Reply to RC3

The manuscript investigates the daily and seasonal variability of soot particle mixing state coupling black carbon measurements and volatility tandem differential mobility analyzer data collected in a suburban site of the North China Plain (NCP).

The introduction reports that several other studies investigated the mixing state of soot particles using volatility measurements in the NCP. The introductions underlines that the present study differs from the previous ones because it encompasses two different seasons during a 5-month period. It is important to highlight what are the novelty of the results of this study compared to the previous ones, thanks to the multiple season measurements.

RE: In the revised manuscript, we further highlight the novelty of this study in the introduction. Most previous studies about mixing state of soot particles are based on the measurement of single-particle soot photometer (SP2) or soot particle aerosol mass spectrometer (SP-AMS). However, these measurement results only denote the accumulation-mode soot particles. This is because the lower measurement size limit of SP2 and SP-AMS is larger than 70 nm. VTDMA can make up this deficiency because its measurement is based on the aerosol number concentration, which is always high in the nucleation mode. This study for the first time reports that the anthropogenic emissions and aging processes have different effects on the mixing state of nucleation- and accumulation-mode soot particles. Thanks to the five-month VTDMA measurement, factors influencing the coating depth of soot particles are found and their relationships are established in this study. All findings are beneficial to study the aging processes of soot particles and improve the accuracy of modeled aerosol optical properties.

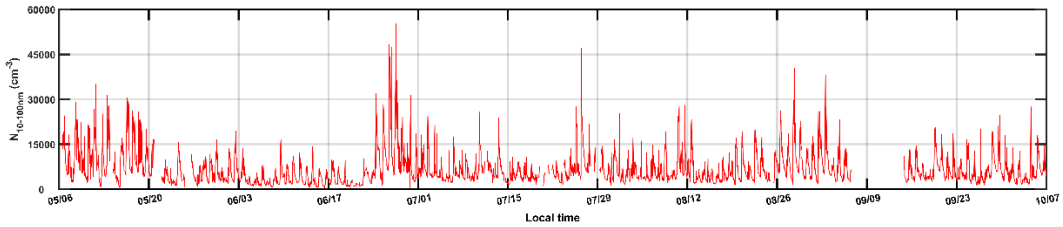
Some of the conclusions are not supported adequately by observations. Figure 4 shows that VV nucleation particles are characterized by a higher volatility during warmer months. On the other hand, the conclusion concerning the seasonal variability of nucleation mode soot particles relies on the assumption that nucleation mode soot is totally internally mixed. This assumption is not adequately supported by the presented results. For example, Figure 3 shows that nucleation mode particles are characterized by a multimodal distribution of SF, and soot could be responsible for the SV and NV peaks, which do not present the temperature trend discussed by the authors (higher values in warmer months). A deeper discussion of the results is encouraged. At line 441 the authors state that "Moreover, enhanced nocturnal liquid chemical reactions were responsible for the enhanced volatility of accumulation-mode soot particles in the nighttime." No clear evidence of liquid or heterogeneous phase reactions during night-time is provided in this study to support such a statement. Furthermore, soot particle coating is controlled by condensation of vapor phase compounds and coagulation with other particles (Bond et al., 2013; Ko et al., 2020). The link between soot coating and NPF events is quite speculative and is not clear (line 274). If the author are interested in investigating such a link, the particle number in the range 10 -100 nm should be investigated, rather than solely the change in

particle number concentration at 40 nm and 80 nm, as done at line 274.

RE: In the conclusions, we suggest that nucleation-mode soot particles were more volatile and had a higher degree of internal mixing than accumulation-mode soot particles, but the soot particles in any modes are not fully internally mixed in our measurement. Figures 6a and S4 suggest that the number fraction of nonvolatile particles (NF_{NV}) in nucleation-mode particles were always smaller than those in accumulation-mode particles but they are always larger than 0.

The line 441 sentence has been revised as: "Moreover, the enhanced nocturnal secondary aerosol formation was responsible for the enhanced volatility of accumulation-mode soot particles in the nighttime."In our previous study (Zhang et al., 2018), we found that the nocturnal chemical processes made the obvious increase of secondary aerosols such as nitrate at Xingtai.

The figure below shows the time series of the total number concentration of 10-100 nm particles ($N_{10\text{-}100\ nm}$). It suggests $N_{10\text{-}100\ nm}$ increased sharply on many days, indicating the frequent occurrence of NPF events. These newly formed particles should have an important impact on the growth of particles. The diurnal variation of $N_{10\text{-}100\ nm}$ is added in the Fig. S3 in the supplement.



Reference:

Zhang, Y., Du, W., Wang, Y., Wang, Q., Wang, H., Zheng, H., Zhang, F., Shi, H., Bian, Y., Han, Y., Fu, P., Canonaco, F., Prévôt, A. S. H., Zhu, T., Wang, P., Li, Z., and Sun, Y.: Aerosol chemistry and particle growth events at an urban downwind site in North China Plain, Atmos. Chem. Phys., 18, 14637-14651, 10.5194/acp-18-14637-2018, 2018.

Specific comments:

Line 166. Please specify if BC concentration was retrieved using the MAC suggested by the manufacturer or a site-specific MAC. In addition, the fact that BC is retrieved form optical measurements and the dependency of MAC on BC coating introduce some limitations in discussing BC concentration variability. The authors should mention this limitation in the discussion of results.

RE: The sentence is added in section 2.2.2 "According to the manufacturer's instructions, the MAC is calculated from the change in optical attenuation at channel 6 (i.e., 880 nm) in the selected time interval using the mass absorption cross section (MAC) of 7.77 $m^2\ g^{-1}$. The dependency of MAC on BC coating may introduce some uncertain in calculating MAC (Drinovec et al., 2015)."

Reference:

Drinovec, L., Močnik, G., Zotter, P., Prévôt, A. S. H., Ruckstuhl, C., Coz, E., Rupakheti, M., Sciare,

J., Müller, T., Wiedensohler, A., and Hansen, A. D. A.: The "dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation, Atmos. Meas. Tech., 8, 1965-1979, 10.5194/amt-8-1965-2015, 2015.

Line 228: It is not clear what the authors mean when they report the wavelength dependent size resolved SF-PDF. It looks like figure 3 reports the SF-PDF for different particle sizes, as selected by DMA1.

RE: It is a mistake. The words "wavelength dependent" are deleted. Thanks for the check.

Line 239 – 240: I suggest the authors to be more accurate, indicating that previous studies observed fresh BC in the lower bound of the accumulation mode. In fact, Levy et al. 2014 reports that the highest frequency of externally mixed fresh BC is observed at 150 nm, while Wu et al., 2017 reported that rBC size distribution measurements in Beijing peaked at about 200 nm, with a secondary less significant mode at 600 nm.

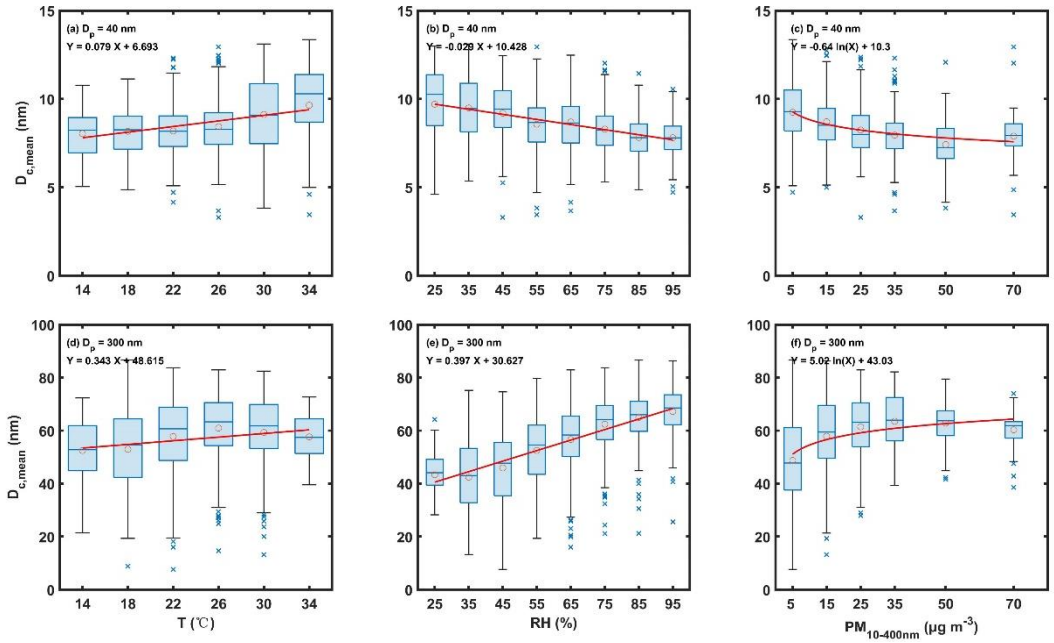
RE: Thanks for the suggestion. The sentence is revised as:"Some studies suggest that freshly emitted refractory particles (like BC) are primarily in accumulation mode. For example, Levy et al. (2013) reported that fresh BC was mostly in the 150–240 nm size range, while Wu et al. (2017) reported that refractory BC size distribution measurements in Beijing peaked at about 200 nm, with a secondary less significant mode at about 600 nm."

Paragraph 3.3.2 The statistical significance of the differences between day-time and night time observed in Figure 7 looks small. Could the authors comment on the observed variability?

RE: In Fig. 7, the daytime hours are 07:00~19:00, and the nighttime to 19:00~07:00. Figure S4 in the supplement suggests that NV mode particles increased obviously during the morning and evening rush hours, which influences the comparison results of SF_{mean} and NF_{NV} between the daytime and nighttime. The observed variability is mainly caused by the data in rush hours.

Figure 10: Did the author explore a different type of fitting for the relationship between coating thickness (Dc) and $PM_{10\text{-}400}$ (for example a logarithmic fitting rather than a linear fitting)?

RE: That is a good suggestion. The new fitting figures are shown below, showing a logarithmic relationship between D_c and $PM_{10\text{-}400}$. We add more discussion in this section.



Technical corrections:

Line 71-72. This statement is true in polluted environments

RE: This sentence has been revised to "This is why aerosol volatility can characterize the mixing state of soot particles in polluted environments".

Line 115. A list of the measured meteorological parameters should be added to complete this sentence.

RE: The sentence is added "The measured meteorological variables including ambient temperature, relative humidity (RH), wind direction and speed was used in this study.".

Line 137: The scope of DMA1 is to select particles with a specific mobility dimeter, thus it would be more accurate to write: "the water-based condensation particle counter (WCPC, model 3787, TSI Inc.), measuring the number of particles ranging from 10 to 400 nm.

RE: It is revised. Thanks.

Line 192: From Figure 2 it looks like in July wind from southeast was present instead of prevalent. Please revise the sentence accordingly.

RE: The sentence is revised as "In July, weak southeast winds were also present, beneficial to the accumulation of air pollutants due to the stable atmospheric environment.".

Line 194: please specify when wind speed is considered high. From figure 2 it is difficult to understand if winds in August were stronger than in the other months.

RE: It is not appropriate. The words "always strong" are deleted. The sentence is revised as "In August, the other prevailing wind was from the north, which was beneficial for atmospheric diffusion.".

Line 204: please add a reference for the assumed particle density.
RE: The reference of Y. Wang et al. (2017) is added.

Line 439: coating of soot takes place for condensation of newly formed material and not newly formed particles.
RE: It is revised. Thanks.

References:
Ko et al., Atmos. Chem. Phys., 20, 15635–15664, 2020
Bond et al., J. Geophys. Res.-Atmos., 118, 5380–5552, 2013