

Author Responses to Reviewer #2

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

Schum et al. present a unique dataset collected on Pico Mountain Observatory to study the physiochemical properties of aerosol in the remote marine free troposphere. They analyzed three aerosol samples that had elevated organic carbon concentration, and attributed the differences in their molecular and physical characteristics to emission sources as well as their transport pathways. They observed a lower O/C ratio in two samples that they believed were likely from biomass burning plumes that were transported mostly in the free troposphere, and the aerosols were in a solid state that resisted oxidation. Before this work is published in ACP, the authors need to provide careful clarification and further discussion of several important aspects in this manuscript. Please find the comments below.

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

Major comments

1. The O/C values for PMO-1 and PMO-3 are surprisingly low for particles that had been transported for 7-10 days. In Section 2.3, the authors pointed out that “losses of highly water soluble, low molecular weight organic compounds are expected”. Highly water soluble compounds are presumably quite polar and thus should have higher O/C. Authors need to address how the SPE artifacts affect the overall sample O/C. The same issue applies to the artifacts of water extraction that the water-soluble compounds in the samples were preferably collected for the subsequent analysis. Please provide a discussion of possible bias, what is roughly the fraction that had been extracted versus not-extracted, and how it might affect the results of the analysis.

We thank the reviewer for this comment. The sample preparation step is necessary because electrospray ionization (ESI) is used to study complex organic matter. The soft ionization method is susceptible to salt adducts that can complicate the mass spectra. Furthermore, low molecular weight (MW) compounds can be analyzed using other analytical techniques (e.g., gradient anion chromatography is suitable for several common low MW organic anions).

As suggested by the reviewer, the loss of low MW compounds with high O/C values does likely correspond to a decrease in the total water-soluble organic carbon O/C value. The magnitude of this depends on how the O/C value is determined. An overall larger difference is associated with relative abundance weighted O/C values (RA-weighted or O/C_w). On the other hand, a negligible difference is associated with arithmetic mean values (due to the very high number of identified molecular formulas). For this reason, a majority of the values reported in the discussion paper were arithmetic mean values. For a more complete comparison of arithmetic mean values of O/C from several studies, we refer the reviewer to Table 3 from Dzepina et al. (2015) shown below.

Table 3. Chemical characterization of the molecular assignments detected in selected studies. All values are average (arithmetic mean).

Sample name	Sample type	Measurement site	O / C	H / C	OM / OC	DBE	DBE / C	MW	Reference
Pico 9/24	Aerosol	Free troposphere	0.46	1.17	1.73	10.7	0.47	478	This study
Pico 9/25	Aerosol	Free troposphere	0.42	1.28	1.67	9.4	0.42	462	
Storm Peak Lab S4SXA	Aerosol	Remote	0.53	1.48	1.91	6.2	0.34	414	Mazzoleni et al. (2012)
Millbrook, NY ¹	Aerosol	Rural	0.32	1.46	1.60	6.30	0.33	366	Wozniak et al. (2008)
Harcum, VA ¹	Aerosol	Rural	0.28	1.37	1.54	7.45	0.38	360	
K-Pusza 2004 (KP2004) ²	Aerosol	Rural	0.48	1.40	1.84	7.36	0.37	408	Schmitt-Kopplin et al. (2010)
K-Pusza 2005 (KP2005) ²	Aerosol	Rural	0.39	1.22	1.69	10.1	0.46	430	
Pearl River Delta, China	Aerosol	Urban, Suburban, Rural, Regional	0.46	1.34	1.85	5.3	0.45	265	Lin et al. (2012a)
Atlantic Ocean ³	Aerosol	Marine layer boundary	0.35	1.59	1.67	4.37	0.28	317	Schmitt-Kopplin et al. (2012)
North Atlantic Ocean – All ⁴	Aerosol	Marine layer boundary	0.42	1.49	1.74	6.76	0.32	445	Wozniak et al. (2014)
North Atlantic Ocean – Aged Marine ⁴	Aerosol	Marine layer boundary	0.36	1.56	1.70	5.88	0.28	423	
Storm Peak Lab CW1	Cloud water	Remote	0.62	1.46	2.08	6.3	0.38	402	Zhao et al. (2013)
Storm Peak Lab CW2	Cloud water	Remote	0.61	1.46	2.06	6.3	0.38	400	
Fresno fog	Fog water	Rural	0.43	1.39	1.77	5.6	0.40	289	Mazzoleni et al. (2010)
Camden and Pinelands, NJ ⁵	Rainwater	Urban impacted	1.02	1.49	2.73	3.24	0.44	220	Altieri et al. (2009a, b)

Values were calculated. ¹ For each sample presented in Wozniak et al. (2008). ² For only two samples (KP2004 and KP2005) presented in Schmitt-Kopplin et al. (2010). ³ For only one, marine aerosol, sample presented in Schmitt-Kopplin et al. (2012). ⁴ For all samples (and only one PCA group) presented in Wozniak et al. (2014). ⁵ By combining the negative mode FT-ICR MS data available in Altieri et al. (2009a) (CHO, CHOS and CHNOS) and Altieri et al. (2009b) (CHON).

After consideration of all of the comments (including those of Reviewer 1 and the editor), we opted to instead focus on the RA-weighted values consistently throughout the manuscript. These values do help distinguish important trends in the data (e.g., Fig. 2 and 4). However, we note both here, and in the manuscript (lines 327-328), that the RA is not expected to directly correspond to the analyte concentrations because the ionization efficiencies depend on several factors such as polarity, surface activity, and pH (Cech and Enke, 2001).

We estimated the impact of the missing low MW species on the overall O/C using the five highest mass concentrations (oxalate, acetate, lactate, formate, and malonate) as measured using ion chromatography. The measured mass concentrations were converted to their percent abundance relative to the total organic mass (estimated using an OM/OC conversion of 2 (El-Zanan et al., 2005)). The total ion abundance identified using ultrahigh resolution FT-ICR MS was assumed to represent as little as 50% of the total WSOC. 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. These abundance values were then used to estimate the weighted average O/C value for each of the samples. The following table was added to the Supplement (Table SM4).

Table SM4. Estimated average O/C 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 O/C from the O/C without ions considered.

Sample	RA Weighted O/C without Ions (100%)	Ions and RA Weighted O/C (100%)	Ions and RA Weighted O/C (70%)	Ions and RA Weighted O/C (50%)
PMO-1	0.48	0.53 (10.42%)	0.55 (14.58%)	0.58 (20.83%)
PMO-2	0.57	0.70 (22.81%)	0.75 (31.58%)	0.81 (42.11%)
PMO-3	0.45	0.52 (15.56%)	0.54 (20.00%)	0.57 (26.67%)

PMO-2 is still by far the most oxidized sample overall. PMO-1 and PMO-3 were still somewhat unoxidized relative to our pre-conceived expectations based on transport time (Bougiatioti et al., 2014; Aiken et al., 2008). Oxalate is by far the most abundant organic ion and has the highest O/C, thus it yields the largest impact. Note that these O/C values are likely the upper limit of the average high MW O/C for these samples. The ionization preferences associated with negative mode ESI favor more highly oxidized higher molecular weight species, thus high MW molecular species detected by other ionization methods would likely only decrease the O/C.

To clarify the impact of the missing anions on the average O/C, the following has been added (see 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 ≤ 2.5 %, which was deemed relatively insignificant (Table SM5).”**

A description of the estimation method and data discussed above were added to the Supplement (Page 5).

2. The authors use the method developed by DeRieux et al. to estimate particle phase state and heavily rely on the result to explain their findings. However, the authors use this method without further comment and discussion, especially regarding its uncertainty. Solid, semisolid and liquid state are qualitative descriptions which do not provide much insight into diffusion time-scale of water or organic molecules into/out of particles. Diffusion is a key process that determines the evolution of particle composition, and the connection of phase state and diffusivity involves multiple-step estimations with large uncertainties, as shown in a couple of studies [1][2]. Is it possible that the uncertainty of the method is large enough that it changes the major conclusions of this paper? The authors need to provide a much more comprehensive discussion of these issues.

We thank the reviewer for this comment.

This work expands the understanding of the long-range transported aerosol collected at the Pico Mountain Observatory (PMO) presented in previous studies (Dzepina et al., 2015, China et al., 2015; China et al. 2017; Zhang et al., 2015; Zhang et al., 2017). As described, the site is located in the North Atlantic free troposphere on the Azores archipelago, and as such, it is quite remote. Additionally, the site is uniquely well-suited for the observation of long range transported aerosol due to the low marine boundary layer which is frequently below the site (See also Image 1 in the Supplement for a photo of the site and the mountain). Specifically, this paper attempts to advance the interpretation of pollution events arriving from North America using the detailed molecular chemistry.

We agree that diffusion is a key process in determining the evolution of particle compositions; however according to the FLEXPART retroplumes, the aerosol have been aloft for several days and the compositions that we measured are mostly low volatility compounds (Fig. 6 of manuscript). Our intent was not to provide exact predictions of diffusion or viscosity for the aerosol collected during the sampling periods (predictions for which our available sample and measurements would not be appropriate), but to provide an estimate of the most probable phase state for the organic aerosol during transport using the GFS meteorological fields (specifically ambient T and RH) associated with the FLEXPART retroplumes for a few upwind days. We then used the ratio of glass transition temperatures (T_g) to the ambient temperature (T_g/T) coupled with chemical markers to assist in the interpretation of our observations of the samples.

At present, we do not have enough information to predict the diffusion of species in the aerosol particles. Insufficient knowledge on the composition of aerosol particles and a lack of available methods to accurately measure viscosity for ambient samples at low concentrations limit the possibility to estimate diffusion, as described in a recent review by Reid et al. (2018). Therefore, we used general literature ideas about phase state and its impact on diffusion and viscosity to support the hypothesis that phase state limits the atmospheric oxidation of organic aerosol, which is consistent with several other studies (Shrivastava et al. 2017, Berkemeier et al., 2014, Lignell et al., 2014, Zelenyuk et al., 2017). Research reported in Ye et al. (2016), has shown that low volatility compounds resist diffusion even at high RH.

To be more accurate and avoid confusion, we removed the classification of molecular species as “solid”, “semi-solid”, and “liquid”, and instead show only the estimated T_g . We also focused our discussion on the uncertainties in the T_g estimates with respect to the DeRieux et al. (2018) defined error and the range of meteorological conditions extracted from FLEXPART. In fact, the range of ambient conditions presents a larger range of estimated T_g values. As such, Figure 7 from the revised manuscript has revised and an additional version of the plot which demonstrates the distribution of T_g values using just the mean RH for the RH dependent T_g was added to the supplement (Fig. S17).

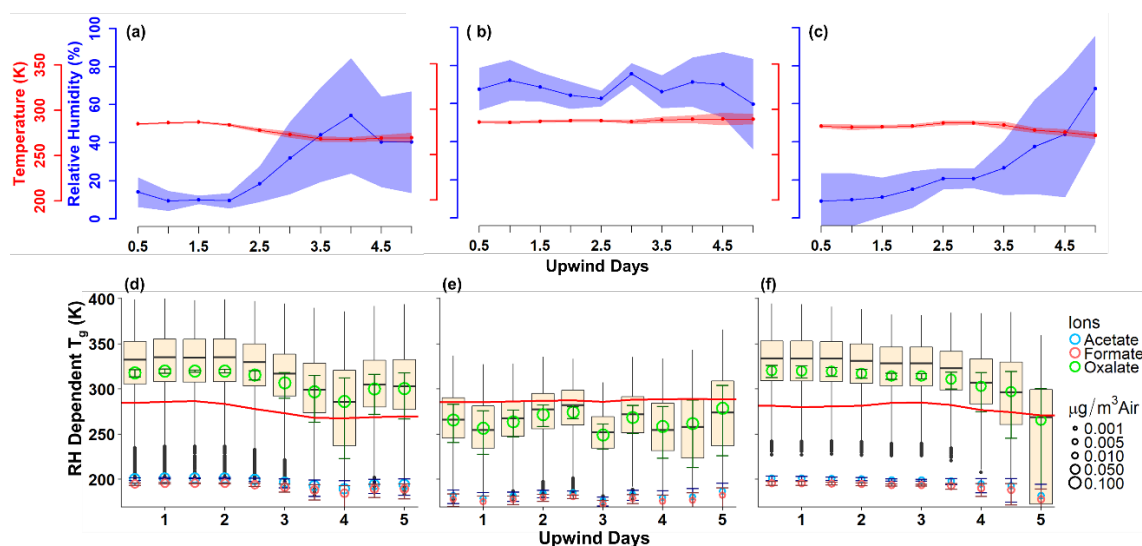


Figure 7. Panels a-c contain the ambient conditions extracted from the GFS analysis along the FLEXPART modeled path weighted by the residence time for PMO-1, PMO-2, and PMO-3, respectively. The line represents the mean value and the shading represents one standard deviation of values. Panels d-f contain the boxplot distributions of the relative humidity dependent T_g values for molecular formulas using the maximum, mean, and minimum RH for PMO-1, PMO-2, and PMO-3, respectively. The T_g values for the full composition of each sample were calculated using the maximum, mean, and minimum RH and then all three sets of data are combined and plotted as a single distribution for each time period. The open circles represent the abundance and Boyer-Kauzmann estimated T_g for the acid forms of the three most abundant low MW organic ions, the bars around the circles represent the range of possible T_g values for those compounds when the range of RH is considered. The red line demonstrates the ambient temperature at each time point, as extracted from GFS. The centerline of the boxplot represents the median, the top and bottom of the “box” represent the third and first quartiles, respectively. The “whiskers” represent $Q3 + 1.5 \cdot \text{IQR}$ (maximum), and $Q1 - 1.5 \cdot \text{IQR}$ (minimum).

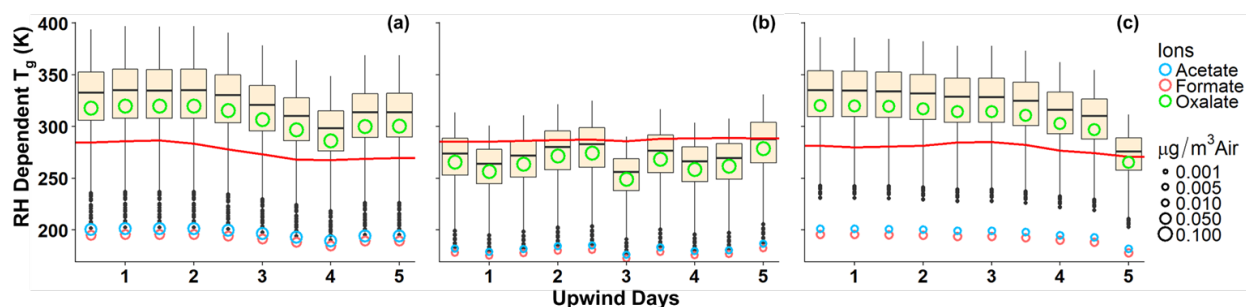


Figure S17. Boxplots showing the distributions of the relative humidity dependent T_g values for each sample over the last five days of transport. The open circles represent the Boyer-Kauzmann estimated T_g values for the acid forms of the three most abundant low MW organic ions not observed in FT-ICR mass spectra. The symbols are scaled by their ambient concentration. The red line represents the mean ambient temperature from the GFS analysis. The samples PMO-1, PMO-2, and PMO-3 are shown in panels (a), (b), and (c), respectively. The centerline of the boxplot represents the median, the top and bottom of the “box” represent the third and first quartiles, respectively. The “whiskers” represent $Q3 + 1.5 \cdot \text{IQR}$ (maximum) and $Q1 - 1.5 \cdot \text{IQR}$ (minimum).

According to DeRieux et al. 2018, the estimation of T_g has an error of ± 21 K when considering only a single compound. They also mention that when considered as a group, the error decreases substantially, owing largely to some species being overestimated and some being underestimated, leading to the final result being reasonably accurate. In order to test the limit of the potential error, we added and subtracted 21 K from all the estimated T_g values and replotted the distributions as presented in the manuscript.

As expected, the range of T_g values increased. However, despite this increase, the majority of the T_g distribution was still below the ambient temperature for PMO-2. Figure S18 (below) illustrates the results of these tests. However, to have the equation under or overestimate the T_g of all formulas by the maximum reported error and the same extent with the same direction is highly unlikely and so it seems likely that our results are robust. Furthermore, an individual molecular formula represents a mixture of isomers with slightly different T_g values, thereby potentially decreasing the error consistent with the description by DeRieux et al. (2018). For example, ultrahigh resolution MS/MS work by LeClair et al. (2012) has shown that most molecular formulas have more functional group losses (neutral losses of hydroxyl, carboxyl, etc.) than could be expected from a single isomer of a molecule. This has also been observed in the MS/MS analysis of PMO-1 which is the subject of a forthcoming paper.

To make the potential error due to the estimation clear the following has been added to the manuscript (Lines 213-217): “DeRieux et al. (2018) reported an uncertainty of ± 21 K for the prediction of any single compound, but the uncertainty is expected to decrease when a mixture of compounds is considered. Nonetheless, we assumed an uncertainty range of ± 21 K on T_g and found that it did not significantly change the T_g trends presented in Section 3.5. Further discussion the uncertainty on T_g is provided in the Supplement.”

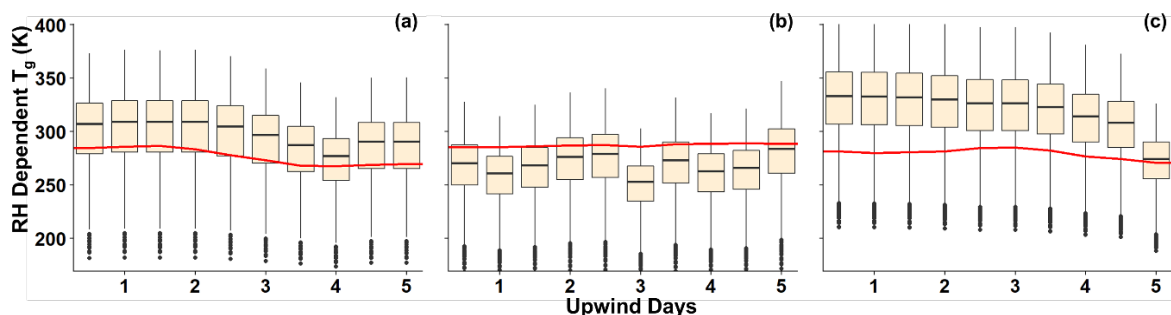


Figure S18. Relative humidity dependent T_g distribution box plots with ± 21 K uncertainty (DeRieux et al., 2018) applied. Panels (a), (b), and (c) show the distributions for PMO-1, PMO-2, and PMO-3, respectively. Three distributions were calculated for each sample, one with 21 K added to the dry T_g , one with 21 K subtracted from the dry T_g , and one with the original T_g values. The three data sets were combined here. The inclusion of the ± 21 K uncertainty does not significantly impact the range of observations. The centerline of the boxplot represents the median, the top and bottom of the “box” represent the third and first quartile respectively. The “whiskers” represent $Q3 + 1.5 \times \text{interquartile range (IQR, } Q3-Q1)$ (maximum) and $Q1 - 1.5 \times \text{(IQR)}$ (minimum).

Minor comments

1. In line 20, “This suggests that biomass burning emissions injected into the free troposphere are longer-lived than emissions in the boundary layer.” The term “longer lived” is vaguely used here, as well as in a couple places in the main text. Do the authors mean the particles from biomass burning have lower oxidation state, or the authors are referring to the chemical life time of the compounds from biomass burning that were transported in the free troposphere?

The intent was to indicate that aerosol in the free troposphere appear to be more resistant to removal, due in part to the ambient conditions. In this case, we specifically contrast this finding to previously reported lifetimes of biomass burning brown carbon species, which were predicted to have a lifetime of ~1 day within the boundary layer (Forrister et al., 2016; Laing et al., 2016). To clarify, we changed “long lived” to “persistent”, everywhere as appropriate in the manuscript.

2. In Section 3.1, chloride is presented in Table 1 but not discussed in the main text. Some studies show that biomass burning can produce chlorine-containing particles [3][4].

We thank the reviewer for this interesting observation. To reflect this, we added the following to Section 3.1 (lines 250-251) of the paper: **“Chloride was also present in PMO-1 and PMO-3, which has been shown in some studies to be a minor product of biomass burning, depending on the fuel burned (Levin et al., 2010; Liu et al., 2017).”**

3. In Figure 1 (c), the air mass spent a couple of days over Europe, and based on (f), the height of the air mass was quite low during those days. Could there be any influence from emissions from Europe on the sample?

We thank the reviewer for this comment. First, the altitude profile plots were inadvertently misplaced, so the altitude of the air mass over Europe was not as low as shown there. We corrected this as soon as we realized the mistake during the discussion. We also corrected the plot in the final manuscript and added additional retroplumes with 12 hour time differences. Looking at the correct plots, the altitude was still somewhat low and the RH increased indicating potential influence from Europe. However, the molecular species identified in PMO-3 were much more similar to the more strongly influenced biomass burning sample (PMO-1) than they were to the anthropogenic, albeit North American, influenced sample (PMO-2). There is the possibility of European influence roughly 5 days before reaching the PMO, shown by the spike in altitude and RH during that time period, but it does not seem to be a major component based on the chemical comparisons of the three samples. Additionally, the source apportionment modeling did not predict European influence for that sample.

4. In Section 3.2, regarding the CO source apportionment in Figure S1, what is the uncertainty associated with the CO modeling?

We add a few sentences in Section 2.4 (highlighted in bold below) to discuss the uncertainty and features associated with the FLEXPART CO simulations. We would like to point out that the FLEXPART CO tracer does not reproduce the actual CO concentration at the site because FLEXPART only simulates the transport of emissions but not the chemistry or deposition. FLEXPART CO was set to have a cutoff lifetime of 20 days in the model, but in reality, the CO lifetime varies from weeks to months depending on the location and atmospheric conditions. In this work, FLEXPART CO simulations were used as an indicator to show the relative contributions from anthropogenic and biomass burning emissions rather than an estimate of CO concentrations at Pico.

Manuscript excerpt (Lines 191-207):

“FLEXPART modeling was used to determine the sources, ages, and transport pathways of the aerosol samples collected at PMO. FLEXPART backward simulations (also called retroplumes) were driven by meteorology fields from the Global Forecast System (GFS) and its Final Analysis (FNL) with 3-hour

temporal resolution, 1° horizontal resolution, and 26 vertical levels. The output was saved in a grid with a horizontal resolution of 1° latitude by 1° longitude, and eleven vertical levels from the surface to 15,000 m a.s.l. **For each simulation, 80 thousand air parcels were released from the receptor and transported backwards for 20 days to calculate a source-receptor relationship (in units of s kg^{-1} , Seibert and Frank, 2004).** FLEXPART retroplumes (~~upwind distributions of residence time~~) are then multiplied with CO emission inventories (kg s^{-1}) from the Emissions Database for Global Atmospheric Research (EDGAR version 3.2 (Olivier and Berdowski, 2001)) and the Global Fire Assimilation System (Kaiser et al., 2012) to estimate the influence from anthropogenic and wildfire sources, respectively. **The FLEXPART CO tracer calculated with this approach indicates the relative contributions from anthropogenic and biomass burning emissions. Since CO chemistry and dry deposition are not considered in the FLEXPART setup, the absolute FLEXPART CO value does not reproduce the actual CO concentrations at Pico. FLEXPART does not consider the background CO accumulated in the atmosphere. The difference between FLEXPART CO and the actual CO largely depends on these factors. In previous applications of this approach, FLEXPART CO was able to estimate the episodes of CO enhancement due to transport of emissions (e.g., Brown et al., 2009; Stohl et al., 2007; Warneke et al., 2009).** This ~~modeling~~ approach has been used in several PMO studies and **successfully captured elevated CO periods (e.g., Dzepina et al., 2015; Zhang et al., 2014, 2017) and it is used here to assist in the interpretation of the chemical composition in this work”**

5. In Section 3.3, line 285-287, 78% of the formulas in PMO-2 are found to be common with sample from the boundary layer aerosol, and PMO-3 has similarity of 76%. Are 78% and 76% significantly different? This piece of information might not be a strong evidence to support the conclusion that PMO-2 was largely influenced by North America outflow transported within the boundary layer while PMO-3 was not.

As mentioned in the manuscript, there are many species (especially CHO molecular formulas) that are present in all samples. In addition, PMO-3 does not have a large number of unique species relative to PMO-1 or PMO-2. This is largely due to the sampled air as shown in the retroplume being somewhat more diffuse with a less certain path of transport and also origin, than either PMO-1 or PMO-2. Despite the large percentage of common species between PMO-3 and the boundary layer sample from Storm Peak Laboratory (SPL), PMO-3 had much more in common with a previous free troposphere wildfire sample (91%) (September 24, 2012, Dzepina et al., 2015). This suggests PMO-3 is more similar to PMO-1 than PMO-2, but there is the potential for a non-negligible influence from the European boundary layer. The point of the percentages, was to show that PMO-1 and PMO-3 have more in common with free tropospheric wildfire aerosol, than they do with the continental boundary layer aerosol of somewhat mixed sources (SPL aerosol).

To clarify, we revised the text (lines 313 – 318): **“In fact, when we compared the molecular formula composition of the free tropospheric aerosol sample “9/24” from the study by Dzepina et al. (2015) to the free tropospheric samples in this study (PMO-1 and PMO-3), we observed that 86% and 91% of the formulas are common. FLEXPART simulations from both studies suggested these samples were all affected by wildfire emissions, contributing to their similarity. In contrast, only 75% of the formulas found in the boundary layer sample (PMO-2) were common with those in Dzepina et al. (2015). These comparisons are provided in Table S2.”**

6. In Figure 2, an obvious difference of the three spectra is the much higher fraction of high molecular weight materials in PMO-2. Little is discussed about the sources of the high molecular weight compounds in the text. Are they from oligomerization? In contrast, Lee et al. [5] observed abundant high molecular weight compounds from biomass burning in Canada using an aerosol mass spectrometer.

Considering the percentage of species with a mass greater than 350, PMO-2 actually has the smallest percentage of its total formulas in that range both by number of formulas and percentage of total abundance. PMO-1 has 70% of its formulas above 350 and PMO-3 has 71% of its formulas in that range, and PMO-2 has 64% of the formulas in this range. In terms of percentage of total abundance, they make up 63% of PMO-1, 59% of PMO-2, and 65% of PMO-3. These numbers are admittedly similar, but PMO-1 and PMO-3 are more similar and are both somewhat higher than PMO-2. These results may support the observations made in Lee et al. (2016) regarding high molecular weight compounds from biomass burning in Canada.

The main reason why those species ($m/z > 350$) stand out so much is due to their normalized relative abundance, where each measured intensity was normalized by the total ion intensity of the assigned molecular formulas in each sample. The implications of this increased O/C and subsequently, oxidation is the major focus of this paper and is discussed several times. The tall peaks that really stand out (norm. RA > 0.1) only make up 136 of 1349 masses above m/z 350 in PMO-2. Additionally, while analyzing the samples, we investigated the potential of SOA type oligomerization, and were unable to find any clear evidence, and thus did not include it in this manuscript. Also, interestingly, the fire studied by Lee et al. (2016) is likely the same fire that impacted the air mass that intercepted PMO on June 27-28, 2013 (PMO-1), so the relative increase in higher molecular mass compounds is consistent between the two studies.

7. In section 3.5, line 387, "Volatility can also play a role in the phase state". This expression is vague. Do the authors mean phase state depends on volatility? Or they both relate to structures of molecules in particles? Please make clarification.

The sentence was replaced with the following (Lines 424-426): **"In general, lower volatility typically inversely correlates with T_g (Shiraiwa et al., 2017) and viscosity. As such it was important to estimate the volatility of the PMO aerosol."**

8. In section 3.5, line 392, "This highlights the correlation between O/C and volatility, where volatility is expected to decrease as O/C increases." What about fragmentation?

Fragmentation can definitely contribute to both a decrease in O/C and an increase in volatility which requires other chemical changes in the compounds, namely a decrease in mass. The general mass ranges for all three samples is consistent and so fragmentation is unlikely to be the source of lower O/C in PMO-1 or PMO-3. Fragmentation may have occurred in PMO-2, helping to contribute to the increased O/C value observed, but it does not change the observation that the predicted volatility for the high abundance species in PMO-2 was lower than for the high abundance species in PMO-1 or PMO-3, or that the high abundance species in PMO-2 were also those with elevated O/C. Furthermore, the estimation of volatility includes a term regarding the carbon and oxygen interactions (Donahue et al., 2011; Li et al., 2016) indicating a relationship between O/C and volatility. Also, studies have shown a relationship between O/C and volatility before (Ng et al., 2011).

To address this, the following has been added (Lines 429-432):

"This highlights the relationship between O/C and volatility, where volatility is expected to decrease as O/C increases when the mass range is constant (Ng et al., 2011); the relationship between oxygen and carbon and its effect on volatility is used by both Donahue et al. (2011) and (Li et al., 2016) to estimate volatility. Similarly, lower volatility is expected to lead to lower diffusivity in aerosol even at elevated RH as demonstrated by Ye et al. (2016)."

9. Lastly, how generalizable are these findings in the paper in terms of predicting the oxidation state of aerosols having different transport pathways?

We thank the reviewer for this interesting question. The idea of phase state having an impact is likely fairly generalizable because it has been shown in several studies to have an impact on the rate of chemical reaction in aerosol samples (Koop et al., 2011; Berkemeier et al., 2014; Lignell et al., 2014; Shrivastava et al., 2017; Zelenyuk et al., 2017). Thus, it is fair to say that aerosol traveling high in the atmosphere, effectively since emission, can be anticipated to have a relatively low oxidation state. However, more samples are needed to be studied using multiple ionization modes to get a more complete analysis of what is present in these samples.

Regarding this question we added the following to the manuscript (lines 512-514):

“More work is needed to better constrain the molecular composition of long range transported aerosol and the processes that affect it during transport. The presented results have broader implications for the aging of long range transported biomass burning organic aerosol rapidly convected to the free troposphere.”

References

- [1] Frances H Marshall, Rachael EH Miles, Young-Chul Song, Peter B Ohm, Rory M Power, Jonathan P Reid, and Cari S Dutcher. Diffusion and reactivity in ultraviscous aerosol and the correlation with particle viscosity. *Chemical Science*, 7(2):1298–1308, 2016.
- [2] Lindsay Renbaum-Wolff, James W Grayson, Adam P Bateman, Mikinori Kuwata, Mathieu Sellier, Benjamin J Murray, John E Shilling, Scot T Martin, and Allan K Bertram. Viscosity of alpha-pinene secondary organic material and implications for particle growth and reactivity. *Proc Natl Acad Sci U S A*, 110(20):8014–9, May 2013.
- [3] EJT Levin, GR McMeeking, CM Carrico, LE Mack, SM Kreidenweis, CE Wold, H Moosmuller, WP Arnott, WM Hao, JL Collett, et al. Biomass burning smoke aerosol properties measured during fire laboratory at missoula experiments (FLAME). *Journal of Geophysical Research: Atmospheres*, 115(D18), 2010.
- [4] Xiaoxi Liu, L Gregory Huey, Robert J Yokelson, Vanessa Selimovic, Isobel J Simpson, Markus Muller, Jose L Jimenez, Pedro Campuzano-Jost, Andreas J Beyersdorf, Donald R Blake, et al. Airborne measurements of western US wildfire emissions: Comparison with prescribed burning and air quality implications. *Journal of Geophysical Research: Atmospheres*, 122(11):6108–6129, 2017.
- [5] Alex KY Lee, Megan D Willis, Robert M Healy, Jon M Wang, Cheol-Heon Jeong, John C Wenger, Greg J Evans, and Jonathan PD Abbatt. Single-particle characterization of biomass burning organic aerosol (BBOA): evidence for non-uniform mixing of high molecular weight organics and potassium. *Atmospheric Chemistry and Physics*, 16(9):5561–5572, 2016.

Additional References

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, Metzger, A., Baltensperger, U., and Jimenez J. L.: O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry, *Environ. Sci. Technol.*, 42(12), 4478–4485, doi:10.1021/es703009q, 2008.

- Berkemeier, T., Shiraiwa, M., Pöschl, U. and Koop, T.: Competition between water uptake and ice nucleation by glassy organic aerosol particles, *Atmos. Chem. Phys.*, 14(22), 12513–12531, doi:10.5194/acp-14-12513-2014, 2014.
- Bougiatioti, A., Stavroulas, I., Kostenidou, E., Zampas, P., Theodosi, C., Kouvarakis, G., Canonaco, F., Prevot, A. S. H., Nenes, A., Pandis, S. N. and Mihalopoulos, N.: Processing of biomass-burning aerosol in the eastern Mediterranean during summertime, *Atmos. Chem. Phys.*, 14(9), 4793–4807, doi:10.5194/acp-14-4793-2014, 2014.
- Cech, N. B. and Enke, C. G.: Practical implications of some recent studies in electrospray ionization fundamentals, *Mass Spec. Rev.*, 20(6), 362–387, doi:10.1002/mas.10008, 2001.
- China, S., Scarnato, B., Owen, R. C., Zhang, B., Ampadu, M. T., Kumar, S., Dzepina, K., Dziobak, M. P., Fialho, P., Perlinger, J. A., Hueber, J., Helmig, D., Mazzoleni, L.R. and Mazzoleni, C.: Morphology and mixing state of aged soot particles at a remote marine free troposphere site: Implications for optical properties, *Geophys. Res. Lett.*, 42(4), 1243–1250, doi:10.1002/2014gl062404, 2015.
- China, S., Alpert, P. A., Zhang, B., Schum, S., Dzepina, K., Wright, K., Owen, R. C., Fialho, P., Mazzoleni, L.R., Mazzoleni, C., and Knopf, D. A.: Ice cloud formation potential by free tropospheric particles from long-range transport over the Northern Atlantic Ocean, *J. Geophys. Res.-Atmos.*, 122(5), 3065–3079, doi:10.1002/2016jd025817, 2017.
- DeRieux, W.-S. W., Li, Y., Lin, P., Laskin, J., Laskin, A., Bertram, A. K., Nizkorodov, S. A. and Shiraiwa, M.: Predicting the glass transition temperature and viscosity of secondary organic material using molecular composition, *Atmos. Chem. Phys.*, 18(9), 6331–6351, doi:10.5194/acp-18-6331-2018, 2018.
- Donahue, N., Epstein, S., Pandis, S. and Robinson, A.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, *Atmos. Chem. Phys.*, 11(7), 3303–3318, doi:10.5194/acp-11-3303-2011, 2011.
- Dzepina, K., Mazzoleni, C., Fialho, P., China, S., Zhang, B., Owen, R. C., Helmig, D., Hueber, J., Kumar, S., Perlinger, J. A., Kramer, L. J., Dziobak, M. P., Ampadu, M. T., Olsen, S., Wuebbles, D. J., and Mazzoleni, L. R.: Molecular characterization of free tropospheric aerosol collected at the Pico Mountain Observatory: a case study with a long-range transported biomass burning plume, *Atmos. Chem. Phys.*, 15(9), 5047–5068, doi:10.5194/acp-15-5047-2015, 2015.
- El-Zanan, H. S., Lowenthal, D. H., Zielinska, B., Chow, J. C. and Kumar, N.: Determination of the organic aerosol mass to organic carbon ratio in IMPROVE samples, *Chemosphere*, 60(4), 485–496, doi:10.1016/j.chemosphere.2005.01.005, 2005.
- Forrister, H., Liu, J., Scheuer, E., Dibb, J., Ziemba, L., Thornhill, K. L., Anderson, B., Diskin, G., Perring, A. E., Schwarz, J. P., Campuzano-Jost, P., Day, D. A., Palm, B. B., Jimenez, J. L., Nenes, A. and Weber, R. J.: Evolution of brown carbon in wildfire plumes, *Geophys. Res. Lett.*, 42(11), 4623–4630, doi:10.1002/2015gl063897, 2015.
- Kaiser, J. W., Heil, A., Andreae, M. O., Benedetti, A., Chubarova, N., Jones, L., Morcrette, J.-J., Razinger, M., Schultz, M. G., Suttie, M., and van der Werf, G. R.: Biomass burning emissions estimated with a global fire assimilation system based on observed fire radiative power, *Biogeosciences*, 9(1), 527–554, doi:10.5194/bg-9-527-2012, 2012.
- Koop, T., Bookhold, J., Shiraiwa, M. and Pöschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, *Phys. Chem. Chem. Phys.*, 13(43), 19238–19255, doi:10.1039/c1cp22617g, 2011.

- Laing, J. R., Jaffe, D. A., and Hee, J. R.: Physical and optical properties of aged biomass burning aerosol from wildfires in Siberia and the Western USA at the Mt. Bachelor Observatory, *Atmos. Chem. Phys.*, 16(23), 15185–15197, doi:10.5194/acp-16-15185-2016, 2016.
- LeClair, J. P., Collett, J. L. and Mazzoleni, L. R.: Fragmentation Analysis of Water-Soluble Atmospheric Organic Matter Using Ultrahigh-Resolution FT-ICR Mass Spectrometry, *Environ. Sci. Technol.*, 46(8), 4312–4322, doi:10.1021/es203509b, 2012.
- Li, Y., Pöschl, U. and Shiraiwa, M.: Molecular corridors and parameterizations of volatility in the chemical evolution of organic aerosols, *Atmos. Chem. Phys.*, 16(5), 3327–3344, doi:10.5194/acp-16-3327-2016, 2016.
- Lignell, H., Hinks, M. and Nizkorodov, S.: Exploring matrix effects on photochemistry of organic aerosols, *P. Natl. Acad. Sci.*, 111(38), 13780–13785, doi:10.1073/pnas.1322106111, 2014.
- Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H. and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, *Atmos. Chem. Phys.*, 11(13), 6465–6474, doi:10.5194/acp-11-6465-2011, 2011.
- Olivier, J.G.J. and Berdowski, J.J.M.: Global emissions sources and sinks, in: *The Climate System*, Berdowski, J., Guicherit, R. and Heij, B.J., A.A. Balkema Publishers/Swets & Zeitlinger Publishers, Lisse, The Netherlands. 33-78, 2001.
- Reid, J. P., Bertram, A. K., Topping, D. O., Laskin, A., Martin, S. T., Petters, M. D., Pope, F. D. and Rovelli, G.: The viscosity of atmospherically relevant organic particles, *Nat. Commun.*, 9(1), 956, doi:10.1038/s41467-018-03027-z, 2018.
- Seibert, P. and Frank, A.: Source-receptor matrix calculation with a Lagrangian particle dispersion model in backward mode, *Atmos. Chem. Phys.*, 4, 51-63, <https://doi.org/10.5194/acp-4-51-2004>, 2004.
- Shiraiwa, M., Li, Y., Tsimpidi, A., Karydis, V., Berkemeier, T., Pandis, S., Lelieveld, J., Koop, T. and Pöschl, U.: Global distribution of particle phase state in atmospheric secondary organic aerosols, *Nat. Commun.*, 8, ncomms15002, doi:10.1038/ncomms15002, 2017.
- Shrivastava, M., Lou, S., Zelenyuk, A., Easter, R., Corley, R., Thrall, B., Rasch, P., Fast, J., Simonich, S., Shen, H. and Tao, S.: Global long-range transport and lung cancer risk from polycyclic aromatic hydrocarbons shielded by coatings of organic aerosol, *P. Natl. Acad. Sci.*, 114(6), 1246–1251, doi:10.1073/pnas.1618475114, 2017.
- Stohl, A., Forster, C., Frank, A., Seibert, P. and Wotawa, G.: Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2, *Atmos. Chem. Phys.*, 5(9), 2461–2474, doi:10.5194/acp-5-2461-2005, 2005.
- Ye, Q., Robinson, E. S., Ding, X., Ye, P., Sullivan, R. C. and Donahue, N. M.: Mixing of secondary organic aerosols versus relative humidity, *P. Natl. Acad. Sci.*, 113(45), 12649–12654, doi:10.1073/pnas.1604536113, 2016.
- Zelenyuk, A., Imre, D. G., Wilson, J., Bell, D. M., Suski, K. J., Shrivastava, M., Beránek, J., Alexander, M. L., Kramer, A. L. and Massey-Simonich, S. L.: The effect of gas-phase polycyclic aromatic hydrocarbons on the formation and properties of biogenic secondary organic aerosol particles, *Faraday Discuss.*, 200, 143–164, doi:10.1039/c7fd00032d, 2017.
- Zhang, B., Owen, R., Perlinger, J., Kumar, A., Wu, S., Martin, M., Kramer, L., Helmig, D. and Honrath, R.: A semi-Lagrangian view of ozone production tendency in North American outflow in the summers of 2009 and 2010, *Atmos. Chem. Phys.*, 14(5), 2267–2287, doi:10.5194/acp-14-2267-2014, 2014.

Zhang, B., Owen, R. C., Perlinger, J. A., Helmig, D., Val Martín, M., Kramer, L., Mazzoleni, L. R. and Mazzoleni, C.: Ten-year chemical signatures associated with long-range transport observed in the free troposphere over the central North Atlantic, *Elem. Sci. Anth.*, 5, doi:10.1525/elementa.194, 2017.