

A point-by-point response to reviewer

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 the valuable comments and suggestions. The main concern of the reviewer is about the method which we used to retrieve the In-BC, Ex-BC and Non-BC. And he/she argued that the uncertainties were not carefully analyzed in the manuscript. This is a good point. Therefore, according to the comments, we just have included a careful analysis of the uncertainties of the retrieved method, 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 **Lines 121-134**, as follows:

“The detailed correlations between mass concentration of non-volatile particles estimated from VTDMA and BC measured by AE-33 in this study are shown in Fig. S2. The total mass concentration of non-volatile particles 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). The calculated non-volatile particle mass concentration distributed on both sides of the line 1:1. We further evaluated the mass fraction of non-volatile compounds except BC, which accounted for ~1.8 %. This result suggests that BC can explain almost of 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. S3), 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.”

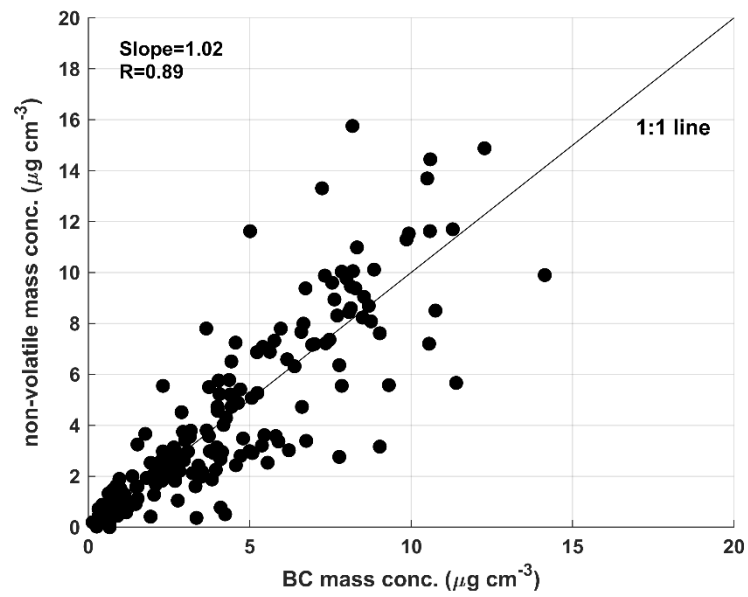


Figure R1. Black carbon (BC) mass concentration measured by AE-33 vs. the non-volatile mass concentration estimated from the VTDMA for winter 2019 periods. Estimation of the non-volatile mass concentration was made assuming a density of 1.6 g cm^{-3} .

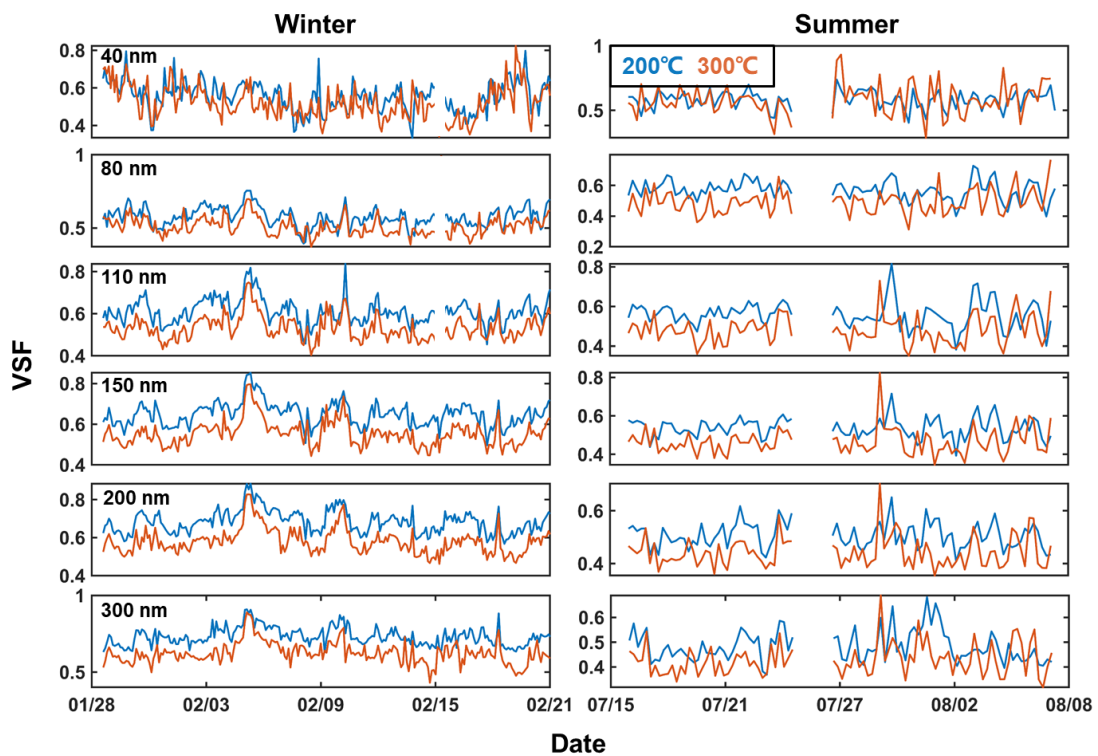


Figure R2. The mean volatility shrink factor (VSF) of all measured size particles after heating at 200 (blue line) and 300 °C (red line) during the winter and summer periods.

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 comments).

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 167-169**, as follows:

“The retrieval result, which has been compared with the measurements by single particle aerosol mass spectrometer (SPAMS) in the Fig. S5 and in the previous study (Chen et al., 2020), both the overall temporal variations and proportion for BC-containing and Ex-BC particles measured by SPAMS and calculated from VTDMA using the retrieved method are consistent, confirming this method is reliable for deriving the mixing state of BC.”

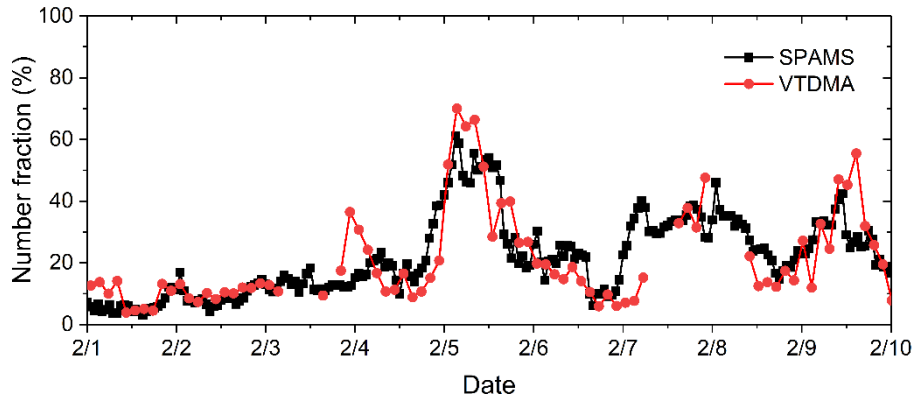


Figure R3. Time series of number fraction of Ex-BC particles measured by SPAMS (in black) and calculated from VTDMA (in red), the 200 nm particles from VTDMA are chosen.

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:

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

A statement has also been included in the revised version, see **lines 147-148**, 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. $\eta_{D_p,T} = N_r(\text{NaCl})/N_{D_p}(\text{NaCl})$).”

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: ①The NPF events took place frequently during the summer sampling periods, 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. S7).

②The 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.

③The 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. R4.

Some discussions have been included in the revised text of **Lines 220-224** and **Lines 229-234**, 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. 4g 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. S7). 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.”

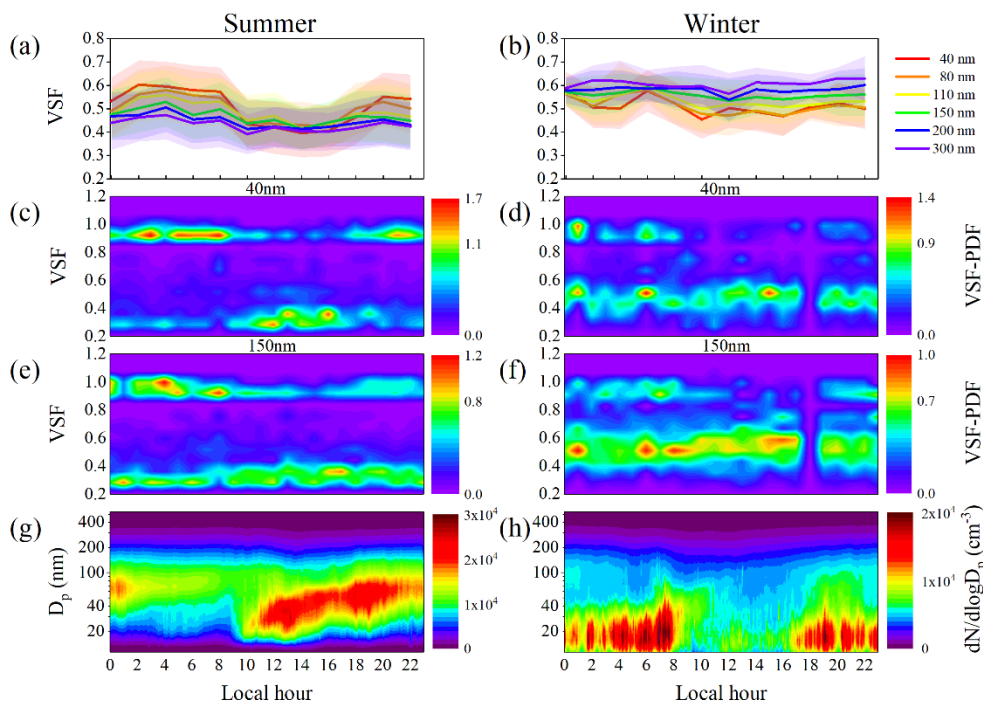


Figure R4. Diurnal variation of (a-b) mean VSF for all measured dry particle sizes, (c-f) mean VSF-PDF for 40- and 150-nm particles, and (g-h) mean particle number size distribution during the summer (left) and winter (right) periods. The shade regions in (a-b) denote the standard deviations.

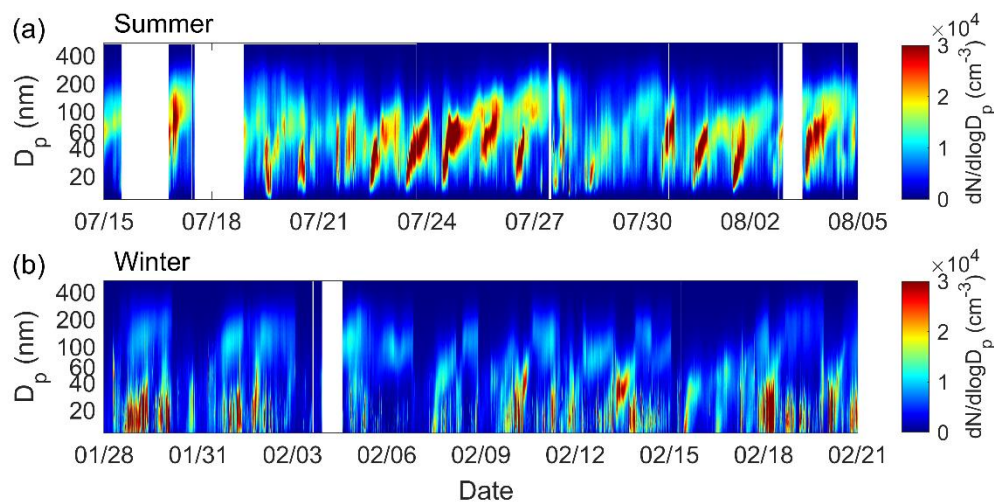


Figure R5. Time series of the aerosol particle number size distribution measured by the SMPS during the (a) summer and (b) winter periods.

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 329–331**, as follows:

“Here, particles with diameters of 150 nm are presented as examples (Fig. S10), 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.”

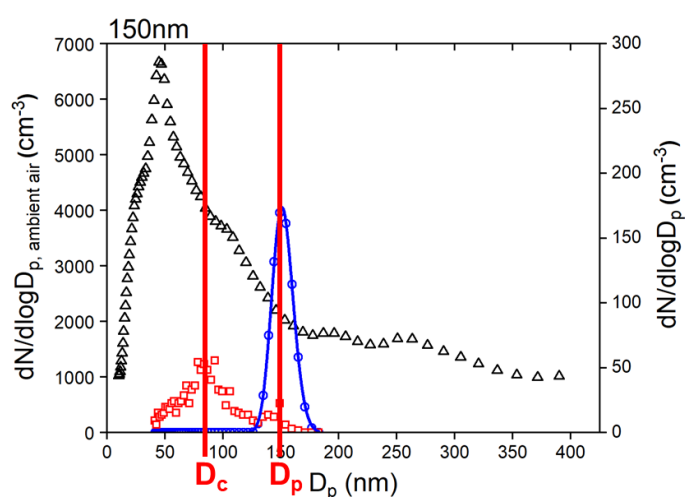


Figure R6. Number size distributions of ambient aerosols (in black), DMA₁-selected particles with D_p equal to 150 nm (in blue), residual particles after heating at 300 °C (in red), and the fitting curves.

Reference

Birmili, W., Weinhold, K., Nordmann, S., Wiedensohler, A., Spindler, G., Müller, K., Herrmann, H., Gnauk, T., Pitz, M., Cyrys, J., Flentje, H., Nickel, C., Kuhlbusch, T. A. J., and Löschau, G.: Atmospheric aerosol measurements in the German Ultrafine Aerosol Network (GUAN): Part 1 – soot and particle number size distribution, *Gefahrst. Reinh. Luft.*, 69, 137–145, 2009.

Birmili, W., Heinke, K., Pitz, M., Matschullat, J., Wiedensohler, A., Cyrys, J., Wichmann, H.-E., and Peters, A.: Particle number size distributions in urban air before and after volatilisation, *Atmos. Chem. Phys.*, 10, 4643–4660, doi:10.5194/acp-10-4643-2010, 2010.

Cheng, Y.F., Eichler, H., Wiedensohler, A., Heintzenberg, J., Zhang, Y.H., Hu, M., Herrmann, H., Zeng, L.M., Liu, S., Gnauk, T., Brüggemann, E., He, L.Y., 2006. Mixing state of elemental carbon and non-light-absorbing aerosol components derived from in situ particle optical properties at Xinken in Pearl River Delta of China. *J. Geophys. Res.: Atmosphere* 111, D20204.

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., Pöschl, U., 2012. Size-resolved measurement of the mixing state of soot in the megacity Beijing, China: diurnal cycle, aging and parameterization. *Atmos. Chem. Phys.* 12, 4477e4491.

Cheung, H.H.Y., Tan, H., Xu, H., Li, F., Wu, C., Yu, J.Z., Chan, C.K., 2016. Measurements of non-volatile aerosols with a VTDMA and their correlations with carbonaceous aerosols in Guangzhou, China. *Atmos. Chem. Phys.* 16, 8431e8446.

Cappa, C. D. and Jimenez, J. L.: Quantitative estimates of the volatility of ambient organic aerosol, *Atmos. Chem. Phys.*, 10, 5409–5424, doi:10.5194/acp-10-5409-2010, 2010. Chen, L., Zhang, F., Yan, P., Wang, X., Sun, L., Li, Y., Zhang, X., Sun, Y., and Li, Z.: The large proportion of black carbon (BC)-containing aerosols in the urban atmosphere, *Environmental Pollution*, 263, 114507, <https://doi.org/10.1016/j.envpol.2020.114507>, 2020.

Frey, A., Rose, D., Wehner, B., Müller, T., Cheng, Y., Wiedensohler, A., Virkkula, A., 2008. Application of the volatility-TDMA technique to determine the number size distribution and mass concentration of less volatile particles. *Aerosol Sci. Technol.* 42, 817e828.

Häkkinen, S. A. K., Äijälä, M., Lehtipalo, K., Junninen, H., Backman, 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.

Levy, M. E., Zhang, R., Zheng, J., Tan, H., Wang, Y., Molina, L. T., Takahama, S., Russell, L. M., and Li, G.: Measurements of submicron aerosols at the California–Mexico border during the Cal–Mex 2010 field campaign, *Atmos. Environ.*, 88, 308–319, doi:10.1016/j.atmosenv.2013.08.062, 2014.

Philippin, S., Wiedensohler, A., and Stratmann, F.: Measurements of non-volatile fractions of pollution aerosols with an eight-tube volatility tandem differential mobility analyzer (VTDMA-8), *Journal of Aerosol Science*, 35, 185–203, <https://doi.org/10.1016/j.jaerosci.2003.07.004>, 2004.

Pöschl, U.: Atmospheric Aerosols: Composition, Transformation, Climate and Health Effects, *Angewandte Chemie International Edition*, 44, 7520–7540, doi:10.1002/anie.200501122, 2005.

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 the tropospheric research site Melpitz, Germany, *Atmos. Chem. Phys.*, 14, 10145–10162, doi:10.5194/acp-14-10145-2014, 2014.

Rose, D., Gunthe, S. S., Su, H., Garland, R. M., Yang, H., Berghof, M., Cheng, Y. F., Wehner, B., Achtert, P., Nowak, A., Wiedensohler, A., Takegawa, N., Kondo, Y., Hu, M., Zhang, Y., Andreae, M. O., and Pöschl, U.: Cloud condensation nuclei in polluted air and biomass burning smoke near the mega-city Guangzhou, China – Part 2: Size-resolved aerosol chemical composition, diurnal cycles, and externally mixed weakly CCN-active soot particles, *Atmos. Chem. Phys.*, 11, 2817–2836, doi:10.5194/acp-11-2817-2011, 2011.

Wang, X., Shen, X. J., Sun, J. Y., Zhang, X. Y., Wang, Y. Q., Zhang, Y. M., Wang, P., Xia, C., Qi, X. F. and Zhong, J. T.: Size-resolved hygroscopic behavior of atmospheric aerosols during heavy aerosol pollution episodes in Beijing in December 2016, *Atmos. Environ.*, 194, 188–197, doi:10.1016/j.atmosenv.2018.09.041, 2018.

Wang, Z., W. Birmili, A. Hamed, B. Wehner, G. Spindler, X. Pei, Z. Wu, Y. Cheng, H. Su, and A. Wiedensohler: Contributions of volatile and nonvolatile compounds (at 300°C) to condensational growth of atmospheric nanoparticles: An assessment based on 8.5 years of observations at the Central Europe background site Melpitz, *J. Geophys. Res. Atmos.*, 122, 485–497, doi:10.1002/2016JD025581, 2017.

Wehner, B., Berghof, M., Cheng, Y. F., Achtert, P., Birmili, W., Nowak, A., Wiedensohler, A., Garland, R. M., Pöschl, U., Hu, M., and Zhu, T.: Mixing state of nonvolatile aerosol particle fractions and comparison with light absorption in the polluted Beijing region, 114, 10.1029/2008jd010923, 2009.

Xu, L., Williams, L. R., Young, D. E., Allan, J. D., Coe, H., Massoli, P., Fortner, E., Chhabra, P., Herndon, S., Brooks, W. A., Jayne, J. T., Worsnop, D. R., Aiken, A. C., Liu, S., Gorkowski, K., Dubey, M. K., Fleming, Z. L., Visser, S., Prévôt, A. S. H., and Ng, N. L.: Wintertime aerosol chemical composition, volatility, and spatial variability in the greater London area, *Atmos. Chem. Phys.*, 16, 1139–1160, <https://doi.org/10.5194/acp-16-1139-2016>, 2016.

Zhang, S. L., Ma, N., Kecorius, S., Wang, P. C., Hu, M., Wang, Z. B., Größ, J., Wu, Z. J., and Wiedensohler, A.: Mixing state of atmospheric particles over the North China Plain, *Atmos. Environ.*, 125, Part A, 152–164, doi:10.1016/j.atmosenv.2015.10.053, 2016.

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.