

## 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  $SO_2$  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  $\sim 0.4$ , meaning that the residual particle size after heating was  $\sim 16$  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  $PM_{10}$  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  $SO_2$  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

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- 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, 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.
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- 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.

#### 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.

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  $\text{NO}_2$  and  $\text{NH}_3$  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  $M_{\text{BC}}$  and  $\text{PM}_{10-400}$  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.

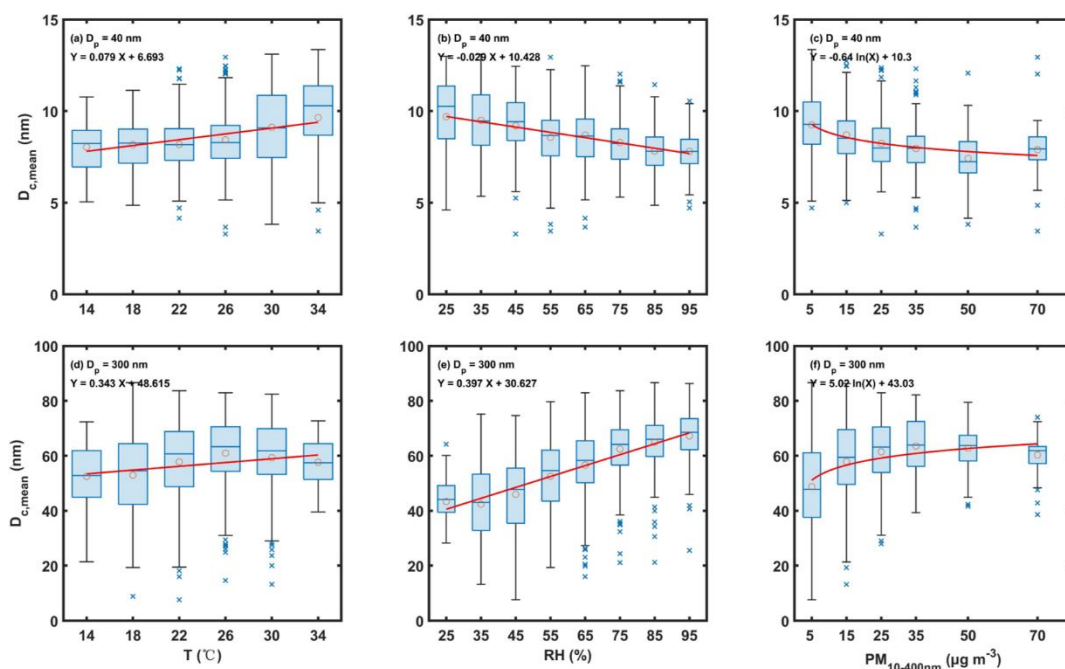


Figure R1. Relationships between ensemble mean coating depth ( $D_{c,mean}$ ) and ambient T (a, d) and RH (b, e), and  $PM_{10-400nm}$  (c, f) for 40-nm (top panels) and 300-nm (bottom panels) particles. The circles show the mean  $D_{c,mean}$  with boxes showing the 25th, 50th, and 75th percentiles 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.