

1 **Response to reviewers for “Secondary organic aerosol formation from in situ OH, O<sub>3</sub>, and NO<sub>3</sub>**  
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, O<sub>3</sub>, and NO<sub>3</sub> 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 NO<sub>3</sub> and O<sub>3</sub> oxidation at all times of day.  
15 O:C and H:C ratios of the SOA formed by O<sub>3</sub>, NO<sub>3</sub> 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 O<sub>3</sub> and NO<sub>3</sub> 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 O<sub>3</sub> and NO<sub>3</sub> oxidation of ambient S/IVOCs does  
22 not yield appreciable SOA amounts. The difference between the OH and O<sub>3</sub>/NO<sub>3</sub> 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 HO<sub>2</sub> (or O<sub>3</sub> or NO<sub>3</sub>). 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 O<sub>3</sub> or NO<sub>3</sub> 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(<sup>1</sup>D), O(<sup>3</sup>P), O<sub>3</sub>, 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<sub>x</sub>/O<sub>x</sub> 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<sub>x</sub>/O<sub>x</sub> 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(<sup>1</sup>D), O(<sup>3</sup>P), O<sub>3</sub>, 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, O<sub>3</sub>, and NO<sub>3</sub> 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 O<sub>3</sub> and NO<sub>3</sub> 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 NO<sub>3</sub> 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<sub>x</sub>, 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<sub>x</sub> (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 NO<sub>3</sub> exposure estimates here and in supplemental material is  
123 appreciated. It seems worth considering how representative one equivalent day of NO<sub>3</sub> aging would be  
124 of atmospheric conditions. Given the typical diel pattern of NO<sub>3</sub>, 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 NO<sub>3</sub> concentrations in the atmosphere are**  
128 **much more variable than those of OH or O<sub>3</sub>. This means that the eq. NO<sub>3</sub> ages calculated assuming an**  
129 **average of 1 pptv of NO<sub>3</sub> 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 **NO<sub>3</sub>. 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 NO<sub>3</sub> 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. NO<sub>3</sub> 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 NO<sub>3</sub> 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 O<sub>3</sub> or NO<sub>3</sub> 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 NO<sub>3</sub> 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 O<sub>3</sub> and NO<sub>3</sub> 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 NO<sub>3</sub> 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 N<sub>2</sub>O<sub>5</sub> 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 O<sub>3</sub>**  
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 O<sub>3</sub>  
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 O<sub>3</sub> oxidation at these highest levels of aging?

187 The apparent uptick in OA enhancement at the highest O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> or NO<sub>3</sub> over the range of eq. ages**  
192 **achieved in this work, but will still react with OH and may lead to SOA formation. Future O<sub>3</sub> and NO<sub>3</sub>**  
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<sup>-1</sup> 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 –ONO<sub>2</sub> group (with  
211 its mass of 62 g mol<sup>-1</sup>), then the molecular mass of the full pRONO<sub>2</sub> molecules would be an average of  
212 620 g mol<sup>-1</sup> (giving the slope of 62 g mol<sup>-1</sup> / 620 g mol<sup>-1</sup> = 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 NO<sub>3</sub>, why are there not average values for the  
215 high monoterpene case at high levels of NO<sub>3</sub> eq. age?

216 The range of eq. NO<sub>3</sub> ages achieved in the OFR was strongly influenced by ambient temperature, which  
217 controlled the equilibrium between N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub>+NO<sub>3</sub> from the injected N<sub>2</sub>O<sub>5</sub>. During nighttime (when  
218 MT concentrations were higher) it was colder and less NO<sub>3</sub> exposure was realized in the OFR. During  
219 daytime (with lower MT concentrations), warm ambient temperatures led to more NO<sub>3</sub> 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. NO<sub>3</sub> ages were achieved when MT concentrations  
222 were higher, and higher eq. NO<sub>3</sub> 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 N<sub>2</sub>O<sub>5</sub> and away from NO<sub>2</sub>+NO<sub>3</sub> (from the injected N<sub>2</sub>O<sub>5</sub>), meaning  
225 lower NO<sub>3</sub> 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 NO<sub>3</sub> 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. NO<sub>3</sub>  
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 NO<sub>3</sub> 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 N<sub>2</sub>O<sub>5</sub> 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.

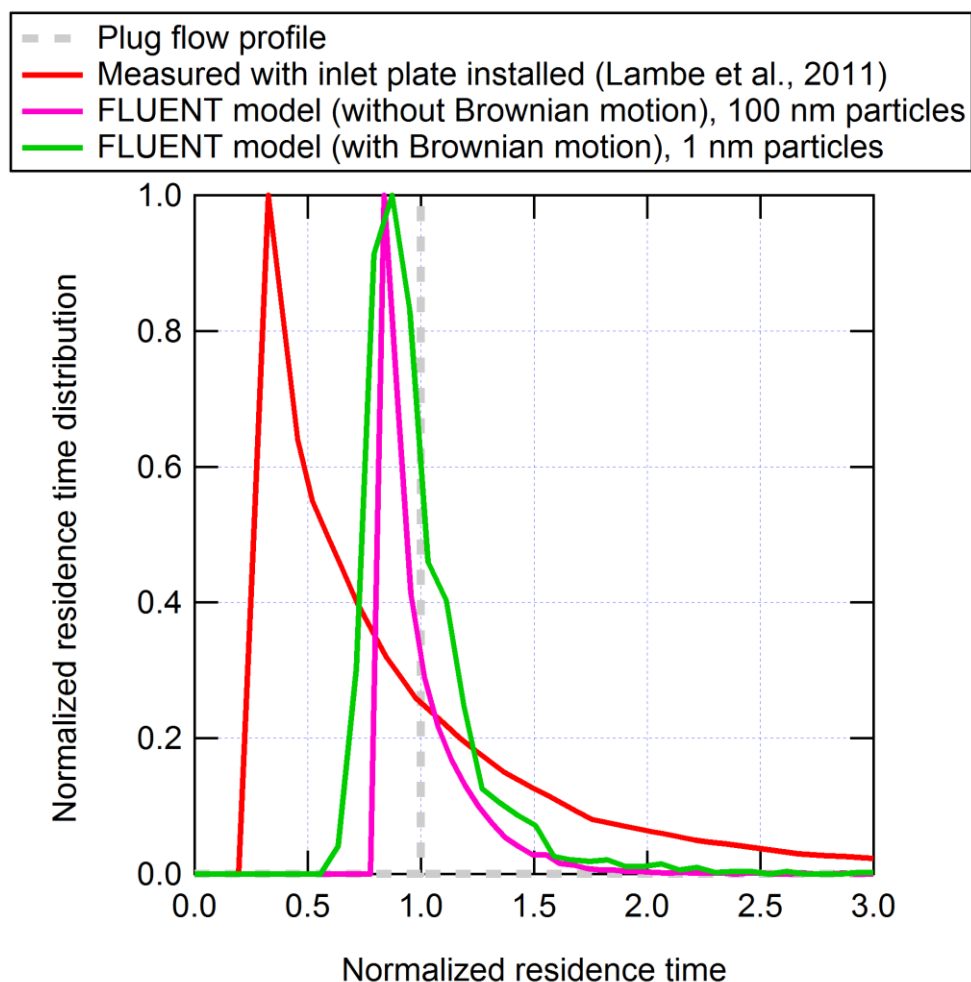


251 [Other Changes:](#)

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**

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