is supported by Fig. 7. For example, for 40-nm particles, there seems to be a morning peak at 08:00 LT for non-BC concentration in winter. For 150-nm particles, I am not sure whether there was any significant diurnal cycle for non-BC concentration / fraction. Please further elaborate to support your analysis.

Re: Yes, the diurnal cycle of Non-BC concentration for 150-nm particles is less obvious than that for 40-nm particles. A slight increase for both the number concentration and fraction can be found for 150-nm particles during nighttime. The average Non-BC number concentration was ~1470 cm^{-3} during nighttime (21:00-05:00 LT), and the number fraction was ~40 %, while the average Non-BC concentration during daytime (06:00-20:00 LT) was ~942 cm^{-3}, and the corresponding fraction was ~30 %, showing Non-BC concentration/fraction was lower during daytime and higher during nighttime. According to the reviewer's suggestion, we have added more detailed descriptions in the revised version, see **Lines 340-343**, as follows:

"Compared to the summer, the Non-BC concentration/fraction in the winter was lower during daytime and higher during nighttime, with the average number concentration of ~1470 cm^{-3} during nighttime (21:00-05:00 LT), corresponding to number fraction of ~40 %, but only ~942 cm^{-3} (~30%) during daytime (06:00-20:00 LT)."

8. The analysis method for the ratio of BC diameter discussed in Section 3.6 should be added in Section 2.

Re: Revised.

Reference

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