

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.

(1) Please pay attentions to the in-text citation format

Reply: All corrected.

(2) 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 Bertscher 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 250°C or even 300°C, 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 ($\sim 3000 m/\Delta m$). 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 PM_{2.5} 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/Q_{expected} showed the lowest value at $f_{\text{peak}}=0$; the varied f_{peak} 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, $f_{\text{peak}} = 0$ 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 CO_2^+ 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 NO_x 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 NO_x 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 ($R^2=0.96-0.97$) 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 $\text{C}_3\text{H}_3\text{O}^+$ 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 (BC_{tr}) and BC from biomass burning (BC_{bb}). Thus, an external tracer, BC_{bb}, 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 ($R^2=0.64$) was much higher than with nitrate ($R^2=0.27$), which is a typical result. For LO-OOA, its correlation with sulfate ($R^2=0.59$) was indeed a little bigger than with nitrate ($R^2=0.46$), 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 ($R^2=0.01-0.15$) 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%·°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.”

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

Anonymous Referee #2

Received and published: 29 September 2017

This manuscript describes the volatilities of the PM₁ chemical components by using the Thermo-Denuder – Aerosol Mass Spectrometer (TD-AMS) system, along with the positive matrix factorization (PMF) analysis. The results make some very important implications on the atmospheric chemistry of aerosol particles, as there appears to be the first report about such study under a polluted environment in China. Overall, the content of this study fits within the scope of ACP. I agree that this campaign was well-designed. However, the authors need to consider making more further clarifications/ evidences to support a couple of ambiguous discussion and/or conclusions in this paper. Numerous corrections on the text editing are needed, including reference and abbreviation formats as well as language issues, etc. Please the authors carefully check that throughout the manuscript. Therefore, a major revision is needed before it would be accepted in ACP.

General comments:

When I finished reading this manuscript, I feel like that the authors did not fully analyze such comprehensive data set, then, highlight the new findings during the discussion of this study, because I found a lot of “consistent comparison” between this study and previous studies. I can understand that the authors would like to support your results/ discussion/conclusions, and I am not saying that you should not do that. But the authors should try to find something new as those comparisons with previous works. More analysis could also be done to understand such data set. For example, for both TD-path and non-TD-path data: temporal variations (PM₁ species and PMF-OA factors)? chemical changes under the different environment conditions? any evidence for potential origins of changing volatilities for these species (e.g., what’s difference between marine and continental air masses)? Variations of size distributions, rather than averaged ones? etc. More details of experimental materials need to be shown wherever in the main text or supplementary. What’s the duration for TD-path data? It’s easier to understand for readers if the authors could show that, for instance, in the time series of Figure 2a. What’s the time resolution of your measurements during the campaign? How did the authors calibrate the AMS, and what were the results, e.g., values of IE, RIENH₄, RIESO₄? The authors should show one figure for the relationship between measured NH₄ and predicted NH₄ for TD-path and non-TD-path data, respectively. I am not convinced by the state of a finding about “: : that HOA, rather than BBOA or COA, could be a potentially important source of LO-OOA: :”, as shown in the abstract and the main text elsewhere, just based on current TD-AMS-PMF results. The authors should perform more analysis to support that. For example, typical cases analysis? Since the authors have the data of seven-wavelength light absorption, it will be useful to support your PMF-POA factors by performing source apportionment of black carbon (BC) with aethalometer data (Elser et al., 2016).

Reply: All revised as described in the reply to the detailed questions below.

Comments/suggestions in details:

(1). Please note that abbreviations should be used in the same format throughout all the manuscript. For example, page 1, line 12: “a TD-AMS (Thermo-Denuder – Aerosol Mass Spectrometer)” and page 1, line 20: “a hydrocarbon-like OA (HOA, : : :)”. For the consistency, the authors may replace “a TD-AMS (Thermo-Denuder – Aerosol Mass Spectrometer)” by “a Thermo-Denuder – Aerosol Mass Spectrometer (TD-AMS)”. Somewhere else if the same issue should also be done.

Reply: All similar issues have been corrected throughout the paper.

(2). Please define abbreviations when using it for the first time. For instance, Page 1, line 13: submicron particulate matter (PM₁); page 1, line 19: positive matrix factorization (PMF). Somewhere else if the same issue should also be done.

Reply: All similar issues have been corrected throughout the paper.

(3). Page 2, lines 15-25, the authors should also introduce more about the major findings reported by those previous studies. Then, the authors may tell readers the missing knowledge according to the new findings of your study.

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 Burtcher 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.”

(4). Page 2, lines 29-31, I cannot understand the relationship of this sentence with the major story of this introduction.

Reply: This sentence is now deleted.

(5). Page 3, line 15, Duplicate definition for “thermo-denuder (TD)”, it has been defined in the first time in Page 2 line 15. In addition, abbreviation should be followed hereafter when it has been defined at the first time. The authors should carefully check the similar issues as others, e.g., black carbon, organic aerosol, etc.

Reply: All similar issues have been corrected throughout the paper.

(6). Page 5, lines 9-15, it's hard to read these sentences Please re-edit. The authors may introduce your data treatment procedure, then/at the same time, you could give the reference(s) to support yours as well as explain why.

Reply: Re-edited as the following:

“In addition, the PMF results with the data obtained only under ambient temperatures were also explored and the best solution was presented in Figure S2 in the supplement. 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 CO_2^+ in the HOA mass spectrum (Figure S2). Therefore, the PMF solution with the inclusion of the thermally denuded data was confirmed as the final results for later discussion. Huffman et al. (2009b) also suggested that the PMF solution of all data collected both with and without TD-processing could facilitate the separation of different OA factors by enhancing the contrast of the time series of these factors.”

(7). Page 5, line 23, the AE-31 should be described in the experimental method section. More details should be also given, e.g., cutoff, and which wavelength you used for the equivalent black carbon concentration. It is same for SMPS in line 29, for which more description should be given in this section too.

Reply: Information added as below:

“An aethalometer (AE-31, Magee, US) coupled with a $\text{PM}_{2.5}$ 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. A scanning mobility particle sizer (SMPS, TSI Inc.) was used to measure the particle number size distribution (mobility diameter: 15–600 nm) with a time resolution of 5 min. By assuming the densities of the components obtained in the literature (Kuwata et al., 2012; Poulain et al., 2014; Hu et al., 2017), the corresponding mass concentration can be calculated from the particle number size distribution.”

(8). Page 5, lines 24-25, “: :due to rain: :”, to state this, the authors should provide related rain data to prove it. And what's the link of “: :sulfate showed a relatively stable: :” to this “rain case” in this sentence? and I don't understand why the relatively stable time series of sulfate can be considered as regional transportation? The authors may perform more analysis on chemical species along with your ground-measured meteorological parameters. Also, for instance, air mass trajectory analysis would be also useful to help figure it out.

Reply: We didn't get the rain data, but we took sampling notes if there was obvious precipitation events. The vague statement about the indication of regional transport was removed. Since the focus of this paper is to characterize aerosol volatility, section 3.1 actually

serves as the background information of the sampling campaign, and we would not extend the discussion much about the relationship between the chemical species and meteorology. The relevant sentences have been rephrased 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. However, all the species decreased their concentrations largely during January 12–13 due to a heavy rain event.”

(9). Page 5, lines 23-30: It's hard to read such long sentence. The authors should separate it for each information what you want to discuss. Such kind of long sentences is also frequently showing somewhere in this paper. The authors should keep the similar modification.

Reply: Sentences rephrased.

(10). Page 6, lines 2-3: The authors should make the plot to support this discussion. And it would be also interesting to see what's the different ratio of measured and predicted NH₄ from TD-path and non-TD-path data.

Reply: The plots of the measured and predicted NH₄⁺ data with and without the TD have been added in the supporting information. The relative sentences have been rephrased as below:

“The measured and predicted ammonium showed a similar correlation ($R^2=0.96-0.97$) 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).”

(11). Page 6, line 4: Double meanings between “diurnal variation” and “during the day” in one sentence. Please reword it and somewhere same is also needed.

Reply: Sentences re-edited.

(12). Page 6, line 5: Please the authors provide any evidence to prove the contribution of “the activity of heavy duty vehicles” to BC in the evening. If it's a case, and what's the difference sources that contribute BC particles between morning and evening peaks? Indeed, I feel more like that biomass burning emissions (according to the next discussion of BBOA variations) might also contribute the evening peak of BC. That's also one of reasons that I propose the authors to perform the BC source apportionment.

Reply: Following this comment, we did the BC source apportionment using the method in Sandradewi et al. (2008), and the sentences have been re-edited according to the results as below:

“The two peaks in the diurnal variation of BC obviously match the traffic rush hours at approximately 8:00 in the morning and the activities of heavy duty vehicles in the evening. When BC source apportionment was applied for our BC dataset with the method in Sandradewi et al. (2008), the results indicated that biomass burning-emitted BC also made a small contribution to the evening peak of BC (Figure S4).”

(13). Page 6, lines 6-10: The authors should be careful to state the nitrate variations just according to such diurnal peaks between BC and nitrate. For example, how did the authors

indicate that the peak of nitrate after the BC one should be linked to photochemistry, and that the peak at around 14:00 is due to “the enhancement of sunlight”? And, why there was no influence of gas-particle partitioning on nitrate, as discussed only for chloride?

Reply: The analysis of the diurnal variation of nitrate has been improved 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 NO_x 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.”

(14). Page 6, lines 10-11: The authors should provide/link your evidence or any published work(s) to prove such kind of discussions. In the manuscript, somewhere else with the similar issue should be modified too.

Reply: Sentences modified as below:

“Similar to ammonium nitrate, ammonium chloride is also quite semi-volatile as revealed in section 3.2. Therefore, its diurnal variation was largely influenced by the ambient temperature, as well as the height of the PBL. Also according to section 3.2, sulfate is a less-volatile species and thus would not lose significant particulate mass when the ambient temperature increases.”

(15). Page 6, lines 11-13: Remove “during the day”. I cannot understand that “: : a regional product of oxidation by SO₂ that is transported ...”, since I did not see the transported evidence of sulfate in this study. The authors may further analyze the temporal variations along with the size distribution of sulfate, and considering meteorological influence.

Reply: “during the day” removed; the sentences have been modified to be more reasonable, as below:

“As a secondary species from SO₂ oxidation, sulfate showed a slight diurnal variation, indicating that it was less affected by the variation of the PBL. This implies that sulfate was not a typical ground-emitted species and could be better mixed in the PBL. Actually, aerosol sulfate in Shenzhen has been proved to be a species mostly from regional air mass transport (He et al., 2011; Huang et al., 2014).”

(16). Page 6, lines 14-15: Please provide the neutralization plot. It seems an odd sentence for “: : so the diurnal variation of ammonium was influenced by sulfate, nitrate and chloride”. It’s generally true that ammonium measured by the aerodyne AMS is mainly in the form of ammonium sulfate, ammonium nitrate, and/or ammonium chloride. I do more trust that diurnal variations of ammonium can be also affected by such inorganic salts formation processes, besides other factors, e.g., atmospheric physical processes. So, the authors should reword it.

Reply: The neutralization plot is added in the supporting information (Figure S5). The sentence has been reworded as below:

“Since ammonium exists mostly in the forms of (NH₄)₂SO₄, NH₄NO₃ and NH₄Cl, its diurnal variation should be significantly affected by the formation processes of all these inorganic salts, besides atmospheric physical processes and semi-volatility.”

(17). Page 6, lines 15-16: I don’t think the authors need to repeat such information of organic

aerosols as already provided in the introduction before (page 2 lines 13-14). Introduced before. Again, somewhere else, such kind of discussion, at least, the authors should provide reference(s) to support it. I suggest the authors to reedit and combine this sentence with the next one (lines 16-18).

Reply: Suggestion taken. The sentence has been re-edited with reference supporting and combined with the next sentence, as below:

“The diurnal variation of organics showed more fluctuation and a few peaks, consistent with its complex origins, e.g., vehicles, biomass burning, and secondary formation (He et al., 2011; Elser et al., 2016), which will be discussed in detail in section 3.3.”

(18). Page 6, lines 19-21: It's complicate to read here with a lot of comparison in only one sentence. Were all the averaged reference values only from Chen et al. (2015)? In addition, why did not the authors compare those values of O/C and H/C with some results observed under other polluted environments of China? It might make sense to understand such knowledge over the regional scale for developing countries in Asia (e.g., China).

Reply: Yes, all the averaged reference values are from Chen et al. (2015). Following the suggestion, we now only compare the O/C values with other polluted environments in China, as below:

“The average values of O/C and H/C of organic aerosol were 0.52 and 1.61, respectively. The average O/C value in this campaign is within the typical O/C range of 0.28–0.56 previously observed under polluted urban environments in China (Huang et al., 2011, 2012; He et al., 2011; Xu et al., 2016b; Hu et al., 2016; Lee et al., 2013).”

(19). Page 6, lines 21-25: The authors did not explain those diurnal variations of O/C and H/C. And why only a small H/C peak at noon was discussed, but no explanation at the peak during the nighttime? Do the authors think the biomass burning could also influence H/C variations, in addition to traffic and cooking emissions?

Reply: The discussion has been re-edited as below:

“The diurnal variation of O/C plotted in Figure 2c shows elevated values during the daytime, which is a clear indicator of the formation of secondary organic aerosol with more oxygen, while H/C reasonably showed an opposite diurnal trend, with decreased values during the daytime. The quick elevation of H/C in the evening should be a combined result of various primary emissions, e.g., traffic, cooking, and biomass burning, which is supported by the source apportionment results discussed in section 3.3.”

(20). Page 6, line 26: The authors should avoid highlighting “non-refractory species measured by the AMS” too many times over the manuscript, because readers will know that after you explain it at the first time (except for the special case). Please the authors carefully check that elsewhere.

Reply: All corrected.

(21). Page 6, lines 26-28: Be careful making the conclusion of averaged “approximately 500 – 700 nm in the accumulation modes” linking to “all the species” being aged particles. For example, were “all the species” including primary emissions, as below discussed HOA and

BBOA, as well as fresh OOA? In addition, the authors already discussed that nitrate can be formed just after the morning traffic rush hours, so is this also included? To understand so, the authors can do the time series of size distribution of each chemical species (including both inorganic aerosols and PMF-OA factors) instead of showing here.

Reply: We have re-edited the sentences to avoid indicating all species are aged, as below. Since this manuscript focuses on aerosol volatility rather than size distribution, we will not extend the discussion of size distribution more.

“The peaks of all the species were at approximately 500 – 700 nm in the accumulation modes, while organics apparently had more mass distribution at smaller sizes down to ~100 nm.”

(22). Page 6, line 30: I don’t understand why “a similar average size distribution” of these inorganic species is because of this.

Reply: This vague statement is now removed.

(23). Page 6, lines 30-32: As reported the comment of 21, the authors should provide the size distribution of PMF-OA factors to prove this. In addition, how to prove “products of photochemical reactions of VOCs have a significant influence on the organic pollution.”, while rather than other formation processes?

Reply: Since PMF only works on the bulk OA mass spectrum data, it will not produce size distribution of OA factors. To be more rigorous, this statement has been re-edited 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).”

(24). Page 7, lines 1-2: How to understand here, the large size of sulfate being aged and from regional transports?

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).”

(25). Page 7, line 8: Again, “measured by the AMS”, such kind of words, does not need to be iterate.

Reply: All corrected.

(26). Page 7, line 10: What does mean by “measured directly by the AMS.”? Is it meaning the measured particles from non-TD-path channel?

Reply: Yes. Now it is reworded as “The MFR is calculated as the ratio of the species mass concentrations with and without TD-processing.”

(27). Page 7, lines 12-13: The authors stated “: : of the total non-refractory species and organics all: :”. Was this “all” including all inorganic salts and PMF-OA factors? If yes, I do not suggest saying, “the fact that they consist of various compounds with a wide range of volatilities”, then

I prefer to say, “the fact that they include various compounds with a wide range of volatilities”.

Reply: Suggestion taken. The relative sentence is corrected to “the fact that they include various compounds with a wide range of volatilities”.

(28). Page 8, lines 4-7: I suggest the authors to separate this long sentence to be clearer.

Page 8, lines 7-11: Again, please separate this too much long sentence to be clearer.

Page 8, lines 12-14: Just as an example to separate a long sentence, “;” can be changed to “.”.

Reply: All corrected.

(29). Page 8, lines 16-18: I don’t think that Jimenez et al., (2009) stated such conclusion. The authors could try to see variations of both total mass spectra and organic spectra, respectively, at different TD temperatures. The mass fraction of total NR-PM1 and total PMF-OA could be shown also.

Reply: Jimenez et al. (2009) is removed. New discussion has been 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 CO_2^+ . 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.”

(30). Page 9, lines 4-5: May replace “classes/species” by “species”. And replace “the total PM1 composition” by “the total PM1 mass loading”.

Reply: Corrected.

(31). Page 9, lines 5-7: Duplicate definition for “positive matrix factorization (PMF)”. I don’t think this sentence is useful here, as the authors said, “as discussed in section 2.4.”. Please remove or reword it.

Reply: Sentence removed.

(32). Page 9, lines 7-9: Same issue, this kind of information has been shown before in “2.4 Source Apportionment Method”. Please reword. Page 9, lines 9-11: Same again, this information has been shown in “2.4 Source Apportionment Method”. And Duplicate definition for the abbreviation. Please reword.

Reply: The sentences have been reworded as below:

“As discussed in section 2.4, PMF modelling was applied to the high-resolution mass spectra of organics and five factors were identified with their MS profiles shown in Figure 4a. Under ambient temperatures, HOA, COA, BBOA, LO-OOA, and MO-OOA averagely accounted for 13.5%, 20.6%, 8.9%, 39.1%, and 17.9% of the total organic mass, respectively (Figure 4d).”

(33). Page 9, lines 11-13: How are the relative contributions of them at different TD temperature conditions? The authors could be able to show that.

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.”

(34). Page 9, lines 14-16: Please separate this sentence mixed with different information. For example, the authors could discuss the characteristics of your HOA mass spectrum, and give supporting reference. Then to compare your H/C value with typical ones as published, to further prove your reasonable HOA factor.

Reply: The sentence is re-edited as below:

“HOA is most often dominated by long chain hydrocarbon ion series of $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$ in previous findings (Canagaratna et al., 2004; Mohr et al., 2009; Ng et al., 2010), which is also the case in this campaign. The average O/C of HOA was 0.10 in this campaign, which was in its range (0.03 to 0.17) reported in previous publications (e.g., Aiken et al., 2009; Huang et al., 2010; Mohr et al., 2012).”

(35). Page 9, line 16: Duplicate definition for “Black carbon (BC)”.

Reply: Corrected.

(36). Page 9, lines 16-17: Please provide reference(s) to support this discussion. Page 9, lines 17-19: “as identified by previous publications (Zhang et al., 2007a; Lanz et al., 2007; Ulbrich et al., 2009)” seems not really needed here, as compared to the last sentence. It will be more useful to compare HOA with BC from traffic emissions (as I proposed above), because biomass burning emissions can also contribute BC here. Also, this will be helpful to support the Page 9, lines 17-19.

Reply: Following the suggestion, we made BC source apportionment and compare HOA to BC from traffic to support the discussion. The sentences are reworded as below:

“BC is regarded as a tracer of HOA, and can be significantly emitted from both fossil fuel combustion and biomass burning (Zhang et al., 2007a; Lanz et al., 2007; Lan et al., 2011). The good correlation ($R^2=0.82$) of HOA and BC from traffic (Figure 4b) suggested that HOA was mainly from traffic emissions. The diurnal variation of HOA was influenced by PBL dynamics and also showed peaks that matched the rush hours, further supporting the dominant role of traffic emissions to the HOA.”

(37). Page 9, line 23: Related reference(s) is(are) needed to be at the end of “: : which are mainly ionized from alkanes, alkenes and, possibly, long chain fatty acids: : ”.

Reply: References added with (He et al., 2010; Huang et al., 2010; Mohr et al., 2009; Mohr et al., 2012).

(38). Page 9, lines 23-24: “COA is characterized” can be removed. As presented “which are

mainly ionized from alkanes, alkenes and, possibly, long chain fatty acids”, what are such m/z 41 and m/z 55 from for the COA factor?

Reply: This sentence is now removed since its information is duplicate to the next sentence.

(39). Page 9, lines 25-27: I did not get the meaning by mentioning this sentence about the results of Mohr et al. (2012). The authors even did not discuss your results about ratio of “m/z 55 to m/z 57”.

Reply: The new sentence has been added as below:

“In this study, COA showed much more $C_3H_3O^+$ than HOA, and the ratio of m/z 55 to m/z 57 showed values larger than 2, indicating the origin of cooking emissions.”

(39). Page 10, line 3: What are they different between “biomass burning” and “wood burning”, as showing here together?

Reply: It’s a mistake. “wood burning and” is removed.

(40). Page 10, lines 7-9: Reword this sentence.

Page 10, lines 10-12: I did not understand the relationship between “an O/C of 0.32 and showed a similar diurnal trend” and “indicating the significant influence: : :”. If the authors would like to highlight the significant role of biomass burning emissions in aerosol pollution, you should provide the relative contribution to the PM loading. And please reword line 12.

Reply: The sentences have been reworded as below:

“The O/C ratios of BBOA varied a lot in previous studies. Laboratory studies reported O/C ratios of 0.18–0.26 for six types of biomass burning emissions (He et al., 2010), and O/C ratios of 0.31 for lodgepole pine burning and 0.42 for sage/rabbitbrush burning (Aiken et al., 2008). Decarlo et al. (2010) reported an O/C ratio of 0.42 for ambient biomass burning aerosol. The BBOA in this study showed an O/C ratio of 0.33, which is within the range of previous studies. The diurnal trend of BBOA showed a large peak in the evening, well consistent with the diurnal peak of BC from biomass burning in Figure S4.”

(41). Page 10, lines 13-16: Please reword this sentence. Separate it. And don’t repeat to define LO-OOA and MO-OOA as shown before already.

Reply: Corrected

(42). Page 10, lines 16-18: Please separate this sentence. And provide the evidence of both sulfate and MO-OOA from regional transports.

Reply: The sentence has been rephrased and citations have been added to support, as below:

“The factor with a relatively higher O/C ratio (0.95) of OOA and higher f44 than f43 is identified as MO-OOA. It showed a good correlation ($R^2=0.64$) with sulfate, which was less volatile and had been identified as a regional pollutant in Shenzhen (He et al., 2011; Huang et al., 2014), implying MO-OOA could also be aged aerosol from regional transport.”

(43). Page 10, lines 20-21: How to get this conclusion of “denoting their secondary nature.” only according to “: : higher concentrations during the daytime,”. Please explain it more.

Reply: The sentence has been modified as below:

“Unlike the primary organic components, which had lower concentrations during the daytime due to the elevated PBL, the diurnal variations of both LO-OOA and MO-OOA showed higher concentrations during the daytime, suggesting that photochemical secondary production should be their main source.”

(44). Page 12, line 5: I feel like that almost findings relative to the OA volatility in this section “were consistent with” previous studies. For example, lines 9-10 (HOA), line 12 (BBOA), line 18 (COA), page 13 line 5 (OOA). I am not saying that the authors should not compare your findings with previous ones. But, the authors should find something new or that may improve our understanding. In addition, a couple of sentences are needed to be reworded/separated. E.g., some long sentences with “;” and with many times of “which attributive clause”, etc.

Reply: We have made a new discussion for this part, highlighting the features and significance of our study, 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%·°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.”

(45). Page 13, lines 8-17, and page 14, lines 13-15: As many previous studies, I do trust that some POA emissions are semivolatile, which might be a missing source of secondary organic aerosols. However, the authors did not provide direct and enough evidence that may support the conclusion of “HOA, rather than BBOA or COA, could be a potentially important source of LO-OOA” via “the oxidizing process of “Evaporation – Oxidation in gas phase - Condensation”, although according to only the volatility sequence of the PMF-OA factors.

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.”

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

Anonymous Referee #3

Received and published: 22 September 2017

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 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%·°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.”

Revision list

P2L18:

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., 2016a). The TDs designed by Bertscher 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.

P3L5:

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.

P3L27:

The AMS was set into two sampling ion optical modes: the V mode with unit mass resolution (UMR) 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/ Δ 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).

P4L8:

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.

P4L13:

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.

P4L17:

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).

P4L22:

An aethalometer (AE-31, Magee, US) coupled with a PM_{2.5} 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. A scanning mobility particle sizer (SMPS, TSI Inc.) was used to measure the particle number size distribution (mobility diameter: 15–600 nm) with a time resolution of 5 min. By assuming the densities of the components obtained in the literature (Kuwata et al., 2012; Poulain et al., 2014; Hu et al., 2017), the corresponding mass concentration can be calculated from the particle number size distribution. The AE-31 and SMPS were used only for ambient sampling.

P6L6:

In addition, the PMF results with the data obtained only under ambient temperatures were also explored and the best solution was presented in Figure S2 in the supplement. 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). Therefore, the PMF solution with the inclusion of the thermally denuded data was confirmed as the final results for later discussion. Huffman et al. (2009b) also suggested that the PMF solution of all data collected both with and without TD-processing could facilitate the separation of different OA factors by enhancing the contrast of the time series of these factors.

P6L16:

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.

P6L26:

The two peaks in the diurnal variation of BC obviously match the traffic rush hours at approximately 8:00 in the morning and the activities of heavy duty vehicles in the evening. When BC source apportionment was applied for our BC dataset with the method in Sandradewi et al. (2008), the results indicated that biomass burning-emitted BC (BC_{bb}) also made a small contribution to the evening peak of BC (Figure S4). Nitrate showed a significant peak about 2 hours after the morning peak of BC, which was likely a result of photochemical oxidization of NO_x 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.

P7L6:

As a secondary species from SO₂ oxidation, sulfate showed a slight diurnal variation, indicating that it was less affected by the variation of the PBL. This implies that sulfate was not a typical ground-emitted species and could be better mixed in the PBL. Actually, aerosol sulfate in Shenzhen has been proved to be a species mostly from regional air mass transport (He et al., 2011; Huang et al., 2014).

P7L11:

The measured and predicted ammonium showed a similar correlation ($R^2=0.96-0.97$) with a similar slope of 0.84–0.85 for both the ambient temperatures and 50 °C (Figure S5), implying that the aerosols showed some acidity in the real ambient temperature range (Zhang et al., 2007b).

P7L16:

The average values of O/C and H/C of organic aerosol were 0.52 and 1.61, respectively. The average O/C value in this campaign is within the typical O/C range of 0.28–0.56 previously observed under polluted urban environments in China (Huang et al., 2011, 2012; He et al., 2011; Xu et al., 2016b; Hu et al., 2016; Lee et al., 2013). The diurnal variation of O/C plotted in Figure 2c shows elevated values during the daytime, which is a clear indicator of the formation of secondary organic aerosol with more oxygen, while H/C reasonably showed an opposite diurnal trend, with decreased values during the daytime. The quick elevation of H/C in the evening should be a combined result of various primary emissions, e.g., traffic, cooking, and biomass burning, which is supported by the source apportionment results discussed in section 3.3.

P7L26:

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). 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).

P8L13:

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 CO_2^+ . 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.

P10L15:

BC is regarded as a tracer of HOA, and can be significantly emitted from both fossil fuel combustion and biomass burning (Zhang et al., 2007a; Lanz et al., 2007; Lan et al., 2011). The good correlation ($R^2=0.82$) of HOA and BC from traffic (BC_{tr}) (Figure 4b) suggested that HOA was mainly from traffic emissions. The diurnal variation of HOA was influenced by PBL dynamics and also showed peaks that matched the rush hours, further supporting the dominant role of traffic emissions to the HOA.

P11L11:

In this study, COA showed much more $\text{C}_3\text{H}_3\text{O}^+$ than HOA, and the ratio of m/z 55 to m/z 57 showed values larger than 2, indicating the origin of cooking emissions.

P12L4:

The correlation of MO-OOA with nitrate ($R^2=0.27$) is much lower than with sulfate, which is a typical result. Meanwhile, LO-OOA, which is less oxygenated (O/C = 0.76), showed a narrow gap between f43 and f44. The correlation of LO-OOA with sulfate ($R^2=0.59$) was indeed a little bigger than with nitrate ($R^2=0.46$), which could be a combined result of the precursors, formation mechanisms, as well as volatility of LO-OOA. Unlike the primary organic components, which had lower concentrations during the daytime due to the elevated PBL, the diurnal variations of both LO-OOA and MO-OOA showed higher concentrations during the daytime, suggesting that photochemical secondary production should be their main source.

P14L5:

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.

P16L1:

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%·°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.

P16L22:

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.

Volatility measurement of atmospheric submicron aerosols in an urban atmosphere in southern China

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Abstract. Aerosol pollution has been a very serious environmental problem in China for many years. The volatility of aerosols can affect the distribution of compounds in the gas and aerosol phases, the atmospheric fates of the corresponding components and the measurement of the concentration of aerosols. Compared to the characterization of chemical composition, few studies have focused on the volatility of aerosols in China. In this study, a Thermo-Denuder – Aerosol Mass Spectrometer (TD-AMS) system was deployed to study the volatility of non-refractory submicron particulate matter (PM₁) species during winter in Shenzhen. To our knowledge, this paper is the first report of the volatilities of aerosol chemical components based on a TD-AMS system in China. The average PM₁ mass concentration during the experiment was $42.7 \pm 20.1 \mu\text{g m}^{-3}$, with organic aerosol (OA) being the most abundant component (43.2% of the total mass). The volatility of chemical species measured by the AMS varied, with nitrate showing the highest volatility, with a mass fraction remaining (MFR) of 0.57 at 50 °C. Organics showed semi-volatile characteristics (the MFR was 0.88 at 50 °C), and the volatility had a relatively linear correlation with the TD temperature (from the ambient temperature to 200 °C), with an evaporation rate of $0.45 \% \cdot ^\circ\text{C}^{-1}$. Five subtypes of OA were resolved from total OAs by positive matrix factorization (PMF) for data obtained under both ambient temperature and high temperatures through the TD, including a hydrocarbon-like OA (HOA, accounting for 13.5%), a cooking OA (COA, 20.6%), a biomass burning OA (BBOA, 8.9%) and two oxygenated OAs (OOA): a less-oxidized OOA (LO-OOA, 39.1%) and a more-oxidized OOA (MO-OOA, 17.9%). Different OA factors presented different volatilities, and the volatility sequence of the OA factors at 50 °C was HOA (MFR of 0.56) > LO-OOA (0.70) > COA (0.85) \approx BBOA (0.87) > MO-OOA (0.99), which was not completely consistent with the sequence of their O/C ratios. The high volatility of HOA implied that it had a high potential to be oxidized to secondary species in the gas phase. The aerosol volatility measurement results in this study provide useful parameters for the modelling work of aerosol evolution in China and are also helpful in understanding the formation mechanisms of secondary aerosols.

Introduction

Atmospheric aerosol pollution has important impacts on climate change, visibility and human health (Bohnenstengel et al., 2014; Baklanov et al., 2015). Aerosols can be emitted, naturally or anthropogenically, by primary sources or produced by secondary chemical reactions from gaseous precursors (IPCC, 2013). Volatility is one of the most important properties of aerosols, as it can determine the gas-particle phase partitioning of aerosols directly. The saturation vapour pressure, which is affected by temperature and vaporization enthalpies as described by the Clausius-Clapeyron equation, is the main factor that dominates the gas-particle phase partitioning of compounds. Volatility can be determined by the saturation vapour pressure or saturation concentration, while the deposition rates of aerosols for wet or dry deposition are greatly influenced by the phase of aerosols (Bidleman, 1988). The chemical mechanism and reaction rates of gas, liquid and heterogeneous reactions can also result in a great difference because of the phase, the concentration and the lifetime of aerosols can also be influenced (Huffman et al., 2009a). The volatility of organic aerosol (OA) also contributes greatly to the uncertainty in predicting the atmospheric aerosol concentration (Donahue et al. 2006; Pankow and Barsanti 2009). Since OAs contribute 30-80% of total aerosol mass according to previous studies (Hallquist et al., 2009; Zhang et al., 2007a), further research regarding the volatility of atmospheric aerosols, especially organic aerosols, is very important in the understanding of aerosol characterization and source apportionment. Some previous studies examined several kinds of OA emission sources, including traffic emissions, combustion sources and the oxidation of primary OA (POA), and showed differences in volatility according to their different compositions (Huffman et al., 2009a; Xu et al., 2016a; Paciga et al., 2016).

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., 2016a). 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.

Aerosol pollution has been one of the most important air quality problems in China. Many studies focused on aerosol source apportionment and chemical and physical properties have been carried out in most of the regions in China, especially in the Yangtze River Delta Region, the Pearl River Delta Region, the Beijing-Tianjin-Hebei Region and northwest China in the past few years (Huang et al 2010, 2012, 2013; He et al., 2011; Xu et al., 2014; Li et al., 2017). However, the volatility of aerosols is rarely researched in China currently. 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. In this paper, the TD-AMS system was first deployed to determine the volatilities of non-refractory PM₁ species in China. With the high-resolution mass spectra of organics, the volatilities of OAs from different sources and their implications for organic aerosol ageing were also explored.

Experimental methods

2.1 Sampling site description

Shenzhen (113.9°E, 22.6°N) is located on the southeast coast of China, in the southeast corner of the Pearl River Delta region with Hong Kong neighbouring to the south and Dongguan (a famous industrial city in China) to the north. The climate in Shenzhen is a subtropical oceanic climate that is deeply influenced by monsoon. The sampling site was located on the campus of Shenzhen Graduate School, Peking University in the western urban area of Shenzhen. The area surrounding the sampling site was mostly covered by subtropical plants, and there was only a local road that was approximately 100 m away, which can be regarded as an anthropogenic emission source. The measurement was taken from 31 December 2014 to 23 January 2015 in winter, which is the season with the highest air pollution due to regional transportation from northwest and northeast China. The average ambient temperature was 15.9 ± 4.2 °C, and the relative humidity was 62.9 ± 17.5 %. The wind was mostly from the northeast and northwest with an average speed of 0.8 ± 0.7 m/s.

2.2 Instruments and methodology

The aerosol volatility measurements were conducted with a TD – AMS system. The thermo-denuder and the high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, referred to hereafter as AMS) were both manufactured by Aerodyne Research Inc., US. The principle theory of an AMS can be found in previous studies (DeCarlo et al., 2006; Canagaratna et al., 2007). The AMS was set into two sampling ion optical modes: the V mode with unite mass resolution (UMR) 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/ Δm). 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). The TD used in this experiment is based on the design of Huffman et al. (2008). It consists of two parts: the heating section and the denuder section. The stainless steel heating section is 22.25 inches (56.5 cm) in length with a 1-inch OD (2.5 cm) and a 0.875-inch ID (2.2 cm), wrapped with three fibreglass-coated heating tapes. The heating section is then joined to a 22-inch (56 cm) denuder section. The denuder section is filled with activated charcoal at room temperature to adsorb the gas phase species evaporated from particles. The temperature in the heating section was set at 48, 95, 143 and 192 °C to make the real temperature at the centreline, measured with a thermocouple, reach 50, 100, 150 and 200 °C, respectively. 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 TD was placed upstream of the AMS. The aerosol flow can go through the heating and denuder sections (TD path) before being sampled by the AMS or flowing directly (ByPass path) into the AMS. The residence time of aerosols in the heating section was approximately 27.9 s with a flow rate of 0.45 L/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.

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).

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2.3 Particle Loss Correction

The particle losses through the TD should be of concern for quantitative measurements with the TD, as it can decrease the transmission efficiency through the TD. There are three mechanisms of particle loss inside the TD: sedimentation, thermophoretic and diffusional processes (Burtscher et al., 2001; Wehner et al., 2002). Burtscher et al. (2001) determined that

the dominant effects would be determined by the temperature and particle size: sedimentation increases as the particle size increases and would be negligible when the TD is vertical; diffusive losses increase with decreasing particle size; and thermophoresis is not strongly dependent on particle size, is important in the denuder section and will partly compensate for diffusion in the heating section.

- 5 The transmission efficiency in this research was calculated via an experiment. CsCl solution was atomized and then measured by Differential Mobility Analyzer (DMA, TSI Inc.)/Condensation Particle Counter (CPC, TSI Inc.) before and after the TD. The transmission efficiency of the ByPass path was regarded as 1. The average transmission efficiency through the TD is approximately 90%, at 50, 100, 150 and 200 °C, as shown in Figure 1, which is similar to previous studies (Huffman et al., 2008; Xu et al., 2016a). The transmission efficiency would be applied in the calculation of the mass concentration of particles
10 flowed through the TD.

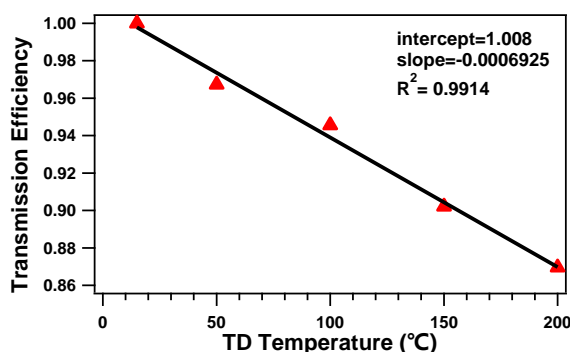


Figure 1. Temperature related transmission efficiency through the TD.

2.4 Source Apportionment Method

- PMF was applied to the high resolution organic mass spectra using the PMF evaluation tool developed by Ulbrich et al. (2009).
15 The data and error matrix were processed according to the signal-to-noise ratio (SNR) as reported in previous papers (Ulbrich et al., 2009; Huang et al., 2010; He et al., 2011). Weak ions ($0.2 < \text{SNR} < 2$) were downweighted by a factor of 2, bad ions ($\text{SNR} < 0.2$) were removed from the analysis (Paatero and Hopke, 2003), and CO_2^+ related ions (O^+ , HO^+ , H_2O^+ and CO^+) were also downweighted (Ulbrich et al., 2009).

- The PMF analysis was based on the full high-resolution organic dataset (including both data sampled under ambient
20 temperature and that was thermally denuded) for 1 to 10 factors with f_{peak} varying from -1 to 1 (seed), increasing with a step of 0.1, and seed varying from 0 to 250 ($f_{\text{peak}} = 0$) in steps of 10. The diagnostic plots of the solutions are shown in Figure S1 in the supplement, including the Q/Q_{expected} ratio, the characteristics of the different mass spectra, the scaled residuals, and the correlation of the component time series with the external tracers. The solutions with more than five factors showed no distinct

information but splitting of the factors; the Q/Q_{expected} showed the lowest value at $f_{\text{peak}}=0$; the varied f_{peak} 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, $f_{\text{peak}} = 0$ and seed = 0, was determined as the optimal solution for this experiment, and the five factors are hydrocarbon-like organic aerosol (HOA), cooking organic aerosol (COA), biomass burning organic aerosol (BBOA), less-oxidized oxygenated organic aerosol (LO-OOA) and more-oxidized oxygenated organic aerosol (MO-OOA).

In addition, the PMF results with the data obtained only under ambient temperatures were also explored and the best solution was presented in Figure S2 in the supplement. 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 CO_2^+ in the HOA mass spectrum (Figure S2). Therefore, the PMF solution with the inclusion of the thermally denuded data was confirmed as the final results for later discussion. Huffman et al. (2009b) also suggested that the PMF solution of all data collected both with and without TD-processing could facilitate the separation of different OA factors by enhancing the contrast of the time series of these factors.

3 Results and discussion

3.1 PM_{10} chemical compositions

Figure 2 shows the chemical compositions for only bypass conditions. Figure 2a shows the time series of the mass concentration of non-refractory species measured by the AMS and black carbon measured with an Aethalometer during the experiment. 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. However, all the species decreased their concentrations largely during January 12–13 due to a heavy rain event. The sum of the non-refractory species and BC was regarded as PM_{10} , which showed a high correlation ($R^2=0.94$, slope=1.1, in Figure S3) with the mass concentration derived from the particle number concentration measured by SMPS. In result, the average mass concentration of PM_{10} was $42.7 \pm 20.1 \mu\text{g m}^{-3}$, ranging from 3.9 to $134.1 \mu\text{g m}^{-3}$, while organics were the most abundant PM_{10} component, contributing 43.2% to the total PM_{10} mass concentration, followed by sulfate (21.2%), black carbon (12.2%), nitrate (11.4%), ammonium (10.4%) and chloride (1.6%). The measured and predicted ammonium showed a high correlation ($R^2=0.97$) with a slope of 0.85, implying that the aerosols showed some acidity (Zhang et al., 2007b).

The diurnal variation of the PM_{10} species are shown in Figure 2b. The two peaks in the diurnal variation of BC obviously match the traffic rush hours at approximately 8:00 in the morning and the activities of heavy duty vehicles in the evening. When BC source apportionment was applied for our BC dataset with the method in Sandradewi et al. (2008), the results indicated that biomass burning-emitted BC (BC_{bb}) also made a small contribution to the evening peak of BC (Figure S4). Nitrate showed a significant peak about 2 hours after the morning peak of BC, which was likely a result of photochemical oxidization of NO_x

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. Similar to ammonium nitrate, ammonium chloride is also quite semi-volatile as revealed in section 3.2. Therefore, its diurnal variation was largely influenced by the ambient temperature, as well as the height of the PBL. Also according to section 3.2, sulfate is a less-volatile species and thus would not lose significant particulate mass when the ambient temperature increases. As a secondary species from SO₂ oxidation, sulfate showed a slight diurnal variation, indicating that it was less affected by the variation of the PBL. This implies that sulfate was not a typical ground-emitted species and could be better mixed in the PBL. Actually, aerosol sulfate in Shenzhen has been proved to be a species mostly from regional air mass transport (He et al., 2011; Huang et al., 2014). Since ammonium exists mostly in the forms of (NH₄)₂SO₄, NH₄NO₃ and NH₄Cl, its diurnal variation should be significantly affected by the formation processes of all these inorganic salts, besides atmospheric physical processes and semi-volatility. The measured and predicted ammonium showed a similar correlation ($R^2=0.96-0.97$) with a similar slope of 0.84–0.85 for both the ambient temperatures and 50 °C (Figure S5), implying that the aerosols showed some acidity in the real ambient temperature range (Zhang et al., 2007b). The diurnal variation of organics showed more fluctuation and a few peaks, consistent with its complex origins, e.g., vehicles, biomass burning, and secondary formation (He et al., 2011; Elser et al., 2016), which will be discussed in detail in section 3.3.

The average values of O/C and H/C of organic aerosol were 0.52 and 1.61, respectively. The average O/C value in this campaign is within the typical O/C range of 0.28–0.56 previously observed under polluted urban environments in China (Huang et al., 2011, 2012; He et al., 2011; Xu et al., 2016b; Hu et al., 2016; Lee et al., 2013). The diurnal variation of O/C plotted in Figure 2c shows elevated values during the daytime, which is a clear indicator of the formation of secondary organic aerosol with more oxygen, while H/C reasonably showed an opposite diurnal trend, with decreased values during the daytime. The quick elevation of H/C in the evening should be a combined result of various primary emissions, e.g., traffic, cooking, and biomass burning, which is supported by the source apportionment results discussed in section 3.3.

Figure 2d shows the average size distribution of the five non-refractory species. The peaks of all the species were at approximately 500 – 700 nm in the accumulation modes, while organics apparently had more mass distribution at smaller sizes down to ~100 nm. The inorganic aerosol species showed a similar average size distribution during the experiment as described in previous studies in Shenzhen (He et al., 2011). 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). 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).

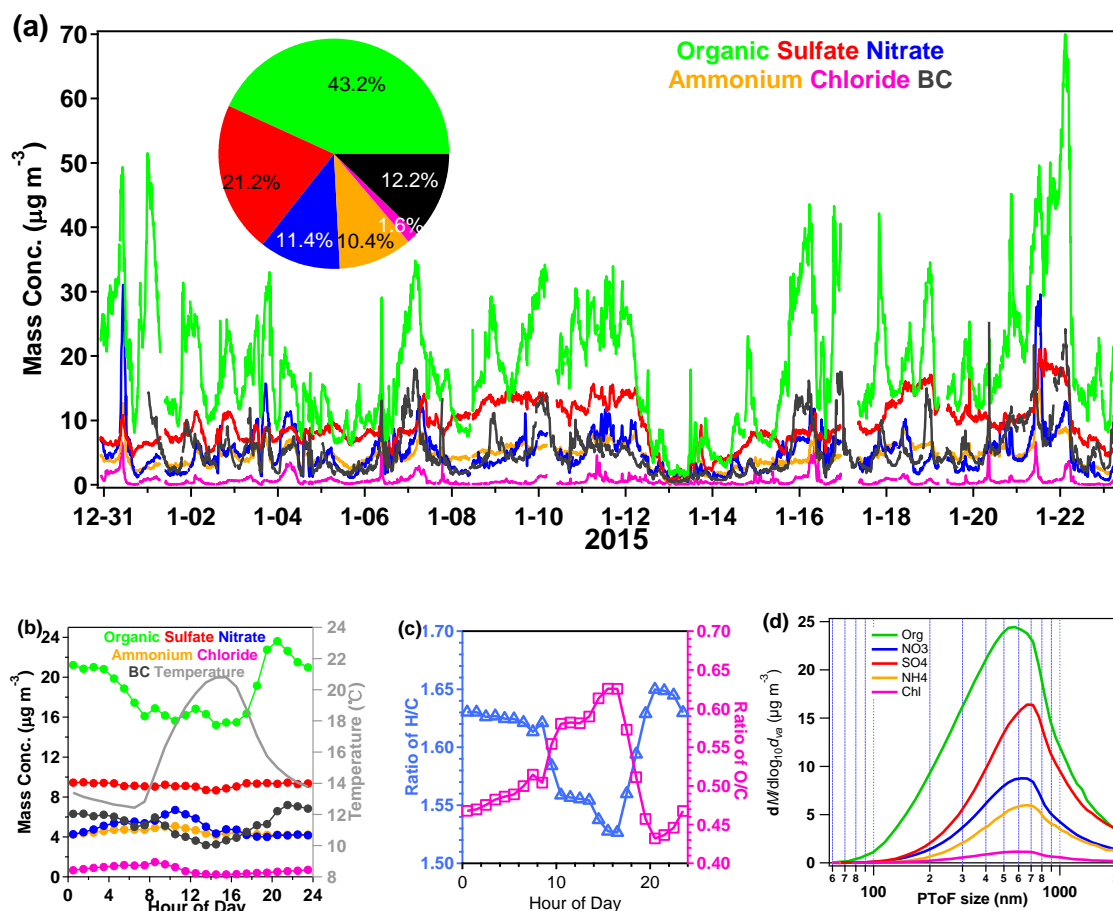


Figure 2. Chemical composition for only bypass conditions: (a) Time series and the mass percentages of PM₁ composition; (b) diurnal variation of PM₁ species and ambient temperature; (c) diurnal variation of H/C ratio and O/C ratio; (d) average size distribution of non-refractory PM₁ species.

3.2 Volatility of PM₁ species

Figure 3 shows the mass fraction remaining (MFR) of the non-refractory species. The MFR is calculated as the ratio of the species mass concentrations with and without TD-processing. The narrow average MFR \pm standard deviation regions show that the volatilities of these species were stable during the measurement. The MFRs of the total non-refractory species and organics both showed nearly linear correlations with the TD temperature, which is consistent with the fact that they include various compounds with a wide range of volatilities. For organics, the MFR was 0.88 at 50 °C, 0.63 at 100 °C, 0.32 at 150 °C and, finally, 0.16 at 200 °C. Based on the linear relationship of the MFR of organics and the TD temperature, the evaporation rate of organics is approximately 0.45% °C⁻¹. 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 CO_2^+ . 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.

Figure 3 also shows the MFRs of inorganic species with different temperature, and all the inorganic species showed trends similar to the results shown by Huffman et al. (2008). Nitrate and chloride show similar trends: they both decreased sharply from ambient temperature to 50 °C, reaching approximately 0.57; then decreased at a lower rate from 50 to 150 °C. When the TD temperature increased to 200 °C, the MFRs of nitrate and chloride were at approximately 0.08, which are lower than those of all the other species. Sulfate is the least volatile species among all PM_{10} species. The MFR of sulfate does not show a significant decreasing trend with temperature below 100 °C (0.93 at 50 °C and 0.89 at 100 °C); when the temperature reached 150 °C, the MFR decreased sharply to 0.43, with 11% left at 200 °C. The trend of MFR of sulfate is consistent with the discussion in Burtscher et al. (2001): sulfuric acid would evaporate under temperatures of 30–125 °C, while ammonium sulfate and bisulfate would evaporate between 125 to 175 °C.

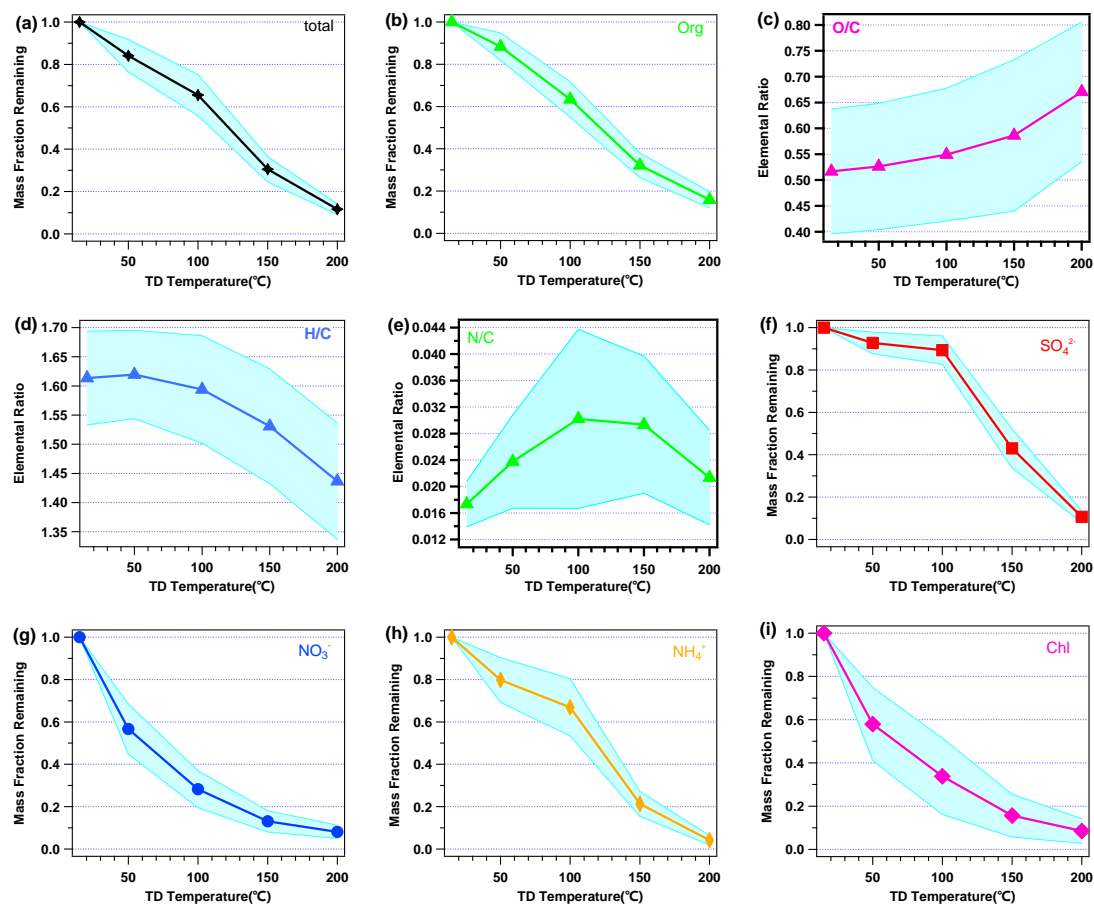


Figure 3. Variation of the average mass fraction remaining (MFR) of the total of non-refractory species and the ratios of O/C, H/C, and N/C with the TD temperature. The shaded regions indicate the average \pm standard deviation.

3.3 Source Apportionment

Organics are one of the most important chemical species in aerosol pollution in Shenzhen, contributing 43.2% to the total PM₁ mass loading. As discussed in section 2.4, PMF modelling was applied to the high-resolution mass spectra of organics and five factors were identified with their MS profiles shown in Figure 4a. Under ambient temperatures, HOA, COA, BBOA, LO-OOA, and MO-OOA averagely accounted for 13.5%, 20.6%, 8.9%, 39.1%, and 17.9% of the total organic mass, respectively (Figure 4d).

HOA is most often dominated by long chain hydrocarbon ion series of $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$ in previous findings (Canagaratna et al., 2004; Mohr et al., 2009; Ng et al., 2010), which is also the case in this campaign. The average O/C of HOA was 0.10 in this campaign, which was in its range (0.03 to 0.17) reported in previous publications (e.g., Aiken et al., 2009; Huang et al., 2010; Mohr et al., 2012). BC is regarded as a tracer of HOA, and can be significantly emitted from both

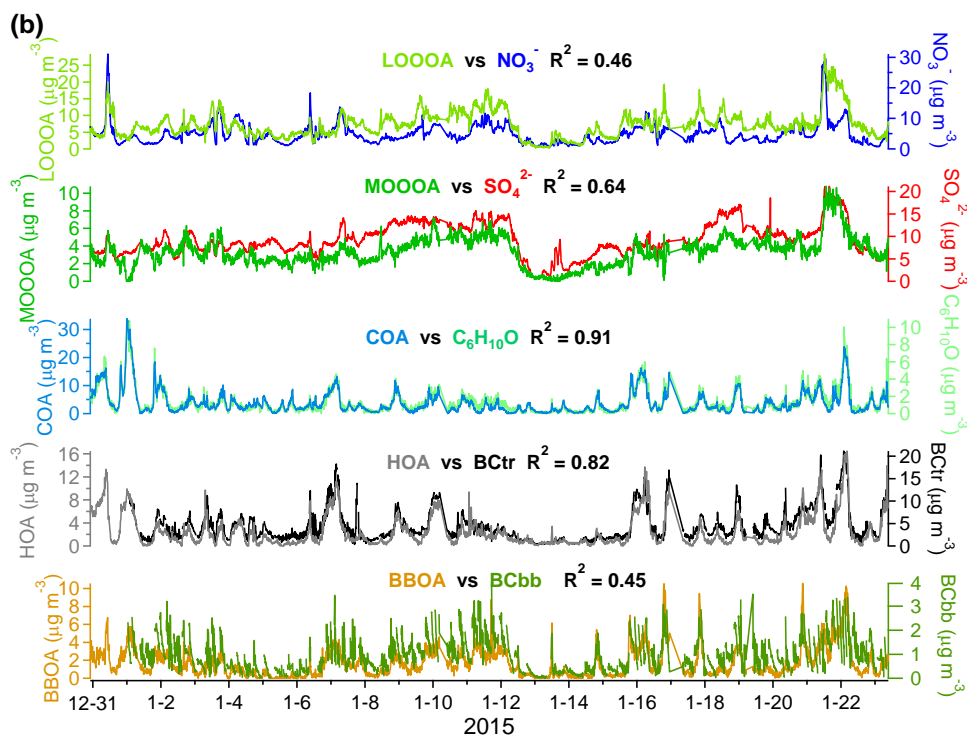
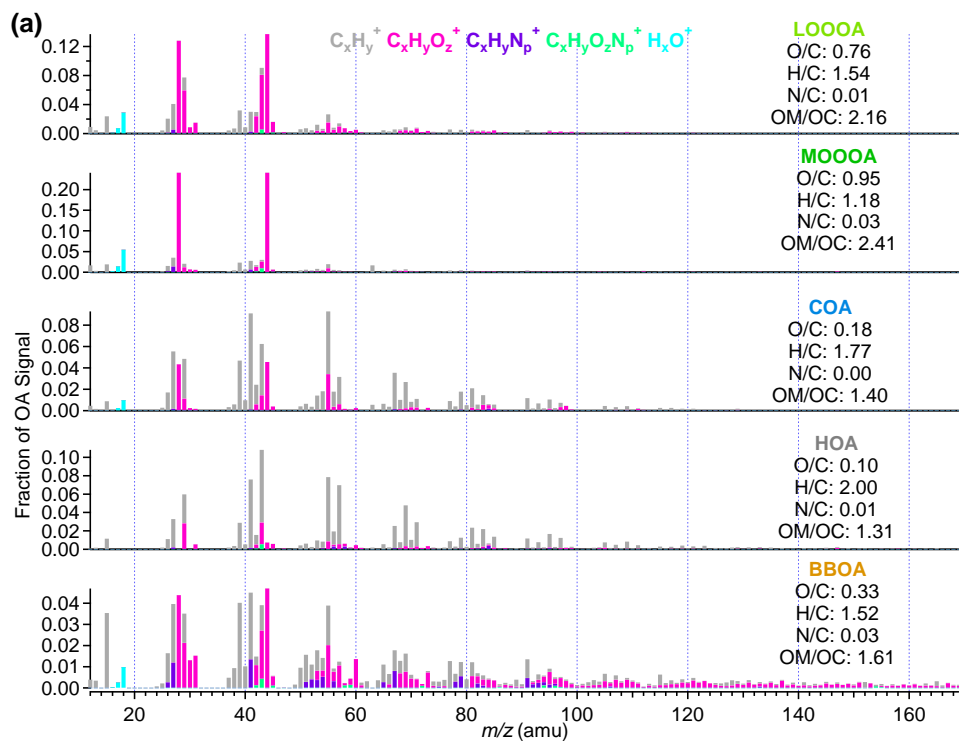
fossil fuel combustion and biomass burning (Zhang et al., 2007a; Lanz et al., 2007; Lan et al., 2011). The good correlation ($R^2=0.82$) of HOA and BC from traffic (BCtr) (Figure 4b) suggested that HOA was mainly from traffic emissions. The diurnal variation of HOA was influenced by PBL dynamics and also showed peaks that matched the rush hours, further supporting the dominant role of traffic emissions to the HOA.

- 5 The O/C ratio of COA is 0.18, which is similar to the previous results shown in Mohr et al. (2012). The mass spectral signature of COA is dominated by the ion series of $C_nH_{2n+1}^+$ and $C_mH_{2m+1}CO^+$ (m/z 29, 43, 57, 71, 85...), $C_nH_{2n-1}^+$ and $C_mH_{2m-1}CO^+$ (m/z 41, 55, 69, 83...), which are mainly ionized from alkanes, alkenes and, possibly, long chain fatty acids (He et al., 2010; Huang et al., 2010; Mohr et al., 2009; Mohr et al., 2012). Mohr et al. (2012) also identified COA from HOA by comparing the signals of m/z 55 and m/z 57 and determined that the differentiation between COA and HOA is mainly driven by the oxygen-containing ions of $C_3H_3O^+$ and $C_3H_5O^+$; especially if the signal ratio of m/z 55 to m/z 57 is larger than 2, it probably can be recognized as COA. In this study, COA showed much more $C_3H_3O^+$ than HOA, and the ratio of m/z 55 to m/z 57 showed values larger than 2, indicating the origin of cooking emissions. The diurnal variation of COA in Figure 4c shows a small peak at approximately 8:00 am, breakfast time, and the second peak at approximately 14:00 corresponds with lunch time. The mass concentration of COA also rises after 17:00, which is the time for dinner and partly because of the decreasing PBL height. The good correlation of COA with the tracer ion $C_6H_{10}O$ ($R^2=0.91$) (Sun et al., 2011; Crippa et al., 2013; Elser et al., 2016) also demonstrated the presence of COA.

- The most abundant signals in BBOA are m/z 29 (CHO^+) and m/z 43 ($C_2H_3O^+$), and there are more fragments in the range of $m/z > 100$ for BBOA than for COA and HOA (He et al., 2010). BBOA can be identified by the contribution of m/z 60 (mostly $C_2H_4O_2^+$), which is distinct fragment of ionized levoglucosan, the molecular marker of biomass burning (Alfarra et al., 2007; Aiken et al., 2009; Mohr et al., 2009). Some previous studies have shown that the background level of m/z 60 /OA is approximately 0.3% in urban areas without biomass burning impacts (DeCarlo et al., 2008; Docherty et al., 2008). The signal of m/z 60 in BBOA is 1.36% in this study, indicating the presence of BBOA during this experiment, and the BBOA correlated well with m/z 60 ($R^2=0.83$). The O/C ratios of BBOA varied a lot in previous studies. Laboratory studies reported O/C ratios of 0.18–0.26 for six types of biomass burning emissions (He et al., 2010), and O/C ratios of 0.31 for lodgepole pine burning and 0.42 for sage/rabbitbrush burning (Aiken et al., 2008). DeCarlo et al. (2010) reported an O/C ratio of 0.42 for ambient biomass burning aerosol. The BBOA in this study showed an O/C ratio of 0.33, which is within the range of previous studies. The diurnal trend of BBOA showed a large peak in the evening, well consistent with the diurnal peak of BC from biomass burning in Figure S4.

- OOA is recognized by the most intense signal of m/z 44 (CO_2^+), and the signals at higher values of m/z are lower relative to those of other OA factors (Ng et al., 2010). Furthermore, the OOA can be divided into two factors, LO-OOA (typically named semi-volatile OOA) and MO-OOA (typically named less-volatile OOA), according to the O/C ratios and f44 (Jimenez et al.,

2009; Ng et al., 2010; Xu et al., 2015). The factor with a relatively higher O/C ratio (0.95) of OOA and higher f44 than f43 is identified as MO-OOA. It showed a good correlation ($R^2=0.64$) with sulfate, which was less volatile and had been identified as a regional pollutant in Shenzhen (He et al., 2011; Huang et al., 2014), implying MO-OOA could also be aged aerosol from regional transport. The correlation of MO-OOA with nitrate ($R^2=0.27$) is much lower than with sulfate, which is a typical result. Meanwhile, LO-OOA, which is less oxygenated (O/C = 0.76), showed a narrow gap between f43 and f44. The correlation of LO-OOA with sulfate ($R^2=0.59$) was indeed a little bigger than with nitrate ($R^2=0.46$), which could be a combined result of the precursors, formation mechanisms, as well as volatility of LO-OOA. Unlike the primary organic components, which had lower concentrations during the daytime due to the elevated PBL, the diurnal variations of both LO-OOA and MO-OOA showed higher concentrations during the daytime, suggesting that photochemical secondary production should be their main source. The diurnal variation of MO-OOA was relatively stable compared to that of LO-OOA, which is consistent with that MO-OOA is a more aged and regional component. The contribution of the two OOAs to total OAs is 57.0%, indicating that OOA contributes the majority of the OA pollution in wintertime in Shenzhen.



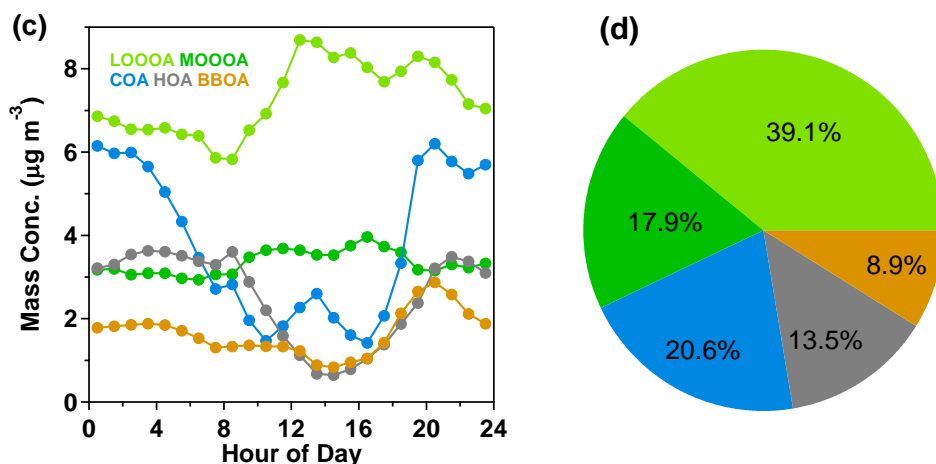


Figure 4 (a) MS profiles of the five OA factors identified by PMF; (b) time series of the five OA factors and the correlation with the relevant species during the experiment; (c) the diurnal variation of the five OA factors; (d) the average contributions of the five OA factors to total OAs. The time series, diurnal variation and pie chart display the results only for ambient conditions.

5 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

10 following section.

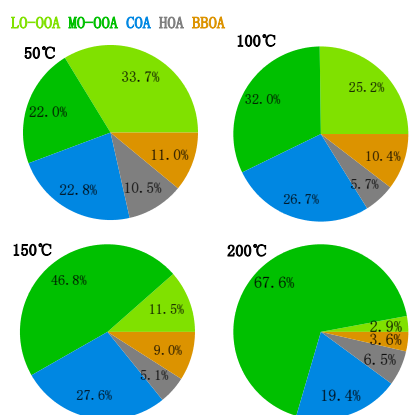


Figure 5. The average compositions of the total OA at different TD temperatures.

3.4 Volatility of OA factors

Figure 6 shows the MFRs of the different OA factors identified by PMF. The MFR of HOA was 0.56 at 50 °C and decreased by 1.26 %·°C⁻¹ from the ambient temperature to 50 °C, and got to only 17.8% at 100 °C. Then, the evaporation rate slowed down significantly, with a MFR of 7.6% at 200 °C. BBOA showed significant volatility in this study, with an evaporation rate of 0.37%·°C⁻¹ near the ambient temperature and an MFR of 0.87 at 50 °C. In addition, it was noted that the evaporation rate of BBOA got quicker when the TD temperature increased from 100 °C to 150 °C, indicating that BBOA contained more compounds that favour evaporating in this temperature range. COA showed a similar volatility to that of BBOA, with an MFR of 0.85 at 50 °C, but it kept a stable evaporation rate throughout the whole temperature range (~0.44%·°C⁻¹). The volatility of LO-OOA (MFR=0.70 at 50 °C) was higher than those of MO-OOA (MFR=0.99 at 50 °C), COA, and BBOA, but lower than that of HOA. The MFR curve of MO-OOA remained relatively stable below 100 °C and then decreased significantly when the temperature increased further. The MFR of MO-OOA was as high as 51.5% even at 200 °C. Thus, MO-OOA was the least volatile one among the five factors. The OOA (LO-OOA+MO-OOA) in Figure 6 presents the MFR variation of the combination of LO-OOA and MO-OOA. The MFR of OOA, which is regarded as a good surrogate of SOA, showed a good linear decline at the temperatures under 150 °C, with an evaporation rate of 0.54 %·°C⁻¹. The evaporation rates of the different OA factors identified by PMF in this study provide the first hand information of semi-volatility of organic aerosols in China, which will be helpful in constraining parameters in the atmospheric chemical models.

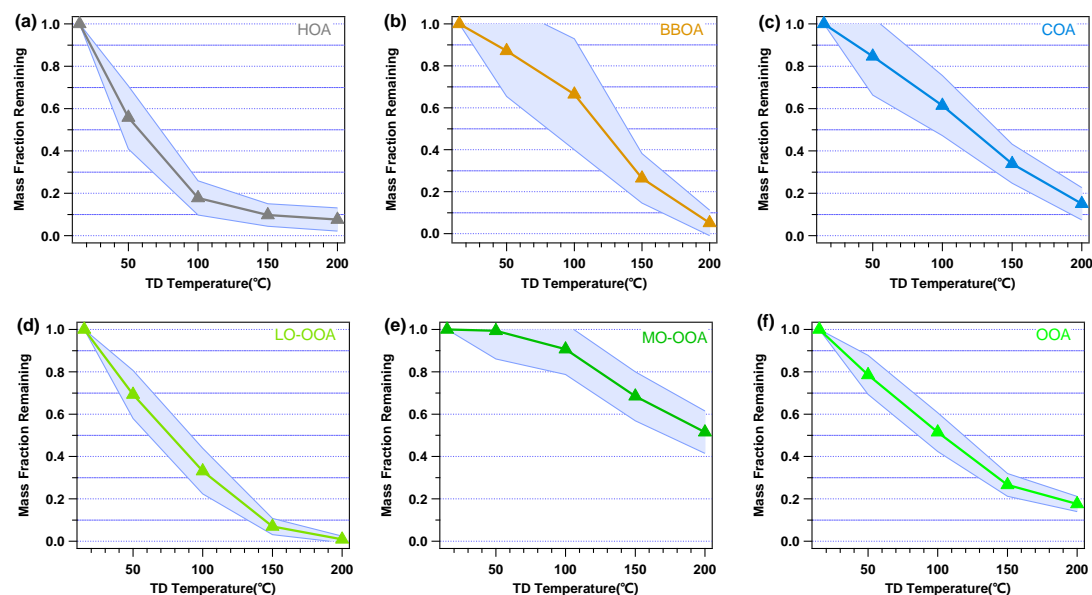


Figure 6 Average mass fraction remaining (MFR) of the five OA factors and OOA (calculated as the combination of MO-OOA and LO-OOA). The shaded region is the average MFR±standard deviation.

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%·°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.

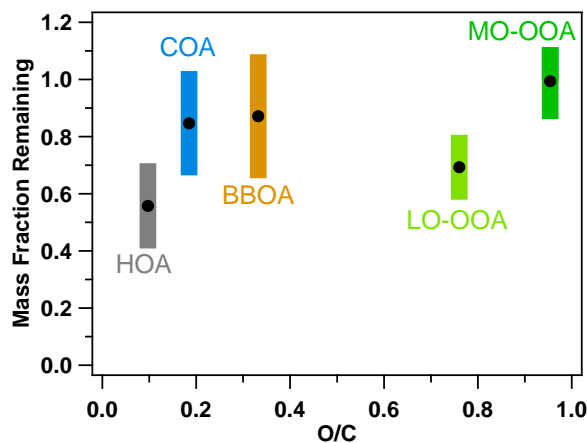


Figure 7 Comparison of the volatilities (MFRs at 50 °C) and O/C ratios of the five OA factors in this study. The colourful regions indicate the standard deviations of the MFRs.

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.

5 4. Conclusions

The source apportionment and volatility of the PM₁ chemical composition during winter in Shenzhen were investigated based on the TD-AMS system. The mean PM₁ mass concentration was $42.7 \pm 20.1 \mu\text{g m}^{-3}$ during the experiment, with organics (accounting for 43.2%) as the most abundant species. Sulfate, black carbon, nitrate, ammonium and chloride contributed 21.2%, 12.2%, 11.4%, 10.4% and 1.6% to the total PM₁, respectively. The chemical species in PM₁ exhibited a range of volatilities. Nitrate showed the highest volatility among the five species measured with the lowest MFR (0.57) at 50 °C. Organics exhibited a relatively linear MFR decrease, with a rate of $0.45 \% \cdot ^\circ\text{C}^{-1}$, as the TD temperature increased from ambient to 200 °C, which is mainly due to the complex composition of organics in the atmosphere. The organics were grouped into five subtypes by the PMF analysis, including primarily emitted HOA, COA, BBOA and two secondarily formed oxygenated OAs: LO-OOA and MO-OOA, and they accounted for 13.5%, 20.6%, 8.9%, 39.1% and 17.9% of the total OA, respectively. Among all the five OA factors, HOA was the most volatile species, whereas MO-OOA had the lowest volatility with the slowest evaporation rate. According to the MFR of different OA factors at 50 °C, the volatility sequence of the five OA factors was HOA (MFR of 0.56 at 50 °C) > LO-OOA (0.70) > COA (0.85) \approx BBOA (0.87) > MO-OOA (0.99), which was not completely consistent with the sequence of their O/C ratios. The most volatile HOA had a high potential to be oxidized to secondary species in the gas phase.

20 Acknowledgments

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