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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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This manuscript by Cao et al. presents the field measurement results using an AMS coupled with a TD conducted in China. As the application of TD-AMS is for now still rare in the atmospheric chemistry studies in China. The manuscript contains useful and valuable information. However, this reviewer finds that in the current version, many necessary details are missing, and many statements and important conclusions appear to be over-interpreted, not well supported by the data or at least is not well explained, which limits the scientific value of the work. The current version needs major revision before its acceptance. The current version fails to make good use of the wealthy data

obtained by the HR-AMS, and it should be extensively expanded. Here below I list the comments below that need to be addressed. Please pay attentions to the in-text citation format Reply: All corrected.

In the introduction part, please provide more details regarding previous TD-AMS studies, focused the important findings. Reply: New review of previous findings has been added into the introduction part as below: "A thermo-denuder (TD) is a device that is widely used to estimate aerosol volatility distributions (Wehner et al., 2002; An et al., 2007; Huffman et al., 2008; Xu et al., 2016). The TDs designed by Burtscher et al., 2001 and Wehner et al., 2002 are typically operated under temperatures higher than 200 °C and have average residence times from 0.3 to 9 s, focusing on very low volatility species. An et al., 2007 and Huffman et al., 2008 developed TDs with longer residence times to make them more suitable for measuring the volatility of semi-volatile organic aerosols. The combined TD and Aerodyne Aerosol Mass Spectrometer (TD-AMS) system was firstly applied in ambient study by Huffman et al. (2008) to quickly characterize the volatility of chemically-resolved ambient aerosol in a field campaign, and the temperature profiles, particle losses and key factors affecting the results were discussed. Huffman et al. (2009a) then measured the volatility of OA from different sources, including biomass-burning OA, meat-cooking OA, trash-burning OA, and chamber SOA formed from α-pinene and gasoline vapours, and found semi-volatility for all the OAs, which is opposite to the previous atmospheric models that only regarded POAs as non-volatile species. Huffman et al. (2009b) also analyzed the positive matrix factorization (PMF) results based on the TD-AMS data and demonstrated that all types of OA should be regarded as semi-volatile species in the models. Lee et al. (2010) measured the volatility of aerosols with two different residence time sets and suggested that longer residence time was required to constrain the variation of OA volatility at lower concentrations. Obviously, OA volatilities, especially for different OA types, are still quite uncertain and need more ambient measurements to constrain."

(3) Introduction: Recently, Xu et al. (Atmos. Chem. Phys. 2014, 14, 12593-12611),

and Li et al. (Atmos. Environ. 2017, 158, 270-304.) have provided a summary of the AMS studies in China, these two papers should be cited. Reply: They are now cited.

(4) Section 2.2: The authors tested the transmission efficiencies, do these numbers are included to calculate the MFR? Besides, some theoretical calculations by Chris Cappa et al. regarding TD kinetics should be included. Reply: Yes, the transmission efficiencies were included to calculate the MFR, which has been clarified in the revised text. The model in Cappa et al. (2010) assumed many parameters and theoretical enthalpy to calculate the MFR, while our paper is currently focused on the experimental determination of MFR. Thus, the complex modeling of MFR will be considered in our future study.

Cappa, C. D.: A model of aerosol evaporation kinetics in a thermodenuder, Atmos. Meas. Tech., 3, 579-592, https://doi.org/10.5194/amt-3-579-2010, 2010.

(5) Section 2.2: why not to try a higher TD temperature, for example 250C or even 300C, there can be extremely low volatility species remained at such temperatures Reply: There are two main reasons for our temperature selection: 1. We referred to Huffman et al. (2008) for the setting of the range of the TD temperatures. 2. Only four temperature levels can be set in the software, which does not allow setting more temperature steps, and we care more about the relatively lower temperatures. It will be interesting to set the TD temperature up to 250 or 300 °C, and we would do it in future studies.

(6) Section 2: Some details regarding the TD is not provided. For example, what is the temperature cycle. What is the sampling time at each TD temperature? Do the authors change the absorption materials of the TD? And how often? Reply: The relevant information has been added as below: “The configuration of temperatures was: 35 min at 50 °C, 5 min for the temperature increasing to 100 °C, 22 min at 100°C, 5 min for the temperature increasing to 150 °C, 24 min at 150°C, 5 min for the temperature increasing to 200 °C, 25 min at 200 °C, and then 15 min for the temperature decreasing

to 50 °C. The complete temperature cycle was about 136 min.” “The AMS was set with 4 menus: ByPass path in V-mode, TD path in V-mode, TD path in W-mode and ByPass path in W-mode, with 2 min in each menu. Only the data sampled during the stable temperature plateau (1839 points for V mode and 1842 points for W mode in TD-path, respectively) were selected for the calculation of volatility”. We didn’t change the absorption materials because the TD used was a rather new one in this campaign.

(7) Section 2: A lot of details are not provided. You should give a bit more details regarding the instrumental and operational details about the AMS, for the convenience of readers not in the AMS community. Calibrations? Relative ionization efficiencies? Size calibration? What are the chemical resolution? As your PMF includes ions with m/z up to 170, does these ions can be well separated from their neighborhood ions? Any instrument details about AE31? Reply: More details of the AMS and AE-31 have been added into the paper, as below. In our data processing, the high resolution of the W mode made the ions separated properly from their neighborhood ions when fitting the ions. “The AMS was set into two sampling ion optical modes: the V mode with UMR(unite mass resolution) was used for quantification of the UMR mass concentration and size distribution of the non-refractory species (including organics, sulfate, nitrate, ammonium, and chloride); the W mode was used to obtain the high-resolution mass spectra (∼3000 m/∆m). The calibrations were conducted at the beginning and end of the campaign with the method described previously (Jayne et al., 2000; Jimenez et al., 2003; Drewnick et al., 2005), including the inlet flow rate, ionization efficiency calibration (IE), and particle size calibrations. The relative ionization efficiencies (RIE) used in the study were 1.2 for sulfate, 1.1 for nitrate, 1.3 for chloride, 1.4 for organics, and 4.0 for ammonium, respectively (Jimenez et al., 2003).” “An aethalometer (AE-31, Magee, US) coupled with a PM2.5 cyclone was used to measure the mass concentration of black carbon (BC) with a time resolution of 5 min. The wavelength of 880 nm was used to calculate the BC mass concentration in the data processing.”

(8) Section 2.3: As this study are the very first few ones that used combined TD and

Bypass data to perform the PMF analyses, more details should be provided. The determination of optimal solution, what are the profiles of other solutions? What are the diagnostic plots of the currently chosen solution? What are the correlations of the factors with external tracers? what the PMF results are if only consider bypass data, and then to show clearly what are the advantages (please provide such information in the forms of plots in details not only a brief description) by running PMF on the combined TD and Bypass data. Such details are missing, but they are very helpful and also necessary to evaluate the robustness of your PMF results. Reply: In the supplement, the following plots are now presented: the profiles/time-series/diurnal variations/pie charts of the 4- and 6-factor solutions with combined TD and Bypass data; the diagnostic plots of the currently chosen solution; the PMF results of the profiles and time series of the 4-, 5-, and 6- factor solutions that only used the bypass data. The correlations of the factors with external tracers were also given. Relevant discussions are as below: "The solutions with more than five factors showed no distinct information but splitting of the factors; the Q/Qexpected showed the lowest value at fpeak=0; the varied fpeak did not improve the results; and the varied value of seed also made no significant difference of the solution. Therefore, the solution of five factors, fpeak = 0 and seed = 0, was determined as the optimal solution for this experiment..." "Compared to the results including the thermally denuded data, the HOA and OOA were mixed to some extent, with a signature of the high fraction of CO2+ in the HOA mass spectrum (Figure S2)."

(9) Results: P5L20 It is not convincing to state that sulfate is due to regional transport while other species are influenced by local emissions, only based on the extents of data variability (and the variability can be quantified, from xx to xx and what are the standard deviations?) Reply: This statement has been rephrased to be more rigorous, as below: "Sulfate showed a relatively stable time series, with a relative standard deviation (RSD) of 38.8%, compared to the other species, such as organics (RSD=56.1%), nitrate (RSD=69.6%), and black carbon (RSD=70.2%), indicating that sulfate was less affected by local emission sources."

(10) P5L25: the BC contribution seems to be quite high in PM1 (12.2%), is this number consistent with previous values in Shenzhen? Is this due to heavy traffic? That's also why I asked the calibration and operational details of AE31. Reply: The BC fraction in PM1 in November, 2009 was 14.0% in Shenzhen (He et al., 2011), which is even higher than that in this study. Actually, the high proportion of BC has been a feature of fine aerosol particles in Shenzhen, due to the high amounts of heavy-duty vehicles and ship emissions in this coastal city, with one of the top container ports in the world.

(11) P5L25: Is this composition for bypass conditions or others? Please indicate it clearly. Reply: It's only for the bypass conditions. We have made it clear.

(12) P5L29-: Please add the meteorological parameters, such as temperatures, solar radiation data to help explain the variations of nitrate. For example, it is not convincing to state the photochemical oxidation of NOx only based on the peak after BC peak. Similar for chloride, NH4NO3 is also semi-volatile, so why G/P partitioning drives chloride but not nitrate? Also, if you have PBL data, then add its diurnal pattern as well. Reply: The diurnal variation of temperature (which is available) is added into Figure 2b, and we have re-edited the discussion of the diurnal variation of nitrate, as below: "Nitrate showed a significant peak about 2 hours after the morning peak of BC, which was likely a result of photochemical oxidization of NOx emitted from the morning traffic. Then, the concentration of nitrate decreased because of both the lifting of the planetary boundary layer (PBL) and its evaporation at higher ambient temperatures (also shown in Figure 2b). Nitrate maintained at a stable concentration level in the evening."

(13) P6L7: Why not provide the neutralization plot? You can do that to support your statement. Reply: The neutralization plot has been added in the supporting information now. Relevant discussion has also been added as below: "The measured and predicted ammonium showed a similar correlation (R2=0.96–0.97) with a similar slope of 0.84–0.85 for both the ambient temperatures and 50 °C, implying that the aerosols showed some acidity in the real ambient temperature range (Zhang et al., 2007b)."

(14) P6L12: Do the elemental ratios calculated by Aiken 2008 method, or Canagaratna 2015 method? Please explain. Also, if it is from Canagaratna 2015 method, can it compare with previous values fairly? Reply: The elemental ratios were calculated based on the Canagaratna 2015 method, which has been clarified now in the text, as below. “The data analysis was performed with SQUIRREL 1.57 and PIKA 1.16 (http://cires1.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html) with the method in DeCarlo et al. (2006). The mass concentration was corrected with composition-dependent collection efficiency (Middlebrook et al., 2012). All the elemental ratios calculated here were based on the Improved–Ambient (I-A) method (Canagaratna et al., 2015), while the previous Aiken–Ambient (A-A) method was also used for comparison in Table S1 in the supporting information (Aiken et al., 2008).”

(15) P6L23: I don’t think “which may be caused by the internal mixing and similar gas-particle distribution processes” is correct. If this is correct, then why you state previously that nitrate is due to photochemistry while chloride is due to G/P partitioning? They are not consistent. Reply: This incorrect statement is now removed.

(16) P6L25: “products of photochemical reactions of VOCs have a significant influence on the organic pollution” I don’t think your data presented till here can indicate this. And why only photochemical reactions of VOCs, and other possible processes are excluded? Reply: We agree that this statement may be ambiguous, and it has been re-analyzed as below: “Compared to other species, the peak of organics was slightly smaller, which was a result of the much broader size distribution of organics towards smaller sizes. This character of organic size distribution implies that urban fresh primary emissions contributed significantly to organic aerosol (Canagaratna et al., 2004; He et al., 2011).”

(17) P6L27: why a large size would mean a more aged sulfate? and why it would then mean it had been transported regionally? Reply: The sentence is now rephrased as below: “The peak of sulfate was slightly larger than the other species, suggesting sulfate was mostly associated with larger particles that had grown through gas to particle conversion and coagulation processes during air mass transport (Zhang et al., 2005; Huang et al., 2008).”

(18) P7L6: Is your AE31 downstream of the TD? If so, can you plot the MFR of BC measured by AE31? You didn’t mention the instrument setup of AE31 at all. Reply: Only the AMS was downstream of the TD. The AE-31 was only used for ambient sampling, which has been clarified in the revised manuscript.

(19) P8L7: “sulphuric acid can be distinguished with temperature between 30 and 125 °C”, what does this mean? I don’t quite understand. Reply: Sentence rephrased as: “sulfuric acid would evaporate under temperatures of 30–125 °C, while ammonium sulfate and bisulfate would evaporate between 125 to 175 °C.”

(20) P8L10: this paragraph is not well written. You should provide the average OA MS at different TD temperatures to give more explanations. You didn’t explain why a more rapid increase occurred from 150-200C, and “OA is heated and oxidized into more aged compounds”, there is lacking any supporting evidence. Jimenez et al., 2009 does not say so. “the results is consistent with the OA evolution process (Jimenez et al., 2009)?” Please be more specific and not so vague, this paper doesn’t have any TD-AMS results, although it does show that the O/C ratio of OA increases with the decrease of saturation of OA. Reply: Jimenez et al. (2009) is removed. The discussion has been re-edited, as below: “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+. The O/C variation should be attributed to loss of more volatile species at lower temperatures, especially after 150 °C. 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.”

(21) P9L15: In my viewpoint, your BC and HOA diurnal patterns don't have clear matched with traffic times. It is overall high during evening to noon, and low during afternoon, more relevant to PBL dynamics, likely. Reply: Yes, we agree that PBL also took effects on the diurnal pattern significantly, and we have mentioned the roles of both PBL and traffics in the revised sentences.

(22) P9L23: Your writing logistic is strange. Sometimes you mentioned the results of previous studies, normally, the readers expect to see what your data show, but instead you didn't mention them. Here, you mention the findings of Mohr et al., 2012 regarding m/z 55 and 57, then how does them behave in your MS? If you are not going to describe them for your data, then why you mention Mohr's results? Their results don't support your explanation. Reply: We have supplemented the description of our data, as below: "In this study, COA showed much more C_3 H_3 Oˆ+ than HOA, and the ratio of m/z 55 to m/z 57 showed values larger than 2, indicating the origin of cooking emissions."

(23) P9L28: That's what I am talking about, you mention PBL influence on COA, why not on HOA, etc. Reply: PBL has influence on all the species, and we have added the description of PBL influence on HOA accordingly.

(24) P10L5: Do you have data of external BB tracer to use? Reply: In the revised manuscript, we have made BC source apportionment based on its light absorption spectrum, as suggested by another reviewer. Thus, we got BC from traffic (BCtr) and BC from biomass burning (BCbb). Thus, an external tracer, BCbb, is used for BBOA, and good correlation is also found, as shown in Figure 4b.

(25) P10L15: What are the correlation coefficients of LOOOA with sulfate, as well as MOOOA with nitrate? Typically, the important criteria is to compare the correlations coefficients, and then postulate the assignment of LOOOA and MOOOA (although it is not always the case.) It seems like LOOOA might have a better correlation with sulfate, while MOOOA is better correlated with nitrate from Figure 4b, how to explain? What are the cross correlation coefficients between diurnal patterns of these species? A more

comprehensive discussion regarding these SOA should be combined with meteorological data and also gaseous species, if available. Reply: For MO-OOA, its correlation with sulfate (R2=0.64) was much higher than with nitrate (R2=0.27), which is a typical result. For LO-OOA, its correlation with sulfate (R2=0.59) was indeed a little bigger than with nitrate (R2=0.46), which could be a combined result of the precursors, formation mechanisms, as well as volatility of LO-OOA. The above explanation has been added into the revised text. In terms of the cross correlation between the diurnal patterns, not any good correlation (R2=0.01-0.15) was found due to the limited data points (only for 24 hours). The analysis between OOA and meteorological and gaseous data was ever done, but no helpful information was obtained due to the complexity of formation of OOA, which is not the most important focus of this study.

(26) P10L20: When you talk about the mass contributions of different OA factors, do you mean the average contributions over all data including bypass and TD? Or it is only for the case of bypass conditions? You didn't indicate this clearly at all throughout the manuscript. Reply: It's only for the case of bypass conditions throughout the paper. We have clarified it in the relevant figure captions.

(27) P12Section 3.4: Can you show the mass fractions of different OA factors at different TD temperatures? Reply: This figure is added as Figure 5, and the following discussion is also added: "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."

(28) P12Section3, 4: As I suggested before, this section doesn't discuss any compositional changes of OA, but only mention the variations of MFR. You have an HR-AMS

which can provide chemical information in very details, which is in fact the unique advantage of HRAMS, why not do so? Reply: We have added the compositional changes as in the reply to the above question. Utilizing the advantages of HR-MS, we can obtain the elemental composition change of OA (O/C, H/C, and N/C) with the temperature increasing, which is now added into section 3.2, and the new discussion is 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."

(29) P13L10: It is not that convincing to state that HOA rather than BBOA or COA was a more important source of LO-OOA, based on only the volatility sequence. The sequence may change at different temperatures, then the conclusion will change according to the logistic used here. To prove this, molecular level analyses are required. For example, a HOA tracer compound get oxidized, and the products appear in LO-OOA. Also, heterogeneous or condensed-phase reactions may also produce LO-OOA related species, it is not definitive that the reactions have to proceed via evaporation-gas-phase oxidation-condensation. Such statement is high speculative without any solid evidence in my opinion. Reply: We have removed this speculation and 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."

(30) P13: Basically, I think it is dangerous to state the evolution process of different OA factors based on only volatility data. Even you are lacking of other data, you can perform more analyses, such as the temporal variations, compositional changes, correlations with other species, and discuss these in more details. This can be done for a few cases. Reply: We have made a new discussion for this part, with the addition of the comparison of O/C and volatility for different OA factors, 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%Âů°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."

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