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 three referees 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.

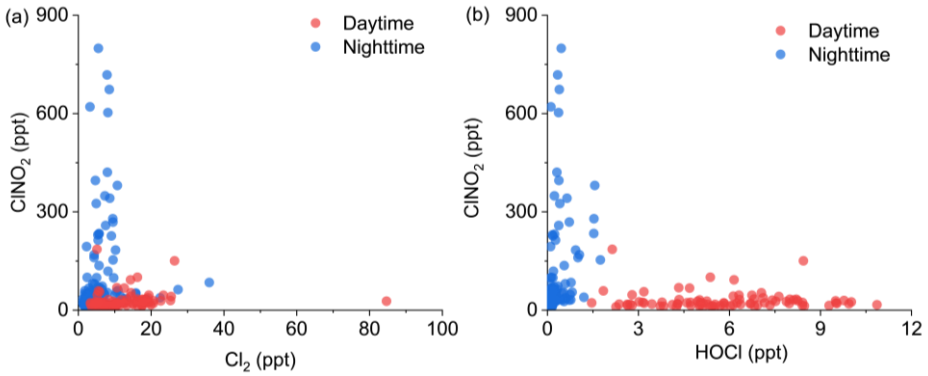

Fig. R1 Dependence of $ClNO_2$ on Cl_2 and HOCl concentrations. Scatter plots of $ClNO_2$ versus (a) Cl_2 and (b) HOCl concentrations, with data points colored by daytime (10:00~17:00) and nighttime (20:00~04:00) period.

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).

Referee #2:

1. The manuscript entitled " Nocturnal production of N_2O_5 and $ClNO_2$ in Delhi: driving factors and impacts" presents data and and analyses from a field study at a site in the megacity of Delhi conducted from 23rd Feb 2023 to 14th March 2023 (~21 days). A FIGAERO-I CIMS (Filter Inlet for Gases and AEROsols Iodide-Chemical Ionization-Time of Flight Mass Spectrometer) was used for measurements of several species including N2O5 and $ClNO_2$ and HCl and on the basis of these measurements and data from air quality monitoring stations made near the site, the authors have sought to explain the influence of factors that affect night time chemistry and elevated levels of observed N_2O_5 and $ClNO_2$ observed during their campaign relative to an earlier study conducting in the winter of 2019, which had reported lower levels of these species. While such a topic is certainly interesting and measurements using such instruments have rarely been made in India, I have serious concerns concerning the present work that prevent me from recommending publication of the paper in ACP.

Response: We sincerely thank the referee for the recognition of our research topic and the critical feedback, which motivates us to improve the manuscript substantially. We have carefully addressed all the concerns and revised the manuscript accordingly, particularly regarding the data quality issue and interpretation. Below please find our point-by-point responses and revisions.

These major concerns are summarized below:

2. Analyses that rests on multiple- assumptions whose basis seems unsound further compounded by use of non-research grade data measured at a nearby monitoring station

for parameters that are fundamental for the analyzes such as accurate NO, NOx measurements. Although the authors have tried to compensate through purely statistical checks, unfortunately in my view these do not seem to be adequate to be able to trust the primary dataset used for the analyses. Here I am not referring to the CIMS data which also seems to have experienced some major technical issues pertaining to in field calibrations and sensitivity being off due to application of Levoglucosan based sensitivity**,** which the authors have characterized, acknowledged and corrected as best they could but the co-measured datasets from other instruments operated by the pollution control agencies. See for example Figure S5 where there are big differences between the NO nighttime levels at IITD site and RK Puram site (which was actually used) for analyses of the CIMS data at IITD. The temporal resolution has not been mentioned but it appears that at night there are occasions when the ozone is non zero despite several ppb of NO at the same time, which is a clear indication of suspect data quality. Since the entire discussion about the night time chemistry rests strongly on the accuracy of NO measurements, I see this as a major red flag in the design/limitation of the study. The complete lack of discussion of seasonality and seasonal emissions in comparison of the wintertime study and the present spring time study and vast generalization reflected in the title also render the scientific quality weak. It is strange that the authors did not include any speciated VOC measurements of alkenes and aromatics compounds and also for the surface area simply used the winter time value by Gani et al despite obviously different aerosol type and source affecting between winter and spring. Their main premise of changed NOx levels isn't even explained in terms of why that should have happened between 2019 and 2023, despite more vehicles and sources. The present analyses being policy prescriptive, there is a need for caution in using just a month's data, some of which though fundamental to the analyses is also of suspect quality to make sweeping assertions concerning nighttime processes. There also seem to be several important previous works from the region that the authors have missed to include including some recent ones published in ACP and GRL and STOTEN that shed light on the chemistry of halogenated species and other night time oxidants like Stabilized Criegee intermediates.

Response: We thank the reviewer for the thorough and critical reading. Our responses to the concerns and revisions are as follows:

(1) <u>Data quality and assumptions</u>

Key data:

- **NO data from IIT Delhi site the R.K. Puram station:**

The NO data from the IIT Delhi site was obtained using the ECOTECH Serinus 40 research instrument and was the fundamental data used for analyzing N_2O_5-$ClNO_2$ chemistry in the manuscript. The NO data from the R.K. Puram station were mainly used to gain a general understanding of the long-term NO variations in Delhi, which was *<u>not</u>* used for the analysis of the CIMS data.

In addition, as described in Text S1.3 in the SI, we have applied rigorous data quality control procedures to the data from the R.K. Puram station following previous studies[10, 11], including removing duplicates, outliers, and constant data. Specifically

for the NO data, we validate NO and NO_2 measurement by comparing them with NO_x: consider NO and NO_2 are reported correctly in unit of $\mu g/m^3$ and assess if NO_x calculated from these is within 2% of reported NO_x + 2.5 ppb. We note that data from the continuous monitoring station in Delhi are widely used for research purposes after careful screening as described above, e.g., a recent publication in Nature Sustainability[11].

Although overall well-correlated (Fig. S6a, $r = 0.89$), absolute NO concentrations differed between the IIT Delhi site and the R.K. Puram station, primarily due to differences in measurement location (Fig. R2). The R.K. Puram station is situated close to a main road, with its sampling inlet 4~5 m above the ground (Fig. R2b), indicating NO concentrations are likely heavily influenced by nearby traffic emissions. In contrast, the sampling inlet at IIT Delhi is located approximately 30 m above ground (on the 8th floor) and about 300 m from the main road (Fig. R2c). Consequently, NO concentrations at IIT Delhi are more representative of regional atmospheric conditions, free from the influence of strong local emission sources or surrounding obstacles, and are generally lower than those measured at the R.K. Puram station. Furthermore, unlike the R.K. Puram station, which is surrounded by dense tree growth that may block wind and trap pollutants, the IIT Delhi site experiences less localized influences.

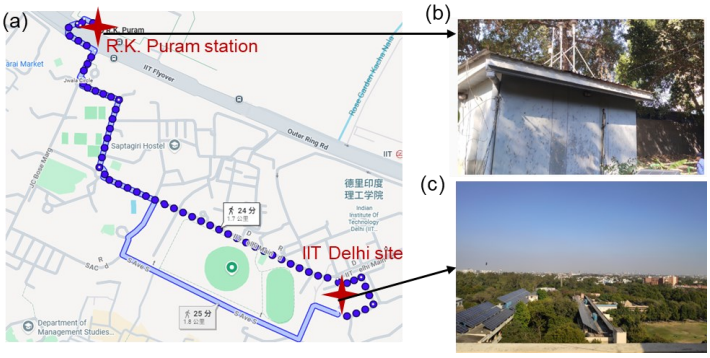

Fig. R2 (a) Locations of the IIT Delhi site and R.K. Puram station. Views from the (b) R.K. Puram station and (c) IIT Delhi site. The picture for the R.K. Puram station was obtained from https://www.newslaundry.com/2024/12/31/exclusive-delhi-aqi-data-is-unreliable-air-monitors-flout-norms-blocked-by-trees and the views from IIT Delhi site was taken from this study on 2023-2-7.

The NO and O_3 data shown in Fig. S6a are hourly averages. As illustrated in Fig. R3, hourly O_3 concentrations are generally close to zero when NO exceeds 10 ppb. On several occasions, O_3 levels of 10–20 ppb were observed alongside NO concentrations exceeding 100 ppb, which likely results from the mixing of O_3-rich and NO-rich air masses. Similar patterns have been reported in Germany[12] and the UK[13] around 2000, as well as in India in 2020 (see Fig. S2 in this reference[14]). Given that the strong negative correlation between NO and O_3 persists in our measurements, and that the N_2O_5 concentrations in the 2023 campaign largely overlapped with those from the 2019 campaign when NO concentrations were within the same range (Fig. 2), we don't expect the few high-NO, low-O_3 cases to significantly affect our main conclusion regarding the nighttime N_2O_5-$ClNO_2$ chemistry.

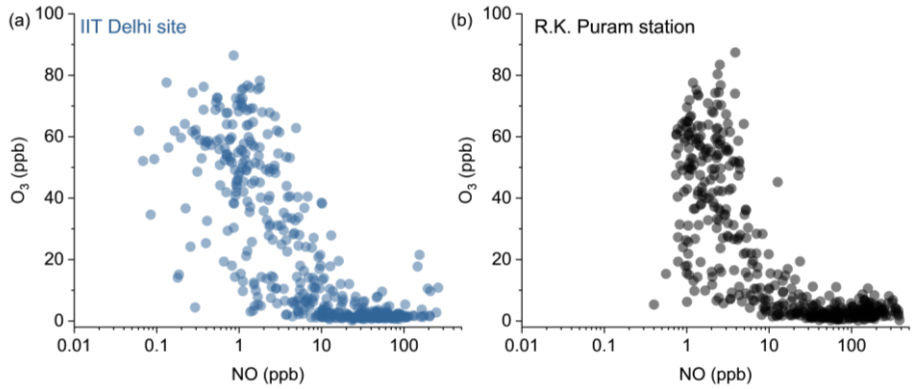

Fig. R3 Scatter plots between hourly NO and O_3 concentrations at (a) IIT Delhi site and (b) R.K. Puram station

- **CIMS data**:

As described in Section 2.1 of the main text, the sensitivities of N_2O_5 and $ClNO_2$, which are key to this study, were directly calibrated, rather than applying the levoglucosan-based sensitivity. Furthermore, the CIMS sensitivity drift during the field measurement was tracked periodically by calibrating acetic acid sensitivity and background measurements.

- **Assumptions about VOCs and aerosol surface area concentrations:**

VOCs and aerosol surface area (Sa) data were primarily used to estimate $NO_3\cdot$ reactivity in this study, but direct measurements of both parameters are lacking due to the unavailability of instrumentation during the campaign.

We therefore applied the same value of 0.081 s^{-1} for $NO_3\cdot$ reactivity to VOCs as derived in the previous 2019 winter study[15]. As shown in Fig. R4, the campaign-averaged $NO_3\cdot$ reactivity to NO in 2023 is ~15.6 s^{-1}, which is approximately 2 orders of magnitude higher than that to the previous winter reactivity to VOCs. Previous studies[14, 16] 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.

Regarding aerosol surface area, we clarify that we did not use the same value as reported by Gani et al.[17]. Instead, based on a linear correlation between $PM_{2.5}$ and Sa measured by Gani et al.[17] from February to March in 2018, we used $PM_{2.5}$ concentrations from our 2023 campaign as proxies to estimate Sa (Fig. S6b). This type of estimations of Sa using $PM_{2.5}$ has also been employed and validated in other studies[14, 18]. The campaign averaged heterogenous NO_3 loss from N_2O_5 uptake is about 0.091 s^{-1}, which is also about 2 orders of magnitude lower than the $NO_3\cdot$ reactivity to NO.

In conclusion, we expect that variations in VOCs between the two campaigns and the uncertainties in the calculated Sa would impose a negligible impact on the overall $NO_3\cdot$ reactivity, which is largely dominated by its reaction with NO.

We have further clarified these assumptions in the main text.

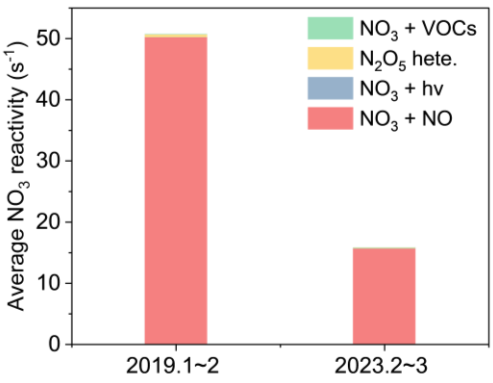

Fig. R4 Campaign-averaged NO_3· reactivity in 2019 and 2023. N_2O_5 hete. indicates loss of NO_3· via N_2O_5 heterogeneous uptake on aerosols.

Revision in the main text:

Line 186-192: *Supporting measurements at IIT Delhi include trace gases O_3 (ECOTECH Serinus 10), NO and NO_2 (ECOTECH Serinus 40), SO_2 (ECOTECH Serinus 50), and CO (ECOTECH Serinus 30) and meteorological parameters (T, RH, wind speed, and wind direction), which were measured by an automated weather station (AWS) (Davis Vantage Pro 2, Davis Instruments Corporation, USA). These concurrent online supporting measurements at IIT Delhi were used for key kinetic parameters calculations, such as P(NO_3·) and NO_3· reactivity, and the analysis of the CIMS data.*

Line 216-222: *Sa is aerosol surface area, $m^2 \cdot m^{-3}$, which was not directly measured but inferred from $PM_{2.5}$ data. Based on the linear correlation between $PM_{2.5}$ and Sa observed by Gani et al. [17] from February to March 2018, we used $PM_{2.5}$ concentrations from our 2023 campaign to derive the corresponding Sa values (Fig. S6b, r = 0.78). This estimation of Sa using $PM_{2.5}$ has also been employed and validated in other studies [14, 18]; t0 is the current time point, t1 is the subsequent time point, and dt is the time interval (in seconds) between them.*

Line 251-256 *: As shown in Fig. S7a and Table S2, the campaign-averaged NO_3· reactivity to NO in 2023 is ~15.6 s^{-1}, which is approximately 2 orders of magnitude higher than the reactivity to VOCs and the heterogenous loss of NO_3 from N_2O_5 uptake (0.091 s^{-1}). Previous studies[14, 16] 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.*

(2) <u>Seasonal variations and drivers of NO changes, and policy implications</u>

We agree with the referee that the seasonal characteristics and drivers of N_2O_5–$ClNO_2$ chemistry should be more clearly articulated. We have addressed these concerns as follows.

Seasonal variability in NO concentrations in Delhi is the main driver of the differences in NO observed between the spring campaign in 2023 and the winter

campaign in 2019. Like the referee mentioned, as shown in Fig. R5(a), the NO emissions in Delhi almost doubled in recent years, mainly driven by the increase in the number of vehicles. The observed decrease in NO concentrations during the 2023 campaign is therefore not driven by the changes in emissions, but the inter-month variability of NO (**Fig. R5(b)**). Elevated O_3 production was observed in spring compared to winter, which facilitates the removal and decrease of NO, thereby promoting N_2O_5 and subsequent $ClNO_2$ production.

We have also revised the title to more accurately reflect the seasonal and comparative nature of the study and avoid vast generalization based on two short-term field campaigns.

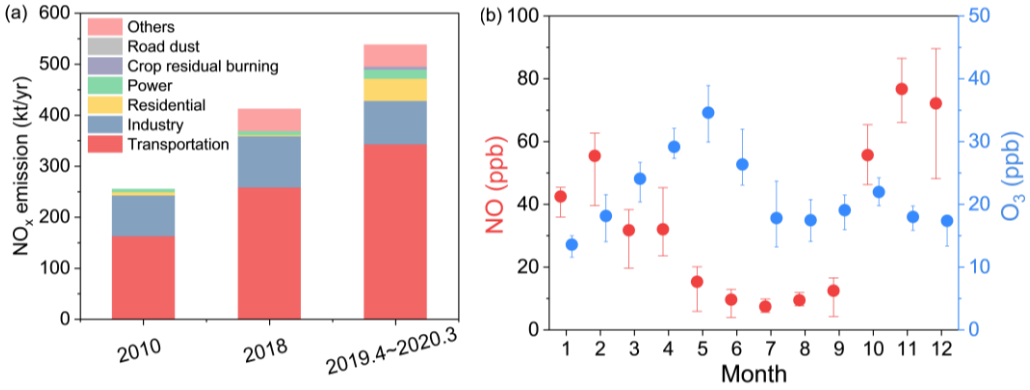

Fig. R5 (a) NOx emissions in Delhi from the year of 2010[19], 2018[20] and 2019.4~2020.3[21]. (b) Average monthly variations of NO and O_3 concentrations from 2017 to 2024 in Delhi. The dots represent the averages and the whiskers denote the 25th to 75th percentile ranges. Data were obtained from the R.K. Puram national monitoring station.

We agree with the reviewer that using only one month's data to make policy prescriptions requires caution. We weakened relevant policy suggestions about the biomass burning regulations.

Revision in the title:

Enhanced nocturnal N_2O_5-$ClNO_2$ chemistry in Delhi under lower-NO conditions.

Revision in the main text:

Line 358-365: *As is shown in Fig. S1c, NO emissions in Delhi almost doubled in recent years, mainly driven by the increase in the number of vehicles. The observed decrease in NO concentrations during the 2023 campaign is therefore not driven by the changes in emissions. Notably, the 2019 and 2023 measurements were conducted in different seasons, i.e., January to early February (winter) in 2019 and late February to mid-March (early spring) in 2023. As is shown in Fig. S14, elevated O_3 concentrations were observed in spring compared to winter, which facilitates the removal and decrease of NO and $P(NO_3)$. Overall, the seasonal variability in NO concentrations is the main driver of the differences in NO and $P(NO_3)$ observed between the two campaigns.*

Line 561-563: ~~*Chloride is mostly of anthropogenic origins in Delhi [22, 23] and we identified biomass burning as one of the major sources of chlorine during our measurements. It is expected that regulations on biomass burning along with transition*~~

~~*to clean residential fuels (e.g., natural gas and electricity) would benefit $PM_{2.5}$ abatement in Delhi by not only cutting primary particle emissions, but also suppressing secondary pollutant formation. To support such strategies,*~~ *an updated chlorine emission inventory combined with modelling studies, is necessary to quantitatively evaluate the contribution of chlorine chemistry to $PM_{2.5}$ formation under different NO_x conditions and inform targeted emission control strategies.*

(3) Missing references

After further screening of the literature, important references[14, 24-26] relevant to the chemistry of halogenated species in the Indo-Gangetic Plain were added to the manuscript. Discussions on stabilized Criegee Intermediates (sCI)[27] were shown below. References listed below were added:

- **Box modeling of $ClNO_2$:** 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.
- **Box modeling of $ClNO_2$ and Cl_2:** Soni M, Sander R, Sahu L K, et al. Comprehensive multiphase chlorine chemistry in the box model CAABA/MECCA: Implications for atmospheric oxidative capacity[J]. Atmospheric Chemistry and Physics, 2023, 23(23): 15165-15180.
- **GEOS-Chem modeling of $ClNO_2$**: Patel A, Reddy M C, Zhang B, et al. Linking anthropogenic chlorine emissions to regional air quality in India[J]. npj Clean Air, 2026, 2(1): 23.
- **Measurements of C_2H_3Cl and $C_6H_4Cl_2$:** 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): 13129-13150.

Previous studies in this region have mainly focused on measurements of chloride using AMS or ACSM (Fig. S3 and Table S4). Observations of gaseous chlorinated species[15, 26] remain limited. Several recent modeling studies[14, 24, 25] have indicated the potential for substantial $ClNO_2$ production, resulting in concentrations up to 5.5 ppb, in this region; however, the scarcity of field observations leaves these model predictions largely unvalidated, limiting our ability to quantify the impacts of chlorinated species on O_3 and secondary aerosol formation.

Atmospheric CIs are produced from the cycloaddition of O_3 to alkenes and can be a major source of OH at night[28]. Shabin et al[27] quantified the abundance of sCI (average 4.4×10^3 molec/cm^3) during the summertime in this region and found that sCI dominates the nighttime oxidation of SO_2 to sulfate. As chloride activation via N_2O_5 uptake is the major source of $ClNO_2$, we did not include sCI-initiated chloride oxidation in the manuscript. Nevertheless, this pathway could be a source of Cl_2 during nighttime in Delhi and is worth future investigation.

Revision in the main text, Line 78-92:

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. Previous studies in this region have mainly focused on measurements of chloride using AMS or ACSM (Fig. S2 and Table S1). Observations of gaseous chlorinated species [15, 26] remain limited. Several recent modeling studies [14, 24, 25] have indicated the potential for substantial $ClNO_2$ production, resulting in concentrations up to several ppb in this region; however, the scarcity of field observations leaves these model predictions largely unvalidated, limiting our ability to quantify the impacts of chlorinated species on O_3 and secondary aerosol formation.

The field measurement conducted in winter 2019 found that nighttime N_2O_5 and $ClNO_2$ levels are rather low in Delhi [15], which is attibuted to the extremely high NO concentrations (hundreds of ppb) and the fast reaction rate constant between NO and NO_3· (k_{NO+NO3}, 2.6×10^{-11} $cm^3 \cdot molec^{-1} \cdot s^{-1}$ at 298 K) [29], thereby largely quenching nocturnal NO_3· (reaction scheme R1) and limiting subsequent N_2O_5 and $ClNO_2$ production.

Specific comments:

1. L74-L77: ..far exceeding typical ranges….please justify….many recent works and data even post 2021 show such levels still occur…

Response: Thanks. We agree that extreme levels of NO concentrations continue to occur in Delhi in recent years, mainly from October to February (Fig. S14a). The term "typical ranges" used in our manuscript refers to the NO concentrations with the highest occurrence frequency based on the measurements from 2017 to 2024 in Delhi (Fig. R6a).

As is shown in Fig. R6a, the most frequent nighttime NO concentrations in Delhi typically fall within the 50~100 ppb range, while the average nighttime NO concentrations (124 ppb) during the 2019 campaign largely sits at the extreme tail of the distribution. As for chloride, the campaign-averaged concentration (21 μg/m^3) in 2019 largely exceeds the levels observed in recent years such as 2022 and 2023 (Fig. R6b). The description "far exceeding typical ranges" was intended to highlight that compared to the campaign in winter 2019, our campaign in spring 2023 recorded relatively lower NO and chloride concentrations, which corresponds to the more frequently occurring levels observed in Delhi in recent years.

To ensure scientific rigor and avoid ambiguity, we have revised the expression and elaborated on the direct comparison between the NO and chloride conditions captured in the two campaigns.

Revision in the main text, Line 92-97:

Notably, the 2019 campaign predominantly captured the extremely polluted episodes during the wintertime in Delhi, with the peak occurrence frequencies of NO (124 ppb) and chloride (21 μg/m^3) concentrations largely falling at the high end of the concentration distributions commonly observed during the recent years (Fig. S3b, c).

Due to the scarcity of field observations, the characteristics of N_2O_5-$ClNO_2$ chemistry outside of such extreme NO and chloride conditions in Delhi remain unclear.

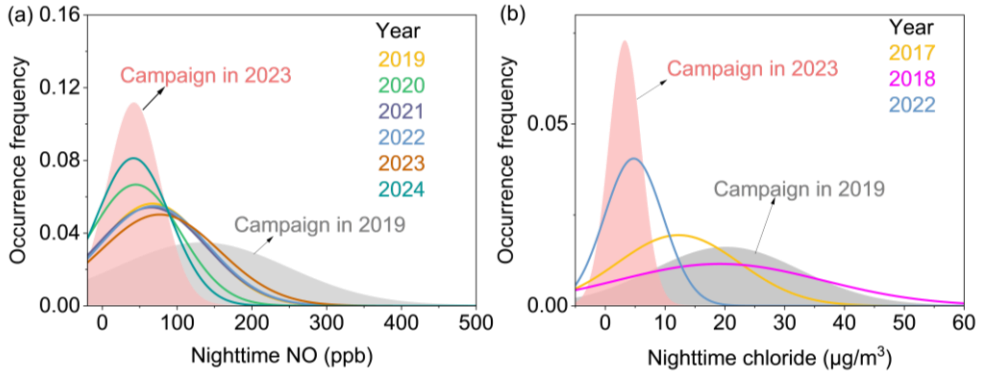

Fig. R6 Representativeness of the two field-campaigns in Delhi. Gaussian-fitted frequency distributions of nightly (a) NO from 2017 to 2024 and (b) chloride concentrations during winter and spring (January to April) in Delhi. The data for NO is obtained from the R.K. Puram monitoring station. Chloride concentrations were unavailable at the station and are retrieved from previous studies [30, 31]. The gray and red shaded area denote the respective concentration distribution of NO and chloride during the 2019 and 2023 campaign, respectively.

2. L94-104: How would the local vegetation and canopy and buildings at IIT Delhi affect dry and wet deposition also considering that you actually use data from a site faraway for your calculations ?

Response: Thanks. We clarify that we use the trace gas and meteorological data concurrently measured at the IIT Delhi site (rather than the R.K. Puram station) for calculations of $P(NO_3\cdot)$, $NO_3\cdot$ reactivity, and etc. Data from the R.K. Puram station was mainly used for characterization of the long-term variations of NO and O_3 in Delhi.

Sampling views from the IIT Delhi site is shown in Fig. R2, where the sampling inlet is located above the local vegetation canopy and thus the observation is representative of an urban background condition. Both the campaigns during winter 2019 and spring 2023 fall within the dry season in Delhi. There were no significant precipitation events during the periods selected for intensive chemical analysis. Consequently, wet deposition was not a significant factor in our nocturnal chemical budget and was omitted from the calculations.

We have added a brief discussion to clarify the use of R.K. Puram data and the negligible impact of dry and wet deposition.

Revision in the main text:

Line 121-125: *All the instruments were installed in an air-conditioned laboratory on the 8th floor, at a sampling height (~30 m) above the local vegetation canopy, and thus the observation is representative of an urban background condition. There were no significant precipitation events during the periods selected for intensive chemical analysis. Consequently, wet deposition was not a significant factor in our nocturnal chemical budget and was omitted from the calculations.*

Line 186-192: *Supporting measurements at IIT Delhi include trace gases O_3 (ECOTECH Serinus 10), NO and NO_2 (ECOTECH Serinus 40), SO_2 (ECOTECH Serinus 50), and CO (ECOTECH Serinus 30) and meteorological parameters (T, RH, wind speed, and wind direction), which were measured by an automated weather station (AWS) (Davis Vantage Pro 2, Davis Instruments Corporation, USA). These concurrent online supporting measurements at IIT Delhi were used for key kinetic parameters calculations, such as P(NO_3·) and NO_3· reactivity, and the analysis of the CIMS data.*

3. L118-L121: Please provide calibration plots Vs RH for the RH regimes experienced during the campaign period to provide more confidence ….

Response: The calibrations plots for N_2O_5 and $ClNO_2$ under different IH_2O^- to I^-ratios (an indicator of ambient RH) are shown in the following Fig. R7. The sensitivities of N_2O_5 and $ClNO_2$ vary little under the RH regimes experienced during the campaign. Fig. R7(b)-(c) has been added to Fig. S19 in the manuscript.

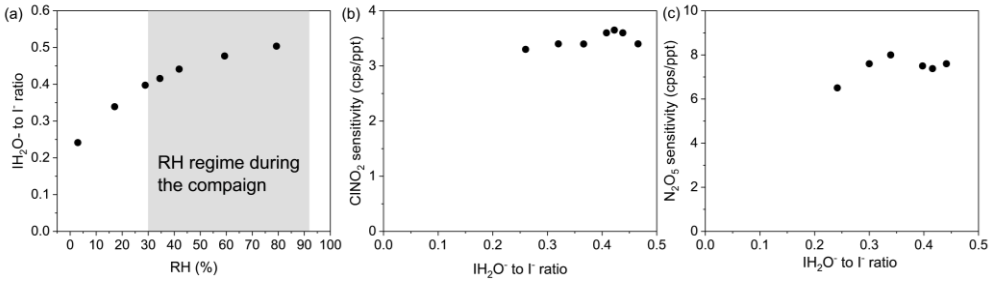

Fig. R7 RH dependency of $ClNO_2$ and N_2O_5 sensitivities. Calibrations of (a) IH_2O^- to I^- ratio, (b) $ClNO_2$ sensitivities, and (c) N_2O_5 sensitivities under different RH.

4. L124-126: What additional precautions were taking to ensure the bottle supplied zero air used was free of VOC contaminants? Was this screened or further cleaned using catalytic convertors which is std practice ?

Response: We used ultrahigh-purity nitrogen cylinder (Laser gases) rather than zero air for background measurements and as the carrier gas for the reagent ion (I^-) and the calibrants (acetic acid and perfluoropentanoic acid). We used a double manifold system with two nitrogen cylinders. This allowed to switch from any empty cylinder to a full one without interrupting instrument's operation. Regular background measurements were achieved by periodically overflowing the CIMS inlet with ultrahigh purity N_2 (Fig. R8). We also applied background subtraction to minimize potential interference from contamination. The detection limits, defined as three times the standard deviation of the hourly averaged background signals, were 0.6 ppt and 1.6 ppt for N_2O_5 and $ClNO_2$, respectively, which were also much lower than the ambient concentrations (several to thousands of ppt).

Revision in the main text, Line 134-137: *The background signals were measured by periodically overflowing the inlet with ultrahigh purity N_2 (Laser gases), and background subtractions were performed to minimize potential interference from*

contamination.

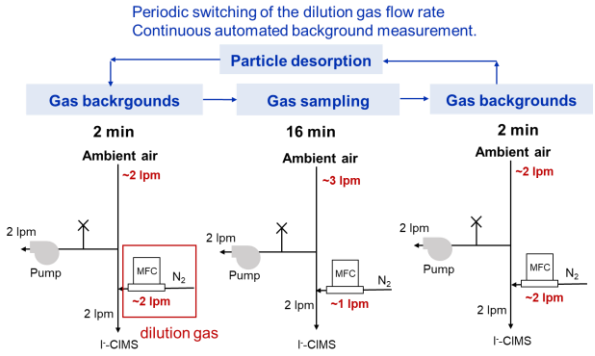

Fig. R8 Configurations of the gas sampling inlet.

5. EDXRF: Details of the instrument and analysis methods are missing..also please check as it is not clear how 83 samples were obtained as 20 x 2= 40 samples. For what dates was freq increased to every 4 h? what were the PM mass concentration loadings? Was any check done with other techniques or BAM for mass closure?

Response: Details of the instrument and analysis methods are added as follows. The specific sampling periods are shown in Table. R1. The sampling frequency was increased to every 4 h from 2023/3/2 9:00 to the end of the campaign. The $PM_{2.5}$ mass loadings on the filter measured by the manual weighing method were overall in good agreement with those measured using BAM (Fig. R9, r = 0.96). The $PM_{2.5}$ data measured using BAM was obtained from the US embassy in Delhi (https://www.airnow.gov/international/us-embassies-and-consulates/#India$New_Delhi, last access, 2024/7/5).

Table. R1 Sampling time information for offline EDXRF analysis.

No.	Time midpoint	Date	Hour	Duration (hrs)
1	2023/2/22 13:00	2023/02/22	07:00-19:00	12
2	2023/2/23 2:00	2023/02/22	19:00-09:00	14
3	2023/2/23 14:00	2023/02/23	09:00-19:00	10
4	2023/2/24 1:00	2023/02/23	19:00-07:00	12
5	2023/2/24 13:00	2023/02/24	07:00-19:00	12
6	2023/2/25 1:00	2023/02/24	19:00-07:00	12
7	2023/2/25 13:00	2023/02/25	07:00-19:00	12
8	2023/2/26 1:00	2023/02/25	19:00-07:00	12
9	2023/2/26 13:00	2023/02/26	07:00-19:00	12
10	2023/2/27 1:00	2023/02/26	19:00-07:00	12
11	2023/2/27 13:00	2023/02/27	07:00-19:00	12
12	2023/2/28 1:00	2023/02/27	19:00-07:00	12
13	2023/2/28 10:00	2023/02/28	07:00-13:00	6
14	2023/2/28 16:00	2023/02/28	13:00-19:00	6
15	2023/2/28 22:15	2023/02/28	19:00-01:30	6.5
16	2023/3/1 14:38	2023/03/01	10:23-19:00	8.62

17	2023/3/2 1:00	2023/03/01	19:00-07:00	12
18	2023/3/2 9:00	2023/03/02	07:00-11:00	4
19	2023/3/2 13:00	2023/03/02	11:00-15:00	4
20	2023/3/2 17:00	2023/03/02	15:00-19:00	4
21	2023/3/3 1:00	2023/03/02	19:00-07:00	12
22	2023/3/3 9:00	2023/03/03	07:00-11:00	4
23	2023/3/3 13:00	2023/03/03	11:00-15:00	4
24	2023/3/3 17:00	2023/03/03	15:00-19:00	4
25	2023/3/4 1:00	2023/03/03	19:00-07:00	12
26	2023/3/4 9:00	2023/03/04	07:00-11:00	4
27	2023/3/4 13:00	2023/03/04	11:00-15:00	4
28	2023/3/4 17:00	2023/03/04	15:00-19:00	4
29	2023/3/4 21:00	2023/03/04	19:00-23:00	4
30	2023/3/5 1:00	2023/03/04	23:00-03:00	4
31	2023/3/5 9:00	2023/03/05	07:00-11:00	4
32	2023/3/5 13:00	2023/03/05	11:00-15:00	4
33	2023/3/5 17:00	2023/03/05	15:00-19:00	4
34	2023/3/5 21:00	2023/03/05	19:00-23:00	4
35	2023/3/6 1:00	2023/03/05	23:00-03:00	4
36	2023/3/6 5:00	2023/03/06	03:00-07:00	4
37	2023/3/6 8:30	2023/03/06	07:00-11:00	4
38	2023/3/6 13:00	2023/03/06	11:00-15:00	4
39	2023/3/6 17:00	2023/03/06	15:00-19:00	4
40	2023/3/6 21:00	2023/03/06	19:00-23:00	4
41	2023/3/7 1:00	2023/03/06	23:00-03:00	4
42	2023/3/7 5:00	2023/03/07	03:00-07:00	4
43	2023/3/7 9:00	2023/03/07	07:00-11:00	4
44	2023/3/7 13:00	2023/03/07	11:00-15:00	4
45	2023/3/7 17:00	2023/03/07	15:00-19:00	4
46	2023/3/7 21:00	2023/03/07	19:00-23:00	4
47	2023/3/8 5:00	2023/03/08	03:00-07:00	4
48	2023/3/8 9:00	2023/03/08	07:00-11:00	4
49	2023/3/8 13:00	2023/03/08	11:00-15:00	4
50	2023/3/8 17:00	2023/03/08	15:00-19:00	4
51	2023/3/8 21:00	2023/03/08	19:00-23:00	4
52	2023/3/9 1:00	2023/03/08	23:00-03:00	4
53	2023/3/9 5:00	2023/03/09	03:00-07:00	4
54	2023/3/9 9:00	2023/03/09	07:00-11:00	4
55	2023/3/9 13:00	2023/03/09	11:00-15:00	4
56	2023/3/9 17:00	2023/03/09	15:00-19:00	4
57	2023/3/9 21:00	2023/03/09	19:00-23:00	4
58	2023/3/10 1:00	2023/03/09	23:00-03:00	4
59	2023/3/10 5:00	2023/03/10	03:00-07:00	4
60	2023/3/10 9:00	2023/03/10	07:00-11:00	4

61	2023/3/10 13:00	2023/03/10	11:00-15:00	4
62	2023/3/10 17:00	2023/03/10	15:00-19:00	4
63	2023/3/10 21:00	2023/03/10	19:00-23:00	4
64	2023/3/11 1:00	2023/03/10	23:00-03:00	4
65	2023/3/11 5:00	2023/03/11	03:00-07:00	4
66	2023/3/11 9:00	2023/03/11	07:00-11:00	4
67	2023/3/11 13:00	2023/03/11	11:00-15:00	4
68	2023/3/11 17:00	2023/03/11	15:00-19:00	4
69	2023/3/11 21:00	2023/03/11	19:00-23:00	4
70	2023/3/12 1:00	2023/03/11	23:00-03:00	4
71	2023/3/12 5:00	2023/03/12	03:00-07:00	4
72	2023/3/12 9:00	2023/03/12	07:00-11:00	4
73	2023/3/12 13:00	2023/03/12	11:00-15:00	4
74	2023/3/12 17:00	2023/03/12	15:00-19:00	4
75	2023/3/12 21:00	2023/03/12	19:00-23:00	4
76	2023/3/13 1:00	2023/03/12	23:00-03:00	4
77	2023/3/13 5:00	2023/03/13	03:00-07:00	4
78	2023/3/13 9:00	2023/03/13	07:00-11:00	4
79	2023/3/13 13:00	2023/03/13	11:00-15:00	4
80	2023/3/13 17:00	2023/03/13	15:00-19:00	4
81	2023/3/13 21:00	2023/03/13	19:00-23:00	4
82	2023/3/14 1:00	2023/03/13	23:00-03:00	4
83	2023/3/14 5:00	2023/03/14	03:00-07:00	4

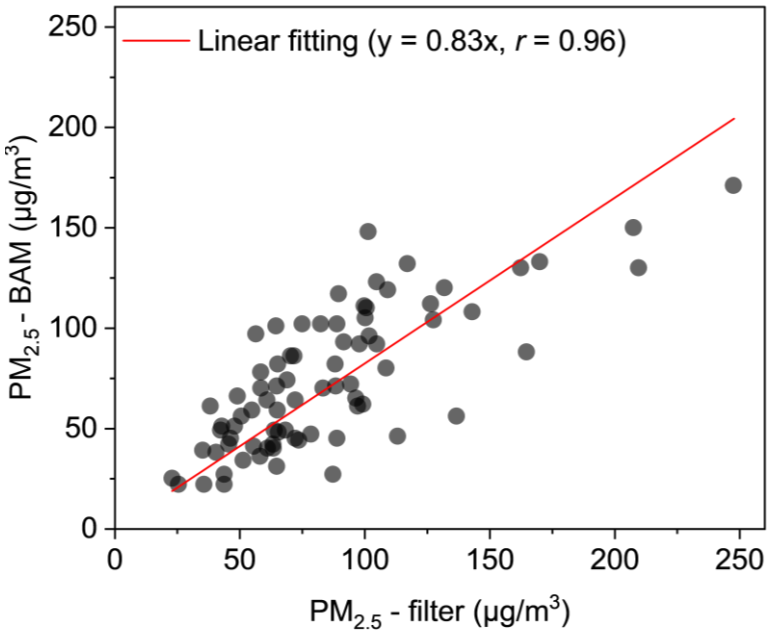

Fig. R9 Comparison of $PM_{2.5}$ measured by the manual weighing method and BAM.

Revision in the main text:

Line 160-177 : *Ambient $PM_{2.5}$ filter samples were collected for offline Energy Dispersive X-ray Fluorescence (EDXRF; SPECTRO-XEPOS, AMETEK Inc.) analysis.*

ED-XRF is a sensitive and non-destructive technique which requires negligible sample pre-treatment and has been widely used for measuring elements in ambient particles[32, 33]. A total of 83 $PM_{2.5}$ samples were collected at 3 lpm on polytetrafluoroethylene (PTFE) filters (25 mm in diameter of 0.4 μm) via a $PM_{2.5}$ cyclone (Casella Solutions, UK) every 12 hours from 2/22 to 2/28 and every 4 hours from 3/1 to 3/14. We increased the frequency of filter switches by the end of the campaign to capture the variations of Cl element concentrations within a night, i.e., before (19:00~23:00) and post (23:00~3:00) midnight. The mid-point of the measurement period, i.e., 1:00 indicates measurement from 23:00~3:00, 5:00 for 3:00~7:00, 9:00 for 7:00~11:00, 13:00 for 11:00~15:00, 17:00 for 15:00~19:00, and 21:00 for 19:00~23:00, was used as the representative timestamp for each filter sample. Four blank filters (without any air sampling) were collected during the daytime (7:00~19:00) on 3/5 and 3/11, and during nighttime (19:00~7:00) on 3/5 and 3/8. These blank filters underwent the same analytical procedures as the sample filters. The filter samples were directly analyzed by EDXRF without any pretreatment. Each sample was analyzed for approximately 22 minutes. The instrument measured 26 elements, i.e., Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Sr, Ba, Ti, Pb and Bi, based on their characteristic fluorescence (150 eV to 600 eV). This manuscript reports the blank-subtracted concentrations of K and Cl.

6. L149-150: Two orders of magnitude lower is of grave concern!

Response: This sentence has been revised to avoid confusion.

Revision in the main text:
Line 181-185: *The trend of chloride measured by CIMS (pCl^--CIMS) largely followed that of the XRF-measured chloride (Cl-XRF) ($r = 0.70$) (Fig. S6c). Since pCl^--CIMS was not directly calibrated, it was only used qualitatively to complement the average diurnal variations of Cl-XRF in Fig. 1d. Cl-XRF was used for further analysis throughout the manuscript.*

7. L175: Please specify what you mean by neighbouring measurements…

Response: Neighboring measurements mean two consecutive sampling time points, usually at a time resolution of about 1 hour, e.g., 2023/2/23 20:00 and 2023/2/23 21:00.

Revision in the main text, Line 221-222:
t0 is the current time point, t1 is the subsequent time point, and dt is the time interval (in seconds) between them.

8. L183-187: Too many assumptions linking to each other?

Response: The descriptions are revised as follows:

Revision in the main text, Line 225-227:
However, nocturnal transport, i.e., changes in air masses, can invalidate this method and yield values exceeding 0.1 (sharp increases in $ClNO_2$, occurrence frequency of

~17%) which were discussed separately (Section 3.2).

9. L207-L211: lack of VOC measurements and assumption of same value as was in 2019 in wintertime is definitely not valid….what is your basis? Even if for a moment one assumes NOx was much lower in 2023 relative to 2019 , then why would VOCs not have changed too…this is an example of inconsistent logic that one comes across on several occasions in the manuscript…

Response: Thanks for pointing this out. We have clarified the assumption of the VOCs data in response to reviewer's general comment 2. The key point is that VOCs data were primarily used to derive NO_3· reactivity in this study, but direct measurements VOCs are lacking due to the unavailability of instrumentation during the campaign.

We applied the same value of 0.081 s^{-1} for NO_3· reactivity to VOCs as estimated in winter 2019[15]. 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[14, 16] 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 campaign-averaged NO_3· reactivity to NO in 2023 is ~15.6 s^{-1}, which is approximately 2 orders of magnitude higher than the reactivity to VOCs and the heterogenous loss of NO_3 from N_2O_5 uptake (0.091 s^{-1}). Previous studies[14, 16] 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.

10. Overall, I think the novel aspect of the study are the CIMS measurements and my recommendation is that the authors should resubmit a new MS focusing only on those and comparing it with world-wide levels in other regions, removing flawed and speculative aspects that aim to be policy prescriptive without sound scientific basis.

Response: Thanks for the suggestions. We have revised the title more focusing the comparison between two CIMS measurements rather than aiming to be policy prescriptive, and clarified the data sources, assumptions and uncertainties in response to the reviewer's comments as listed above.

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[23, 34] 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[35, 36].

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 $NO_3\cdot$ reactivity to NO in 2023 is ~15.6 s^{-1}, which is approximately 2 orders of magnitude higher than that to VOCs. Previous studies[14, 16] 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 $NO_3\cdot$ 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[14, 16] 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.

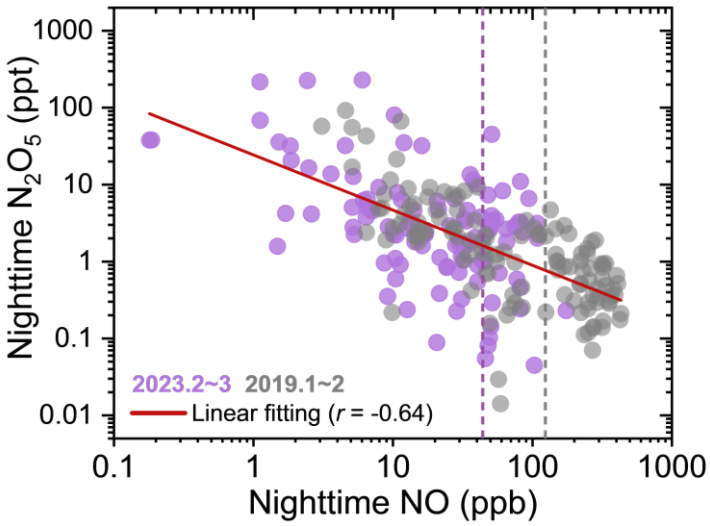

Fig. R10 Scatter plot of nighttime NO versus N_2O_5. Nighttime is defined as the period from 20:00 to 04:00, excluding the transition period between day and night when the air mass was unstable. The purple and grey dashed lines indicate the average NO concentrations during the 2023 and 2019 campaign, 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 [23, 34]. 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[37]. 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[37, 38].

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[37].
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[15]. 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 $ClNO_2$[39].

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.

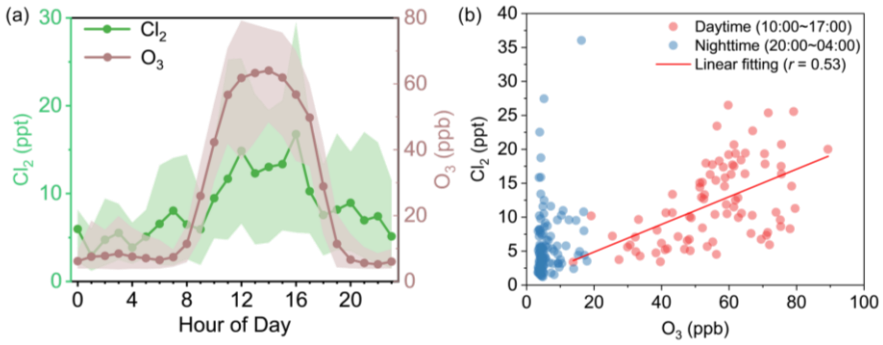

Fig. R11 (a) Average diurnal variations of Cl_2 and O_3 in Delhi. The dots indicate the averages while the shaded area shows the 10th and 90th percentiles. (b) Scatter plot between O_3 and Cl_2 in Delhi. The linear fitting line between the daytime O_3 and Cl_2 is also plotted.

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[40, 41]

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

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

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.

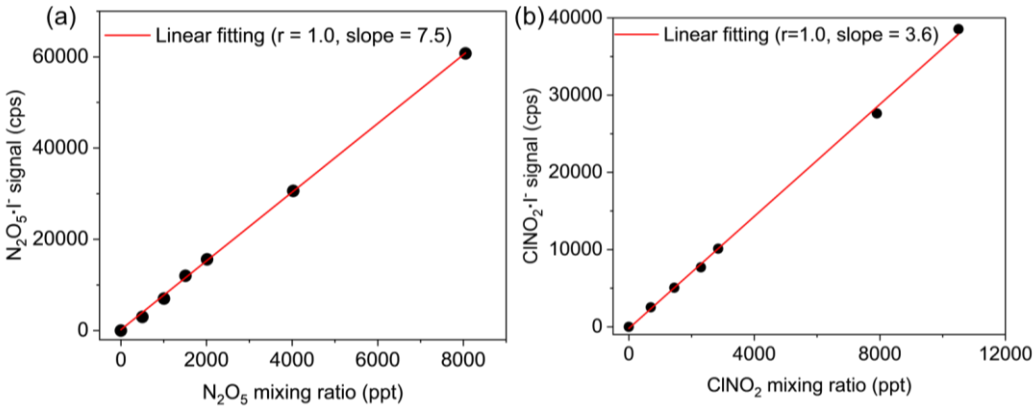

Fig. R12 Calibrations of (a) N_2O_5 and (b) $ClNO_2$.

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.

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