Responses to Referee #2's comments

We are grateful to the reviewers for their valuable and helpful comments on our manuscript "Rapid formation of hydroxymethyl hydroperoxide and its vital role in methanesulfonic acid-methylamine nucleation: impacts of urban industrial and forested areas" (MS No.: **egusphere-2025-4960**). We have revised the manuscript carefully according to reviewers' comments. The point-to-point responses to the Referee #2's comments are summarized below:

General comments:

Major comments: While I am not an expert in quantum calculations or molecular dynamics, this manuscript clearly addresses the enhanced formation of HMHP via MSA-catalyzed hydrolysis of CH_2OO and highlights its importance in new particle formation. The theoretical results presented provide valuable guidance for future research on SA- and MSA-derived nucleation.

However, as shown in Figure 6, the MSA concentrations are around 1×10^4 in all locations, which is near the detection limit of the CIMS, if that is the instrument used. It is unclear how reliable these data are for quantifying MSA's contribution to nucleation or HMHP formation. I suggest that the authors tone down the emphasis on the importance of MSA-HMHP formation in urban industrial regions. Because, as usual, SA-MA or SA-NH_3 are the main nucleation mechanisms in the urban industrial regions.

Specific Comments:

Comment 1.

Lines 53-59: The manuscript should clarify why MSA is important in this study. Its atmospheric abundance varies widely: typically high in the marine atmosphere and free troposphere, but often very low over continental regions. The authors should provide an estimate of the average MSA concentration in continental areas. Compared to H_2O dimers, MSA is much lower in concentration, so the text should explicitly explain why its role in nucleation is significant despite its low abundance.

Response: Thanks for your valuable comments. In fact, MSA, one of the simplest organic organosulfur acids in the atmosphere, is a prominent oxidation product from organosulfur compounds that originate from biological processes, biomass combustion, industrial emissions, and agriculture, which appreciably contribute to atmospheric NPF events in certain conditions (***Chem. Rev.*** 2006, 106, 940-975.; ***Environ. Sci. Technol.***, 2017, 51, 243-252.; ***Environ. Sci. Technol.,*** 2010, 44, 1566-1572). MSA has been measured in atmospheric aerosol particles nearly all geographic regions, ranging from coastal areas to the continental. Notably, in coastal regions characterized by elevated MSA levels, MSA concentrations range from approximately 10% to 250% of gaseous sulfuric acid concentration (***Atmos. Chem. Phys.***, 2022, 22, 6103-6114; ***Atmos. Environ.*** 2022, 269, 118826), whereas in continental regions with lower MSA levels, MSA concentrations are typically ~10%-50% of gaseous sulfuric acid concentrations (***J. Geophys. Res.*** 2002, 107, 7101-7116; ***Atmos. Environ.*** 2020, 222, 117161).

Despite its much lower atmospheric abundance than H_2O, MSA can act as an efficient catalytic species owing to its strong acidity and versatile hydrogen-bonding capability. By forming stable pre-reactive complexes and facilitating multiple proton-transfer pathways, MSA substantially lowers the reaction barriers for CH_2OO hydrolysis.

Based on the above analysis, we emphasized the importance of MSA in the Introduction section. In Lines 54-64 on Pages 2-3 of the revised manuscript, the sentence of "In fact, MSA is a major oxidation product of organosulfur compounds originating from a variety of sources, including biological processes, biomass combustion, industrial emissions, and agricultural activities. As a result, it has been widely detected in atmospheric aerosol particles across diverse geographic regions, spanning from coastal to inland areas (Barnes et al., 2006; Gaston et al., 2010). Notably, in coastal regions characterized by elevated MSA levels, MSA concentrations range from approximately 10% to 250% of gaseous sulfuric acid concentration (Ning et al., 2022; Ning and Zhang, 2022), whereas in continental regions with lower MSA levels, including many inland urban and industrial regions, MSA concentrations are typically on the order of ~10%-50% of gaseous sulfuric acid concentrations (Berresheim et al., 2002; Chen et al., 2020). Furthermore, MSA is characterized by strong acidity and the ability to act as a proton-transfer bridge, suggesting a potentially important role in modulating the hydrolysis of CH_2OO." has been reorganized.

Comment 2.

Lines 79-81: The current sentence about discrepancies between measured and modelled global NPF rates is unclear. It is not accurate to attribute differences solely to MSA-driven nucleation. The authors should clarify that global NPF simulations can be influenced by multiple factors, including missing nucleation mechanisms, NH_3 concentrations, and other environmental parameters. A rephrasing is needed to reflect these more accurately.

Response: Thanks for your valuable comments. As noted by the reviewer, the binary MSA-MA nucleation mechanism underestimates the nucleation rates compared to field observations. Therefore, seeking the involvement of other gaseous species to better understand the MSA-MA-driven NPF. In Lines 85-88 on Page 4 of the revised manuscript, the sentence of "However, the binary MSA-MA nucleation mechanism is insufficient to explain the high NPF rates observed under realistic atmospheric conditions. This implies that other potential gaseous precursors may participate in and further enhance binary MSA-MA nucleation (Lee et al., 2019; Zhang et al., 2022)" has been reorganized.

Comment 3.

Lines 84-85: MSA in urban industrial areas and forested areas are low. And the NPF mechanisms are SA-base plus AP. MSA's importance on NPF in these areas can not convince me.

Response: Thanks for your valuable comments. We sincerely apologize for the insufficiently comprehensive assessment of the impact of HMHP on MSA-MA nucleation in the previous version of the manuscript. The earlier analysis focused primarily on regions with elevated HMHP concentrations, while the concentration distributions of the precursor species MSA and MA were not adequately considered. Indeed, the regions in which HMHP influences the MSA-MA nucleation process should be determined through a comprehensive evaluation of the concentration characteristics of HMHP, MSA and MA. In the revised manuscript, we therefore systematically account for the combined effects of HMHP, MSA and MA concentrations on the formation rate of the HMHP-involved MSA-MA system.

Our results indicate that HMHP's contribution to MSA-MA nucleation is most pronounced under conditions of high HMHP concentrations accompanied by relatively low concentrations of both MSA and MA. A review of the existing literature shows that regions with high HMHP concentrations are mainly associated with urban industrial areas and forested regions, whereas low concentrations of MSA and MA are predominantly observed in urban industrial environments.

Based on these integrated lines of evidence, we predict that the influence of HMHP on the MSA-MA system is most significant in urban industrial regions. The corresponding main revision has been made as follows.

(a) In the revised manuscript, the title of "Rapid formation of hydroxymethyl hydroperoxide and its vital role in methanesulfonic acid-methylamine nucleation: impacts of urban industrial and forested areas" has been changed as "Rapid formation of hydroxymethyl hydroperoxide and its vital role in methanesulfonic acid-methylamine nucleation: impacts of urban industrial areas".

(b) In Lines 91-92 on Page 4 of the revised manuscript, the sentences of "This will limit our knowledge of frequent NPF events, especially in urban industrial areas and forested areas." has been changed as "This will limit our knowledge of frequent NPF events, especially in urban industrial areas."

(c) In Lines 231-232 on Pages 8-9 of the revised manuscript, the sentences of "Finally, the atmospheric implication of HMHP for MSA-MA nucleation were calculated for urban industrial areas and forested areas." has been changed as "Finally, the atmospheric implication of HMHP for MSA-MA nucleation were calculated for urban industrial areas."

(d) In Lines 319-321 on Page 12 of the revised manuscript, the sentences of "These results highlight that HMHP exerts a markedly stronger influence on MSA-MA nucleation at elevated concentrations, particularly in urban industrial and forested regions, where its contribution to NPF can be substantial." has been changed as "These results highlight that HMHP exerts a markedly stronger influence on MSA-MA nucleation at elevated concentrations, particularly in urban industrial regions, where its contribution to NPF can be substantial."

(e) In Lines 351-353 on Page 13 of the revised manuscript, the sentences of "These results predict that HMHP substantially enhances MSA-MA-driven NPF in urban industrial and forested regions, helping to explain previously unaccounted NPF sources and improve nucleation models." has been changed as "These results predict that HMHP substantially enhances MSA-MA-driven NPF in urban industrial regions, helping to explain previously unaccounted NPF sources and improve nucleation models."

(f) In Lines 355-356 on Page 13 of the revised manuscript, the sentences of "It also reveals the potential contribution of other organic peroxides to NPF, offering a plausible explanation for part of the unaccounted particle fluxes in both urban industrial regions." has been changed as "It also reveals the potential contribution of other organic peroxides to NPF, offering a plausible explanation for part of the unaccounted particle fluxes in urban industrial regions."

Comment 4.

Lines 178-180: At this MSA level, the reaction is reported to be more favorable than that with NH_3. How does it compare to the response with H_2O?

Response: Thanks for your valuable comments. Based on the calculated effective rate constants, when the MSA concentration ranges from 10^6 to 10^8 molecules·cm^{-3}, its catalytic effect is substantially stronger than that of NH_3, for which concentrations of 10^7-10^{11} molecules·cm^{-3} are considered. Similarly, at MSA concentrations between 10^5 and 10^8 molecules·cm^{-3}, MSA exhibits significantly higher catalytic activity than SA ([SA] = 10^4-10^7 molecules·cm^{-3}). Taken together, these results indicate that MSA is a more effective catalyst than both NH_3 and SA. Nevertheless, because atmospheric H_2O concentrations are orders of magnitude higher than those of MSA, the overall catalytic efficiency of MSA remains lower than that of H_2O. In Lines 185-193 on Page 7 of the revised manuscript, the sentence of "When the MSA concentration ranges from 10^6 to 10^8 molecules·cm^{-3}, its catalytic effect is substantially stronger than that of NH_3 ([NH_3] = 10^7-10^{11} molecules·cm^{-3}), with k'_{MSA} being approximately 2-6 orders of magnitude over the temperature range of 280.0-320.0 K. Similarly, for MSA concentrations between 10^5 and 10^8 molecules·cm^{-3}, MSA exhibits a significantly higher catalytic activity than SA ([SA] = 10^4-10^7 molecules·cm^{-3}). In this case, k'_{MSA} exceeds k'_{SA} by about 1-3 orders of magnitude. Taken together, these results demonstrate that MSA is a more effective catalyst than both NH_3 and SA under atmospherically relevant conditions. Nevertheless, even under extreme conditions, with MSA at its upper-limit concentration ([MSA] = 10^8 molecules·cm^{-3}) and H_2O at its lower-limit concentration ([H_2O] = 10^{16} molecules·cm^{-3}), k'_{MSA} is approximately five orders of magnitude smaller than $k'_{\mathrm{WM},}$, indicating that the catalytic efficiency of MSA remains lower than that of H_2O." has been reorganized.

Comment 5.

Section 3.3 and 3.4: When assessing the importance of HMHP in MSA-MA nucleation, it is essential to investigate and compare the behavior of HMHP-MSA-MA clusters with that of SA-MA clusters. Such a comparison would help clarify the relative importance of HMHP-MSA-MA nucleation.

Response: Thanks for your valuable comments. In response to the reviewer's suggestion, comparing the formation rates of the MSA-MA-HMHP system with those of the SA-MA and SA-A systems is crucial for assessing the nucleation potential of HMHP. Accordingly, in the revised manuscript, we have included a quantitative comparison of the formation rates (J) for the MSA-MA-HMHP, SA-MA and SA-A systems (Fig. S7) and added the corresponding discussion in section 3.4. The corresponding main revision has been made as follows.

(a) In the supplement, the cluster formation rates of the MSA-MA-HMHP systems have been compared to those of the SA-MA (***Atmosphere***, 2024, 15(4), 467) and SA-A (***Atmosphere***, 2024, 15(4), 467) systems, which are widely regarded as key contributors to new particle formation in urban industrial areas (***Environ. Sci. Technol.***, 2021, 55(16), 10994-11005; ***Atmos. Chem. Phys.***, 2021, 55(16), 10994-11005). This corresponding comparison is presented in Fig. S7.

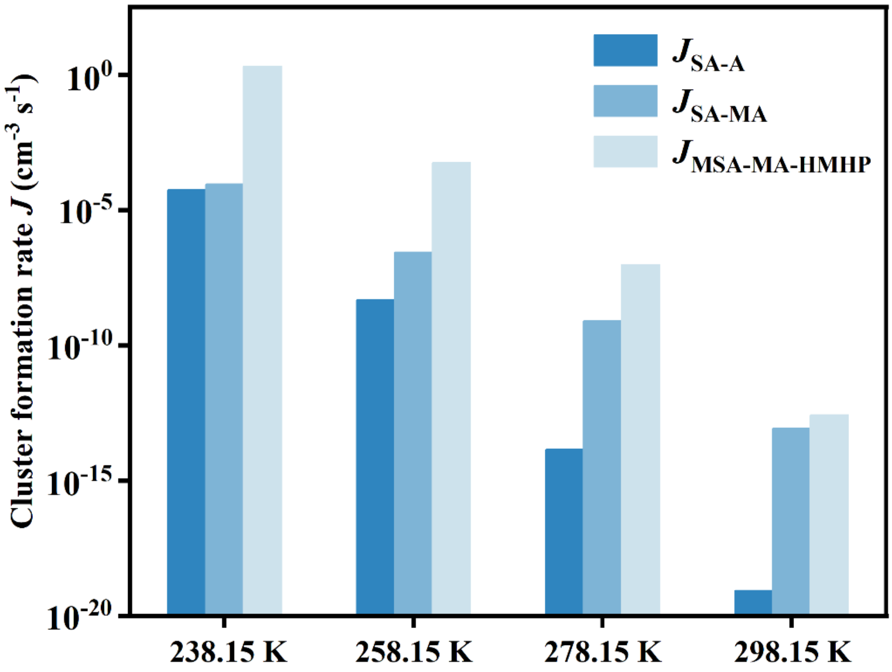

Fig. S7 Comparison of cluster formation rates (J) between the MSA-MA-HMHP system ([MSA] = 1.00×10^{6} molecules·cm^{-3}, [MA] = 1.00×10^{8} molecules·cm^{-3}, [HMHP] = 1.00×10^{9} molecules·cm^{-3}), the SA-MA system ([SA] = 1.00×10^{6} molecules·cm^{-3}, [MA] = 1.00×10^{8} molecules·cm^{-3}) and the SA-A system ([SA] = 1.00×10^{6} molecules·cm^{-3}, [A] = 1.00×10^{10} molecules·cm^{-3})

(b) In Lines 322-331 on Page 12 of the revised manuscript, the sentence of "Previous studies have revealed that SA-MA and SA-A nucleation mechanisms are widely regarded as key contributors to new particle formation in urban industrial regions (Yin et al., 2021; Liu et al., 2021).

To underscore the importance of MSA-MA-HMHP nucleation in urban industrial regions, the cluster formation rates (*J*) of the MSA-MA-HMHP system have been compared with those of the SA-MA and SA-A systems (Qiao et al., 2024) (Fig. S7). The results show that, over the temperature range of 238.15 K-298.15 K, the *J* of MSA-MA-HMHP system is 1-5 orders of magnitude higher than that of SA-MA system at equivalent precursor concentrations ([SA] = 1.00×10^6 molecules·cm^{-3} and [MA] = 1.00×10^8 molecules·cm^{-3}). Similarly, under the conditions of [SA] = 1.00×10^6 molecules·cm^{-3} and [A] = 1.00×10^{10} molecules·cm^{-3}, the *J* of MSA-MA-HMHP systems slightly exceeds that of SA-A system by approximately 5-6 orders of magnitude. These comparisons suggest that HMHP plays a key role in enhancing MSA-MA nucleation, particularly in urban industrial environments." has been added.

Comment 6.

Section 3.4: All the locations discussed in this section exhibit extremely low MSA concentrations. It is unclear why a site with higher MSA levels was not selected for analysis. Additionally, it would be important to compare your proposed mechanism with existing pathways such as SA-NH_3, SA-MA, SA-AP, and others. Without such comparisons, the claim regarding the importance of HMHP-MSA-MA nucleation may not be fully justified.

Response: Thanks for your valuable comments. In response to the reviewer's suggestion, we have clarified the rationale for adopting the minimum MSA concentration in Section 3.4 firstly. Then, a comparison of the formation rates between the MSA-MA-HMHP system and the SA-MA and SA-A systems is performed for assessing the nucleation potential of HMHP. The corresponding main revision has been made as follows.

(a) In this study, the concentration of MSA spans a range of 10^4-10^8 molecules·cm^{-3}. As shown in Fig. 5, the contribution of HMHP to MSA-MA nucleation is most pronounced under conditions of low MSA concentrations. Accordingly, in Section 3.4, the MSA concentration is fixed at its lower-limit value ([MSA] = 1.00×10^4 molecules·cm^{-3}).

(b) Previous studies have revealed that the SA-MA and SA-A systems are widely regarded as key contributors to new particle formation in urban industrial regions (***Environ. Sci. Technol.***, 2021, 55(16), 10994-11005; ***Atmos. Chem. Phys.***, 2021, 55(16), 10994-11005). To highlight the importance of MSA-MA-HMHP nucleation in urban industrial regions, the formation rates (*J*) of the MSA-MA-HMHP, SA-MA and SA-A systems are compared (Fig. S7). The detail information is provided in Comment 5. Meanwhile, it is generally acknowledged that new particle formation in urban industrial regions is predominantly governed by SA-base nucleation mechanisms, such as SA-MA and SA-A, whereas the contribution of SA-AP nucleation is comparatively minor.

Comment 7.

Lines 330-332: What is the main nucleation mechanism in Niwot Ridge and the southeastern United States? Is MSA-MA-driven NPF the main mechanism there?

Response: Thanks for your valuable comments. As the reviewer's suggestion, in the revised manuscript, the dominant formation pathways for Niwot Ridge (Fig. S5) and the southeastern United States (Fig. S6) have been added. Correspondingly, the associated discussion has been incorporated into Section 3.4. The corresponding main revision has been made as follows.

(a) In the supplement, the cluster formation pathways in Niwot Ridge (Fig. S5) and the southeastern United States (Fig. S6) are presented.

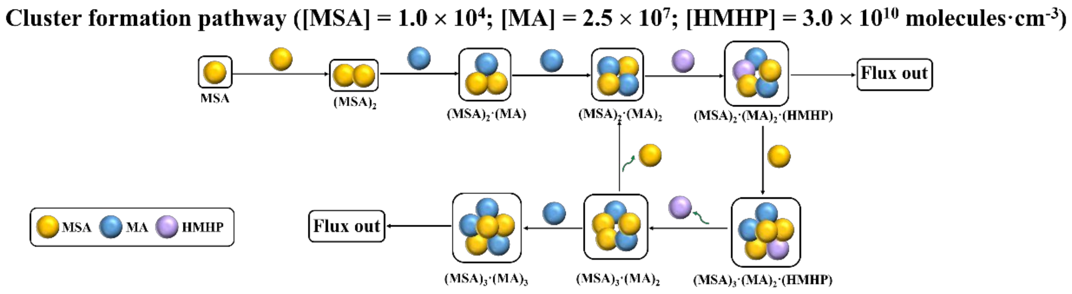

Fig. S5 The cluster formation pathway of the MSA-MA-HMHP system at [MSA] = 1.0×10^4 molecules·cm^{-3}, [MA] = 2.5×10^7 molecules·cm^{-3} and [HMHP] = 3.0×10^{10} molecules·cm^{-3}.

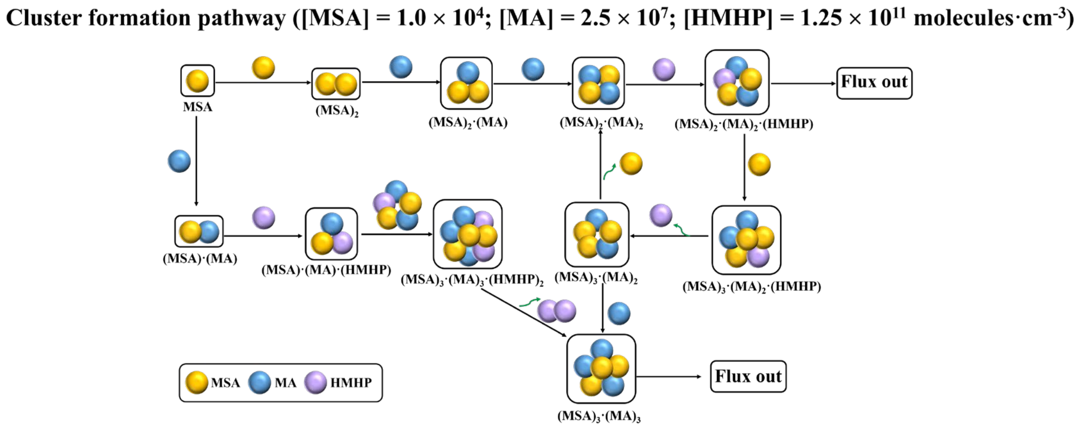

Fig. S6 The cluster formation pathway of the MSA-MA-HMHP system at [MSA] = 1.0×10^4

molecules·cm^{-3}, [MA] = 2.5 × 10^7 molecules·cm^{-3} and [HMHP] = 1.25 × 10^{11} molecules·cm^{-3}.

(b) In Lines 315-319 on Page 12 of the revised manuscript, the sentence of "In contrast, in environments characterized by high HMHP concentrations, such as the southeastern United States (1.25 × 10^{11} molecules·cm^{-3}) and Niwot Ridge (3.00 × 10^{10} molecules·cm^{-3}), HMHP-involving nucleation pathways become dominant. Under these conditions, HMHP acts both as a "catalyst", facilitating the formation of MSA-MA clusters, and as an "participant" in the assembly of critical clusters (Figs. S5 and S6). These two roles contribute up to 59% and 42%, respectively, to the overall nucleation process." has been reorganized.

Comment 8.

Figure 6: Please clarify the sources of the vapor concentrations used in this figure. Where were these values obtained?

Response: Thanks for your valuable comments. We apologize for not clearly explaining the settings of the MSA, MA and HMHP concentrations in Fig. 6. A detailed explanation is provided below.

(a) As shown Fig. 5, lower concentrations of MSA and MA tend to enhance the role of HMHP in MSA-MA nucleation. Accordingly, the concentrations of MSA and MA in Fig. 6 are set to low values ([MSA] = 1.00 × 10^4 molecules·cm^{-3} and [MA] = 2.50 × 10^7 molecules·cm^{-3}).

(b) Atmospheric HMHP concentrations exhibit substantial variability across different environments worldwide. Accordingly, to further evaluate the implication of HMHP in the MSA-MA nucleation. Fig. 6 presents an analysis of the branch ratios of the major flux-out pathways under varying HMHP concentrations (2.50 × 10^9 molecules·cm^{-3}-1.25 × 10^{11} molecules·cm^{-3}).

Overall, in Fig.6, the concentrations of MSA and MA are fixed at [MSA] = 1.00 × 10^4 molecules·cm^{-3} and [MA] = 2.50 × 10^7 molecules·cm^{-3}, respectively. Atmospheric HMHP concentrations are then prescribed according to observations from different regions: values range from 2.50 × 10^9 to 6.25 × 10^9 molecules·cm^{-3} in Central Portugal, Pabstthum, and Beijing; increase to 1.15 × 10^{10}-3.00 × 10^{10} molecules·cm^{-3} in Guang Zhou and Niwot Ridge and reach 1.25 × 10^{11} molecules·cm^{-3} in the southeastern United States.