

Response to comments:

We sincerely thank the reviewers for their helpful comments and guidance. Addressing the major points raised during the review process has substantially improved the quality of the manuscript. In the text that follows, reviewer comments in normal text are followed by author responses in italics.

Reviewer #1:

This manuscript presents measurements of aerosol composition made with an Aerodyne HRAMS in Houston, TX. The measurements were carried out in two different seasons, and the focus of the analysis is on differences in the OA composition and sources during these different times. Overall, this is a novel data set and the topic is certainly appropriate for ACP. The writing is generally good and the manuscript is well-organized. I do have a number of major issues with the manuscript – some addressed here, some in the section below – that prevent me from endorsing it for publication at this time. It may be suitable for publication after a major revision.

My greatest concern deals with the analyses and discussion related to Figure 9 (lines 482 - 494) and Figure 11 (lines 550 - 560). This seems like the definition of “cherry picking” data to support one’s view, when the entire data set does not. There is no rationale for excluding such large amounts of data until one achieves a good linear fit. It supports the authors’ narratives, but I think the conclusions involving these Figures (which are central to the entire manuscript) need substantial revision since they are not consistent with the data.

Response:

We thank the reviewer for highlighting this point, but we respectfully disagree with the reviewer that the data analysis involves cherry picking. Please note the fact that it is possible to find a distinct regression relationship between two observed variables for part of a given data set, in contrast to the whole data set. We can find many examples in the literature: for example, the third figure in Li et al. (2016) and the eighth figure in Guo et al. (2016). In this

work, OOA presented a non-linear relationship with LWC for our whole dataset, which is in agreement with a previous study (Xu et al., 2017). The main focus of their work was to investigate the effects of aqueous-phase and photochemical processing on secondary organic aerosol formation and evolution. Their data suggested that the OOA exhibited a non-linear relationship with RH for their whole dataset in different seasons. However, based on least squares regression correlation analysis, Sullivan et al. (2016) reported a relationship of an increasing water-soluble organic carbon with LWC for RH increased from 40% to 70% during a specific short period. Thus, our aim is to examine if there is a linear relationship between OOA and LWC during specific loadings of LWC.

Classical regression methods, such as linear least squares regression, were developed to specify a global function to fit a model to an entire data set. However, as mentioned by the reviewer, no rationale for determining what fraction of the data is appropriate for a good linear fit was provided. In general, data are usually chosen arbitrarily. Here we provide the detailed strategy for choosing the appropriate fraction of data points utilized in subsequent local linear regression analyses.

The first step is to examine the linear or non-linear relationships between two variables by fitting the given data with a locally weighted scatter plot smoothing algorithm (LOWESS). Further details on the LOWESS technique is available in Cleveland (1981). We take the relationship between LO-OOA and LWC during the summer campaign as an example. The LOWESS function has a “span” argument (f) that represents the proportion of the total number of points that contribute to each local fitted value. The fitting curve is constructed by connecting the “fitted” value with lines for each data point, with colors from red to blue to show the effect of the smoothing parameter choice. The red curve ($f=0.01$, where f is equal to the proportion of points) is “looser” than the blue curve ($f=1$), as the blue curve is fitted to all data points. As shown in Figure S14(C) (named as in the current SI), the blue curve fitted for data points with LWC concentration great than $5 \mu\text{g m}^{-3}$ is likely a straight line. To further verify this assumption, we resampled the original data by using a bootstrap method and recalculated the LOWESS curves. Figure S14(D) presents the 400 LOWESS curves for all resampled data. A strong linear relationship between LO-OOA and LWC can be found for data with LWC great than $6 \mu\text{g m}^{-3}$. Because the number of the corresponding data points

decreased as the LWC increased, the fitted curve is sparsely distributed for high LWC data. Although these resampled data points are not as representative compared to the data at lower LWC, the linear relationship is apparent.

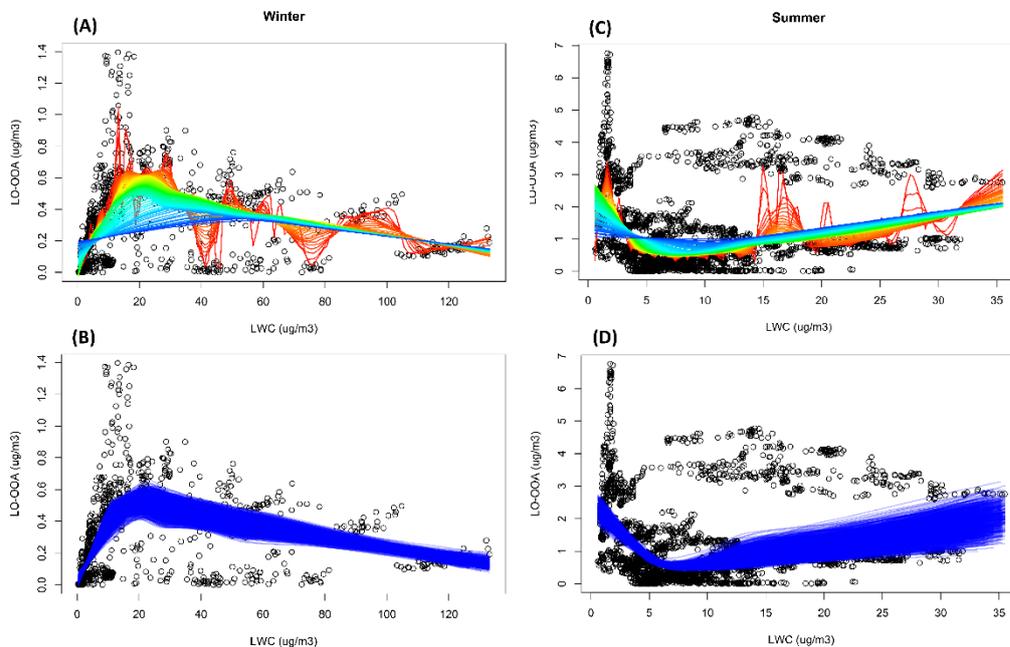


Figure S14. LOWESS curves for the nighttime LO-OOA vs. LWC during winter (A) and summer (C) and for the associated resampled data obtained by bootstrap method (B for winter and D for summer).

Author's changes in manuscript:

Our revision to this comment is included in the following bulleted list:

1. Added the results of LOWESS analysis into supplementary materials (Figures S14-17).
2. Added a paragraph before the discussion of Figure 8 to clarify the potential relationship between OOA and LWC during nighttime:

“The potential linear relationship between OOA and LWC for the nighttime data was investigated by fitting the data with a locally weighted scatter plot smoothing algorithm (LOWESS, (Cleveland, 1981)). According to the LOWESS curves fitted for the original nighttime data and the resampled data obtained by a bootstrap method (Figs. S14-15), there likely exists a linear relationship between LO-OOA and LWC for data points with LWC less than $20 \mu\text{g m}^{-3}$ and greater than $6 \mu\text{g m}^{-3}$ for the winter and summer periods, respectively. As

for MO-OOA, such a linear relationship likely exists when LWC is less than 50 and $7 \mu\text{g m}^{-3}$ for the winter and summer periods, respectively.”

3. Added another paragraph before the discussion of Figure 10 to clarify the potential relationship between OOA and O_x during daytime:

“According to the LOWESS curves fitted for the original daytime data and resampled data obtained using a bootstrap method (Figs. S16-17), there likely exists a linear relationship between LO-OOA and O_x when O_x is less than 35 ppb and greater than 20 ppb for the winter and summer periods, respectively. As for MO-OOA, the linear relationship likely exists for data points with O_x less than 35 ppb for the winter period, but the linear relationship is less prominent.”

4. Deleted the discussion of the linear relationship between MO-OOA and O_x for the summer campaign.

Specific comment 1:

I think that the quantification of the aerosol organic nitrates (ON) have a large uncertainty that needs to be discussed. Equations 3, 4, and 5 indicate the derived ON concentrations are very sensitive to the R_{ON} value. Although the authors have used an R_{ON} value from a very well cited source, there is major uncertainty because the source they cite is based upon a study of SOA from β -pinene oxidation by the nitrate radical. Clearly, the ON formation in this study will be more complex, which adds significant uncertainty to the R_{ON} value and thus to the derived ON concentrations. Much more discussion of this point, including bounds on the ON concentration is warranted.

Response:

Previous studies found that isoprene was the main biogenic VOC in Houston (Leuchner and Rappengluck, 2010; Kota et al., 2014), and Brown et al. (2013) reported that monoterpenes and isoprene were frequently present within the nocturnal boundary layer in the Houston area and underwent rapid oxidation, mainly by nitrate radical. Given the large abundance of monoterpene and isoprene in the Houston area, similar to Xu et al. (2015), we assume organic nitrates formed via isoprene and beta-pinene oxidation are representative. Fry et al.

(2013) assumed that the $R_{ON}/R_{NH_4NO_3}$ value is instrument-independent, and further estimated the average $R_{ON}/R_{NH_4NO_3}$ of 2.25 for the organic nitrate standards. The $R_{ON}/R_{NH_4NO_3}$ values vary with precursor VOC. We utilized the average $R_{ON}/R_{NH_4NO_3}$ of isoprene (2.08, (Bruns et al., 2010)) and beta-pinene organic nitrates (3.99, (Boyd et al., 2015)) from the literature to obtain an estimate range of R_{ON} by using the NO_x^+ method. The mass range of ON is estimated by assuming that the average molecular weights of organic molecules with nitrate functional groups are 200 to 300 $g\ mol^{-1}$ (Surratt et al., 2008; Rollins et al., 2012).

The result of estimated ON is available in Table S2. The associated Figures and content in the original manuscript were updated accordingly. Here we retain the results estimated with R_{ON} value of 0.166 in the manuscript.

Table S2. Results of organic nitrates estimated using the NO_x^+ ratio method.

	$NO_{3,ON}$ conc. ($\mu g\ m^{-3}$)		$NO_{3,ON}/NO_{3,obs}$		ON/OA	
	lower	upper	lower	upper	lower	upper
Winter	0.22	0.34	34%	35%	31%	66%
Summer	0.05	0.06	61%	81%	9%	17%

Specific comment 2:

The COA factor seems quite problematic given that 1) it is present in winter but absent in summer (cooking is presumably still occurring in the city during this period?), and 2) the diurnal profile of COA (Fig. 4) is inconsistent with both cooking activity and results from many urban areas.

Response:

1) There is a restaurant situated directly northeast of the measurement site (UHSL). The northeasterly winds were observed at the measurement site with a high frequency during the winter campaign but not the summer (Fig. 1), which is likely to be responsible for the impact of emissions from cooking activities on this site during winter. It also is possible that increased processing in the summer led COA to be oxidized and included in one of the OOA factors.

2) In our previous supplemental material, we have interpreted the COA factor by comparing the factor mass spectra with other factors, examining the relationship of COA factor versus cooking-tracer ion ($C_3H_3O^+$) and investigating the factor's signal ratio of m/z 55 to m/z 57. As shown in the following figure (now S13), the signals for m/z 55 to m/z 57 for COA in the summer is close to that for LO-OOA and MO-OOA, and higher than that for BBOA and HOA. This is a strong evidence for the interpretation of the COA factor (Mohr et al., 2012).

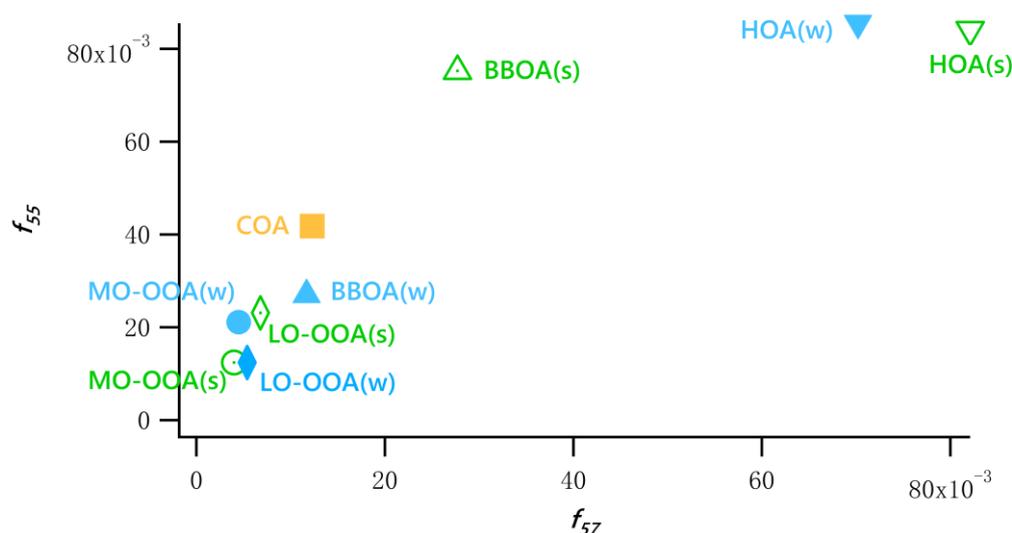


Figure S13. f_{55} vs. f_{57} of PMF factors for the winter and summer periods. (w) and (s) denote the winter and summer data, respectively.

Although there is no routine peak during mealtime in the diurnal pattern of COA, the COA factor mass spectra correlated moderately with previously reported COA factors deduced from PMF analysis (as shown in the table below), which further supports the interpretation of COA factor in this work.

Table Correlation (r) of COA mass spectra with previously published spectral database.

(<http://cires1.colorado.edu/jimenez-group/HRAMSsd/>)

References	Study area	r
(Mohr et al., 2012)	Barcelona	0.76
(Crippa et al., 2013)	Paris	0.58

(Elser et al., 2016)	Xi'an and Beijing	0.65
(Hu et al., 2016)	Beijing	0.65

Specific comment 3:

The brief discussion on aerosol acidity (Lines 318-320) is completely wrong: briefly, the thermodynamic modeling did not include gas-phase ammonia or nitric acid, which significantly limits the ability to characterize acidity. See the extensive body of work from R. Weber and A. Nenes on this topic.

Response:

The original sentence (original lines 318-320) has been deleted.

Specific comment 4:

I had a lot of difficulty with Figure 1 and the associated discussion (Lines 349-360). I realize many published papers (including many in ACP) follow this standard formula for a paper reporting the results from a ground-based field study. However, I find it almost impossible to actually get anything useful out of Figure 1-there is simply too much data presented in too small a space. This is especially true for the discussions about pollutants and wind direction, which cannot be distinguished in Figure 1. If the discussion is central to the manuscript, then additional figures in the Supplemental and likely necessary. If not, then I'd suggest removing (or greatly modifying) Figure 1.

Response:

For the sake of clarity, we have removed the panels of elemental ratios (O/C, H/C, OM/OC, and N/C), ON and MSA from the stacked time series plot and put these panels into the supplemental material (Figure S2).

Specific comment 5:

Perhaps this is just a miscalculation, mis-labeled figure or a typo in the manuscript, but the ON concentration estimates (12% and 37% of OA) do not seem consistent with the results in Figure 2, Figure 6, and Table 1. For example, Fig. 2 lists ON contributions to NR-PM₁ as 3.4% and 1.5% in winter and summer, respectively. Based on the reported averages (NR-PM₁ concentrations of 6 and 3.6 $\mu\text{g}/\text{m}^3$ in winter and summer, respectively), this would give ON concentrations of 0.204 and 0.054 $\mu\text{g}/\text{m}^3$. These levels do not seem consistent with Figure 6, nor with the reported contributions to OA.

Response:

We apologize for the error. As suggested, we estimated the bounds of ON based on the R_{ON} values (and their precursor VOCs) that are relevant to the Houston area in the revised manuscript. The estimated result is available in Table S2. The ON concentrations in Tables, Figures and text have been updated in the revised manuscript.

Specific comment 6:

All of the discussion about wet removal is misguided (lines 448-452, 468). The authors seem to imply here that the highest levels of aerosol LWC correspond to periods of precipitation. I seriously doubt that is the case, as precipitation events will greatly reduce all of the aerosol species, as well. Either way, the authors should have access to accurate precipitation data, so this point should be backed by evidence rather than speculated upon.

Response:

Precipitation totals from a nearby Texas Commission on Environmental Quality (TCEQ) monitor site were added to Figure 1 (b, g). The periods of precipitation events correspond to high levels of RH. Indeed, the wet removal effect works on all species. We have rephrased the statement on wet removal effect in response to this comment.

Lines 436-441: "This result indicates that wet removal may dominate under an extremely high RH environment coupled with stagnant air ($WS < 2 \text{ m/s}$, Fig. 7(E)), as the OA concentration decreased at extremely high LWC level (Fig. 7(A)). In summer, the OA mass decreased when LWC increased from 1.25 to 6.25 $\mu\text{g m}^{-3}$ but increased when LWC increased

further, suggesting the wet removal effect is likely not as strong as that in winter because of the relatively lower LWC in summer.”

Specific comment 7:

This discussion linking MSA with aqueous processing is confusing (lines 507-520). It is entirely possible for aqueous processing to produce OOA and at the same time for the OOA factors to exhibit weak (or no) correlations with MSA (e.g., if the air mass had a continental origin).

Response:

The discussion linking MSA with aqueous processing supports the idea that the summertime MO-OOA formation was more likely associated with aqueous processing than LO-OOA, as MO-OOA positively correlated with MSA but LO-OOA exhibited weak correlation with MSA. This result also indicates that MO-OOA was impacted by marine aerosol and that LO-OOA likely originated from continental areas.

Specific comment 8:

This is a relatively minor point, but I question the label of “summer” applied to the May measurements. Can the authors use comparison to priori measurement campaigns in Houston to show that May is representative of summertime conditions in terms of source influences, emissions, chemistry, etc.? Further, because of the short duration of the winter measurement period (2 weeks), the limitation that this campaign may not have fully characterized the winter season in Houston should be discussed.

Response:

We agree with the reviewer that the sampling periods are too short to cover the whole seasons thus we have added a comment in Section 2.1:

“The data collected during winter campaign are limited in duration; thus, the following discussion focuses primarily on the summer campaign. The label of “winter/summer” in the text denotes the measurement period in the winter/summer.”

The fourth paragraph of the Introduction section has been deleted, and we have shortened the discussion about winter data in the text. It should also be noted that even though May officially is part of spring, the temperatures in Texas in May are high enough that they are much more characteristic of summer meteorology.

Specific comment 9:

The paragraph in lines 64-70 seems contradictory with the current results: the reported measurement seem to indicate that Houston is well below the current (and future) standard.

Response:

The original statement has been deleted.

Specific comment 10:

I understand that it is common to sample an AMS downstream of a Nafion drier (lines 150-152), but can the authors comment on potential artifacts from this measurement setup? E.g., the potential loss of semi-volatile organics.

Response:

The work of El-Sayed et al. (2016) indicates that drying of aerosol water led to the evaporation of condensed-phase organics (for both daytime and nighttime sampling periods). For the purposes of this study, therefore, we may be underestimating the contribution of aqueous-SOA (i.e., IEPOX as an example in El-Sayed et al. (2016)).

We have added comment in Section 2.3.2:

“As suggested by El-Sayed et al. (2016), drying of aerosol water may have led to the evaporation of condensed-phase organics. Thus, the mass concentrations of resolved OA factors here are a lower-bound, conservative estimate due to potential losses of aqueous-SOA in the Nafion dryer element.”

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Reviewer #2:

Specific Comment 1:

My major concern is that the authors claimed seasonal differences between winter and summer, but the measurements were only made for 2-week period during wintertime with high frequencies of RH>60% (~70% in Fig.1). As a result, there might be a significant uncertainty when comparing the summer and winter data. The authors need to address such uncertainties in the revised manuscript.

Response:

Please see response to similar comment from Reviewer #1.

Specific Comment 2:

The uncertainties for the quantification of S/C and N/C AMS was operated in V-mode ($m/\Delta m \sim 2000$) in this study, separation of N-containing and S-containing are challenging. What are the uncertainties in quantification of S/C and N/C.

Response:

Because of the lack of measurement results for standard organic nitrates and organic sulfates, we are unable to estimate quantitatively the uncertainties in N/C and S/C. Since the elemental ratio packages in PIKA indicate that the calibration factors for S/C ratios are “not measured/published”, we have deleted the S/C data in the revised manuscript.

The uncertainties in quantification of N/C include: 1) the important nitrogen-containing ion (CH_2N^+ , m/z 28 (Ge et al., 2017)) was excluded from the AMS elemental analysis due to the overwhelming interference of adjacent N_2^+ ion, resulting in the current N/C ratio being underestimated by ~20% on average (Struckmeier et al., 2016); 2) because the signals of $\text{C}_x\text{H}_y\text{N}_p^+$ and $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$ are much lower than C_xH_y^+ and $\text{C}_x\text{H}_y\text{O}_z^+$, the determination of N/C relies on the mass resolution ($m/\Delta m$). The mass resolution of V-mode AMS is just half of that of W-mode, making separation and quantification of the nitrogen-containing ions above m/z 50 impossible (Xu et al., 2017); and 3) N-containing ion peaks are very often on tails of larger peaks, thus small errors in m/z calibration can generate uncertainty in estimated N/C. Aiken et al. (2007) compared the N/C ratios for methylamine, ethylamine, and hydrogen cyanide from a NIST electron-ionization database and from elemental analysis using an AMS. The analysis of AMS (NIST) spectra indicates that quantification of N/C is possible with an average error of 20%.

Specific Comment 3:

What the values of CE and RIE used for MSA quantification? Please elaborate.

Response:

Following previous studies by Zorn et al. (2008) and Huang et al. (2015), the relative ionization efficiency (RIE) of MSA (1.3) was assumed to be the average of the value for organic species ($RIE_{org} = 1.4$) and sulfate species ($RIE_{so4} = 1.2$). The collection efficiency of all ions composing MSA was calculated using the composition-dependent collection efficiency developed by Middlebrook et al. (2015). The resulting collection efficiency was 0.5 for 7.3% and 4.2% of time of the summer and winter campaign, respectively, and was 1.0 for the remaining time of the two campaigns.

Specific Comment 4:

What's the basis of LWC bin division (Fig.8)? Why didn't you use the uniformly-spaced LWC bin as Fig. 10 (O_x binned in 10 ppb).

Response:

Unlike the O_x concentration, the LWC in the winter and summer show a power function distribution and a lognormal distribution, respectively. We used uniformly-spaced LWC bins for most of the data. The summer data are binned in $5 \mu\text{g m}^{-3}$ increments from 0 to $20 \mu\text{g m}^{-3}$ (covering 83% of data points), and winter data are binned in $2.5 \mu\text{g m}^{-3}$ increments from 0 to $15 \mu\text{g m}^{-3}$ (covering 91% of data points). The number of data points within each bin is too small to produce a reasonable result if the remaining data at higher values are binned using the same increment. This data processing method is common in literature (Huang et al., 2015).

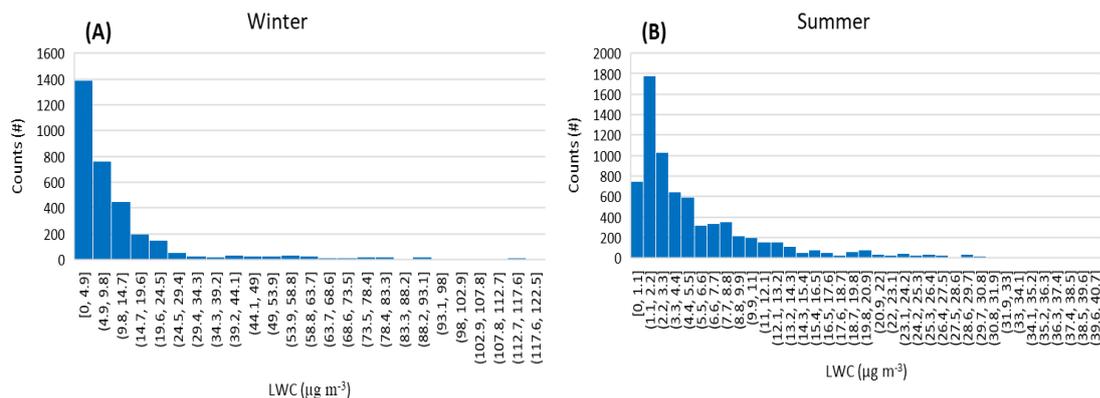


Figure The frequency histograms of LWC in the winter and summer.

Specific Comment 5:

Are there any specific reasons that you used two different versions of software to do data analysis (PIKA1.16 for time series (line 176) and PIKA 1.19D to do PMF analysis (line 235))?

Response:

We performed updated data analysis in the version of PIKA 1.19D, and all data presented in Figures, Tables and the text have been updated in the revised manuscript.

Specific Comment 6:

How the density of organics was calculated? Was it the I-A method (you mentioned in line 183?) or A-A methods?

Response:

The organic density was estimated using an empirical equation based on elemental ratios (Kuwata et al., 2012):

$$\rho_{Org} = 1000 \times \left[\frac{12 + \frac{H}{C} + 16 \times \frac{O}{C}}{7.0 + 5 \times \frac{H}{C} + 4.15 \times \frac{O}{C}} \right]$$

The elemental ratios were estimated using the updated I-A method (Canagaratna et al., 2015).

Specific Comment 7:

Line 199-200, $\text{NO}_2^+/\text{NO}^+=0.1-2.0$, that is to say, the $\text{NO}^+/\text{NO}_2^+=0.5-10$, which is contradictory with the cited study (5-10) (Xu et al., 2015). What is the ON with $R_{\text{ON}}=0.5$? Please mention it here.

Response:

This is an error. The $\text{NO}_2^+/\text{NO}^+$ ratio is in the range of 0.1-0.2. This mistyping has been deleted and the bounds of ON have been estimated. Please see response to Reviewer #1 regarding uncertainties in ON.

Specific Comment 8:

Line 417, what is the correlation coefficient between LO-OOA/MO-OOA vs. aq-OOA in summer? Are there any further support other than the mass spectra? In fact, the correlation between LO-OOA/MO-OOA vs. SO_4 is moderate in Fig. 7.

Response:

The correlation coefficients of summertime LO-OOA/MO-OOA mass spectra with aq-OOA is 0.95/0.96, respectively. This result suggests that the formation of LO-OOA in summer and MO-OOA in both seasons likely involved aqueous processing. The correlation between OOA and MSA also supports this. MSA has a relatively higher correlation coefficient with MO-OOA ($r=0.45$) compared to LO-OOA ($r=0.30$), though the correlation also is influenced by many other factors. Additionally, the high correlation coefficients of SO_4 with MO-OOA in both seasons ($r=0.74$ and 0.79 for winter and summer, respectively) further support the conclusion, although the correlation of LO-OOA and SO_4 is not as strong as expected. We believe that the strong correlation between the mass spectra of OOA and aq-OOA is strong enough to support our conclusion.

Specific Comment 9:

Line 448, the authors attributed the decreased MO-OOA concentration at $\text{LWC} > 40 \mu\text{g}/\text{m}^3$ to wet removal. How about other species? Besides, in Fig.8 (I), the continuous increase of

MO-OOA under $LWC < 40 \mu\text{g}/\text{m}^3$ appeared not very clear.

Response:

Please see response to Reviewer #1. The continuous increase of MO-OOA under $LWC < 40 \mu\text{g}/\text{m}^3$ is not very clear, but the maximum and minimum values of each bin increased obviously. We further investigated the relationship between MO-OOA and LWC for nighttime data only, and the MO-OOA shows a significant increase trend under $LWC < 40 \mu\text{g}/\text{m}^3$ during nighttime.

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