Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-663-AC2, 2017

Atmospheric Chemistry and Physics
Discussions
Open Access

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

**Li-Ming Cao et al.**

huangxf@pku.edu.cn

Received and published: 16 November 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

Printer-friendly version

Discussion paper

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

Printer-friendly version

Discussion paper

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 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 $\alpha$-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 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."

(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 PM2.5 cyclone was used to measure the mass concentration of black carbon (BC) with a time resolution of 5 min. The wavelength of 880 nm was used to calculate the BC mass concentration in the data processing. 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 (R2=0.96–0.97) with a similar slope of 0.84–0.85 for both the ambient temperatures and 50 °C, implying that the aerosols showed some acidity in the real ambient temperature range (Zhang et al., 2007b)."

(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 NOx emitted from the morning traffic. Then, the concentration of nitrate decreased because of both the lifting of the planetary boundary layer (PBL) and its evaporation at higher ambient temperatures (also shown in Figure 2b). Nitrate maintained at a stable concentration level in the evening."

(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 meteoro-

Printer-friendly version

Discussion paper

logical 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 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."

(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_n H_(2n+1)ˆ+ and C_n H_(2n-1)ˆ+ 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 (R2=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_3 H_3 Oˆ+ than HOA, and the ratio of m/z 55 to m/z 57 showed values larger than 2, indicating the origin of cooking emissions."

(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

Printer-friendly version

Discussion paper

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 (R2=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 ≈ BBOA > MO-OOA. It can be easily found that the sequence of the volatilities of the OA factors does not completely follow the sequence of the O/C ratios. For example, although LO-OOA has a higher O/C ratio than BBOA and COA, LO-OOA is also more volatile (or with a lower MFR) than BBOA and COA. This clearly indicates the volatility of the OA factors depends not only on the oxygenation of organic compounds, but also other factors, e.g., molecular weight and mixing state. HOA is identified as the most volatile OA factor while MO-OOA is nearly non-volatile near the real atmospheric temperatures in Shenzhen, which is consistent with the results observed in Mexico and Paris (Cappa and Jimenez, 2010; Paciga et al., 2016). However, LO-OOA is the second volatile OA factor after HOA in Shenzhen, which is different from that in Mexico, where BBOA is more volatile than LO-OOA. Actually, the volatility of the aerosols directly from biomass burning have been measured to be quite variable, with an evaporation rate of 0.2–1.6%Âů°C-1, depending on the kinds of wood and combustion conditions (Huffman et al., 2009a). The relatively lower volatility of COA was also identified in previous studies and attributed to the abundant fatty acids of low volatility in COA (Mohr et al., 2009; Paciga et al., 2016). Hong et al. (2017) recently reported the estimation of the organic aerosol volatility in a boreal forest in Finland using two independent methods, including using a VTDMA with a kinetic evaporation model and applying PMF to HR-AMS data. Semi-volatile and low-volatility organic mass fractions were determined by both methods, similar to our study in China. This implies that MO-OOA and LO-OOA, with different volatilities, could be popular organic aerosol components across the world. Hong et al. (2017) also pointed out that determining of extremely low volatility organic aerosols from AMS data using the PMF analysis should be explored in future studies."

(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 Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-663, 2017.