

Response to the editor's and reviewers' comments on "Enhanced nocturnal N₂O₅-ClNO₂ chemistry in Delhi under lower-NO conditions" by Chen et al.

We thank the editor and referees for their time and efforts in reviewing our revised manuscript. We carefully addressed the comments and further revised the manuscript accordingly. Below we give the itemized responses. The referees' comments are shown in black font. Our responses are shown in blue font. Revised text as it appears in the main text and SI is shown in red italic font. Revisions in the main text and SI are highlighted in yellow. The Line numbers mentioned in the response letter refer to those in the revised manuscript.

Editor:

The authors have substantially revised this manuscript in response to extensive comments from both reviewers. There are remaining comments to address, including consideration of a change in title and in the representation of VOC observations that require attention prior to acceptance.

Response: We appreciate the editor's time in handling our manuscript and the positive evaluation of our previous revisions. We have addressed the remaining comments mainly regarding the VOC representations and the manuscript title, as detailed in responses below. We have also checked the manuscript carefully for typos, grammar, terminology, numbering, updates of data in tables, and updates of variables in equations.

Referee #2:

My apologies for the delay. I acknowledge the efforts and work of the authors to address the major concerns raised in my previous review.

The revised MS has significantly improved and I have just two remaining points below (one major concern and the other a suggestion):

Major concern

1) In the response to reviewers and based on the cited works the authors state that: "Previous studies^[14, 16] have shown that total VOCs concentrations vary by less than a factor of 2 between winter and spring in India."

This statement is not backed by the papers cited and is very misleading. First of all the cited papers do not report VOC data over India but rather in different seasons and years from two sites in Delhi and Mohali. The current status over India remains that there is very little measured VOCs data that is comprehensive and long term and India is a subcontinent not just two sites in north India. Further the number of VOCs measured and reported even in these studies while covering major VOCs are also by no means adequate to claim complete VOC quantification. So the authors should be careful and clarify this and also acknowledge that there remains a major knowledge gap in terms of VOC speciation and year round variability and reactivity to oxidants even in the Delhi-

NCR region for winter and spring. Future studies should incorporate VOC measurements so that one can overcome limitations in terms of process based understanding. This is clearly borne by the present work too.

in fact, the more recent study by Mishra et al. which the authors cite reported that for monsoon and post-monsoon seasons, the average total mass concentration of the same set of pure hydrocarbons during post-monsoon season was 3.7 times greater than in monsoon season while the average total mass concentration of OVOCs during post-monsoon was 2.6 times greater than the monsoon season values in Delhi.

Response: We thank the reviewer for raising the critical point about the lack of comprehensive characterization of VOCs in the original manuscript. We agree with these comments and further clarified the representation and limitation of the VOCs observations in the revised manuscript.

Specifically, we have added a citation to the recent work by Mishra et al. to more accurately reflect the temporal variability in VOC speciation and concentrations. Furthermore, we emphasize in the main text that long-term and dense measurement networks of VOCs in India are needed in future studies, which serve as a basis for better quantifying NO_3 reactivity.

Revision in the main text,

Line 253-262: *As shown in Fig. S7a and Table S2, the campaign-averaged NO_3 reactivity to NO in 2023 is $\sim 15.6 \text{ s}^{-1}$, which is approximately 2 orders of magnitude higher than the reactivity to VOCs and the heterogeneous loss of NO_3 from N_2O_5 uptake (0.091 s^{-1}). Limited field measurements in Mohali^[1] and Delhi^[2, 3] showed that the total VOC concentrations exhibit inter-annual and seasonal variations ranging from a factor of less than two to approximately four. In this context, though we don't expect that the lack of concurrent VOCs observations would significantly influence the estimated total NO_3 reactivity during the 2023 campaign, which is likely dominated by reactions with NO, it should be emphasized that the exact value of NO_3 reactivity towards VOCs may deviate from the assumed value (0.081 s^{-1} on average). This uncertainty stems from the temporal and spatial changes in VOC speciation, concentration and reactivity. Long-term and dense VOCs measurements will help to better quantify NO_3 reactivity in Delhi.*

Suggestion point

2) While the authors have mentioned in their response that based on the work by Shabin et al. that sCI-initiated chloride oxidation pathway could be a source of Cl_2 during nighttime in Delhi and is worth future investigation, the relevant discussion is missing in the revised MS and may be good to add for future investigations:

Response: Thanks for the suggestion. As noted in the response file, because our current study focuses on ClNO_2 , and chloride activation via N_2O_5 uptake is the major source of ClNO_2 , we did not include discussions about sCI-initiated chloride oxidation in the manuscript. We will certainly incorporate the work by Shabin et al. into our future investigations of Cl_2 chemistry in Delhi.

Referee #3:

The manuscript has been improved significantly, however, I still think that the title of the revised manuscript is confusing. Although the NO concentration has reduced significantly to about 44 ppb in 2023, this level is still consider high. The usage of “under lower-NO conditions” sounds inappropriate and misleading. Suggest to revise the title again.

Response: We agree with the referee’s suggestion. We have revised the title to “Enhanced nocturnal N_2O_5 -ClNO₂ chemistry under reduced NO conditions in Delhi”. We have also carefully reviewed the manuscript text to ensure that our discussions of NO concentrations properly convey that they remain elevated despite the reduced level observed in 2023.

Revision in the title,

Enhanced nocturnal N_2O_5 -ClNO₂ chemistry in Delhi under reduced NO conditions

References

- [1] MEIDAN D, BROWN S S, SINHA V, et al. Nocturnal atmospheric oxidative processes in the Indo-Gangetic plain and their variation during the COVID-19 lockdowns [J]. Geophysical Research Letters, 2022, 49(7): e2021GL097472.
- [2] WANG L, SLOWIK J G, TRIPATHI N, et al. Source characterization of volatile organic compounds measured by proton-transfer-reaction time-of-flight mass spectrometers in Delhi, India [J]. Atmospheric Chemistry and Physics, 2020, 20(16): 9753–70.
- [3] MISHRA S, SINHA V, HAKKIM H, et al. Reactive chlorine-, sulfur-, and nitrogen-containing volatile organic compounds impact atmospheric chemistry in the megacity of Delhi during both clean and extremely polluted seasons [J]. Atmospheric Chemistry and Physics, 2024, 24(22): 13129–50.