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):

Yield (%) = (Δ[organic acid] / Δ[toluene]) × 100% 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.

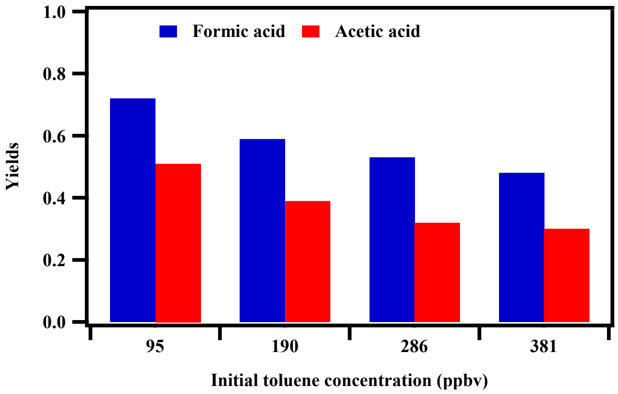

Figure S4. Effects of initial toluene concentrations on the yields of formic acid and acetic acids.

(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

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