

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 #3***

49

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

59 *Main Comments*

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

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

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

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

83 We reworded the sentence (indicated above):

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

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

87 **R3.2a)** *Aging The authors use FLEXPART to expect that there is more aging in the 9/25 airmasses*
88 *(15 days) than the 9/24 airmasses (>12 days). What is the evidence for this from the mass spectra?*
89 *It is not clear exactly what criteria in the spectra are being used to indicate aging (what are O/C,*
90 *H/C, DBE, and Carbon number supposed to do in the aging picture that the authors are trying to*
91 *present?)*

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

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

100 Yes, the biomass burning plume was observed on both days, but it was much stronger on 9/24.
101 There seems to be a lingering of the biomass burning pollution through the period starting Sep 24,
102 2012 to at least Sep 27, 2012 (Fig. 1). However, the observed event with strong pollution plume
103 started on Sep 25, 2012 ~ 4:00 and lasted until Sep 26, 2012 ~2:00 (on-line measurements in Fig.
104 1b-d and Fig. 3b-f). Note that another strong pollution event was recorded by all measurements in
105 June 2012 and corresponding to 6/29 filter sample. However, 6/29 filter sample was collected for
106 a period much longer (142 hours) than other filter samples, which makes the separation of different
107 aerosol contributions difficult. Thus, we never analyzed it in details.

108 We now see this observation may not have been clearly described. Therefore, we added the
109 following clarification early in the paper, in section “3.2 Characterization of the air masses during
110 24–26 September 2012” on page 24769 starting in line 10:

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

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

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

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

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

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

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

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

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

147 **R3.3) This work presents O/C and H/C as well as carbon number ranges observed in WSOC from**
148 **2 different airmasses. It would be very helpful if these values were put in context of other previous**
149 **measurements from different airmasses. While the authors mention some comparisons in the text**
150 **in sections 3.3.2 to 3.3.4, it is hard to quickly get an overview of how the observations at this aged**
151 **site differ from the other measurements at other sites. For example, what is the difference between**
152 **this aged site and less aged sites measured in previous campaigns? I recommend the authors**
153 **present these values as well as values from previous sites (including a brief description of the site**
154 **type (rural, remote, urban, fresh biomass etc..)) in a table so that it will be easier to compare. Since**
155 **the authors mention DBE and OM/OC, these would be useful to add to this table as well.**

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

159 **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

160 Values were calculated:

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

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

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

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

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

166 2009b (CHON).

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

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

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

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

198 Nevertheless, from the presented AI values, we observed the fraction of aromatic species in the
199 Pico WSOM data to be very small (Table 2). Likewise, the results of doing DBE/C analysis show
200 ~95% of detected species does not have aromatic character (please see **R2.14** in our response to
201 Reviewer 2 for more details). Finally, there is no evidence of numerous aromatic compounds in
202 van Krevelen diagram, such as ones detected in the study of Zhao et al. (2013), which would have
203 high DBE values accompanied by low O/C ratio and an H/C ratio of approximately 1.

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

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

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

223 “... processed aerosol. **High molecular weight species unique for this study are likely**
224 **oligomers produced by mechanisms involving aqueous-phase oxidation of biomass burning**
225 **species, as previously observed in laboratory studies (Holmes and Petrucci, 2006; Sun et al.,**
226 **2010).”**

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

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

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

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

239 *Other comments*

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

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

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

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

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

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

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

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

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

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

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

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

276 -We added the description further elaborating the importance of NMHC measurements and
277 $\ln[(\text{propane})/(\text{ethane})]$ ratio at the opening of section “3.2.1 Non-methane hydrocarbon
278 measurements” on page 24770 in lines 25-28:

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

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

290 The ions were measured using ultrahigh resolution mass spectrometry. From these accurate mass
291 measurements, molecular formulas are determined using sophisticated algorithms. The most likely
292 source of the aerosol organic matter is the wildfires in North America as indicated by Figs. 2, S3-
293 S5. To our knowledge, no other study of free tropospheric long range transported aerosol has been
294 reported. The Pico Mountain Observatory often intercepts polluted air masses from North America
295 and the primary source of an increase in measured gas- and particle-phase compounds is often
296 biomass burning (e.g., Lapina et al., 2006; Val Martin et al., 2006, 2008a; Fialho et al., 2005,
297 2006).

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

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

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

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

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

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

320 We deleted the second part of the sentence mentioned by the reviewer on page 24780 in lines 24-
321 29, in an effort to concentrate the “Big Picture” discussion on chemical composition of Pico
322 samples to section “4. Conclusions”.

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

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

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

330 We changed the caption of this figure to state the difference between N₁ and N₂ by the following
331 insertion (**bolded**) (note that the number of Fig. S9 of the ACPD manuscript was changed to Fig.
332 10S):

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

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

337 **R3.14)** Figure 5b and Figure 7c. What are the strong ions that dominate the signal between 200-
338 300 amu?. These ions are not strong in Figure 5a. Do the authors have any insight into what these
339 ions are? It would be good to at least mention their formulas.

340 We believe the reviewer is referring here to the feature of strong ions between *m/z* 200-300 in MS
341 of 9/25 sample (Fig. 5e). These strong ions are composed of C, H and O atoms and mainly have 4
342 oxygen atoms. They do not form particular homologous series, although we did detect one small
343 C₁₁H₁₈(CH₂)₁₋₃O₄ one. With oxygenation and saturation lower than other CHO class compounds
344 detected in this study (with average values and standard deviation being O/C = 0.30 ± 0.08, H/C =
345 1.49 ± 0.26, DBE = 4.15 ± 1.34 and DBE/C = 0.33 ± 0.14), the enhancement of these species in
346 9/25 sample over 9/24 one might be an additional indication of marine aerosol contribution to 9/25.
347 We briefly summarize this by inserting additional text in the comparison of two samples on page
348 24785 in line 8:

349 “**An enhancement of several common ions between *m/z* 200-300 was observed in 9/25 (Fig.**
350 **10c). These strong CHO and one CHOS ions have the following molecular formulas:**
351 **C₁₁H₁₀O₄, C₁₀H₁₀(CH₂)₁₋₂O₄, C₁₂H₂₀(CH₂)₁₋₂O₂, C₁₂H₂₀O₃, C₁₁H₁₈(CH₂)₁₋₂O₄, C₁₂H₁₈(CH₂)₁₋
352 **3O₄, C₁₂H₁₈(CH₂)₁₋₂O₄ and C₁₂H₂₆O₄S. With lower oxygenation and higher saturation than**
353 **other CHO compounds detected in this study (their average values ± standard deviation were**
354 **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**
355 **enhancement of these species in 9/25 over 9/24 might be an additional indication of species**
356 **such as fatty acids and thus marine aerosol contribution to 9/25.”****

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

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

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

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

373

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

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