

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

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

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

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 ***R1.2b) 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 ***R1.3) 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 **R1.4)** *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 **R1.5)** *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 **R1.6a)** *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 ***R1.6b) 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 ***R1.6c) 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 ***R1.6d) 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 suwannee 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 ***R1.6e) 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 ***R1.6f) Page 24776 Line3-5: 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 constraints 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; Helming 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 **R1.10)** *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 **R1.11)** *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 **R1.12)** *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 **R1.13a)** *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 **R1.13b)** *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 **R1.14)** *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 **R1.15)** *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 **R1.16)** *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 **R1.1**. 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 **R1.17)** *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 **R1.18)** *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 **R1.19)** *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 **R1.20) 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 **R1.21) Page 24755 line 11: delete “with an”**

458 Done.

459 **R1.22) 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 **R1.23) 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 **R1.24) Page 24767 line 17: delete “during 2012”**

474 Done.

475 **R1.25) 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 **R1.26)** *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 **R1.27)** *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 **R1.28)** *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 **R1.29)** *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 **R1.30)** *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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