

The authors' edits and responses to both reviewers have substantially improved this manuscript. However, three concerns from the first round of reviews remain only partially addressed, and the manuscript would benefit from more careful consideration of each, as detailed below.

5 We thank the reviewer for further comments and have addressed each additional comment below. Our responses are in blue text, with changes to the manuscript noted in **bold**.

A. Wall loss:

10 **A1.** The additional discussion of wall loss effects remains unconvincing for a number of reasons. First, because this manuscript argues that the chemistry of camphene (especially NO_x dependence) is very different from the other precursors for which wall loss has been tested in the Riverside chamber, it can't be expected that wall losses will act similarly. The extent to which vapor wall loss influences measured yields depends on many factors including the distribution of volatilities of SOA-contributing products under all different oxidation conditions -- which may or may not be comparable between camphene oxidation and that of other precursors -- and the speed at which semivolatile vapors are formed, which is likely not comparable to past experiments on systems that used higher [HC]0.

We would first like to emphasize that this is the first time that an explicit gas-phase chemical mechanism has been used to better understand the fate of RO₂ radicals in the context of observed SOA formation in the UCR chamber. Therefore, while we can say that the NO_x dependence of SOA formation was the inverse of what is typically observed, we can't say that similar chemistry did not occur in other previous studies in our chamber or in other chambers.

20 We acknowledge that vapor wall losses are highly dependent on the volatility distribution of the oxidation products, which may differ between parent VOCs. We have performed a large number of seeded and unseeded experiments with different parent VOCs in the UCR chamber, yielding oxidation products over a large range of volatilities and at varying generation rates, without reproducing vapor wall loss dependence that has been observed in other studies and described in published literature. There is no evidence that the volatility distribution or the timing of the oxidation products in the camphene experiments were significantly different than the ranges of products previously studied and thus, that more significant vapor wall losses occurred for camphene oxidation. This is further discussed in response to comment #A3 below.

30 We acknowledge that the systems described above do not include wall loss characterization at low [HC] vapor concentrations and thus the possibility of an underestimation of SOA yield for the low [HC] experiments exists. This is further discussed in response to comment #A3 below.

A2. Second, a lack difference between seeded and unseeded experiments does not alone imply the absence of wall effects - see Krechmer et al. 2020 (DOI: 10.1021/acs.est.0c03381).

Regarding the utility of seeded vs. non-seeded experiments for demonstrating wall loss, we thank the reviewer for sharing the Krechmer paper and have cited the reference in the revised manuscript. The theoretical framework and

35 model simulations presented by Krechmer et al. in fact demonstrate the competition between seed and the chamber walls for condensable organics, though it was concluded that high seed concentrations do not negate wall loss effects and an underestimation of SOA yield by 25-35% occurs even when the condensation rate to particles is similar to the condensation rate to chamber walls. These simulation results presented by Krechmer et al. likely overestimate the effects of wall losses, relative to our measured yields for camphene oxidation in the UCR chamber, because: 1) the results are presented for continuous flow experiments which have higher wall loss relative to batch flow experiments, and 2) the wall loss rates are based on those reported for chambers that are 6-20 m³. The UCR chamber used in the camphene oxidation studies was 90 m³, 4.5 times larger than the largest chamber studied in the shared paper, and as noted by Krechmer et al. and others, the wall loss rates are dependent on surface-volume ratio. While additional wall loss characterization for these experiments is not possible, as the UCR chamber has since been rebuilt and reconfigured, we agree with the concluding suggestions by Krechmer et al. that wall loss experiments should be performed for systems characterization, and we will continue to probe this question in the UCR chambers.

A3. Third, it's not clear why else these experiments would exhibit such a strong dependence on dHC (and on top of that, why there'd be so much delay in SOA formation which is also dependent on HC₀) if not for the influence of wall losses.

50 The dependence of SOA mass yield on $\Delta[\text{HC}]$ is expected at low $\Delta[\text{HC}]$ due to the non-linear dependence of partitioning on M_0 ; this is assuming consistent chemistry across $\Delta[\text{HC}]$ (i.e., an increase in products but not a change in the distribution of products). At a given photochemical aging time (equivalent to the OH level), the amount of $\Delta[\text{HC}]$ will increase with $[\text{HC}]_0$ and thus the SOA mass yield will also increase. This contributes to an apparent, but not actual, delay in SOA mass/SOA mass yield as a function of $[\text{HC}]_0$ shown in Fig. 4. By plotting M_0 vs $\Delta[\text{HC}]$ in all experiments (Figure S9-with added NO_x and S10-w/o added NO_x), it is clear that in the lowest $[\text{HC}]_0$ experiments, SOA is formed at very low $\Delta[\text{HC}]$, which would not be the case if the majority of the condensable compounds were being lost to the walls. We do not maintain that there is absolutely no wall loss, but that there is no real delay in SOA formation as a function of $[\text{HC}]_0$. Based on the shape of the curves (i.e., as described by Ng et al. 2006) there is evidence for oxidation products contributing to SOA mass that are being formed more slowly than camphene is being consumed, which is consistent with the mechanistic description presented in the manuscript (see Fig. S5).

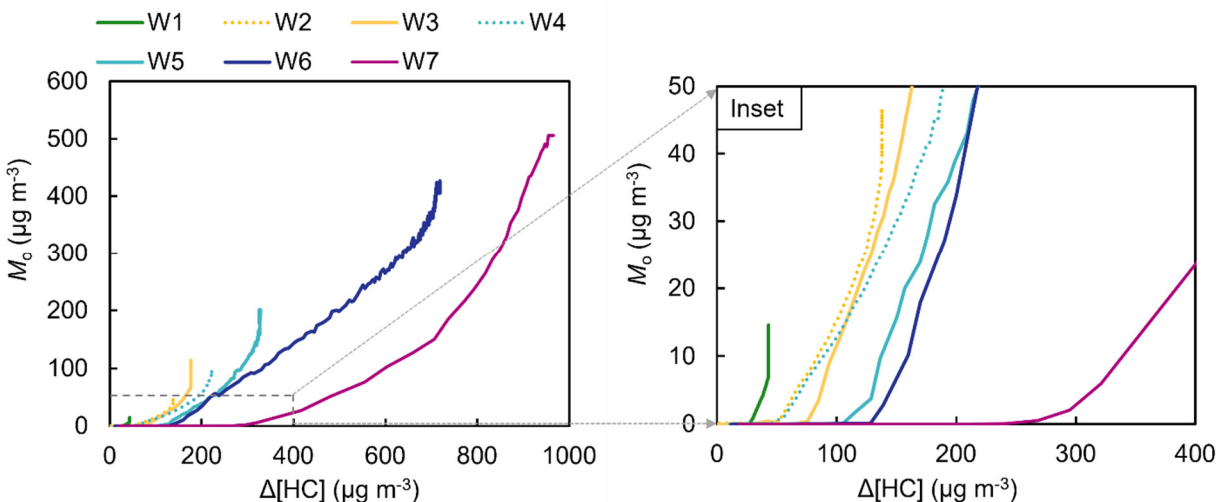
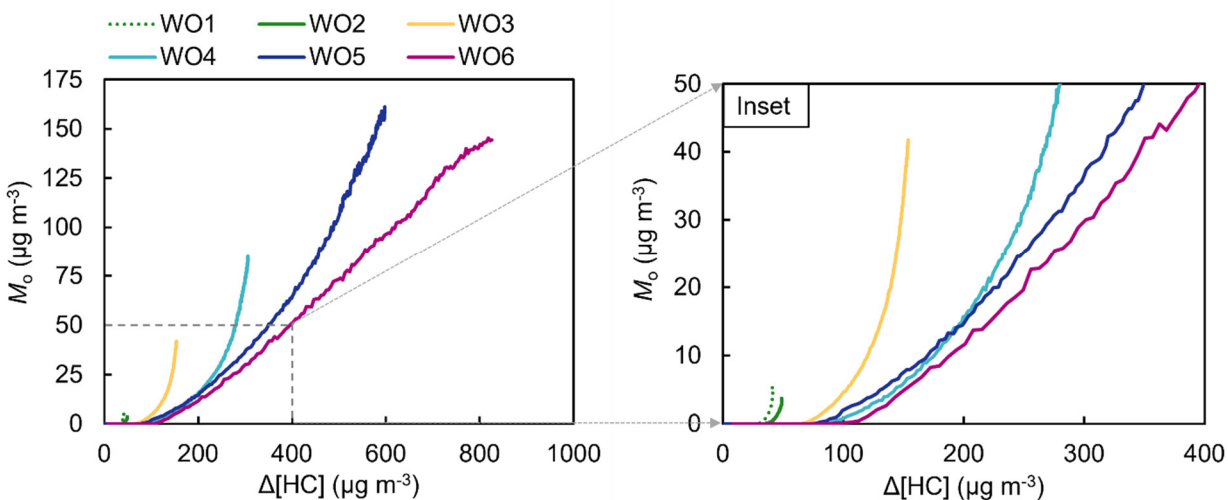


Figure S9. Measured SOA mass concentrations as a function of reacted camphene concentration with added NO_x ; inset shows the lowest camphene concentrations from 0 – 400 $\mu\text{g m}^{-3}$.



65 Figure S10. Measured SOA mass concentrations as a function of reacted camphene concentration without added NO_x ; inset shows the lowest camphene concentrations from 0 – 400 $\mu\text{g m}^{-3}$.

We have added the following text referencing the new SI figures (line 288):

“In the camphene experiments presented herein, the aging effects were determined to be less important than RO_2 chemistry, since the SOA mass yield curves as a function of photochemical aging already plateau or nearly plateau by the end of experiments (Fig. 4) and the shapes of the growth curves (Fig. S9 and Fig. S10) indicate different kinetics and contributions from oxidation products that form slowly among and between the experiments with and without added NO_x (Ng et al., 2006).”

70 A4. All these reasons merit stronger caveats on the results presented herein. Most importantly, although it is suggested that vapor wall loss "would not affect the following discussion or conclusions regarding the role of RO_2 chemistry", this is not entirely accurate; if wall-loss correction of SOA yields in experiments W1-2, for which the correction will

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be largest out of the high-NO_x experiments, were sufficiently large, they might counteract the observed decrease in yield at "extreme NO_x", or at least render them statistically insignificant.

In response to comments A1-A4, and in an effort to make our assumptions clearer, we have made the following changes to the manuscript.

80 We have revised the discussion of vapor wall loss under section 2.1 (Chamber Facility and Instrumentation) to read as follows:

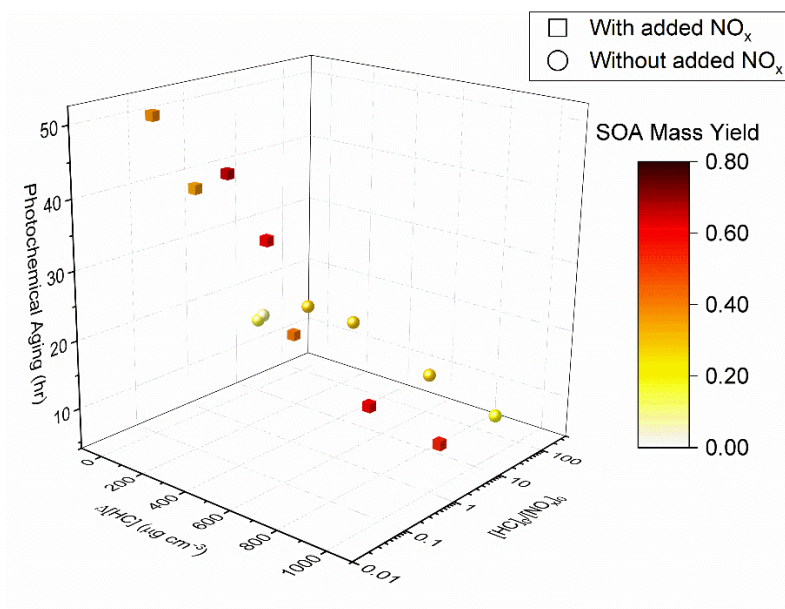
85 **Particle wall loss corrections were performed following the method described in Cocker et al. (2001). Vapor wall loss of organics has been reported in multiple chambers (e.g., Zhang et al., 2015, 2014; Schwantes et al., 2019); and has been modeled as a function of the mass and volatility of the condensing compounds, condensation sink, and characteristics of the chamber (e.g., La et al., 2016; Zhang et al., 2014; Ye et al., 2016). The extent to which these observations and modeling simulations are relevant in the UCR chamber is unclear, given the significant difference in chamber sizes. The UCR chamber is 4.5 times larger (90 m³) than the largest referenced chamber in these studies (20 m³) and most are ~10 m³. In the UCR chamber, the role of vapor wall loss has been investigated in SOA experiments using various precursor compounds (including α -pinene and *m*-xylene) under seed and no seed conditions (Clark et al., 2016; Li et al., 2015). There has been no evidence of non-negligible vapor wall loss in those experiments, including no measurable differences in SOA formation in experiments with and without seed. In this work, stability tests on camphene demonstrated negligible vapor wall loss of the parent compound. Thus without evidence to suggest otherwise, negligible vapor wall loss was assumed for these experiments. This assumption is further discussed where it may affect the major conclusions regarding the role of gas-phase chemistry on SOA formation.**

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We have also added the following caveats:

- In the presentation of the SOA mass and yield (section 3.2), line 251: **The SOA mass yields measured at the lowest [HC]₀/ Δ [HC] may be an underestimate due to the assumption of negligible vapor wall loss, which would have the largest effect at low [HC] (Krechmer et al., 2020).**
 - In the discussion of Fig. 5: "Only over low Δ [HC] ranges, the SOA mass yield increases with Δ [HC] in experiments without added NO_x due to the dependence of partitioning on M_o (or Δ [HC]). **This trend may be exaggerated due to the assumption of negligible vapor wall loss, which could result in an underestimation of SOA mass yield particularly at low Δ [HC] (Krechmer et al., 2020).**"
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105 We have additionally revised Fig. 5, which we think more clearly shows the following: 1) the role of Δ [HC] at low Δ [HC] particularly for the experiments without added NO_x; 2) the generally higher SOA yields in experiments with added NO_x; and 3) the generally higher SOA yields at "moderate" [HC]₀/[NO_x]₀ values.



110 **Figure 5. SOA mass yield (color bar) as a function of $\Delta[\text{HC}]$, $[\text{HC}]_0/[\text{NO}_x]_0$, and photochemical aging time, with added NO_x experiments square markers and without added NO_x experiments round markers.**

115 The text associated with Fig. 5 has been modified to read: “Over low $\Delta[\text{HC}]$, SOA mass increased in experiments without added NO_x due to the dependence of partitioning on M_o (or $\Delta[\text{HC}]$). This trend may be exaggerated due to the assumption of negligible vapor wall loss, which could result in an underestimation of SOA mass yield particularly at low $\Delta[\text{HC}]$ (Krechmer et al., 2020). The sensitivity of SOA formation to $[\text{HC}]_0/[\text{NO}_x]_0$ over the range of $[\text{HC}]$ sampled is also shown. At a given $\Delta[\text{HC}]$ level, a lower $[\text{HC}]_0/[\text{NO}_x]_0$ (when within 0.5–200) led to a higher SOA mass yield (decreasing $[\text{HC}]_0/[\text{NO}_x]_0$ by ~ 2 orders of magnitude resulted in a factor of two increase in SOA mass yield). **The chamber data presented here indicate that the highest SOA mass yields from camphene were observed in a regime of high $\Delta[\text{HC}]$ and moderate $[\text{HC}]_0/[\text{NO}_x]_0$; this regime is distinguished from an extreme $[\text{NO}_x]$ regime, proposed in section 4.2, in which SOA mass yields are suppressed at the lowest $[\text{HC}]_0/[\text{NO}_x]_0$ (also shown in Fig. 5). These observations are different from those in studies of α -pinene, in which lower $[\text{HC}]_0/[\text{NO}_x]_0$ generally led to lower SOA mass yield (Eddingsaas et al., 2012). **The observed trends are further explored in the following sections, particularly the role of RO_2 based on SAPRC simulations.**”**

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Regarding experiments W1 and W2 and the existence of an extreme NO_x regime, we provide the following analysis. In the table below, the with added NO_x experiments are ordered from low to high $[\text{HC}]_0/[\text{NO}_x]_0$. It can be seen that for experiments W3-W7, SOA mass yield decreases as $[\text{HC}]_0/[\text{NO}_x]_0$ increases. As has been described in the manuscript, this trend is plausibly explained by the SAPRC modeling simulations. Experiments W1 and W2 are clearly outliers and do not follow the same trend. If we assume, as arguably an extreme upper limit, the observed SOA mass concentrations in W1 and W2 were $\sim 25\%$ low (using the estimate in Krechmer et al.), the calculated SOA mass yields increase to 46% and 41%, respectively, which is not enough to negate our conclusions regarding an extreme NO_x regime.

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Expt.	$\Delta[\text{HC}]$ ($\mu\text{g m}^{-3}$)	$[\text{HC}]_0/[\text{NO}_x]_0$ (ppb/ppb)	SOA Mass Yield
W1	40	0.08	0.36
W2	140	0.18	0.33
W3	177	0.51	0.64
W5	334	0.64	0.60
W6	724	1.33	0.59
W7	950	2.88	0.52
W4	237	5.91	0.41

We have added the following in 4.2, before the description of the extreme NO_x regime: “The relatively low SOA mass yields in experiments W1 and W2 (0.36 and 0.33) also can be explained by differences in product distribution. **An underestimation of the SOA mass yields in these experiments due to the assumption of negligible wall loss is not sufficient to explain these relatively low yields.**”

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B. Uncertainty: the +/- 6.65% experimental uncertainty on an individual experiment's measured yield is a useful number and good to have included in the revisions. What's missing now is any discussion of how that uncertainty might affect the conclusions drawn here. Given that uncertainty range, for example, it does not necessarily seem that the decreased SOA yield observed at high SOA mass under both high- and low- NO_x conditions (the purple points in Figure 2) can be statistically significantly distinguished from the plateaus (the yellow, light blue, and dark blue points). It seems from my reading (and without doing any quantitative statistical analysis) that this is the only place where the uncertainty bounds may be large enough to affect the significance of the conclusions, but it would be reassuring if the authors could comment further on statistical significance throughout.

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Uncertainty in observed SOA mass and calculated SOA mass yields is often approximated by the cumulative uncertainty in the measured quantities and sometimes by performing replicate experiments (e.g., during characterization). The uncertainty reported here is of the latter type, but was calculated for other experimental systems; thus using that reported value for quantitative statistical analysis would not necessarily result in a robust result. We agree with the reviewer that the decreased yields at high $\Delta\text{HC}/\text{SOA}$ mass may not be statistically different than the plateaus but because we saw the same behavior in the GECKO-A simulations, we thought it was worth exploring with the SAPRC model. The SAPRC modeling results provide a plausible explanation, though as with any model simulations, further experiments should be done to confirm and constrain the predictions. We have made an effort to make the above points clearer through the following modifications.

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- We have revised the text in section 2.1 to read: “**A prior characterization of this UCR chamber system (Li et al., 2016) reported an experimental uncertainty in SOA yields of < 6.65%.**”

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- In section 3.2, after the Fig. 3 description we have added: “**The difference between the peak SOA mass yield and the SOA mass yield at the highest $[HC]_0$ was ~ 0.12 with added NO_x and ~ 0.08 without added NO_x . While the SOA mass yields at the highest $[HC]_0$ may not be statistically different within the uncertainty of the measurements, this trend was also observed in the GECKO-A model simulations (see Sect. 5) and thus was further investigated, and reasonably explained, by the RO_2 fate based on box model simulations (see Sect. 4 & 5).**”
- In section 4.2, line 413: “**While the decreasing SOA mass yields at high $[HC]_0$ and M_0 in experiments with and without added NO_x (shown in Fig. 3) may not be statistically different within the uncertainty of the measurements, RO_2 chemistry was explored as an explanation for the apparent trends.**” In all occurrences, “led to” was replaced by “can explain” to better convey that while the observations can be explained by the SAPRC model predictions further experiments are needed to confirm and constrain.

C. Figure 3 (now 4): Putting these on the same axes does indeed make it easier to see that at any given point, the high- NO_x yield is higher than the low- NO_x yield, and it's good this point was highlighted in the text. However, it does not convincingly show that the yields have all plateaued or nearly plateaued by the end of the experiment, or that the trends would remain as pronounced as you show if the low- NO_x experiments were allowed to run longer. In fact, the new figure draws greater attention to the delay in SOA formation in low- HC experiments -- and whether or not this is a consequence of wall losses (see above), it merits some explanation. It still seems likely that the yields in low- NO_x experiments would be higher than reported if they were allowed to run longer. A similar comparison across experiments to Figure 3 (now 4) but in the growth curve space ($\Delta[M(0)]$ vs $\Delta[HC]$, e.g. Ng et al., ES&T, 2006, DOI 10.1021/es052269u) might help to distinguish whether the different shapes of these curves imply differences in chemistry or just in oxidation extent, and help to visualize the remaining SOA that might be formed if the experiments were allowed to continue.

We thank the reviewer for the suggestion to plot M_0 vs. $\Delta[HC]$. Two new figures were created and added to the SI (Fig. S9 and Fig. S10). The figures are shown and discussed in the response to comment A3.

Regarding the SOA mass yield curves as a function of photochemical aging time, we have revised the manuscript to read:

“Experiments with added NO_x generally had longer photochemical aging times than experiments without added NO_x ; without added NO_x , **all experiments may not have fully plateaued and thus would have had higher SOA mass yields at longer irradiation times.** However, even at the same aging time (Fig. S8), the SOA yields were higher in the experiments with added NO_x .”

Fig. 5 illustrates that SOA yield is not only dependent on $\Delta[HC]$, but also on $[HC]_0/[NO_x]_0$. Beyond the differences in OH levels, as discussed in the manuscript, this is indicative of the RO_2 chemistry changing with $\Delta[HC]$, particularly the fates of the RO_2 radicals as a function of $[HC]_0/[NO_x]_0$. The different shapes of the curves in Fig. S9 and Fig. S10

190 are consistent with our conclusions that the chemistry is different among the experiments with added NO_x and without added NO_x, and between the with and without added NO_x experiments.