Response to Reviewer's comments

For clarity, the reviewer's comments are listed below in *black italics* type, our responses are in black normal type, and changes in the revised version are highlighted in blue.

Reviewer #1:

The article High Yields of Formic Acid and Acetic Acid during Multi-generational Oxidation of Toluene provides laboratory based evidence for substantial formation of formic acid (FA) and acetic acid (AA) under high OH exposure, equivalent to multi-day atmospheric oxidation. The article is well written, and the main conclusions are generally well supported with figures and discussion. I recommend this article for publication pending a few minor corrections as noted below.

We gratefully thank you for your comments and suggestions to improve the manuscript. We have revised the manuscript by carefully considering the comments. The major revisions are specified as follows: (1) We have softened the claims regarding the closure of the organic acid budget and added a discussion of the limitations of our study. (2) We have provided a more detailed description of experiments. (3) We have added a new supplementary figure showing the concentration dependence of organic acid yields. More details about the revisions can be found in the revised manuscript and in our response below.

(Q1) *Although the experimental evidence for FA and AA formation from toluene oxidation is strong, the claim that this pathway could close the budget of missing FA and AA in urban and petroleum emissions needs further discussion or softened. This is particularly true considering that much of the recent literature points to aerosol sources being the main missing FA/AA formation pathway. Two key places to clarify. Line 408–411: This claim assumes that the FA/AA yields seen for toluene in this study also apply to other aromatics. At a minimum this should be explicitly stated as a limitation of the study, while literature evidence for similar oxidation schemes would strengthen the argument. Can the authors apply a more quantitative approach to how much of the budget this pathway could account for? For example, is there enough BTEX in urban emissions to yield the needed quantities for FA and AA to close the budget? Does this also apply to other emission sources such as biomass burning? What are the limitations imposed by only using one VOC in the flow reactor? Would competitive OH reactions change the yield and/or main conclusions?*

Response: Thank you for your suggestion. We agree that our original discussion overstated the generalizability of our findings and have revised the manuscript accordingly.

We have softened the relevant statements to explicitly acknowledge that our experiments were conducted solely with toluene and that direct extrapolation to other aromatic compounds or complex emission mixtures requires caution. Nevertheless, we note that previous studies have demonstrated that biogenic VOCs can also produce organic acids through multi-generational oxidation (Friedman and Farmer, 2018), suggesting that enhanced organic acid formation during multi-generational oxidation may be a common feature across different VOC classes. If the high yields observed here are applicable to the broader BTEX class, the contribution of aromatic oxidation to the atmospheric organic acid budget could be substantially higher than currently estimated. However, we acknowledge that this extrapolation carries some uncertainty. Under ambient conditions, the presence of numerous co-emitted VOCs would compete for available OH radicals, effectively reducing the •OH exposure per molecule of

toluene and potentially lowering the organic acid yield per unit of toluene oxidized. We have added a brief discussion of this limitation in the revised manuscript. Additionally, biomass burning emissions contain a complex mixture of VOCs, including substantial amounts of aromatic compounds, and have been identified as a significant source of atmospheric organic acids (Permar et al., 2023; Bruns et al., 2017). Our findings suggest that multi-generational oxidation of aromatic compounds within biomass burning plumes may contribute to the rapid organic acid formation observed during plume aging, although more studies employing realistic fuel mixtures under controlled conditions are needed to quantitatively constrain this contribution.
We have revised the corresponding paragraphs in Section 4 to reflect these considerations.

Page 17: "If the high yields of organic acids observed during the multi-generational oxidation of toluene are broadly applicable to other aromatics, the elevated yields of formic and acetic acids at high •OH exposures reported in this study may help explain these discrepancies."

Page 18: "It is noted that biomass burning emissions also contain substantial amounts of aromatic compounds, and multi-generational oxidation within biomass burning plumes may similarly produce significant quantities of organic acids, as supported by both laboratory experiments and field observations (Bruns et al., 2017; Permar et al., 2023)."

(Q2) *Please provide a brief description of how you calculated % yield from the experiments.*
Response: We have added a description of the yield calculation in Section 2.2. Specifically, the molar yield of each organic acid was calculated as:
Yield (%) = (Δ[organic acid] / Δ[toluene]) × 100%
where Δ[organic acid] is the concentration of formic acid or acetic acid (ppbv) produced under a given condition, and Δ[toluene] is the corresponding amount of toluene consumed (ppbv) under that condition. Both quantities were determined from direct measurements at each axial sampling port, which correspond to different residence times and thus different OH exposures within the reactor. It is important to note that the reported yields are apparent yields and were not corrected for the subsequent reactions of the organic acids with OH radicals, as stated in the original manuscript.

Page 7: "The molar yields of formic acid and acetic acid were calculated relative to the amount of toluene consumed at each sampling position as show in equation E(1):

$$\text{Yield (\%)} = (\Delta[\text{organic acid}] / \Delta[\text{toluene}]) \times 100\% \qquad \text{E1}$$

where Δ[organic acid] is the concentration of formic acid or acetic acid (ppbv) produced at a given sampling position, and Δ[toluene] is the corresponding amount of toluene consumed (ppbv) at that position. It should be noted that the reported yields are apparent yields and were not corrected for the subsequent reactions of organic acids with •OH."

(Q3) *Figures 2 a and d: Why does the % yield start at 20 % and 40 % before any production has occurred? See previous comment about explaining the % yield calculation more clearly.*
Response: We clarify that the first data points in Figures 2b and 2d do not represent conditions before reaction. These data points correspond to the earliest sampling position along the reactor (at 5% of the reactor length, corresponding to a residence time of ~3.9 s), where both toluene consumption and organic acid formation have

already commenced. The non-zero yields at the lowest OH exposure therefore reflect product formation that has occurred within the reactor. To improve clarity, we have revised the figure caption for Figure 2.

Page 9: "Figure 1. Production of formic acid and acetic acid during the photooxidation of toluene as a function of •OH exposure. Panels (a) and (b) correspond to 20% RH, and panels (c) and (d) correspond to 70% RH. The initial toluene concentration was ~94 ppbv. Error bars represent standard deviations of repeated experiments under identical conditions. Note that the first data point in each panel corresponds to a condition where measurable toluene consumption has already occurred, with •OH exposures of 0.07 equivalent days at 20% RH and 0.2 equivalent days at 70% RH, respectively."

(Q4) *Line 84: Consider adding Permar et al., 2023 for wildfire emissions (https://doi.org/10.1039/D3EA00098B). This article also supports that FA is rapidly formed in environments with high OH exposure, although the authors see no AA production on the same time scale. The MCM is similarly evaluated and shows the model is missing most FA and AA production.*

Response: We have added this reference in the revised manuscript.

(Q5) *Line 245: What was the OH exposure in these other studies? How different is it relative to this work?*

Response: Thank you for your suggestion. We have added a comparison of •OH exposures with previous studies in the revised manuscript. The detailed comparisons are as follows:

(1) Seuwen and Warneck (1996) conducted their toluene oxidation experiments in small glass vessels (2–10 L) with reaction times of 15−30 minutes and estimated •OH concentration of ~1.25×10^7 molecules cm^{-3}, corresponding to an OH exposure of ~0.04–0.07 equivalent days (based on a reference •OH concentration of 3.6×10^6 molecules cm^{-3} for urban Beijing). This is substantially lower than the OH exposures at which we observed peak organic acid yields (1–3 equivalent days).

(2) Berndt et al. (1999) investigated benzene oxidation using a flow tube with short residence times of 0.26–0.42 s and a high initial OH concentration of 4×10^{12} molecules cm^{-3}, corresponding to ~3–5 equivalent days. However, the dominant chemistry under such extreme OH conditions and short timescales may differ fundamentally from atmospherically relevant multi-generational oxidation.

(3) Wyche et al. (2009) employed a chamber with •OH concentration of ~10^5−10^6 molecules cm^{-3} and residence times of ~500–600 minutes, yielding •OH exposures of ~0.01–0.1 equivalent days under high-NO_x conditions, where a formic acid yield of 14% was observed. Under low-NO_x conditions, using HONO as •OH precursor, the •OH exposure was about three times higher (~0.03–0.3 equivalent days), and the maximum formic acid yield increased significantly to 49%. This trend is consistent with our findings that higher OH exposures promote greater organic acid formation.

(4) Murschell and Farmer (2018) employed an OFR and achieved very high •OH exposures of about 3 equivalent days, reporting formic acid yields of up to 43% from the oxidation of a chlorinated aromatic compound. Notably, the organic acid yield increased rapidly with increasing •OH exposure, further demonstrating the critical role of •OH exposure in controlling organic acid formation. This result is broadly consistent with our findings.

Taken together, these comparisons reinforce our conclusion that organic acid yields are strongly dependent on •OH exposure, and that the relatively low yields reported in earlier studies can be attributed to the limited •OH exposures achievable in conventional experiments.

Page 10: "This discrepancy may be ascribed to the differences in •OH exposure levels. Previous chamber studies were typically conducted under •OH exposures of <0.1 equivalent days (Seuwen and Warneck, 1996; Wyche et al., 2009), which are substantially lower than those (1–3 equivalent days) at which peak organic acid yields were observed in our study. Under such limited •OH exposures, primary oxidation products dominate, whereas formic and acetic acids likely form as secondary or later-generation products requiring higher •OH exposures (Lambe et al., 2012; Isaacman-VanWertz et al., 2018; Drozd et al., 2019)."

(Q6) *Line 258–260: Would the presence of other VOCs be expected to similarly decrease yields compared to the toluene only experiments in this work (see major comment)?*

Response: In the presence of other VOCs, competitive •OH reactions would reduce the effective •OH exposure per molecule of toluene, which would likely decrease the organic acid yield from toluene oxidation. However, it should be noted that (1) under atmospherically relevant conditions, the multi-generational oxidation of other VOCs may also produce organic acids through analogous fragmentation pathways, potentially compensating for the reduced yield from any single precursor; and (2) the total OH exposure in the atmosphere integrated over several days is sufficient to drive multi-generational oxidation of multiple VOC species. Therefore, while the yield from toluene alone would likely decrease in a multi-VOC system, the total organic acid production from the VOC mixture may still be substantial.

(Q7) *Line 261–264: Is there a figure for this?*

Response: We have added a figure in the revised manuscript.

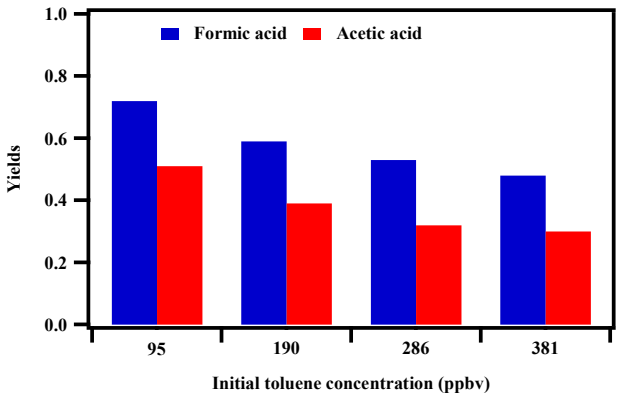

Figure S4. Effects of initial toluene concentrations on the yields of formic acid and acetic acids.

(Q8) *Figure 5: Can the authors comment on why there is 2x more aerosol mass formed during the 70 % RH experiments relative the 20 % ones? Could this account for some of the lower FA and AA yields at higher RH (Fig 1)?*

Response: Thank you for your suggestion. We think that the higher SOA mass observed at 70% RH compared to 20% RH can be attributed to several factors: (1) Enhanced particle-phase aqueous chemistry. Higher humidity promotes the uptake of water-

soluble intermediates (e.g., glyoxal and methylglyoxal) into the particle phase, where aqueous-phase reactions can produce low-volatility products that contribute to SOA mass (Ervens et al., 2011; Jia and Xu, 2014). (2) Enhanced formation of low-volatility organic hydroperoxides. Water vapor can facilitate the formation of organic hydroperoxides, thereby increasing SOA yields (Wang et al., 2023).
These factors may also partially explain the lower organic acid yields at higher RH. Greater partitioning of water-soluble intermediates into the particle phase could reduce their availability for gas-phase fragmentation to organic acids, while enhanced peroxide formation may divert intermediates toward non-acid-producing pathways. We have added this analysis to the revised manuscript.

Page 15: "Additionally, it is worth noting that a greater aerosol mass was formed at 70% RH than at 20% RH under comparable •OH exposures (Figure 5). This enhanced SOA formation at higher humidity may partially account for the lower organic acid yields observed under high-RH conditions. Specifically, the larger partitioning of water-soluble intermediates into the particle phase could reduce their availability for gas-phase fragmentation into organic acids, and enhanced peroxide formation may divert intermediates toward non-acid-producing pathways."

(Q9) *Line 336–339: Consider moving the clarification at line 352 further up in this discussion as this statement is specific to toluene oxidation and doesn't rule out a broader aerosol pathway under real-world conditions.*
Response: We agree that it is important to clarify that our conclusion regarding the minor role of SOA photodegradation is specific to toluene-derived SOA under our experimental conditions and does not preclude the potential importance of aerosol-derived organic acids in the real atmosphere, where SOA composition is more diverse and may contain more photo-labile species. We have added some discussion in the revised manuscript.

Page 14: "Although SOA photodegradation can produce small oxygenated VOCs (including formic acid and acetic acid), previous studies showed that aromatic-derived SOA generates much lower yields of such products compared to biogenic SOA (e.g., derived from isoprene or α-pinene) (Malecha and Nizkorodov, 2016). It should be noted that this conclusion is specific to toluene-derived SOA under our experimental conditions. In the real atmosphere, SOA formed from other precursors (e.g., biogenic VOCs or biomass burning emissions) may exhibit substantially higher organic acid yields upon photodegradation, and the contribution of aerosol-phase chemistry to the overall organic acid budget cannot be excluded based on our results alone."

References

Berndt, T., Böge, O., and Herrmann, H.: On the formation of benzene oxide/oxepin in the gas-phase reaction of OH radicals with benzene, Chem. Phys. Lett., 314, 435–442, 1999.

Bruns, E. A., Slowik, J. G., El Haddad, I., Kilic, D., Klein, F., Dommen, J., Temime-Roussel, B., Marchand, N., Baltensperger, U., and Prévôt, A. S. H.: Characterization of gas-phase organics using proton transfer reaction time-of-flight mass spectrometry: fresh and aged residential wood combustion emissions, Atmospheric Chem. Phys., 17, 705–720, 2017.

Friedman, B. and Farmer, D. K.: SOA and gas phase organic acid yields from the sequential photooxidation of seven monoterpenes, Atmos. Environ., 187, 335–345, 2018.

Murschell, T. and Farmer, D. K.: Atmospheric OH oxidation of three chlorinated aromatic herbicides, Environ. Sci. Technol., 52, 4583–4591, 2018.

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Wyche, K. P., Monks, P. S., Ellis, A. M., Cordell, R. L., Parker, A. E., Whyte, C., Metzger, A., Dommen, J., Duplissy, J., Prevot, A. S. H., Baltensperger, U., Rickard, A. R., and Wulfert, F.: Gas phase precursors to anthropogenic secondary organic aerosol: detailed observations of 1,3,5-trimethylbenzene photooxidation, Atmospheric Chem. Phys., 9, 635–665, 2009.

Reviewer #2:

This study investigates the formation of formic and acetic acid during the photooxidation of toluene using an oxidation flow reactor (OFR). The authors report unexpectedly high peak molar yields at equivalent atmospheric aging times of 1–3 days. The authors concluded that these findings suggest current chemical mechanisms, such as MCM v3.3.1, which underestimate these yields by a factor of five, are missing significant multi-generational oxidation pathways.

However, the authors did not provide sufficient experimental details for me to examine whether their conclusion is valid. The source of OH radical in the OFR experiments of this study was O_3. Its concentration was not reported in the paper.

Usually O_3 concentrations in such experiments should be very high (compared to ambient concentrations) to sustain strong OH production. If this is the case in this study, the alkenes formed after the first 1-2 steps of oxidation of toluene are likely also ready to react with O_3. Reactivity of the ozonides formed is likely insensitive to NOx. It is possible that ozonides and subsequent products (e.g. Criegee Intermediates) convert into organic acids in the aqueous phase. It is an open question whether the abovementioned processes are relevant to the atmosphere. In any case, the authors should discuss the possibility and quantify their contribution to the observed organic acids.

If O_3 concentrations used in the experiments of this study were not very high (as in the OH exposure calibration experiments reported in Figure S3), to achieve high aging, the lamps needed to be very strong, and significantly photolyzed toluene and oxygenated alkenes at 254 nm. These processes have been very poorly constrained. They may or may not lead to organic acid formation, but they are experimental artifacts that should be avoided, or at least deducted.

The authors should report more details of their experiments, carefully examine the possibility of the organic acid formation pathways I discussed above, and update their discussions and conclusion in the paper as needed before this paper can be accepted for publication in ACP.

We gratefully thank you for your comments and suggestions to improve the manuscript. We have revised the manuscript by carefully considering the comments. The major revisions include: (1) quantitative assessment of the relative contributions of O_3 reactions and 254 nm photolysis versus •OH-initiated reactions; (2) detailed experimental conditions for the high-NO_x experiments with model-simulated radical concentrations; (3) wall loss data for organic acids; and (4) expanded discussion on NO/NO_2 roles, RH dependence, and organic acid decay at high •OH exposures. More details about the revisions can be found in the revised manuscript and in our response below.

(Q1) *The source of OH radical in the OFR experiments of this study was O_3. Its concentration was not reported in the paper. Usually O_3 concentrations in such experiments should be very high (compared to ambient concentrations) to sustain strong OH production. If this is the case in this study, the alkenes formed after the first 1-2 steps of oxidation of toluene are likely also ready to react with O_3. Reactivity of the ozonides formed is likely insensitive to NOx. It is possible that ozonides and subsequent products (e.g. Criegee Intermediates) convert into organic acids in the aqueous phase.*

It is an open question whether the abovementioned processes are relevant to the atmosphere. In any case, the authors should discuss the possibility and quantify their contribution to the observed organic acids. If O_3 concentrations used in the experiments of this study were not very high (as in the OH exposure calibration experiments reported in Figure S3), to achieve high aging, the lamps needed to be very strong, and significantly photolyzed toluene and oxygenated alkenes at 254 nm. These processes have been very poorly constrained. They may or may not lead to organic acid formation, but they are experimental artifacts that should be avoided, or at least deducted.

Response: Thank you for your suggestions. We appreciate the opportunity to clarify the experimental conditions and to evaluate the relative contributions of O_3 reactions and 254 nm photolysis compared to •OH reactions.

Regarding the O_3 concentrations, we note that the initial O_3 concentration was in fact reported in the original manuscript (Section 2.2): "the initial concentration of O_3 was about 1580 ppbv". Moreover, the O_3 concentrations at different sampling positions under various experimental conditions were also provided in the original manuscript (Figure 1). Compared with typical OFR studies, our O_3 concentrations (< 2 ppmv) are relatively modest, being ~50 times higher than typical ambient levels. However, the OH radical concentrations in the OFR exceed 10^9 molecules cm^{-3}, which is ~10^3 times higher than typical atmospheric concentrations. To quantitatively assess the relative importance of these two oxidation pathways, we calculated the contribution of O_3 reactions relative to •OH reactions for a series of species under our reactor conditions. As shown in Figure R1, even for species containing multiple unsaturated bonds, the relative contribution of O_3 reactions is less than 20%, while for most species the O_3 contribution is less than 5%. These results confirm that the oxidation process in our OFR is predominantly driven by •OH.

We have also performed an assessment of the potential contribution of 254 nm photolysis. As shown in Figure R2, except for a few species containing multiple chromophores, the contribution of 254 nm photolysis is generally minor compared to •OH-initiated oxidation. For example, the absorption cross section of toluene at 254 nm is relatively small (~5×10^{-19} cm^2 $molecule^{-1}$), and the resulting photolysis rate under our photon flux (~2.9×10^{15} photons cm^{-2} s^{-1}) is approximately 0.0015 s^{-1}, which is more than one order of magnitude lower than the corresponding •OH reaction rate. Therefore, direct photolysis of toluene at 254 nm is not a significant pathway.

In summary, although the O_3 concentrations and 254 nm photon flux in our OFR are higher than ambient levels, •OH concentrations are enhanced to an even greater extent, ensuring that •OH -initiated reactions remain the dominant oxidation pathway. We have added a brief discussion to Section 2.2.

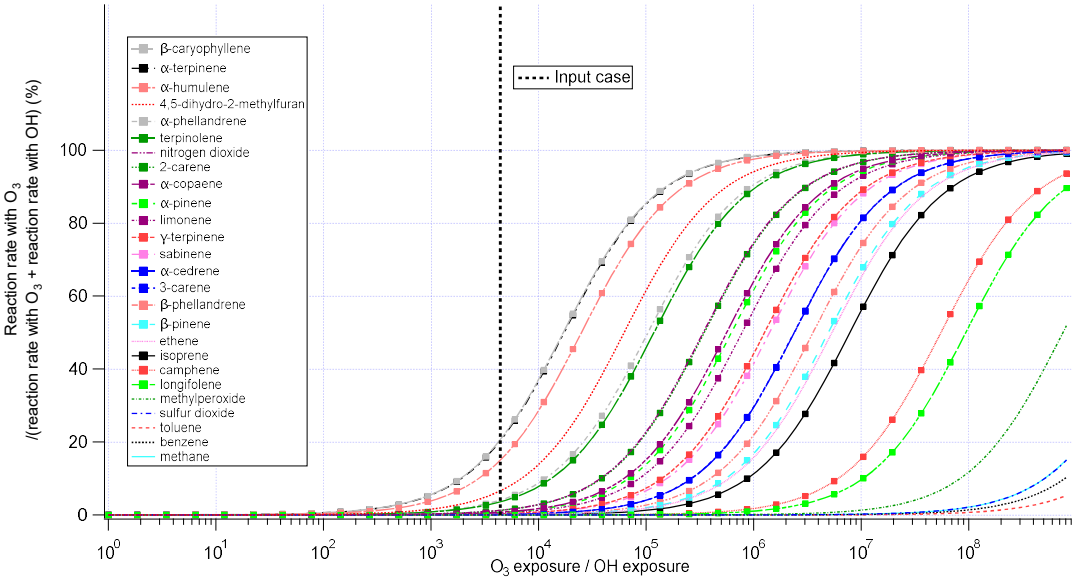

Figure R1. Relative contributions of O_3 reactions versus •OH reactions in the oxidation flow reactor.

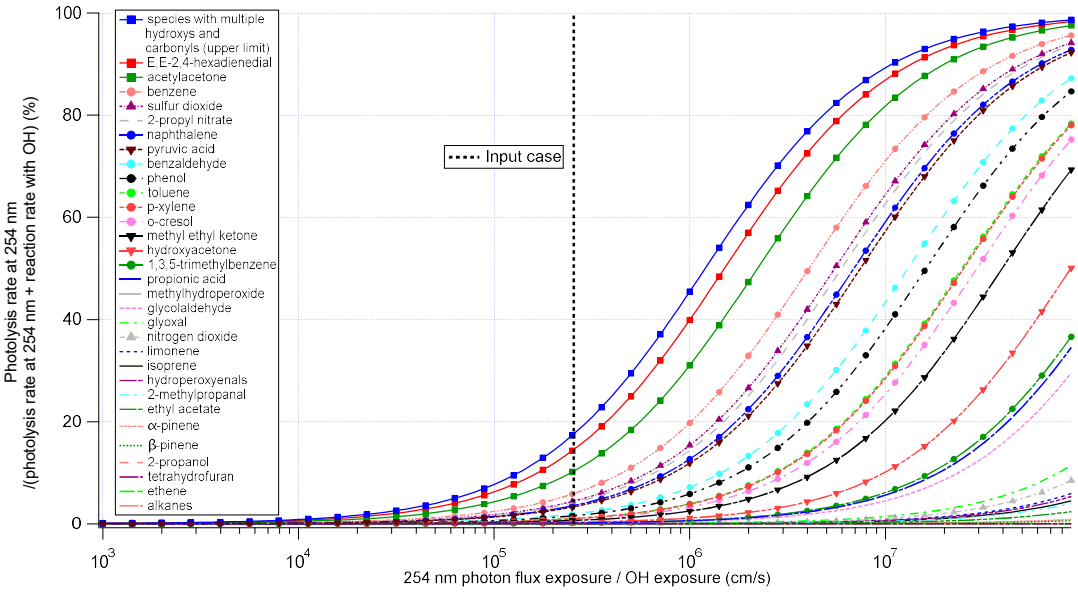

Figure R2. Relative contributions of 254 nm photolysis versus •OH reactions in the oxidation flow reactor.

Page 6: "It should be noted that although both the O_3 concentration and the 254 nm photon flux in the OFR substantially exceed typical ambient levels, •OH concentration is enhanced to an even greater extent, ensuring that •OH-initiated reactions remain the dominant oxidation pathway."

(Q2) *Line 111: this OFR is much more tube-like than typical OFRs (e.g. PAM). More details are needed to convince me that its wall losses are negligible.*

Response: Thank you for your suggestion. We acknowledge that our OFR design (2 L volume, 1 m length, 5 cm inner diameter) is more tubular in geometry compared to typical OFRs such as the PAM reactor. We have conducted detailed wall loss experiments using this reactor configuration. Given the short residence times employed in our study (3.9–60 s), wall losses have a minor impact on the experimental results. The wall loss rate constants for formic acid and acetic acid were measured as 4.3×10^{-4}

s^{-1} and 3.4×10^{-4} s^{-1} at 20% RH, and 4.7×10^{-4} s^{-1} and 3.9×10^{-4} s^{-1} at 70% RH, respectively. Compared with the •OH reaction rate at the •OH concentrations in our OFR, the wall loss rates account for less than 5% of the total removal rates. Therefore, wall losses were not corrected for in our yield calculations and do not affect the conclusions of this study. We have added a statement to this effect in Section 2.2 of the revised manuscript.

Page 7: "In addition, the wall loss rates of formic acid and acetic acid were measured to be less than 5% of their respective •OH reaction rates under our experimental conditions and were therefore not corrected for in the yield calculations."

(Q3) *Line 142: I can expect NO and NO_2 to play very different roles in toluene oxidation chemistry. The authors should discuss the roles of NO and of NO_2 in these experiments separately.*

Response: Thank you for your suggestion. In our experiments, NO was generated via the reaction $O(^1D) + N_2O \rightarrow 2NO$, followed by $NO + O_3 \rightarrow NO_2 + O_2$. The resulting NO_x mixture therefore contained both NO and NO_2. Based on our model simulations, NO and NO_2 concentrations exhibit a strong linear correlation ($R_2 = 0.98$) across all experimental conditions, making it difficult to fully decouple their individual effects on organic acid formation. Nevertheless, we note that the primary role of NO in toluene oxidation chemistry is to react with peroxy radicals (RO_2• and HO_2•), diverting them from the RO_2• + HO_2• pathway toward NO reaction channels that favor alkoxy radical formation. Since our results show that organic acid yields are insensitive to the NO level, this implies that the dominant organic acid formation pathway is not mediated by traditional peroxy radical chemistry, regardless of whether NO or NO_2 is the predominant species. We have added a brief discussion of this point in the revised manuscript.

Page 11: "It should be noted that NO and NO_2 were produced simultaneously in our experiments (via $O(^1D) + N_2O \rightarrow 2NO$, followed by $NO + O_3 \rightarrow NO_2 + O_2$), and model simulations indicate that their concentrations were strongly correlated ($R^2 = 0.98$). NO primarily reacts with RO_2 to form alkoxy radicals (RO•), which can divert the traditional organic acid formation pathway toward carbonyl products. NO_2 can react with peroxyacyl radicals to form peroxyacyl nitrates (PANs), potentially sequestering acyl peroxy intermediates, and can also react with •OH, thereby affecting •OH concentration."

Page 11: "These results indicate that neither the NO-mediated RO_2• diversion pathway nor the NO_2-related pathways significantly control organic acid production."

(Q4) *Line 214: the organic acid formation pathways I proposed above both become more important relative to multi-generation OH oxidation at lower RH. None of these reactions directly involve water vapor, but OH is produced from it. More organic acid formed at lower RH is a piece of evidence AGAINST OH oxidation pathways.*

Response: As demonstrated in our quantitative assessment above, O_3 reactions and 254 nm photolysis are minor compared to •OH -initiated reactions under our experimental conditions and therefore cannot account for the observed RH dependence. The lower organic acid yields at higher RH can be attributed to two alternative factors rather than a reduced role of •OH chemistry: (1) substantially more SOA is formed at 70% RH than at 20% RH, and greater partitioning of water-soluble intermediates into the particle phase could reduce their availability for gas-phase fragmentation to organic acids; and

(2) enhanced formation of organic hydroperoxides at higher humidity may divert reactive intermediates toward non-acid-producing pathways. We have added this discussion to Section 3.1.1 of the revised manuscript.

Page 15: "Additionally, it is worth noting that a greater aerosol mass was formed at 70% RH than at 20% RH under comparable •OH exposures (Figure 5). This enhanced SOA formation at higher humidity may partially account for the lower organic acid yields observed under high-RH conditions. Specifically, the larger partitioning of water-soluble intermediates into the particle phase could reduce their availability for gas-phase fragmentation into organic acids, and enhanced peroxide formation may divert intermediates toward non-acid-producing pathways."

(Q5) *Line 225: the authors need to clarify that the decay after 3 days of aging was likely due to the fragmentation of the precursors of formic and acetic acids. The acids react with OH too slowly to be consumed at such a low age.*

Response: Thank you for your suggestion. We have clarified it in the revised manuscript.

Page 8: "The decrease in organic acid concentrations at higher •OH exposure is likely due to kinetic competition between organic acid formation and their subsequent degradation (including direct •OH reaction and depletion of their precursors) as OH exposure increases."

(Q6) *Line 275: I do not believe that NO:HO_2 can reach 1000 with much O_3 added, which reacts with NO very rapidly and sustains HO_2 concentration through HOx radical recycling. The authors should also report the details of these "high-NOx" experiments.*

Response: We clarify that the method of NO generation in our experiments differs from the conventional approach of direct NO injection. Although the reaction of NO with O_3 is rapid, in our system, NO is produced in situ throughout the reactor via the reaction $O(^1D) + N_2O \rightarrow 2NO$, rather than being introduced at a single point. The NO concentration was systematically varied by adjusting the N_2O flow rate (0, 20, 40, 80, 120, 160, and 200 mL min^{-1}). All NO_x experiments were conducted using a single lamp, with sampling at the reactor outlet corresponding to a residence time of 60 s.

The model-simulated NO concentrations increased approximately linearly with N_2O flow rate, reaching a maximum of ~29 ppbv. The NO:HO_2• ratio increased from approximately 3 to ~10^3 as the N_2O flow rate increased, transitioning the dominant radical chemistry from HO_2• -controlled to NO-controlled regimes. The model-simulated •OH and HO_2• concentrations as a function of NO concentration are shown in Figure R3. We have added detailed experimental conditions in the revised manuscript.

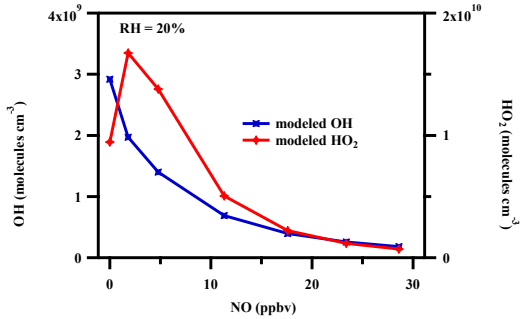

Figure R3. Model-simulated •OH and HO_2• concentrations as a function of NO

concentration.

Page 6: "The influence of NO_x on organic acid formation was investigated by adding N_2O to the OFR. NO and NO_2 were produced via the reaction $O(^1D) + N_2O \rightarrow 2NO$, followed by $NO + O_3 \rightarrow NO_2 + O_2$ (Lambe et al., 2017). The NO concentration was systematically varied by adjusting the N_2O flow rate (0, 20, 40, 80, 120, 160, and 200 mL min^{-1}). All NO_x experiments were conducted using a single lamp, with sampling at the reactor outlet corresponding to a residence time of 60 s. It should be noted that although both the O_3 concentration and the 254 nm photon flux in the OFR substantially exceed typical ambient levels, •OH concentration is enhanced to an even greater extent, ensuring that •OH-initiated reactions remain the dominant oxidation pathway."

(Q7) *Line 314: Fittschen et al. (2014) reported a very high overall rate constant but did not conclude that HCOOH is the only C-containing product. Other pathways were also discussed that paper and the branching ratios of different channels were not specified.*

Response: Thank you for your suggestion. In our model implementation, we assumed a 100% yield of formic acid from this pathway, which represents an upper-limit estimate. Even under this favorable assumption, the modeled formic acid concentrations remain approximately five times lower than the experimental measurements. If the actual branching ratio is lower, the contribution of this pathway would be even smaller, further strengthening the conclusion that additional unidentified pathways are needed. We have revised the discussion in Section 3.2 to acknowledge the uncertain branching ratio and to clarify that our model estimate represents an upper bound for this pathway.

Page 13: "It should be noted that the branching ratio for formic acid formation from this reaction remains uncertain, thus, the yield of 100% was assumed in our model, representing an upper-limit estimation."

Page 13: "Even under this upper-limit assumption, the modeled concentrations of formic acid are still approximately five times lower than the experimental measurements (Figures 4c–d)."

(Q8) *Line 364: NO can facilitate glyoxal and methylglyoxal formation through ring-opening. Could their low yields at high exposures simply because almost all NO was oxidized in these experiments?*

Response: Experiments presented in Figure 6 were conducted without NO_x addition. Therefore, the decrease in glyoxal and methylglyoxal yields at high •OH exposures cannot be attributed to the oxidation of NO. At low •OH exposure, the measured glyoxal yield (~11%) in this study is consistent with previous studies reporting glyoxal yields of 10–15% from toluene oxidation under low-NO_x conditions (Gery et al., 1985; Bandow et al., 1985).

(Q9) Technical correction: *Table S1: "Rquivalent" -> "Equivalent" in the first row*

Response: We have corrected it in the revised manuscript.

References

Bandow, H. and Washida, N.: Ring-cleavage Reactions of Aromatic Hydrocarbons Studied by FT–IR Spectroscopy. III. Photooxidation of 1,2,3-, 1,2,4-, and 1,3,5-Trimethylbenzenes in the NO_x–Air System, Bull. Chem. Soc. Jpn., 58, 2549–2555, 1985.

Gery, M. W., Fox, D. L., Jeffries, H. E., Stockburger, L., and Weathers, W. S.: A continuous stirred tank reactor investigation of the gas-phase reaction of hydroxyl radicals and toluene, Int. J. Chem. Kinet., 17, 931–955, 1985.

Reviewer #3:

This study investigated the formation of formic acid and acetic acid during multi-generational photooxidation of toluene using an oxidation flow reactor (OFR). The authors found that the yields of these organic acids increased significantly with OH exposure, reaching 74% for formic acid and 40% for acetic acid at 1–3 equivalent atmospheric aging days. This finding challenges the traditional view of relatively low organic acid yields and provides a new explanation for the widespread underestimation of organic acids in atmospheric models. The study design is rigorous, with a wide range of experimental conditions (different RH, OH exposure levels, NOx concentrations), and the data quality is high. However, several issues regarding the generalizability of the conclusions, depth of mechanistic interpretation, and appropriateness of model comparisons need to be clarified or addressed. Until these concerns are adequately resolved, publication in ACP is not recommended.

We gratefully thank you for your comments and suggestions to improve the manuscript. We have revised the manuscript by carefully considering the comments. The major revisions include: expanded discussion on multi-generational oxidation mechanisms, additional analysis and discussion on the NO_x dependence experiments, conducted wall loss experiments, and quantitative assessment of the relative contribution of 254 nm photolysis. More details about the revisions can be found in the revised manuscript and in our response below.

(Q1) *Discussion of "multi-generational oxidation mechanisms" is overly speculative. The title and core conclusion emphasize that "multi-generational oxidation" is key to high organic acid yields, but the paper's discussion of specific chemical mechanisms is relatively weak:*

Section 3.3 rules out the dominant roles of SOA photodegradation and known gas-phase pathways (e.g., glyoxal/methylglyoxal oxidation) but does not propose clear multi-generational oxidation pathways. The authors mention that "fragmentation of five-membered oxygen-containing heterocyclic compounds" may yield acetic acid, but note that "this pathway remains controversial." This makes "multi-generational oxidation" sound more like a descriptive label than a mechanistic explanation.

Section 3.2 tests four formic acid formation pathways, with only the CH_3O_2 + OH pathway contributing significantly, yet the model still underestimates observations by ~5-fold. This suggests the existence of unidentified pathways, but the authors do not further explore potential candidate pathways (e.g., Criegee intermediate chemistry, peroxy radical isomerization). It is recommended to propose more specific mechanistic hypotheses in the discussion based on recent literature, to guide future research.

Response: Thank you for your suggestions. We agree that the mechanistic discussion in the original manuscript was insufficiently developed and have expanded it in the revised manuscript.

Regarding the term “multi-generational oxidation”, we retain it because it accurately describes the experimental observation that organic acid yields increase with progressive oxidation (i.e., higher •OH exposure) and that the acids are predominantly later-generation products rather than primary oxidation products. We do not intend the term to imply a fully resolved mechanism. We would also like to clarify that the model evaluation itself constitutes a mechanistic discussion. The original model did not

consider formic acid formation; we explicitly added four possible formation pathways and evaluated their contributions. Although we concluded that only the CH_3O_2• + •OH pathway contributes significantly, this exercise was itself a test of specific chemical mechanisms. More importantly, after adding these four pathways, the modeled formic acid yield reaches only ~13% of the observed value, and the predicted NO_x dependence does not match observations. This discrepancy is not as a model failure, but as evidence that unidentified multi-generational pathways contribute substantially to organic acid formation. Furthermore, we have used experimental constraints to narrow down the possible mechanisms: based on the lack of relative humidity dependence, we rule out a dominant role of Criegee intermediate chemistry; based on the lack of correlation with SOA mass, we rule out SOA photodegradation as a major source; and based on the correlation with primary oxidation markers of carbonyl species, we confirm that the organic acids are multi-generational oxidation products. These are all mechanistic arguments grounded in experimental data. Based on the observed NO_x independence of organic acid yields, we propose alkoxy radical (RO•) β-scission as a key multi-generational pathway. Multi-generational oxidation produces increasingly oxygenated intermediates. Alkoxy radicals formed through RO_2• + NO or RO_2• + RO_2• reactions can undergo β-scission, producing smaller carbonyl compounds and organic acids. As oxidation proceeds to later generations, the intermediates become smaller and more oxygenated, making fragmentation to C1–C2 acids increasingly favorable. Notably, this pathway would be facilitated rather than suppressed under high-NO_x conditions, consistent with our observation of NO_x-independent organic acid formation. We have updated the discussion of these points in the revised manuscript.

We believe this framework transforms "multi-generational oxidation" from a speculative label into a structured, falsifiable research direction. Further mechanistic confirmation will require additional laboratory and theoretical studies, which we have highlighted as future work.

Page 11: "It should be noted that NO and NO_2 were produced simultaneously in our experiments (via $O(^1D) + N_2O \rightarrow 2NO$, followed by $NO + O_3 \rightarrow NO_2 + O_2$), and model simulations indicate that their concentrations were strongly correlated ($R^2 = 0.98$). NO primarily reacts with RO_2 to form alkoxy radicals (RO•), which can divert the traditional organic acid formation pathway toward carbonyl products. NO_2 can react with peroxyacyl radicals to form peroxyacyl nitrates (PANs), potentially sequestering acyl peroxy intermediates, and can also react with •OH, thereby affecting •OH concentration."

(Q2) *The observed NOx independence presents a profound conflict with existing mechanistic understanding and is insufficiently explained. The authors report that increasing NO concentrations up to 29 ppbv (corresponding to a NO/HO_2 ratio >1000) did not suppress the formation of formic and acetic acid (Section 3.1.2). This finding, while intriguing, presents a fundamental paradox with established atmospheric chemical mechanisms: Traditional atmospheric chemistry holds that organic acids are primarily formed through reactions of RO_2 with HO_2. Under high-NO conditions, RO_2 should preferentially react with NO to form nitrates or carbonyl compounds, which would strongly suppress organic acid formation.*

However, authors provide no concrete chemical mechanism to explain how such high yields (up to 74% for formic acid) can persist when traditional RO_2+HO_2 pathways are effectively shut down. The current MCM model underestimates observations by approximately five-fold, confirming that the model captures neither the magnitude nor

the NOx-independent nature of the observed production. This represents a critical gap: if the mechanism is truly insensitive to NOx at levels exceeding 1000:1 NO:HO_2 ratios, it would require a fundamental rethinking of aromatic oxidation chemistry. Yet the authors offer little speculation on what such a pathway might entail.

Response: Thank you for your suggestions. We agree that the NO_x independence of organic acid formation is one of the most significant findings of our study and deserves a more thorough discussion.

First, we note that the MCM model does not include any formic acid formation pathway from toluene oxidation (as discussed in Section 3.2). The model's underestimation of formic acid is therefore not a failure to capture the NO_x dependence of a known pathway, but rather a complete absence of the relevant chemistry. For acetic acid, the model includes only the CH_3CO_3• + HO_2• and CH_3CO_3• + RO_2• pathways (reactions R1 and R2), both of which are indeed NO_x-sensitive. The model's underestimation of acetic acid yields and its prediction of NO_x sensitivity (contrary to our observations) confirm that these traditional peroxy radical pathways are not the dominant source of the observed organic acids. We propose that the NO_x-insensitive formation of organic acids may proceed through pathways that are not mediated by the traditional RO_2• + HO_2• mechanism. One plausible candidate is alkoxy radical β-scission: RO_2• + NO → RO• + NO_2, followed by fragmentation of RO• to produce organic acids. This could explain why organic acid yields do not decrease with increasing NO_x. Under this mechanism, the overall process would be NO_x-facilitated rather than NO_x-suppressed, which is consistent with our observation that organic acid yields remain high (or even increase slightly) with increasing NO_x. We acknowledge that the specific pathways responsible for the high organic acid yields remain to be fully elucidated, and that this represents a critical gap in current mechanistic understanding.

(Q3) *In lines 109–126, the 2 L small-scale reactor has an extremely high surface-to-volume ratio. Formic acid and acetic acid, as highly polar molecules, may undergo adsorption and reversible release on surfaces, which could significantly affect concentration measurements at the outlet. The authors need to provide recovery rate calibration data (measured or simulated) for these two acids under different humidity conditions.*

Response: Thank you for your suggestions. Our OFR is made of quartz, which has lower wall adsorption for polar organic molecules compared to Teflon chambers. We have conducted wall loss experiments for formic acid and acetic acid under both 20% and 70% RH conditions. The measured wall loss rate constants were 4.3×10^{-4} s^{-1} and 3.4×10^{-4} s^{-1} at 20% RH, and 4.7×10^{-4} s^{-1} and 3.9×10^{-4} s^{-1} at 70% RH, respectively. Compared with the •OH reaction rate at the •OH concentrations in our OFR, the wall loss rates account for less than 5% of the total removal rates. Additional evidence supporting the minor role of wall effects is that when the reaction was terminated (by removing precursors or turning off the lamps), the concentrations of formic acid and acetic acid decreased to less than 10% of their peak values, indicating that reversible wall adsorption is negligible.

(Q4) *In lines 386–419, the authors do not discuss the potential influence of photolysis. A critical flaw is that important intermediate products of toluene oxidation (such as glyoxal, methylglyoxal, pyruvic acid, etc.) have large absorption cross-sections at 254 nm. In the real atmosphere, these species are primarily degraded via long-wavelength UV photolysis or reaction with OH radicals; however, inside the OFR, the intense 254*

nm radiation may induce rapid photolysis of these intermediates and directly release formic acid, leading to artificially enhanced yields. The authors should discuss this potential artifact and, if possible, quantify the contribution of direct photolysis to the observed formic acid production under their experimental conditions. Without such analysis, the reported "multi-generational oxidation" yields may significantly overestimate the true atmospheric formation potential.

Response: Thank you for your suggestions. We have performed a quantitative assessment of the potential contribution of 254 nm photolysis relative to OH-initiated oxidation for key intermediates under our experimental conditions. As shown in Figure R4, the contribution of 254 nm photolysis is generally minor (< 20%) compared to OH-initiated oxidation for most intermediates.

Furthermore, even if 254 nm photolysis of key carbonyl intermediates (e.g., glyoxal, methylglyoxal) were to produce formic acid with 100% yield, this artifact could not explain the observed high organic acid concentrations. The molar yields of glyoxal and methylglyoxal at low •OH exposure are only ~11% each, and these decrease to ~1% at high •OH exposures (Figure 6). Even assuming complete conversion of all glyoxal and methylglyoxal to formic acid via photolysis, the resulting formic acid yield would be far below the observed peak value of 74%.

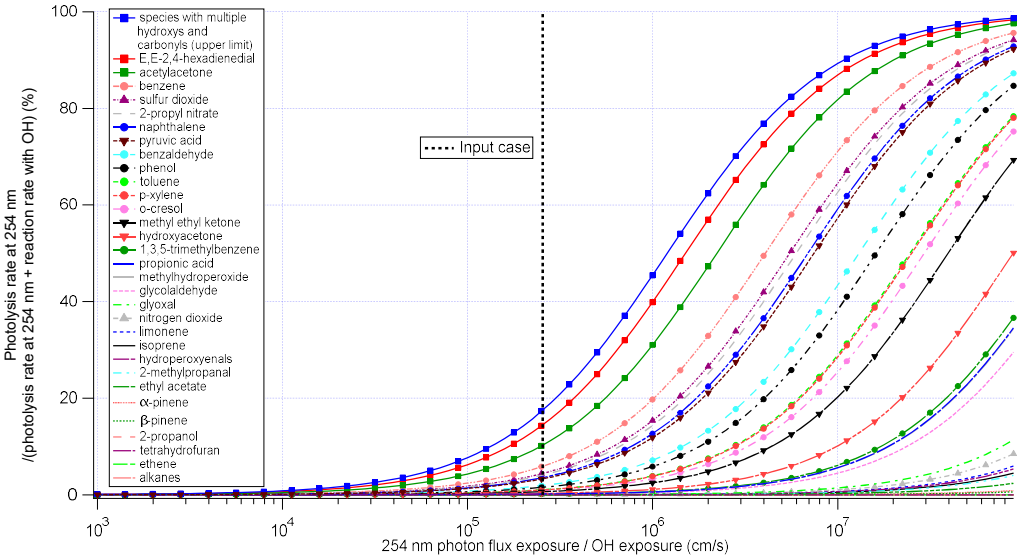

Figure R4. Relative contributions of 254 nm photolysis versus •OH reactions in the oxidation flow reactor.

(Q5) *The temperature effect should be addressed. What was the internal temperature of the OFR? Did the temperature increase as a function of OH exposure, even with the use of a water jacket?"*

Response: As stated in the original manuscript, the OFR was maintained at 298 ± 1 K using a continuously circulating water jacket. The temperature remained stable at 298 ± 1 K across all experimental conditions, including when all eight lamps were illuminated simultaneously, confirming that the water jacket effectively dissipates the heat generated by the UV lamps. No systematic temperature increase was observed with increasing lamp number or •OH exposure.

(Q6) *Since N_2O absorbs a significant amount of photons, have the authors calibrated the OH exposure under high-NO_x conditions during N_2O injection? The manuscript lacks a description of this. It is important to note that OH exposure at a constant lamp*

voltage certainly differs significantly between high-NOx and low-NOx conditions. The results shown in Fig. 3 are inconsistent with expectations, suggesting that the same calibration factors may have been applied regardless of whether N_2O was injected. If so, this approach would be technically inaccurate, as N_2O significantly alters the photolysis environment and OH exposure within the reactor.

Response: In our study, •OH exposures were determined through model simulations rather than direct calibration, and the results were validated by comparing simulated and measured toluene decay, which showed good agreement (slope =1.08 and R^2 = 0.97), confirming the accuracy of our •OH exposure estimates. We acknowledge, however, that Figure 3 in the original manuscript did not properly account for the change in •OH exposure under high-NO_x conditions. With increasing N_2O addition, the model simulated •OH concentration decreased substantially (from 2.92×10^9 to 1.8×10^8 molecules cm^{-3}). Nevertheless, the organic acid yields remained high even under these reduced •OH conditions (at 20% RH: ~40% for formic acid and ~19% for acetic acid; at 70% RH: ~58% and ~24%, respectively). This suggests that the NO_x-insensitive nature of organic acid formation is robust, and that NO may even facilitate organic acid production through enhanced alkoxy radical formation and subsequent fragmentation.

(Q7) *Line 167: Please also provide the volume concentrations of the produced SOA.*

Response: Thank you for your suggestion. We have revised it in the manuscript.

Page 7: "Before each experiment, high concentrations of O_3 were introduced into the OFR with two lamps illuminated until particle concentrations measured by the SMPS were negligible (< 50 cm^{-3} or 0.1 μg m^{-3}) and no impurities were detected by GC-FID."

(Q8) *The wall loss of formic acid, acetic acid, and LVOCs (Low Volatility Organic Compounds) must be accounted for in the yield calculations."*

Response: Thank you for your suggestion. We have conducted detailed wall loss experiments. The measured wall loss rate constants for formic acid and acetic acid were measured as 4.3×10^{-4} s^{-1} and 3.4×10^{-4} s^{-1} at 20% RH, and 4.7×10^{-4} s^{-1} and 3.9×10^{-4} s^{-1} at 70% RH, respectively. Compared with the •OH reaction rate at the OH concentrations in our OFR, the wall loss rates account for less than 5% of the total removal rates. Therefore, wall losses were not corrected for in our yield calculations and do not affect the conclusions of this study.

Page 7: "In addition, the wall loss rates of formic acid and acetic acid were measured to be less than 5% of their respective •OH reaction rates under our experimental conditions and were therefore not corrected for in the yield calculations."

(Q9) *Line 208–209: As shown in Fig. 2, while the decay of toluene increases with OH exposure, it is not completely consumed. A more plausible explanation for the observed organic acid yield curves would be the kinetic competition between acid formation and their subsequent degradation (or other non-acid producing pathways) as OH exposure increases.*

Response: Thank you for your suggestion. We agree that the organic acid yield curves reflect kinetic competition between formation and degradation processes as •OH exposure increases. We have revised the relevant statement in the manuscript accordingly.

Page 8: "The decrease in organic acid concentrations at higher •OH exposure is likely due to kinetic competition between organic acid formation and their subsequent

degradation (including direct •OH reaction and depletion of their precursors) as OH exposure increases."