

1 **Response to reviewers for “Secondary organic aerosol formation from in situ OH, O₃, and NO₃**
2 **oxidation of ambient pine forest air in an oxidation flow reactor.”**

3 **B. B. Palm, J. L. Jimenez, et al.**

4 We thank the reviewers for their comments on our paper. To facilitate the review process we have
5 copied the reviewer comments in black text. Our responses are in regular blue font. We have responded
6 to all the referee comments and made alterations to our paper (in bold text).

7 **Anonymous Referee #1**

8 Overview

9 R1.0. This well-written and impressive manuscript summarizes oxidation flow reactor (OFR) experiments
10 aimed at studying in situ SOA formation from ambient pine forest air during the BEACHON-ROMBAS
11 campaign after oxidation by OH, O₃, and NO₃ radicals. Since SOA formation was measured semi-
12 continuously during this study, the authors were able to capture diurnal and daily changes. More SOA
13 was formed from precursors present in nighttime air than in the daytime air for all 3 oxidations.
14 Interestingly, OH oxidation produced ~ 4 times more SOA than NO₃ and O₃ oxidation at all times of day.
15 O:C and H:C ratios of the SOA formed by O₃, NO₃ and several eq. hours of OH oxidation yielded similar
16 oxidation levels of ambient organic aerosol (OA). The authors previously demonstrated that ambient
17 VOC concentrations alone could not explain the amount of SOA formed in the OFR by OH oxidation. This
18 behavior was likely due to SOA being formed from semivolatile/intermediate volatility organic
19 compounds (S/IVOCs) that entered the OFR. However, for SOA formed from O₃ and NO₃ oxidation, the
20 measured VOCs were found in the present study to be sufficient in explaining the amount of SOA
21 formed in the OFR. More specifically, this means that for O₃ and NO₃ oxidation of ambient S/IVOCs does
22 not yield appreciable SOA amounts. The difference between the OH and O₃/NO₃ OFR experiments
23 provides some support for their hypothesis that ambient S/IVOCs generally lacking double bonds in their
24 structures (especially since double bonds in VOCs emitted upwind of the site are likely already oxidized
25 before they enter the OFR). Using ambient mixtures in this study provides important insights into SOA
26 formation potential and chemical evolution in the real atmosphere, and thus, this work will be of high
27 interest to the larger atmospheric chemistry community. I only have a few minor comments below that I
28 kindly ask the authors to address before publication. As a result, I recommend that this manuscript be
29 accepted with minor revisions noted below.

30 R1.1. My biggest comment is related to timescales in the OFR for multi-phase chemical processes. Since
31 the authors appear to justify that their OFR experiments can produce similar oxidation states (O:C
32 ratios) in OA found in the atmosphere, my question is this a result of the "correct" processes that
33 actually occur in the atmosphere? Besides for heterogeneous oxidation (through OH oxidation), what
34 about aqueous-phase processes such as accretion or decomposition reactions of epoxides and or
35 hydroperoxides? There is a lot of work published now by the Caltech, UNC, Oberlin College, and other
36 groups that have shown epoxides are really important in aqueous-phase chemical processes. Recently,
37 the Harvard (Martin) and UNC groups have shown that multi-phase chemical reactions of
38 hydroperoxides could be important as well (Liu et al., 2016, PCCP; Riva et al., 2017, Atmos. Environ.).
39 There is evidence from this site that even MBO oxidation products can undergo aqueous-phase
40 reactions within aerosol to yield organosulfates (Zhang et al., 2012, ES&T). I'm not sure authors can
41 really address this issue now, but I think some discussion needs to be included that acknowledges that

42 these processes may explain some part of ambient oxidation states, which can't be reflected on the
43 reaction timescales of the OFR.

44 We thank the reviewer for pointing out this caveat. We have included the following text as a new
45 paragraph starting after page 16, line 22:

46 **“While these two vectors describe the possible oxidation processes in the OFR, there may be other**
47 **vectors (e.g., from condensed phase chemistry or reactive uptake) occurring in the atmosphere. As**
48 **documented in Hu et al. (2016), SOA formation processes that require reactive uptake or within-**
49 **particle non-radical chemistry (such as uptake of isoprene epoxydiols to form IEPOX-SOA) on time**
50 **scales longer than the several minute residence time in the OFR are not captured with the OFR**
51 **method used in this work. This is because the rate of reactive uptake and non-radical particle-phase**
52 **chemistry do not speed up proportionally to increased OH and HO₂ (or O₃ or NO₃). However, to our**
53 **knowledge the only precursor for which reactive uptake of epoxides has been shown to be a major**
54 **pathway is isoprene, which was a very minor precursor at this site (Karl et al., 2012). The formation of**
55 **epoxides during MBO oxidation has been proposed to play a role during BEACHON-RoMBAS (Zhang**
56 **et al., 2012). However, recent results suggest that formation of epoxides during MBO oxidation is not**
57 **important in the atmosphere (Knap et al., 2016). Thus, at this time it is not clear whether any**
58 **important SOA-forming processes in this environment are missed by the OFR setup, and this question**
59 **should be investigated in future studies.”**

60 R1.2. In section 2.2 of the experimental methods section, can the authors provide more information or
61 clarify on how the ambient might or might not change upon entering the OFR? Specifically, is it drier in
62 the OFR compared to the ambient RH? If the RHs aren't the same, how might this affect the
63 interpretation of the results?

64 To address this comment, we have added the following text to the experimental methods section at
65 page 5, line 16:

66 **“The OFR was located on top of the measurement trailer in order to sample ambient air directly**
67 **without using an inlet. Therefore the temperature and RH inside the OFR were the same as ambient**
68 **conditions, with the exception of minor heating from the UV lamps mounted inside the OH-OFR (up to**
69 **~2°C heating at the highest lamp settings, and ~0.5°C at the settings producing the most SOA; Li et al.,**
70 **2015). No heating occurred during O₃ or NO₃ modes. Thus RH within the OFR was the same or slightly**
71 **lower than ambient, depending on the operating mode.”**

72 R1.3. I'm curious if the authors know how hydroperoxides behave in their OFR? Do they photolyze quite
73 easily due to the UV radiation you are using? How might this affect the interpretation of the results?

74 Non-OH chemistry, such as photolysis of hydroperoxides, has indeed been investigated via modeling in
75 Peng et al. (2016). That investigation concluded that for a wide variety of gases and for OH-OFR
76 conditions in BEACHON-RoMBAS, reactions with OH dominated over other possible reactions, including
77 O(¹D), O(³P), O₃, and photolysis at 185 nm or 254 nm. This was also the case for OH oxidation at other
78 field campaigns where ambient air was oxidized in the OFR. Peng et al. (2016) illustrated that non-OH
79 reactions can become significant under certain circumstances, such as very low RH, high external OH
80 reactivity, or when the gases involved are particularly reactive towards a non-OH pathway. However,
81 these conditions are more commonly found in laboratory studies, where they can also be avoided by

82 carefully designing such experiments. Peng et al. (2016) also investigated photolysis of SOA, and found
83 that while photolysis could affect a small but non-negligible percentage of SOA, photolysis of SOA across
84 the lifetime of particles in the atmosphere would play a much larger role.

85 To address this comment, we have moved the sentence “The gas-phase HO_x/O_x chemistry inside the OFR
86 has also been investigated with kinetic modeling (Li et al., 2015; Peng et al., 2015, 2016).” from page 5,
87 lines 12-13, to page 5, line 25, and altered it to read:

88 **“The gas-phase HO_x/O_x chemistry and possible non-OH chemistry inside the OFR was investigated**
89 **with kinetic modeling (Li et al., 2015; Peng et al., 2015, 2016). For the wide variety of compounds**
90 **investigated in Peng et al. (2016), reactions with OH dominated over other possible reactions,**
91 **including O(¹D), O(³P), O₃, and photolysis at 185 nm or 254 nm, under the conditions of OH oxidation**
92 **in the OFR during this campaign.”**

93

94 **Anonymous Referee #2**

95 Overview

96 R2.0. This work describes the first field observations of in-situ OH, O₃, and NO₃ exposures to ambient air
97 using an oxidative flow reactor. This is highly important work in the field of atmospheric chemistry
98 today, with extensive field and lab studies being performed to better understand the chemical
99 mechanisms and potential to form (or fragment) secondary organic aerosol. Observations here are
100 conducted in a forested environment with biogenic precursor gases (monoterpene dominant) and
101 highlight the dominance of OH oxidation chemistry, but show potential for O₃ and NO₃ reactions with
102 C=C bond VOC species at night. Several studies have been performed using a similar method since the
103 2011 BEACON-RoMBAS study described here, making the analysis and results of this study very relevant
104 for upcoming manuscripts for this research team and others. In-situ NO₃ chemistry and modeling is
105 especially novel. Specific comments to be addressed:

106 R2.1. Pg. 4, Line 22: Discussing MT's here, but haven't defined how these are measured, if cumulative
107 MT's by PTR, or summed by GC/MS.

108 **We have changed the sentence starting at page 4, line 21, to: "VOC concentrations at the site**
109 **(quantified using proton-transfer-reaction time-of-flight mass spectrometry; PTR-TOF-MS) varied on a**
110 **diurnal cycle..."**

111 R2.2. Pg. 5, Line 5: Please provide average concentration increases for "moderate increases" of NO_x, CO,
112 and anthro VOCs. Also, what anthro VOCs?

113 **We have changed the text at page 5, line 5 to: "...leading to moderate increases in NO_x (up to ~5 ppbv**
114 **from ~2 ppbv), CO (up to ~140 ppbv from ~100 ppbv), and anthropogenic VOCs (e.g., benzene up to**
115 **~50 pptv from ~20 pptv, and toluene up to ~150 pptv from ~50 pptv) during the late afternoon and**
116 **evening (Fry et al., 2013; Ortega et al., 2014)."**

117 R2.3. Pg. 5, Line 20: Are periods with very high local winds excluded from the analysis?

118 **We have added the following text to the manuscript at page 5, line 20:**

119 **"The data were not screened for high local wind speeds. However, periods of high wind speeds were**
120 **infrequent during the campaign, and the influence of local winds was likely tempered by the fact that**
121 **the OFR was located within the canopy of the forest."**

122 R2.4. Pg. 6: The thorough explanation of NO₃ exposure estimates here and in supplemental material is
123 appreciated. It seems worth considering how representative one equivalent day of NO₃ aging would be
124 of atmospheric conditions. Given the typical diel pattern of NO₃, and relatively low concentrations,
125 would it ever be expected that a whole day's worth of oxidation could occur prior to further oxidation
126 from OH?

127 **The reviewer touches on a very important point, which is that NO₃ concentrations in the atmosphere are**
128 **much more variable than those of OH or O₃. This means that the eq. NO₃ ages calculated assuming an**
129 **average of 1 pptv of NO₃ in this work need to be interpreted in the context of that assumption, which is**
130 **only strictly applicable to this research site. Other sites may have much more or less average ambient**
131 **NO₃. We had already made this point in the paragraph starting on page 6, line 24. To more strongly**

132 make the point that, even for a given location, the NO₃ concentrations can be variable from one night to
133 the next, we have altered the text starting on page 7, line 3 to read:

134 **“Estimated eq. NO₃ ages from this study are therefore shown simply for a common metric of**
135 **comparison for all of the data during this study, interpretable in terms of the average chemistry**
136 **occurring at the BEACHON site. Interpretation of measurements at other sites would need to be**
137 **adjusted to local NO₃ concentrations.”**

138 R2.5. Pg.8, Line 22: Can further argument be provided for the assumption in this modeled correction (of
139 no fragmentation for O₃ or NO₃ reaction LVOC products)? I’m wondering to what extent does the
140 assumption drive conclusions? Figure 5 suggests lower OA concentrations at 2-3 days NO₃ eq. aging
141 compared to 1 day eq. aging.

142 To address this comment, we have added the following text to page 8, line 24:

143 **“This assumption is reinforced by the fact that for the highest O₃ and NO₃ eq. ages achieved in this**
144 **work, no net decrease of OA was observed when SOA-forming gases were not present (see Sect. 3.2.1**
145 **and Fig. 5). If fragmentation reactions in the gas phase (or from heterogeneous oxidation) were**
146 **important for the range of eq. ages studied here, observations would show a net loss of OA at the**
147 **highest eq. ages when SOA-forming gases (e.g., MT) were not present.”**

148 Regarding the lack of SOA formation observed at the highest NO₃ ages in Fig. 5, those data points were
149 coincident with low ambient MT concentrations (all blue on the MT concentration color bar), so little to
150 no SOA formation was expected. This comment is also addressed by our response to R2.14 below.

151 R2.6. Pg. 9, line 1: The acronym for sesquiterpene (SQT) has not yet been defined.

152 We thank the reviewer for catching this mistake. We have changed the page 9, line 1 instance of SQT to
153 **“sesquiterpenes (SQT)”**.

154 R2.7. Pg. 10, line 15: The negative values in Figure 2d for the fraction of monoterpenes reacted, along
155 with the instances of OFR output MT concentrations that exceed ambient levels shown in Figure S7,
156 should be mentioned. Can this be attributed to instrument uncertainty, or are there other factors at play
157 that give these apparent MT generation events?

158 To address this comment, we have added the following text at page 10, line 15:

159 **“The scatter in the measurements is thought to be due mainly to incomplete and/or variable mixing of**
160 **the injected N₂O₅ flow into the sampled ambient air (see Sect. S1 for more details), with some**
161 **contribution from measurement variability at low ambient MT concentrations.”**

162 We have also added the following text to the end of the Fig. S7 caption:

163 **“Note that the ambient MT were sampled through a separate inlet within the canopy, several meters**
164 **from the OFR. Short periods of higher MT concentrations measured through the OFR (at low O₃**
165 **exposures) may be due to spatial heterogeneity in ambient MT concentrations within the canopy.”**

166 R2.8. Pg. 10, line 24: Change “didn’t” to “did not”.

167 Done.

168 R2.9. Pg. 12, Line 6: please provide average daytime MT+SQT concentration and average nighttime
169 MT+SQT concentration here.

170 We have changed the text at page 12, line 6 to:

171 **“This is consistent with the general increase in MT and SQT (average of 1.1 and 0.04 ppbv in the**
172 **canopy during nighttime, and 0.4 and 0.03 ppbv during daytime, respectively) and related precursor**
173 **concentrations in the shallower nighttime boundary layer.”**

174 We have also clarified the related text in Sect. 2.1. The VOC concentrations quoted in the original text
175 referred to the measurements at 25 m, above the forest canopy. As shown in Palm et al. (2016), the in-
176 canopy concentrations were higher, and those are the concentrations that are relevant to this analysis.
177 Therefore, the text on page 4, line 24 was changed to:

178 **“During BEACHON-RoMBAS, the concentration of MBO+isoprene in the forest canopy ranged from**
179 **about 2 ppb during daytime to 0.4 ppb at nighttime (see Palm et al., 2016).”**

180 The text at page 5, line 2 was changed to:

181 **“MT concentrations in the canopy spanned from 0.4 ppb during the day to 1.1 ppb at night, on**
182 **average.”**

183 R2.10. Pg. 12, line 19: In Figure 6, there is an uptick in OA enhancement with the highest level of O₃
184 oxidation for the nighttime air. However, in Figure S7 it appears that the MTs are largely depleted prior
185 to reaching this extent of aging. Would this suggest that something beyond the measured
186 monoterpenes is contributing to SOA formation from O₃ oxidation at these highest levels of aging?

187 The apparent uptick in OA enhancement at the highest O₃ eq. ages is most likely a result of
188 measurement variability due to the limited number of measurements in each eq. age bin. To address the
189 possibility that the O₃ ages used in this study were not high enough to lead to SOA formation from non-
190 VOC precursors, we have changed the text at page 12, line 19 to read:

191 **“Such molecules would typically not react appreciably with O₃ or NO₃ over the range of eq. ages**
192 **achieved in this work, but will still react with OH and may lead to SOA formation. Future O₃ and NO₃**
193 **oxidation studies should include higher eq. age ranges in order to investigate if additional SOA could**
194 **be formed from ambient precursors at higher ages.”**

195 R2.11. Pg. 13, Line 11: abstract says factor of 3.4. Here it states factor of 4.4. Are these numbers
196 referring to the same discrepancy?

197 We have clarified the relationship between these two numbers by changing the text at page 13, line 10
198 to:

199 **“This is in contrast to the analysis for OH oxidation in Palm et al. (2016), where a factor of 4.4 times**
200 **more SOA was formed from OH oxidation than could be explained by measured VOC precursors. As**
201 **shown in that analysis, the additional SOA-forming gases in ambient air were likely S/IVOCs, where**
202 **the SOA formation from S/IVOCs was 3.4 times larger than the source from VOCs. This conclusion was**
203 **supported by unspiciated measurements of total S/IVOC concentrations (classified by volatility).”**

204 R2.12. Pg. 18, line 24: Change “formed from primary VOCs” to “formed from reaction with primary
205 VOCs”.

206 We have changed this text to read:

207 **“formed from reaction with primary VOCs.”**

208 R2.13. Pg. 20, line 13: Please explain further where 620 g mol⁻¹ is coming from.

209 We have clarified this point by changing the text at page 20, line 11 to:

210 **“To put this in context, if every SOA molecule formed in the OFR contained a single –ONO₂ group (with
211 its mass of 62 g mol⁻¹), then the molecular mass of the full pRONO₂ molecules would be an average of
212 620 g mol⁻¹ (giving the slope of 62 g mol⁻¹ / 620 g mol⁻¹ = 0.10 in Fig. 13).”**

213 R2.14. Figure 5: This method of binning seems to limit comparison of low and high monoterpene
214 conditions at the same levels of oxidation. Particularly for NO₃, why are there not average values for the
215 high monoterpene case at high levels of NO₃ eq. age?

216 The range of eq. NO₃ ages achieved in the OFR was strongly influenced by ambient temperature, which
217 controlled the equilibrium between N₂O₅ and NO₂+NO₃ from the injected N₂O₅. During nighttime (when
218 MT concentrations were higher) it was colder and less NO₃ exposure was realized in the OFR. During
219 daytime (with lower MT concentrations), warm ambient temperatures led to more NO₃ exposure. To
220 make this clearer, we have added the following text on page 11, line 21:

221 **“As seen in Fig. 5 (and in Fig. 6 below), lower eq. NO₃ ages were achieved when MT concentrations
222 were higher, and higher eq. NO₃ ages were achieved when MT concentrations were lower. This was
223 because the higher MT concentrations occurred during nighttime, when lower ambient temperatures
224 shifted the equilibrium towards N₂O₅ and away from NO₂+NO₃ (from the injected N₂O₅), meaning
225 lower NO₃ exposures were realized in the OFR.”**

226 Due to the data limitations, we did not bin data by multiple MT concentrations for day or night;
227 however, the non-binned data points are shown as well (and colored by MT) in order to give a sense of
228 the relationship between SOA formation and MT concentrations for similar oxidation levels. That
229 relationship is also borne out in the measured vs. modeled discussion in Section 3.2.2 and Fig. 7.

230 Supplemental Information:

231 R2.15. Fig S3: Should reiterate in figure caption that these fractional fates are modeled, not measured.
232 Additionally, it seems that the fraction of LVOCs condensing on the aerosol will decrease slightly at
233 higher NO₃ exposures. Would this be due to a greater frequency of fragmentation reactions occurring as
234 opposed to functionalization?

235 We have changed the first line of the Fig. S3 caption from “Fractional fates” to **“Modeled fractional
236 fates”** as suggested. The slightly lower apparent fraction that condenses on particles at higher eq. NO₃
237 ages is a result of the slightly lower condensational sink (i.e., lower aerosol concentrations) during the
238 daytime when those high eq. ages were achieved (see also response to comment R2.14). Fragmentation
239 at high exposures was not included in the model, as described in Sect. 2.3 and in response to comment
240 R2.5.

241 R2.16. Fig S6: why higher NO₃ exposures on the limited data points on Aug9-10?

242 We have changed the last sentence of the Fig. S6 caption to read:

243 **“For these examples, the amount of injected N₂O₅ was held roughly constant (with a higher constant**
244 **value injected on Aug. 9–10).”**

245 R2.17. Fig S8: Which quantile averages are being shown by the black trace?

246 We have changed the last sentence of the Fig. S8 caption to read:

247 **“Quantile averages of OA enhancement per ppbv MT are shown for each oxidant, with error bars**
248 **corresponding to the standard error of the mean of each quantile.”**

249 R2.18. Table S2: revisit for formatting.

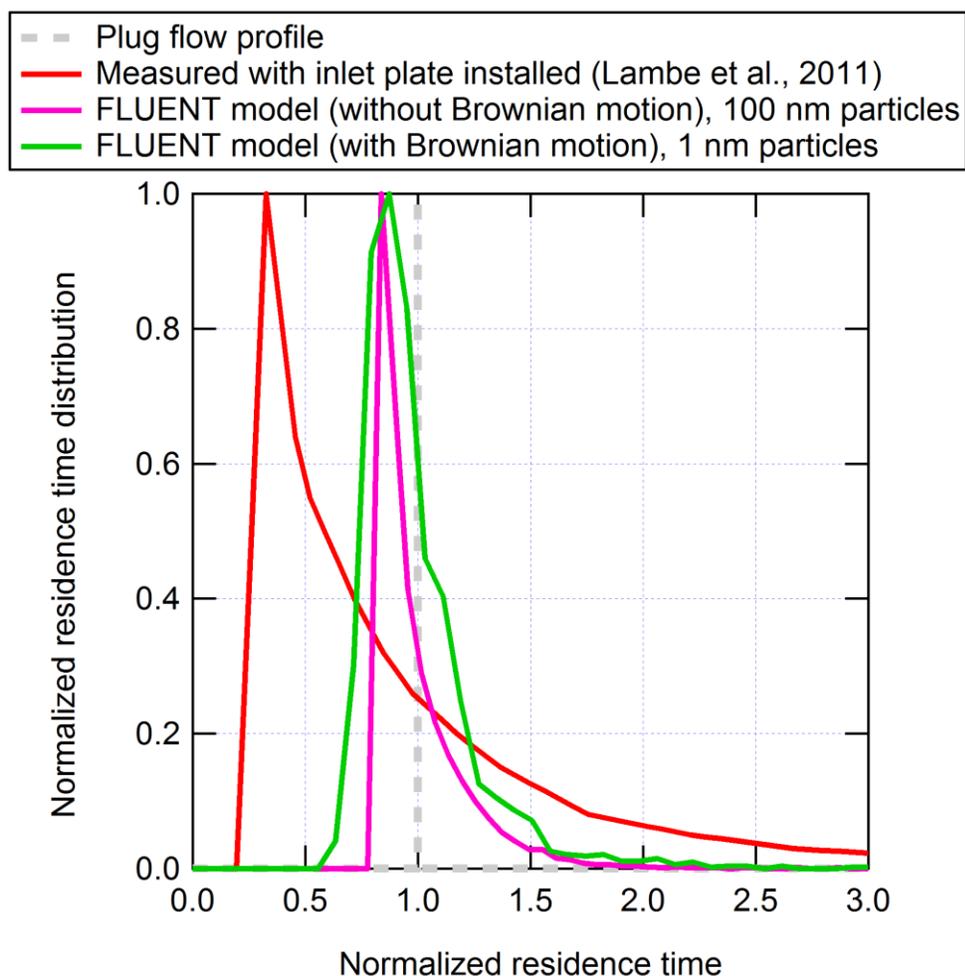
250 We thank the reviewer for pointing out the issue with the formatting of line numbers. It has been fixed.

251 [Other Changes:](#)

252 1: On page 7, line 20, we changed the typo “Scanning Particle Mobility Analyzer” to “**Scanning Mobility**
253 **Particle Sizer**”.

254 2: The author list in the Supplemental Information was changed to match the author list in the main
255 paper.

256 3: We have corrected Fig. S1 to reflect a small change in the FLUENT model results. The new figure is
257 presented here:



258

259 **Fig. S1. Normalized residence time distributions in the OFR as a function of normalized residence time**
260 **(1 = avg. residence time of each distribution). The FLUENT model was used to calculate residence**
261 **times for 1 nm particles (with Brownian motion) and 100 nm particles (without Brownian motion) for**
262 **the OFR configuration without the inlet plate to represent conditions used during BEACHON-RoMBAS.**
263 **These distributions are compared to the bis(2-ethylhexyl) sebacate (BES) particle residence time**
264 **distribution measured with the inlet plate installed in Lambe et al. (2011) and to the ideal plug flow**
265 **distribution (where all particles have equal residence time calculated as the OFR volume divided by**

266 the total flow rate through the OFR). The residence time distribution without the inlet plate is much
267 narrower than with the plate and is close to plug flow, although local winds may at times create a
268 broader distribution than the model shows.

269 **References**

- 270 Fry, J. L., Draper, D. C., Zarzana, K. J., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Brown, S. S., Cohen,
271 R. C., Kaser, L., Hansel, A., Cappellin, L., Karl, T., Hodzic Roux, A., Turnipseed, A., Cantrell, C., Lefer, B. L.
272 and Grossberg, N.: Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011,
273 *Atmos. Chem. Phys.*, 13, 8585–8605, doi:10.5194/acp-13-8585-2013, 2013.
- 274 Hu, W., Palm, B. B., Day, D. A., Campuzano-Jost, P., Krechmer, J. E., Peng, Z., de Sá, S. S., Martin, S. T.,
275 Alexander, M. L., Baumann, K., Hacker, L., Kiendler-Scharr, A., Koss, A. R., de Gouw, J. A., Goldstein, A.
276 H., Seco, R., Sjostedt, S. J., Park, J.-H., Guenther, A. B., Kim, S., Canonaco, F., Prévôt, A. S. H., Brune, W. H.
277 and Jimenez, J. L.: Volatility and lifetime against OH heterogeneous reaction of ambient isoprene-
278 epoxydiols-derived secondary organic aerosol (IEPOX-SOA), *Atmos. Chem. Phys.*, 16, 11563–11580,
279 doi:10.5194/acp-16-11563-2016, 2016.
- 280 Karl, T., Hansel, A., Cappellin, L., Kaser, L., Herdinger-Blatt, I. and Jud, W.: Selective measurements of
281 isoprene and 2-methyl-3-buten-2-ol based on NO⁺ ionization mass spectrometry, *Atmos. Chem. Phys.*,
282 12, 11877–11884, doi:10.5194/acp-12-11877-2012, 2012.
- 283 Knap, H. C., Schmidt, J. A. and Jørgensen, S.: Hydrogen shift reactions in four methyl-buten-ol (MBO)
284 peroxy radicals and their impact on the atmosphere, *Atmos. Environ.*, 147, 79–87,
285 doi:10.1016/j.atmosenv.2016.09.064, 2016.
- 286 Lambe, A. T., Ahern, A. T., Williams, L. R., Slowik, J. G., Wong, J. P. S., Abbatt, J. P. D., Brune, W. H., Ng, N.
287 L., Wright, J. P., Croasdale, D. R., Worsnop, D. R., Davidovits, P. and Onasch, T. B.: Characterization of
288 aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation
289 and cloud condensation nuclei activity measurements, *Atmos. Meas. Tech.*, 4, 445–461,
290 doi:10.5194/amt-4-445-2011, 2011.
- 291 Li, R., Palm, B. B., Ortega, A. M., Hlywiak, J., Hu, W., Peng, Z., Day, D. A., Knote, C., Brune, W. H., de
292 Gouw, J. A. and Jimenez, J. L.: Modeling the Radical Chemistry in an Oxidation Flow Reactor: Radical
293 Formation and Recycling, Sensitivities, and the OH Exposure Estimation Equation, *J. Phys. Chem. A*, 119,
294 4418–4432, doi:10.1021/jp509534k, 2015.
- 295 Ortega, J., Turnipseed, A., Guenther, A. B., Karl, T. G., Day, D. A., Gochis, D., Huffman, J. A., Prenni, A. J.,
296 Levin, E. J. T., Kreidenweis, S. M., DeMott, P. J., Tobo, Y., Patton, E. G., Hodzic, A., Cui, Y. Y., Harley, P. C.,
297 Hornbrook, R. S., Apel, E. C., Monson, R. K., Eller, A. S. D., Greenberg, J. P., Barth, M. C., Campuzano-Jost,
298 P., Palm, B. B., Jimenez, J. L., Aiken, A. C., Dubey, M. K., Geron, C., Offenberg, J., Ryan, M. G., Fornwalt, P.
299 J., Pryor, S. C., Keutsch, F. N., DiGangi, J. P., Chan, A. W. H., Goldstein, A. H., Wolfe, G. M., Kim, S., Kaser,
300 L., Schnitzhofer, R., Hansel, A., Cantrell, C. A., Mauldin, R. L. and Smith, J. N.: Overview of the Manitou
301 Experimental Forest Observatory: site description and selected science results from 2008 to 2013,
302 *Atmos. Chem. Phys.*, 14, 6345–6367, doi:10.5194/acp-14-6345-2014, 2014.
- 303 Palm, B. B., Campuzano-Jost, P., Ortega, A. M., Day, D. A., Kaser, L., Jud, W., Karl, T., Hansel, A., Hunter, J.
304 F., Cross, E. S., Kroll, J. H., Peng, Z., Brune, W. H. and Jimenez, J. L.: In situ secondary organic aerosol
305 formation from ambient pine forest air using an oxidation flow reactor, *Atmos. Chem. Phys.*, 16, 2943–
306 2970, doi:10.5194/acp-16-2943-2016, 2016.
- 307 Peng, Z., Day, D. A., Stark, H., Li, R., Lee-Taylor, J., Palm, B. B., Brune, W. H. and Jimenez, J. L.: HO_x radical
308 chemistry in oxidation flow reactors with low-pressure mercury lamps systematically examined by

309 modeling, *Atmos. Meas. Tech.*, 8, 4863–4890, doi:10.5194/amt-8-4863-2015, 2015.

310 Peng, Z., Day, D. A., Ortega, A. M., Palm, B. B., Hu, W., Stark, H., Li, R., Tsigaridis, K., Brune, W. H. and
311 Jimenez, J. L.: Non-OH chemistry in oxidation flow reactors for the study of atmospheric chemistry
312 systematically examined by modeling, *Atmos. Chem. Phys.*, 16, 4283–4305, doi:10.5194/acp-16-4283-
313 2016, 2016.

314 Zhang, H., Worton, D. R., Lewandowski, M., Ortega, J., Rubitschun, C. L., Park, J.-H., Kristensen, K.,
315 Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Gilman, J.,
316 Kuster, W. C., de Gouw, J., Park, C., Schade, G. W., Frossard, A. A., Russell, L., Kaser, L., Jud, W., Hansel,
317 A., Cappellin, L., Karl, T., Glasius, M., Guenther, A., Goldstein, A. H., Seinfeld, J. H., Gold, A., Kamens, R.
318 M. and Surratt, J. D.: Organosulfates as Tracers for Secondary Organic Aerosol (SOA) Formation from 2-
319 Methyl-3-Buten-2-ol (MBO) in the Atmosphere, *Environ. Sci. Technol.*, 46, 9437–9446,
320 doi:10.1021/es301648z, 2012.

321