A point-by-point response to reviewer

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 Atmospheric Chemistry and Physics.

We'd like to thank you for your efforts and time on handling the paper. We also thank the reviewer 1 for the further comments, which we have addressed in the revision (a point-by-point response to the reviewer as follows).

Yours sincerely,

Fang Zhang

On behalf of all authors

Comments from the reviewer 1:

Even though the author made some revisions to their manuscript and answered some of my comments, I still have some doubts with respect to their answers and hope the authors could clarify:

1. Fig 3 in your revised manuscript. How could you compare the bulk BC mass concentration with size-resolved one, as VTDMA measured the size-resolved VSF. And you obtained a slope of 1.02, which makes you results even suspicious. The bulk one should be larger than the size-resolved one, as the mode size of BC-containing particles should be larger than 300 nm.

Re: Thanks for the comments. We are afraid that the method for calculating the bulk mass concentration of the non-volatile material in this study has not been addressed clearly. Therefore, in the revision, we have included more details to clarify this, see **Lines 173-181**, or as follows,

"…To investigate the composition of the refractory component and verify whether they consist mainly of BC, we first quantify the bulk mass concentration of these non-volatile material. For the calculation, the number concentrations of the residual non-volatile particles at each size (40, 80, 110, 150, 200 and 300 nm) is calculated by integrating the residual PNSD of each selected particle size that directly measured by VTDMA at the temperature of 300 ℃. Then, the size resolved mass concentration of

the residual non-volatile particles was calculated by assuming the particles are spherical and with a density of 1.6 g cm^{-3} (Häkkinen et al., 2012; Poulain et al., 2014). Finally, by fitting the size-resolved mass concentration and integrating the fitted curves, the bulk mass concentration of non-volatile particles was retrieved…"

2. Similar as figure 4. Did you use size-resolved information from SPAMS, otherwise how did you compare this two information? There should be some difference, otherwise it is erroneous. Please clarify.

Re: According to the reviewer's comments, we have updated and compared the results at 200 nm from both the VTDMA and SPAMS instruments (Fig. R1) in the revised text, see **Lines 194-205**, or as follows,

"…To further verify the reliability of the retrieved results, the number fraction of Ex-BC and In-BC for 200 nm particles calculated from the VTDMA is compared with the measurements by single particle aerosol mass spectrometer (SPAMS), as shown in the Fig. 4. The comparison can only be confined to the size of 200 nm because which is the lower limit of the measured size for SPAMS (Bi et al., 2015). It exhibits that the variations of number fractions of both the Ex-BC and In-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…"

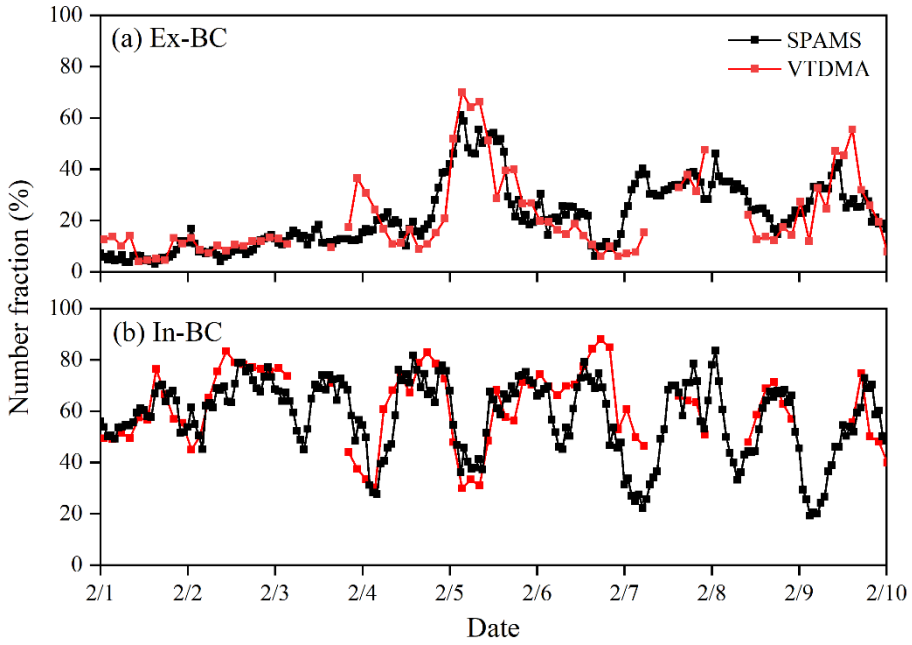

Figure R1. Time series of number fraction of **(a)** Ex-BC particles and **(b)** In-BC particles measured by SPAMS (in black) and calculated from VTDMA (in red), the 200 nm particles from VTDMA and SPAMS are chosen for comparison.

3. Since SPAMS could measure the mixing state of BC-containing particles, which is

probably more accurate than VTDMA, what is the reason using VTDMA instead of SPAMS in current study? Your study is neither introducing a new method (actually out of date in my opinion), nor presenting a new result (actually I see you have published half of them in Chen et al. (2020)). What is the reason to use these data again? Then you should emphasis the contribution or objectives for current dataset, for instance, modifying your intro part as well as the result structure.

Re: Thanks a lot for the comments.

We agree the reviewer that the SPAMS could measure the mixing state of BC-containing particles, which is probably more accurate than VTDMA. But, the dataset of VTDMA can be used to investigate the aerosol volatility and link the volatility to the particle's formation and growth during cold and warm seasons. In addition, because only a short time period of synchronous data from SPAMS and VTDMA was obtained during the winter campaign, we just used the SPAMS data to verify the inverted mixing state of BC particles. Also, because of restrictions on the data sharing terms, we cannot obtain the right to use and analyze these data from SPAMS more deeply. As the reviewer stated, SPAMS is probably more accurate than VTDMA. In the future, if more dataset from SPAMS is available, further study and analysis can be done.

In this study, we mainly present the size-dependent VSF to characterize and contrast the volatility behavior of fine particles between cold and warm seasons of urban Beijing. The mixing state of ambient fine particles, which is retrieved from the size-resolved VSF, is further analyzed and compared between the two seasons with an aim of understanding of the effects of particle growth on volatility and mixing state in different atmospheric conditions. While Chen et al (2020) only focused on retrieving and quantifying the mass and number concentrations of BC particles with different mixing states. In addition, the data used in this study includes measurements from both summer and winter, while in Chen et al (2020), only winter data were analyzed. More importantly, this study is with new findings that the non-BC particles that primarily from nucleation processes accounted for 52–69 % of the total number concentration in the summer. This thus leads to more volatile particles in the summer than in the winter. This is further evidenced from the diurnal cycles of the retrieved aerosol mixing state and an outstanding high-volatile mode around noontime on new particle formation (NPF) days in summer. While Chen et al (2020) found that large proportions of aerosols are BC-containing particles in the winter of urban Beijing, implying the dominant role of BC in increasing aerosol loadings due to their rapid aging in polluted urban area.

According to the reviewer's suggestion, we just have included some more statements to clarify and emphasis the contribution or objectives for current dataset in the main text and conclusion results (**Lines 77-85, 412-430** or as follows).

"…Here, we used the size-dependent VSF as a parameter to characterize the volatility behavior of fine particles in cold and warm seasons of urban Beijing; In addition, the mixing state of ambient fine particles in the summer, which is retrieved

from the size-resolved VSF, is also compared to that in the winter. By contrasting the volatility and mixing state in the two seasons, this study is with aim of linking the aerosol particles volatile properties and mixing state to its atmospheric chemical and physical processes under different ambient conditions in polluted urban areas…"

"…In this study, the volatility of the fine particles is characterized as VSF and the results from wintertime and summertime are shown and compared. Results show that the measured VSF-PDF is almost always bimodal, with one high-volatile and one less- or non-volatile mode, both in the summer and winter. The mean VSF-PDF has a pronounced HV mode in the summer, generally with a VSF minimum at ~0.2, while in the winter a broad MV mode spans much of the measured VSF range (with VSF minimum at 0.45-0.65), reflecting lower average volatility in the winter. Diurnal variations in VSF of 40-nm particles are evident only in the summer, with a prominent HV mode resulting from new particle formation and growth present around noontime and early afternoon and a dominant LV mode during nighttime. No such feature is evident in the winter measurements. The mixing state of ambient fine particles was calculated from the size-resolved VSF and the results for summer and winter compared and contrasted. On average, nucleation and particle growth results in a dominant population of volatile, Non-BC, particles, which account for 52–69 % of the total concentration in the measured size range in the summer. However, black carbon (BC)-containing particles contributed 67–77 % toward the total number concentration in the winter, indicating that BC particles are a dominant component of the wintertime Beijing. The diurnal cycles of the retrieved particle mixing state in the summer further show that rapid photochemical processing and nucleation are the main contributors to Non-BC particles. By analyzing the ratio of the BC particle diameter before and after heating at 300 ºC, we show that the BC particles are more thickly coated in wintertime than in summertime. The observed results on aerosols volatility and mixing state in this study can help understanding the formation and growth of fine particles and determining their effect on environment and climate…"

4. The discussion part for Sect 3.3 is too weak without sufficient comparison with other studies that deal with particle nucleation and growth. Thus only quite limited information could be extracted for current study.

Re: More discussions have been included in the revised paper, see **Lines 283-293**, as follows:

"…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 during the campaign. It has been shown that ~97 % of newly formed particles are volatile because they are dominated by non-refractory sulfate and organics in Beijing (Wehner et al., 2009). Wu et al (2017) also observed that a clear decrease in VSFs for 30- and 50-nm particles in rural area of north China during the NPF events,

indicating that more volatile compounds could be produced during the growth process of newly formed particles. However, some earlier campaign measurements that were conducted in various atmospheric environments, such as urban (Sakurai et al., 2005), and forest (Ehn et al., 2007), showed that the volatility of newly formed particles varied with the atmospheric environments, indicating distinct particle growth mechanisms....”

Reference

Bi, X., Dai, S., Zhang, G., Qiu, N., Li, M., Wang, X., Chen, D., Peng, P.a., Sheng, G., Fu, J., Zhou, Z., 2015. Real-time and single-particle volatility of elemental carbon-containing particles in the urban area of Pearl River Delta region, China. Atmos. Environ. 118, 194-202.

Ehn, M., Petäjä, T., Birmili, W., Junninen, H., Aalto, P., and Kulmala, M.: Non-volatile residuals of newly formed atmospheric particles in the boreal forest, Atmos. Chem. Phys., 7, 677-684, 10.5194/acp-7-677-2007, 2007.

Häkkinen, S. A. K., Äijälä, M., Lehtipalo, K., Junninen, H., Back man, J., Virkkula, A., Nieminen, T., Vestenius, M., Hakola, H., Ehn, M., Worsnop, D. R., Kulmala, M., Petäjä, T., and Riipinen, I.: Long-term volatility measurements of submicron atmospheric aerosol in Hyytiälä, Finland, Atmos. Chem. Phys., 12, 10771–10786, doi:10.5194/acp-12-10771-2012, 2012.

Poulain, L., Birmili, W., Canonaco, F., Crippa, M., Wu, Z. J., Nordmann, S., Spindler, G., Prévôt, A. S. H., Wiedensohler, A., and Herrmann, H.: Chemical mass balance of 300 ◦C non-volatile particles at thetropospheric research site Melpitz, Germany, Atmos. Chem. Phys., 14, 10145–10162, doi:10.5194/acp-14-10145-2014, 2014.

Sakurai, H., Fink, M. A., McMurry, P. H., Mauldin, L., Moore, K. F., Smith, J. N., and Eisele, F. L.: Hygroscopicity and volatility of 4–10 nm particles during summertime atmospheric nucleation events in urban Atlanta, Journal of Geophysical Research: Atmospheres, 110, https://doi.org/10.1029/2005JD005918, 2005.

Wu, Z. J., Ma, N., Größ, J., Kecorius, S., Lu, K. D., Shang, D. J., Wang, Y., Wu, Y. S., Zeng, L. M., Hu, M., Wiedensohler, A., and Zhang, Y. H.: Thermodynamic properties of nanoparticles during new particle formation events in the atmosphere of North China Plain, Atmospheric Research, 188, 55-63, https://doi.org/10.1016/j.atmosres.2017.01.007, 2017.