

Reply to RC1

This paper shows some VTDMA data from China, with the intent of investigating factors affecting the mixing state of refractory material in a polluted environment. The results are interesting and within the remit of ACP, and the manuscript is reasonably well written. Also, because measurements of this nature are particularly common, there is an element of novelty in its own right. However, this paper is slightly let down by the fact that the results are interpreted in a very self-contained manner, without really considering the wider body of knowledge. Addressing this should be fairly straightforward, however this could potentially change the character of the paper, therefore I recommend publication after 'major' corrections.

RE: The reviewer raised an important issue. In the revised manuscript, we further highlight the novelty of this study following a more comprehensive review of more previous studies. Our study is unique in the analysis of the volatility and mixing state of nucleation-mode soot-containing particles. The findings help understand the aging processes of soot particles and improving the accuracy of modeled aerosol absorption. Meanwhile, we add more results to validate our results against previous findings in the revised manuscript.

Major comments:

The authors give an interesting discussion investigating the potential reasons for the phenomena they observe, however they do not place this in the context of wider atmospheric implications. In particular, this paper would benefit from a comparison with equivalent measurements in other locations, or alternative methods of measuring BC mixing state (e.g. doi: 10.5194/acp-20-3645-2020). This will allow for a deeper insight into the processes and phenomena under investigation.

RE: The reviewer provides a good reference for us to compare the two studies. Yu et al. (2020) characterize mass-resolved mixing state of mass-resolved black carbon (BC) in Beijing based on the measurement of a coupled combination of a centrifugal particle mass analyzer (CPMA) and a single-particle soot photometer (SP2). A new inversion algorithm was used to characterize the mixing state of rBC-containing particles in Beijing. We characterize the size-resolved mixing state of soot particles based on the measurement of VTDMA in Xingtai using a different observation method but the measurement result is comparable. For example, Yu et al. (2020) finds that a more even distribution of rBC and non-rBC material mass fractions in summer, which may be caused by higher amount of secondary material. In our study, we find that the coating effect of volatile matter on soot particles was stronger in warm months (i.e. in summer) than in cold months. Another example is that Yu et al. (2020) finds that polluted air from the Southern Plateau dominated the aged rBC-containing particles in Beijing. In our study, the measurement site (Xingtai) is in the south of Beijing where highly aged soot particles (less NV particles) were observed.

In addition, more comparisons are made with reference to other studies in the discussion.

It would also better justify this as an ACP research article (as opposed to a

measurement report) if either novel implications for wider atmospheric science could be specifically identified, or if newly-identified phenomena could be singled out.

RE: 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 measurements only denote the accumulation-mode soot particles. This is because the lower observation limit of particle size by 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 firstly reports that the anthropogenic emissions and aging processes have different effects on the mixing state of nucleation- and accumulation-mode soot particles based on the five-month VTDMA measurement. Furthermore, factors influencing the coating depth of soot particles are found in this study. Some of the findings are new and important to improve the accuracy of modeled aerosol optical properties.

The discussion in the above has been added in the revised manuscript.

Minor comments:

Line 23: Taken in isolation, “weaken the volatility of soot particles” is a strange statement to make because many use the term “soot” synonymously with the refractory components like black carbon. I would rephrase.

RE: Agreed. It is revised as “weaken the mean volatility of soot-containing particles”.

Page 69: Co-emitted organic carbon from biomass burning can be refractory (sometimes referred to as ‘tar’ or ‘tarballs’).

RE: Adachi et al. (2018, 2019) suggests that tarballs are mainly from biomass burning events (such as wildfires) and these particles are also refractory. The sentence is revised as “Aerosol volatility refers to the shrinking extent of particles at a certain temperature. The mixing state of soot particles or tarballs is closely related to aerosol volatility at high temperatures (Philippin et al., 2004; Wehner et al., 2009; Adachi et al., 2018, 2019).”.

Line 157: This repeats a statement already made earlier.

RE: It is deleted.

Line 166: I presume the factory calibration was used to calculated MBC, but this should still be stated.

RE: Yes, it was. We have added the corresponding description in the revised manuscript.

Line 217: “better atmospheric diffusion conditions” needs to be better explained

RE: In August, there are more and stronger northerly winds, which is beneficial to the diffusion of air pollutants. The sentence is revised as “PM₁₀₋₄₀₀ was lower in August than in July, likely because of the better atmospheric diffusion conditions (more and stronger northerly winds) in August.”.

Line 222: This paragraph doesn’t really say anything substantial and can probably

be removed.

RE: This paragraph has been removed.

Reply to RC2

The authors present a five-month aerosol volatility measurement at a suburban site in North China Plain, focusing on analysis and interpretation of data from a volatility tandem differential mobility analyzer (VTDMA). The manuscript is like a measurement report. Throughout the manuscript, the authors tried to explain their measurements by some reasons that they could not demonstrate, using the sentences "likely caused by..." "likely due to..." "likely because of..." to interpret their results. Some discussions and conclusions are not reasonable and even wrong. For example, the authors conclude that anthropogenic emissions could weaken the volatility of soot particles and enhanced their degree of external mixing, which can not be supported by the measurement results that show increased fractions of non-volatile mode soot (i.e., externally mixed BC) and decreased coating depth with size increase. These measurement results follow the diffusion growth theory, namely condensation process of secondary aerosol components (i.e., coating materials) on soot surface is more sensitive to smaller size particles, in other word, the coating growth is effective for smaller soot particles.

RE: We appreciate the critical and constructive comments and have strived to address them to the capacity permitted by our measurements that are analyzed in more depth with reference to more previous studies concerning the mixing state of refractory BC in the NCP. Some conclusions of our study are consistent with previous studies. For example, Yu et al. (2020) found more evenly distributed rBC and non-rBC material mass fractions in summer, caused by higher amount of secondary material, while we find that the coating effect of volatile matter on soot particles was stronger in warm months (i.e, in summer) than in cold months.

As shown in Fig. 6a and Fig. S4 in the supplement, the fractions of non-volatile mode particles ($N_{F_{NV}}$) increased obviously in the rush hours for both nucleation and accumulation mode particles. Figure 8 in the manuscript revealed that the ensemble mean shrink factor (SF_{mean}) increased in the rush hours. All these suggest that anthropogenic sources can weaken the mean volatility of soot-containing particles and enhance their degree of external mixing by emitting more fresh and externally mixed soot particles. Cheng et al. (2012) also observed the same phenomenon at a suburban site in Beijing. Wu et al. (2017) and Zhang et al. (2021) reported that refractory BC mass size distribution measurements in Beijing peaked at about 200 nm. This means that anthropogenic sources emitted more externally mixed soot particles in the accumulation mode than that in the nucleation mode.

The chemical processes on the surface of BC is complex, which is not only controlled by the diffusion growth theory. Recently, some new theories are put forward. For example, Zhang et al. (2020) demonstrates that BC-catalyzed sulfate formation involving NO_2 and NH_3 plays an important role in the particle growth and the development of hazes in China. This BC

catalytic chemistry can occur even at low SO₂ and intermediate relative humidity levels. In addition, the coagulation with preexisting aerosols is also important for the coating of soot particles (e.g., He et al., 2015).

We added more references in the revised manuscript to confirm our measurements. Some new findings are firstly reported in our study. For example, we find that the variation of meteorological conditions and pollution levels has different effect on the aging of the nucleation-mode and accumulation-mode soot particles based on the five-month VTDMA measurement.

Reference:

- He, C., Liou, K. N., Takano, Y., Zhang, R., Levy Zamora, M., Yang, P., Li, Q., and Leung, L. R.: Variation of the radiative properties during black carbon aging: theoretical and experimental intercomparison, *Atmos. Chem. Phys.*, 15, 11967-11980, 10.5194/acp-15-11967-2015, 2015.
- Wu, Y., Wang, X., Tao, J., Huang, R., Tian, P., Cao, J., Zhang, L., Ho, K. F., Han, Z., and Zhang, R.: Size distribution and source of black carbon aerosol in urban Beijing during winter haze episodes, *Atmos. Chem. Phys.*, 17, 7965-7975, <https://doi.org/10.5194/acp-17-7965-2017>, 2017.
- Yu, C., Liu, D., Broda, K., Joshi, R., Olfert, J., Sun, Y., Fu, P., Coe, H., and Allan, J. D.: Characterising mass-resolved mixing state of black carbon in Beijing using a morphology-independent measurement method, *Atmos. Chem. Phys.*, 20, 3645-3661, 10.5194/acp-20-3645-2020, 2020.
- Zhang, F., Wang, Y., Peng, J., Chen, L., Sun, Y., Duan, L., Ge, X., Li, Y., Zhao, J., Liu, C., Zhang, X., Zhang, G., Pan, Y., Wang, Y., Zhang, A. L., Ji, Y., Wang, G., Hu, M., Molina, M. J., and Zhang, R.: An unexpected catalyst dominates formation and radiative forcing of regional haze, *Proceedings of the National Academy of Sciences*, 117, 3960, 10.1073/pnas.1919343117, 2020.
- Zhang, Y., Liu, H., Lei, S., Xu, W., Tian, Y., Yao, W., Liu, X., Liao, Q., Li, J., Chen, C., Sun, Y., Fu, P., Xin, J., Cao, J., Pan, X., and Wang, Z.: Mixing state of refractory black carbon in fog and haze at rural sites in winter on the North China Plain, *Atmos. Chem. Phys.*, 21, 17631-17648, 10.5194/acp-21-17631-2021, 2021.

General Comments:

The authors took 40-nm and 80-nm particles to explore volatility of nucleation-mode soot particles. The VTDMA measurement show that the particles in nucleation mode (represented by 40-nm particles) had strong volatility and a high degree of internal mixing with shrink factor of ~ 0.4 , meaning that the residual particle size after heating was ~ 16 nm. These residual materials after heating at 300 degree for 40-nm particles are dominated by extremely low-volatile components rather than soot, taking into account that a carbon spherule of soot agglomerates has size of 15-30 nm. The authors claimed that the number concentration of 40-nm and 80-nm particles increased quickly due to the influence of new particle formation (NPF) events. Previous studies (e.g., Ehn et al., 2014) have demonstrated that the importance of extremely low-volatile

organic components for the initial growth of new formed particles. These extremely low-volatile organic components remain in the particle phase after heating at 300 degree. How the authors to demonstrate that the residual materials after heating at 300 degree for 40-nm particles are soot rather than extremely low-volatile organic components?

RE: The measurement site (Xingtai) is located in a highly polluted area in the central-south NCP because this region is heavily industrialized. Major industrial manufacturers include coal-based power plants, steel and iron works, glassworks, and cement mills (Wang et al., 2018). Wang et al. (2021) finds that both the mass concentration and mass fraction of BC in PM₁ are larger at Xingtai than those at urban Beijing in the north NCP. All these suggest that the emission of soot particles from the fossil fuel combustion is a lot at Xingtai.

The measurement of nucleation-mode soot particles is not easy because of their small volume and mass. Recently, Zhang et al. (2021) reports the size distribution of refractory BC in the mass equivalent diameter range of 70-500 nm based on the measurement of SP2 at the Gucheng site (between Beijing and Xingtai). It is found that the nucleation-mode soot particles are plentiful but they cannot be fully measured due to the limit of measurement size range by SP2. Considering that industrial emission at Xingtai is stronger than that at Gucheng, it is expected that more nucleation-mode soot particles are discharged at Xingtai. In addition, Fig. S4 in the supplement shows that the number fraction of nonvolatile particles (N_{nv}) in the nucleation mode increased obviously during morning and evening rush hours, implying that traffic emission is also one of sources for nucleation-mode soot particles.

Ehn et al. (2014) demonstrates that extremely low-volatile components (ELVOCs) plays a considerable role in particle formation and growth in the forest area because forests emit large quantities of volatile organic compounds (VOCs). However, the primary aerosol sources are mainly from anthropogenic emissions in the NCP, leading to the heavy hazes in this region. The Xingtai site is located at the foothill of the Taihang Mountains. The weak diffusion conditions make it more easily influenced by the accumulation of air pollutants. The high concentrations of gaseous precursors and strong atmospheric oxidation capacity make new particle formation (NPF) occurring frequently at Xingtai (Wang et al., 2018; 2021).

Wehner et al. (2009) indicates that some nonvolatile material is produced during particle formation and growth in the polluted Beijing region, but usually ~97% of the particle material is volatile at 300 °C. On the other hand, 97% of the newly formed particles consists of volatile particle material which is most likely dominated by sulfate but also volatile organic compounds. Cheng et al. (2012) also suggests that particles in the size range of 30-320 nm with non-volatile residuals at 300 °C are mostly soot particles, which is measured at Yufa (another site in the NCP). In our previous studies, we found that the frequent NPF events are closely related to the formation of sulfate at Xingtai because this site is located in one of SO₂ pollution centers. (Wang et al., 2018, 2021).

According to the discussion above, we think most of nonvolatile particles in the nucleation mode are soot rather than ELVOCs although the contribution of ELVOCs is possible.

Reference:

- Cheng, Y. F., Su, H., Rose, D., Gunthe, S. S., Berghof, M., Wehner, B., Achtert, P., Nowak, A., Takegawa, N., Kondo, Y., Shiraiwa, M., Gong, Y. G., Shao, M., Hu, M., Zhu, T., Zhang, Y. H., Carmichael, G. R., Wiedensohler, A., Andreae, M. O., and Pöschl, U.: Size-resolved measurement of the mixing state of soot in the megacity Beijing, China: diurnal cycle, aging and parameterization, *Atmos. Chem. Phys.*, **12**, 4477-4491, 2012.
- Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, *Nature*, **506**, 476-479, [10.1038/nature13032](https://doi.org/10.1038/nature13032), 2014.
- Wang, Y., Li, Z., Zhang, Y., Du, W., Zhang, F., Tan, H., Xu, H., Fan, T., Jin, X., Fan, X., Dong, Z., Wang, Q., and Sun, Y.: Characterization of aerosol hygroscopicity, mixing state, and CCN activity at a suburban site in the central North China Plain, *Atmos. Chem. Phys.*, **18**, 11739-11752, [10.5194/acp-18-11739-2018](https://doi.org/10.5194/acp-18-11739-2018), 2018.
- Wang, Y., Wang, J., Li, Z., Jin, X., Sun, Y., Cribb, M., Ren, R., Lv, M., Wang, Q., Gao, Y., Hu, R., Shang, Y., and Gong, W.: Contrasting aerosol growth potential in the northern and central-southern regions of the North China Plain: Implications for combating regional pollution, *Atmos. Environ.*, **267**, 118723, <https://doi.org/10.1016/j.atmosenv.2021.118723>, 2021.
- Wehner, B., Berghof, M., Cheng, Y. F., Achtert, P., Birmili, W., Nowak, A., Wiedensohler, A., Garland, R. M., Pöschl, U., and Hu, M.: Mixing state of nonvolatile aerosol particle fractions and comparison with light absorption in the polluted Beijing region, *Journal of Geophysical Research Atmospheres*, **114**, 85-86, 2009.
- Zhang, Y., Liu, H., Lei, S., Xu, W., Tian, Y., Yao, W., Liu, X., Liao, Q., Li, J., Chen, C., Sun, Y., Fu, P., Xin, J., Cao, J., Pan, X., and Wang, Z.: Mixing state of refractory black carbon in fog and haze at rural sites in winter on the North China Plain, *Atmos. Chem. Phys.*, **21**, 17631-17648, [10.5194/acp-21-17631-2021](https://doi.org/10.5194/acp-21-17631-2021), 2021.

Specific comments:

Abstract: I don't think the May, September and October with temperatures in the range of 15-30 degrees are cold months.

RE: As mentioned in the abstract, warm months (June, July and August) and cold months (May, September and October) are relative to emphasize the difference of ambient temperature in these months. Actually, other meteorological variables are also distinct between the cold and warm months, such as the ambient RH shown in Fig. 2a, and the winds shown in Fig.2b and Fig. S1. This is because the weather system affecting the measurement site differ markedly between the warm and cold months. For example, this site is influenced periodically by strong cold fronts in cold months but not in warm months. Therefore, the meteorological variables changed periodically in cold months but not in warm months. The difference of meteorological variables can cause the variation of aerosol volatility and soot mixing state, as discussed in this paper. In addition, Fig. 2c shows that the heavy haze is more likely to appear in cold months.

Introduction (Page 3/Lines 61-62): The authors stated that “However, studies on the mixing state of BC or soot particles in the actual atmosphere are few due to limited observations.” To my knowledge, there have been many field measurements to investigate the mixing state of ambient BC particles using a single-particle soot photometer (SP2) and a soot particle aerosol mass spectrometer (SP-AMS) in recent years.

RE: The sentence “However…” is deleted. The paragraph about the measurement results using SP2 and SP-AMS in the NCP was added.

“The online measurement instruments quantifying the mixing state of BC-containing particles are limited. Based on the measurement of single-particle soot photometer (SP2), Wu et al. (2017) indicated that the mass of refractory black carbon (rBC) had an approximately lognormal distribution as a function of the volume-equivalent diameter (VED) in Beijing. Yu et al. (2020) suggested that the mixing state of rBC particles was related to air pollution levels and air mass sources. Zhang et al. (2021) further indicated that meteorological conditions had a large impact on the mixing state of rBC particles. Moreover, the Aerodyne soot particle aerosol mass spectrometer (SP-AMS) can also be used to study the mixing state of rBC. For example, J. Wang et al. (2019) found that the formation of secondary aerosols through photochemical and aqueous chemical reactions was responsible to the coating of rBC based on the measurement of SP-AMS in winter Beijing. However, the lower measurement size limit of SP2 and SP-AMS is larger than 70 nm. Therefore, they cannot quantify the mixing state of BC-containing particles in the small nucleation mode.”.

Thanks for the suggestion.

2.2 Measuring BC: The raw data of AE33 measurement have a large uncertainty due to filter-loading and multiple-scattering effects. However, the authors did not make any corrections for measurement data.

RE: Sorry, we didn't elaborate the correction but we did it. Drinovec et al. (2015) reported that a new real-time loading effect compensation algorithm is used in AE33 based on a two parallel spot (i.e., dual-spot) measurement of optical absorption. The dual-spot compensation algorithm determines the value of the compensation parameter k with high temporal resolution, which indicates changes in aerosol properties on the daily timescale. Intercomparison studies show excellent reproducibility of the AE33 measurements and very good agreement with post-processed data obtained using earlier Aethalometer models and other filter based absorption photometers. A wavelength-independent multiple-scattering compensation factor (2.90) adapted in eastern China recommended by Zhao et al. (2020) is used to process the data of AE33.

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.

Zhao, G., Yu, Y., Tian, P., Li, J., Guo, S., and Zhao, C.: Evaluation and Correction of the Ambient

Particle Spectral Light Absorption Measured Using a Filter-based Aethalometer, *Aerosol Air Qual. Res.*, 20, 1833-1841, 10.4209/aaqr.2019.10.0500, 2020.

Page 7/Line 188: Average temperatures in warm (June, July, and August) and cold (May, September, and October) months only have a difference of ~6 degree. The authors should reconsider classification criteria to discuss monthly variations.

RE: As described in the above, the warm and cold months are relative terms. The difference of meteorological conditions made different air pollution levels at Xingtai, leading to distinct aerosol properties between warm and cold months.

Page 8/Lines 218-219: The similar changes in concentrations of BC and PM can not suggest the non-trivial role of BC in the formation processes of aerosol pollution. Both concentrations of BC and PM strongly depend on planetary boundary layer height.

RE: We can't confirm the role of BC in the formation processes of aerosol pollution in this study, but a recent study demonstrated that BC catalyzed sulfate formation involving NO_2 and NH_3 may play an important role in the formation of haze events in China (Zhang et al., 2020). For this reason, this sentence is revised as: "Figure 2c also shows that changes in M_{BC} and PM_{10-400} were similar, suggesting the **possible** role of BC in the formation processes of aerosol pollution."

Reference:

Zhang, F., Wang, Y., Peng, J., Chen, L., Sun, Y., Duan, L., Ge, X., Li, Y., Zhao, J., Liu, C., Zhang, X., Zhang, G., Pan, Y., Wang, Y., Zhang, A. L., Ji, Y., Wang, G., Hu, M., Molina, M. J., and Zhang, R.: An unexpected catalyst dominates formation and radiative forcing of regional haze, *Proceedings of the National Academy of Sciences*, 117, 3960, 10.1073/pnas.1919343117, 2020.

Page 9/Lines 246: should be "non-volatile"

RE: It is revised. Thanks for the detailed check.

Page 12/Lines 326-328: There are only two sizes in nucleation mode. The authors made conclusion that the volatility of nucleation-mode soot particles became larger with increasing particle size, which is not solid.

RE: The sentence is deleted.

Figure 10: The coating depth and temperature have a poor correlation ($R^2=0.03-0.04$), which can not support that coating depth depends on temperature as discussed by the authors.

RE: There are multiple factors influencing the coating depth of soot particles ($D_{\text{c,mean}}$), leading to a weak correlation when analyzing the relationship of $D_{\text{c,mean}}$ with one of these factors. In the revised manuscript, we analyzed the relationships using the box plots instead of scatter plots and fit the relationship of $D_{\text{c,mean}}$ and $\text{PM}_{10-400\text{nm}}$ using the logarithmic function instead of linear function. The results are shown in the figure below, showing the better relationships with these factors. We added more discussions about their relationships in this section.

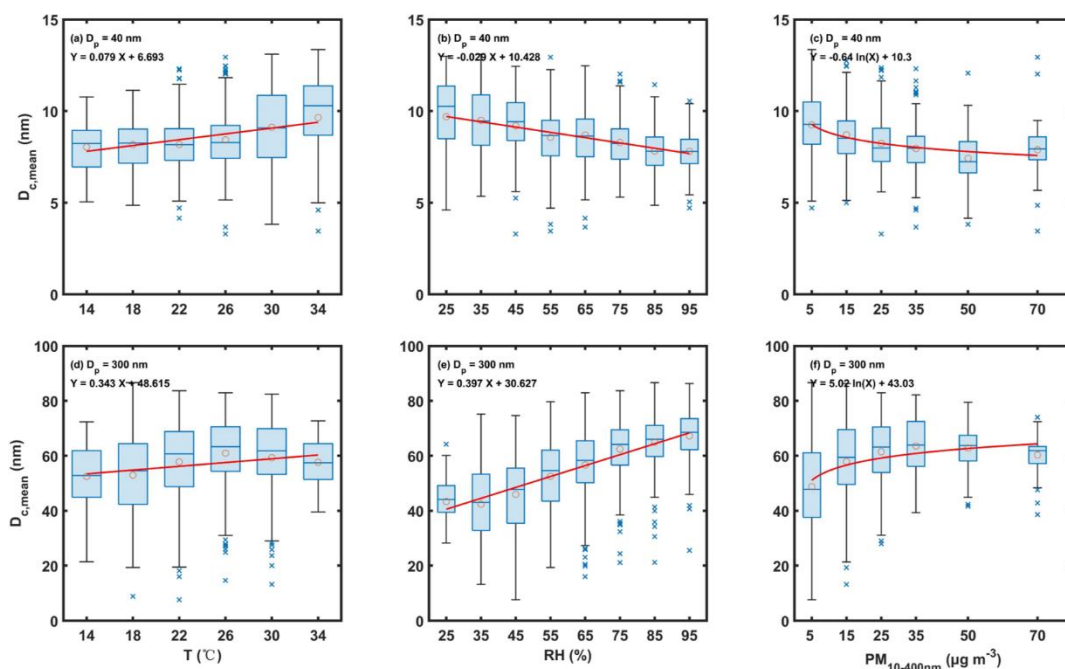


Figure R1. Relationships between ensemble mean coating depth ($D_{c,mean}$) and ambient T (a, d) and RH (b, e), and $\text{PM}_{10-400\text{nm}}$ (c, f) for 40-nm (top panels) and 300-nm (bottom panels) particles. The circles show the mean $D_{c,mean}$ with boxes showing the 25th, 50th, and 75th percentiles and extremities show the 5th and 95th percentiles. Red lines show the linear or logarithmic fitting lines through the data, and best-fit relations are given in each panel.

Reference:

- Wang, Y., Li, Z., Zhang, R., Jin, X., Xu, W., Fan, X., Wu, H., Zhang, F., Sun, Y., Wang, Q., Cribb, M., and Hu, D.: Distinct Ultrafine- and Accumulation-Mode Particle Properties in Clean and Polluted Urban Environments, *Geophys. Res. Lett.*, 46, 10918-10925, 10.1029/2019GL084047, 2019.
- Zhang, Y., Liu, H., Lei, S., Xu, W., Tian, Y., Yao, W., Liu, X., Liao, Q., Li, J., Chen, C., Sun, Y., Fu, P., Xin, J., Cao, J., Pan, X., and Wang, Z.: Mixing state of refractory black carbon in fog and haze at rural sites in winter on the North China Plain, *Atmos. Chem. Phys.*, 21, 17631-17648, 10.5194/acp-21-17631-2021, 2021.

Page 17/Lines 441-442: Which measurement results can demonstrate enhanced nocturnal liquid chemical reactions?

RE: This sentence is revised as: "Moreover, the enhanced nocturnal secondary aerosol formation was responsible for the enhanced volatility of accumulation-mode soot particles in the nighttime.". Zhang et al. (2018) reported that the nocturnal chemical processes made the obvious increase of secondary aerosols such as nitrate at Xingtai.

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.

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 introduction 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.

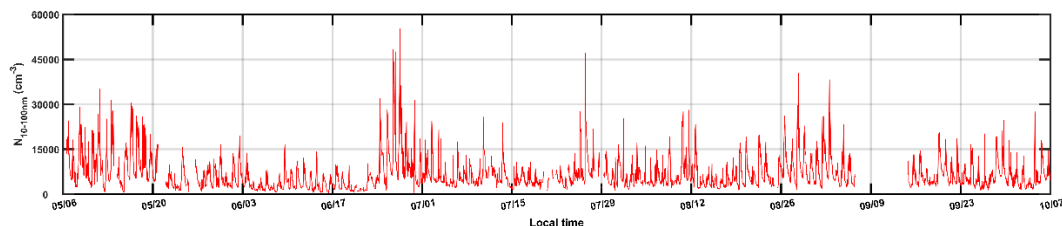
Some of the conclusions are not supported adequately by observations. Figure 4 shows that VV nucleation particles are characterized by a higher volatility during warmer months. On the other hand, the conclusion concerning the seasonal variability of nucleation mode soot particles relies on the assumption 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 (N_{FV}) 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 ($N_{10-100\text{ nm}}$). It suggests $N_{10-100\text{ nm}}$ 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 $N_{10-100\text{ nm}}$ 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 from 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 $7.77\text{ m}^2\text{ g}^{-1}$. 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.

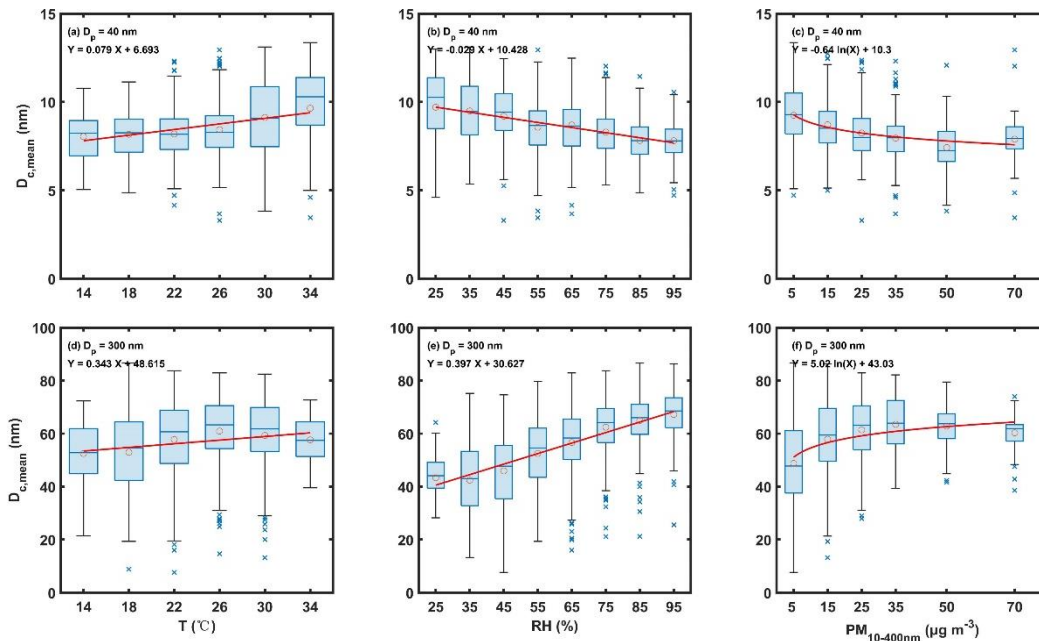
RE: Thanks for the suggestion. The sentence is revised as: "Some studies suggest that freshly emitted refractory particles (like BC) are primarily in accumulation mode. For example, Levy et al. (2013) reported that fresh BC was mostly in the 150–240 nm size range, while Wu et al. (2017) reported that 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 (D_c) and PM_{10-400} (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_{10-400} . 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 diameter, 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