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 #1:

The authors present field measurements of N_2O_5 and $ClNO_2$ concentrations and other species conducted in New Delhi, India in Spring 2023 and compare results to previous measurements conducted in winter 2019. The authors find that concentrations of N_2O_5 and $ClNO_2$ are higher in 2023 compared to 2019, and concentrations of NO_x and particulate chloride are lower. N_2O_5 appears to be inversely related to concentrations of NO_x, and $ClNO_2$ is positively correlated with particulate chloride. Measurements of other organic compounds show evidence for the importance of Cl initiated oxidation reactions. These results would suggest that reductions in NO_x can increase formation of secondary pollutants in Delhi (since Cl concentrations will be higher), which has important policy implications. Overall, the manuscript is well written and covers and important area of atmospheric chemistry research. In my opinion, the manuscript should be published in ACP after taking into consideration the comments below:

Response: We appreciate the reviewer's overall positive assessment and constructive suggestions. Please find our point-by point response and revisions below.

Main comment:

Considering the complex dependence of $ClNO_2$ on N_2O_5 observed in New Delhi, would the authors like to discuss the possibility of processes other than N_2O_5 influencing concentrations of $ClNO_2$?

Response: Thanks for the insightful comment. The heterogeneous uptake of N_2O_5 on chloride containing particles is in general the main production mechanism of atmospheric $ClNO_2$, which proceeds rapidly with the aqueous reaction between NO_2^+ and Cl^-. In addition, some studies[1, 2] have shown that the aqueous reactions of NO_2^- and HONO with Cl_2, HOCl and NH_2Cl are potential sources of $ClNO_2$, with a reaction rate constant about 3~4 orders of magnitude lower than the reaction between NO_2^+ and Cl^- (Table R1). In addition, the reaction between HCl and N_2O_5 on surfaces is not considered due to the relatively slow reaction rate constant[3].

Considering that besides N_2O_5, NO_2^-, NH_2Cl, Cl_2, and HOCl are potential important precursors of $ClNO_2$, we further examined the correlation between Cl_2, HOCl and $ClNO_2$. The importance of NO_2^- reaction with NH_2Cl is not investigated due to the

lack of measurements. No significant correlation was observed between $ClNO_2$ and Cl_2 or HOCl (Fig. R1), which was mainly due to both Cl_2 and HOCl peaked during the day while daytime $ClNO_2$ levels were consistently low in Delhi, indicating insignificant daytime $ClNO_2$ production. As is shown in Fig. 1e in the main text, nighttime $ClNO_2$ shows a strong positive correlation with N_2O_5 when chloride is low, indicating N_2O_5-driven $ClNO_2$ production under chloride-deficient conditions in Delhi. Significant increase of $ClNO_2$ concentrations was observed after midnight when chloride is high, with N_2O_5 concentrations close to zero, suggesting efficient N_2O_5 to $ClNO_2$ conversion under chloride-rich conditions in Delhi. The average nighttime variations of $ClNO_2$ can also be reproduced with the N_2O_5-related mechanism incorporated (Fig. S13b).

We therefore conclude that the N_2O_5 and chloride concentrations are the critical parameters controlling $ClNO_2$ production in Delhi. Additionally, as mentioned in the main text, besides the local N_2O_5 uptake, $ClNO_2$ levels in Delhi were influenced by the transport of $ClNO_2$-laden biomass burning plumes from upwind regions, and vertical intrusion associated with the breakup of the residual layer. Discussions about other potential chemical processes affecting $ClNO_2$ concentrations were added.

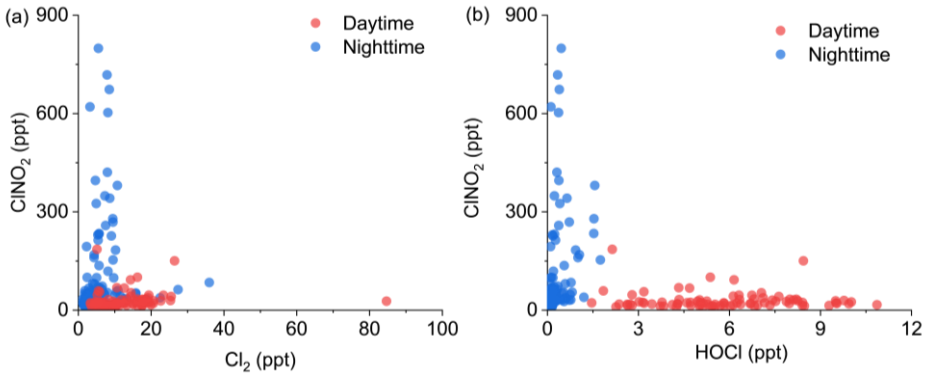

Fig. R1 Dependence of $ClNO_2$ on Cl_2 and HOCl concentrations. Scatter plots of $ClNO_2$ versus (a) Cl_2 and (b) HOCl concentrations, with data points colored by daytime (10:00~17:00) and nighttime (20:00~04:00) period.

Table R1 Summary of $ClNO_2$ production mechanism[1, 2]

No.	Reaction	Reaction rate constant
1	$Cl^-(aq) + NO_2^+(aq) \rightarrow ClNO_2(aq)$	3.9×10^{10} $M^{-1}\cdot s^{-1}$
2	$Cl_2(aq) + NO_2^-(aq) \rightarrow ClNO_2(aq) + Cl^-(aq)$	2.5×10^{6} $M^{-1}\cdot s^{-1}$
3	$HOCl(aq) + NO_2^-(aq) \rightarrow ClNO_2(aq) + OH^-(aq)$	2.0×10^{7} $M^{-1}\cdot s^{-1}$
4	$Cl_2(aq) + HONO(aq) \rightarrow ClNO_2(aq) + Cl^-(aq) + H^+(aq)$	2.5×10^{6} $M^{-1}\cdot s^{-1}$
5	$HOCl(aq) + HONO(aq) \rightarrow ClNO_2(aq) + H_2O(l)$	2.0×10^{7} $M^{-1}\cdot s^{-1}$
6	$NH_2Cl(aq) + H^+(aq) + NO_2^-(aq) \rightarrow ClNO_2(aq) + NH_3(aq)$	7.6×10^{6} $M^{-2}\cdot s^{-1}$

Revision in the main text,

Line 55-61: *The heterogeneous uptake of N_2O_5 on chloride containing particles is in general the main production mechanism of atmospheric $ClNO_2$, which proceeds rapidly with the aqueous reaction between NO_2^+ and Cl^-. In addition, some studies[1, 2] have shown that the aqueous reactions of NO_2^- and HONO with Cl_2, HOCl and NH_2Cl are*

potential sources of $ClNO_2$, with a reaction rate constant about 3~4 orders of magnitude lower than the reaction between NO_2^+ and Cl^- (R5). Additionally, the reaction between HCl and N_2O_5 on surfaces is not considered due to the relatively slow reaction rate constant[3].

Specific comments

1. The figure numbers are not in chronological order throughout the text.

Response: Thanks for the reminder. We have carefully revised the figure numbers in both the main text and the SI, and they now appear in chronological order.

2. Line 51-52: There seems to be references missing

Response: Thanks, several original references[4-7] listed below are added.

(1) Finlayson-Pitts B J, Ezell M J, Pitts J N. Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and $ClONO_2$[J]. Nature, 1989, 337(6204): 241-244

(2) Behnke W, George C, Scheer V, et al. Production and decay of $ClNO_2$ from the reaction of gaseous N_2O_5 with NaCl solution: Bulk and aerosol experiments[J]. Journal of Geophysical Research: Atmospheres, 1997, 102(D3): 3795-3804.

(3) Thornton J A, Abbatt J P D. N_2O_5 reaction on submicron sea salt aerosol: Kinetics, products, and the effect of surface active organics[J]. The Journal of Physical Chemistry A, 2005, 109(44): 10004-10012.

(4) Osthoff H D, Roberts J M, Ravishankara A R, et al. High levels of nitryl chloride in the polluted subtropical marine boundary layer[J]. Nature Geoscience, 2008, 1(5): 324-328.

Revision in the main text, Line 54-55:

N_2O_5 is formed from the reaction between $NO_3\cdot$ and NO_2 (R1), and the heterogeneous reactions of N_2O_5 on atmospheric particles produce particulate nitrate and gaseous $ClNO_2$ (R2-R5) (Bertram and Thornton, 2009;Finlayson-Pitts et al., 1989;Behnke et al., 1997;Thornton and Abbatt, 2005;Osthoff et al., 2008).

3. Line 77: Should this be S2b,c instead of S2b,d?

Response: Yes, we have revised the figure numbers to ensure they appear in chronological order.

Revision in the main text, Line 93-95:

...with the peak occurrence frequencies of NO (124 ppb) and chloride (21 $\mu g/m^3$) concentrations largely falling at the high end of the concentration distributions commonly observed during the recent years (Fig.S3b, c).

4. Line 184: "invalidate" instead of "invalid"?

Response: Thanks, revised.

Revision in the main text, Line 225:

However, nocturnal transport, i.e., changes in air masses can invalidate this method….

5. Line 207: Is this the same Keq described in supplement line 134? If so, why are different expressions used?

Response: Yes, the Keq values in the main text and SI are the same. The main text uses the expression from Wängberg et al[8]., while the SI originally cited Cantrell et al[9]. We have revised the SI to match the main text expression, which was used for our analysis.

Revision in the SI, Line 144:

$$K_{eq} = 5.5 \times 10^{-27} \times \exp(10724/T)$$

6. Line 280-281: shown in (d) instead of "shown in (c)"?

Response: Thanks for the careful check.

Revision in the main text, Line 323:

Gaseous HCl and particulate Cl measured by CIMS are also shown in (d).

References

[1] Dalton E Z, Hoffmann E H, Schaefer T, et al. Daytime atmospheric halogen cycling through aqueous-phase oxygen atom chemistry[J]. Journal of the American Chemical Society, 2023, 145(29): 15652-15657.

[2] Dale W. Margerum L M S, Jolynn Hobson, and Elizabeth E. Moore. Water chlorination chemistry: Nonmetal redox kinetics of chloramine and nitrite ion[J]. Environmental Science & Technology, 1994, 28(2): 331-337.

[3] Raff J D, Njegic B, Chang W L, et al. Chlorine activation indoors and outdoors via surface-mediated reactions of nitrogen oxides with hydrogen chloride[J]. Proceedings of the National Academy of Sciences, 2009, 106(33): 13647-13654.

[4] Finlayson-Pitts B J, Ezell M J, Pitts J N. Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and $ClONO_2$[J]. Nature, 1989, 337(6204): 241-244.

[5] Behnke W, George C, Scheer V, et al. Production and decay of $ClNO_2$ from the reaction of gaseous N_2O_5 with NaCl solution: Bulk and aerosol experiments[J]. Journal of Geophysical Research: Atmospheres, 1997, 102(D3): 3795-3804.

[6] Thornton J A, Abbatt J P D. N_2O_5 reaction on submicron sea salt aerosol: Kinetics, products, and the effect of surface active organics[J]. The Journal of Physical Chemistry A, 2005, 109(44): 10004-10012.

[7] Osthoff H D, Roberts J M, Ravishankara A R, et al. High levels of nitryl chloride in the polluted subtropical marine boundary layer[J]. Nature Geoscience, 2008, 1(5): 324-328.

[8] Wängberg I, Etzkorn T, Barnes I, et al. Absolute determination of the temperature behavior of the $NO_2 + NO_3 + (M) \leftrightarrow N_2O_5 + (M)$ equilibrium[J]. The

Journal of Physical Chemistry A, 1997, 101(50): 9694-9698.

[9] Cantrell C A, Davidson J A, Mcdaniel A H, et al. The equilibrium constant for $N_2O_5 \rightleftharpoons NO_2+NO_3$: Absolute determination by direct measurement from 243 to 397 K[J]. The Journal of Chemical Physics, 1988, 88(8): 4997-5006.