Reply to the Reviewers

---For the manuscript “egusphere-2025-5992”

Reviewer 1#:

This is a chamber study on SOA formation promoted by atmospheric ammonia. This manuscript investigates the influence of NH_3 on secondary organic aerosol (SOA) formation during the photo-oxidation of mixed anthropogenic (n-heptylcyclohexane) and biogenic (α-pinene) volatile organic compounds using a large outdoor photochemical smog chamber. The study demonstrates that NH_3 significantly accelerates VOC degradation and enhances SOA production by facilitating nucleation and participating in particle-phase reactions, including the formation of nitrogen-containing light-absorbing substances such as imidazoles. The work addresses an important gap in understanding NH_3-involved interactions in complex mixed precursor systems and provides valuable insights into the formation of light-absorbing aerosols in AVOC-BVOC mixtures. The experimental design using a large-scale outdoor chamber is a notable strength, offering realistic atmospheric conditions. Overall, this research contributes meaningfully to the scientific basis for assessing NH_3 effects on the co-oxidation of anthropogenic and biogenic gases in urban environments.

1. It is not clear if these figures are from specific experiments (which ones) or an average of all experiments (which wouldn't make sense). Are these averages from all experiments, or data from specific experiments in Fig.1? Are there corresponding blank measurements from the chamber that are used for a baseline subtraction?

   Thank you for your helpful question. The data presented in the figures are from one of multiple replicate experiments, rather than averages across all experiments. Since consistent results from replicate experiments effectively ruled out interference from random uncertainties, this study selected one representative dataset for presentation. The mass spectrometry data shown in the figures are from the MIX-N2, AL-N1, and AP-N5 experiments. Under background conditions (i.e., blank measurements), the SO_2 concentration in the chamber environment was ≤ 0.5 ppb, NOx ≤ 2 ppb, O_3 ≤ 0.5 ppb, and released or generated VOCs and particulate matter were negligible (<0.01 μg m^{-3}). Therefore, even without additional background subtraction for each experiment, the results remain reliable. We have added clarifications regarding these questions to the revised manuscript. Detailed revisions can be found on page 5, line 148−149, and page 4, line 97−98 of the revised manuscript.

2. What were the starting concentrations of all trace gases in a clean chamber? How were the trace gases measured? When were filter collected from the chamber? This is not clear in the text, the whole first 3.5 hours?

   Thanks for the question. In a clean chamber, the SO_2 concentration was ≤0.5 ppb, NOx ≤2 ppb, and O_3 ≤0.5 ppb, as measured by online SO_2 (EC 9850, Ecotech, Australia), NOx (EC 9841, Ecotech, Australia) and O_3 analyzers (EC 9830, Ecotech, Australia), respectively. Sampling commenced immediately when the enclosure was opened. The first filter collected samples continuously for 3.5 hours, and was then replaced with a fresh one for an additional 3.5 hours of continuous collection. We have added clarifications regarding these questions to the revised manuscript. Detailed revisions can be found on page 4, line 97−98 and 112−114, and page 3, line 93−96 of the revised manuscript.

3. Figure 8 is scaled by Nitrogen number which may create a massive bias in that plot toward nitrogen containing species. Why is this done?

   Thanks for the question. The nitrogen-number scaling was intentionally applied to visually distinguish how molecular species distributions vary across different nitrogen -number ranges, thereby potentially offering preliminary clues for subsequent analysis of NH_3-involved reaction pathways in mixed organic oxidation systems. From a methodological perspective, this scaling approach was justified by its intended purpose. We have added clarifications regarding this issue to the revised manuscript. Detailed revisions can be found on page 14, line 304−307 of the revised manuscript.

4. How do the authors make an estimation of the mass concentration of the different functional groups in Figure 4?

Thanks for the question. In FTIR spectroscopy, the relative magnitudes of absorbance peak areas were used to estimate the relative mass concentrations of different functional groups. In UV spectroscopy, the absolute values of mass absorption efficiency (MAE) were employed for similar estimations. It is important to note that we only assessed the relative mass concentrations across different experiments, rather than estimating absolute mass concentration values. We have added clarifications regarding this issue to the revised manuscript. Detailed revisions can be found on page 9, line 226−228 of the revised manuscript.

5. The figure caption should explain the content of the figure, and the meanings of different symbols or patterns should be clarified. For example, what do the solid and hollow patterns represent in Figure 1(b) and 1(c)?

Thanks for the recommendation. In Fig(b) and (c), the solid and hollow symbols denoted NH_3-free and NH_3-containing experimental systems, respectively. We have clarified the meanings of different symbols or patterns. Detailed revisions can be found on page 6, line 167–168 of the revised manuscript.

Reviewer 2#:

In this study, the key role of NH_3 on SOA formation during the photo-oxidation of mixed VOCs of anthropogenic (n-heptylcyclohexane) and biological (α-pinene) sources was revealed by a large-scale outdoor photochemical smog chamber experiment. The results showed that NH_3 significantly accelerated the degradation of VOCs and increased the quantity and mass concentration of SOA by promoting nucleation and particle-phase reactions (e.g., acid-base interaction, Maillard reaction). It especially enhanced the production of nitrogenous light-absorbing substances (e.g., imidazoles), which may contribute to climatic impacts through the radiative effect of brown carbon and cloud interaction. Meanwhile, NH_3 inhibits the formation of OOMs by mediating the gas-particle partitioning of medium molecular weight compounds, which hinders the cross-reactions necessary for OOMs production. Additionally, elevated temperatures inhibit SOA production. The study elucidates how NH_3 affects the co-oxidation of ambient anthropogenic and biogenic gases, and deepen the understanding of its role in SOA generation, particularly light-absorbing aerosols, in the AVOC-BVOC mixed system. It is recommended that the paper be accepted after major revision. In addition, there are some issues that need to be clarified, which are list below:

1. The NH_3 concentrations tested (74.85–748.5 ppb) span a wide range. Does the particle size distribution reveal any systematic trends with NH_3 concentration?

   Thanks for the question. When NH_3 at varying concentrations was introduced into the reaction system, the SOA particle size distribution exhibited rapid growth within the first hour, subsequently approaching a steady state after approximately two hours. Notably, lower NH_3 concentrations (74.8 ppb) corresponded to larger maximum particle diameters observed during the reaction period, whereas at elevated NH_3 concentrations (133.7 ppb and 748.5 ppb), the maximum particle sizes were comparable between the two experimental groups. By the conclusion of the reaction, the maximum particle diameters under all three NH_3 concentration conditions converged to statistically similar values. These findings have been incorporated into the revised manuscript. Detailed revisions can be found on page 5, line 153–154 of the revised manuscript and Figure S1 of the revised supporting information.

2. Why was n-heptylcyclohexane chosen to represent AVOC? Is its chemical structure (cyclically branched alkanes) prevalent in the actual urban atmosphere?

   Thanks for the question. n-Heptylcyclohexane, as a representative long-chain alkane, significantly influences the yield and production efficiency of anthropogenic SOA (ASOA) as well as atmospheric oxidizing capacity. This compound is ubiquitously distributed in the urban atmosphere, originating from diverse sources including volatile chemical products such as coatings and vehicular exhaust emissions, thereby representing an important potential contributor to ASOA. The photochemical reactivity and SOA formation potential of long-chain alkanes are profoundly governed by their structural characteristics: cycloalkanes exhibit the highest reactivity and greatest SOA formation potential, followed by branched alkanes, with linear alkanes being the least reactive. Consequently, cyclic branched alkanes serve as ideal model species for investigating SOA formation under varying conditions. n-Heptylcyclohexane, a hybrid hydrocarbon possessing both cyclic and branched alkyl moieties, provides critical insights that can be extrapolated as an important reference for ASOA derived from long-chain alkanes. We have added clarifications regarding this issue to the revised manuscript. Detailed revisions can be found on page 2, line 49–51 and 56–58 of the revised manuscript.

3. Is the mixing effect of other BVOCs (e.g. isoprene) considered for α-pinene as a typical representative of BVOCs? Are the experimental results generalizable?

   Thanks for the question. This study primarily focuses on the mixed oxidation of representative AVOCs and BVOCs, with the latter being predominantly monoterpenes; the effects of other BVOCs such as isoprene were not considered. Given the robust representativeness of α-pinene within the monoterpene class, the experimental results are inferred to possess a certain degree of generalizability to the reaction systems involving AVOCs and monoterpenes.

4. Were multiple replications of the experiment performed to verify the stability of the results?

   Thanks for the question. Repeated experiments were conducted in this study to ensure the stability and reliability of the results. Details are provided in Table S1.

5. Some of the terms (e.g., "VOC/NOx ratio") are not clearly explained in their abbreviated meanings, which may affect the understanding of lay readers.

   Thanks for the recommendation. “VOC/NOx ratio” means the reactive organic compounds-to-primary NOx concentration ratio. We have added clarifications regarding this issue to the revised manuscript. Detailed revisions can be found on page 5, line 153–154 of the revised manuscript.