Response to reviewers' comments on "Nocturnal production of N_2O_5 and $ClNO_2$ in Delhi: driving factors and impacts" by Chen et al.

We thank the referee for the helpful comments. We carefully addressed them and 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.

Referee #3:

Chen et al. present a comprehensive field measurement study investigating nocturnal N_2O_5-$ClNO_2$ chemistry in Delhi. The study identifies the primary driver of N_2O_5 and $ClNO_2$ enhancement in 2023 compared to 2019 as a substantial reduction in nocturnal NO concentrations, which mitigated the suppression of NO_3 radical formation, and high particulate chloride concentration in Delhi also facilitated efficient conversion of N_2O_5 to $ClNO_2$. This study is an additional piece of work which is important for better understanding of N_2O_5 heterogenous chemistry in high NO regions such as India. Overall, the manuscript is interesting but I think it needs to be significantly improved and strengthened prior to the decision of acceptance for publication. My detail comments are as below:

Response: We sincerely thank the reviewer for the positive assessment of our work and for recognizing its importance in advancing the understanding of N_2O_5 heterogenous chemistry in high NO regions. We appreciate the constructive and insightful comments. In response, we have thoroughly revised the manuscript and significantly strengthened our analysis and discussions according to the reviewer's suggestions. A point-by-point response to the specific comments is provided below.

1. Title: I would suggest the authors to revise the title to be more specific and relevant to the major finding of this study.

Response: Thanks, we have revised the title to "*Enhanced nocturnal N_2O_5-$ClNO_2$ chemistry in Delhi under lower-NO conditions*".

2. Line 43: It is good to recommend, however, I think the authors should be more realistic when concluding. Stringent chlorine emissions control is preferable but at this stage it is not clear how chlorine emissions can be control since there are both anthropogenic and natural sources.

Response: We agree with the reviewer that we should be more realistic when concluding. Delhi is an inland city, located far away from any ocean or sea. The nearest coastline (the Arabian Sea to the west or the Bay of Bengal to the east) is roughly 1,000

kilometers away. Therefore, we do not expect significant impacts from natural chlorine emissions. Previous studies[1, 2] have also identified intense anthropogenic/continental chlorine emissions in Delhi. We have revised the sentence as follows.

Revision in the main text:
Line 43-45: *Our findings highlight the need for increased attention to atmospheric secondary pollution and stringent anthropogenic chlorine emissions control under lower-NOx conditions in Delhi.*
Line 423-425: *Delhi is an inland city located roughly 1,000 kilometers away from the nearest coastlines. Significant chlorine emissions from natural sea salt aerosols are not expected. The high chloride levels observed in Delhi point to intense chlorine emissions from anthropogenic sources.*

3. Line 61: Revise "arctic" to remote polar and marine regions.

Response: Thanks, revised.

Revision in the main text:
Line 75: *…which are about an order of magnitude higher than those observed in the remote polar…*

4. Line 69: "ingredients" does not sound scientific. Maybe precursors will be better.

Response: Thanks, revised.

Revison in the main text:
Line 78-80: *Delhi is one of the world's most polluted megacities. Intense air pollutant emissions from transport, residential, industrial, and other sources provide abundant precursors (i.e., particulate chloride and NOx, Fig. S1a, b) for N_2O_5 and $ClNO_2$ production.*

5. Line 128-129: What type of remaining detected gaseous compounds? Be more specific. Any basis for choosing the maximum sensitivities of chloroacetic acid?

Response: The remaining detected gaseous compounds are oxygenated organics consisting of CHO or CHON. These compounds are expected to be polar or acidic semi-volatile and intermediate-volatile organic compounds (S/IVOCs), as the iodide ion is sensitive to species with high polarity and hydrogen bonding capablity[3, 4].

Chloroacetic acid was selected as a representative surrogate standard for these uncalibrated species, containing a carboxylic acid group (high hydrogen-bonding capability) and a polar halogenated moiety. Our choice to apply its maximum sensitivity serves as a conservative, lower-bound estimation approach for quantifying the remaining uncalibrated S/IVOCs.

Revison in the main text:
Line 153-155: *For the remaining detected gaseous compounds, mainly oxygenated organics consisting of carbon, hydrogen, and oxygen (abbreviated as CHO) or carbon,*

hydrogen, oxygen, and nitrogen (abbreviated as CHON).

6. Line 209-211: Agreed that the NO might still be the dominant loss for NO_3. However, depends on the level of VOCs (I presumed that Delhi is a high VOCs emission region), the NO_3 loss via VOCs might be a significant contribution to NO_3. Can the authors clarify that the loss via VOC is not significant or is negligible?

Response: We have addressed this issue in response to the general comment 2 raised by reviewer 2. The key point is that as shown in Fig. R4, the campaign-averaged NO_3· reactivity to NO in 2023 is ~15.6 s^{-1}, which is approximately 2 orders of magnitude higher than that to VOCs. Previous studies[5, 6] have shown that total VOCs concentrations vary by less than a factor of 2 between winter and spring in India. Therefore, we don't expect that changes in VOCs concentrations would significantly influence the overall NO_3 reactivity.

Revision in the main text:
Line 251-256: *As shown in Fig. S7a and Table S2, the average NO_3· reactivity to NO in 2023 is ~15.6 s^{-1}, which is approximately 2 orders of magnitude higher than that to VOCs and the heterogenous loss of NO_3 from N_2O_5 uptake (0.091 s^{-1}). Previous studies[5, 6] have shown that total VOCs concentrations vary by less than a factor of 2 between winter and spring in India. Therefore, we don't expect that changes in VOCs concentrations would significantly influence the overall NO_3 reactivity.*

7. Line 236-237: Any support for the efficient conversion of N_2O_5 to $ClNO_2$?

Response: As discussed in Line 274 to 283, the maximum N_2O_5 levels in Delhi are up to an order of magnitude lower than those in other global urban areas. By contrast, the peak $ClNO_2$ concentrations are comparable to or higher than those reported in North America and Europe, indicating a high $ClNO_2$ production efficiency driven by the high chloride and ALWC described in the manuscript.

Revision in the main text:
Line 282-283: *The observed pattern of low N_2O_5 and high $ClNO_2$ indicates efficient conversion of N_2O_5 to $ClNO_2$ in Delhi.*

8. Line 243-244: From Fig. S9, the authors did not do correlation analysis, so need to be careful with the description here. If there is please, please provide the correlation value.

Response:.Thanks, we have revised the description.

Revision in the maintext:
Line 297-299: *Overall, the nocturnal N_2O_5 mixing ratio shows a significant negative dependency ($r = -0.64$, $p<0.01$) on the NO concentration (Fig. 2a), and high $ClNO_2$ levels were accompanied by abundant chloride (Fig. S11a).*

9. Line 262-263: Clarify what is the new N_2O_5 driven $ClNO_2$ enhancement pattern in

2023?

Response: The new N_2O_5-driven $ClNO_2$ enhanced pattern in 2023 indicates the dashed linear fitting line shown in Fig. 1e, which is absent in 2019. This pattern is characterized by a strong positive correlation (r = 0.93) between N_2O_5 and $ClNO_2$ under conditions of elevated N_2O_5 (10~400 ppt) and limited chloride (0.1~3.4 μg/m^3).

Revision in the maintext:
Line 306-309: *The emerging early evening peak of N_2O_5 leads to a new N_2O_5-driven $ClNO_2$ enhancement pattern in 2023 (the dashed linear fitting line in Fig. 1e), characterized by a strong positive correlation (r = 0.93) between N_2O_5 and $ClNO_2$ under conditions of elevated N_2O_5 (10~400 ppt) and limited chloride (0.1~3.4 μg/m^3).*

10. Line 270-271: I do not think a unity of $ClNO_2$ yield will necessary occur even there is a high chloride concentration. Please revise the statement.

Response: Thanks for pointing this out. We have revised the statement.

Revision in the maintext:
Line 314: *Additionally, the estimated $ClNO_2$ yield may reach unity in Delhi (**Fig. S13a**).*

11. Line 285: I think drivers is not an appropriate word as the study only investigated a few factors. Please find a suitable description and revise them throughout the text.

Response: We agree with the reviewer that our study focused on a limited number of critical factors influencing N_2O_5-$ClNO_2$ chemistry, specifically NO and chloride, while other potentially important factors (e.g., particulate nitrate and organics) were not extensively discussed. To ensure scientific rigor, we have replaced "drivers" with "influencing factors" throughout the revised manuscript. Additionally, the word "driver" has been removed from the title.

12. Figure 2a: Suggest to revise the Figure 2a as it is hard to follow.

Response: Fig. 2a has been simplified as follows (Fig. R10), where the purple and grey dashed lines indicate the average NO concentrations during the 2023 and 2019 campaign, respectively.

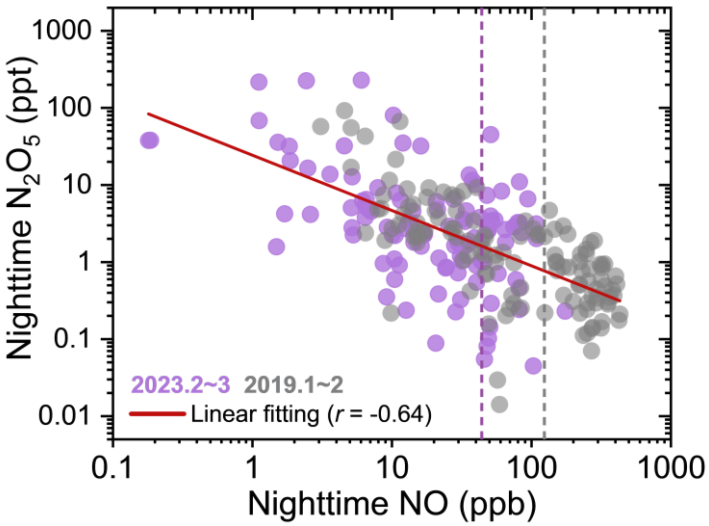

Fig. R10 Scatter plot of nighttime NO versus N_2O_5. Nighttime is defined as the period from 20:00 to 04:00, excluding the transition period between day and night when the air mass was unstable. The purple and grey dashed lines indicate the average NO concentrations during the 2023 and 2019 campaign, respectively.

13. Line 340: Any proof to support that the chloride is in the form of semi-volatile NH_4Cl?

Response: We summarize the proof here in three points. (1) XRF measured the total chloride concentrations, including refratory alkali chlorides like NaCl and KCl and non-refractory NH_4Cl while CIMS can only measure the non-refractory chloride. We observed concurrent increase in the chloride measured by CIMS and Cl element concentrations measured by XRF after midnight (Fig. 1d), indicating the semi-volatile nature of particulate Cl (i.e., NH_4Cl) in Delhi. (2) As is shown in Fig 3b, the observed particle-phase Cl fraction amounted to up to 89% on average at 6:00 whereas it remained below 20% in the afternoon (12:00-18:00). This diurnal variation is attributed to lower temperatures (15-25 °C) and higher RH (56-92%) in the early morning hours, which favored the co-condensation of HCl and water vapor into particles as NH_4Cl under the NH_3-rich conditions commonly found in Delhi. (3) The observed thermodynamically-driven partitioning behavior of Cl agrees with previous model simulations [1, 2]. These discussions have been included in the orginal manuscript (Line 383-397).

14. Line 366: What is the justification for vertical intrusion contribute to the night-time $ClNO_2$ as the nocturnal boundary layer is relatively stable at night?

Response: We thank the reviewer for pointing out this potential source of confusion. Our statement was meant to highlight the vertical transport during the early morning period (06:00~08:00 LT) rather than during the deep night. At this time, the breakup of the residual layer initiates strong vertical mixing, which delivers high levels of $ClNO_2$ produced aloft down to the surface, resulting in the observed sharp increase.We have revised the manuscript to explicitly constrain the timing and mechanism of this process, ensuring it is not misinterpreted as nocturnal vertical transport.

Revision in the maintext:

Line 412-413:... *and vertical intrusion initiated by the breakup of the residual layer during the early morning (6:00~8:00).*

15. Line 413-414: The authors calculated the Cl atom production from photolysis of Cl_2, $ClNO_2$, $NHCl_2$, and NCl_3. However, it is unknown how the calculations were done. I cannot find any information on the concentrations of Cl_2, $NHCl_2$, and NCl_3.

Response: The calculations were done according to Eq. 5 in the manuscript. Details of the calculations were also described in 2.2 Kinetic Calculations. Concentrations of Cl_2, $NHCl_2$, and NCl_3 were determined according to our previous study[7]. In brief, the sensitivities for Cl_2, NCl_3, and $NHCl_2$ were estimated applying their relative sensitivities to $ClNO_2$. Previous direct calibration results suggest consistent sensitivity ratios among the inorganic chlorinated species. An uncertainty of 11%, 32%, and 41% was estimated for the sensitivities of Cl_2, NCl_3, and $NHCl_2$ based on the differences in their relative sensitivity ratios to $ClNO_2$ in previous studies[7, 8].

Revision in the maintext:

Line 148-150: *Sensitivities for Cl_2 (3.4 cps/ppt), NCl_3 (3.1 cps/ppt), and $NHCl_2$ (0.05 cps/ppt) were estimated using their relative sensitivities to $ClNO_2$* reported in our previous study[7].

Line 453-454: *The average daytime P(Cl·) (Eq. 5) from $ClNO_2$ photolysis in 2023 (0.035 ppb/h) is about approximately twice that observed in 2019 (0.015 ppb/h).*

16. Line 420: While the increase in chlorine-containing organic products is clear, the statement about "pronounced Cl-initiated oxidation" could be more nuanced.

Response: Thanks. We agree that the phrase "pronounced Cl-initiated oxidation" was somewhat overstated. To provide a more nuanced discussion, we have revised the statement in the updated manuscript.

Revision in the maintext:

Line 461-462: *suggesting non-negligible Cl-initiated oxidation of VOCs under these conditions in Delhi*.

17. Figure 6: I am not clear what is the main purpose of showing Fig. 6? The schematic is helpful but could be made more detailed to visually summarize the key differences (e.g., include relative sizes of NO, and the resulting radical and SOA outputs for 2019 vs. 2023). Furthermore, the N_2O_5 uptake can also produce Cl_2 together with $ClNO_2$. How do the authors consider about this pathway?

Response: This figure serves as the manuscript's TOC. We thank the reviewer for the suggestion. Differences in NO and the resulting radical outputs are represented by arrow thickness and the bar plot. We are unable to visualize changes in SOA because these results were not reported in the previous study[9]. Still, differences in SOA were described in the manuscript via changes in the bulk O/C ratio (Line 506-510). Yes, the N_2O_5 uptake can also produce Cl_2 along with $ClNO_2$[10].

In Delhi, our preliminary results show that Cl_2 concentrations exhibit little correlation with $ClNO_2$ (daytime r = 0.19, nighttime r = 0.18), suggesting that Cl_2 is unlikely to be a coproduct of $ClNO_2$ from N_2O_5 uptake. Notably, Cl_2 peaks during the daytime and correlates well with O_3 (Fig. R11), indicating that O_3-involved chloride oxidation may be an important source of Cl_2 in Delhi. This finding requires further investigation and is largely beyond the scope of the current study, which focuses on N_2O_5-$ClNO_2$ chemistry.

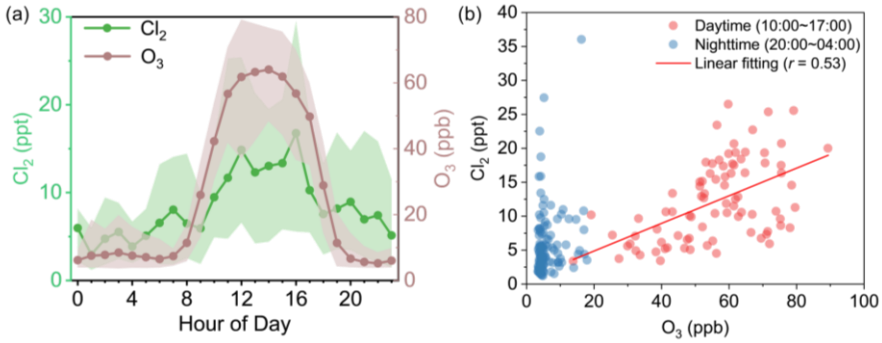

Fig. R11 (a) Average diurnal variations of Cl_2 and O_3 in Delhi. The dots indicate the averages while the shaded area shows the 10th and 90th percentiles. (b) Scatter plot between O_3 and Cl_2 in Delhi. The linear fitting line between the daytime O_3 and Cl_2 is also plotted.

18. Line 494: "extensive characterization" is over-stated.

Response: Thanks, the statement has been revised.

Revision in the maintext:
Line 532: *This study characterized N_2O_5-$ClNO_2$ chemistry in Delhi.*

19. Line 556: Double check the references as there are some duplications.

Response: Thanks. We have carefully checked the references and unified the formatting.

20. Supplementary info, Line 66: I have a concern on the measurement and calibration of N_2O_5 and $ClNO_2$. Did the author check on the inlet loss or artefact of these compounds generated in the inlet? As the PM loadings are very high in Delhi, how did the measurements can assure that the inlet chemistry does not play significant role? This information should be added to the supplement.

Response: Thanks. We agree that in highly polluted environments like Delhi, ensuring minimal inlet loss and preventing artifact production of N_2O_5 and $ClNO_2$ within the sampling line are essential. We addressed these concerns through strict sampling designs and regular maintenance, including increasing the flow rate to reduce residence time while maintaining laminar flow. An impactor with a cut-off of $PM_{2.5}$ was placed at the gas inlet to reduce large particle deposited in the sampling system.

Experiments like injecting N_2O_5 into a used sampling tube to examine N_2O_5 losses and $ClNO_2$ production would be benificial, however, we were unanble to do this due to

limited resources in Delhi. Previous measurements in other polluted areas like Hong Kong and Beijing show that loss of N_2O_5 to inlet partiles is about 10%, while that loss of $ClNO_2$ is neglibible due to its insoluble and relatively inert properties. These details are now explicitly described in the revised Supplementary Info.

Revision in the SI:
Line 48-52: *An impactor with a cut-off of $PM_{2.5}$ was placed at the gas inlet to reduce large particle deposited in the sampling system. The bypass flow was utilized to ensure a short residence time (~1.6 s) while maintaining a laminar flow (Reynolds number = 840 <2300) within the tubing, thereby suppressing both wall loss and gas-particle reactions within the inlet.*

21. Supplementary info, Line 91: Provide the standard deviation or error values for the gravimetric weight loss analysis of chloroacetic acid.

Response: Thanks, added.

Revision in the SI:
Line 98-99: *...determined by gravimetric weight loss analysis, was 177.3 ± 0.8 ng/min.*

22. Supplementary info, Line 139: What is RH parameterization? How to validate?

Response: RH parameteriztion refers to that γ_{N2O5} was parametrized using Eq. 5 (the following equation) according to the experimental measurements of N_2O_5 uptake on aqueous organic aerosols[11, 12]

$$\gamma(N_2O_5) = RH \times 5.2 \times 10^{-4} \quad (RH \leqslant 57\%) \text{ (Eq. 5.1)}$$

$$\gamma(N_2O_5) = 0.03 \quad (RH > 57\%) \quad \text{(Eq. 5.1)}$$

This parameterization method was supported by the consistency between the simulated nocturnal $ClNO_2$ variations using the RH-parameterized γ_{N2O5} and the observed $ClNO_2$ levels, as detailed in Text S2. We have clearly show the RH parameterization equations in the revised manuscript.

23. Supplementary info, Line 177: I am confused by the authors on what is the purpose of showing the $ClNO_2$ in residual layer. The calculation has very high uncertainties and may not really represent the "real" concentration of $ClNO_2$. Please clarify or delete this unnecessary calculation.

Response: Thanks for the suggestions. The estimation of residual-layer $ClNO_2$ was originally included to support that the morning $ClNO_2$ increases were associated with downward transport from aloft. We agree that without direct measurements, such calculations carry large uncertainties and may not accurately reflect the "real" concentrations.We now have deleted these unnecessary calculations and related descriptions in the main text.

24. Supplementary info, Figure S19: The smallest mixing ratios of N_2O_5 and $ClNO_2$ points for the calibration are more than 2 ppb. I am concern about the response of CIMS

on lower concentration region as the measured ambient concentrations typically fall below this low value. Have the authors conducted calibration for lower concentration? In addition, the HCl calibration also used "extremely" high concentration, how can this represent the ambient concentrations?

Response: We thank the reviewer for raising the point regarding the calibration range for N_2O_5, $ClNO_2$, and HCl. We have conducted calibrations for lower N_2O_5 and $ClNO_2$ concentrations by proportionally increasing the dilution N_2 flow (Fig. R8, 0, 0.5 lpm, 1 lpm, and 1.5 lpm). Results are shown in the following Fig. R12. These calibration points have been added to further validate the linear response of CIMS under ambient concentrations. In addition, the detection limits (as three times the standard deviation of the hourly averaged backrgound signals) for N_2O_5 and $ClNO_2$ are 0.6 ppt and 1.6 ppt, respectively, which are well below their ambient concentrations. This further confirms that CIMS is capable of quantifying ambient levels with sufficient signal to noise ratio and linear dynamic ranges.

Regarding HCl, we attempted calibration at lower concentrations, but the CIMS could not detect discernible HCl signals unless "extremely" high HCl concentrations were used. This is likely because HCl is sticky and suffers from wall losses at low concentrations, and because the ionization efficiency of HCl by iodide is low. The calibrated sensitivity under Delhi's RH conditions is 0.013 cps/ppt. Nevertheless, given the strong linearity of the multipoint calibration at high HCl concentrations, and the verified linear response of the CIMS at lower concentrations for N_2O_5 and $ClNO_2$, we assume that the calibrated HCl sensitivity is applicable to ambient measurements.

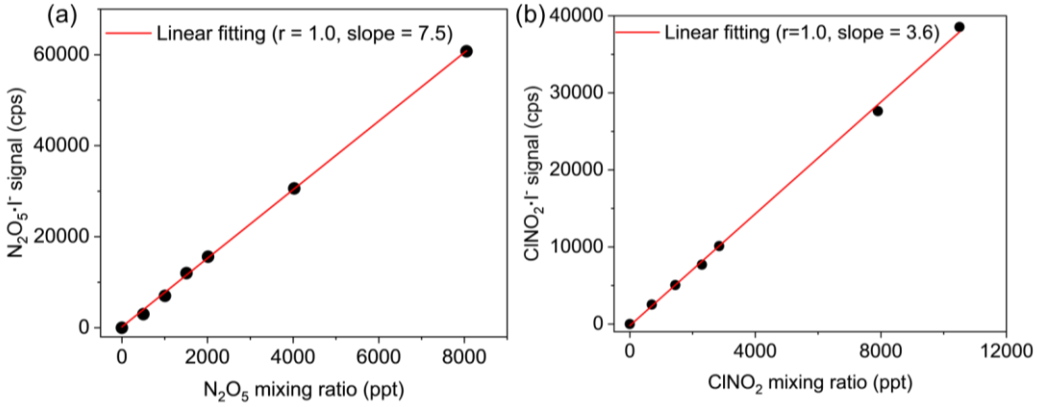

Fig. R12 Calibrations of (a) N_2O_5 and (b) $ClNO_2$.

Revision in the SI:

Calibration plots for N_2O_5 and $ClNO_2$ have been revised accordingly.

Line 100-105: *It is noted that HCl was calibrated in the concentration range about 2~3 orders of magnitude higher than the ambient level. Nevertheless, given the strong linearity of the multipoint calibration at high HCl concentrations, and the verified linear response of the CIMS at lower concentrations for N_2O_5 and $ClNO_2$, we assume that the calibrated HCl sensitivity is applicable to ambient measurements.*

25. The authors should further polish the manuscript for grammatical errors and better

clarity in the text.

Response: Thanks for the suggestions. We have carefully proofread the manuscript to eliminate grammatical errors, correct typos, and enhance overall clarity.

References

[1] Gunthe S S, Liu P, Panda U, et al. Enhanced aerosol particle growth sustained by high continental chlorine emission in India[J]. Nature Geoscience, 2021, 14(2): 77-84.

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[3] Lee B H, Lopez-Hilfiker F D, Mohr C, et al. An iodide-adduct high-resolution time-of-flight chemical-ionization mass spectrometer: Application to atmospheric inorganic and organic compounds[J]. Environmental Science & Technology, 2014, 48(11): 6309-6317.

[4] Iyer S, Lopez-Hilfiker F, Lee B H, et al. Modeling the detection of organic and inorganic compounds using iodide-based chemical ionization[J]. Journal of Physical Chemistry A, 2016, 120(4): 576-587.

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[7] Chen Y, Xia M, Zhang J, et al. Chloramine chemistry as a missing link in atmospheric chlorine cycling[J]. Science Advances, 2025, 11(44): eadv4298.

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[9] Haslett S L, Bell D M, Kumar V, et al. Nighttime NO emissions strongly suppress chlorine and nitrate radical formation during the winter in Delhi[J]. Atmospheric Chemistry and Physics, 2023, 23(16): 9023-9036.

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[12] Thornton J A, Braban C F, Abbatt J P D. N_2O_5 hydrolysis on sub-micron organic aerosols: the effect of relative humidity, particle phase, and particle size[J]. Physical Chemistry Chemical Physics, 2003, 5(20): 4593-4603.