

Interactive comment on “Volatility measurement of atmospheric submicron aerosols in an urban atmosphere in southern China” by Li-Ming Cao et al.

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huangxf@pku.edu.cn

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In this study, the authors deployed a TD-AMS to investigate the volatility of different chemical compositions of PM₁ in Shenzhen. Aerosol volatility studies are important but rare in China. This work, as far as I know, could be the 1st report on the online measurement of the volatilities of aerosol chemical components using a TD-AMS in China, and thus provide valuable information. In addition, OA was classified into several groups using PMF and tested their volatility separately, which help to understand their sources and characters. The manuscript is overall well written and documented. The topic fits well in the scope of ACP. I recommend this manuscript can be published

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Discussion paper



after some revisions.

1) In general, aerosol is a really complex system, especially in China. The analysis in this work is a bit too simple. Some more discussions are recommended, e.g. size resolved volatility study, organic aerosol volatility in different events, e.g. heavy haze events or NPF events. Reply: According to this comments and other comments of this reviewer and other reviewers, we have added many new useful materials to support the data analysis in this paper, with the major revisions summarized below: (1) The elemental composition change of organic aerosol with TD temperature, as below: “The relationship of the O/C, H/C, and N/C ratios with the TD temperature is also shown in Figure 3. It can be seen that O/C kept increasing as the temperature increased, especially after 150 °C, which is consistent with previous studies (Xu et al., 2016a). When examining the organic mass spectra at difference temperatures (in Figure S6), the elevation of O/C with temperature increasing was found to be reasonably related to increasing of CO₂+. Previous PMF results usually correlated higher volatility with reduced species and lower volatility with more oxygenated species (Ng et al., 2010; Huang et al., 2012). In this study, the elevation of O/C with temperature increasing was closely related to the evaporation of more reduced organic components, as the PMF results indicated later. On the other hand, H/C showed a reasonable reverse trend relative to that of O/C. N/C generally had an increasing trend with the TD temperature increasing, but N/C varied largely at the different TD temperatures, suggesting that the volatilities of N-containing compounds are complex.” (2) The mass fractions of the five OA factors at different TD temperatures, with the discussion as below: “Figure 5 showed the mass fractions of the five factors at different TD temperatures. It is found that when the temperature increasing, the fraction of MO-OOA quickly increased up to 67.6% at 200 °C, while LO-OOA showed a reverse trend, accounting for only 2.9% at 200 °C, indicating that they had quite different volatilities. For HOA, COA, and BBOA, they also exhibited different volatilities, with HOA accounting for only 5-7% above 100°C, while the fraction of COA did not change much with the temperature increasing. The different volatilities of different OA factors will be discussed in more

detail in the following section.” (3) The comparison between the volatility and the O/C ratios for the OA factors, with the new discussion as below: “Figure 7 compares both the volatilities (MFR at 50 °C) and the O/C ratios of the five factors. The sequence of the volatilities can be summarized as HOA > LO-OOA > COA \approx BBOA > MO-OOA. It can be easily found that the sequence of the volatilities of the OA factors does not completely follow the sequence of the O/C ratios. For example, although LO-OOA has a higher O/C ratio than BBOA and COA, LO-OOA is also more volatile (or with a lower MFR) than BBOA and COA. This clearly indicates the volatility of the OA factors depends not only on the oxygenation of organic compounds, but also other factors, e.g., molecular weight and mixing state. HOA is identified as the most volatile OA factor while MO-OOA is nearly non-volatile near the real atmospheric temperatures in Shenzhen, which is consistent with the results observed in Mexico and Paris (Cappa and Jimenez, 2010; Paciga et al., 2016). However, LO-OOA is the second volatile OA factor after HOA in Shenzhen, which is different from that in Mexico, where BBOA is more volatile than LO-OOA. Actually, the volatility of the aerosols directly from biomass burning have been measured to be quite variable, with an evaporation rate of 0.2–1.6% $\text{Å}^{\circ}\text{C}^{-1}$, depending on the kinds of wood and combustion conditions (Huffman et al., 2009a). The relatively lower volatility of COA was also identified in previous studies and attributed to the abundant fatty acids of low volatility in COA (Mohr et al., 2009; Paciga et al., 2016). Hong et al. (2017) recently reported the estimation of the organic aerosol volatility in a boreal forest in Finland using two independent methods, including using a VTDMA with a kinetic evaporation model and applying PMF to HR-AMS data. Semi-volatile and low-volatility organic mass fractions were determined by both methods, similar to our study in China. This implies that MO-OOA and LO-OOA, with different volatilities, could be popular organic aerosol components across the world. Hong et al. (2017) also pointed out that determining of extremely low volatility organic aerosols from AMS data using the PMF analysis should be explored in future studies.”

2) The last sentence of conclusion part, “HOA, rather than BBOA or COA, could be

a potentially important source of LO-OOA”. More discussions are needed to support this statement. Reply: We have made a more cautious statement as below: “It should also be noted that, as the most volatile species in this study, HOA could be evaporated easily and thus have a larger potential to experience the “evaporation–oxidation in gas phase–condensation” process, forming SOA (e.g., LO-OOA) as described in Huang et al. (2012). This potential can be further supported by the fact that it is difficult to resolve HOA in downwind regions far from urban and industrial areas in China (Huang et al., 2011; Zhu et al., 2016). Other studies also showed that semi-volatile hydrocarbons from diesel exhaust (Robinson et al., 2007) and crude oil (de Gouw et al., 2011) can be easily oxidized to SOA. Therefore, the modelling work needs to consider the process from HOA to SOA in future.”

3) Hong et al., 2017 has reported a similar work that estimate of the organic aerosol volatility using two independent methods including a VTDMA and HR-AMS. They compared the direct measurement result from VTDMA and PMF result from HR-AMS. It would be good to add some discussions to compare the methods and results between this two works. Hong, J., Äijälä, M., Häme, S. A. K., Hao, L., Duplissy, J., Heikkinen, L. M., Nie, W., Mikkilä, J., Kulmala, M., Prisle, N. L., Virtanen, A., Ehn, M., Paasonen, P., Worsnop, D. R., Riipinen, I., Petäjä, T., and Kerminen, V. M.: Estimates of the organic aerosol volatility in a boreal forest using two independent methods, *Atmos. Chem. Phys.*, 17, 4387-4399, 10.5194/acp-17-4387-2017, 2017. Reply: The discussion about Hong et al. (2017) has been added into the text as below: Hong et al. (2017) recently reported the estimation of the organic aerosol volatility in a boreal forest in Finland using two independent methods, including using a VTDMA with a kinetic evaporation model and applying PMF to HR-AMS data. Semi-volatile and low-volatility organic mass fractions were determined by both methods, similar to our study in China. This implies that MO-OOA and LO-OOA, with different volatilities, could be popular organic aerosol components across the world. Hong et al. (2017) also pointed out that determining of extremely low volatility organic aerosols from AMS data using the PMF analysis should be explored in future studies.

4) I suggest adding a summary of volatility studies in China. Although there should be no other studies using a TD-AMS, but some related work using VTMDA are still worth to be summarized, e.g. Cheung et al., 2016; Nie et al., 2017. Cheung, H. H. Y., Tan, H., Xu, H., Li, F., Wu, C., Yu, J. Z., and Chan, C. K.: Measurements of non-volatile aerosols with a VTDMA and their correlations with carbonaceous aerosols in Guangzhou, China, *Atmos. Chem. Phys.*, 16, 8431-8446, 10.5194/acp-16-8431-2016, 2016. Nie, W., Hong, J., Häme, S. A. K., Ding, A., Li, Y., Yan, C., Hao, L., Mikkilä, J., Zheng, L., Xie, Y., Zhu, C., Xu, Z., Chi, X., Huang, X., Zhou, Y., Lin, P., Virtanen, A., Worsnop, D. R., Kulmala, M., Ehn, M., Yu, J. Z., Kerminen, V. M., and Petäjä, T.: Volatility of mixed atmospheric Humic-like Substances and ammonium sulfate particles, *Atmos. Chem. Phys. Discuss.*, 2016, 1-26, 10.5194/acp-2016-839, 2016. Reply: The following sentences have been added into the introduction part: “Cheung et al. (2016) studied the aerosol volatility in Guangzhou, China, based on the volatility tandem differential mobility analyzer (VTDMA) measurement, and found that non-volatile organic aerosol may contribute significantly to the non-volatile residuals. Also using a VTDMA, Nie et al. (2017) studied the volatility of aerosol humic-like substances (HULIS) in Nanjing, China, and figured out that the interaction between HULIS and ammonium sulfate tended to decrease the volatility of organic aerosols.”

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