

1 **Molecular characterization of free tropospheric aerosol collected at the Pico**
2 **Mountain Observatory: A case study with a long range transported biomass**
3 **burning plume**

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30 ***AUTHOR'S RESPONSE TO COMMENTS FROM***
31 ***ANONYMOUS REVIEWERS 1, 2 and 3***

32 We would like to thank Anonymous Reviewers 1, 2 and 3 for their review of the manuscript
33 and useful comments, many of which we have adopted and which helped us improve the
34 manuscript. The reviewers agree that this work makes an important addition to existing knowledge
35 of organics aerosol, and that it should be published after taking into account suggested comments.

36 In this reply all the original comments were copied, numbered by reviewer and comment
37 (e.g., **R1.1**, **R1.2**, **R1.3**, ...) and *italicized*. Original comments that required answers to multiple,
38 different points were further separated (e.g., **R1.1a**, **R1.1b**, **R1.1c**, ...) for increased clarity of this
39 reply. Our reply is given after each comment in non-italic font. Any text that we added or modified
40 to address comments from reviewers is written in **bold font** and has noted the exact placement of
41 the new text in the published ACPD manuscript (page and line(s)). All the references cited in both
42 this reply and the original ACPD manuscript are given with the same format as in the manuscript
43 and are not cited here. The references cited by Anonymous Reviewers and the authors of the
44 manuscript that are NOT included in the original ACPD manuscript are cited at the end of each
45 reply. Finally, for the ease of each reviewer in reading this reply, comments which address the
46 same issue were copied and referenced to the first instance when they appear.

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48 ***Response to Comments from Anonymous Reviewer #1***

49

50 *This manuscript describes the characterization of air parcels observed at the Pico Mountain*
51 *Observatory. Transport of air particles to the observatory are determined using FLEXPART*
52 *analysis along with observations of gas and particle phase species. Monitored gas phase species*
53 *include non- methane hydrocarbons and ozone. Particle phase species were determined using*
54 *continuous measurements of black carbon, aerosol light scattering, and number concentration.*
55 *Molecular characterization was conducted for 24 hr filter collected aerosol samples using an*
56 *OC/EC analyzer, ion chromatography, SEM, and ultrahigh-resolution electrospray ionization*
57 *fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS). Based on the*
58 *suite of measurements, FLEXPART back trajectories, and satellite data from the time periods, two*
59 *plume sources were determined and studied in detail, one representing aged biomass burning*
60 *aerosol from 12 days traversing the Atlantic and the other representing 15 day old marine aerosol.*
61 *The detailed molecular composition analysis of the two air parcels and aerosol particle*
62 *constituents represents a unique contribution to the literature. The manuscript is well written,*
63 *however, is rather lengthy with no clear discussion of the results and implications. I support*
64 *publication in ACP after the following comments are addressed.*

65 ***Major Comments:***

66 ***RI.1) Page 24755 line 19-22: Why would increased fragmentation reduce the O/C? Most studies***
67 ***suggest aging and fragmentation actually increases O/C? See Comment #16.***

68 In this study, we report the molecular characterization of aerosol after long range transport in the
69 free troposphere and 12.4 and 14.7 days of aging for the two collected samples. The aging
70 processes likely include re-equilibration of aerosol constituents to the gas phase (evaporation),
71 photolysis (fragmentation) and other condensed phase reactions (e.g., cloud processing). The
72 cumulative results of aging and the removal of aerosol constituents are observed. This means that
73 we observe the aerosol components that are long-lived. Compounds with high O/C ratios are highly
74 water-soluble and were likely removed during transport. The text has been revised to indicate
75 cumulative effects are responsible for the observed molecular composition.

76 We are not aware of other studies with molecular characterization of long range transported free
77 tropospheric aerosol, thus making it difficult to support our hypothesis with literature citations.
78 Therefore, all mentions of the low O/C ratio due to fragmentation have been removed from the
79 main text and our hypothesis is discussed in section “4. Conclusions”.

80 We reworded the sentence (indicated above):

81 **“These aged aerosol WSOM compounds had an average O/C ratio of ~ 0.45, which is**
82 **relatively low compared to O/C ratios of other aged aerosol.”**

83 ***RI.2a) Page 24762 line 4-7: Why is the Cl⁻ in the blank such a large fraction of the aerosol***
84 ***samples? Is this due to very low Cl⁻ concentrations in the aerosol? It seems the errors in the***
85 ***estimation of Cl⁻ in the ambient aerosol (Table 2) would be higher with such a large background***
86 ***subtraction.***

87 Measurements of inorganic ions are best done using Teflon filters. In this study, we did all of the
88 chemical measurements from quartz fiber filters because of site logistics and power limitations.
89 Quartz filters have low-level chloride contamination as reported. We note this limitation in the
90 revised text with the following insertion on page 24762 in line 6:

91 **“We report averages of the two measurements, blank subtracted for Cl⁻ only; the Cl⁻ in the
92 blank was 48% (SD=21%) of the Cl⁻ in aerosol samples.”**

93 *RI.2b) Along the same lines. For marine aerosol of 9/25, one would think that the concentration
94 of Cl⁻ would increase.*

95 The observed composition of 9/25 indicates a contribution of marine aerosol, but this free
96 tropospheric aerosol was highly aged. Chloride concentrations are known to decrease with aging
97 (Fomba et al., 2014) and sample storage (Witz et al., 1990). Regardless, the high blank subtraction
98 may have obscured the differences between the two samples.

99 *RI.3) Data processing section is very wordy. Most of this information has been published already.
100 I would suggest substantial shortening of text. Most of section 2.3.3 could reside in the
101 supplemental information.*

102 We agree that most of the information contained in section “2.3.3. Data processing and assignment
103 of molecular formulas” (as well as in the entire section “2.3 Ultrahigh-resolution ESI FT-ICR MS
104 analysis of WSOC”) has been previously described. We moved most of this section to the
105 Supplement. Section 2.3 of the ACPD manuscript starting on page 24762 in line 8 and ending on
106 page 24766 in line 21 has been revised to new Section 2.2.2, which now reads:

107 **“We selected two samples named 9/24 and 9/25 (filter-collection periods were
108 September 24 at 15:00 to September 25 at 15:00 and September 25 at 15:00 to September 26
109 at 15:00) for detailed chemical characterization by ultrahigh resolution mass spectrometry
110 (Table 2). In this paper, unless noted otherwise, “9/24” and “9/25” always refer to the filter
111 samples collected during these time periods.**

112 **A detailed description of the sample preparation, ESI FT-ICR MS measurements and
113 data processing is given in the Supplement. Briefly, WSOM samples for FT-ICR MS analysis
114 were prepared using reversed-phase solid-phase extraction (Mazzoleni et al., 2010, 2012;
115 Zhao et al., 2013). The analysis was performed at the Woods Hole Oceanographic Institution
116 (Woods Hole, MA) Fourier Transform Mass Spectrometry facility with the ultrahigh-
117 resolution hybrid linear ion trap and FT-ICR (7 tesla) mass spectrometer (LTQ FT Ultra,
118 Thermo Scientific, San Jose, CA) with an ESI source. Three replicate measurements were
119 done for each sample in the negative ion mode. The mass resolving power was set at 400,000
120 and the mass accuracy was < 2 ppm. Transient co-addition and molecular formula
121 assignment were performed with Composer software (Sierra Analytics, Modesto, CA version
122 1.0.5) (Mazzoleni et al., 2012). The molecular formula calculator, which uses a Kendrick
123 mass defect (KMD) analysis (Hughey et al., 2001) to sort ions into user-defined homologous
124 series, was set to allow up to 100 carbon, 400 hydrogen, 100 oxygen, 3 nitrogen and 1 sulfur
125 atom per molecular formula. All molecular formula assignments presented in this paper
126 were assigned using CH₂ homologous series consistent with the PREDATOR algorithm
127 (Blakney et al., 2011). The final data set for all samples is composed of the results of two
128 methods for formula assignments: Method A, with a *de novo* cutoff of *m/z* 500 and C, H, N,**

129 **O, S elemental composition; and Method B, with a *de novo* cutoff of m/z 1000 and C, H, O**
130 **elemental composition (details are given in the Supplement).”**

131 *RI.4) The average amounts listed in the text should also be listed in Table 1. Perhaps the last row*
132 *could contain information of the averaged ambient mass concentrations.*

133 We added an extra column at the end of Table 1, which provides the measured average total mass
134 concentrations and their standard deviation.

135 *RI.5) Page 24768 line 1-11: This is a long winded way of saying this. It would be easier to just*
136 *state that you measure 1.7 for the OM/OC ratio. The authors already state they are using the*
137 *suggested literature value of 1.8 from Pitchford et al. (2007). Include a similar statement: the*
138 *measured value (1.7) is the lower limit of OM/OC due to low retention of highly oxygenated low*
139 *molecular weight species (Hallar et al. 2013).*

140 We shortened the text on page 24768 in lines 2-11 to the following:

141 **“The OM/OC ratio of 1.8 adopted in our analysis is slightly higher than the OM/OC ratio of**
142 **~1.7 (Table 2) calculated from FT-ICR MS analysis of WSOM elemental compositions**
143 **(Mazzoleni et al., 2010). The measured value of 1.7 is expected to be lower than the total,**
144 **because of the low sample recovery of highly oxygenated, low molecular weight species**
145 **(Hallar et al. 2013).”**

146 *RI.6a) Through-out the results section, small sentences of discussion are inserted into the text and*
147 *feel out of place. The flow of the paper would be better, if these comments were deleted or moved*
148 *to one section. The authors’ conclusions would be stronger if these comments were grouped*
149 *together.*

150 *I believe the authors prove the source of the air masses from sections 3.1-3.2. I would say you*
151 *should rephrase the discussion to state that your data is representative of these air masses and*
152 *therefore the chemical composition is obtained. I do not believe you have enough evidence to say*
153 *that any one feature from the mass spectra proves the aerosol source. Rather, the authors should*
154 *say because they know the source of the aerosol, the obtained mass spectra represent the chemical*
155 *composition of these aerosols.*

156 *I will list the sentences I think should either be removed or moved to a consolidated section.*

157 In this paper, we decided to combine results and discussion in a single section “3. Results and
158 discussion” (page 24767 in line 15). We believe this is the best way to present our findings, as the
159 results are immediately compared to previously published work whenever possible. Therefore, we
160 prefer to keep the format of this section as in the submitted ACPD manuscript. However we agree
161 that: i) highlighting the specific sentences pointed out in this comment by the reviewer would very
162 much strengthen the unique observations of these highly aged aerosol; and ii) this would greatly
163 help the flow of the paper. We thank the reviewer for this comment. In response, we either deleted
164 mentioned text or moved it to section “4. Conclusions” in an effort to concentrate the “Big Picture”
165 discussion on the importance and implications of this study.

166 We agree with the reviewer that after first establishing the emission sources of aerosol, we can
167 then infer that the results of aerosol measurements are representative for those sources. To stress
168 it early on in section “3.2 Characterization of the air masses during 24–26 September 2012”, we
169 changed the sentence in the opening of section on page 24768 in lines 25-26 to:

170 **“This section describes the two sampling periods selected for this case study and provides**
171 **evidences that the aerosol is representative of the described sources.”**

172 *RI.6b) Page 24768 line 21-23: I would adjust this statement to: This indicates your 24 hr filter*
173 *samples capture the major trends observed by the continuous measurements.*

174 We changed the sentence on page 24768 in lines 21-23 to:

175 **“This indicates that the measurements of filter-collected aerosol captured the major trends**
176 **observed by the continuous aerosol measurements (Fig. 1).”**

177 *RI.6c) Page 24774 line 4-5: How is this statement supported? It would be better to say that the*
178 *higher molecular weight ranges could be an indicator of aging processes associated in long range*
179 *transport? However, as mentioned in #11 it is a long stretch to compare ESI-MS spectra and make*
180 *conclusions based on intensity.*

181 We re-worded the statement on page 24774 in lines 3-5 to:

182 **“The higher molecular weight ranges observed in the PMO WSOM are likely a consequence**
183 **of the combined oxidative aging and aqueous-phase oligomers formation during the long**
184 **range transport.”**

185 *RI.6d) Page 24774 line 26 – Page 24775 line 1: Why is this an indication of highly processed*
186 *aerosol? Other than Suwannee fulvic acid, because although it has similar optical properties to*
187 *HULIS (definition of HULIS), it does not mean it has similar molecular composition. It also does*
188 *not confirm the aged nature of the aerosol (Page 24775 line 3-4). Please include references to the*
189 *use of suwanne river fulvic acid as a marker of the age of an aerosol if the authors wish to use this*
190 *as an indicator.*

191 The ESI FT-ICR MS analysis of molecular composition of Suwannee River Fulvic Acid has been
192 reported by Stenson et al., 2003. The similar Kendrick distribution may be a result of similar
193 structures from the lignin. It is established that chemical properties of processed ambient organic
194 aerosol resemble those of terrestrial fulvic acid such as its standard Suwannee River Fulvic Acid
195 (Cappiello et al., 2003; Dinar et al., 2006). Regardless, we decided to remove the comment
196 regarding aerosol processing by deleting (~~bolded and strikethrough~~) the following words from
197 the sentence on page 24775 in lines 1-4:

198 “Ultrahigh-resolution FT-ICR MS measurements of a Suwannee River Fulvic Acid standard, a
199 model for HULIS, yield very similar distribution in the Kendrick plot (Stenson et al., 2003);
200 ~~confirming the very aged and processed nature of PMO aerosol WSOC.”~~ :

201 *RI.6e) Page 24775 line 19-21: Please move this discussion to the end of all the results and discuss*
202 *with all the results, rather than one at a time.*

203 We deleted the following sentence mentioned by the reviewer on page 24775 in lines 19-21:

204 ~~“As discussed in the following sections, this tight distribution might be characteristic of very~~
205 ~~processed aerosol.”~~

206 *RI.6f) Page 24776 Line 3-5: Include in discussion section.*

207 We deleted the following sentence mentioned by the reviewer on page 24776 in lines 3-5:

208 ~~“The distribution of molecular assignments in DBE vs. number of carbon atoms is both wide~~
209 ~~and uniform, which might be characteristic for highly aged and processed aerosol.”~~

210 ***R1.6g)** Page 24777 Line 26-29: Include in discussion section. Also explain how a high DBE value*
211 *suggests more SOA formation?*

212 We incorporated the text on page 24777 in lines 26-29 in section “4. Conclusions”.

213 The idea of a decrease in H/C and increase in DBE value with increased aging was shown to be a
214 consequence of chemical processing of organic aerosol as they age for a large number of Aerodyne
215 Aerosol Mass Spectrometer (AMS) data sets as presented in Heald et al., 2010 (please see van
216 Krevelen diagram in Fig. 2 of Heald et al. (2010) for an overview) and further corroborated in Ng
217 et al., 2011 (please see parameterization in Fig. 2 as well as van Krevelen diagram in Fig. 4 of Ng
218 et al. (2011) for an overview). For species consisting only of C, H and O atoms, the work of Heald
219 et al. (2010) has shown that addition of oxygen to a molecule during chemical processing (a.k.a.
220 aging) on average increases an O/C ratio and decreases H/C one. E.g., the OH radical oxidation of
221 an organic molecule R-CH₂-R' could produce R-(C=O)-R' species and thus increase DBE,
222 consistent with an increase of DBE values on a molecular level. Note that no molecular level
223 information is available from AMS data as presented in the above mentioned studies.

224 ***R1.6h)** Page 24779 Lines 1-6: Include in discussion section. I think it would be better worded as;*
225 *biomass burning aerosol processed by clouds have the characteristics (...) seen in the mass spec.*
226 *Your observations are not confirming the source, but rather informing the community what the*
227 *chemical composition of these aerosol types are.*

228 We incorporated the text on page 24779 in lines 1-6 to section “4. Conclusions”. We also changed
229 the first sentence mentioned in this comment on page 24779 in lines 1-3 to clearly reflect that our
230 observations are not confirming the source. The new sentence now reads:

231 **“The presence of markers characteristic for aqueous-phase processing of biomass burning**
232 **aerosol suggests the biomass burning aerosol was processed by clouds and remained in the**
233 **particle-phase after the evaporation of water.”**

234 ***R1.6i)** Page 24779 line 16-18: Why would similar average values indicate the same emission*
235 *source? Should not the greater O/C value go to the more aged sample 09/25?*

236 O/C ratio is an intensive property and one of the key constrains for understanding sources and
237 transformations of aerosol on local, regional and global scale (e.g. Canaragatna et al., 2015 and
238 references therein). For example, the work of the AMS community has shown that different
239 emission sources and processing mechanisms produce aerosol with distinctly different O/C ratios.
240 We do not claim similar O/C ratios of 9/24 and 9/25 samples are a definite proof of identical
241 aerosol sources. Rather, we use it as an indicator of very similar sources and transformations of
242 aerosol sampled at the PMO.

243 Note that somewhat longer transportation path of aerosol collected in 9/25 sample is consistent
244 with the observed lower O/C ratio. Air masses that brought 9/25 aerosol went low in the marine
245 boundary layer, where higher humidity and sea spray would allow more aqueous-phase processing
246 and therefore increased removal of highly polar compounds. Please see also answer **R1.1** for more
247 details.

248 ***R1.6j)** Page 24779 line 23-25: Include in discussion.*

249 We incorporated the text on page 24779 in lines 23-25 to section “4. Conclusions”.

250 **R1.6k)** *Page 24780 line 24-29: Include in discussion, How would molecular fragmentation,*
251 *mentioned in the other sections as a sign of aging, fit in with high DBE values?*

252 We deleted the second part of sentence mentioned by the reviewer on page 24780 in lines 24-29,
253 in an effort to concentrate the “Big Picture” discussion on chemical composition of Pico samples
254 to section “4. Conclusions”. Please also see answers **R1.1** and **R1.6g**.

255 ~~“... studies, confirming the unsaturation feature of the aerosol after long range transport and~~
256 ~~the same emission source regions and transformational processes of CHO and CHNO group~~
257 ~~species.”~~

258 **R1.6l)** *Page 24784 line 20-21: Please include in the discussion section why increased*
259 *fragmentation of molecular species would produce an aerosol with a lower O/C ratio and a*
260 *reference to the literature articles supporting this?*

261 Please see our answer **R1.1**. To address this comment from the reviewer, we deleted the following
262 mention of low O/C ratio due to fragmentation on page 24784 in lines 20-21:

263 ~~“... which might have resulted in increased fragmentation of molecular species and a lower~~
264 ~~O/C ratio.”~~

265 **R1.7)** *There is no description of the gas phase measurements mentioned in the abstract in the*
266 *experimental section. Page 24770 page 25-27: At least list the name of the methods and a small*
267 *description of the measurements methods. This should be included in the experimental.*

268 As suggested, we added the description of all gas-phase measurements to the methods section by
269 inserting a new section “2.3 Gas-phase measurements at the Pico Mountain Observatory” to page
270 24767 in line 1:

271 **“Nonmethane hydrocarbons were measured at PMO with a cryogen-free, custom-**
272 **built inlet system interfaced to a gas chromatography with flame ionization detection**
273 **(Tanner et al., 2006; Helmig et al., 2008, 2015).**

274 **Continuous surface ozone measurements were made by a Thermo-Scientific 49I UV**
275 **absorption ozone analyzer using ultraviolet absorption of ozone at 254 nm and the Beer-**
276 **Lambert Law to relate the attenuation of light in sample cells to ozone concentration; an**
277 **inlet was located 10 meters above the ground level. This instrument has been calibrated to a**
278 **U.S. National Institute of Standards and Technology (NIST) traceable standard, maintained**
279 **at NOAA Global Monitoring Division in Boulder, Colorado (McClure-Begley et al., 2014).”**

280 **R1.8a)** *Page 24771 lines 4-18: This is a confusing paragraph with no explanation of why this is*
281 *important. Are the authors suggesting ethane and propane are gas-phase indicators of aged*
282 *biomass burning plumes? Or is this already established in the literature? The authors need to*
283 *explain why ethane and propane matter and what they suggest about the age of aerosol in an air*
284 *parcel, including references.*

285 We added the explanation about why ethane and propane, as well as their ratio, matter. The
286 revisions to the ACPD manuscript are described below.

287 -We added the description (**bolded**) of the importance of ethane and propane as pollution tracers
288 to section “1. Introduction” on page 24759 in line 5:

289 “... (Honrath et al., 2008). **Previous research at PMO has shown several-fold increases of**
290 **NMHC in anthropogenic and biomass burning plumes. Furthermore, it has been**
291 **demonstrated that isoprene and ratios of selected NMHC pairs have characteristic**
292 **signatures that were used for identification of upslope flow conditions (Kleissl et al., 2006)**
293 **and pollution plume characterization (Helmig et al., 2008).”**

294 -We added the description further elaborating the importance of NMHC measurements and
295 $\ln([\text{propane}]/[\text{ethane}])$ ratio at the opening of section “3.2.1 Non-methane hydrocarbon
296 measurements” on page 24770 in lines 25-28:

297 “**NMHC have been widely used as tracers for anthropogenic and biomass burning**
298 **emissions (Helmig et al., 2008). Due to their different oxidation rates, mole fractions of**
299 **different NMHC exponentially decline at different rates during atmospheric transport**
300 **allowing the natural log of $\text{NMHC}_1/\text{NMHC}_2$ (e.g., $\ln([\text{propane}]/[\text{ethane}])$) to be used as a**
301 **linear measure of photooxidation and transport time. $\ln([\text{propane}]/[\text{ethane}])$ has been**
302 **demonstrated to be a sensitive indicator for identifying pollution signatures and transport**
303 **time to PMO (Helmig et al., 2008, 2015).”**

304 *R1.8b) Page 24771 lines 6-8: I do not understand the notation in this sentence. What does “ethane*
305 *(propane) increased from 0.78 (0.09)” mean? Do you mean “ethane and propane” increased?*

306 We agree with a reviewer that this abbreviated notion might not have been sufficiently clear. Thus,
307 we changed the mentioned sentence to:

308 “**The mixing ratios of ethane and propane increased from 0.78 and 0.09 ppbv at 19:20 in the**
309 **evening of September 24 to a maximum of 1.25 and 0.22 ppbv at 9:30 in the morning of**
310 **September 25.”**

311 *R1.8c) Page 24771 line 13: What is the significance of “ $\ln(\text{propane}/\text{ethane})$ ” ? Is this a quantity*
312 *often reported in the literature?*

313 Please see the answer to the comment **R1.8a**.

314 *R1.9) Page 24772 lines 4-22: I am also confused by this section. What is the purpose of mentioning*
315 *the other studies in the results sections? Are you confirming your results with those from other*
316 *literature? That does not make sense because you are studying aerosol aged for 12 days and*
317 *comparing with fresh and very near fresh (1-2h) aerosols in the literature. Please revise this*
318 *section for clarity.*

319 The main reason for investigating the fraction of tar balls (TBs) was to provide additional evidence
320 that the plume was influenced by biomass burning emissions. Per the reviewer’s suggestion and
321 for improved clarity, we removed the discussion on the TBs fraction and size from other studies.
322 We replaced section “3.2.2 Scanning electron microscopy (SEM) analysis” of the ACPD
323 manuscript with the following text:

324 “**Representative SEM images for 9/24 and 9/25 are shown in Figs. 4a and b,**
325 **respectively. A higher fraction of spherical particles was observed on 9/24 (43%) compared**

326 to 9/25 (18%). However, the fraction of near spherical particles was lower on 9/24 (23%)
327 compared to 9/25 (29%). Spherical particles observed on 9/24 and 9/25 were likely tar balls
328 (TBs) with diameters in the range of 70–1800 nm (Fig. 4c-d). TBs are spherical, organic
329 amorphous particles composed of carbon and oxygen abundant in biomass burning aerosol
330 (Adachi and Buseck, 2011; China et al., 2013; Pósfai et al., 2003, 2004; Tivanski et al., 2007).
331 The EDS analysis of spherical and near spherical particles shows that they were mostly
332 composed of C and O, consistent with the hypothesized identification. As described by China
333 et al. (2013), soot particles emitted from biomass burning are often heavily coated
334 (embedded) with other material. Thus, we visually classified the soot particles and found that
335 for the 9/24 event, 46% of the soot particles (with respect to the total number of classified
336 soot particles) were heavily coated (Fig. 4e-h) compared to only 17% on 9/25. The higher
337 fraction of heavily coated soot particles observed for 9/24 is consistent with the air mass being
338 most likely influenced by biomass burning. Finally, 34% and 58% of soot was partly coated,
339 11% and 17% thinly coated and 7% and 8% partially encapsulated, for 9/24 and 9/25
340 respectively. Note that tar balls are likely not water-soluble and therefore, the ultrahigh
341 resolution mass spectrometry analysis of WSOM presented below probably does not probe
342 them.”

343 *RI.10) Page 24772 lines 25-27: The authors mention the low O/C measured in this study and here*
344 *mention that there is likely a large portion of material that is not included. This portion of material*
345 *not extracted would likely have a very low O/C and would reduce the measured O/C even further.*
346 *This caveat should be mentioned again in a discussion section.*

347 The discussion of the observed low O/C was based on ultrahigh resolution mass spectrometry
348 analysis of WSOM. However, we agree with the reviewer that tar balls are perhaps not water
349 soluble and therefore are not included in the WSOM analysis. The text on page 24772 in lines 25-
350 28 the reviewer is mentioning in this comment was included in the discussion section noting that
351 in our samples there is a significant portion of material that is not water soluble and overall the
352 O/C can be even lower than that observed for WSOM.

353 *RI.11) Page 24773 Lines 23 – 24774 line 3: Can this be attributed to tuning of the MS electronics?*
354 *Can one compare the ESI intensity between different instruments and compare the concentrations*
355 *in each sample? ESI intensity is not necessarily correlated to solution concentration, due to*
356 *charging and matrix effects among others factors.*

357 All of the instrument parameters used here are exactly the same as in our previous work. The
358 instrument is tuned using Suwannee River Fulvic Acid as described by Soule et al., 2010. The ion
359 optics do indeed affect the proportion of ions, thus we purposely do not adjust them. The
360 observations described here are qualitative descriptions of the mass spectra differences we have
361 observed. The high abundance of lower molecular weight ions as reported in Mazzoleni et al.,
362 2010, 2012 and Zhao et al., 2013 are consistent with those reported in Wozniak et al., 2008 and
363 Schmitt-Kopplin et al., 2010. In each of those cases, the studied samples of aerosol or cloud water
364 were collected at continental sites, whereas the samples reported in this study were collected at a
365 remote free tropospheric site in the North Atlantic.

366 *RI.12) Page 24781 line 1-13: This paragraph can be deleted the topic was already discussed on*
367 *page 24780 lines 10-15.*

368 The paragraph on page 24781 in lines 1-13 reports our observation of a very uniform distribution
369 of the number of oxygen atoms in the assigned molecular formulas of two different CHNO classes
370 (N_1 and N_2). This trend has not been observed previously. For example, Zhao et al. (2013) show
371 the same representation for cloud water samples collected at the Storm Peak Laboratory in
372 Steamboat springs, CO (Fig. S5 in the Supplement). In comparison, the distribution of the CHNO
373 classes of Pico aerosol WSOM is more evenly distributed. We hypothesize this is the result of
374 aging processes during long range transport of atmospheric aerosols, including aqueous-phase
375 processing. We are not sure how to explain it at this point as there is no comparable data available
376 yet and have therefore decided to show it in Fig. S10 of the Supplement. (Note, similar reasoning
377 can be applied to CHOS classes shown in Fig. S11, and compared to Fig. S6 of Zhao et al., 2013).

378 ***RI.13a)** Section on CHOS group. This seems a lot of text for such a small subset of compounds. I
379 think the authors should stress in the beginning that the statistics are not great. The authors should
380 not bother trying to report in the text all the subtleties of the dataset. Table 2 and Figure 8 are
381 enough.*

382 We are intrigued by the lack of sulfur-containing compounds in Pico WSOM and have therefore
383 dedicated sufficient space in this publication in an attempt to understand it. This is reflected in the
384 length of section “3.3.4 Molecular formula assignments of the CHOS group”. We believe that the
385 lack of sulfur-containing compounds that have otherwise been regularly observed in ultrahigh
386 resolution MS studies is worth reporting. For example, nearly complete lack of compounds
387 corresponding to molecular assignments of CHNOS group might indicate the removal of these
388 highly oxygenated species by aqueous-phase processing. We noted this observation on page 24774
389 in lines 20-25 of the ACPD manuscript and in answer **R2.15** to Reviewer 2. Therefore, we prefer
390 to keep here mentioned section 3.3.4 in the current format.

391 ***RI.13b)** In addition, there was recent study of organosulfates in the atmosphere from CalNex and
392 China.¹ It could be interesting to note the absence of organosulfates in the Pico Mountain
393 Observatory compared with urban aerosols.*

394 We thank the reviewer for bringing to our attention an important study of urban organosulfates by
395 Tao et al. (2014). We referenced this work in our manuscript and added the following text to
396 section 3.3.4 on page 24783 in line 9:

397 **“Conversely, our finding of a low number of sulfur-containing species in long range
398 transported aerosol is in contrast to a recent study of urban aerosol in Los Angeles and
399 Shanghai, which was dominated by organosulfates (Tao et al., 2014).”**

400 ***RI.14)** Page 24784 line 19-20: I thought the air masses were aged 12 and 15 days? I am confused
401 by the 9.5 and 7 days statement.*

402 We apologize for the confusion. We refer here only to the time period air masses spent above the
403 ocean. To avoid ambiguity, we clarified the sentence on page 24784 in lines 17-21 to:

404 **“In addition, air masses that transported the aerosol collected in 9/25 underwent longer
405 transport times at substantially lower altitudes in cleaner marine atmosphere (the averaged
406 residence time spent over the North Atlantic Ocean for the retroplumes of 9/25 was 9.5 days
407 vs. 7 days for 9/24).”**

408 **RI.15)** Page 24785 line 22-23: *It would be nice to explicitly mention what the critical insights this*
409 *work provided.*

410 We agree with the reviewer that the ACPD manuscript did not address well the critical insights
411 and implications of this study. To improve this, we rewrote section “4. Conclusions” to clearly
412 review the importance and implications of the presented work.

413 **RI.16)** Page 24786 lines 9-10: *I am not sure of the authors conclusions that aged SOA have low*
414 *O/C and that the low O/C can be explained by fragmentation. The authors have certainly not*
415 *proven this in this manuscript. In fact papers have found an increase in O/C from again*
416 *processes.²⁻⁵ The authors need to discuss these and/or similar papers and support their conclusion*
417 *that low O/C SOA can be an indicator of aging through a fragmentation pathway.*

418 Please see our answer **RI.1**. To address this comment from the reviewer, we deleted the following
419 mention of low O/C ratio due to fragmentation on page 24784 in lines 20-21:

420 “... , ~~suggesting transformation processes leading to the fragmentation of aged SOA.~~”

421 **Minor Comments:**

422 **RI.17)** Figure 1: *The caption of Figure 1 mentions that the filter samples in (a) do not align with*
423 *the continuous measurements in (b) (c) and (d) because of being shown for the entire overlapping*
424 *period. Why not line them up? There are already breaks in the axis of (b) (c) and (d). A small*
425 *break in (a) around 09/24 would seem like it would line them up.*

426 Per reviewers’ suggestion, we changed the x-axis of panels (b)-(d) in Fig. 1 to exactly match the
427 time periods of the filter-based aerosol measurements with the on-line ones. The slight mismatch
428 in Figure 1 of the ACPD manuscript was the result of small spaces between bars representation of
429 filter samples (Fig. 1a) that are not present in the time series of continuous measurements (Figs.
430 1b-d). For the first two filter samples (6/29 and 7/26), their data is already matching the time series
431 of continuous measurements as those filter samples were: i) separated in time from other filter
432 measurements; and ii) measured for periods longer than 24 hours (142 and 52 hours, resp., as
433 shown in Table 1). To make the match in x-axis of different aerosol measurements more clear, we
434 also inserted the black horizontal dashed lines and visually separated each filter-sampling period;
435 the lines represent the exact start and end times of filter sampling. Note that for the 9/24 and 9/25
436 samples presented in the manuscript, this was already done in Fig. 3.

437 The text of Fig.1 caption was changed accordingly by modifying the sentence on page 24801 in
438 line 5 to:

439 **“On-line measurements are shown for all overlapping periods and each filter-collection**
440 **period in (a) matches the continuous measurements in (b-d). Black dashed lines denote the**
441 **start and end times of filter sampling.”**

442 **RI.18)** Figure 2: *It is difficult to read the white numbers. Perhaps they can be outlined?*

443 We highlighted the label of upwind time in days at each locations of the plume that was previously
444 indicated by white numbers in Fig. 2. In the new Fig. 2 version, the days are shown with white
445 font on a black background, which was the best representation of many tested options.

446 **RI.19)** Page 24755 line 2: *spell out acronym, m.a.s.l.*

447 The acronym “a.m.s.l” was removed from the Abstract (page 24755, line 2). It was defined at its
448 first mention in the main text of the ACPD manuscript on page 24758 in line 18.

449 *RI.20) Page 24755 line 8-10: What about the other 5%?*

450 The 5% remainder of total filter-collected aerosol mass is divided between elemental carbon (2%)
451 and particulate chloride (2%). We added this information to the abstract and now the sentence on
452 page 24755 in lines 8-10 reads:

453 **“The average ambient concentration of aerosol was $0.9 \pm 0.7 \mu\text{g m}^{-3}$. On average, organic**
454 **aerosol components represent the largest mass fraction of the total measured aerosol ($60 \pm$**
455 **51%), followed by sulfate ($23 \pm 28\%$), nitrate ($13 \pm 10\%$), chloride ($2 \pm 3\%$), and elemental**
456 **carbon ($2 \pm 2\%$).”**

457 *RI.21) Page 24755 line 11: delete “with an”*

458 Done.

459 *RI.22) Page 24758 line 27-29: Insert reference for the article described*

460 We changed the text mentioned by the reviewer so that new sentence now reads:

461 **“Previous measurements at PMO (e.g., Val Martin et al., 2008a; 2008b) and dispersion model**
462 **simulations (e.g. Owen et al., 2006) indicated that North American outflow of tropospheric**
463 **ozone and its precursors are frequently encountered at the site.”**

464 *RI.23) Page 24762 line 24: Include location of woods hole oceanographic institute.*

465 Done. We added the location of the institution so that now this sentence reads:

466 **“Prepared extracts were stored in a freezer until cold overnight shipment on freezer packs**
467 **to the Woods Hole Oceanographic Institution (Woods Hole, MA) Fourier Transform Mass**
468 **Spectrometry facility for analysis.”**

469 Note that this sentence has been moved to the Supplement. Therefore, the location of the Woods
470 Hole Oceanographic Institution was added to its mention in the newly revised section “2.2.2
471 Ultrahigh-resolution ESI FT-ICR MS analysis of WSOM”. Please refer to answer to comment
472 **R1.3** above.

473 *RI.24) Page 24767 line 17: delete “during 2012”*

474 Done.

475 *RI.25) Page 24769 line 11-17: This seems rather long winded.*

476 We thank the reviewer for this comment, this text was indeed too long. Due to the long range
477 transport, we examined many possibilities for the observed trends. With this particular text, we
478 wanted to give clear evidence that the event observed for 9/24 sample was indeed due to the
479 biomass burning plume. The text has been revised so that interested readers can find the additional
480 information on the NOAA website by following the reference given in the text. We significantly
481 shortened the text the reviewer is commenting on here. The new text now reads:

482 **“September was a dry month and several US states were experiencing an intense drought**
483 **(NOAA National Climatic Data Center, 2012). Consequently, widespread wildfires were**
484 **observed in the US northwest and northern Rockies.”**

485 *RI.26) Page 24772 line 6-7: Include a brief description of where 12 days comes from, i.e.*
486 *FLEXPART analysis.*

487 We changed the sentence on page 24772 in lines 6-7 and removed the mention of the plume age.
488 Note that the entire opening paragraph of section “3.2.2 Scanning electron microscopy (SEM)
489 analysis” with the sentence mentioned here was rewritten in a reply to the comment **R1.9**. The
490 particular sentence mentioned by the reviewer here now reads:

491 **“Spherical particles observed on 9/24 and 9/25 were likely tar balls (TBs) with diameters in**
492 **the range of 70–1800 nm (Fig. 4c-d).”**

493 *RI.27) Page 24774 line 11- 12: The statement about CHO has already been made in this*
494 *manuscript.*

495 We deleted this sentence from the manuscript.

496 *RI.28) Page 24775 line 11-13: Delete sentence: This statement is unnecessary at this point in the*
497 *manuscript.*

498 We deleted the sentence on page 24775 in lines 12-14 from the manuscript. The following sentence
499 on page 24775 in lines 14-15 of the original ACPD manuscript was slightly changed to reflect this
500 and moved to the Supplement:

501 **“Elemental ratios determined from the assigned molecular formulas of the ESI FT-ICR mass**
502 **spectrum are visualized using van Krevelen diagrams (Kim et al., 2003) with the H/C ratio**
503 **plotted against the O/C, or N/H or S/H ratio (Wu et al., 2004).”**

504 *RI.29) Page 24776 line 17: Define isoabundance. What is the difference from abundance?*

505 Isoabundance is the total relative abundance of the overlaid species shown with a color scale. The
506 plot type is a contour plot. To clarify this, we added this definition after the opening sentence of
507 Section 3.3.2 on page 24776 in line 19:

508 **“ ... (Table 2). Isoabundance is defined as the total relative abundance of the overlapped**
509 **species in the van Krevelen diagram depicted with a color scale.”**

510 *RI.30) Page 24784 line 29: This is a confusing sentence. The unique formulas are fewer than*
511 *what?*

512 We believe this comment refers to the sentence in the ACPD manuscript that starts on page 24783
513 in line 28 and ends on page 24784 in line 2. Here, we explain that the molecular formulas assigned
514 to ions observed in the FT-ICR mass spectra of both 9/24 and 9/25 samples (aka “common”
515 molecular formulas) are far more abundant in each spectra than those detected in only one sample
516 (aka “unique” molecular formulas). To improve this, we changed the text that starts on page 24783
517 in line 26 and ends on page 24784 in line 2 to:

518 **“A total of 3426 molecular formulas were common to both of the samples (“common”**
519 **molecular formulas) and they spanned the entire m/z range (Figs. 10a-d). Molecular formulas**

520 **detected in only one sample (“unique” molecular formulas) were fewer in number (N = 541**
521 **and 1372 for 9/24 and 9/25). Most of the unique molecular formulas had low relative**
522 **abundances.”**

523 *RI.31) Page 24785 line 19: Include the uncertainty of the average mass concentration.*

524 We included the uncertainty of the average mass concentration here.

525 *RI.32) Page 24786 line 3-5: Was the pollution events both days? I thought one day was clean and*
526 *one day was polluted.*

527 Yes, the biomass burning plume was observed on both days, but it was much stronger on 9/24.
528 There seems to be a lingering of the biomass burning pollution through the period starting Sep 24,
529 2012 to at least Sep 27, 2012 (Fig. 1). However, the observed event with strong pollution plume
530 started on Sep 25, 2012 ~ 4:00 and lasted until Sep 26, 2012 ~2:00 (on-line measurements in Fig.
531 1b-d and Fig. 3b-f). Note that another strong pollution event was recorded by all measurements in
532 June 2012 and corresponding to 6/29 filter sample. However, 6/29 filter sample was collected for
533 a period much longer (142 hours) than other filter samples, which makes the separation of different
534 aerosol contributions difficult. Thus, we never analyzed it in details.

535 We now see this observation may not have been clearly described. Therefore, we added the
536 following clarification early in the paper, in section “3.2 Characterization of the air masses during
537 24–26 September 2012” on page 24769 starting in line 10:

538 **“The event of interest started on September 25 at approximately 4:00 and lasted until the 26**
539 **at approximately 2:00 (Fig. 1b-d). The observed elevated ...”**

540 We also rewrote the sentence on page 24770 in lines 14-17 that now reads:

541 **“Therefore, the air masses arriving at PMO during September 24-26 were influenced by the**
542 **US biomass burning, while those that arrived during 9/25 were also influenced by the marine**
543 **boundary layer.”**

544 In this work, we do not report that the observed aerosol likely has a small contribution of aged
545 urban anthropogenic emissions. During both days, the FLEXPART analysis shows that the air
546 masses arriving to the Observatory went over continental US (Figs. S4 and S5 of the Supplement).
547 Thus, the filter-collected aerosol samples might have a contribution from the regional and/or global
548 background pollution. This contribution might be more significant during days in which no
549 pollution event was observed. From chemical composition data during days that were not
550 influenced by the pollution plume, regional/global background contribution to organic aerosol is
551 indeed small and amounts to maybe ~15% of total mass measured during strong biomass burning
552 event (Fig. 1 and Table 1). However, it is not clear how to divide urban anthropogenic vs.
553 regional/global background vs. biomass burning aerosol contributions of it. This type of analysis
554 is beyond the scope of this publication.

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593 ***Response to Comments from Anonymous Reviewer #2***

594

595 *Anonymous Review: This manuscript describes the characterization of free tropospheric aerosol*
596 *particles collected at the Pico Mountain Observatory. It describes data obtained using a suite of*
597 *instruments (OC/EC analyzer, ion chromatograph, aethalometer, particle counter, FLEXPART*
598 *retroplume analysis, etc.) to identify two samples collected on subsequent days with very different*
599 *air mass histories and chemical characteristics. One sample was influenced by biomass burning*
600 *from the northwestern United States, and the other showed a primarily marine influence. These*
601 *two samples were studied in extensive detail using Fourier transform ion cyclotron resonance*
602 *mass spectrometry (FTICR MS) and compared to each other and data from the literature. The*
603 *dataset from these unique and difficult to obtain samples represent valuable information that can*
604 *be a great asset to the community. The manuscript is, for the most part, clearly written, but it is*
605 *unnecessarily long and at times unfocused - reading more as a cataloguing of FTICR MS data*
606 *from two samples rather than concentrating on a discussion of the implications of these data on*
607 *processes in the atmosphere. The manuscript will be suitable for publication in ACP if the*
608 *following comments are addressed.*

609 *Detailed Comments:*

610 **R2.I) Title:** *the title gives the impression that it will study multiple biomass burning plumes, but*
611 *only one of the samples contains a biomass burning plume. The title should be changed to reflect*
612 *this.*

613 We agree with the reviewer that only one strong biomass burning plume was observed on these
614 two days. Thus, we modified the title to reflect this:

615 **“Molecular characterization of free tropospheric aerosol collected at the Pico Mountain**
616 **Observatory: A case study with a long range transported biomass burning plume”.**

617 **R2.II) Methods:**

618 **R2.1) There is no need to discuss methods for analyses and activities that are not presented in the**
619 **results. Details about the 18 samples collected but not used (lines 23-24, page 24760), analysis of**
620 **organic and inorganic (F-, Br-, NO₂-, PO₄³⁻) anions (page 24761), that the field site is difficult**
621 **to get to (line 20, page 24760), that positive ion mass spectra were analyzed but not discussed,**
622 **and anything else that isn't germane to the presented results are not needed.**

623 We addressed the reviewer's comments (labeled below as **R2.1a – R2.1d**) as described below.

624 **R2.1a)** Details about the 18 filter samples collected but not used were removed. The mentioned
625 sentence on page 24760 in lines 23-25 was changed to:

626 **“Eighteen filters collected during the 2012 field campaign were selected for further**
627 **laboratory analysis (Table 1).”**

628 **R2.1b)** Details about the organic and inorganic ions that were below the detection limit were
629 removed. The mentioned sentence on page 24761 in lines 24-27 was changed to:

630 “Samples were analyzed for NO₃⁻, SO₄²⁻ and Cl⁻ with ion chromatography (ICS–2000 ion
631 chromatograph with an IonPac AS11 separator column (Dionex Corporation, Bannockburn,
632 IL, USA)).”

633 To accompany this change, we also deleted the following sentence on page 24762 in lines 3-4:
634 “NO₃⁻, SO₄²⁻ and Cl⁻ only were present at concentrations above the detection limit.”

635 **R2.1c)** We did not remove the mention that the Pico Mountain Observatory is difficult to reach on
636 page 24760 in lines 20-21. The site logistics are a limiting factor that is unique to this site. It is
637 hard to appreciate the efforts of the PMO team to transport the newly installed aerosol
638 instrumentation (e.g., four high volume samplers, nephelometer, gas bottles, power cable, etc.)
639 by foot to the site. More importantly, we operate the station to minimize the physical stress
640 imposed by the strenuous hike. We revised the mentioned sentence to read:

641 “This was done, because the site is reachable only via a strenuous hike on rugged terrain
642 (Honrath et al., 2004).”

643 **R2.1d)** We removed the mention of the positive mode data on page 24763 in line 11. We also
644 deleted the following sentence on page 24763 in lines 13-14: “~~In this paper, we report only the~~
645 ~~findings from the negative ion mode measurements.~~” Note that in revised paper this text has
646 been moved to the Supplement.

647 **R2.2)** *Along these same lines, the details for the measurements of ethane and propane, and the*
648 *SEM analyses (and any other measurements included in the results) should be added to the*
649 *methods.*

650 We addressed the reviewers’ comments (labeled below as **R2.2a** – **R2.2b**) as described below.

651 **R2.2a)** Measurements of the gas-phase species were added to the methods section. This comment
652 was addressed as a reply to Reviewer 1 in answer **R1.7**. For the ease of following our response to
653 Reviewer 2, we copied the same answer below.

654 As suggested, we added the description of all gas-phase measurements to the methods section by
655 inserting a new section “2.3 Gas-phase measurements at the Pico Mountain Observatory” to page
656 24767 in line 1:

657 “Nonmethane hydrocarbons were measured at PMO with a cryogen-free, custom-
658 built inlet system interfaced to a gas chromatography with flame ionization detection
659 (Tanner et al., 2006; Helmig et al., 2008, 2015).

660 Continuous surface ozone measurements were made by a Thermo-Scientific 49I UV
661 absorption ozone analyzer using ultraviolet absorption of ozone at 254 nm and the Beer-
662 Lambert Law to relate the attenuation of light in sample cells to ozone concentration; an
663 inlet was located 10 meters above the ground level. This instrument has been calibrated to a
664 U.S. National Institute of Standards and Technology (NIST) traceable standard, maintained
665 at NOAA Global Monitoring Division in Boulder, Colorado (McClure-Begley et al., 2014).”

666 **R2.2b)** The SEM analysis was already described in the ACPD manuscript on page 24761 in lines
667 8-14 as the last paragraph of the section “2.1 Aerosol measurements at the Pico Mountain
668 Observatory”. Nevertheless, to address the reviewers’ concerns and improve the description of the
669 SEM analysis, we did the following two modifications: i) we made a new section “2.2.3 Single

670 particle morphology using scanning electron microscopy” to which additional details of the SEM
671 analysis were added; and ii) we moved some of the text that was in the ACPD manuscript reported
672 with the results in section “3.2.2 Scanning electron microscopy (SEM) analysis” to aforementioned
673 new section 2.2.3, which describes the method. The new description of the SEM analysis methods
674 starting on page 24761 in line 8 now reads:

675 **“Quartz filter samples from 9/24 and 9/25 were further analyzed with scanning**
676 **electron microscopy (SEM) to investigate the morphology of particles and their possible**
677 **sources. Four portions (5 mm × 5 mm) were used from different areas of each quartz filter,**
678 **to obtain a representative sample statistics. The samples were coated with a 1.8 nm thick**
679 **platinum layer using a sputter coater (Hummer 6.2) and then imaged using a Hitachi S-4700**
680 **field emission SEM (FE-SEM). Over 2000 individual particles from each sample were**
681 **classified to investigate the relative abundance of spherical, near spherical, soot and other**
682 **irregularly shaped particles. Furthermore, we visually classified the soot particles (N = 433**
683 **and 550 for 9/24 and 9/25, respectively) into four classes: (1) heavily coated (embedded soot),**
684 **(2) partly coated, (3) bare or thinly coated, and (4) attached with other material (partially**
685 **encapsulated) to investigate the degree of internal mixing after long range transport (China**
686 **et al., 2013, 2015). Elemental compositions of individual particles were investigated using**
687 **Energy Dispersive X-Ray spectroscopy (EDS).**

688 *R2.3) Page 24762, line 10: What percentage of WSOM do Strata X SPE cartridges isolate? How*
689 *do Strata X SPE cartridges eluted with acetonitrile compare to other SPE cartridges (e.g., C-18,*
690 *PPL, etc.) and elution solvents in terms of the characteristics of organic matter that they extract?*

691 To date, we do not have an accurate measurement of the recovered WSOM due to analytical
692 challenges and instrument limitations and thus we have not quantified the performance of the SPE
693 cartridges. Strata-X cartridges are composed of a polymeric divinyl benzene resin with carbonyl
694 and tertiary amine functional groups and are expected to be similar to the modified styrene divinyl
695 benzene polymer type sorbent (PPL) cartridges studied by Dittmar et al. (2008) and the Oasis HLB
696 cartridges studied by Varga et al. (2001). These cartridges retain neutral polar compounds and
697 hydrophobic compounds using pi-pi bonding, hydrogen bonding (dipole-dipole interactions), and
698 hydrophobic interaction. We use acetonitrile for the extraction to avoid artifacts that may result
699 from methanol as described by Bateman et al. (2011).

700 *R2.4) Equations: There are several problems with the equations in the manuscript. Presumably,*
701 *these are typographic errors, and the calculations were made correctly. However, the calculations*
702 *should be checked to ensure this is the case, and the numbers in the manuscript are correct.*
703 *Additionally, the text needs to be changed to reflect the following:*

704 *R2.4a) Equation 1, the Kendrick Mass is calculated using the exact mass of compound C not the*
705 *observed mass.*

706 We calculated the Kendrick mass defect as described by Hughey et al. (2001). In that paper, for
707 CH₂ homologous series, Kendrick mass analysis is defined as:

$$708 \quad \text{Kendrick mass} = \text{IUPAC mass} * \frac{14}{14.01565} \quad (1)$$

$$709 \quad \text{Kendrick mass defect} = \text{nominal Kendrick mass} - \text{exact Kendrick mass} \quad (2)$$

710 The masses measured by the ultrahigh resolution ESI FT-ICR MS are defined as IUPAC mass.
711 Kendrick mass analysis is routinely performed on the measured mass as described by Hughey et
712 al. (2001). Therefore, we left Equation 1 as it is in the ACPD manuscript. Note that this equation
713 has been moved to the Supplement.

714 **R2.4b)** Equation 2, the Kendrick Mass Defect is calculated by subtracting the nominal Kendrick
715 Mass from the Kendrick Mass (not vice versa): $KMD = KM - \text{Nominal Kendrick Mass}$

716 Please see the answer **R2.4a** above. Briefly, our KMD formula is consistent with Hughey et al.
717 (2001). Therefore, we left Equation 2 as it is in the ACPD manuscript. Note that this equation has
718 been moved to the Supplement.

719 **R2.4c)** Equation 4 is incorrect in the text. The *o* and *s* are subtracted in the numerator. It should
720 read:

$$721 \quad AI = DBEAI/CAI = (1 + c - o - s - 0.5 * h)/(c - o - s - n)$$

722 We thank the reviewer for catching this typo, which has been corrected. The calculation of AI was
723 performed with a correct equation. Note that this equation has been moved to the Supplement.

724 **R2.4d)** Equations 5 and 6 are incorrect. In equation 5, the *O* and *C* should be lowercase as
725 designated by the defined elemental composition. In equation 6, the *O* and *H* should be replaced
726 with *h* and *c*. Further, equations 5-8 can be combined into one equation replacing *O/C*, *H/C*, *DBE*,
727 and *OM/OC* with *X* then defining *X* as *O/C*, *H/C*, *DBE*, or *OM/OC* in the text following the
728 equation.

729 We thank the reviewer for catching these typos. The typos (upper case) have been corrected. Yes,
730 we are aware the equations can be combined as suggested. Meanwhile with the goal to shorten the
731 manuscript, the equations have been moved to the Supplement, therefore we prefer to list them
732 individually.

733 **R2.5)** The AI calculation as used in the manuscript assumes that all oxygen atoms are in the form
734 of carbonyl bonds which is not true for aerosol WSOM where carboxyl and alcohol (as well as
735 nitrate and sulfate) functional groups are abundant. The modified AI described in Koch and
736 Dittmar (2006) assumes that half of the oxygens are in C=O bonds and half are in C-O bonds, a
737 more likely scenario. Regardless of whether the modified AI is used, this assumption about the
738 bonding of oxygen should be stated explicitly.

739 The AI calculation of Koch and Dittmar (2006) used in the manuscript provides a conservative
740 lower boundary for the aromaticity of the molecular formulas. Thus, the molecular formulas may
741 be more aromatic than indicated using this index. Clarification of this important limitation was
742 added to the definition of AI as described below. Note that the description of AI has been moved
743 to the Supplement.

744 **“The AI calculation of Koch and Dittmar (2006) assumes that all oxygen atoms are in the**
745 **form of carbonyl C=O bonds and provides a conservative lower boundary for the**
746 **aromaticity of the molecular formulas. This is not true for aerosol WSOM where carboxyl**
747 **and alcohol (as well as nitrate and sulfate) functional groups are abundant. Thus, the**
748 **molecular formulas may be more aromatic than indicated using this index.”**

749 **R2.6)** *Throughout the manuscript, WSOC should be changed to WSOM to reflect that water*
750 *soluble organic matter is being characterized rather than water soluble organic carbon which*
751 *typically refers to a quantity of carbon.*

752 We changed each mention of WSOC in the ACPD manuscript to WSOM in the revised manuscript.

753 **R2.7)** *Page 24768, lines 2-11: There are a few problems with the rationale in these arguments.*
754 *The OM/OC ratio of 1.8 takes into account the entire OM. What has been analyzed by FTICR MS*
755 *here is the WSOM that is isolated by the extraction technique. One would expect WSOM to be*
756 *higher because it inherently excludes low oxygenated hydrocarbon compounds (in addition to the*
757 *highly oxygenated, low MW compounds cited by the authors). Do Strata X cartridges bias against*
758 *high O/C compounds? If no, the actual OM/OC ratio in the aerosol OM at this site may be much*
759 *lower than the value of 1.8 used here.*

760 As described in the text, the measured OM/OC value for the SPE recovered WSOM was 1.7 and
761 yes, we expect the value to be higher because some of the very low molecular weight, highly
762 oxygenated compounds like oxalic acid are not retained by these cartridges. This specific text
763 when taken out of context as indicated by the reviewer does not provide sufficient evidence for
764 adopting a ratio of 1.8. In the preceding lines on page 24767 lines 19–21, we report that the
765 literature consensus on OM/OC value for remote areas is 1.8. Thus, our measurement is fairly
766 close to the expected value. To clarify this point, the text on page 24768 in lines 2-11 was modified
767 as given below:

768 **“The OM/OC ratio of 1.8 adopted in our analysis is slightly higher than the OM/OC ratio of**
769 **~1.7 (Table 2) calculated from FT-ICR MS analysis of WSOM elemental compositions**
770 **(Mazzoleni et al., 2010). The measured value of 1.7 is expected to be lower than the total,**
771 **because of the low sample recovery of highly oxygenated, low molecular weight species**
772 **(Hallar et al. 2013).”**

773 **R2.8)** *Page 24768, lines 18-23: These correlations are cited in the abstract but are only presented*
774 *as a supplementary figure. This seems to be a disconnect in its value to the paper. In lines 21-23,*
775 *the correlations are described as indicating that the measurements follow the same trends which*
776 *is self-evident. More in depth analysis and interpretation of the implications of these results and*
777 *their importance in the atmospheric conditions or processes at this site are needed. Otherwise, the*
778 *correlations should be removed from the manuscript.*

779 We agree with the reviewer that the abstract should highlight only the most important contributions
780 from presented work. Therefore, we deleted the mention of filter samples vs. on-line aerosol
781 measurements correlations on page 24755 in lines 10-12 of the Abstract.

782 As pointed out by the reviewer, these correlations and accompanying figures are one way to show
783 an agreement between three very different types of aerosol measurements. We prefer to keep the
784 figures in the way not essential to the discussion of the results, which is expressed by the placement
785 in the Supplement. The correlations strengthen the point that all aerosol measurements saw the
786 same trends during the 2012 field campaign. We believe it is important to show it in this subtle
787 way. As shown in Fig. 4 of Hallquist et al. (2009), there is yet no perfect technique for a complete
788 chemical characterization of organic aerosol. With mentioned correlations, we also wish to stress
789 the necessity for high quality filter-based aerosol measurements, which are becoming less common
790 with emerging of state-of-the-art, on-line measurements of organic aerosol.

791 **R2.9)** Section 3.2, first paragraph: this information belongs in the methods section.

792 We moved the text starting on page 24768 in line 26 and ending on page 24769 in line 3 to the
793 very beginning of the section describing the ultrahigh-resolution ESI FT-ICR MS analysis. The
794 new, slightly modified text now reads:

795 **“We selected two samples named 9/24 and 9/25 (filter-collection periods were September 24**
796 **at 15:00 to September 25 at 15:00 and September 25 at 15:00 to September 26 at 15:00) for**
797 **detailed chemical characterization by ultrahigh resolution mass spectrometry (Table 2). In**
798 **this paper, unless noted otherwise, “9/24” and “9/25” always refer to the filter samples**
799 **collected during these time periods.”**

800 **R2.10)** What is the purpose of the ethane and propane mixing ratios? This needs to be made clear
801 to the reader. The methods need to be added to the methods section as well.

802 This comment was addressed as a reply to Reviewer 1 in answers **R1.7** and **R1.8a**. For the ease of
803 following our response to Reviewer 2, we inserted the same answers below.

804 **R2.10a)** The purpose of the ethane and propane mixing ratios (identical to answer to Reviewer 1
805 **R1.8a)**:

806 We added the explanation about why ethane and propane, as well as their ratio, matter. The
807 revisions to the ACPD manuscript are described below.

808 -We added the description (**bolded**) of the importance of ethane and propane as pollution tracers
809 to section “1. Introduction” on page 24759 in line 5:

810 **“... (Honrath et al., 2008). Previous research at PMO has shown several-fold increases of**
811 **NMHC in anthropogenic and biomass burning plumes. Furthermore, it has been**
812 **demonstrated that isoprene and ratios of selected NMHC pairs have characteristic**
813 **signatures that were used for identification of upslope flow conditions (Kleissl et al., 2006)**
814 **and pollution plume characterization (Helmig et al., 2008).”**

815 -We added the description further elaborating the importance of NMHC measurements and
816 $\ln([\text{propane}]/[\text{ethane}])$ ratio at the opening of section “3.2.1 Non-methane hydrocarbon
817 measurements” on page 24770 in lines 25-28:

818 **“NMHC have been widely used as tracers for anthropogenic and biomass burning**
819 **emissions (Helmig et al., 2008). Due to their different oxidation rates, mole fractions of**
820 **different NMHC exponentially decline at different rates during atmospheric transport**
821 **allowing the natural log of $\text{NMHC}_1/\text{NMHC}_2$ (e.g., $\ln([\text{propane}]/[\text{ethane}])$) to be used as a**
822 **linear measure of photooxidation and transport time. $\ln([\text{propane}]/[\text{ethane}])$ has been**
823 **demonstrated to be a sensitive indicator for identifying pollution signatures and transport**
824 **time to PMO (Helmig et al., 2008, 2015).”**

825 **R2.10b)** The description of NMHC measurements method (identical to answer to Reviewer 1
826 **R1.7)** was addressed in a reply to comment **R2.2a** above.

827 **R2.11)** Perhaps Figure 4 should be altered to note that contributions that each particle type are
828 attributed to each sample. The numbers are difficult to follow in the text.

829 We modified the caption of the Figure 4 and provided the fraction of tar balls and embedded soot
830 particles. The new, modified caption of Figure 4 now reads:

831 “**Representative SEM images of particles collected on 9/24 (a) and 9/25 (b). Also shown are**
832 **examples of spherical (43% and 18% in 9/24 and 9/25, respectively) (c), near spherical**
833 **particles (23% and 29% in 9/24 and 9/25, respectively) (d), and embedded soot particles**
834 **(46% and 17% in 9/24 and 9/25, respectively) (e-h).”**

835 *R2.12) Throughout section 3.3: I caution the authors in being clear how they are comparing the*
836 *results from this study to those from other studies. In addition to differences in WSOM source and*
837 *processing, WSOM mass spectra can differ depending on the methodologies used in each study*
838 *(e.g., the extraction conditions (choice of SPE cartridge, eluting solvent, etc.), the tuning*
839 *parameters of each individual FTICR MS instrument). The best comparisons (especially of*
840 *abundances, mass ranges, etc.) are made for samples that have been processed and analyzed in*
841 *the same way over similar time periods.*

842 Part of the answer to this comment was addressed as an answer to Reviewer 1 in comment **R1.11**.

843 We understand and acknowledge this concern for caution. We agree that the best comparisons
844 between the results of ESI FT-ICR MS analysis of ambient aerosol are between samples that have
845 been processed and analyzed following an identical protocol. However, there is a very limited
846 number of studies of this type and we feel that it is important for the context of our work to
847 comment on those observations.

848 All of the instrument parameters used here are exactly the same as in the previous work of the
849 Mazzoleni research group. The instrument is tuned using Suwannee River Fulvic Acid as described
850 by Soule et al., 2010. The ion optics do indeed affect the proportion of ions, thus we purposely do
851 not adjust them. The observations described here are qualitative descriptions of the mass spectra
852 differences we have observed. The high abundance of lower molecular weight ions as reported in
853 Mazzoleni et al., 2010, 2012 and Zhao et al., 2013 are consistent with those reported in Wozniak
854 et al., 2008 and Schmitt-Kopplin et al., 2010. In each of those cases, the studied aerosol or cloud
855 water were collected at continental sites, whereas the samples reported in this study were collected
856 at a remote free tropospheric site in the North Atlantic.

857 *R2.13a) Throughout section 3.3: The presentation (Figures 6-10) and description of the FTICR*
858 *MS results is extensive and repetitive and would benefit from a more targeted approach that*
859 *effectively describes the important, unique features in these samples that can be linked to important*
860 *potential effects in the atmosphere/environment.*

861 This comment was addressed as a part of reply to Reviewer 1 in answer **R1.6**. Note that the entire
862 answer **R1.6** is long and thus we did not copy and paste it here. For the ease of following our
863 response to Reviewer 2, here we mainly copied and slightly rewrote answer to Reviewer 1 subtitled
864 **R1.6a**. Please refer to the complete answer **R1.6** to Reviewer 1 for a detailed explanation on how
865 we improved the presentation of Section 3.3.

866 In this paper, we decided to combine results and discussion into a single section “3. Results and
867 discussion” (page 24767 in line 15). We believe this is the best way to present our findings, as
868 explained results are immediately compared to the previously published work whenever possible.
869 Therefore, we prefer to keep the format of this section as in the ACPD manuscript.

870 However we agree that: i) highlighting the specific sentences Reviewer 1 pointed out in his
871 comment would very much strengthen the unique observations of these highly aged aerosol (details
872 are described in comments **R1.6a-R1.6l**); and ii) this would greatly help the flow of the paper. In
873 response, we either deleted mentioned text or moved it to section “4. Conclusions” in an effort to
874 concentrate the “Big Picture” discussion on the importance and implications of this study.

875 **R2.13b)** *Many details included in the presentation have been established in several other FTICR*
876 *MS studies – such as the high isobaric complexity in samples, that homologous series can be*
877 *observed in DBE and KMD plots (e.g., page 24775, line 10; page 24776, lines 7-9 – are there*
878 *specific importances to these series?), and that lines of apparent saturation/unsaturation,*
879 *oxidation/reduction, and alkylation can be observed in van Krevelen diagrams.*

880 We moved to the Supplement the mention of high complexity in graphical representation of ESI
881 FT-ICR MS data and all panels in Fig. 6 associated with it (Figs. 6b, 6e and 6h). More precisely,
882 in the revised manuscript we deleted the following text from the ACPD manuscript (only the
883 beginning and the end of each deleted part is noted):

884 - Mention of complexity in Kendrick plot on page 24775 in lines 4-11:

885 ~~“Due to the presence... and $(\text{CH}_2)_{1,2,5,7}\text{C}_7\text{H}_{16}\text{SO}_4$, respectively.”~~

886 - Mention of complexity in van Krevelen diagram on page 24775 in lines 21-14:

887 ~~“Molecular assignments in... and iii) functionalization or fragmentation.”~~

888 - Mention of complexity in Kendrick plot on page 24776 in lines 5-9:

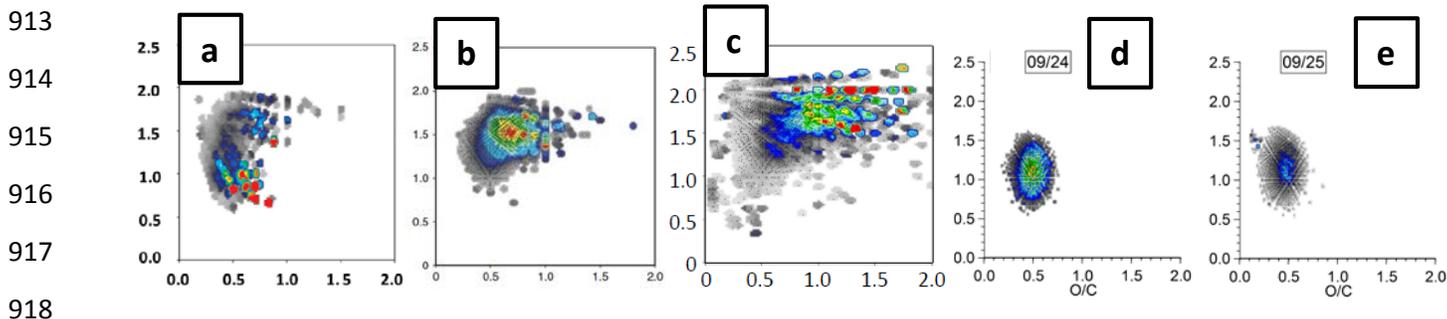
889 ~~“Numerous homologous series... and $\text{C}_{16}\text{H}_{11}\text{NO}_{11}(\text{CH}_2)_n$.”~~

890 - Middle panels of Figure 6 have been moved to the Supplement as new Figure S9.

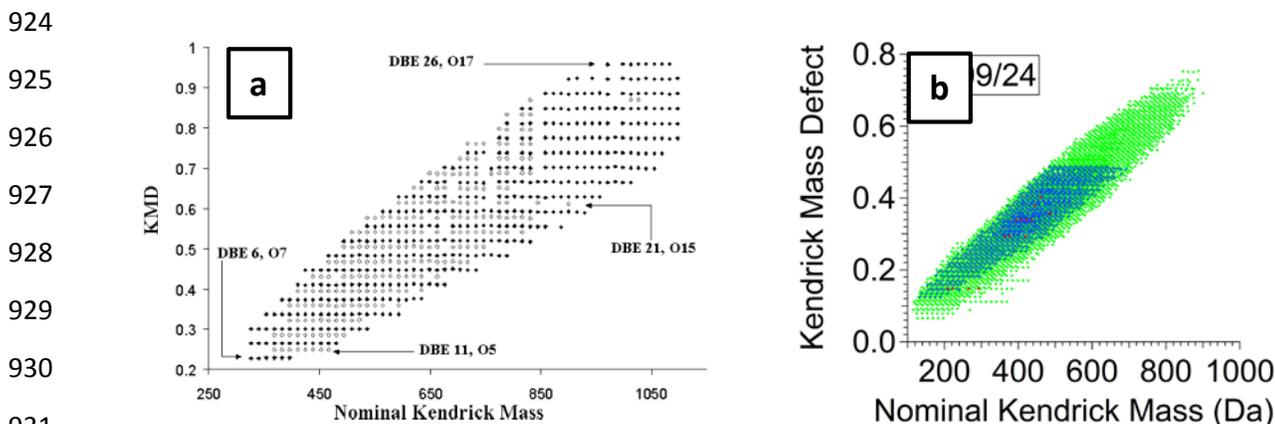
891 **R2.13c)** *Additionally, descriptions of Kendrick plots as, for example, “narrow and uniform” (e.g.,*
892 *page 24774, line 28) are vague and do not have particular value unless they are linked to specific*
893 *molecular components which one cannot tell from the Kendrick plots themselves. Backing up the*
894 *vague terminology with more quantitative measures describing the distributions and what they*
895 *mean molecularly will improve the manuscript. Otherwise, they are simply describing differences*
896 *in a graph shape.*

897 We agree with the reviewer vague terminology is far from an ideal way of describing the features
898 of the studied aerosol in scientific work. At the same time, a comparison of the statistical
899 characteristics of different ESI FT-ICR MS data has not been shown to be the best way to quantify
900 the differences in data sets. Averages of large numbers of points in the data sets sometimes yield
901 similar values, although the data looks quite different. Also, the description of shape in the
902 graphical representation of aerosol data has been used before (e.g., Markowski, G.R.: Improving
903 Twomey's Algorithm for Inversion of Aerosol Measurement Data, Aerosol Science and
904 Technology, 7, 127-141, 1987). We do not have much data to compare our findings with. While
905 looking at the available studies of the Mazzoleni research group, we noticed that Pico aerosol is
906 truly unique (an example is given in Fig. R2.F1 below). Looking at the work published by other
907 research groups, we again found this remarkable uniformity observed in the graphical
908 representations of the Pico aerosol to be almost unique (a rare example of similar distribution in
909 the Kendrick plot is given in Fig. R2.F2 below). Therefore we concluded that the observed

910 uniformity in the graphical representations of the Pico aerosol may be an indication of highly
 911 processed aerosol in which aging mechanisms have smoothed out wider distributions observed for
 912 other samples.



919 Figure R2.F1: Comparison of van Krevelen diagrams (H/C vs. O/C) for molecular assignments in
 920 CHNO group for Mazzoleni et al., 2010 (a), Mazzoleni et al., 2012 (b), Zhao et al., 2013 (c) and
 921 9/24 (d) and 9/25 (e) samples presented in this study. Figures were copied from the original papers
 922 and thus axis do not have same dimensions and some are a bit foggy; however, all panels have the
 923 same range of x- and y-axis.



932 Figure R2.F2: Comparison of KMD vs. NKM representations of SRFA sample as reported by
 933 Stenson et al. (2003) (a) and 9/45 sample from this study (b).

934
 935 Therefore, we made a compromise between visual observations and reviewers concern of vague
 936 terminology. To address reviewers comment, we mainly quantified the observed uniformity in
 937 graphical representations as described below.

938 - Mention of narrow and uniform distribution in Kendrick plot in sentence on page 24774 in line
 939 28 has been quantified by adding a sentence (**bolded**) preceding it:

940 **“For example, in comparison with the cloud water WSOM reported by Zhao et al. (2013) the**
 941 **free tropospheric aerosol WSOM studied here had a narrower spread in the NKM over the**
 942 **observed mass ranges.** This narrow and uniform distribution has not been observed in other

943 Kendrick plots of aerosol WSOM (e.g., Kourtchev et al., 2013) and may indicate highly processed
944 aerosol.”

945 - Mention of narrow and homogeneous distribution in van Krevelen diagram in sentence on page
946 24775 in lines 16-17 has already been quantified by the sentence after it (underlined):

947 “The van Krevelen diagrams for the 9/24 and 9/25 in Figures 6b and 6e showed a narrow and
948 homogeneous distribution with aliphatic and olefinic species (Table 2). For example, the range of
949 values of O/C ratio for aerosol WSOM collected at the PMO vs. the Storm Peak Laboratory
950 (Mazzoleni et al., 2012) is 0.13 - 1.48 vs. 0.07 – 1.80 (Table 3).”

951 - Comparison of CHO group distribution in van Krevelen diagram on page 24776 in lines 24-27
952 was quantified by adding a sentence (**bolded**) after it (note that in this case the averaged values
953 are quite similar, while distributions look different in van Krevelen diagram):

954 “The distribution of elemental ratios for the CHO molecular assignments in this study was similar
955 to the aerosol reported by Mazzoleni et al. (2012) and narrower than the cloud water values
956 reported by Zhao et al. (2013), both of which were measured at the Storm Peak Laboratory. **This**
957 **is consistent with the observed lower average values of O/C and H/C in this study (~0.44 and**
958 **1.22) compared to that of Mazzoleni et al. (2012) (0.47 and 1.42) and Zhao et al. (2013) (0.54**
959 **and ~1.42).”**

960 - Finally, we replaced three mentions of “tight distribution” with “narrow distribution” (page
961 24779 in line 8, page 24782 in line 4 and page 24782 in line 22). We hope that by quantifying
962 narrow distribution several times prior to page 24779, we convinced interested readers of its
963 validity. Therefore, we offer no quantification the last three times we mention “narrow
964 distribution”.

965 ***R2.14) Throughout section 3.3: DBE values are frequently cited as evidence for the unsaturation***
966 ***of samples, and they are evidence for the total number of double bonds. However, because WSOM***
967 ***compounds vary in size within a sample and between studies, DBE is limited in terms of how much***
968 ***structural information it can give. A better idea of WSOM structural components can be gained***
969 ***using the DBE/C ratio (Hockaday et al., 2006), the aromaticity index, or the aromaticity***
970 ***equivalence (Yassine et al. 2014).***

971 We thank the reviewer for this suggestion. In the case of the very high molecular weight species
972 as those we encountered in our study, the high DBE number has less significance as the increase
973 in the number of C atoms in a molecule is likely to be naturally followed by an increase in DBE.
974 Indeed, a way to analyze structural characteristics of molecular formulas is to use a DBE/C ratio
975 or the aromaticity index. We included in the manuscript the analysis of DBE/C at each important
976 discussion of DBE values. More precisely, we modified the manuscript and Supplement as
977 described below. Finally, note that we kept the discussion and graphical representation of DBE
978 and AI analysis for the sake of comparison with previously published work.

979 - We inserted the following explanation on page 24777 in line 6:

980 “**Another indicator of molecular saturation for high molecular weight species such as those**
981 **found in the Pico aerosol is the carbon-normalized DBE (DBE/C) (Hockaday et al., 2006;**

982 detailed explanation is in the Supplement). The average DBE/C values of CHO group for
983 9/24 and 9/25 were 0.46 and 0.41 (Table 2), confirming the lower degree of saturation
984 compared to Mazzoleni et al. (2012) and Zhao et al. (2013) ($DBE/C_{CHO} = 0.37$ and 0.35).
985 However, nearly all of the CHO molecular assignments were below the aromaticity criteria
986 of $DBE/C \geq 0.7$ (95% and 97% for 9/24 and 9/25), indicating an overall lack of aromaticity.
987 The CHO species ...”

988 - We inserted the following description to the Supplement (note that the calculation of DBE/C_w
989 was added as the last equation describing the relative abundance weighted values):

990 “Another indicator of molecular saturation is the carbon-normalized DBE, defined as
991 the ratio of DBE to the number of C atoms (DBE/C) for each molecular assignment, i.e.:

$$992 \quad DBE/C = \frac{DBE(C_c H_h N_n O_o S_s)}{c(C_c H_h N_n O_o S_s)} \quad (4)$$

993 Hockaday et al. (2006) introduced DBE/C as a criterion for identifying molecular species
994 with condensed aromatic ring structures. The value of $DBE/C \geq 0.7$ is a threshold for
995 molecular assignments with fused-ring structures, and thus a proxy for combustion derived
996 species and their degradation products (Hockaday et al., 2006).

$$997 \quad DBE/C_w = \frac{\sum w_i * DBE_i}{\sum w_i * c_i} \quad (10)''$$

998 - We inserted the following clarification for CHNO group species on page 24780 in line 24:

999 “... 10.3 and 9.8, and DBE/C ones of 0.51 and 0.49 (Table 2), with nearly all molecular
1000 formula with DBE/C below the aromaticity criteria of 0.7 (92% and 94%).”

1001 - We rewrote the sentence on page 24781 in lines 20-21 and inserted the following clarification
1002 for CHOS group species:

1003 “Relatively high saturation of 9/24 CHOS species was confirmed by their significantly lower
1004 average DBE (Fig. 9c) and DBE/C value of 0.20 (Table 2). Furthermore, no molecular
1005 assignments in 9/24 (as well as in 9/25) were found above the DBE/C aromaticity threshold
1006 of 0.7.”

1007 - We rewrote the sentence on page 24782 in lines 10-11 so that it now reads:

1008 “Much lower DBE and DBE/C values than those observed for CHO and CHNO compounds
1009 were consistent with the higher saturation of CHOS species (Fig. 9d and Table 2).”

1010 - We rewrote the sentence on page 24785 in lines 9-10 so that it now reads:

1011 “The average DBE values (and DBE/C in the parenthesis) of 9/24 and 9/25 were 10.7 (0.47)
1012 and 9.4 (0.42) (Fig. 10g) and these values were similar to the average DBE found in the CHO
1013 and CHNO groups (Tables 2 and 3).”

1014 Finally, we kept the use of aromaticity index (AI) while defining its limitations. This comment
1015 was already addressed as an answer to reviewer comment **R2.5**.

1016 **R2.15)** Page 24774, line 22: Why is it “not likely that nitrooxy organosulfates will be observed
1017 after long range transport?” Do you have a rationale and citation for this?

1018 According to the FLEXPART backtrajectory analysis, the observed WSOM is expected to be
1019 highly aged over transport that lasted for > 12 days. The vertical pathway in the backtrajectory
1020 also indicates that the aerosol were aloft in the free troposphere for much of their time before
1021 reaching the measurement site. Thus, cloud processing is strongly implicated as a
1022 removal/transformation mechanism. In another study by our group, we have observed
1023 morphological changes to soot that are a surprising consequence of the long range transport with
1024 cloud processing (China et al., 2015). Since nitrooxy organosulfates are highly water-soluble, we
1025 hypothesize they have been removed by cloud processing. However, we do not have evidence for
1026 this hypothesis and we do not know of other studies with molecular characterization of long range
1027 transported free tropospheric aerosol.

1028 To further clarify this in the manuscript, we modified the text on page 24774 in lines 22-25 to:

1029 **“Due to their high water solubility, it is not likely that nitrooxy organosulfates will be**
1030 **observed after long range transport because they are likely removed by cloud processing.**
1031 **This observation is also consistent with the low number of sulfur-containing species. Thus,**
1032 **the CHNOS molecular formula assignments are not presented here.”**

1033 **R2.16)** Page 24775, lines 1-4: Why is a “similar distribution in the Kendrick plot” evidence for
1034 very aged and processed aerosol WSOM? Further, fulvic and humic acids, which are by definition
1035 insoluble in water, have been found in previous studies to be poor analogues for aerosol WSOM
1036 and so-called HULIS (Duarte et al., 2007). Unfortunately, the term HULIS persists in the
1037 literature, but its similarity to SRFA and other fulvics and humics should not.

1038 This comment was addressed in **R1.6d**. For convenience, we inserted the same answer below.

1039 The ESI FT-ICR MS analysis of molecular composition of Suwannee River Fulvic Acid has been
1040 reported by Stenson et al., 2003. The similar Kendrick distribution may be a result of similar
1041 structures from the lignin. It is established that chemical properties of processed ambient organic
1042 aerosol resemble those of terrestrial fulvic acid such as its standard Suwannee River Fulvic Acid
1043 (Cappiello et al., 2003; Dinar et al., 2006). Regardless, we decided to remove the comment
1044 regarding aerosol processing by deleting (~~bolded and strikethrough~~) the following words from
1045 the sentence on page 24775 in lines 1-4:

1046 “Ultrahigh-resolution FT-ICR MS measurements of a Suwannee River Fulvic Acid standard, a
1047 model for HULIS, yield very similar distribution in the Kendrick plot (Stenson et al., 2003),
1048 ~~confirming the very aged and processed nature of PMO aerosol WSOC.~~” :

1049 **R2.17)** Can the authors provide citations and/or mechanisms for how “fragmentation” can result
1050 in higher degrees of unsaturation in the WSOM composition?

1051 This comment was addressed in **R1.1**. For convenience, we copied and pasted the same answer
1052 below.

1053 In this study, we report the molecular characterization of aerosol after long range transport in the
1054 free troposphere and 12.4 and 14.7 days of aging for the two collected samples. The aging
1055 processes likely include re-equilibration of aerosol constituents to the gas phase (evaporation),
1056 photolysis (fragmentation) and other condensed phase reactions (e.g., cloud processing). The
1057 cumulative result of aging and the removal of aerosol constituents is observed. This means that we
1058 observe the aerosol components that are long-lived. Compounds with high O/C ratios are highly
1059 water-soluble and were likely removed during transport. The text has been revised to indicate
1060 cumulative effects are responsible for the observed molecular composition.

1061 We are not aware of other studies with molecular characterization of long range transported free
1062 tropospheric aerosol, thus making it difficult to support our hypothesis with literature citations.
1063 Therefore, all mentions of the low O/C ratio due to fragmentation have been removed from the
1064 main text and our hypothesis is discussed in section “4. Conclusions”.

1065 ***R2.18)** Page 24783, lines 16-24; Page 24785, lines 5-8; Page 24787, lines 7-9: organosulfates
1066 are not specific to marine environments and have been identified in terrestrial environments and
1067 from other sources. Furthermore, fatty acids are a major biological component in all manner of
1068 life and are not specific to marine environments. This line of reasoning must be further supported,
1069 edited to add qualifying statements, or eliminated.*

1070 It is true that aerosol organosulfates are found in various environment, from pristine marine to
1071 highly polluted urban atmosphere. Similarly, fatty acids as biological aerosol components have
1072 been attributed to various emissions as diverse as biomass burning and marine aerosol (Finlayson-
1073 Pitts and Pitts, 2000). From the observations presented in this work, marine aerosol is the most
1074 likely culprit for the observed organosulfates and fatty acids in 9/25. The air masses of both
1075 samples underwent similar transportation histories, with the main difference of the 9/25 air masses
1076 decreasing in altitude shortly before reaching the measurement site. Therefore, the marine
1077 boundary layer emissions are the most likely source of both organosulfates and fatty acids.

1078 ***R2.19)** Section 3.3.5 is largely redundant with the rest of section 3.3. That said, it contains much
1079 of the important comparison of the two samples.*

1080 Yes, this section provides a succinct and important comparison of the two samples. Thus, we kept
1081 it in a current form.

1082 ***R2.20)** The literature is full of marine aerosol or rainwater WSOM studies that have examined the
1083 molecular composition. These studies can be compared to the present study to confirm marine
1084 sources to the 9/25 sample or to delineate differences between the Pico samples (collected in the
1085 middle of the ocean) and these other marine aerosols. See, for example, Altieri et al., 2012; Cavalli
1086 et al., 2004; Decesari et al., 2011; Ovadnevaite et al., 2014; Russell et al., 2010; Wozniak et al.,
1087 2014.*

1088 We thank the reviewer for suggesting this additional set of studies. In reviewing them, we indeed
1089 found some similarities to observed features of Pico aerosol. We summarized those as described
1090 below. Note that Altieri et al., 2012 paper presents results of the positive mode ESI FT-ICR MS

1091 measurements. We analyzed our data also in the positive mode and plan to present those results as
1092 a separate publication.

1093 - We inserted the following text on page 24783 in line 15:

1094 “...2013). **Non-sea-salt sulfate species in marine aerosol have previously been found and**
1095 **attributed to the degradation of marine primary emissions (e.g. Cavalli et al., 2004).**
1096 **Furthermore, the degradation products of marine flora such as methanesulfonic acid have**
1097 **been shown to peak in summer months and produce aliphatic organic species with low**
1098 **oxygenation (Cavalli et al., 2004; Ovadnevaite et al., 2014). Nevertheless, ...”**

1099 - We inserted the following text on page 24783 in line 24:

1100 “... aging. **Recent study of aerosol collected on a research vessel in the North Atlantic Ocean**
1101 **detected 246 CHOS species in aged marine aerosol, a number of CHOS species comparable**
1102 **to our study (Wozniak et al., 2014; “Aged marine” PCA group from their study is given in**
1103 **Table 3). Consistent with Claeys et al. (2010), Wozniak et al. (2014) attributed the observed**
1104 **CHOS species to organosulfate markers of marine aerosol degradation albeit with longer**
1105 **carbon chains. The CHOS species reported in Wozniak et al. (2014) have similar chemical**
1106 **characteristics to those reported here (magnitude-weighted average O/C = 0.36 and H/C =**
1107 **1.57).”**

1108 *Minor Comments (given the length of the manuscript, many of these are suggestions for shortening*
1109 *it):*

1110 **R2.21) Page 24757, lines 10-11: The sentence “Determination of the OA molecular composition**
1111 **is a challenging task.” is redundant with line 1 in this paragraph.**

1112 This sentence has been removed.

1113 **R2.22) Page 24757, the paragraph beginning on line 17 can be condensed considerably to omit**
1114 **details about FTICR MS that have been covered in a great many previous publications.**

1115 The manuscript was prepared from the perspective of the lead author, who is experienced in high
1116 resolution aerosol mass spectrometry and wanted to highlight the new learning experience with
1117 ultrahigh resolution FT-ICR MS. Furthermore this manuscript contains many types of data, which
1118 are not often presented in the ultrahigh resolution mass spectrometry literature. Thus, we anticipate
1119 a broader audience and want to familiarize the reader with the major concepts. We condensed the
1120 paragraph starting on page 24757 in line 17 and ending on page 24756 in line 12 to:

1121 **“The mass spectrometer with the highest mass resolution and accuracy is the Fourier**
1122 **transform ion cyclotron resonance mass spectrometer (FT-ICR MS; Kim et al., 2006).**
1123 **Typically the FT-ICR MS mass resolving power and accuracy used for ambient aerosol**
1124 **analysis are 200,000 – 400,000 and < 2 ppm, respectively (Mazzoleni et al., 2010). When**
1125 **combined with an appropriate ionization technique, FT-ICR MS is capable of resolving**
1126 **thousands of chemically different species in a single mass spectrum, and is ideally suited for**
1127 **the analysis of complex mixtures of ambient OA. Electrospray ionization (ESI) is a soft**
1128 **ionization technique that leaves the sample molecules intact and minimizes their**

1129 fragmentation, and thus is ideal for coupling with FT-ICR MS for detailed molecular level
1130 OA characterization (Nizkorodov et al., 2011). Negative mode ESI is especially useful for the
1131 ionization of multifunctional oxidized compounds such as carboxyl groups. FT-ICR MS was
1132 successfully used for the analysis of ambient OA (Wozniak et al., 2008; Schmitt-Kopplin et
1133 al., 2010; Mazzoleni et al., 2012), dissolved organic matter in rain (Altieri et al., 2009a, 2009b,
1134 2012; Mead et al., 2013; Zhao et al., 2013), fog water (Mazzoleni et al., 2010) and sea spray
1135 aerosol (Schmitt-Kopplin et al., 2012).”

1136 *R2.23) Page 24758-9, the final two paragraphs of the introduction should include some further*
1137 *justification of why the measurements are being made. Simply understanding long range transport*
1138 *is not an end in itself. The atmospheric community wants to understand long range aerosol*
1139 *transport (and the resulting WSOM chemical characteristics) for their effects in the atmosphere*
1140 *and environment. This needs to be made clear. Further, many of the details on the PMO can be*
1141 *more appropriately moved to the methods section as a site description.*

1142 *R2.23a)* We will first address reviewers’ suggestion to move the details of PMO site to the methods
1143 section. Description of the PMO in the introduction of the manuscript is a natural opening for
1144 previous research done at the observatory. Similarly, we believe the reader should know the
1145 specific characteristics of the site before learning about previous research. Thus, we prefer to leave
1146 it in the introduction.

1147 *R2.23b)* Next, we thank the reviewer for the suggestion to strengthen the importance of aerosol
1148 measurements at the Pico Mountain Observatory. To address it, we modified the text as described
1149 below.

1150 - The importance of the long range transported aerosol was strengthen and moved to the first
1151 paragraph of section “1. Introduction” on page 24756 in line 23:

1152 “... (Zhang et al., 2007). **Highly aged and processed long range transported ambient aerosol**
1153 **are of particular interest and have chemical compositions characteristic of global aerosol**
1154 **(Ramanathan et al., 2001). The long range transport of aerosol from Asia to North America**
1155 **has received considerable attention (Ramanathan et al. 2001, 2007; Dunlea et al., 2009), but**
1156 **less attention has been placed on aerosol transported from North America to Europe.**
1157 Ambient ...”

1158 - Next, we added new paragraph to page 24759 in line 15 by moving all of the mention of past
1159 aerosol measurements at the PMO from paragraph starting on page 24758 in line 13 and ending
1160 on page 24759 in line 14.

1161 “Until 2010, the only type of aerosol measured at the PMO was black carbon. Fialho et al.
1162 (2005, 2006) developed a method to determine the contribution of black carbon (BC) and
1163 dust from multiwavelength aethelometer measurements. Although typically average free
1164 tropospheric aerosol concentrations are low, the long range transport events bring elevated
1165 levels of BC and dust mass concentrations to PMO. To study these events, new on- and off-
1166 line aerosol instrumentation was installed in 2012, as described below.”

1167 *R2.24) Page 24763, line 23-24: The sentence beginning “the aim of data processing...” is not*
1168 *necessary.*

1169 We removed the mentioned sentence by moving the detailed description of FT-ICR MS
1170 measurements and data analysis, this sentence included, to the Supplement.

1171 **R2.25) Page 24765 (and in the results): Why are two methods of formula assignments presented**
1172 **and compared? I believe that they were ultimately used in tandem (which seems appropriate). The**
1173 **authors should just state that both methods are used to assign formulas. Any comparison can be**
1174 **moved to the supplementary information.**

1175 The reviewer is correct when saying that two methods of formula assignment were used in tandem
1176 to create a final FT-ICR MS dataset presented in the manuscript. Molecular formulas are the
1177 combination of both Methods A and B, as described in text starting on page 24765 in line 27 and
1178 ending on page 24765 in line 8. We stated this clearly with the final sentence that says “The results
1179 presented here are the combination of both methods without double counting.” To clarify this
1180 further, we changed this sentence to:

1181 **“The assigned molecular formulas presented here are the combination of both methods**
1182 **without double counting.”**

1183 Note that this text has been moved to the Supplement in the final manuscript version.

1184 Finally, we did not present a detailed comparison of Methods A and B in the results and discussion.
1185 Rather, we mentioned basic statistics of molecular formula assignments from both Methods A and
1186 B in section “3.3.1 Mass spectra and molecular formula assignments” on page 24773 in lines 5-
1187 12.

1188 **R2.26) Page 24765, line 10: The assignment thresholds are presented as percentages. To what**
1189 **are these thresholds being compared? The highest peak in the spectrum? This should be clarified.**

1190 Yes, they are relative to the base peak of the mass spectrum. To clarify this further, we changed
1191 the mentioned sentence to:

1192 “...and 0.1% (**relative to the molecular ion peak at 100%**) for 9/24, ...”

1193 Note that this text has been moved to the Supplement in the final manuscript version.

1194 *References:*

1195 *Altieri et al., 2012; Atmos. Chem. Phys., 12, 3557-3571.*

1196 *Cavalli et al., 2004; J. Geophys. Res., 109, D24215, doi:10.1029/2004JD005137*

1197 *Duarte et al., 2007; Atmos. Environ., 41, 8100-8113.*

1198 *Decesari et al., 2011; J. Geophys. Res., 116, D22210, doi:10.1029/2011JD016204*

1199 *Hockaday et al., 2006; Org. Geochem., 37, 501-510.*

1200 *Ovadnevaite et al., 2014; JGR Atmospheres, 10.1002/2013JD021330*

1201 *Russell et al., 2010; PNAS, 107, 6652-6657.*

1202 *Wozniak et al., 2014; Atmos. Chem. Phys. 14, 8419-8434.*

1203 *Yassine et al., 2014; Rapid Commun. Mass Spec. 28, 1-10.*

1204

1205 **Additional References to the Response to the Anonymous Reviewer #2:**

1206 Bateman, A. P., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Photolytic processing of secondary
1207 organic aerosols dissolved in cloud droplets, *Phys. Chem. Chem. Phys.*, 13, 12199–12212,
1208 doi:10.1039/C1CP20526A, 2011.

1209 Dittmar, T., Koch, B., Hertkorn, N., and Kattner, G.: A simple and efficient method for the solid-
1210 phase extraction of dissolved organic matter (SPE-DOM) from seawater, *Limnol. Oceanogr.:*
1211 *Methods*, 6, 230–235, 2008.

1212 Markowski, G.R.: Improving Twomey's Algorithm for Inversion of Aerosol Measurement Data,
1213 *Aerosol Sci. Tech.*, 7, 127-141, 1987

1214 Soule, M.C.K., Longnecker, K., Giovannoni, S.J., and Kujawinski, E.B.: Impact of instrument and
1215 experiment parameters on reproducibility of ultrahigh resolution ESI FT-ICR mass spectra of
1216 natural organic matter, *Org. Geochem.*, 41, 725-733, 2010.

1217 Varga, B., Kiss, G., Ganszky, I., Gelencser, A., Krivacsy, Z.: Isolation of water-soluble organic
1218 matter from atmospheric aerosol, *Talanta*, 55, 561-572, doi:10.1016/S0039-9140(01)00446-5,
1219 2001.

1220

1221 ***Response to Comments from Anonymous Reviewer #3***

1222

1223 *This paper presents ultrahigh-resolution MS analysis of aerosol WSOC from a free tropospheric*
1224 *site at the Pico Mountain Observatory. Measurements of aerosol OC, EC, and inorganics are used*
1225 *together with FLEXPART analysis of air mass histories to classify the overall chemical*
1226 *composition and air mass history of the aerosol sampled at the site. Two events are identified as*
1227 *case studies of biomass influenced and marine influenced airmasses. This data offers a useful*
1228 *opportunity to explore the effect of airmass aging and airmass sources on WSOC composition.*
1229 *The manuscript is well written in sections, but could be tightened to make it clearer and some of*
1230 *the reasoning seems to be erroneous and needs to be rechecked. So, I recommend publication only*
1231 *after the following comments are addressed.*

1232 *Main Comments*

1233 ***R3.1)*** *The argument that the authors present in the abstract (line 19-24) that low O/C ratios in*
1234 *aged aerosol is consistent with evaporation and increased fragmentation does not make sense to*
1235 *me. My understanding is that increased fragmentation results in more oxidized organic aerosol*
1236 *and higher O/C values (see for example, Kroll et al. Nature Chemistry, 3: 133-139). Also, previous*
1237 *work has shown that oxidation is generally accompanied by decrease in volatility of aerosol*
1238 *components. So, I don't understand how evaporation is increasing with aging. The argument about*
1239 *fragmentation is repeated throughout the manuscript and based on the Kroll et al. paper and*
1240 *related papers, I think it is incorrect and should be rethought.*

1241 We thank the reviewer for this point that was brought up by all of the reviewers. This comment
1242 was addressed in our reply to Reviewer 1 in **R1.1**. For your convenience, we inserted that response
1243 here.

1244 In this study, we report the molecular characterization of aerosol after long range transport in the
1245 free troposphere and 12.4 and 14.7 days of aging for the two collected samples. The aging
1246 processes likely include re-equilibration of aerosol constituents to the gas phase (evaporation),
1247 photolysis (fragmentation) and other condensed phase reactions (e.g., cloud processing). The
1248 cumulative results of aging and the removal of aerosol constituents are observed. This means that
1249 we observe the aerosol components that are long-lived. Compounds with high O/C ratios are highly
1250 water-soluble and were likely removed during transport. The text has been revised to indicate
1251 cumulative effects are responsible for the observed molecular composition.

1252 We are not aware of other studies with molecular characterization of long range transported free
1253 tropospheric aerosol, thus making it difficult to support our hypothesis with literature citations.
1254 Therefore, all mentions of the low O/C ratio due to fragmentation have been removed from the
1255 main text and our hypothesis is discussed in section "4. Conclusions".

1256 We reworded the sentence (indicated above):

1257 **"These aged aerosol WSOM compounds had an average O/C ratio of ~ 0.45, which is**
1258 **relatively low compared to O/C ratios of other aged aerosol."**

1259 **R3.2)** *I have several questions regarding how the mass spectra of 9/24 and 9/25 are compared:*

1260 **R3.2a)** *Aging The authors use FLEXPART to expect that there is more aging in the 9/25 airmasses*
1261 *(15 days) than the 9/24 airmasses (>12 days). What is the evidence for this from the mass spectra?*
1262 *It is not clear exactly what criteria in the spectra are being used to indicate aging (what are O/C,*
1263 *H/C, DBE, and Carbon number supposed to do in the aging picture that the authors are trying to*
1264 *present?)*

1265 The point of comparing 9/24 and 9/25 samples was to highlight their similarities and differences,
1266 as well as to stress unique features present in each sample. Both samples are highly aged and thus
1267 processed, with the difference being that air masses bringing the aerosol sampled in 9/24 caught
1268 an intense biomass burning plume, while those of 9/25 were more dilute and additionally
1269 underwent a path low in marine boundary layer before arriving at Pico.

1270 The answer on this important clarification was given as a reply to Reviewer 1 in answer **R1.32**.
1271 For the ease of following our response to Reviewer 3, we copied and pasted the relevant parts of
1272 it below.

1273 Yes, the biomass burning plume was observed on both days, but it was much stronger on 9/24.
1274 There seems to be a lingering of the biomass burning pollution through the period starting Sep 24,
1275 2012 to at least Sep 27, 2012 (Fig. 1). However, the observed event with strong pollution plume
1276 started on Sep 25, 2012 ~ 4:00 and lasted until Sep 26, 2012 ~2:00 (on-line measurements in Fig.
1277 1b-d and Fig. 3b-f). Note that another strong pollution event was recorded by all measurements in
1278 June 2012 and corresponding to 6/29 filter sample. However, 6/29 filter sample was collected for
1279 a period much longer (142 hours) than other filter samples, which makes the separation of different
1280 aerosol contributions difficult. Thus, we never analyzed it in details.

1281 We now see this observation may not have been clearly described. Therefore, we added the
1282 following clarification early in the paper, in section “3.2 Characterization of the air masses during
1283 24–26 September 2012” on page 24769 starting in line 10:

1284 **“The event of interest started on September 25 at approximately 4:00 and lasted until the 26**
1285 **at approximately 2:00 (Fig. 1b-d). The observed elevated ...”**

1286 We also rewrote the sentence on page 24770 in lines 14-17 that now reads:

1287 **“Therefore, the air masses arriving at PMO during September 24-26 were influenced by the**
1288 **US biomass burning, while those that arrived during 9/25 were also influenced by the marine**
1289 **boundary layer.”**

1290 **R3.2b)** *Unique Ions In Figure 10, it looks like the differences between the spectra are due to unique*
1291 *ions on 9/24 ions which have higher O/C values and higher carbon numbers than the unique ions*
1292 *on 9/25. I am not clear on how these differences are reflective of aging. The authors also state but*
1293 *don’t provide much information on why the mass >400 amu, that are uniquely intense in the Pico*
1294 *Mtn spectra are really reflective of aging. In fact, if these are unique for this site, it would be*
1295 *interesting to have more description about the likely compositions of these >400 amu ions.*

1296 As noted in our answer to **R3.2a**, the air masses of the 9/25 sample underwent a transport path
1297 through the marine boundary layer. This would increase the amount of aqueous-phase processing

1298 of organic compounds, which in turn would lead to increased removal of highly polar and water-
1299 soluble species across the entire range of carbon number, including higher carbon number
1300 compounds. Therefore, the higher O/C ratio and carbon numbers in 9/24 sample are consistent
1301 with this hypothesis. We did not convey this message clearly in the ACPD manuscript and have
1302 corrected it in final manuscript version, as described in answer **R3.2a**).

1303 **R3.2c) Common Ions** In Figure 10 a and b it looks as though there is a difference in the
1304 distributions and relative intensities of the common ions $<m/z\ 350$ and those $>m/z\ 350$. Does this
1305 difference mean anything with respect to the air mass histories? This should be discussed.

1306 All ions common to both samples are likely a result of the common aerosol source, which are
1307 biomass burning emissions in the North America. There is likely also a small contribution from
1308 the regional/global background aerosol, the proof and separation of which is beyond the scope of
1309 this publication (please see the answer **R1.32** to Reviewer 1 for more details on this point). We
1310 collected Hi-Vols samples at the Pico Mountain Observatory for 24 hours so there was no
1311 optimization to exclude the biomass burning effect. This is confirmed with on-line aerosol
1312 measurement in Fig. 1b-d with a strong event during the 9/24 sample collection and a smaller one
1313 during the 9/25 sample collection and lingering of much smaller events through the end of
1314 September 2012.

1315 We are reluctant to make statements about the relative intensities in the ESI FT-ICR MS spectra.
1316 The reviewer is correct, the relative intensities of the 9/25 sample are indeed approx. half of those
1317 observed in 9/24, which might be a reflection of the differences in organic aerosol loading between
1318 the two samples. Nevertheless, the results of ESI FT-ICR MS analysis are not quantitative. Thus,
1319 we prefer to keep this conclusion to be tested in the future studies.

1320 **R3.3) This work presents O/C and H/C as well as carbon number ranges observed in WSOC from**
1321 **2 different air masses. It would be very helpful if these values were put in context of other previous**
1322 **measurements from different air masses. While the authors mention some comparisons in the text**
1323 **in sections 3.3.2 to 3.3.4, it is hard to quickly get an overview of how the observations at this aged**
1324 **site differ from the other measurements at other sites. For example, what is the difference between**
1325 **this aged site and less aged sites measured in previous campaigns? I recommend the authors**
1326 **present these values as well as values from previous sites (including a brief description of the site**
1327 **type (rural, remote, urban, fresh biomass etc..)) in a table so that it will be easier to compare. Since**
1328 **the authors mention DBE and OM/OC, these would be useful to add to this table as well.**

1329 We thank the reviewer for this comment; it is indeed much easier to follow the discussion with
1330 key results from previously published work tabulated. To address this comment from the reviewer,
1331 we made new Table 3 (below) and inserted it after Table 2 on page 24800.

1332 **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-Pusztta 2004 (KP2004) ²	Aerosol	Rural	0.48	1.40	1.84	7.36	0.37	408	Schmitt-Kopplin et al, 2010
K-Pusztta 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 boundary layer	0.35	1.59	1.67	4.37	0.28	317	Schmitt-Kopplin et al, 2012
North Atlantic Ocean - All ⁴	Aerosol	Marine boundary layer	0.42	1.49	1.74	6.76	0.32	445	Wozniak et al., 2014
North Atlantic Ocean – Aged Marine ⁴	Aerosol	Marine boundary layer	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 & Pinelands, NJ ⁵	Rainwater	Urban impacted	1.02	1.49	2.73	3.24	0.44	220	Altieri et al., 2009ab

1333 Values were calculated:

1334 ¹For each sample presented in Wozniak et al. (2008).

1335 ²For only two samples (KP2004 and KP2005) presented in Schmitt-Kopplin et al. (2010).

1336 ³For only one, marine aerosol, sample presented in Schmitt-Kopplin et al. (2012).

1337 ⁴For all samples (and only one PCA group) presented in Wozniak et al. (2014).

1338 ⁵By combining the negative mode FT-ICR MS data available in Altieri et al., 2009a (CHO, CHOS and CHNOS) and Altieri et al.,

1339 2009b (CHON).

1340 **R3.4)** *The DBE values are mentioned, but what is the connection between DBE and oxidation. In*
1341 *the situations where DBEs increase and H/C values go down, couldn't this be reflective of either*
1342 *increased aromaticity OR increased addition of oxygen? Is there a correlation between O/C and*
1343 *and DBEs for this data? The authors mention aromaticity index, but don't really use it or report*
1344 *values throughout most of the manuscript text. The authors mention that DBE increases with*
1345 *aging. Is aging known to add C-C double bonds? If so, authors should reference and should clarify*
1346 *how/why DBEs increase with aging.*

1347 This comment was partially addressed in our reply to Reviewer 1 in the answer to **R1.6g**. For the
1348 ease of following our response to Reviewer 3, we copied and pasted the same answer below.

1349 The idea of a decrease in H/C and increase in DBE value with increased aging was shown to be a
1350 consequence of chemical processing of organic aerosol as they age for a large number of Aerodyne
1351 Aerosol Mass Spectrometer (AMS) data sets as presented in Heald et al., 2010 (please see van
1352 Krevelen diagram in Fig. 2 of Heald et al. (2010) for an overview) and further corroborated in Ng
1353 et al., 2011 (please see parameterization in Fig. 2 as well as van Krevelen diagram in Fig. 4 of Ng
1354 et al. (2011) for an overview). For species consisting only of C, H and O atoms, the work of Heald
1355 et al. (2010) has shown that addition of oxygen to a molecule during chemical processing (a.k.a.
1356 aging) on average increases an O/C ratio and decreases H/C one. E.g., the OH radical oxidation of
1357 an organic molecule R-CH₂-R' could produce R-(C=O)-R' species and thus increase DBE,
1358 consistent with an increase of DBE values on a molecular level. Note that no molecular level
1359 information is available from AMS data as presented in the above mentioned studies.

1360 It is indeed true that in theory an increase in the DBE and decrease in H/C ratio could also be
1361 reflective of increased aromaticity. However, the formation of aromatic rings in organic aerosol
1362 molecules requires a lot of energy which is known to be present in combustion processes such as
1363 biomass burning that form molecules consisting of numerous aromatic rings (e.g., polycyclic
1364 aromatic hydrocarbons and soot) (Finlayson-Pitts and Pitts, 2000). It is unlikely that aromatic rings
1365 would continue forming during > 12 days long range transport; on the contrary, atmospheric
1366 oxidation due to aging would probably continually decrease aromaticity of organic aerosol
1367 compounds (Bloss et al., 2005; Ng et al., 2007). As stated above and presented in the manuscript,
1368 we acknowledge the possibility that aromatic species such as lignin and their oxidation products
1369 might have been present in wildfires biomass burning emissions. These types of compounds could
1370 be resistant to chemical transformations of the long range transported aerosol.

1371 Nevertheless, from the presented AI values, we observed the fraction of aromatic species in the
1372 Pico WSOM data to be very small (Table 2). Likewise, the results of doing DBE/C analysis show
1373 ~95% of detected species does not have aromatic character (please see **R2.14** in our response to
1374 Reviewer 2 for more details). Finally, there is no evidence of numerous aromatic compounds in
1375 van Krevelen diagram, such as ones detected in the study of Zhao et al. (2013), which would have
1376 high DBE values accompanied by low O/C ratio and an H/C ratio of approximately 1.

1377 **R3.5)** *The WSOC shown in this manuscript generally have high carbon numbers. Most biogenic*
1378 *VOCs have carbon numbers on the low end of the carbon numbers of WSOC species reported in*
1379 *this paper. They point out that the WSOC ions at m/z >400 amu here are unique and likely reflect*
1380 *aging processes during long range transport. When the authors mention aging, it is not clear*
1381 *whether the authors are suggesting that the large carbon numbers observed here a result of*
1382 *heterogeneous oligomer forming reactions from small carbon number precursors OR do they*

1383 *reflect SOA formation from large carbon number precursors? How different in age are the*
1384 *airmasses observed here compared to those observed in other studies? Can the authors provide*
1385 *some information on how much of the large carbon number distribution is affected by clusters*
1386 *form during electrospray rather than oligomers?*

1387 As reviewer suggests, biogenic VOC are small organic molecules and we believe the vast majority
1388 of the sampled Pico aerosol was emitted from biomass burning which has a complex composition.
1389 For example, biomass burning aerosol sampled during controlled experiments were found to be
1390 composed of numerous highly oxidized, high molecular weight species (Smith et al., 2009).
1391 Furthermore, oxidation reactions of biomass burning, water-soluble species were found to produce
1392 oligomers with molecular weights up to ~2000 (Holmes and Petrucci, 2006). Mechanism involving
1393 aqueous-phase oxidation of biomass burning compounds leading to the formation of oligomers is
1394 likely to produce high molecular weight species observed in this study. To stress this, we added
1395 the following sentence (**bolded**) to section 4. “Conclusions” on page 24786 in line 15:

1396 “... processed aerosol. **High molecular weight species unique for this study are likely**
1397 **oligomers produced by mechanisms involving aqueous-phase oxidation of biomass burning**
1398 **species, as previously observed in laboratory studies (Holmes and Petrucci, 2006; Sun et al.,**
1399 **2010).”**

1400 The air masses observed here are much older than those observed in previous studies of ESI FT-
1401 ICR MS, which makes Pico dataset unique. At the same time, this limits our capability to compare
1402 our samples to similar datasets.

1403 Finally, we do not believe the formation of clusters during electrospray affected the results of the
1404 ESI FT-ICR MS analysis. Clusters formation was not observed in previous measurements with the
1405 same sample preparation and ESI FT-ICR MS instrumental parameters. Note that concentrations
1406 of Pico aerosol are much lower than from other studies, and cluster formation increases with
1407 concentration.

1408 **R3.6)** *Words with two ffs next to each other print the two ffs with different font. Equations 5-8*
1409 *printed out with the letter P randomly placed within each equation.*

1410 We could not address this comment, as we did not encounter this problem when we printed out
1411 both versions of the manuscript.

1412 *Other comments*

1413 **R3.7)** *Title: The manuscript actually compares two different airmasses and doesn't focus only on*
1414 *the biomass burning plume so perhaps title should be changed to reflect this.*

1415 The air masses bringing the aerosol sampled in 9/24 and 9/25 are not completely different and the
1416 differences are subtle, as evident from large fraction of common molecular species detected in the
1417 two samples. Nevertheless, the reviewer has a point that aerosol collected in 9/24 was influenced
1418 by a more intense biomass burning plume.

1419 This comment was also addressed as our reply to Reviewer 2 in answer **R2.I** (first comment). For
1420 convenience, we copied and pasted the same answer below.

1421 We agree with the reviewer that only one intense biomass burning plume was observed on these
1422 two days. Thus, we modified the title to reflect this:

1423 **“Molecular characterization of free tropospheric aerosol collected at the Pico Mountain**
1424 **Observatory: A case study with a long range transported biomass burning plume”.**

1425 *R3.8) Section 3.2. It would be easier if the knowledge about the distinct sources (biomass burning*
1426 *influenced and marine influenced) was presented right away after the definition of the time*
1427 *periods. Then the rest of the observations in this section can be used to support why the airmasses*
1428 *are identified as they are.*

1429 Section “3.2 Characterization of the air masses during 24–26 September 2012” presents the history
1430 of air masses through FLEXPART analysis as well as observed wildfire activity during the
1431 September 2012. Furthermore, we show the results of the collocated measurements as additional
1432 evidence of the differences between the intercepted air masses. We believe that the conclusion
1433 about their somewhat different source influences is drawn after this presentation, and prefer to
1434 keep it as it is.

1435 *R3.9) Section 3.2.1. I see that the absolute concentrations of the VOCs could reflect relative*
1436 *pollution of the two different airmasses, but isn’t clear what new information is offered by the*
1437 *ethane/propane ratios.*

1438 This comment was addressed as a reply to Reviewer 1 in the answer to **R1.8a**. For convenience,
1439 we copied and pasted the same answer below.

1440 We added the explanation about why ethane and propane, as well as their ratio, matter. The
1441 revisions to the ACPD manuscript are described below.

1442 -We added the description (**bolded**) of the importance of ethane and propane as pollution tracers
1443 to section “1. Introduction” on page 24759 in line 5:

1444 “... (Honrath et al., 2008). **Previous research at PMO has shown several-fold increases of**
1445 **NMHC in anthropogenic and biomass burning plumes. Furthermore, it has been**
1446 **demonstrated that isoprene and ratios of selected NMHC pairs have characteristic**
1447 **signatures that were used for identification of upslope flow conditions (Kleissl et al., 2006)**
1448 **and pollution plume characterization (Helmig et al., 2008).”**

1449 -We added the description further elaborating the importance of NMHC measurements and
1450 $\ln[(\text{propane})/(\text{ethane})]$ ratio at the opening of section “3.2.1 Non-methane hydrocarbon
1451 measurements” on page 24770 in lines 25-28:

1452 **“NMHC have been widely used as tracers for anthropogenic and biomass burning**
1453 **emissions (Helmig et al., 2008). Due to their different oxidation rates, mole fractions of**
1454 **different NMHC exponentially decline at different rates during atmospheric transport**
1455 **allowing the natural log of $\text{NMHC}_1/\text{NMHC}_2$ (e.g., $\ln([\text{propane}]/[\text{ethane}])$) to be used as a**
1456 **linear measure of photooxidation and transport time. $\ln([\text{propane}]/[\text{ethane}])$ has been**
1457 **demonstrated to be a sensitive indicator for identifying pollution signatures and transport**
1458 **time to PMO (Helmig et al., 2008, 2015).”**

1459 **R3.10)** Page 24778, line 14-28. *If there is ion signal everywhere, how do the authors know that*
1460 *the ions being presented are actually from biomass burning products and not isobars? Is there*
1461 *some pattern or diagnostic from this or previous studies that the authors are using to confirm the*
1462 *identity of these ions?*

1463 The ions were measured using ultrahigh resolution mass spectrometry. From these accurate mass
1464 measurements, molecular formulas are determined using sophisticated algorithms. The most likely
1465 source of the aerosol organic matter is the wildfires in North America as indicated by Figs. 2, S3-
1466 S5. To our knowledge, no other study of free tropospheric long range transported aerosol has been
1467 reported. The Pico Mountain Observatory often intercepts polluted air masses from North America
1468 and the primary source of an increase in measured gas- and particle-phase compounds is often
1469 biomass burning (e.g., Lapina et al., 2006; Val Martin et al., 2006, 2008a; Fialho et al., 2005,
1470 2006).

1471 We cannot be certain if any of the identified biomass burning markers are the suggested molecules.
1472 We would need additional information about their molecular structure and functionalization that
1473 is not available with the analysis presented in this work.

1474 Nevertheless, the evidence of the air masses source presented in the manuscript gives the strong
1475 indication of biomass burning aerosol. As Reviewer 1 pointed out, by proving that biomass burning
1476 emissions were the source of aerosol measured during the pollution event, we can deduce that the
1477 obtained data are representative of biomass burning aerosol. Please see an answer R1.6a to
1478 Reviewer 1 for more details.

1479 **R3.11)** Section 3.3.3. *How do the authors know whether the N containing species are nitrates or*
1480 *amines? Do the CHNO ion formulas allow for unique identification of one vs. the other?*

1481 A key indicator that CHNO compounds are nitrates is the oxygen number. Additionally, the data
1482 presented here were analyzed by the negative mode ESI FT-ICR MS, which produces negative
1483 molecular ions ($[M+H]^-$) and is thus well suited for the ionization of acidic species such as e.g.,
1484 nitrates and carboxylic acids. On the other hand, positive mode ESI produces positive ions
1485 ($[M+H]^+$ or $[M+Na]^+$) and ionizes only the molecules with a high proton affinity (and Na^+ binding
1486 energy) such as compounds containing amino groups. Therefore, it is unlikely amines will be
1487 produced by negative mode ESI used in this work.

1488 **R3.12)** Page 24780, Line 27-28. *How does unsaturation reflect long range transport related*
1489 *aging? Is the increase in observed unsaturation due to increase in heteroatoms or due to increase*
1490 *in C=C double bonds? What do the authors use to distinguish between these two options?*

1491 This comment was addressed in a reply to Reviewer 1 in **R1.6k**. For convenience, we copied and
1492 pasted the same answer below.

1493 We deleted the second part of the sentence mentioned by the reviewer on page 24780 in lines 24-
1494 29, in an effort to concentrate the “Big Picture” discussion on chemical composition of Pico
1495 samples to section “4. Conclusions”.

1496 “... studies, ~~confirming the unsaturation feature of the aerosol after long range transport and~~
1497 ~~the same emission source regions and transformational processes of CHO and CHNO group~~
1498 ~~species.~~“

1499 Additionally, please refer to an answer **R3.4** above in which we addressed the connection between
1500 the molecular saturation and aging.

1501 **R3.13)** Page 24781, Line 7. In Figure S9, please state the difference between N1 and N2 in the
1502 figure legend.

1503 We changed the caption of this figure to state the difference between N₁ and N₂ by the following
1504 insertion (**bolded**) (note that the number of Fig. S9 of the ACPD manuscript was changed to Fig.
1505 10S):

1506 “Sum of the relative abundance vs. number of oxygen atoms for CHNO compounds **with one and**
1507 **two N atoms (N₁ and N₂)** in the 9/24 (a) and 9/25 (b) WSOM samples.”

1508 Similarly, we changed the caption of Fig. S10 of the ACPD manuscript (Fig. S11 in the revised
1509 manuscript) to explicitly state the number of S atoms in S₁ CHOS compounds as one.

1510 **R3.14)** Figure 5b and Figure 7c. What are the strong ions that dominate the signal between 200-
1511 300 amu?. These ions are not strong in Figure 5a. Do the authors have any insight into what these
1512 ions are? It would be good to at least mention their formulas.

1513 We believe the reviewer is referring here to the feature of strong ions between *m/z* 200-300 in MS
1514 of 9/25 sample (Fig. 5e). These strong ions are composed of C, H and O atoms and mainly have 4
1515 oxygen atoms. They do not form particular homologous series, although we did detect one small
1516 C₁₁H₁₈(CH₂)₁₋₃O₄ one. With oxygenation and saturation lower than other CHO class compounds
1517 detected in this study (with average values and standard deviation being O/C = 0.30 ± 0.08, H/C =
1518 1.49 ± 0.26, DBE = 4.15 ± 1.34 and DBE/C = 0.33 ± 0.14), the enhancement of these species in
1519 9/25 sample over 9/24 one might be an additional indication of marine aerosol contribution to 9/25.
1520 We briefly summarize this by inserting additional text in the comparison of two samples on page
1521 24785 in line 8:

1522 “An enhancement of several common ions between *m/z* 200-300 was observed in 9/25 (Fig.
1523 10c). These strong CHO and one CHOS ions have the following molecular formulas:
1524 C₁₁H₁₀O₄, C₁₀H₁₀(CH₂)₁₋₂O₄, C₁₂H₂₀(CH₂)₁₋₂O₂, C₁₂H₂₀O₃, C₁₁H₁₈(CH₂)₁₋₂O₄, C₁₂H₁₈(CH₂)₁₋
1525 ₃O₄, C₁₂H₁₈(CH₂)₁₋₂O₄ and C₁₂H₂₆O₄S. With lower oxygenation and higher saturation than
1526 other CHO compounds detected in this study (their average values ± standard deviation were
1527 O/C = 0.30 ± 0.08, H/C = 1.49 ± 0.26, DBE = 4.15 ± 1.34 and DBE/C = 0.33 ± 0.14), the
1528 enhancement of these species in 9/25 over 9/24 might be an additional indication of species
1529 such as fatty acids and thus marine aerosol contribution to 9/25.”

1530 **R3.15)** Figure 6e. Line iii shows decreasing O:C and decreasing H:C and is attributed to
1531 functionalization (alkylation) or fragmentation (line 23, page 24775). I don't understand how this
1532 can be. fragmentation would increase O:C and decrease H:C. I would also think that alkylation
1533 would increase H:C and decrease O:C.

1534 We did not intend to interpret the changes in elemental ratios in the subset of van Krevelen diagram
1535 shown in Fig. 6e of the ACPD manuscript as definite claims of chemical processes. Rather, we
1536 intended to highlight the different series of compounds present in van Krevelen diagram and give
1537 examples of likely processes. The arrows at one side of selected lines do not indicate chemical
1538 process. To address reviewers' comment and avoid ambiguity, we deleted the arrow from each
1539 line.

1540 Fragmentation might increase or decrease O/C and H/C ratios, depending on the size and
1541 composition of fragmented part of the molecule. The reviewer is correct with respect to the
1542 alkylation, and to address this comment we removed this mention of alkylation on page 24775 in
1543 line 24 by deleting “(i.e., alkylation in this diagram)”.

1544 Finally, all middle panels of Fig. 6 including Fig. 6e have been removed from the main text and
1545 moved to the Supplement as an answer to the comment **R2.13b** to Reviewer 2.

1546

1547 **Additional References to the Response to the Anonymous Reviewer #3:**

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