**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 #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[1, 2], 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[2].

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.

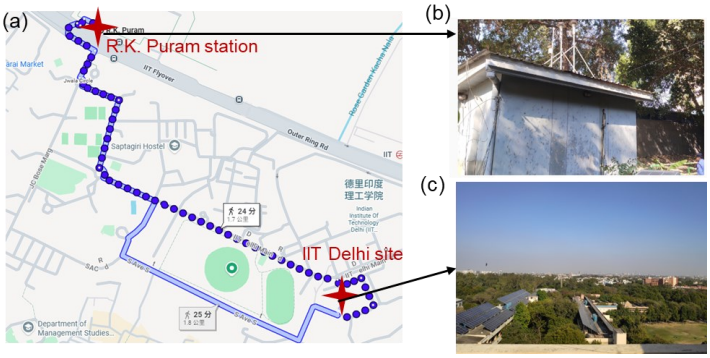


**Fig. R2** (a) Locations of the IIT Delhi site and R.K. Puram station. Views from the (b) R.K. Puram station and (c) IIT Delhi site. The picture for the R.K. Puram station was obtained from https://www.newslaundry.com/2024/12/31/exclusive-delhi-aqi-data-is-unreliable-air-monitors-flout-norms-blocked-by-trees 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[3] and the UK[4] around 2000, as well as in India in 2020 (see Fig. S2 in this reference[5]). 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.

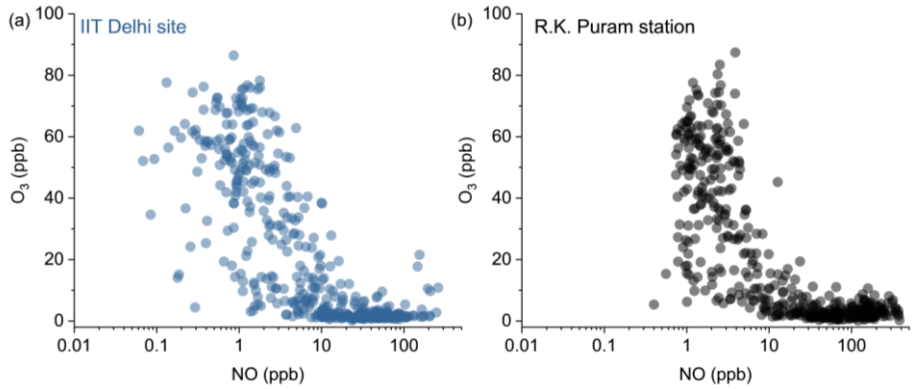


**Fig. R3** Scatter plots between hourly NO and $O_3$ concentrations at (a) IIT Delhi site and (b) R.K. Puram station

- **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[6]. 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[5, 7] 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.[8]. Instead, based on a linear correlation between $PM_{2.5}$ and Sa measured by Gani et al.[8] 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[5, 9]. 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.

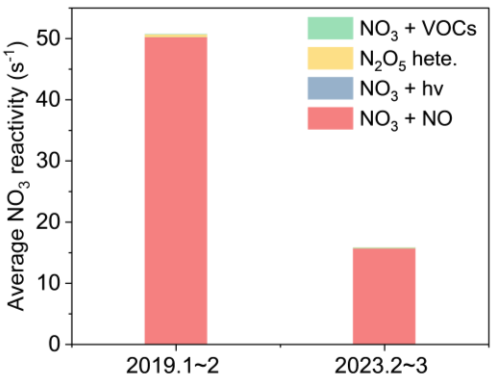


**Fig. R4** Campaign-averaged $NO_3$· reactivity in 2019 and 2023. $N_2O_5$ hete. indicates loss of $NO_3$· via $N_2O_5$ heterogeneous uptake on aerosols.

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. [8] 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 [5, 9]; 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[5, 7] 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.

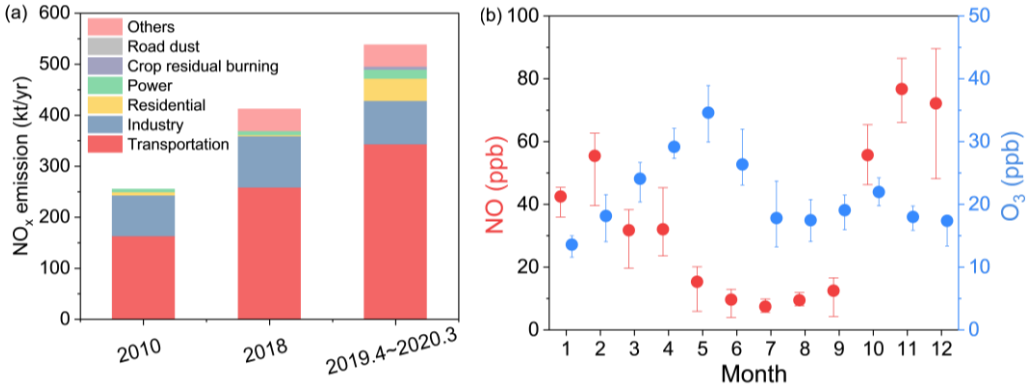


**Fig. R5** (a) NOx emissions in Delhi from the year of 2010[10], 2018[11] and 2019.4~2020.3[12]. (b) Average monthly variations of NO and $O_3$ concentrations from 2017 to 2024 in Delhi. The dots represent the averages and the whiskers denote the 25$^{th}$ to 75$^{th}$ percentile ranges. Data were obtained 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 [13, 14] 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[5, 15-17] relevant to the chemistry of halogenated species in the Indo-Gangetic Plain were added to the manuscript. Discussions on stabilized Criegee Intermediates (sCI)[18] 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[6, 17] remain limited. Several recent modeling studies[5, 15, 16] 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[19]. Shabin et al[18] quantified the abundance of sCI (average $4.4\times10^3$ 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 [6, 17] remain limited. Several recent modeling studies [5, 15, 16] 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 [6], which is attibuted to the extremely high NO concentrations (hundreds of ppb) and the fast reaction rate constant between NO and $NO_3$· ($k_{NO+NO3}$, $2.6\times10^{-11}$ $cm^3 \cdot molec^{-1} \cdot s^{-1}$ at 298 K) [20], 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.*

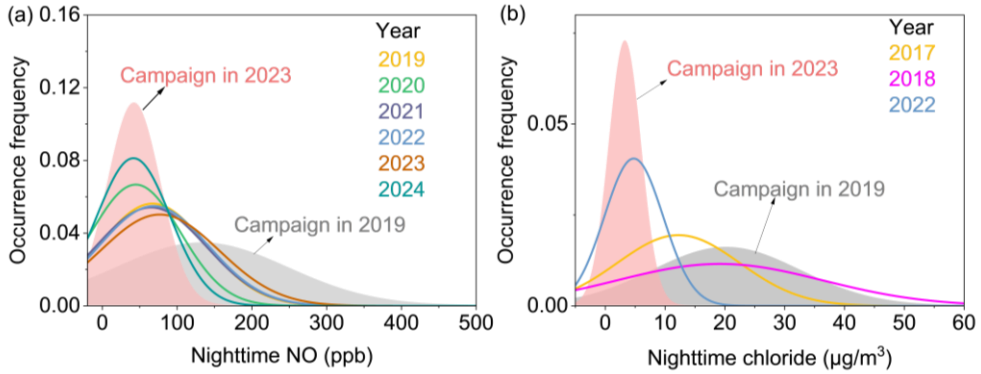


**Fig. R6 Representativeness of the two field-campaigns in Delhi.** Gaussian-fitted frequency distributions of nightly (a) NO from 2017 to 2024 and (b) chloride concentrations during winter and spring (January to April) in Delhi. The data for NO is obtained from the R.K. Puram monitoring station. Chloride concentrations were unavailable at the station and are retrieved from previous studies [21, 22]. 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 8$^{th}$ 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 $P(NO_3\cdot)$ and $NO_3\cdot$ 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.

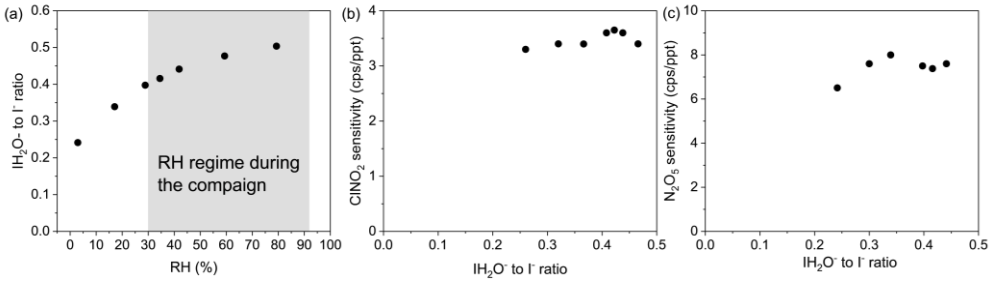


**Fig. R7** RH dependency of $ClNO_2$ and $N_2O_5$ sensitivities. Calibrations of (a) $IH_2O^-$ to $I^-$ ratio, (b) $ClNO_2$ sensitivities, and (c) $N_2O_5$ sensitivities under different RH.

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.*

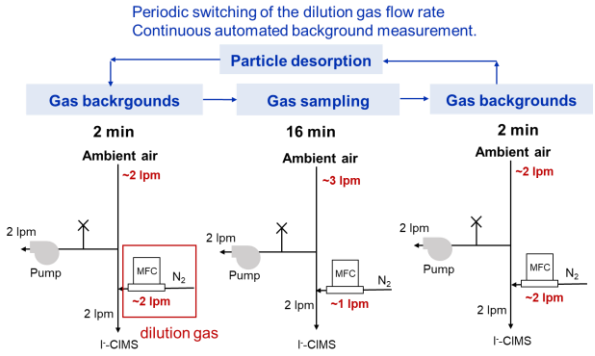


**Fig. R8** Configurations of the gas sampling inlet.

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 |

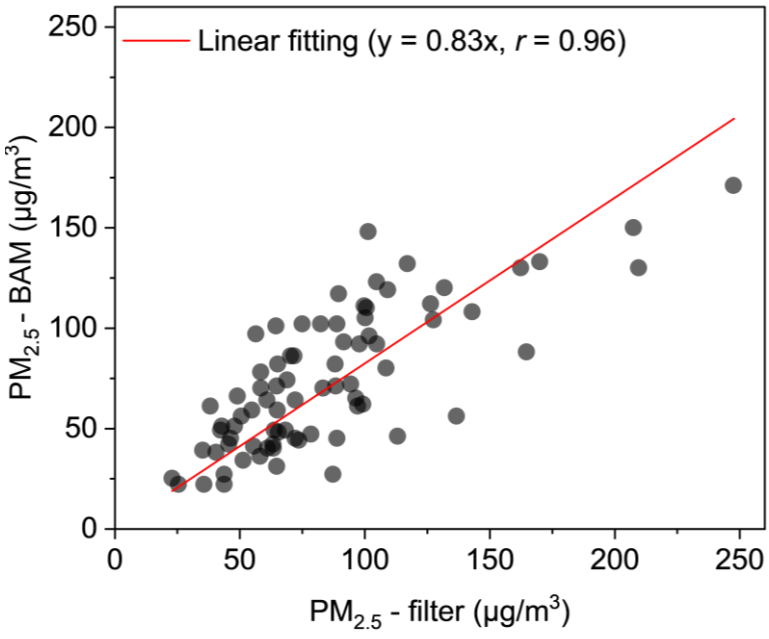


**Fig. R9** Comparison of $PM_{2.5}$ measured by the manual weighing method and BAM.

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[23, 24]. 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[6]. 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, 7] 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[5, 7] 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.

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