

## Author Responses to Reviewer #1

The Reviewer comments are black italic font and the Author responses are blue font.

*The authors describe the analysis of three selected filter samples that were collected within a more comprehensive sampling campaign (a total of 127 filters) at the Pico Mountain Observatory (PMO) on Pico Island / Azores. The samples were chosen because of the high organic carbon (OC) concentration. While major small ions and OC of the three filter samples were measured as well, the focus of the manuscript certainly lies on the analysis using direct infusion electrospray ionization ultra-high resolution mass spectrometry in the negative ion mode ((-)ESI/UHRMS). Differences in the mass spectra are discussed with regard to a back-trajectory analysis. The authors observe signals in one sample (out of three) that exhibits higher O/C ratios compared to the other two samples that likely have undergone a longer atmospheric transport time (and thus aging). The authors argue that the two samples with the lower O/C ratio were transported in the free troposphere (FT) to PMO, and thus the particle phase state during transport was likely solid. They conclude that “biomass burning emissions”, which are directly injected by pyro-convection into the FT, “are longer-lived than emissions in the boundary layer”.*

We thank the reviewer for his comments. We made several changes to both the main paper and the supplemental information. In particular, we made major revisions to section 3.5.

*General comments:*

*Overall, the manuscript presents results from an atmospheric measurement station that is certainly very well suited for studying aerosol transformation processes during long-range transport. Furthermore, the authors demonstrate the need for ultra-high resolution mass spectrometry techniques when it comes to ambient measurements of particulate matter. However, I have major concerns regarding a weak reasoning that is used as a basis for their conclusions and implications for atmospheric aging (see my point (1) below). Also, the authors remain too speculative in many cases, or even state arguments that are not supported by their figures (see (2)). Furthermore, I have serious technical concerns that might have an effect on the outcome of the ESI/UHRMS analysis (see (3)).*

*My major remarks concerning the above mentioned points:*

*(1) The authors argue that particle phase state is affected by the conditions during atmospheric transport. Their observation of a low O/C in the biomass burning samples (PMO-1 and PMO-3) is reasoned by the phase state of the particles during transport. Although, the authors mention that the PMO-2 sample is originating from another source (from the Eastern United States – dominated by a mix of biogenic and anthropogenic emissions), they argue that the high O/C ratio of this sample is caused by the semi-solid phase state, which allows faster aging during atmospheric transport to PMO. Assuming that the back-trajectory analysis is getting the sources right, the authors don't present a convincing argument why we can use the two different sources (biomass burning organic aerosol (BBOA) vs. anthropogenic/biogenic secondary aerosol (A/BSOA)) as an **identical reference point for the onset of atmospheric aging!***

We thank the reviewer for this comment. We agree that biomass combustion and anthropogenic/biogenic aerosol are not identical reference points for the onset of atmospheric aging. However, these are the pollution events that arrived at the Pico Mountain Observatory and they arrived with very different transport conditions. To provide context regarding our expectations for oxidation, we cited studies that demonstrate both the rapid oxidation of anthropogenic/biogenic aerosol (Jimenez et al. 2009) and the lower average oxidation of biomass combustion aerosol relative to anthropogenic/biogenic aerosol (Bougiatioti et al., 2014) see also lines 30-35, 377-378.

We further strengthened this point to avoid confusion with the following new text (Lines 307-309):  
“**Although North American outflow of anthropogenic secondary organic aerosol is expected to have**

**a higher O/C value compared to the wildfire emissions of biomass burning organic aerosol (e.g., Aiken et al., 2008; Jimenez et al., 2009; Bougiatioti et al., 2014) ...”**

We also added the following sentence to the manuscript (lines 504-505), to clarify the role played by emission sources: **“These observations suggest that the transport pathways, in addition to the emission sources, contribute to the observed differences in the organic aerosol oxidation.”**

Regarding the aerosol phase state, we estimated the glass transition temperature (DeRieux et al., 2018) for the identified molecular formulas using the extracted Global Forecast System (GFS) data for the FLEXPART retroplumes. Doing this showed that the majority of species identified in PMO-1 and PMO-3 had  $T_g$  values that exceeded the ambient temperature, which suggests solid state during the last 5 days of transport. Considering the length of transport (~7-10 days), these samples demonstrated low O/C and OS<sub>c</sub> even compared to biomass burning samples analyzed after less transport (Bougiatioti et al., 2014). As described in several papers (Koop et al., 2011; Shrivastava et al., 2017; Zelenyuk et al., 2017), the solid phase is expected to have decreased susceptibility to oxidation and other chemical processes. For this reason, it was hypothesized that the phase state contributes to ambient observations made in this study.

In contrast to PMO-1 and PMO-3, the estimated  $T_g$  values for compounds identified in PMO-2 were often lower than the ambient temperature, indicating a less viscous state and thus an increased susceptibility to oxidation and other chemical processes, relative to PMO-1 and PMO-3. This is consistent with other studies of anthropogenic and biogenic SOA in the planetary boundary layer (Maclean et al., 2017; Ye et al., 2016). Although there are uncertainties in the prediction (DeRieux et al., 2018), PMO-2 organic aerosol species were more likely to be semi-solid/liquid based on the ambient conditions than PMO-1 or PMO-3. Thus, we hypothesized that the higher O/C and oxidation observed in PMO-2 may be due to aqueous phase processing during transport, leading to increased oxidation of atmospheric organic matter (Ervens et al., 2008; Zhao et al., 2014). To support this hypothesis, we examined markers of potential cloud processing. We observed depleted nitrate (Dunlea et al., 2009), elevated sulfate and oxalate (Yu et al. 2005; Sorooshian et al. 2007) in PMO-2 as described in section 3.1.

*In the literature it is now well recognized that these two kinds of organic aerosol (BBOA vs SOA from anthropogenic and biogenic VOCs) are already very different on the molecular level at the time when emitted by their sources or formed in the atmosphere: While BBOA is largely composed of lignin- and cellulose-derived condensed aromatic / polyphenolic structures with low O/C ratios (Lin et al., 2016), numerous studies have shown that the auto-oxidation of (mostly biogenic) VOCs results in highly oxygenated molecules within seconds after the initial attack by an oxidant (Crouse et al., 2013; Ehn et al., 2012; Jokinen et al., 2014). Although it is not yet fully understood what happens to these compounds once they condense, the auto-oxidation mechanism still can explain high aerosol O/C from atmospheric oxidation of VOCs.*

We agree that the two types of organic aerosol (SOA vs. BBOA) are very different on the molecular level. Auto-oxidation as described by Crouse et al. (2013), Ehn et al. (2012), and Jokinen et al. (2014) does increase the O/C, but it also shows clear carbon number preferences associated with the oxidation of terpene precursors. This trend is consistent with our earlier work on condensed SOA where the concept of “auto-oxidation” was described as “oxygen-increasing-reactions” (Kundu et al., 2012). However, in the case of PMO-2, we did not observe carbon number preferences, which would indicate auto-oxidation. While this does not negate the possible influence of auto-oxidation, it does minimize its relative importance for these long range transported aerosol observations. On the other hand, aqueous phase processing as described by Lim et al. (2010) leads to SOA production with a greater array of carbon

numbers; the greater array of carbon numbers matches more closely with our observations of a continuum of carbon numbers from 2 to 33 in PMO-2.

We also compared the molecular composition of PMO-2 to that of cloud water from the Storm Peak Laboratory (Zhao et al., 2014) and Whiteface Mountain (Cook et al., 2017), and fog water from Fresno, California (Mazzoleni et al. 2010). In these comparisons, the common species observed only in cloud water and PMO-2 had higher O/C and oxidation than the species common to other samples. This likely indicates that at least some degree of aqueous phase processing has occurred. The results comparing our study to the Cook et al. (2017) and Mazzoleni et al. (2010) studies are new and have been added to the Supplement of this paper in Table S6. All three samples contain atmospheric water that was impacted by anthropogenic, biogenic, and biomass burning air plumes at one time or another. These results consistently show that high O/C species in PMO-2 are uniquely common with atmospheric organic matter in fog and cloud, indicating the influence of aqueous phase processing. We note that the comparisons of the molecular compositions from Zhao et al. (2014) and Mazzoleni et al. (2010) were more comprehensive because we had more complete datasets. The species common only to PMO-1 and the Cook et al. (2017) dataset also had high O/C, but the two formulas represent only 2% of the formulas used for comparison. On the other hand, the uniquely common formulas between the Cook et al. (2017) dataset and PMO-2 represent over 20% of the formulas used for comparison. As such it seems reasonable to say the same trend holds.

**Table S6. Number of molecular formulas and their average O/C values (unweighted O/C and RA weighted O/C ( $O/C_w$ )) uniquely common between this study and ambient aqueous organic matter (Mazzoleni et al., 2010; Zhao et al., 2015; Cook et al., 2017). Uniquely common means that the formula is common between only one of the PMO samples and the aqueous organic matter sample. CW indicates cloud water, the numbers in parentheses are the percentage of total formulas.**

Sample	# Common Formula	O/C	$O/C_w$
<b>PMO and Fog (Mazzoleni et al., 2010)</b>			
PMO-1	202 (6.4%)	0.38	0.39
PMO-2	48 (2.3%)	0.5	0.55
PMO-3	11 (0.60%)	0.29	0.29
<b>PMO and CW (Cook et al., 2017)</b>			
PMO-1	2 (0.063%)	0.82	0.82
PMO-2	23 (1.1%)	0.8	0.81
PMO-3	1 (0.055%)	0.36	0.36
<b>PMO and CW (Zhao et al., 2015)</b>			
PMO-1	197 (6.2%)	0.42	0.42
PMO-2	70 (3.3%)	0.76	0.8
PMO-3	42 (2.3%)	0.38	0.38

In addition to Table S6, the following sentences were added to the manuscript (Lines 483-486):  
**“Comparisons of the detailed molecular composition of the PMO samples with studies of cloud**

(Zhao et al., 2013; Cook et al., 2017) and fog (Mazzoleni et al., 2010) water organic matter indicates that the formulas uniquely common to only PMO-2 and the literature atmospheric water samples have higher O/C consistent with aqueous processing during transport. These results are provided in Fig. S19 and Table S6.”

*My impression is that the authors do not adequately consider or discuss different reasons for their observations and overemphasize the possible link between atmospheric transport and aging efficiency at different altitudes.*

Our previous paper (Dzepina et al., 2015) provided a discussion of a biomass burning plume event intercepted at the PMO. In that paper, we considered several factors, but not phase state. We also did not have any non-biomass burning influenced aerosol samples like PMO-2 for comparison. The new set of samples provides an opportunity for a new perspective. In this work, we examined the meteorological variables from GFS that corresponded to the FLEXPART transport pathways and used the recently developed estimation methods for volatility and phase state to assist in the interpretation of the observations.

Since in Dzepina et al. 2015 we considered photochemical oxidation and fragmentation, it was deemed unnecessary to go over again in detail for this manuscript. For clarity, the following introductory sentences were revised (Lines 100 – 104): **“The low oxidation observed by Dzepina et al. (2015) was attributed to the dominance of persistent aerosol that resisted removal mechanisms, however it is possible that the phase state of the aerosol during transport played a significant role. The increased resistance to photodegradation (Lignell et al., 2014; Hinks et al., 2015) and water diffusivity (Berkemeier et al., 2014) of solid phase organic aerosol provide a basis for this hypothesis.”**

*To be clear, I am not saying that aerosol phase state does not change aerosol transformation rates, but to extract this effect from ambient observations, one likely needs to consider a larger set of samples (which the authors apparently have).*

We would like to have a larger dataset to extract this valuable information. Unfortunately, there were several limiting factors that are not readily apparent:

- (1) The Pico Mountain Observatory is a research post that was originally designed to be temporary, located on the caldera top of Pico Mountain in the Azores (see also Image 1 in the Supplement). The mountain-top site is one of the highest points for 1500 km in the North Atlantic. The site is only accessible by foot over rugged terrain (Honrath et al., 2004) and has limited infrastructure for aerosol chemical observations (Dzepina et al., 2015). Thus, we conducted a field study with filter collection and conducted off-line analyses.
- (2) The field study and filter collection were limited by the meteorology. Thus, the pollution events were primarily influenced by biomass combustion from North America or dust events from Africa. We also lost samples/observations due to occasional nighttime lenticular cloud formation (Dzepina et al., 2015).
- (3) The detailed molecular analyses were done with an ultrahigh resolution FT-ICR MS instrument at the Woods Hole Oceanographic Institution (WHOI). The WHOI instrument is made available with user fees. The costs of the instrument and travel limited our analyses to only those samples with adequate OC loading to ensure reliable measurements.

(2) The authors argue that the aerosol that was captured on the PMO-2 sample travelled at altitudes below 2 km over Eastern U.S. and stayed below 2 km altitude until it reached PMO 2-4 days later (p. 7, l. 251-253). From Figure 1 (e), I cannot see that. For the upwind days 0-5, the mean height of the plume is consistently higher than 2 km. As stated on p.2, l. 65-67, the marine boundary layer (MBL) around PMO ranges between 500 m and 2 km, and thus below the mean height of the plume.

We thank the reviewer for catching our mistake with Fig. 1. We immediately posted the corrected Fig. 1 in Author Comment #1 during the open discussion of this paper. We also added a few more FLEXPART retroplumes for our sampling periods to the Supplement (Figs S1-S3).

However, the authors argue that **PMO-2 air masses travelled within the MBL layer** to PMO, explaining high relative humidity and a semi-solid phase state during transport. Another argument against the transport within the MBL is given by the authors, mentioning that PMO-2 does not reveal any chemical signature from the MBL (p. 6, l. 232-233). Furthermore, the mean height in PMO-3 appears even lower than PMO-2 for the last five days.

We thank the reviewer for this comment. We noted that the MBL influence, as inferred from the estimated amount of sea salt sulfate and presence of methane sulfonic acid (MSA), does not seem to be the major influence on that sample. (lines 259-261). The relatively low influence of the MBL does not negate transport within the MBL, especially in this case, because the transport was very fast. Clarification regarding this point was added to lines 263-265. **“The influence of marine sources supports boundary layer transport. However, the results indicate that marine aerosol is not likely a major component of PMO-2, perhaps because the rate of PMO-2 transport was very fast.”**

(3) The discussed filters were selected because of their high mass loadings of organic carbon (>1 mg OC / quarter filter). After loading the water-soluble (WS) OC extract onto solid phase extraction (SPE) material for purification, the SPE was then eluted by 2 mL of MeCN/H<sub>2</sub>O and the extract was used for direct infusion. If we assume that half of the OC is WSOC and assume 100% SPE collection efficiency (neglecting losing the small, polar organic compounds), the concentration of the solution for direct injection ESI would be ~0.25 mg/mL. To me, this appears as a huge concentration in which ion source cluster formation (e.g. x-mers of analytes, clusters with solvents or solvent additives, impurities), can become a serious issue. I understand that SPE was done in order to reduce cluster formation with inorganic ions and that a separation technique was apparently not available. However, the authors could have done straight-forward tests to check the extent of cluster formation in these samples by: (1) sample dilution and checks for non-linear reduction of cluster-signal candidates and (2) MS/MS isolation and recording the fragmentation energy of cluster signal candidates.

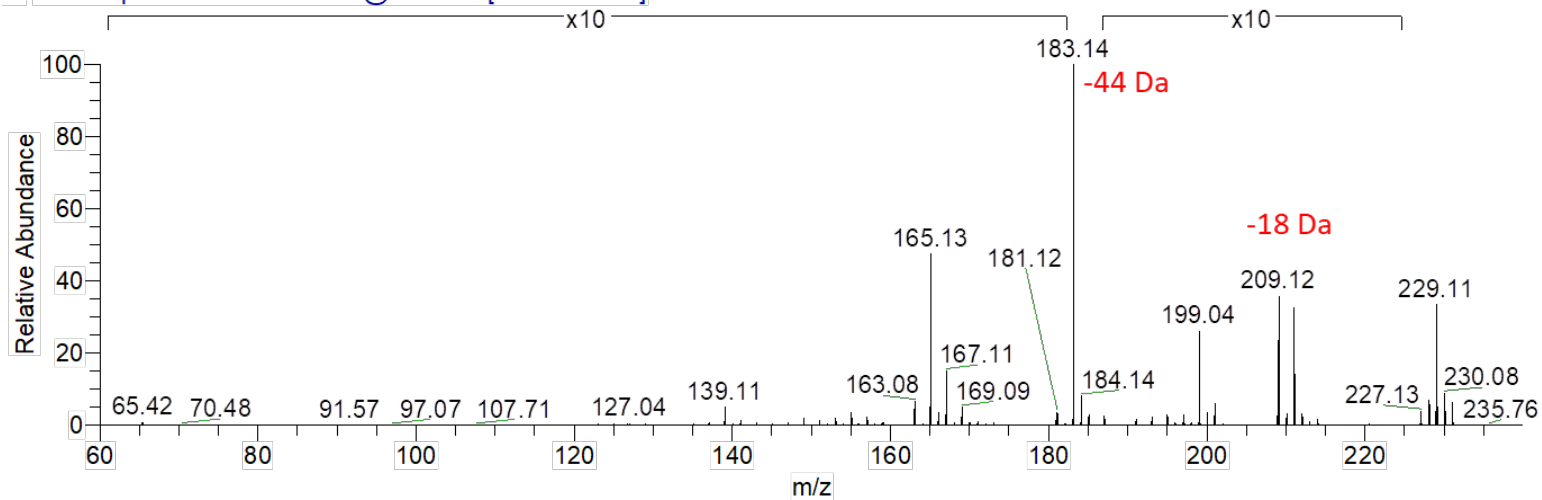
Yes, direct infusion of high concentrations can lead to ESI artifacts. We always dilute our samples to the lowest possible level to obtain a stable current during ESI. This has been described in our previous work (Putman et al., 2012). We also note that negative ion ESI is less prone to adduct artifacts. This is mainly because the low molecular weight negative ions are removed by the SPE procedure.

Although, I understand that MS/MS cannot be done on all ion signals, there are some “suspicious” signals standing out in Figure 2 (the signals > 0.3 rel. abundance) that should have been checked using MS/MS when doing direct injection.

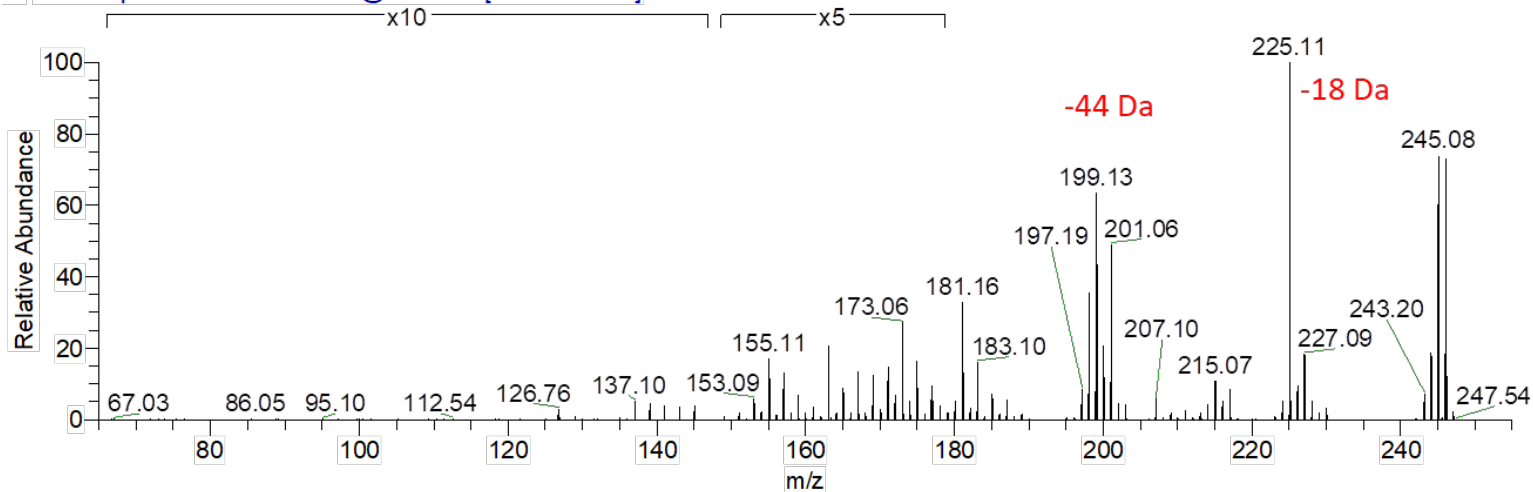
Regarding the suspicious signals, we have done a thorough study using ultrahigh resolution FT-ICR MS/MS on PMO-1 similar to LeClair et al. (2012). The results of the MS/MS are the subject of a forthcoming manuscript. To answer the reviewer’s concern, we re-examined several of the MS/MS

spectra. Overall, the mass spectra show fragmentation patterns consistent with covalently bonded molecules and not ion clusters. On the following pages, the MS/MS spectra for several of the tallest peaks present in PMO-1 are shown. Note that we cannot isolate 1 and only 1 m/z value. Instead we isolate a range of values (for example  $230 \pm 3$ ). In this way, the ions of the entire isolated group are simultaneously fragmented.

P062713w\_230w6\_100k\_CID #1-55 RT: 0.00-3.16 AV: 55 NL: 9.18E4  
T: FTMS - p ESI Full ms2 230.00@cid33.00 [60.00-240.00]

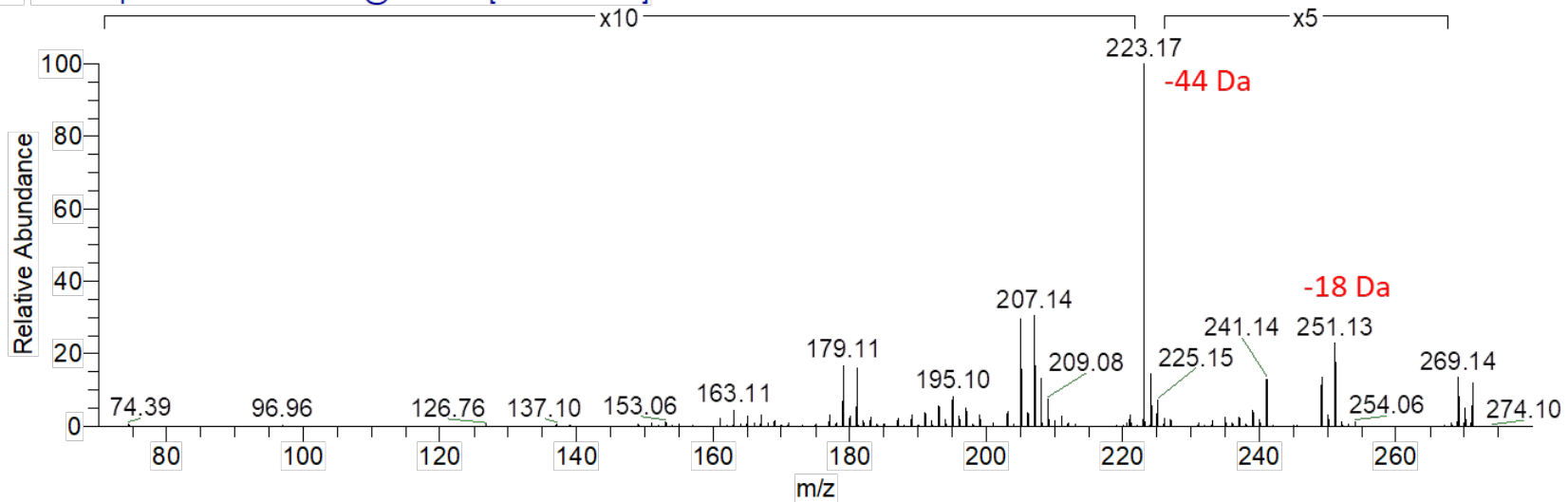


P062713w\_245w6\_100k\_CID #1-55 RT: 0.01-3.10 AV: 55 NL: 1.11E4  
T: FTMS - p ESI Full ms2 245.00@cid32.00 [65.00-255.00]

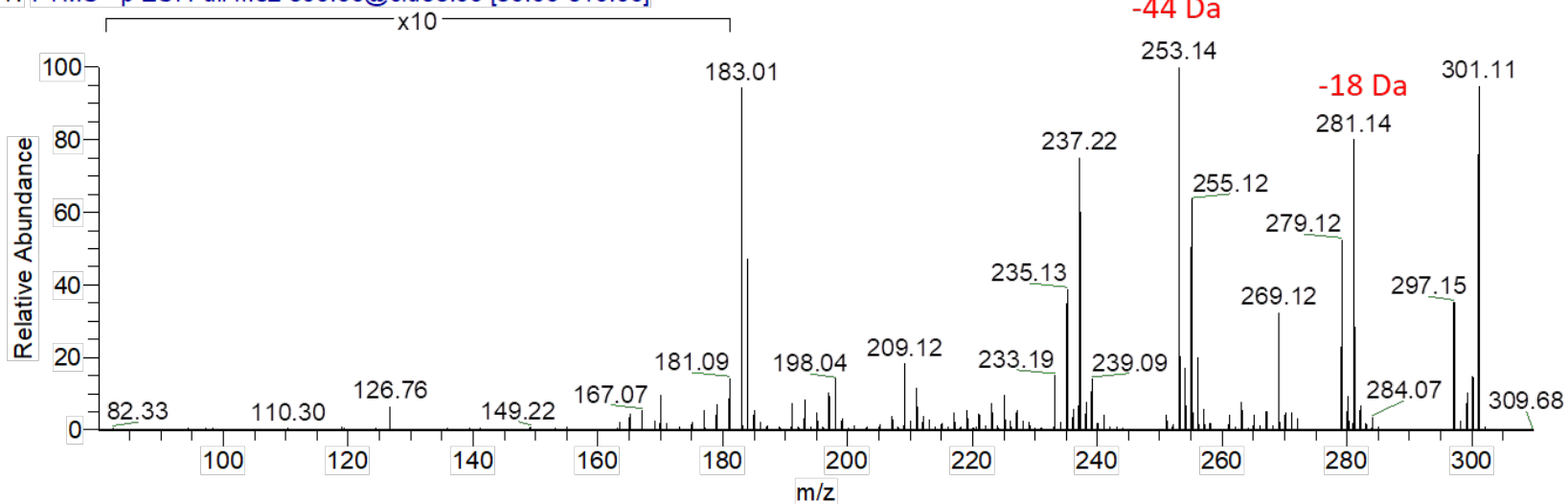




P062713w\_270w6\_100k\_CID #1-54 RT: 0.01-2.47 AV: 54 NL: 1.10E5  
T: FTMS - p ESI Full ms2 270.00@cid35.00 [70.00-280.00]



P062713w\_300w6\_200k\_CID #1-54 RT: 0.02-3.31 AV: 54 NL: 4.85E3  
T: FTMS - p ESI Full ms2 300.00@cid38.00 [80.00-310.00]





*Ion source cluster formation would introduce a bias on the calculated glass transition temperature ( $T_g$ ) by artificially increasing the average number of carbon per molecule. Furthermore, the overall  $T_g$  is already biased toward higher values since small molecules are very likely lost during the SPE procedure (l. 158-159). The manuscript misses in its current form a critical evaluation of these points and its implications on aerosol phase state and aging.*

As shown above, we do not have evidence for ion clustering. However, the lower MW species can be quite important for the average organic aerosol  $T_g$ . We chose to address this in two ways, first we report the distribution of  $T_g$  values in Figure 7 and second, we estimated the influence of the known low MW compounds. Using the concentrations of organic acids (e.g., Table SM1), we found that the relative abundance weighted  $T_g$  for each of the samples changed by  $\leq 2.5\%$  when the abundance of the organic acids was considered (Table SM5). This was done by estimating the  $T_g$  for each of the following organic acids (formic, acetic, oxalic, malonic, and lactic) using the Boyer-Kauzmann rule ( $T_g = g * T_m$ ,  $g = 0.7$ ,  $T_m$  = melting temperature) (Shiraiwa et al. 2017; DeRieux et al. 2018). Oxalic acid is by far the most abundant of all organic acids in these samples and thus has the largest impact. The percentage of total organic mass that each acid made up was calculated by dividing their concentration by the concentration of organic mass, which was estimated by multiplying the OC value by 2 (El-Zanan et al., 2005). Then the individual low MW compound mass fractions were used to estimate their abundance relative to the sum of the total abundance of species identified by FT-ICR MS using the worst-case scenario assumption that the detected species in the mass spectra represent only 50 % of the total organic mass. These abundance values, along with the estimated  $T_g$  values were then used to calculate the abundance weighted average dry  $T_g$  for each sample. When compared to the original weighted  $T_g$  values, the difference was  $\leq 2.5\%$  for all samples, indicating that while the organic acids do impact the  $T_g$  to some extent, the impact is not so significant as to change any of the conclusions of this study. A series of tables showing the values described here are provided in the Supplement (Tables SM1-SM5).

**Table SM1. The concentrations of the ions used for the estimation and the organic mass (OM) concentration. The values are in  $\mu\text{g}/\text{m}^3$  air.**

<b>Ion</b>	<b>PMO-1</b>	<b>PMO-2</b>	<b>PMO-3</b>
<b>Formate</b>	<b>0.0289 <math>\pm</math> 0.0003</b>	<b>0.00438 <math>\pm</math> 0.00007</b>	<b>0.0119 <math>\pm</math> 0.0001</b>
<b>Acetate</b>	<b>0.0519 <math>\pm</math> 0.0001</b>	<b>0.004587 <math>\pm</math> 0.000005</b>	<b>0.0071 <math>\pm</math> 0.0002</b>
<b>Oxalate</b>	<b>0.0938 <math>\pm</math> 0.00070</b>	<b>0.0897 <math>\pm</math> 0.00181</b>	<b>0.0522 <math>\pm</math> 0.00002</b>
<b>Malonate</b>	<b>0.00605 <math>\pm</math> 0.0003</b>	<b>0.00548 <math>\pm</math> 0.0007</b>	<b>0.0045 <math>\pm</math> 0.0003</b>
<b>Lactate</b>	<b>0.0292 <math>\pm</math> 0.0004</b>	<b>0.0019 <math>\pm</math> 0.0001</b>	<b>0.00467 <math>\pm</math> 0.0001</b>
<b>OM</b>	<b>4.14 <math>\pm</math> 0.04</b>	<b>0.956 <math>\pm</math> 0.052</b>	<b>1.74 <math>\pm</math> 0.20</b>

**Table SM5.** Estimated average  $T_g$  values when the ions are considered. The table contains the results for 3 assumptions of the organic mass fraction represented by the FT-ICR MS identified species (100%, 70%, 50%). The numbers in parentheses show the percent change in average  $T_g$  from the  $T_g$  without ions considered. All  $T_g$  values are in K.

Sample	RA Weighted $T_g$ without Ions (100%)	Ions and RA Weighted $T_g$ (100%)	Ions and RA Weighted $T_g$ (70%)	Ions and RA Weighted $T_g$ (50%)
PMO-1	328.75	324.38 (1.33%)	322.67 (1.85%)	320.51 (2.51%)
PMO-2	326.45	324.43 (0.619%)	323.71 (0.839%)	322.85 (1.10%)
PMO-3	326.88	324.41 (0.756%)	323.44 (1.05%)	322.22 (1.43%)

A comment about the estimated impact of small organic acids to the  $T_g$  has been added to the manuscript as follows (lines: 164-171): **“The procedural loss of ionic low MW compounds such as oxalate can lead to an underprediction of the organic aerosol O/C and overprediction of the average glass transition temperatures ( $T_g$ ). To investigate this, we used the concentrations of the prominent organic anions measured with ion chromatography to estimate the abundance of these compound relative to the compounds detected by FT-ICR MS. The low MW corrected average O/C values correlated with the trends of the original O/C values, however the significance of impacts varies with the measured analyte concentrations and the assumptions associated with the uncertain mass fraction of the molecular formula composition (Table SM4). When low MW organic anions were included in the estimated average dry  $T_g$  values, they dropped by  $\leq 2.5\%$ , which was deemed relatively insignificant (Table SM5).**

In the supplement, a discussion of the estimation method was added (pg. 5). In addition, the tables shown above were added to the supplement as well.

*Finally, it would have been interesting to measure also in the positive ESI mode, in which one can observe levoglucosan or nitrogen-heterocycles that are expected in biomass burning aerosol samples.*

We agree with the reviewer, analyses with positive mode ESI would have been interesting. Time constraints limited our ability to do multiple ionization method and we were interested in the oxidation characteristics of long-range transported aerosol. Since oxidation leads to the addition of carboxylic acid groups and in general more polar molecular species, negative mode ESI was the most practical way to analyze the samples.

*Moreover, it is not clear how the blank signal of the DI/ESI-UHRMS was determined. I would expect a measurement of a blank filter that undergoes the whole procedure incl. transport from the field site, sample preparation procedure in laboratory (sonication, filtration, SPE, etc). Only a good blank measurement allows determining the significance level at which individual signals are present in the samples and identifying those signals that emerge from sample preparation. Here, it is especially important since the paper discusses the number of identified compounds between the different samples. If a compound was identified as “not present” in one sample, does that mean after blank subtraction? It is not described what were procedures involving a blank filter, nor are mentioned the criteria and the thresholds for this kind of filtering!*

Blank subtraction is a non-trivial matter in ultrahigh resolution MS (e.g., Zielinski et al., 2018) due to the difference in ion collection times for a sample compared to a blank, and the possibility of resuspension of

sample residues within the instrument when a blank (i.e., clean solvent) is infused. Ion trap instruments (including hybrid FT-ICR MS and Orbitrap MS instruments) also use an auto-gain control (AGC) to avoid space charge artifacts. In our analysis, the AGC was set at the recommended setting of  $1 \times 10^6$  ions. Since samples and blanks generate ions at very different rates, the time necessary for the analysis varies and often a maximum injection period is required. Our maximum inject period was 500 ms for samples and 800 ms for blanks. The actual average injections times for samples were in the range of 20-80 ms, however the blanks “timed-out” at 800 ms before the mass analysis was performed. The injection time differences indicated that the blanks were very clean and the potential for resuspension was non-negligible due to increased accumulation time. Therefore, we compared the intensities of the analytes in the samples and blanks and used a ratio of 3 to determine whether or not a peak should be removed.

In this study, we had both technical instrument blanks and field blanks. We applied the ratio of 3 criteria to both types of blanks, where all of the analytes with a ratio  $< 3$  relative to the technical blank were removed and those  $< 3$  relative to the field blanks were flagged. This led to 2 formulas being flagged because they didn't meet the criteria in 1 of the 3 samples. If the 2 analytes were contamination, they should have appeared equally in all 3 samples, but they were not. Further the 2 analytes were part of a homologous series that was not otherwise in common with the field blanks. The two flagged analytes are  $C_{17}H_{34}O_4$  and  $C_{19}H_{38}O_4$ , which showed very low intensity in that sample. We deemed this to be a fair assessment, especially in light of the very different amounts of time required for the ion injection.

The QA that was performed for the samples is consistent with what has been described in other studies from our group (Putman et al., 2012; Mazzoleni et al., 2012; Dzepina et al., 2015). In short, we removed formulas with extremely high or low O/C ( $>2$ ,  $<0.1$ ), H/C ( $>2.2$ ,  $<0.3$ ), and DBE ( $>20$ ). We also removed known solvent contaminant peaks and isolated assignments that were not part of a  $CH_2$  homologous series. After this was done, we aligned the two replicate analyses of the samples and kept only the formulas that were present in both replicates. If a formula is described as “not present” it means that formula was not present in the sample being referred to after the QA steps described above were performed. This description of the QA procedure was added to the Supplement of the manuscript. To the main manuscript we added the following (lines: 185-188): **“Specifically, two formulas ( $C_{17}H_{34}O_4$  and  $C_{19}H_{38}O_4$ ) observed in PMO-1 could not be classified as pertaining only to the field blank and so they were not removed. Further discussion about the blank subtraction is provided in the Supplement. To produce the final data set for each sample, the replicates were aligned and only the molecular formulas found in both replicates after QA were retained.”**

The description of the blank subtraction procedure given above will be added to the Supplement pg. 4.

*Overall, I cannot recommend the article to be published in ACP, since the conclusions reached remain far too speculative and are not convincingly supported by the presented data. I miss a more critical discussion and evaluation of other potentially important processes (both atmospheric and instrumental) throughout the manuscript. The description of the mass spectrometry analysis is not sufficiently complete and leaves the reader with open questions (e.g. What was the workflow of the data analysis? What did they use as blank samples?). Last but not least, the presentation and language is in many cases not precise.*

Based on the combination of reviewer and editor impressions, we substantially revised the discussion in section 3.5 regarding the observed organic aerosol and its glass transition temperatures ( $T_g$ ). This aspect of the paper is one that is especially unique because we pulled out the GFS ambient conditions along the

FLEXPART retroplume to consider the role of the ambient conditions on the observed chemistry. We paired this with a discussion of the markers of aqueous phase chemistry.

To avoid unnecessary length, our original paper referenced several of our previous papers regarding instrumental method details. However, the reviewers have raised a few interesting questions that we answered more directly in the revised manuscript and the corresponding supplement.

A key point that is especially important to keep in mind is that very little research has been done on the chemistry of free tropospheric aerosol as opposed to the more extensive knowledge of aerosol chemistry from within the continental boundary layer. Our detailed analysis contributes much needed insight to the chemistry of free tropospheric aerosol, where the ambient conditions are colder and drier than in the boundary layer.

The manuscript has been edited for grammar corrections and clarity.

#### *Specific comments*

*p.3, l. 106-109: Please provide a reference stating that long-range transported aerosol is generally acidic in nature. Furthermore, negative ESI is not only sensitive to organic acids, but also to important biomass burning markers (e.g. nitro-phenols (Iinuma et al., 2010)). Have you seen nitro-phenols or similar biomass burning tracers in the biomass burning samples?*

Long range transported aerosol generally has an acidic nature as mentioned in a study by Bougiatioti et al. (2016). Additionally, it is known that during oxidation, carboxylic acid groups will be formed in organic aerosol (Iinuma et al., 2004), providing additional evidence that aged aerosol is generally acidic in nature. The following reference has been added to the manuscript for the citation of acidic transported aerosol at line 112: **(Bougiatioti et al., 2016)**

To clarify our use of negative mode ESI and the reasons for it, the following has been added to lines 175-176 of the manuscript: **“Negative polarity is effective for the deprotonation of polar organic molecules (Mazzoleni et al., 2010), which are expected to dominate the organic aerosol mass fraction and were the focus of this study.”**

Formulas such as  $C_6H_5NO_3$  (nitro-phenol) and  $C_6H_{10}O_5$  (levoglucosan) were detected in the samples. Additionally, all but three of the CHNO and CHO negative mode ESI species connected to brown carbon by Lin et al. (2016) were detected in one or more of the aerosol samples in this study. PMO-1 contained all of them, which supports the biomass combustion source for this sample in particular. For a list of matching formulas see Table S4. This table was added to the Supplement.

**Table S4. Molecular formulas identified in brown carbon by Iinuma et al. 2010 and Lin et al. 2016.**

Formula	Observed	Citation
		Iinuma et al. 2010;
C <sub>7</sub> H <sub>7</sub> NO <sub>4</sub>	Yes	Lin et al. 2016
C <sub>6</sub> H <sub>5</sub> NO <sub>3</sub>	Yes	Lin et al. 2016
C <sub>6</sub> H <sub>5</sub> NO <sub>4</sub>	Yes	Lin et al. 2016
C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>6</sub>	No	Lin et al. 2016
C <sub>6</sub> H <sub>4</sub> NO <sub>4</sub>	No	Lin et al. 2016
C <sub>10</sub> H <sub>9</sub> NO <sub>3</sub>	No	Lin et al. 2016
C <sub>8</sub> H <sub>7</sub> NO <sub>4</sub>	Yes	Lin et al. 2016
C <sub>8</sub> H <sub>7</sub> NO <sub>3</sub>	Yes	Lin et al. 2016
C <sub>9</sub> H <sub>7</sub> NO <sub>4</sub>	Yes	Lin et al. 2016
C <sub>10</sub> H <sub>7</sub> NO <sub>4</sub>	Yes	Lin et al. 2016
C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	Yes	Lin et al. 2016
C <sub>9</sub> H <sub>6</sub> O <sub>3</sub>	Yes	Lin et al. 2016
C <sub>10</sub> H <sub>8</sub> O <sub>4</sub>	Yes	Lin et al. 2016
C <sub>13</sub> H <sub>8</sub> O <sub>5</sub>	Yes	Lin et al. 2016
C <sub>13</sub> H <sub>8</sub> O <sub>6</sub>	Yes	Lin et al. 2016
C <sub>15</sub> H <sub>10</sub> O <sub>6</sub>	Yes	Lin et al. 2016
C <sub>16</sub> H <sub>12</sub> O <sub>6</sub>	Yes	Lin et al. 2016
C <sub>16</sub> H <sub>12</sub> O <sub>7</sub>	Yes	Lin et al. 2016
C <sub>17</sub> H <sub>14</sub> O <sub>8</sub>	Yes	Lin et al. 2016

*p. 5, l. 169: The two references describe different criteria for the molecular formula assignments: Dzepina et al.: max. 100 C, 400 H, 100 O, 3 N, and 1 S. Mazzoleni et al.: max. 70 C, 140 H, 25 O, 3 N, and 1 S.*

The maximum range for C, H, and O is a function of the molecular weight range. Our highest m/z value is 752.3636, thus assuming 100% C ( $752.3636/12 = 62.7$ ), 50% O ( $752.3636/32 = 23.5$ ) and an H/C = 2 ( $62.7 * 2 = 125.4$ ). Thus, it is not necessary to have higher maximum values.

*The elemental windows for nitrogen and sulfur seem very strict. The used limits exclude for example the identification of nitrogen-heterocycles with four nitrogen (e.g Kampf et al., 2012). Given the clear isotopic signature of sulfur, why was not more sulfur allowed? Were the isotopic patterns used to confirm the molecular formulas in case multiple elemental compositions appeared within the instrumental accuracy limits?*

Based on our observations over several iterations of molecular formula assignment with varied elemental tolerances, the number of unreliable (aka chemically unreasonable) molecular formula assignments increases with an increased number of N and S.

Isotopic patterns were used to provide confidence in the molecular formula assignment. Roughly 90% of all species identified were found to have a corresponding  $^{13}\text{C}$  peak and roughly 70% of all sulfur containing formulas were found to have a corresponding  $^{34}\text{S}$  peak. The molecular formulas without isotope confirmation had low relative abundances, thus the polyisotopic ions were likely below the noise threshold.

Reduced S and N (including heterocyclic compounds) are unlikely to be detected in negative ion ESI-MS. Furthermore, several studies have shown that the number of elements and especially the number of multivalent elements must be restricted to obtain reliable molecular formula assignment (Koch et al., 2007; Herzsprung et al., 2015). On the other hand, not allowing probable heteroatoms leads to incorrect assignments (Ohno et al., 2013).

*p. 5, l. 172: According to Putman et al., allowing nitrogen for compounds larger than 500 amu results in multiple results within 1 ppm. Does that mean that the number of elements allowed was chosen such strict that only one molecular formula per signal was obtained?*

In the Putman et al. (2012) paper we discussed the importance of having a *de novo* (aka first in series) cutoff of 500 u when assigning molecular formulas with heteroatoms such as nitrogen. This means that the molecular formula assignments above 500 u are restricted to homologous series of molecular formulas below 500 u. In Composer this relationship is based on Kendrick mass defects to identify homologous series of  $\text{CH}_2$ . This is necessary because the number of chemically reasonable formulas with N and S heteroatoms is greater than 1.

*p. 6, l. 205-222: As mentioned by the editor, this paragraph is not well structured and needs rewriting.*

Upon receipt of the editor's comments, we revised the paragraph from a single long paragraph to 3 shorter paragraphs. To further clarify the paragraph, we removed the following sentence (from Section 3.1) as it was slightly off topic: **“Generally, increased cloud processing is expected to lead to increased oxidation of atmospheric organic species (Ervens et al., 2008; Zhao et al., 2013), but has also been hypothesized that cloud scavenging of oxidized components could lead to lower overall oxidation by leaving behind reduced aerosol (Dzepina et al., 2015).”**

*p. 8, l. 308: Is the high O/C of the CHNO species potentially driven by organic nitrates?*

Yes, we expect the oxygen of nitrate functional groups to contribute to the O/C value. This is why the O/C ratios of CHO and CHNO species were never directly compared and contrasted within a single sample, instead they were only compared across the samples.

*p. 8, l. 310-311: Does the common number of identified molecules in a certain group (here CHNO) really tell us something about the similarity of samples? This is mentioned several times in the manuscript, and I don't understand why intensity of compounds is not given more weight in the discussions.*

The peak intensity is not the only consideration for these compounds, because intensity is not based entirely on the abundance of the compound in the sample. Ionization efficiency also plays an important role (this is mentioned in lines 324-326). For this reason, we tried to limit our reliance on interpreting the samples solely through abundance. However, because the ions represent a mixture of isomers, the trends associated with the molecular formulas are important. For example, although a majority of the CHO molecular formulas between the three samples were in common, we observed much higher normalized relative abundances of the CHO with higher O/C values in PMO-2. It is the same for CHNO species as well, the species with high O/C are more abundant in PMO-2 than in the other two samples.

To eliminate confusion, we moved the non-intensity weighted values to the supplement.

*Why not visualizing the similarity of two different samples by simple scatter plots of the intensity of all ions of sample A vs intensity of all ions of sample B. This would also allow determining the Pearson correlation coefficient.*

As requested, we made a scatter plot (see below). The scatter plots are consistent with our observations regarding the similarities between PMO-1 and PMO-3 and the relative difference between these two and PMO-2. The Pearson coefficients are shown in each plot and demonstrate PMO-1 and PMO-3 are more similar to each other than PMO-2.

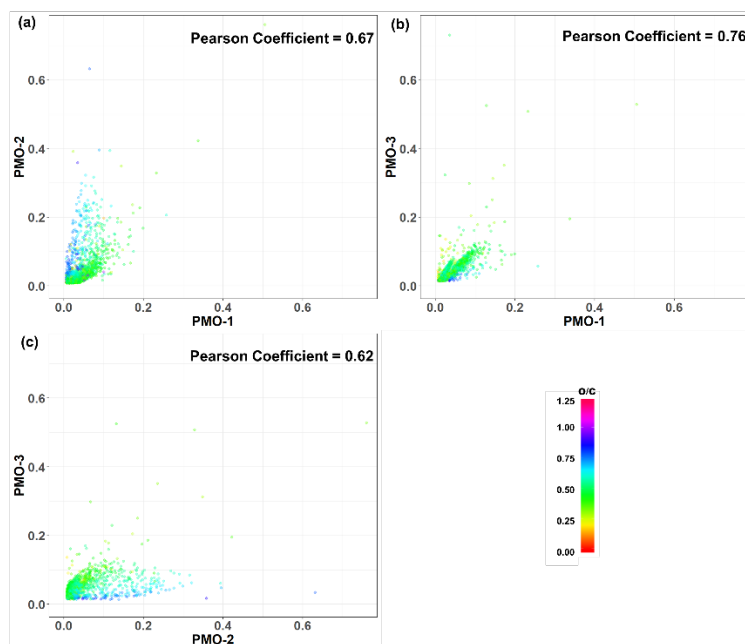
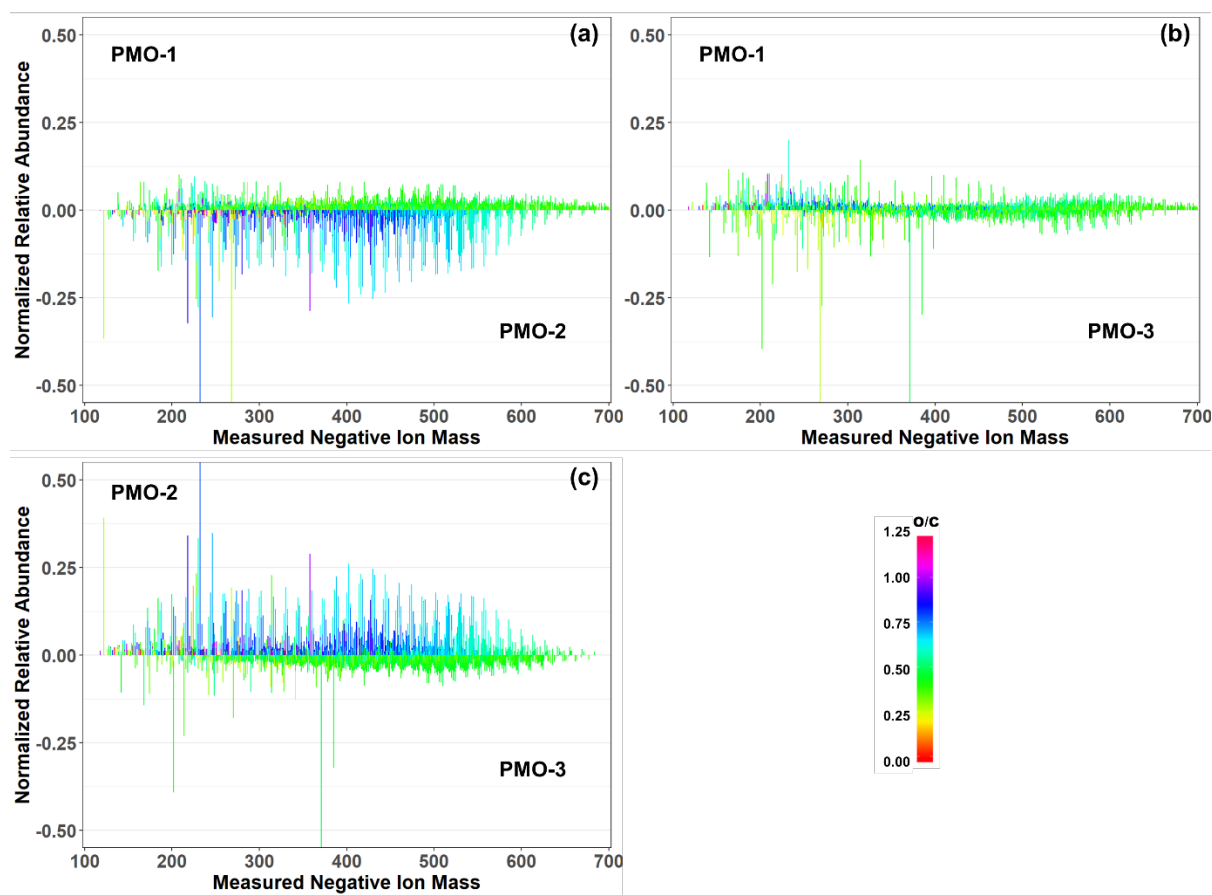


Figure AR1. Scatter plot of the normalized relative abundance of one sample vs. the normalized relative abundance of another. The sample name is on each axis and the numbers denote the normalized relative abundance.

Another way of demonstrating the differences and similarities between these samples while considering their abundance can be done using difference mass spectra. We added 3 difference mass spectra to the Supplement (Fig. S23). In these plots, PMO-2 contains nearly all of the high O/C species, while PMO-1 and/or PMO-3 show the lower O/C species, as described in the manuscript. The plots also show where the species are more abundant. Likewise, similar abundances cancel each other toward zero.





**Figure S23.** Difference mass spectra comparing the three PMO samples. The species more abundant in one sample or another are elevated in the correspondingly labeled half of the plot. PMO-1 vs. PMO-2 (a), PMO-1 vs. PMO-3 (b), and PMO-2 vs. PMO-3 (c).

*p. 8, l. 319: Is the high O/C of the CHOS species potentially driven by organic sulfates? What would be the O/C after accounting for organic sulfates? Is it then still different from the CHO value?*

Yes, the O/C of the CHOS species is impacted by the presence of organic sulfates. If 4 oxygen are removed from the molecular formulas and the O/C is recalculated the O/C decreases to a level somewhat below that of the CHO group (O/C = 0.44 for PMO-2 and O/C = 0.27 for PMO-1 when “sulfate” is removed). This is why the O/C values of the CHOS compounds are not directly compared to the other groups.

*p. 9, l. 334 ff.: The oxygen that originates from organic nitrates and sulfates artificially increases the oxidation state of carbon.*

Yes, this is correct, and in Fig. 4 (manuscript) the  $OS_C$  values used were calculated using the assumption that nitrogen and sulfur were both fully oxidized (Kroll et al., 2011). The average values reported in the tables calculated without this assumption were corrected. To clarify this, a sentence was added to lines 370-371: **“Additionally, we assumed all nitrogen and sulfur were present as nitrate and sulfate functional groups and calculated the  $OS_C$  with the appropriate corrections (Equation S1).”**

*p. 10, l. 394: Was the glass transition temperature determined only for single molecules and not for the intensity weighted population of all ion signals? Obviously the atmospheric particles are mixtures and therefore only the glass transition temperature derived from the whole spectrum is meaningful.*

We thank the reviewer for this question. A similar question was raised by Reviewer 2. Prompting much additional consideration of this topic. Please see also the Authors Response to Reviewer 2.

First, we calculated the  $T_g$  for all components because it provides the distribution of  $T_g$  values. This can be useful because it is unlikely that all particles contain all the species identified (e.g. Riemer and West, 2013), and so some particles may contain species that are more likely to be liquid, while another may be more likely solid. A determination of the chemical mixing at the single particle level would require a different type of analysis (e.g., O'Brien et al., 2015) and is not possible with our samples. The single compound information is lost when all species are treated as if they were uniformly mixed by calculating a single average  $T_g$ .

We agree that the overall  $T_g$  for a particle is what matters in determining the phase state of said particle, but as we have no way of knowing the exact composition of every aerosol particle we feel that showing the distribution of estimated  $T_g$  values is more appropriate. In any case, we did calculate the compositional arithmetic average dry  $T_g$  values for all three samples (RA Weighted  $T_g$  without Ions (100%)), which is shown in the table below. This table has also been added to the Supplement as Table S5.

**Table SM5. Estimated average  $T_g$  values when the ions are considered. The table contains the results for 3 assumptions of the organic mass fraction represented by the FT-ICR MS identified species (100%, 70%, 50%). The numbers in parentheses show the percent change in average  $T_g$  from the  $T_g$  without ions considered. All  $T_g$  values are in K.**

Sample	RA Weighted $T_g$ without Ions (100%)	Ions and RA Weighted $T_g$ (100%)	Ions and RA Weighted $T_g$ (70%)	Ions and RA Weighted $T_g$ (50%)
PMO-1	328.75	324.38 (1.33%)	322.67 (1.85%)	320.51 (2.51%)
PMO-2	326.45	324.43 (0.619%)	323.71 (0.839%)	322.85 (1.10%)
PMO-3	326.88	324.41 (0.756%)	323.44 (1.05%)	322.22 (1.43%)

*Accounting for the fact that small organics are lost during the SPE (which would reduce  $T_g$  of the mixture), what would be the effect on  $T_g$  of the mixture if one assumes that 10, 20 or 50% of total OC consist of small organics?*

It is correct that low MW species are lost during SPE and this can bias the  $T_g$  towards higher values. However, the bias is very minor based on estimations made using the ion concentrations and OM concentrations for these samples, as discussed in the response to reviewer comment #3 (Table SM5). The most prevalent organic anion in all three samples, is oxalate, which has a  $T_g$  estimated to be 324.21 according to the Boyer-Kauzmann rule ( $T_g = g \cdot T_m$ ,  $g = 0.7$ ,  $T_m =$  melting point) (Koop et al., 2011; Shiraiwa et al., 2017; DeRieux et al., 2018). If the assumption is made that half of the total OM is small organics, oxalate would likely make up the largest percentage of the total and would thus have the

greatest effect on the impact of small organics on the  $T_g$ . Just as a theoretical exercise, if we use the assumption that 50% of the OM is oxalate and the method described in detail above, the average dry  $T_g$  drops  $\leq 2.5$  K. It would be lower if we assumed that formate or acetate were the major small organic being lost, but based on our measurements that is not expected.

As explained earlier, our intention was not to definitively calculate the glass transition temperature for the entire mixture in the particle. To clarify this we altered Figure 7 in the manuscript to instead show the distribution of estimated  $T_g$  values based on the ambient relative humidity. In this plot, we included the  $T_g$  and abundance of the most abundant low MW organic ions removed by SPE. This sheds light on their potential impact toward the overall  $T_g$  of the particles. We also plotted the ambient temperature to guide the eye and illustrate where the estimated  $T_g$  values exceed the ambient temperature, which implies a greater likelihood for solid state aerosol (Shiraiwa et al., 2017). Furthermore, the text of the manuscript has been revised to reflect these changes from discussing phase state predictions to estimates of  $T_g$  and their implications.

*Figure 3: The three dots with  $H/C < 0.6$  are cyan in PMO-1, which should mean unique in PMO-1. Why are these three signals in PMO-2 and PMO-3 then grey (common signals)?*

We thank the reviewer for the comment, the figure caption was inaccurate, and the grey symbols were actually all CHNO formulas detected in the three samples. They were included in each plot to make it clear where the differences are between the three samples. The colored circles are the formulas that are unique to each sample, as stated in the figure caption. We clarified the wording by replacing “**common species**” with “**all identified CHNO species**”.

*Figure 1: The Figure quality is not appropriate.*

Corrected.

*Figure 2: X-axis ticks are missing for (a),(b),(d) and (e). It seems as the highest peaks in (b) and (c) are cut at the top, or are they all the same height?*

The tick marks on the bottom plot are accurate for all plots. The tallest peaks are cut off at the top in order to better show the lower intensity species. A comment to clarify this has been added to the caption for Figure 2: “**The tallest peaks in the mass spectra exceed the range, this was done to improve the visibility of the lower abundance species (see also Fig. S6).**” In addition, a plot that shows the entire range of abundance values was added to the Supplement (Fig. S6).

*Figure 4: X-axis ticks are missing for (a), (b), (d) and (e).*

Corrected

*Figure 4: The y-label is number of formulas. The caption is not clear on that. What is the “normalized abundance”? On what is it normalized?*

Thank you for catching this oversight. Instead of normalized abundance, it should have been number of formulas. However, we decided to use the histogram based on the normalized abundance instead of the one that was there, so the caption is now correct as written, and no additional changes are needed. The abundance is normalized to the total abundance of the assigned species.

Figure 6: X-axis ticks are missing for PMO-I.

Corrected

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