Dear Editor

Many thanks for your important comments, which are very helpful for further improving our manuscript quality. We have carefully read you comments and revised our manuscript based on your comments and suggestions. We also made additional revisions for accurate discussions and statements. Following is our response to your comments.

Anything for our manuscript, please feel free to contact me via ghwang@geo.ecnu.edu.cn

All the best,

Gehui Wang

Oct. 30, 2021

Comments from the author:

This manuscript described a very interesting set of results, and the authors have made substantial changes to address reviewers comments. I have some editorial comments to add here, and I consider these requested revisions to be minor.

Author reply: We thank you for the comments. See our response below. Line numbers here refer to those in the revised manuscript:

1. Comment: Line 28 and throughout manuscript: "x" in NOx should be in subscripts
Author reply: All the "NOx" in the manuscript have been fixed as "NO_X".

2. Comment Line 30-33: Information in the abstract should be broadly applicable to the atmosphere. Report yields (which are intensive) rather than mass concentrations (which are specific to the conditions employed by this study only).

Author reply: Suggestion taken. SOA mass concentrations are changed as SOA yield in line 30-33, and shown as follows:

"The SOA yield increased from 28.1% in the absence of NH_3 to 34.7% in the presence of NH_3 but decreased to 19.5% in the presence of NO_X. However, the highest SOA yield of 42.7% and the lowest carbon oxidation state (OS_C) occurred in the presence of both NH_3 and NO_X"

3. Comments: Line 35 and throughout manuscript: "precipitate" usually means transitioning from liquid to solid, or rain/snow. "Partition" is more appropriate.

Author reply: "precipitate" in line 35, 106, 384 and 391 are fixed as "partition".

4. Comments: Line 101: I suggest replacing "artificial" with "anthropogenic", and "biological" with "biogenic" to denote the source of emission, rather than how the compound was created.

Author reply: "artificial" and "biological" in line 101 are fixed as "anthropogenic" and "biogenic", respectively.

5. Comments: Line 124-125: "contributes much to the improvement… compared to SO_2 in winter". Does this mean reduction in NH_3 contributes more to reduction in $PM_{2.5}$ than reductions in SO_2?

Author reply: The content of this expression here is inaccurate. SO_2 emissions have be significantly reduced, while particle concentrations have decreased less. For clarification, the sentence in line 101 is changed to:

"Indeed, field observation and model simulation have pointed out that the simultaneous control of NH_3 emissions in conjunction with SO_2 emission is more effective in reducing $PM_{2.5}$ than the process without NH_3 emissions control, and $PM_{2.5}$ concentration can be more effectively reduced if NH_3 emission is decreased as much as that of SO_2 (Erisman and Schaap, 2004)."

6. Comment: Line 153: "one atmospheric pressure" can be replaced with "atmospheric pressure" or "1 atm"

Author reply: "one atmospheric pressure" is fixed as "atmospheric pressure".

7. Comment: Line 154: "at all times"

Author reply: It is fixed.

8. Comment: Line 155: replace "at last" with "at least"

Author reply: It is fixed.

9. Comment: Line 160: I am curious why the zero air generator does not make RH close to zero.

Author reply: During the zero air generation process, the allochroic silicagel absorbs water vapor, which can make the RH less than 20% but cannot make it down to zero, because the silicagel absorption cannot remove all the water vapor. In most cases, <20% RH is believed to be dry enough for smog chamber simulation as a dry conditions, because such a low RH condition is less than the deliquescent point of most inorganic salts in the atmosphere. Thus, zero air with a ~20% RH has widely been used for smog chamber experiments.

10. Comment: Line 169: it is interesting that there is no change in OH concentration despite changing NOx. This suggests that OH production is mainly from H2O2 photolysis, rather than HOx recycling by NOx.

Author reply: It is due to the nature of the UV-light used in this study, OH production is mainly from H_2O_2 photolysis, rather than HOx recycling by NOx.

11. Comment: Line 175: what is a typical ratio of NO_2 to NO? was this measured?

Author reply: NOx concentration was measured online by the NO-NO_2-NOx analyzer (Model 42C, Thermo Electron Corporation, USA). The typical ratio of $[NO_2]_0$ to $[NO]_0$ is about 30:1.

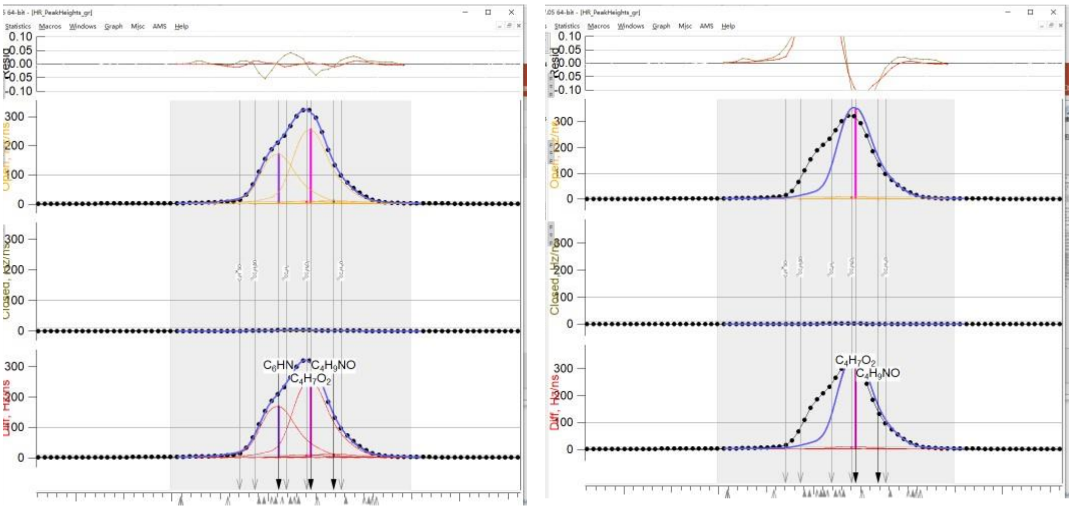
The sentence of "NOx concentration was measured online by the NO-NO_2-NOx analyzer (Model 42C, Thermo Electron Corporation, USA)." is added in line 175.

12. Comment: Line 194: (also pointed out by one of the reviewers) SMPS measures electrical mobility diameter, not "aerodynamic equivalent sizes"

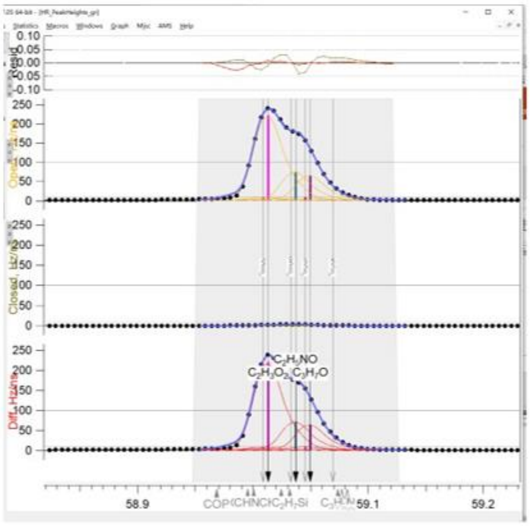
Author reply: "aerodynamic equivalent sizes" is fixed as "electrical mobility diameter".

13. Comment: Line 210: (also pointed out by one of the reviewers) V-mode with mass resolution of 2000 might not be sufficient to separate many isobars, especially when N is included. Can the authors show how well isobars are resolved with this resolution? (W-mode, or V-mode in more recent AMS can achieve mass resolution of 4000, which is more capable of quantifying O/C ratios)

Author reply: We express our appreciation to the editor for this comment. Here are some HR fit with N or without N (see the detailed figures below). As shown in the right column below, if the N fragments are not added in the RH fit, there is a remarkable difference between the signal of AMS (black scatter line) and fitting result (blue line). However, when N fragments are added into the HR fit process, the fitting blue lines are almost entirely overlapping with the AMS signal. In addition, clearly suggesting that in this study the V-mode of AMS with mass resolution of 2000 is capable of separating many isobars including the N-containing organic fragments, and the related results shown by this work are reliable. Similar work has been reported by other AMS work (Liu et al., 2015) and are referenced by this work.



m/z 87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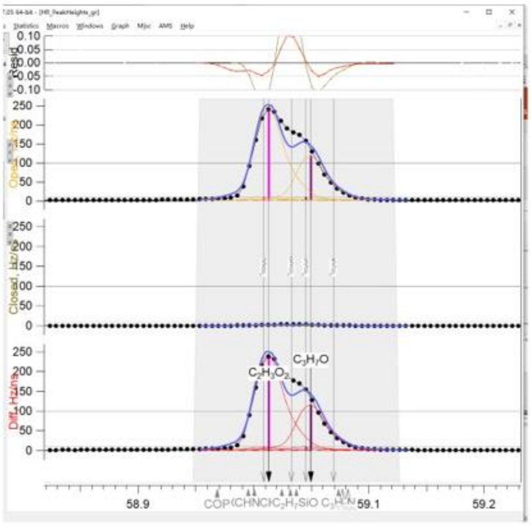
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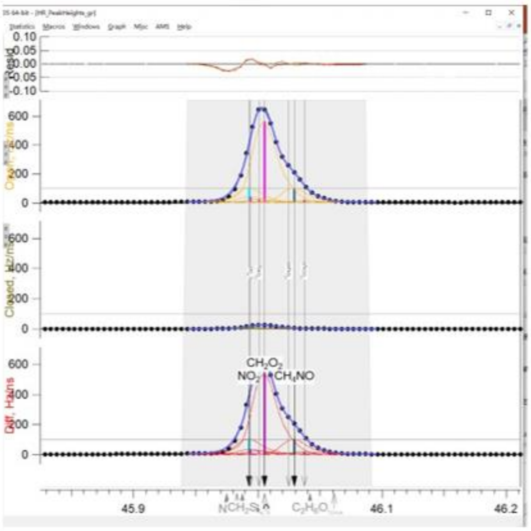
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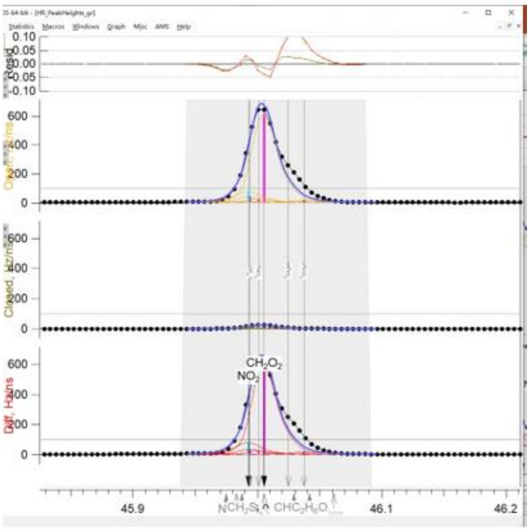
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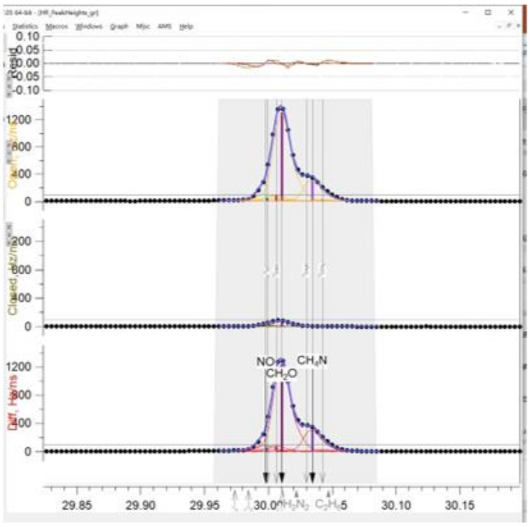
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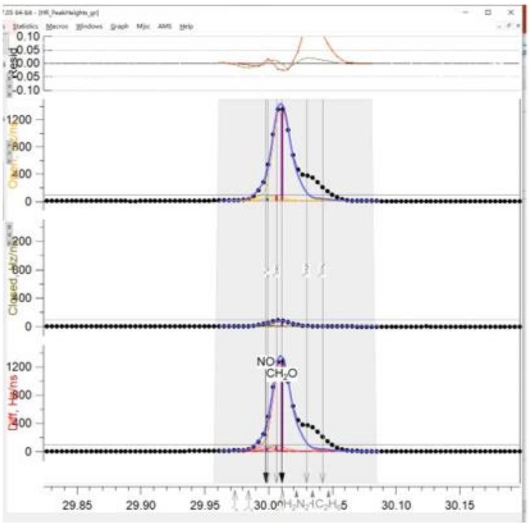
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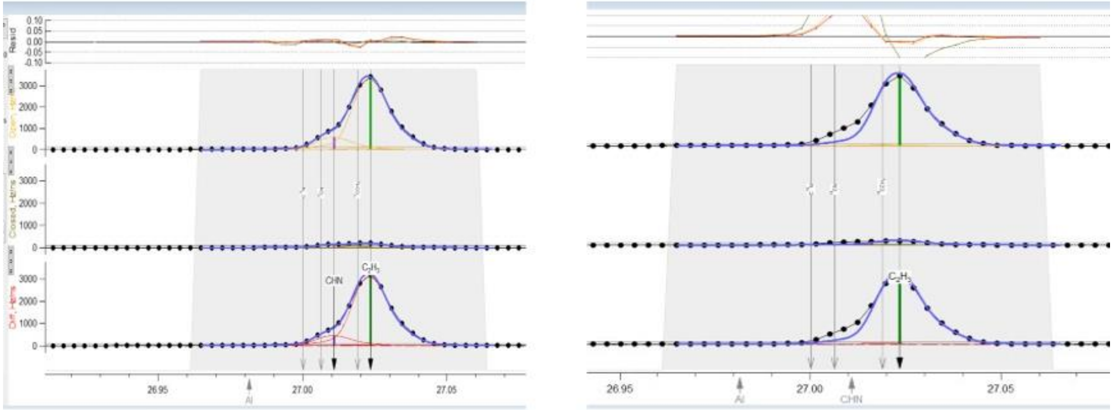

14. Comment: Line 232: (based on response to one of the reviewers) 46.2 mm, not 46.2 nm

Author reply: "46.2 nm" is fixed as "46.2 mm" .

15. Comment: Line 262: this "effect" not "effects"

Author reply: This is fixed in the manuscript.

16. Comment: Lines 267-274: this is a thoughtful response to the reviewer's comment. I suggest rephrasing Lines 267-268 because I don't think the wall loss "problem" is necessarily remedied, especially since the authors reported the interesting phenomenon of accelerated wall loss with NH3 present. I think this phenomenon is now buried in the wall loss correction, and not necessarily understood. The authors seem to suggest that carbonyls in the gas phase are consumed by and reacting with NH3 on the walls (which is entirely plausible), causing carbonyls to leave the suspended particles (to maintain equilibrium). If that is the case, is there any evidence from the AMS, or from the size distribution measured by SMPS (e.g. shifting to smaller diameters after lights are turned off)

Author reply: The sentences of "Interestingly, wall loss is increased 66% and 205% in Exp.2 (in the presence of NH_3) and Exp.3 (in the mixed condition of NH_3 and NO_X), respectively, when compared with the experiments with no NH_3 (Exp.1 and 4). The larger particle wall loss in the presence of NH_3 could be explained by increasing condensation process of oxidized organic vapors onto the Teflon chamber wall via oligomerization (for dicarbonyls) and ionic dissociation/acid-base reaction (for organic acids)." in line 267-274 is deleted.

17. Comment: Line 296: this is a good response to the reviewer's concern about NH_4NO_3 being the source of enhancement. It might be best to rephrase this as what % of the enhancement this source can explain. Also, the author can look at the NH4+ and NO3- signal on the AMS and see how much NH4NO3 is formed.

Author reply: We thank the editor for this concern. Our AMS data showed that NH_4NO_3 formed in he chamber accounted for 6.6% of the SOA mass formed in the chamber.

Therefore, the enhanced particle mass in the chamber are almost entirely due to the SOA formation. Please see the related discussions in page 15, line 294-297.

18. Comment: Line 317-318: this is not a fair statement. SOA aging has received a lot of attention.

Author reply: We deleted the sentence of "but little attention has been paid to the evolution of SOA chemical composition in previous studies" in line 317-318.

19. Comment: Line 361: Avoid starting a sentence with "Or".

Author reply: Suggestion taken, "Or" is deleted, the manuscript here was fixed as "In addition, Or NH_3/NH_4^+ may react with… …".

20. Comment: Line 377-378: formation "of" high volatility oxidation products

Author reply: This is fixed in the manuscript.

21. Comment: Line 389-390: "This result suggested that although NOx promotes the formation of higher volatility compounds." Incomplete sentence

Author reply: We Combine the two sentences of "This result suggested that although NO_X promotes the formation of higher volatility compounds. These higher volatility compounds (e.g. glyoxal) can react with NH_3 and partition into the particle-phase, which could contribute to the increase in SOA formation." into one "This result suggested that although NO_X promotes the formation of higher volatility compounds, these higher volatility compounds (e.g. glyoxal) can react with NH_3 and partition into the particle-phase, which could contribute to the increase in SOA formation."

22. Comment: Line 424: "extra-consumed" is an awkward compound word.

Author reply: "extra-consumed carbonyl" is fixed as "unreacted carbonyl".

23. Comment: Lines 456 and 457: "defend" should be "defined"

Author reply: This is fixed in the manuscript.

24. Comment: Line 473-474: "declining" instead of "decline"

Author reply: This is fixed in the manuscript.

25: Comment: Conclusions: several reviewers pointed out the atmospheric relevance of these results. I recommend adding a discussion about how these results at high NH_3 levels can be extrapolated to lower concentrations found in the atmosphere.

Author reply: Suggestion taken. We added the following discussions into the text. Please see page 29, line 584.

"Although the reactant concentrations including NH_3 used in this work are much higher than those in the real urban environment, our results are applicable for the polluted urban atmosphere. In the urban atmosphere aromatic VOCs consist of numerous species and their total concentration is much higher than a single species such as toluene. On the other hand, carboxylic acids and carbonyls in the urban polluted atmosphere can be produced from aromatics and many other species. Therefore, it is reasonable for our smog chamber experiments to use toluene as a single precursor with a concentration much higher than that in the real atmosphere. Although the mechanisms of SOA formed under high precursor concentrations is expected to be the same as that under low concentrations, the kinetics are probably different. Thus, the effect of NH_3 and NO_X on the photooxidation of toluene with lower concentrations should be checked in the further study."

26: Comment: Data availability: following up on one of the reviewer's comments, I highly recommend uploading the data to an online repository. While AMS raw data files are large and it might not be feasible to do so, at the very least all the data used to make the plots should be shared. This sharing will facilitate data comparisons will increase the impact of this study.

Author reply: The datasets are available from https://doi.org/10.6084/m9.figshare.16910953.

References:

Erisman, J. W., and Schaap, M.: The need for ammonia abatement with respect to secondary PM reductions in Europe, Environ. Pollut., 129, 159-163, 10.1016/j.envpol.2003.08.042, 2004.

Liu, Y. C., Liggio, J., Staebler, R., and Li, S. M.: Reactive uptake of ammonia to secondary organic aerosols: kinetics of organonitrogen formation, Atmos. Chem. Phys., 15, 13569-13584, 10.5194/acp-15-13569-2015, 2015.