

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

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.

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

49

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

64 *Detailed Comments:*

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

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

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

72 **R2.II) Methods:**

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

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

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

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

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

85 “Samples were analyzed for NO_3^- , SO_4^{2-} and Cl^- with ion chromatography (ICS-2000 ion
86 chromatograph with an IonPac AS11 separator column (Dionex Corporation, Bannockburn,
87 IL, USA)).”

88 To accompany this change, we also deleted the following sentence on page 24762 in lines 3-4:
89 “ ~~NO_3^- , SO_4^{2-} and Cl^- only were present at concentrations above the detection limit.~~”

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

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

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

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

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

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

109 As suggested, we added the description of all gas-phase measurements to the methods section by
110 inserting a new section “2.3 Gas-phase measurements at the Pico Mountain Observatory” to page
111 24767 in line 1:

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

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

121 **R2.2b)** The SEM analysis was already described in the ACPD manuscript on page 24761 in lines
122 8-14 as the last paragraph of the section “2.1 Aerosol measurements at the Pico Mountain
123 Observatory”. Nevertheless, to address the reviewers’ concerns and improve the description of the
124 SEM analysis, we did the following two modifications: i) we made a new section “2.2.3 Single

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

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

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

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

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

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

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

163
$$\text{Kendrick mass} = \text{IUPAC mass} * \frac{14}{14.01565} \quad (1)$$

164
$$\text{Kendrick mass defect} = \text{nominal Kendrick mass} - \text{exact Kendrick mass} \quad (2)$$

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

169 **R2.4b)** *Equation 2, the Kendrick Mass Defect is calculated by subtracting the nominal Kendrick*
170 *Mass from the Kendrick Mass (not vice versa): KMD = KM – Nominal Kendrick Mass*

171 Please see the answer **R2.4a** above. Briefly, our KMD formula is consistent with Hughey et al.
172 (2001). Therefore, we left Equation 2 as it is in the ACPD manuscript. Note that this equation has
173 been moved to the Supplement.

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

176 $AI = DBEAI/CAI = (1 + c - o - s - 0.5 * h)/(c - o - s - n)$

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

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

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

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

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

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

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

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

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

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

223 **“The OM/OC ratio of 1.8 adopted in our analysis is slightly higher than the OM/OC ratio of
224 ~1.7 (Table 2) calculated from FT-ICR MS analysis of WSOM elemental compositions
225 (Mazzoleni et al., 2010). The measured value of 1.7 is expected to be lower than the total,
226 because of the low sample recovery of highly oxygenated, low molecular weight species
227 (Hallar et al. 2013).”**

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

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

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

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

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

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

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

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

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

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

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

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

270 -We added the description further elaborating the importance of NMHC measurements and
271 $\ln[(\text{propane})/(\text{ethane})]$ ratio at the opening of section “3.2.1 Non-methane hydrocarbon
272 measurements” on page 24770 in lines 25-28:

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

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

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

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

286 **“Representative SEM images of particles collected on 9/24 (a) and 9/25 (b). Also shown are
287 examples of spherical (43% and 18% in 9/24 and 9/25, respectively) (c), near spherical
288 particles (23% and 29% in 9/24 and 9/25, respectively) (d), and embedded soot particles
289 (46% and 17% in 9/24 and 9/25, respectively) (e-h).”**

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

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

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

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

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

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

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

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

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

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

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

340 **“Due to the presence ... and $(CH_2)_{1,2,5,7}C_7H_{16}SO_4$, respectively.”**

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

342 **“Molecular assignments in ... and iii) functionalization or fragmentation.”**

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

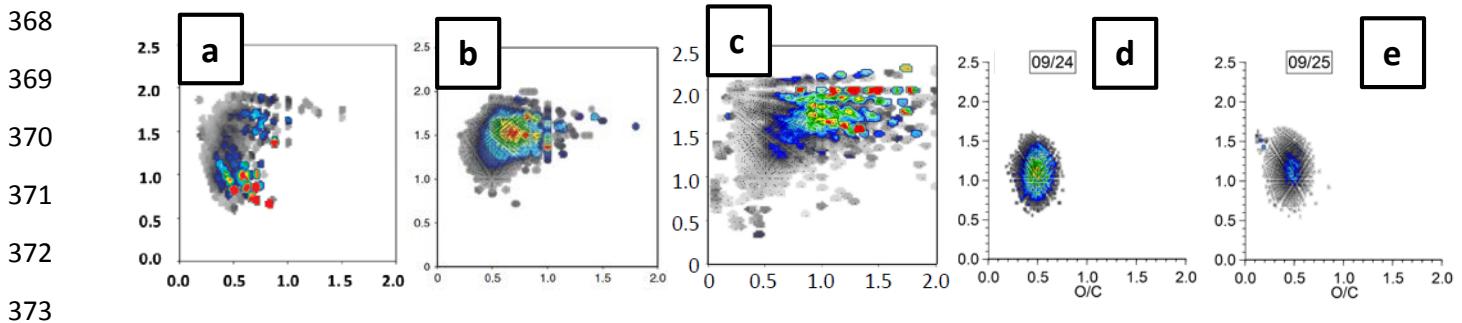
344 **“Numerous homologous series ... and $C_{16}H_{14}NO_{11}(CH_2)_n$.”**

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

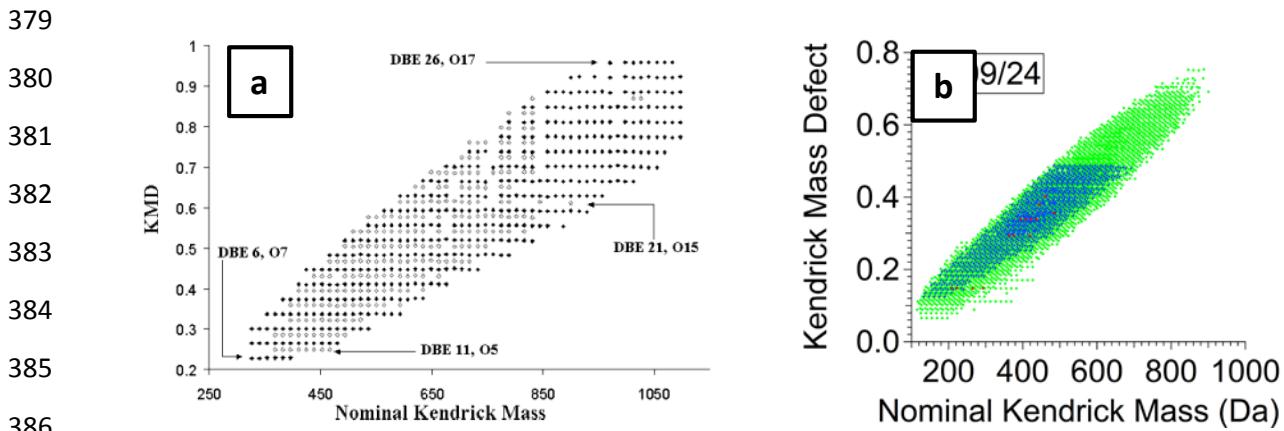
346 **R2.13c)** *Additionally, descriptions of Kendrick plots as, for example, “narrow and uniform” (e.g.,*
347 *page 24774, line 28) are vague and do not have particular value unless they are linked to specific*
348 *molecular components which one cannot tell from the Kendrick plots themselves. Backing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

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

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



374 Figure R2.F1: Comparison of van Krevelen diagrams (H/C vs. O/C) for molecular assignments in
 375 CHNO group for Mazzoleni et al., 2010 (a), Mazzoleni et al., 2012 (b), Zhao et al., 2013 (c) and
 376 9/24 (d) and 9/25 (e) samples presented in this study. Figures were copied from the original papers
 377 and thus axis do not have same dimensions and some are a bit foggy; however, all panels have the
 378 same range of x- and y-axis.



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

389

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

393 - Mention of narrow and uniform distribution in Kendrick plot in sentence on page 24774 in line
 394 28 has been quantified by adding a sentence (**bolded**) preceding it:

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

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

400 - Mention of narrow and homogeneous distribution in van Krevelen diagram in sentence on page
401 24775 in lines 16-17 has already been quantified by the sentence after it (underlined):

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

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

409 “The distribution of elemental ratios for the CHO molecular assignments in this study was similar
410 to the aerosol reported by Mazzoleni et al. (2012) and narrower than the cloud water values
411 reported by Zhao et al. (2013), both of which were measured at the Storm Peak Laboratory. **This**
412 **is consistent with the observed lower average values of O/C and H/C in this study (~0.44 and**
413 **1.22) compared to that of Mazzoleni et al. (2012) (0.47 and 1.42) and Zhao et al. (2013) (0.54**
414 **and ~1.42).**”

415 - Finally, we replaced three mentions of “tight distribution” with “narrow distribution” (page
416 24779 in line 8, page 24782 in line 4 and page 24782 in line 22). We hope that by quantifying
417 narrow distribution several times prior to page 24779, we convinced interested readers of its
418 validity. Therefore, we offer no quantification the last three times we mention “narrow
419 distribution”.

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

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

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

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

437 detailed explanation is in the Supplement). The average DBE/C values of CHO group for
438 9/24 and 9/25 were 0.46 and 0.41 (Table 2), confirming the lower degree of saturation
439 compared to Mazzoleni et al. (2012) and Zhao et al. (2013) (DBE/C_{CHO} = 0.37 and 0.35).
440 However, nearly all of the CHO molecular assignments were below the aromaticity criteria
441 of DBE/C ≥ 0.7 (95% and 97% for 9/24 and 9/25), indicating an overall lack of aromaticity.
442 The CHO species ...”

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

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

447
$$DBE/C = \frac{DBE(C_cH_hN_nO_oS_s)}{c(C_cH_hN_nO_oS_s)} \quad (4)$$

448 Hockaday et al. (2006) introduced DBE/C as a criterion for identifying molecular species
449 with condensed aromatic ring structures. The value of DBE/C ≥ 0.7 is a threshold for
450 molecular assignments with fused-ring structures, and thus a proxy for combustion derived
451 species and their degradation products (Hockaday et al., 2006).

452
$$DBE/C_w = \frac{\sum w_i * DBE_i}{\sum w_i * c_i} \quad (10)''$$

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

454 “... 10.3 and 9.8, and DBE/C ones of 0.51 and 0.49 (Table 2), with nearly all molecular
455 formula with DBE/C below the aromaticity criteria of 0.7 (92% and 94%).”

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

537 **R2.20)** *The literature is full of marine aerosol or rainwater WSOM studies that have examined the
538 molecular composition. These studies can be compared to the present study to confirm marine
539 sources to the 9/25 sample or to delineate differences between the Pico samples (collected in the
540 middle of the ocean) and these other marine aerosols. See, for example, Altieri et al., 2012; Cavalli
541 et al., 2004; Decesari et al., 2011; Ovadnevaite et al., 2014; Russell et al., 2010; Wozniak et al.,
542 2014.*

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

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

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

549 “...2013). **Non-sea-salt sulfate species in marine aerosol have previously been found and**
550 **attributed to the degradation of marine primary emissions (e.g. Cavalli et al., 2004).**
551 **Furthermore, the degradation products of marine flora such as methanesulfonic acid have**
552 **been shown to peak in summer months and produce aliphatic organic species with low**
553 **oxygenation (Cavalli et al., 2004; Ovadnevaite et al., 2014).** Nevertheless, ...”

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

555 “... aging. **Recent study of aerosol collected on a research vessel in the North Atlantic Ocean**
556 **detected 246 CHOS species in aged marine aerosol, a number of CHOS species comparable**
557 **to our study (Wozniak et al., 2014; “Aged marine” PCA group from their study is given in**
558 **Table 3).** Consistent with Claeys et al. (2010), Wozniak et al. (2014) attributed the observed
559 **CHOS species to organosulfate markers of marine aerosol degradation albeit with longer**
560 **carbon chains. The CHOS species reported in Wozniak et al. (2014) have similar chemical**
561 **characteristics to those reported here (magnitude-weighted average O/C = 0.36 and H/C =**
562 **1.57).**”

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

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

567 This sentence has been removed.

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

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

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

584 fragmentation, and thus is ideal for coupling with FT-ICR MS for detailed molecular level
585 OA characterization (Nizkorodov et al., 2011). Negative mode ESI is especially useful for the
586 ionization of multifunctional oxidized compounds such as carboxyl groups. FT-ICR MS was
587 successfully used for the analysis of ambient OA (Wozniak et al., 2008; Schmitt-Kopplin et
588 al., 2010; Mazzoleni et al., 2012), dissolved organic matter in rain (Altieri et al., 2009a, 2009b,
589 2012; Mead et al., 2013; Zhao et al., 2013), fog water (Mazzoleni et al., 2010) and sea spray
590 aerosol (Schmitt-Kopplin et al., 2012)."

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

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

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

605 - The importance of the long range transported aerosol was strengthen and moved to the first
606 paragraph of section "1. Introduction" on page 24756 in line 23:

607 "... (Zhang et al., 2007). **Highly aged and processed long range transported ambient aerosol**
608 **are of particular interest and have chemical compositions characteristic of global aerosol**
609 **(Ramanathan et al., 2001). The long range transport of aerosol from Asia to North America**
610 **has received considerable attention (Ramanathan et al. 2001, 2007; Dunlea et al., 2009), but**
611 **less attention has been placed on aerosol transported from North America to Europe.**
612 **Ambient ...”**

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

616 "Until 2010, the only type of aerosol measured at the PMO was black carbon. Fialho et al.
617 (2005, 2006) developed a method to determine the contribution of black carbon (BC) and
618 dust from multiwavelength aethelometer measurements. Although typically average free
619 tropospheric aerosol concentrations are low, the long range transport events bring elevated
620 levels of BC and dust mass concentrations to PMO. To study these events, new on- and off-
621 line aerosol instrumentation was installed in 2012, as described below."

622 **R2.24)** *Page 24763, line 23-24: The sentence beginning "the aim of data processing..." is not
623 necessary.*

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

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

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

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

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

639 Finally, we did not present a detailed comparison of Methods A and B in the results and discussion.
640 Rather, we mentioned basic statistics of molecular formula assignments from both Methods A and
641 B in section “3.3.1 Mass spectra and molecular formula assignments” on page 24773 in lines 5-
642 12.

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

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

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

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

649 **References:**

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

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

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

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

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

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

656 Russell *et al.*, 2010; *PNAS*, 107, 6652-6657.
657 Wozniak *et al.*, 2014; *Atmos. Chem. Phys.* 14, 8419-8434.
658 Yassine *et al.*, 2014; *Rapid Commun. Mass Spec.* 28, 1-10.
659

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

661 Bateman, A. P., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Photolytic processing of secondary
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666 *Methods*, 6, 230–235, 2008.

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675