

A point-by-point response to reviewers

Dear Editor,

We are very pleased to submit a revised manuscript entitled with “Characterizing the volatility and mixing state of ambient fine particles in summer and winter of urban Beijing” for possible publication in journal of ACP.

I'd like to thank you for your efforts and time on handling the paper. I also would like to thank the reviewers for their valuable comments and suggestions, all of which have been considered carefully during the revision (a point-by-point response to reviewers as follows). We believe all the comments from the reviewers have been addressed, and the paper have been greatly improved after the revision.

Yours sincerely,

Fang Zhang

On behalf of all authors

Comments from the reviewers:

Reviewer #1

This contribution presents size-dependent volatility properties of urban aerosols in Beijing during summer and winter time using VTDMA. This work tries to calculate and compare the number concentration of In-BC, Ex-BC and Non-BC particles from the particle volatility distribution after heating up to 300 °C for aerosols under the studied two seasons. In addition, the extent of aging of BC particles was characterized based on current datasets. Although the comprehensive dataset presented in the manuscript is interesting and may carry certain values for the scientific community, the major conclusion separating In-BC, Ex-BC and Non-BC seems to be poorly supported by current analysis. The mixing state of BC particles derived from VTDMA data is highly uncertain or even not correct, and the uncertainties were not carefully analyzed in the manuscript. I therefore do not recommend publication in ACP.

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

Major comments:

The major results of current manuscript were based on the assumption that in urban areas refractory component in sub micrometer aerosols consists mainly or solely of BC. This assumption might not be true that there are some other important non-volatile aerosol compounds in submicron aerosols, for instance, some extremely low-volatility organic material that does not evaporate even at 300 °C. Nowadays, too many studies (Cappa & Jimenez, 2010; Häkkinen et al., 2012; Poulain et al., 2014; Wang et al., 2017; Zhang et al., 2016) confirmed that besides BC, low-volatility oxygenated organic aerosols also existed in the non-volatile fractions in particles. Specifically, Xu et al. (2016) measured the chemical composition of PM₁ after heating at a rural site (Detling, Kent) and found at 250 °C, OA has the largest contribution (~ 40 %) to the residual mass. Hence, based on aerosol volatility properties, you may not be able to characterize the mixing state of BC particles.

Re: The reviewer is right that there may be some other non-volatile compounds in submicron aerosols will not evaporate even at 300 °C, such as the extremely low-volatile organic material. 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 OA factors 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. 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. Some discussions about this issue have been included in the revised paper, see **section 2.4** or **Lines 177-199**, as follows:

“Therefore, in this study, the retrieval of the mixing state of BC is based on the assumption that the refractory component in sub micrometre aerosols consists mainly or solely of BC. This assumption might not be true that there are some other important non-volatile aerosol compounds in submicron aerosols, for instance, some extremely low-volatility organic material that does not evaporate even at 300 °C (Cappa & Jimenez, 2010; Häkkinen et al., 2012; Poulain et al., 2014; Zhang et al., 2016; Wang et al., 2017). To investigate the composition of the refractory component and verify whether they consist mainly of BC, we first quantify the mass concentration of these non-volatile material, which 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). Then, we correlate it with the BC mass concentrations measured by AE33, which are shown in Fig. 3. 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 OA factors 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. S2), 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.”

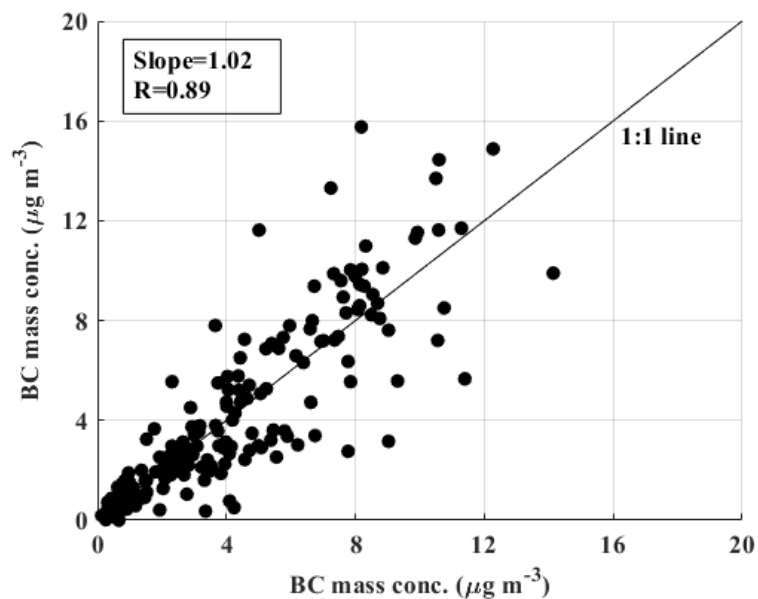


Figure R1. Black carbon (BC) mass concentration measured by AE33 vs. the non-volatile mass concentration estimated from the VTDMA for winter 2019 periods. Estimation of the non-volatile mass concentration was made assuming a density of 1.6 g cm^{-3} .

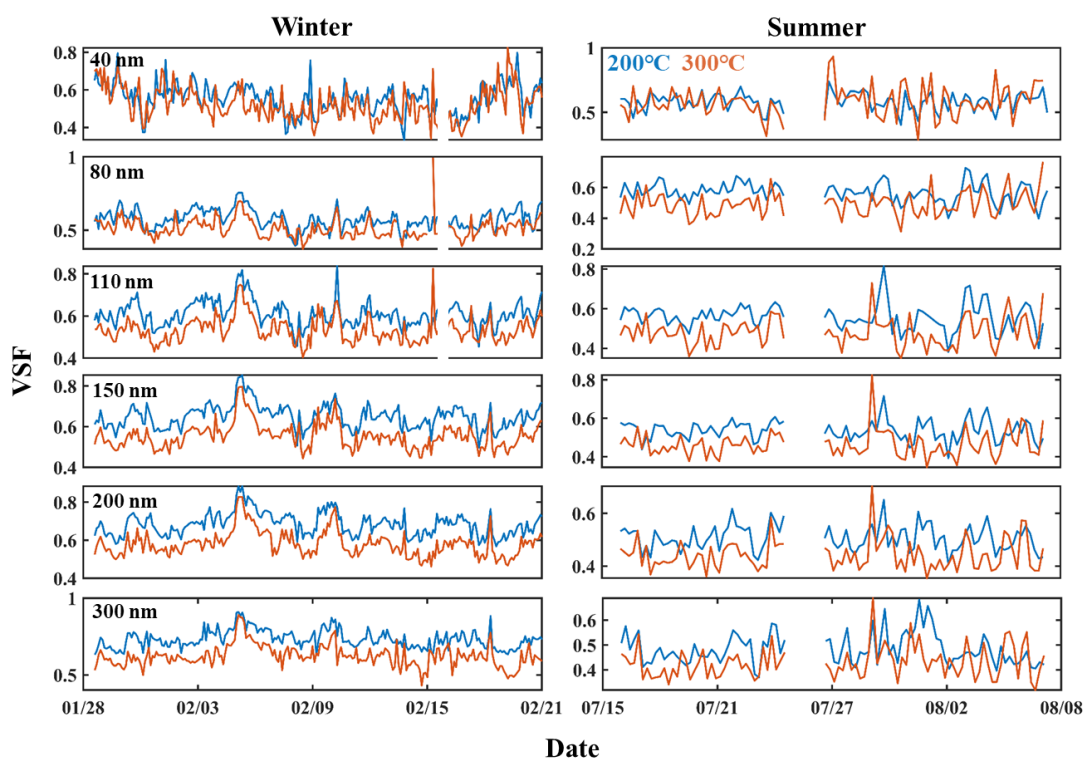


Figure R2. The mean volatility shrink factor (VSF) of all measured size particles after heating at 200 (blue line) and 300 °C (red line) during the winter and summer periods.

Then, it comes with my second comment regarding the method this manuscript used to category In-BC, Ex-BC and Non-BC particles as given in line 146-149. Even though this method has been used in previous studies as in Wehner et al. (2009) and Cheng et al. (2012), it is actually out of date and not recommended to be employed to classify the mixing state of BC-particles. With VSF > 0.82, ambient particles could be composed of only BC, but also In-BC coating with non-volatile organics. Therefore, using current classification, significant uncertainties may be introduced into the estimation of the number fraction of different BC-containing particles. We now rely on some other techniques, for instance, SP2, VTDMA-SP2, SP-AMS to study the mixing state of BC-containing particles.

Re: It is true that currently some advanced techniques such as SP2 and SP-AMS were used widely to investigate the mixing states of BC particles, which is more accurate and intuitive. However, due to the lack of these instruments, and considering various studies have also used the VTDMA to estimate the mixing states of soot particles (Philippin et al., 2004; Rose et al., 2011; Levy et al., 2014; Zhang et al., 2016), so we tried to retrieve the particle mixing state by VTDMA. In previous studies, particles with different volatile fractions (i.e., different VSF values) at 300 °C are often assumed to be soot particles with different mixing states (Cheng et al., 2006; Wehner et al., 2009; Cheng et al., 2012). The further evidence that support this retrieved results in this study is included by comparing the retrieved Ex-BC with that measured by SPAMS data (see the next comment).

Moreover, in line 161-162, you concluded your results were reliable for deriving the mixing state of BC by comparing with SPAMS results. However, Fig.2 in your previous publication (Chen et al., 2020) only compared the total BC-containing particles; separation of Ex-BC particles from In-BC particles was not performed. I did not see any other evidence that could support your conclusion here. If you have, please specify.

Re: 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 retrieve mixing state of BC in the study periods. We have added this part of evidence to the revised paper, see **Lines 200-208**, as follows:

“To further verify the reliability of the retrieved results, the number fraction of Ex-BC calculated from the VTDMA is compared with the measurements by single particle aerosol mass spectrometer (SPAMS) (Bi et al., 2015), as shown in the Fig. 4. It exhibits that the variations of number fractions of the Ex-BC particles retrieved from VTDMA are well consistent with that measured by SPAMS, confirming that the method is reliable for deriving the mixing state of BC during the campaign in urban Beijing.”

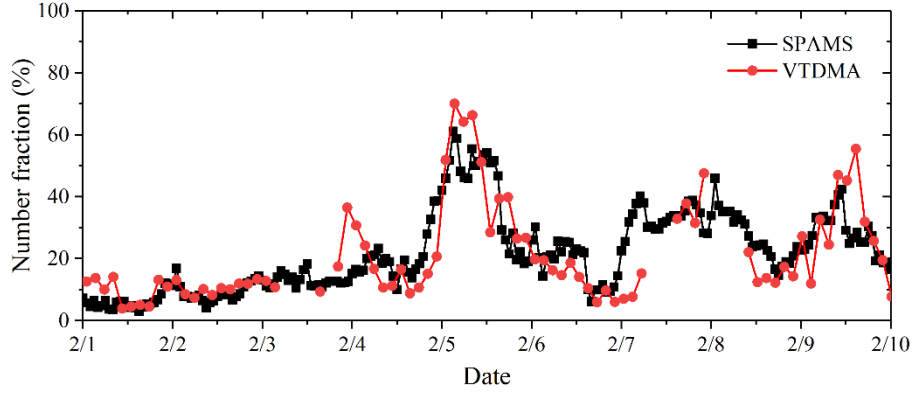


Figure R3. Time series of number fraction of Ex-BC particles measured by SPAMS (in black) and calculated from VTDMA (in red), the 200 nm particles from VTDMA are chosen.

Large uncertainties using Eq. 1 in your manuscript to calculate completely volatile particles may arise. Transportation efficiency as I understand was determined by volatility measurements of NaCl particles or other non-volatile particles at 300 °C in your study. However, ambient aerosols with different volatility could evaporate differently, resulting in different particle size after heating. Therefore, you have to at least consider the number size distribution of particles after heating into the determination of the transportation efficiency. In other words, number concentration of completely volatile particles should be dependent on the volatility of your ambient particles, thus your Eq.1 should be revised as a function of your VSF or your volatility distribution after heating.

Re: The transportation efficiency η was affected by particle diffusional and thermophoretic losses in the sampling lines, and determined at each particle diameter and heating temperature with NaCl particles in laboratory calibrations (Philippin et al., 2004; Cheung et al., 2016), which do not evaporate at the temperature (300 °C) used in our measurements. In this study, we have considered the number size distribution loss of NaCl particles after heating at 300 °C to calculate the η . To describe more detailly, we add an equation to explain the η in line 148, as follows:

$$\eta_{D_p,T} = \frac{N_r(NaCl)}{N_{D_p}(NaCl)} \quad (1)$$

A statement has also been included in the revised version, see **lines 141-143**, as follows:

“In this study, $\eta_{D_p,T}$ at each particle size is determined from the number concentration of sodium chloride (NaCl) particles before and after heating at 300 °C (i.e. $\eta_{D_p,T} = N_r(NaCl)/N_{D_p}(NaCl)$).”

In section 3.3, you studied the effect of the formation and growth of particles on their volatility. However, your discussion and analysis is not thorough. How frequent of NPF events occurred during your studied seasons stated in your manuscript? Did you select the data of the days of NPF events to drive your conclusion, otherwise, how could the

influence of other atmospheric processes be neglected? What are the sources of 40 and 150 nm particles? Your 40 nm particles could be newly formed particles or a mixture of newly formed particles after growth with pre-existing particles. Your analysis should guide the reader to a clear process level, otherwise your conclusion will be quite difficult for us to sink into. Moreover, are the plots in Fig. 4a-h the average or median values of the whole campaign or of the NPF days? I think Fig. 4g or Fig. 4h in your manuscript present a certain NPF day, how could you compare general patterns with a case event? How could we reader withdraw general information or conclusions by case studies?

Re: ① The NPF events took place frequently during the summer sampling periods, with about 10 NPF events occurred (see Fig. R4). The time series of the aerosol particle number size distribution measured by the SMPS during the campaign have been added to the supplement (Fig. S5).

② The pre-existing 40-nm particles could be much fewer as the number concentration was much lower as compared with the contribution by the growth of nucleated particles (Wang et al., 2018). Therefore, the 40-nm particles during the NPF events can represent the newly formed particles.

③ The plots in Fig. 4a-h are the average values of the whole campaign. After checking the original data, we just have updated the Fig. 4g and 4h, or see Fig. R5.

Some discussions have been included in the revised text of **Lines 281-285** and **Lines 290-295**, as follows:

“Here, the VSF-PDFs of 40- and 150-nm particles are shown. The variation of pre-existing 40-nm particles could be much fewer as the number concentration was much lower as compared with the contribution by the growth of nucleated particles (Wang et al., 2018). Therefore, the 40-nm particles during the NPF events can represent the newly formed particles, and the 150-nm particles represent the pre-existing particles.”

“Fig. 8g 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. S5). 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.”

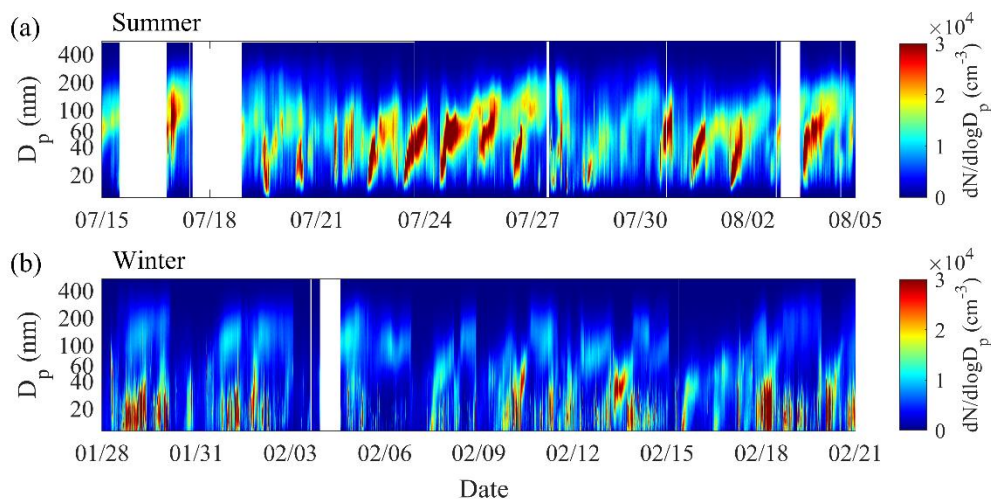


Figure R4. Time series of the aerosol particle number size distribution measured by the SMPS during the (a) summer and (b) winter periods.

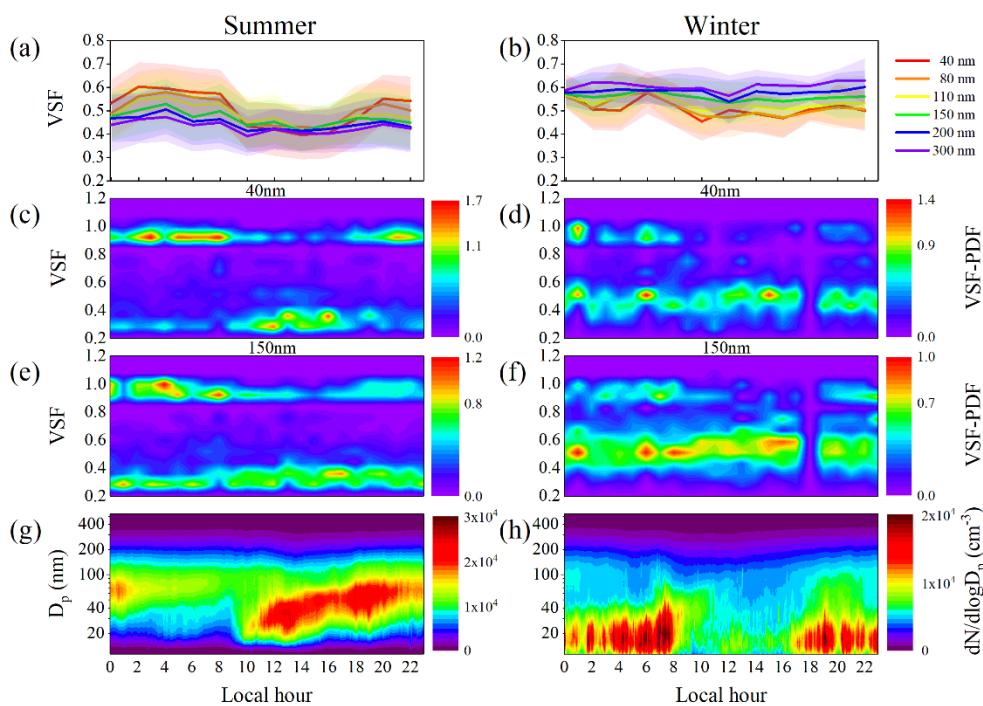


Figure R5. Diurnal variation of (a-b) mean VSF for all measured dry particle sizes, (c-f) mean VSF-PDF for 40- and 150-nm particles, and (g-h) mean particle number size distribution during the summer (left) and winter (right) periods. The shade regions in (a-b) denote the standard deviations.

In section 3.6, you characterized coating thickness by DP/DC ratio. However, I did not find any description or definition about Dp and Dc. You obtained a volatility distribution of particles after heating. How did you get Dc from this distribution? The determination of Dc was quite difficult, even with a SP2, which could accurately

measure the mass of BC. Zhang et al. (2016) gave a thorough discussion of the uncertainties associated with determining D_c from SP2 measurements due to the morphology effect. Similar discussion of the uncertainties in determining D_c should be given in the manuscript.

Re: Bimodal distribution was observed in VTDMA measurements, representing the size distributions of Ex-BC and In-BC cores respectively. The peaks at initially prescribed size ranges represent Ex-BC particles because they did not undergo a size change after heating. The peaks at smaller size represent the sizes of In-BC cores. An example of the measured size distribution is shown in Fig. R6. Here, D_p refers to the peak value of the DMA₁ selected size distribution (particles with diameters of 150 nm are presented as examples), and D_c refers to the peak diameter of residual particles after heating at 300 °C. The heated particles should be more compacted with nearly spherical core, which is expected to be very different from uncoated fresh BC that are with fractal chain morphology. In the revised paper, we have given the definition about D_p and D_c in **Lines 166–168**, as follows:

“Here, particles with diameters of 150 nm are presented as examples (Fig. 4), D_p refers to the peak value of the DMA₁ selected size distribution, and D_c refers to the peak diameter of residual particles after heating at 300 °C.”

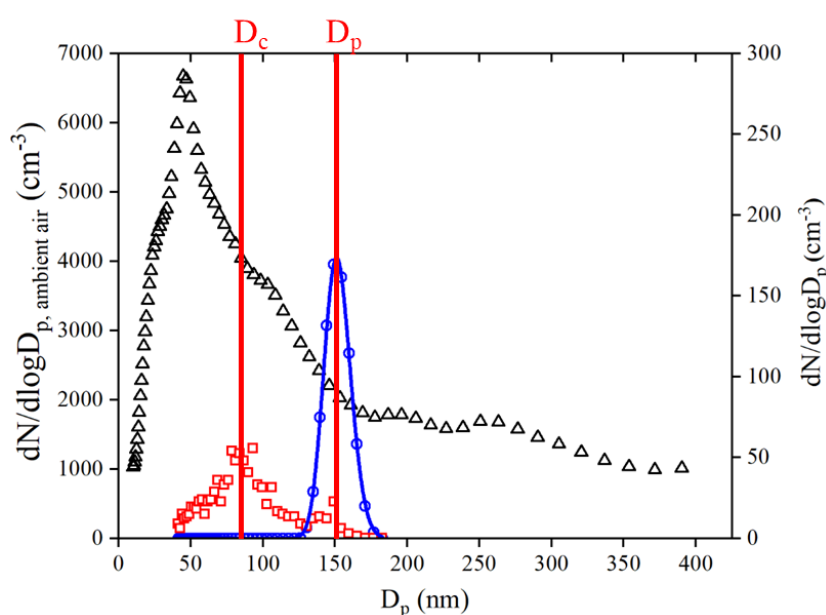


Figure R6. Number size distributions of ambient aerosols (in black), DMA₁-selected particles with D_p equal to 150 nm (in blue), residual particles after heating at 300 °C (in red), and the fitting curves.

Reference

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Zhang, Y., Zhang, Q., Cheng, Y., Su, H., Kecorius, S., Wang, Z., Wu, Z., Hu, M., Zhu, T., Wiedensohler, A., and He, K.: Measuring the morphology and density of internally mixed black carbon with SP2 and VTDMA: new insight into the absorption enhancement of black carbon in the atmosphere, *Atmos. Meas. Tech.*, 9, 1833–1843, <https://doi.org/10.5194/amt-9-1833-2016>, 2016.

A point-by-point response to reviewer

Reviewer #2

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°C. The non-volatile particles that remained in the particle phase upon heating up to 300°C 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 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 **section 2.4** or **Lines 172-208**, as follows:

“Therefore, in this study, the retrieval of the mixing state of BC is based on the assumption that the refractory component in sub micrometre aerosols consists mainly or solely of BC. This assumption might not be true that there are some other important non-volatile aerosol compounds in submicron aerosols, for instance, some extremely low-volatility organic material that does not evaporate even at 300 °C (Cappa & Jimenez, 2010; Häkkinen et al., 2012; Poulain et al., 2014; Zhang et al., 2016; Wang et al., 2017). To investigate the composition of the refractory component and verify whether they consist mainly of BC, we first quantify the mass concentration of these non-volatile material, which 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). Then, we correlate it with the BC mass concentrations measured by AE33, which are shown in Fig. 3. 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 OA factors 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. S2), 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.

To further verify the reliability of the retrieved results, the number fraction of Ex-BC calculated from the VTDMA is compared with the measurements by single particle aerosol mass spectrometer (SPAMS) (Bi et al., 2015), as shown in the Fig. 4. It exhibits that the variations of number fractions of the Ex-BC particles retrieved from VTDMA are well consistent with that measured by SPAMS, confirming that the method is

reliable for deriving the mixing state of BC during the campaign in urban Beijing.”

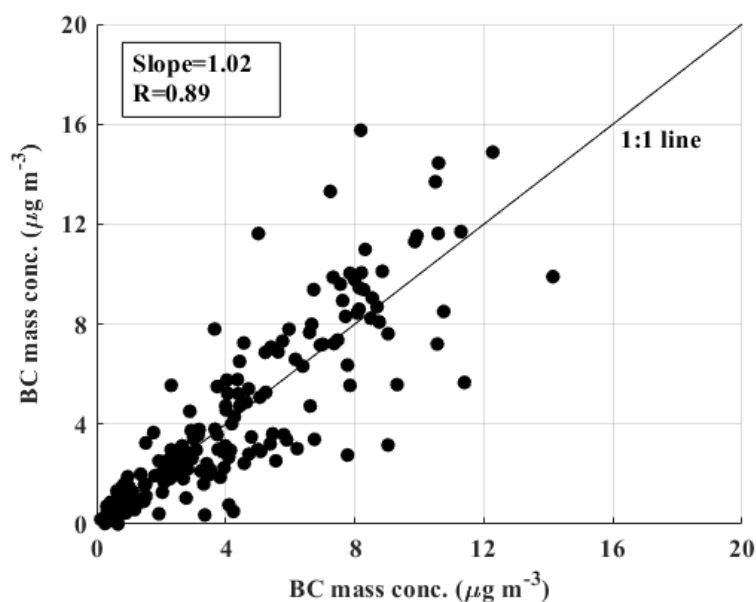


Figure R1. Black carbon (BC) mass concentration measured by AE33 vs. the non-volatile mass concentration estimated from the VTDMA for winter 2019 periods. Estimation of the non-volatile mass concentration was made assuming a density of 1.6 g cm^{-3} .

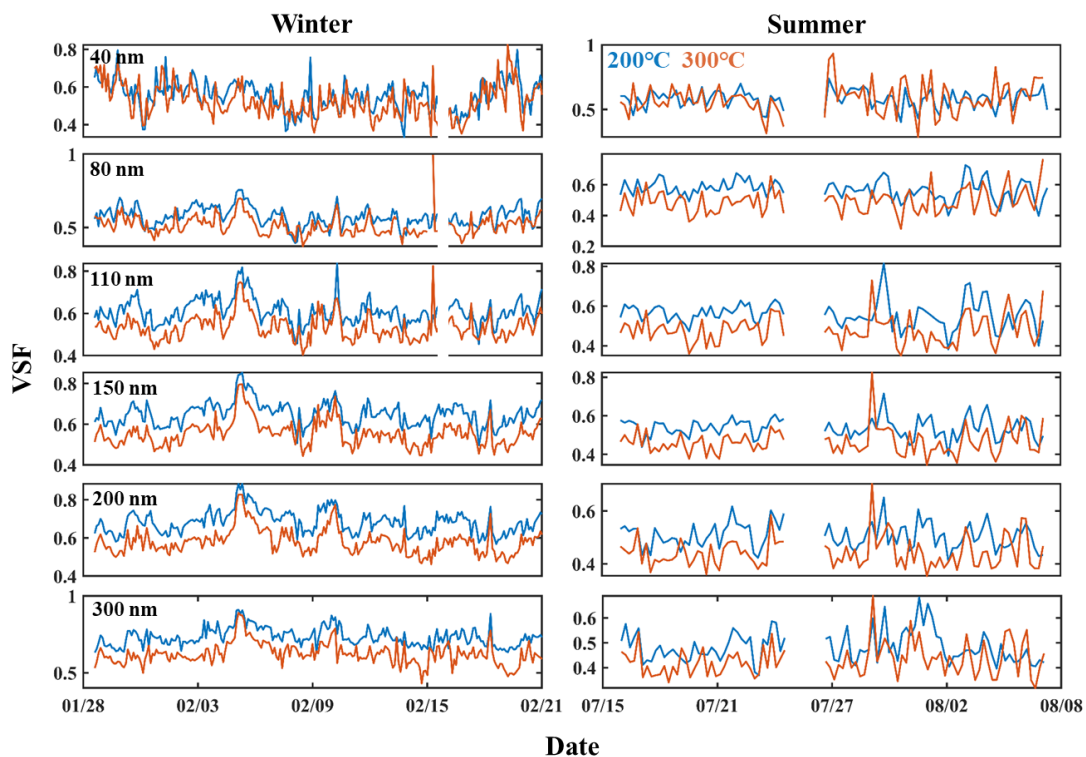


Figure R2. The mean volatility shrink factor (VSF) of all measured size particles after heating at 200 (blue line) and 300 °C (red line) during the winter and summer periods.

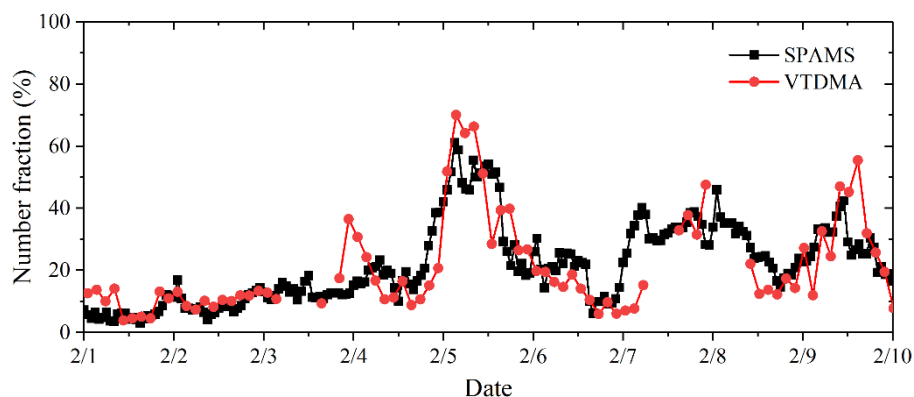


Figure R3. Time series of number fraction of Ex-BC particles measured by SPAMS (in black) and calculated from VTDMA (in red), the 200 nm particles from VTDMA are chosen.

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 257-277**, 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 size-resolved 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 with prevailing northerly wind. The northwest clusters (C2 and C3) were predominant, which associated with the high $PM_{2.5}$ concentrations (Wang et al., 2015). The VSF_{mean} difference of small particle size among different clusters is greater than that of large size, implying the more diverse sources of small particles. In the summer, the air masses were classified into six clusters, with prevailing southerly wind (C1 and C3). It shows that the VSF_{mean} values in both the winter and summer are not closely associated with the variations of trajectories, or the impacts of regional transportation on volatility of the fine aerosol particles are complex. Obviously, the seasonal differences in VSF_{mean} are more significant than that among different clusters especially for larger size particles, e.g. with lower VSF_{mean} value of ~ 0.47 in the summer than that in the winter (~ 0.55).”

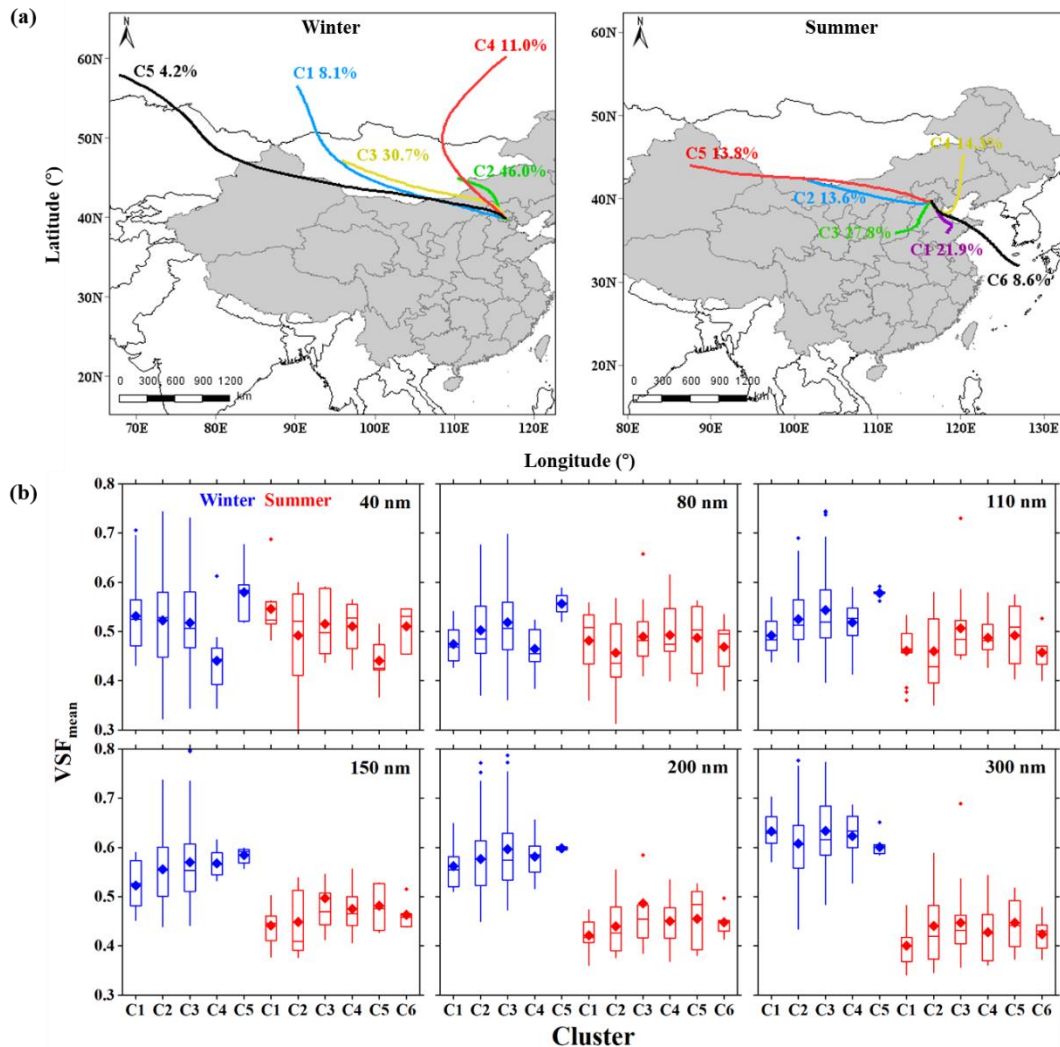


Figure R4. (a) The 72-h back trajectories arriving at Nanjiao site during the winter (left) and summer (right) periods. C1-C6 represent Cluster 1-Cluster 6 respectively. The percentages present the relative occurrences. (b) Box diagram for the mean volatility shrink factor (VSF_{mean}) of all selected diameter particles (40-300 nm) from different clusters during the winter (blue) and summer (red) 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. S5). Fig. R5 shows that almost no NPF events occurred during the campaign. Some statements have been included in the revised text of **Lines 290-295**, as follows:

“Fig. 8g 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. S5). 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.”

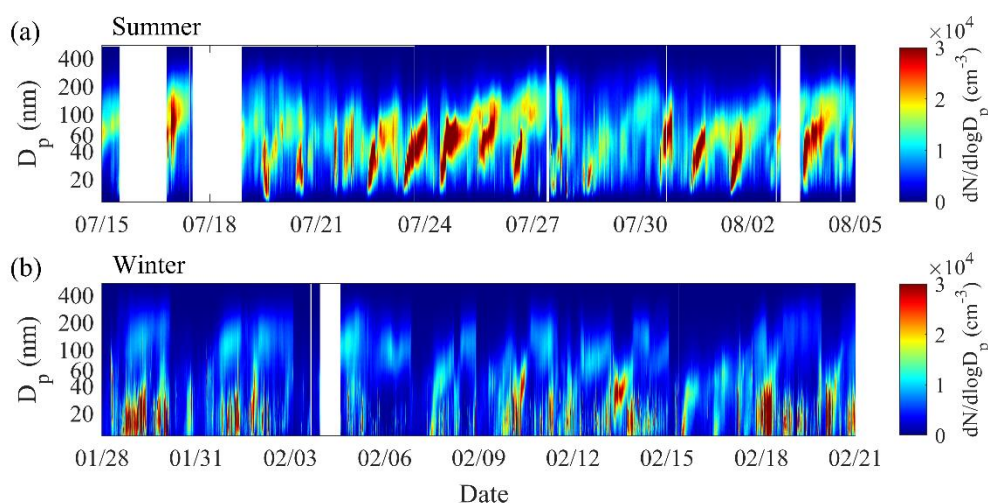


Figure R5. Time series of the aerosol particle number size distribution measured by the SMPS during the (a) summer and (b) winter periods.

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 223-227**, 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 313**, 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. 8c-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):

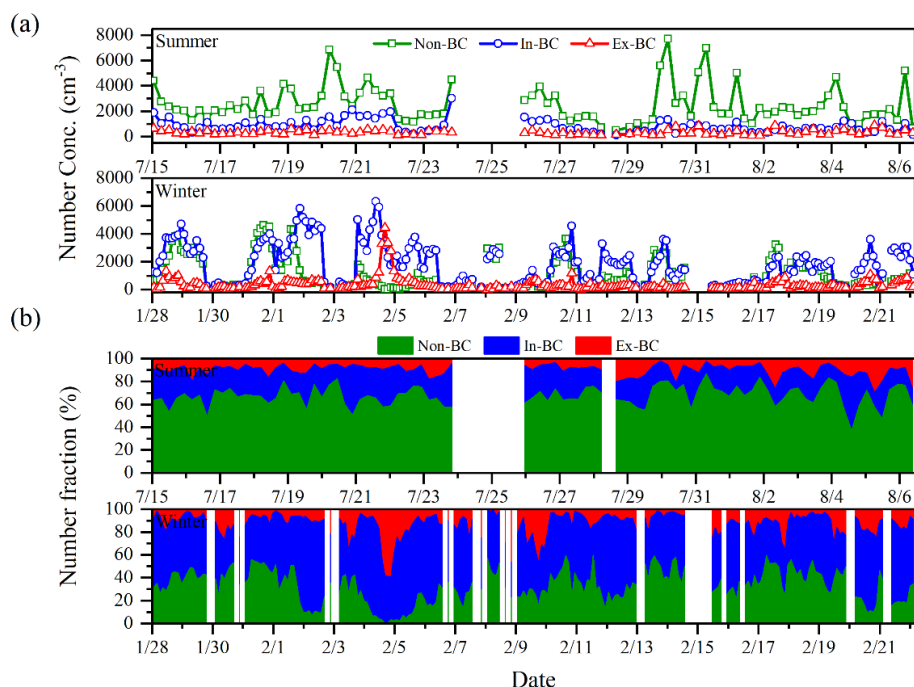


Figure R6. Summer (top) and winter (bottom) time series of (a) number concentrations and (b) number fractions of Non-BC (in green), In-BC (in blue), and Ex-BC (in red) 150-nm particles.

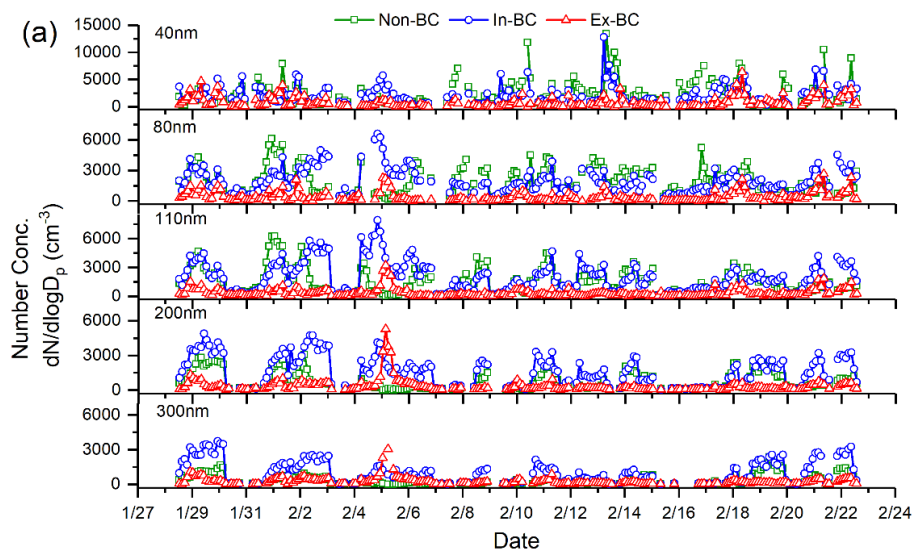


Figure R7. Temporal variation of number concentrations of Non-BC (in green), In-BC (in blue), and Ex-BC (in red) in the range of 40-300 nm particles during the winter periods.

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 $\sim 1470 \text{ cm}^{-3}$ during nighttime (21:00-05:00 LT), and the number fraction was $\sim 40 \%$, while the average Non-BC concentration during daytime (06:00-20:00 LT) was $\sim 942 \text{ cm}^{-3}$, and the corresponding fraction was $\sim 30 \%$, 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 366-369**, 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 $\sim 1470 \text{ cm}^{-3}$ during nighttime (21:00-05:00 LT), corresponding to number fraction of $\sim 40 \%$, but only $\sim 942 \text{ cm}^{-3}$ ($\sim 30\%$) 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.

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