

Response to reviewer comments on “Photochemical aging of aerosols contributes significantly to the production of atmospheric formic acid” by Yifan Jiang et al.

Comments from the reviewers are shown in black *Italic* font. Response from the authors is shown in black regular font. Revisions are shown in blue regular font. The line numbers provided here refer to the ones in the revised manuscript.

*Reviewer 1 Comments:*

*This paper examines the sources of formic acid (HCOOH) in the somewhat polluted marine boundary layer. The authors have an excellent site on the coast near Hong Kong that samples a range of polluted conditions from coastal to marine. The mix of air masses was a bit unusual as the marine was highly polluted in NO<sub>x</sub> with low O<sub>3</sub>, and the land (coastal) air had high O<sub>3</sub> and biogenics. They identify aerosols as a key co-existing species that is related to high formic acid levels. They track the observed air parcels with HYSPLIT back trajectories. They then pursue laboratory-chamber studies to quantify the net production of HCOOH from different aerosols and follow up with a box model study of the kinetics involved. Their conclusions that a major source of HCOOH comes from photochemical aging of organic compounds in aerosols (particularly nitrate-containing aerosols) is indisputable. They note that inclusion of this additional source would reduce some (all) of the model-measurement discrepancy in global models. The paper is very clearly written; and from my fast read-through, I did not find any typos. Altogether, impressive.*

Response: Thank you for your encouraging comments. Below please find our point-to-point response and revisions of the manuscript.

*1. "191.1 ± 167.2 ppt in marine air masses" – the 4th decimal place is unnecessary and only clutters up the major numbers: 191 ± 167.*

Response: We agree that the fourth decimal place is unnecessary. We have revised as the referee suggested.

Revision in the main text:

Abstract:

Line 17-18: The average concentrations of HCOOH were **191 ± 167** ppt in marine air masses and **996 ± 433** ppt in coastal air masses.

Results Section 3.1:

Line 289-296: The average HCOOH concentration in marine air masses was **191 ± 167** ppt; this was higher than those over the remote ocean, due to local emission sources, but significantly lower than those in urban environments (Table 1). In contrast, the ambient HCOOH concentrations in coastal air masses were substantially higher, averaging **996 ± 433** ppt, comparable with other measurements at rural or urban background sites. During the haze period, the concentrations of HCOOH displayed a pattern similar to the concentrations of O<sub>3</sub>, with the daytime peak concentration

increasing from 674 to 2790 ppt.

*2. The lack of atmospheric HCOOH sources in models is duly noted, but do the aerosols in the dominant remote marine atmosphere have the organics and nitrates to generate the missing source? Can the authors assess/speculate on this based on published data, e.g., from ATom. I do not expect them to analyze other observations, but they can comment on whether the aerosols observed over the Pacific would likely produce ~0.1 ppb/hr as at their site.*

Response:

Following the referee's suggestion, we estimated the production rates of HCOOH from aerosols using the Atmospheric Tomography Mission (ATom) data from April to May 2018 (Wofsy et al., 2021). The selected observation data were obtained within the Pacific Ocean with sampling heights below 5 km. The mean values of mass concentration of PM<sub>1</sub>, the surface area density of PM<sub>1</sub>, the photolysis frequency of NO<sub>2</sub> and the mixing ratio of O<sub>3</sub> were 1 μg cm<sup>-3</sup>, 26 μm<sup>2</sup> cm<sup>-3</sup>, 0.01 s<sup>-1</sup> and 24.2 ppb, respectively. The calculated mean production rate of HCOOH from aerosols (P<sub>HCOOH-a</sub>) was 6.6 ppt h<sup>-1</sup>. Considering that the proportion of nitrate in PM<sub>1</sub> was only 3%, which is significantly lower than that at our site (24.3%), the actual P<sub>HCOOH-a</sub> is expected to be even lower. The small P<sub>HCOOH-a</sub> in the remote marine atmosphere is reasonable given the low concentration of HCOOH observed over the Pacific (mean: 10.5 ppt; maximum: 85.6 ppt). In addition, a previous study showed small discrepancy between observed and modelled results (without considering aerosol aging) in remote clean air masses (Chen et al., 2021).

We also assessed the HCOOH production when the remote marine boundary layer is affected by fire plumes by selecting data obtained at heights below 5 km and HCOOH concentrations higher than 1 ppb. The mean values of the mass concentration of PM<sub>1</sub>, the surface area density of PM<sub>1</sub>, the photolysis frequency of NO<sub>2</sub> and the mixing ratio of O<sub>3</sub> were 4.9 μg cm<sup>-3</sup>, 92.6 μm<sup>2</sup> cm<sup>-3</sup>, 0.011 s<sup>-1</sup> and 45.5 ppb, respectively. The resulting P<sub>HCOOH-a</sub> was 84.5 ppt h<sup>-1</sup>, significantly higher than that observed in remote marine atmosphere. After consideration of the low proportion of nitrate in PM<sub>1</sub> (5.1%), P<sub>HCOOH-a</sub> was 17.7 ppt h<sup>-1</sup> assuming a positive linear correlation between P<sub>HCOOH-a</sub> and nitrate concentration. This corresponds to a rate of 2390%/year that organic aerosol (OA) mass (3 μg cm<sup>-3</sup>) is photochemically converted to HCOOH, which is equivalent to a carbon-based HCOOH yield of ~3.8–38% over 1–10 days of aging, close to that required to account for the ATom observations (16–37%) in aged fire air masses (Chen et al., 2021). Therefore, the photochemical aging of aerosols potentially explains a substantial portion of missing HCOOH sources in aged fire plumes. We added discussions above in the main text and the calculation details are shown in SI.

Revision in the main text:

Results Section 3.3:

Line 456-464: To evaluate the role of aerosol photochemical aging on HCOOH production in a broader context, we also examined the HCOOH data over the remote

marine boundary layer obtained from the Atmospheric Tomography Mission (ATom) aircraft campaign which was conducted around the globe during April-May 2018 (Wofsy et al., 2021) (Text S5). Our results show that the photochemical aging of aerosols was insignificant in remote ocean areas due to the low PM and nitrate concentrations found there. However, when these regions are affected by aged fire plumes containing higher levels of organics and nitrate, photochemical aging of aerosols accounts for the substantial sources of HCOOH. These results suggest the photochemical aging appears to be important in relatively polluted atmospheres.

Revision in SI:

Line 100-128:

**Text S5.** Evaluation methods of HCOOH production from photochemical aging of aerosols using the Atmospheric Tomography Mission (ATom) data.

We first assessed the production of HCOOH from aerosols over the Pacific as an illustrative case of the remote marine boundary layer. The selected observation data were obtained within the Pacific Ocean with sampling heights below 5 km. The mean values of mass concentration of PM<sub>1</sub>, the surface area density of PM<sub>1</sub>, the photolysis frequency of NO<sub>2</sub> and the mixing ratio of O<sub>3</sub> were 1 μg cm<sup>-3</sup>, 26 μm<sup>2</sup> cm<sup>-3</sup>, 0.01 s<sup>-1</sup> and 24.2 ppb, respectively. The calculated mean production rate of HCOOH from aerosols (P<sub>HCOOH-a</sub>) was 6.6 ppt h<sup>-1</sup>. Considering that the proportion of nitrate in PM<sub>1</sub> was only 3%, which is significantly lower than that at our site (24.3%), the actual P<sub>HCOOH-a</sub> is expected to be even lower. The small P<sub>HCOOH-a</sub> in the remote marine atmosphere is reasonable given the low concentration of HCOOH observed over the Pacific (mean: 10.5 ppt; maximum: 85.6 ppt). In addition, a previous study showed small discrepancy between observed and modeled results in remote clean air masses in remote clean air masses (Chen et al., 2021).

We also assessed the HCOOH production when the remote marine boundary layer is affected by fire plumes by selecting data obtained at heights below 5 km and HCOOH concentrations higher than 1 ppb. The mean values of the mass concentration of PM<sub>1</sub>, the surface area density of PM<sub>1</sub>, the photolysis frequency of NO<sub>2</sub> and the mixing ratio of O<sub>3</sub> were 4.9 μg cm<sup>-3</sup>, 92.6 μm<sup>2</sup> cm<sup>-3</sup>, 0.011 s<sup>-1</sup> and 45.5 ppb, respectively. The resulting P<sub>HCOOH-a</sub> was 84.5 ppt h<sup>-1</sup>, significantly higher than that observed in remote marine atmosphere. After consideration of the low proportion of nitrate in PM<sub>1</sub> (5.1%), P<sub>HCOOH-a</sub> was 17.7 ppt h<sup>-1</sup> assuming a positive linear correlation between P<sub>HCOOH-a</sub> and nitrate concentration. This corresponds to a rate of 2390%/year that organic aerosol (OA) mass (3 μg cm<sup>-3</sup>) is photochemically converted to HCOOH, which is equivalent to a carbon-based HCOOH yield of ~3.8–38% over 1–10 days of aging, close to that required to account for the ATom observations (16–37%) in aged fire air masses (Chen et al., 2021).

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M., Apel, E. C., Hornbrook, R. S., Blake, D. R., Nault, B. A., Campuzano-Jost, P., Jimenez, J. L., and Dibb, J. E.: HCOOH in the Remote Atmosphere: Constraints from Atmospheric Tomography (ATom) Airborne Observations, *ACS Earth Space Chem*, 5, 1436–1454, <https://doi.org/10.1021/acsearthspacechem.1c00049>, 2021.

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