

Enhanced nocturnal N₂O₅-ClNO₂ chemistry in Delhi under lower-NO conditions

Yijing Chen^{1,2}, Cheng Wu^{2*}, Epameinondas Tsiligiannis², Ravi Kant Pathak^{2,3}, Jan B. C. Pettersson², Harsh Raj Mishra^{2,3†}, Gazala Habib⁴, Geetam Tiwari⁵, Kebin He¹, Jingkun Jiang^{1*}, Mattias Hallquist^{2*}

Affiliations:

¹State Key Laboratory of Regional Environment and Sustainability, School of Environment, Tsinghua University, School of Environment, Tsinghua University; Beijing, 100084, China.

²Department of Chemistry and Molecular Biology, University of Gothenburg; Gothenburg, 40530, Sweden.

³Indo-Gangetic Plains Centre for Air Research and Education (IGP-CARE), Hamirpur, Uttar Pradesh, 210301, India.

⁴Transportation Research and Injury Prevention Centre, Indian Institute of Technology Delhi, New Delhi, 110016, India.

⁵Department of Civil Engineering, Indian Institute of Technology Delhi, New Delhi, 110016, India.

†Present address: School of Earth and Atmospheric Sciences, Queensland University of Technology, Queensland, 4001, Brisbane, Australia.

*Correspondence to: Mattias Hallquist (hallq@chem.gu.se), Jingkun Jiang (jiangjk@tsinghua.edu.cn) and Cheng Wu (cheng.wu@gu.se).

This PDF file includes:

Abstract

Main Text

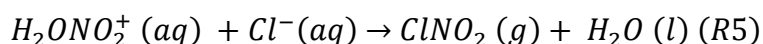
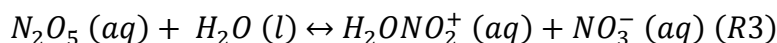
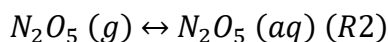
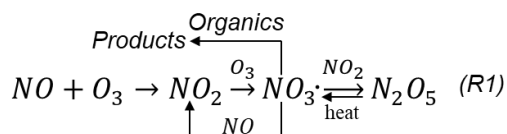
Figures 1 to 6

ABSTRACT.

Nitryl chloride (ClNO_2) is an important $\text{Cl}\cdot$ precursor, originating from the heterogeneous reactions of dinitrogen pentoxide (N_2O_5) on chloride-containing particles. This N_2O_5 - ClNO_2 chemical process plays critical roles in chloride activation, nitrate formation, and thus air pollution. Here we present field measurements made in the early springtime of 2023 in Delhi and compare with a previous study conducted during the winter of 2019. We found elevated nocturnal levels of N_2O_5 and ClNO_2 , averaging 13 and 80 ppt, respectively, which are approximately doubled compared to observations in 2019. This change is primarily driven by the reduced nighttime NO levels, from 124 ± 25 ppb in 2019 to 44 ± 9 ppb in 2023. In addition, the chloride concentration (nighttime average $4.7 \mu\text{g}/\text{m}^3$) in Delhi is among the highest reported globally, driving efficient conversion of N_2O_5 to ClNO_2 . Decreased NO and elevated ClNO_2 levels lead to higher $\text{NO}_3\cdot$ and $\text{Cl}\cdot$ production that promote the oxidation of organics. Consistently, we observed increased fractions of gaseous nitrogen- and chlorine-containing organic products and a higher oxidation state of the organic aerosols. Our findings highlight the need for increased attention to atmospheric secondary pollution and stringent anthropogenic chlorine emissions control under lower- NO_x conditions in Delhi.

1 INTRODUCTION

Atmospheric N_2O_5 - $ClNO_2$ chemistry refers to the conversion of N_2O_5 to $ClNO_2$ on chloride-containing particles (Finlayson-Pitts et al., 1989), which is ubiquitous worldwide (Wang et al., 2019) and exerts profound impacts on nitrogen budgets (Dentener and Crutzen, 1993), chloride activation (Thornton et al., 2010), and atmospheric oxidative capacity (Simpson et al., 2015; Yang et al., 2022). 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). 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^- (R5). Some studies (Dalton et al., 2023; Dale W. Margerum, 1994) 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^- . Other reactions such as HCl reacts with N_2O_5 on surfaces is not considered due to the relatively slow reaction rate constant (Raff et al., 2009).



$ClNO_2$ is rather inert at night and undergoes negligible losses, while it photolyzes to produce $Cl\cdot$ during the daytime (Osthoff et al., 2008). Given the fast photolysis of $NO_3\cdot$ and thermal decomposition of N_2O_5 , the N_2O_5 to $ClNO_2$ conversion is expected to happen mainly at night (Brown and Stutz, 2012). The occurrence of this nocturnal chemistry was confirmed by direct field observations of N_2O_5 and $ClNO_2$ in the urban coastal air (Osthoff et al., 2008; Riedel et al., 2012), and later extended to polluted inland areas (Thornton et al., 2010; Phillips et al., 2012; Le Breton et al., 2018a; Ma et al., 2023; Chen et al., 2023), where abundant NO_x and particulate chloride precursors co-exist, with measured nighttime peak mixing ratios consistently up to several parts per billion by volume (ppb), which are about an order of magnitude higher than those observed in the remote polar and marine regions (McNamara et al., 2019; Eger et al., 2019; Kercher et al., 2009).

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 NO_x , 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 (Mishra et al., 2024; Haslett et al., 2023) remain limited. Several recent modeling studies (Meidan et al., 2022; Soni et al., 2023; Patel et al., 2026) 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 (Haslett et al., 2023), which is attributed to the extremely high NO concentrations (hundreds of ppb) and the fast reaction rate constant between NO and $\text{NO}_3\cdot$ ($k_{\text{NO}+\text{NO}_3}$, $2.6 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 298 K) (Burkholder et al., 2020), thereby largely quenching nocturnal $\text{NO}_3\cdot$ (reaction scheme R1) and limiting subsequent N_2O_5 and ClNO_2 production. 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 ($21 \mu\text{g}/\text{m}^3$) 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.

In this work, we present a recent field measurement of N_2O_5 , ClNO_2 and other relevant inorganic and organic species in both gas and particle-phases during the early springtime of 2023 in Delhi. This timing captures a broader range of NO concentrations (below 0.1 to hundreds of ppb) and chemical conditions, which overlaps with but extends beyond previous studies that primarily focused on the most polluted winter months. We characterize the changes in N_2O_5 - ClNO_2 chemistry relative to the previous observation in winter 2019 (Haslett et al., 2023) and examine the underlying driving factors and impacts. The field derived kinetic parameter, quantified as the product of N_2O_5 uptake coefficient ($\gamma_{\text{N}_2\text{O}_5}$) and ClNO_2 yield (f_{ClNO_2}), is also estimated and compared to those reported from other atmospheric environments. We find enhanced N_2O_5 production driven by decreased NO concentrations, and the formation of ClNO_2 is dependent on the chloride level in Delhi. The product of $\gamma_{\text{N}_2\text{O}_5} \times f_{\text{ClNO}_2}$ (average ~ 0.2) is at the upper end of the values observed around the world, indicating efficient N_2O_5 conversion to ClNO_2 in Delhi. We further investigate the impacts of associated increases in $\text{NO}_3\cdot$ and $\text{Cl}\cdot$ production rates on the atmospheric oxidation of organics, utilizing concurrent measurements of a wide range of molecular-level organic oxidation products.

2 METHODS

2.1 Field observation overview

The field campaign was performed at the Indian Institute of Technology Delhi campus (IIT Delhi, 28.54°N, 77.19°E; ~230 m above the sea level) from 15 February to 14 March in 2023. The valid dataset collected during the early spring period (2/23-3/14) was used for analysis in this study. IIT Delhi is a representative continental urban site situated at the north-western of Indo-Gangetic Plain, which is frequently affected by intense anthropogenic emissions from biomass and waste burning activities, traffic exhaust, power plants, and industries (Kumar et al., 2022; Bryant et al., 2023; Kashyap et al., 2019; Rai et al., 2020), and potential biogenic emissions from the surrounding vegetations (Fig. S4). 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. In addition, considering the high aerosol loading and stable nighttime boundary layer (average nighttime wind speed of 0.6 m/s) in Delhi, N₂O₅ or ClNO₂ losses through dry deposition on building surfaces or vegetation are expected to be minor. 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. Details of the measurement design are found in the supplementary information (Text. S1).

FIGAERO-I-CIMS. N₂O₅, reactive chlorines, and oxygenated organics were identified as iodide clusters (M·I⁻) by a Filter Inlet for Gases and AEROSols Iodide-Chemical Ionization-Time of Flight Mass Spectrometer (FIGAERO-I-HR-ToF-CIMS, hereafter as CIMS) (Lopez-Hilfiker et al., 2014). Basic principles and configurations were described in previous field studies (Le Breton et al., 2018a; Le Breton et al., 2018b). Each CIMS operation cycle consisted of background (~2 min), ambient gas (~16 min), a second background (~2 min), and PM_{2.5} desorption measurements (~50 min) (Fig. S5). The background signals were measured by periodically overflowing the inlet with ultrahigh purity N₂ (Laser gases), and background subtractions were performed to minimize potential interference from contamination. The raw signals in counts per second (cps) were normalized by the sum of the reagent ions (I⁻ + I·H₂O⁻) and multiplied by 10⁶. During the field campaign, ~0.3 lpm perfluoropentanoic acid in N₂ was injected into the CIMS (identified as C₅HF₉O₂I⁻) every 1~2 days for mass calibration. The sensitivities of acetic acid, which was generated from a permeation source (permeation rate of 184.5 ng/min at 40°C), was measured periodically on 2/27, 2/28, 3/5, 3/10, 3/12, and 3/14 to track the instrument stability, which was 0.27 ± 0.05 cps/ppt with a variation of 17.7%.

Calibrations of gaseous species were conducted after the campaign under RH conditions (IH₂O⁻ to I⁻ ratio 0.42 ± 0.02) similar to those observed during the field measurement in Delhi (IH₂O⁻ to I⁻ ratio 0.40 ± 0.08), with sensitivities of 7.5, 3.6, 0.013, 13.6, and 0.29 cps/ppt for N₂O₅, ClNO₂, HCl, chloroacetic acid, and acetic acid, respectively. The sensitivity of acetic acid measured post-campaign (0.29 cps/ppt) agreed well with the on-site calibration result (0.27 cps/ppt), and therefore no additional scaling was applied for the on-site sensitivities of the detected species. Sensitivities for Cl₂ (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 (Chen et al., 2025b). The detection limits were determined as three times the standard deviation of the hourly averaged background signals, which were 0.6 ppt for N_2O_5 , 1.6 ppt for ClNO_2 , 0.6 ppt for Cl_2 , 22.6 ppt for NHCl_2 , 0.3 ppt for NCl_3 , 209.1 ppt for HCl , and 2.5 ppt for chloroacetic acid, respectively. 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), the maximum value of the calibrated sensitivities (chloroacetic acid, 13.6 cps/ppt) was used to derive conservative concentration estimates. For particulate compounds, the calibrated sensitivity of levoglucosan (2.2×10^5 ions/ng) was applied to obtain lower-limit estimates, as the detection of levoglucosan has recently been demonstrated to proceed at the collision limit (Aggarwal et al., 2025).

EDXRF. Ambient $\text{PM}_{2.5}$ 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 (Ogrizek et al., 2022; Unga et al., 2025). A total of 83 $\text{PM}_{2.5}$ samples were collected at 3 lpm on polytetrafluoroethylene (PTFE) filters (25 mm in diameter of 0.4 μm) via a $\text{PM}_{2.5}$ 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.

The EDXRF instrument detects the total concentrations of elements in the collected filter samples, while the CIMS detects compounds that evaporate at temperatures up to 200 °C. Persistent signals of $\text{HCl}\cdot\text{I}^-$ were observed from $\text{PM}_{2.5}$ desorption during the CIMS measurement (Fig. S5), likely originating from the thermal decomposition of non-refractory chloride (e.g., NH_4Cl). 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 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.

Supporting measurements. Supporting measurements at IIT Delhi include trace gases O₃ (ECOTECH Serinus 10), NO and NO₂ (ECOTECH Serinus 40), SO₂ (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 $P(\text{NO}_3^\cdot)$ and NO₃[·] reactivity, and the analysis of the CIMS data. Hourly PM_{2.5} concentrations and solar radiation data were obtained from the nearest national monitoring station, the R.K. Puram station operated by Delhi Pollution Control Committee (DPCC), which is located approximately 3 km northwest of IIT Delhi. Intercomparison of the trace gases, T, and RH measured at IIT Delhi and R.K. Puram showed overall good agreement (Fig. S6a). The solar radiation was converted to photolysis frequency (j) of NO₂ (j_{NO_2}) utilizing the method from Trebs et al (Trebs et al., 2009). The estimated j_{NO_2} was then used to derive real-time photolysis frequency of NO₃[·], O₃ and reactive chlorines (Chen et al., 2025b). Additional details about the field observations are shown in Text S1.

Comparison with the measurements in 2019 (Haslett et al., 2023) was used to investigate the evolution of N₂O₅-ClNO₂ chemistry under different chemical regimes (e.g., NO and chloride concentrations) in Delhi. It is noted that throughout the manuscript, “in 2023” and “in 2019” refer to the corresponding field campaigns conducted from 23 February to 14 March in 2023 (this study) and from 11 January to 5 February in 2019 (the previous campaign), respectively.

2.2 Kinetic calculations

N₂O₅-ClNO₂ chemistry. Key kinetic parameters were derived to investigate factors controlling the variations of N₂O₅ and ClNO₂ and compare with previous studies. The field-constrained uptake parameter, defined as the product ($\gamma_{\text{N}_2\text{O}_5} \times f_{\text{ClNO}_2}$) of the N₂O₅ uptake coefficient ($\gamma_{\text{N}_2\text{O}_5}$) and ClNO₂ yield (f_{ClNO_2}), as is shown in Eq. 1, was calculated hourly using neighboring measurements during the nighttime following Eq. 3b in Mielke et al. (Mielke et al., 2013) (Eq. 1), assuming the local heterogeneous uptake of N₂O₅ was the sole source of the measured ClNO₂ and that ClNO₂ experienced negligible nocturnal losses.

$$[\gamma_{\text{N}_2\text{O}_5} \times f_{\text{ClNO}_2}]_{t_0} = \frac{[\text{ClNO}_2]_{t_1}}{\int_{t_0}^{t_1} \frac{1}{4} \bar{c} S_a [\text{N}_2\text{O}_5]_{t_0} dt} \quad (\text{Eq. 1})$$

$$\bar{c} = \sqrt{\frac{8kT}{\pi M}} \quad (\text{Eq. 2})$$

where $\bar{c}$ is the average molecular velocity of N₂O₅, m·s⁻¹; T is temperature in Kelvin; M_w is the molecular weight of N₂O₅, dimensionless; k is Boltzmann’s constant, 1.38×10⁻²³ m²·kg·s⁻²·K⁻¹; S_a is aerosol surface area, m²·m⁻³, which is 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. (Gani et al., 2020) 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 (Meidan et al., 2022; Zhang et al., 2025); t_0 is the current time point, t_1 is the subsequent time point, and dt is the time interval (in seconds) between them.

The theoretical values of the uptake parameter ($\gamma_{N_2O_5} \times f_{ClNO_2}$) range from 0 to 0.1, as the maximum values of $\gamma_{N_2O_5}$ and f_{ClNO_2} are generally below 0.1 and 1, respectively (Tham et al., 2018). However, nocturnal transport, i.e., changes in air masses, can invalidate this method and yield values exceeding 0.1 (sharp increases in ClNO₂, occurrence frequency of ~17%) which were discussed separately (Section 3.2).

The production rate ($P(NO_3)$) and reactivity ($R(NO_3)$) of NO₃· were calculated to evaluate N₂O₅ budgets, which are shown in Eq. 2 and Eq. 3, respectively. The ClNO₂ production efficiency ($\varepsilon(ClNO_2)$, Eq. 4), indicating the fraction of the total generated NO₃· overnight that is ultimately transformed into ClNO₂, was calculated for comparison with previous studies (Eger et al., 2019; Xia et al., 2025). The integration period was set from 20:00 to 04:00 to minimize influences of potential air mass mixing during the day-night and night-day transition periods.

$$P(NO_3) = k_{NO_2+O_3}[NO_2][O_3] \quad (\text{Eq. 2})$$

$$R(NO_3) = k_{NO+NO_3}[NO] + j_{NO_3} + k_{hete}[NO_2]K_{eq} + \sum k_i[VOC_i] \quad (\text{Eq. 3})$$

$$k_{hete} = \frac{\bar{c}\gamma_{N_2O_5}S_a}{4} \quad (\text{Eq. 4})$$

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

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

$$\varepsilon(ClNO_2) = \frac{[ClNO_2]_{max}}{\int_{20:00}^{04:00} P(NO_3)} \quad (\text{Eq. 6})$$

where $k_{NO_2+O_3} = 1.2 \times 10^{-13} \times \exp(-2450/T) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ and $k_{NO+NO_3} = 1.8 \times 10^{-11} \times \exp(110/T) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (Burkholder et al., 2020); j_{NO_3} is the photolysis frequency of NO₃· and is retrieved from the Tropospheric Ultraviolet and Visible (TUV) radiation model and scaled with the field constrained j as discussed previously; k_{hete} is the first-order heterogenous loss rate coefficient of N₂O₅. $\gamma_{N_2O_5}$ was parametrized using Eq. 5 according to the experimental measurements of N₂O₅ uptake on aqueous organic aerosols (Evans and Jacob, 2005; Thornton et al., 2003). This parameterization method was supported by the consistency between the simulated nocturnal ClNO₂ variations using the RH-parameterized $\gamma_{N_2O_5}$ and the observed ClNO₂ levels, as detailed in Text S2; K_{eq} is the equilibrium constant between NO₃·, NO₂, and N₂O₅, where $K_{eq} = 5.5 \times 10^{-27} \times \exp(10724/T)$ (Wängberg et al., 1997). $\sum k_i[VOC_i]$ is the sum of NO₃· reactivity

with different VOCs and we applied the same value of 0.081 s^{-1} in 2023 as in 2019 (Haslett et al., 2023) due to the lack of concurrent VOCs measurements in 2023. As shown in Fig. S7a and Table S2, the campaign-averaged $\text{NO}_3\cdot$ reactivity to NO in 2023 is $\sim 15.6 \text{ s}^{-1}$, which is approximately 2 orders of magnitude higher than the reactivity to VOCs and the heterogenous loss of $\text{NO}_3\cdot$ from N_2O_5 uptake (0.091 s^{-1}). Previous studies (Meidan et al., 2022; Wang et al., 2020) 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 $\text{NO}_3\cdot$ reactivity.

Production rates of $\text{Cl}\cdot$ and $\text{OH}\cdot$ radicals. The $\text{Cl}\cdot$ production rate ($P(\text{Cl}\cdot)$) is calculated according to Eq. 5. For the 2023 campaign, we calculated $P(\text{Cl}\cdot)$ both from ClNO_2 photolysis and from all the detected photolabile reactive chlorines. A direct comparison between 2019 and 2023 was conducted using $P(\text{Cl}\cdot)$ from ClNO_2 photolysis. In 2019, only ClNO_2 photolysis was considered as a source of $\text{Cl}\cdot$, since mixing ratios of other reactive chlorines were not reported in the previous study (Haslett et al., 2023). Additionally, we estimated a lower-limit $\text{OH}\cdot$ production rate ($P(\text{OH}\cdot)$) in Delhi from the photolysis of O_3 in the presence of water vapor (Eq. 6) (Dunlea and Ravishankara, 2004).

$$P(\text{Cl}) = j_{\text{ClNO}_2}[\text{ClNO}_2] + 2 \times j_{\text{Cl}_2}[\text{Cl}_2] + j_{\text{NCl}_3}[\text{NCl}_3] + j_{\text{NHCl}_2}[\text{NHCl}_2] \quad (\text{Eq. 5})$$

$$P(\text{OH}) = \frac{2 \times j_{\text{O}^1\text{D}}[\text{O}_3] + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]}{k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{N}_2}[\text{N}_2] + k_{\text{O}_2}[\text{O}_2]} \quad (\text{Eq. 6})$$

where $j_{\text{O}^1\text{D}}$ is the photolysis frequency of O_3 , $k_{\text{H}_2\text{O}} = 1.6 \times 10^{-10} \times \exp(60/T)$, $k_{\text{N}_2} = 2.2 \times 10^{-11} \times \exp(110/T)$, and $k_{\text{O}_2} = 3.3 \times 10^{-11} \times \exp(55/T)$ (Burkholder et al., 2020).

3 RESULTS AND DISCUSSION

3.1 Characteristics of N_2O_5 and ClNO_2 variations

We observed pronounced nocturnal enrichment of N_2O_5 and ClNO_2 in 2023 (Fig. 1a, b). N_2O_5 and ClNO_2 up to 566 and 1340 ppt were measured during the nighttime, with mixing ratios frequently exceeding 10 and 100 ppt, respectively (Fig. S8). Overall, the nighttime N_2O_5 and ClNO_2 mixing ratios in 2023, with an average of 13.1 ppt and 80.1 ppt, respectively, are significantly (Mann-Whitney test, $p < 0.01$) higher than those measured in 2019 (4.5 and 36.3 ppt, respectively) (Fig. 1a, b).

As shown in Table S3, the maximum N_2O_5 mixing ratio in Delhi is a third to half of those observed in urban areas of the United States (Thornton et al., 2010; Osthoff et al., 2008) and England (Bannan et al., 2015), and approximately an order of magnitude lower than those measured in aged air plumes from industrial regions in China (Chen et al., 2023; Wang et al., 2016; Ye et al., 2021). By contrast, the peak ClNO_2 level in Delhi is much higher than those reported in urban regions of the North America (Thornton et al., 2010; McNamara et al., 2020; Wang et al., 2023a) and Europe (Bannan et al., 2015; Phillips et al., 2012; Priestley et al., 2018), and similar to or 1~2 times lower than those observed in the North China Plain (Tham et al., 2016; Xia et al., 2021; Peng et al., 2021; Chen et al., 2025a). The observed pattern of low N_2O_5 and high ClNO_2 indicates efficient conversion of N_2O_5 to ClNO_2 in

283 Delhi.

284 We further examined N_2O_5 and ClNO_2 variations every night and classified them into the
285 enhanced and non-enhanced cases (Fig. S9 and Fig. S10). Among the enhanced cases, elevated N_2O_5
286 mixing ratios exceeding 10 ppt were characterized by both relatively low NO (median 3 ppb) and
287 particulate Cl (median $0.7 \mu\text{g}/\text{m}^3$) concentrations, and appreciable ClNO_2 levels larger than 100 ppt
288 were observed under moderate NO (median 7 ppb) and high particulate Cl (median $3.3 \mu\text{g}/\text{m}^3$)
289 conditions (Fig. S9). No notable N_2O_5 or ClNO_2 mixing ratios were measured among the non-enhanced
290 cases when NO levels were relatively high (median 31 ppb) (Fig. S10). The occurrence frequency of
291 the enhanced cases (11 out of total 19 nights) is higher than the non-enhanced (8 nights) cases.

292 The measured N_2O_5 generally presents transient, spike-like patterns in 2023 (Fig. S8), peaking
293 around the early evening (18:00~20:00) when both NO and particulate Cl are relatively low, and
294 tapering off as the night proceeds (Fig. 1a, c-d). In comparison, the ClNO_2 mixing ratio gradually built
295 up after midnight with the increase of particulate Cl, reaching the highest level during the early
296 morning hours (06:00~08:00, Fig. 1b, d). Overall, the nocturnal N_2O_5 mixing ratio shows a significant
297 negative dependency ($r = -0.64$, $p < 0.01$) on the NO concentration (Fig. 2a), and high ClNO_2 levels
298 were accompanied by abundant chloride (Fig. S11a), indicating the critical roles of NO and chloride
299 in controlling N_2O_5 and ClNO_2 formation in Delhi.

300 The nocturnal mean ClNO_2 production efficiency ($\epsilon(\text{ClNO}_2)$) also increases from 3.0% in 2019
301 to 4.3% in 2023, which is comparable to the values reported in marine and coastal areas (Eger et al.,
302 2019; Xia et al., 2025). In addition, the diurnal profile of N_2O_5 in 2023 was inverted compared to 2019,
303 with higher levels in the early evening rather than during the daytime (Fig. 1a). Consistently, distinct
304 diurnal variations of N_2O_5 were also observed under relatively low- and high-NO conditions in 2023
305 (Fig. S12). The emerging early evening peak of N_2O_5 leads to a new N_2O_5 -driven ClNO_2 enhancement
306 pattern in 2023 (the dashed linear fitting line in Fig. 1e), characterized by a strong positive correlation
307 ($r = 0.93$) between N_2O_5 and ClNO_2 under conditions of elevated N_2O_5 (10~400 ppt) and limited
308 chloride ($0.1\sim 3.4 \mu\text{g}/\text{m}^3$). This pattern resembles those observed in other continental air masses
309 (Thornton et al., 2010; Bannan et al., 2015; Zhou et al., 2018), while the ClNO_2 to N_2O_5 ratios are
310 slightly higher in Delhi, ranging from 0.3 to 3.2, with an average of 1.2. Notably, despite the substantial
311 decline in particulate Cl from 2019 ($20.8 \mu\text{g}/\text{m}^3$) to 2023 ($4.7 \mu\text{g}/\text{m}^3$), the higher ClNO_2 levels in 2023
312 indicate that the promoting effect of elevated N_2O_5 potentially outcompetes the limiting impact of
313 reduced chloride. Additionally, the estimated ClNO_2 yield is around unity in Delhi (Fig. S13a).

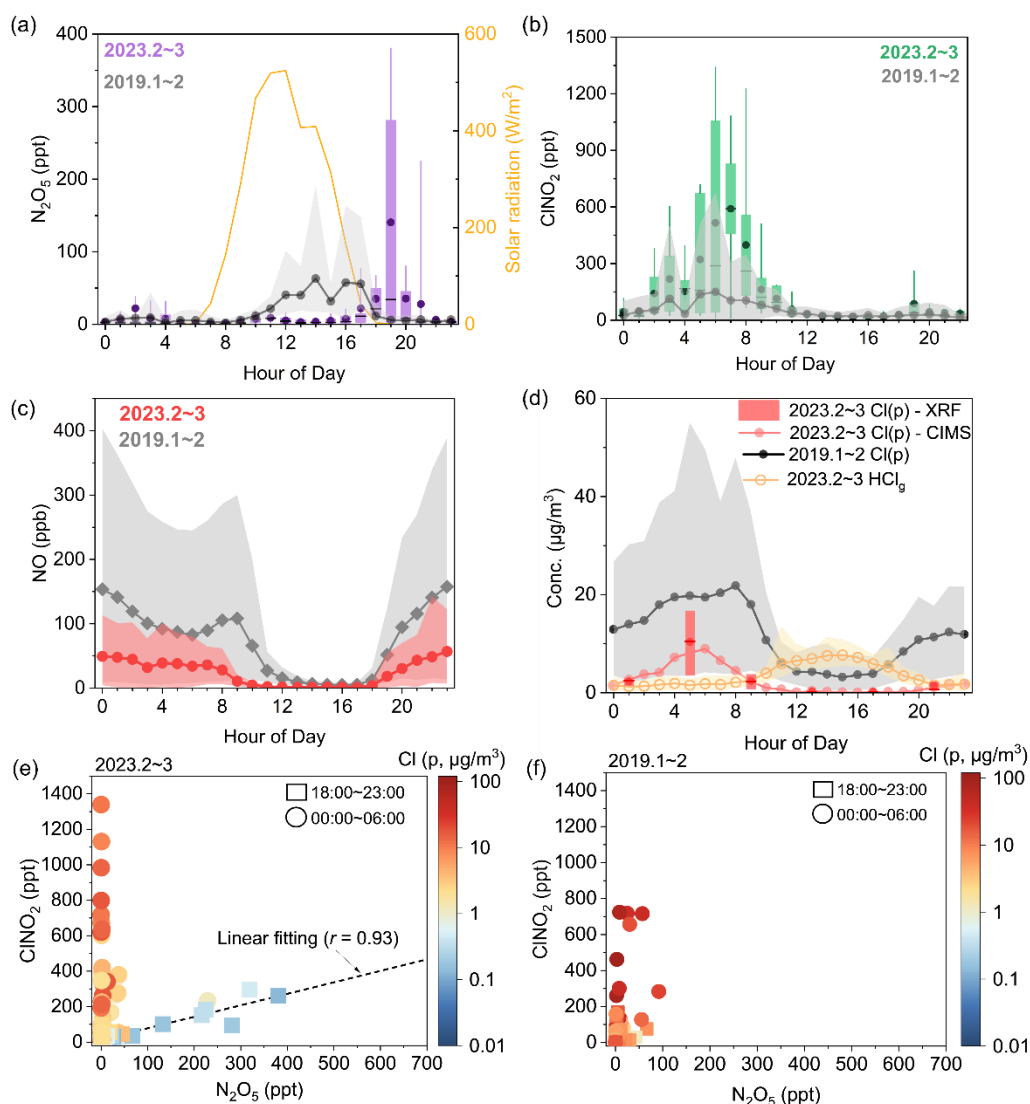


Fig. 1 Field characterization of N_2O_5 and ClNO_2 in Delhi. Campaign-averaged diurnal variations of (a) N_2O_5 , (b) ClNO_2 , (c) NO , and (d) particulate Cl and gaseous HCl . Scatter plots of N_2O_5 versus ClNO_2 mixing ratios in (e) 2023 and (f) 2019, color-coded by the particulate Cl concentrations. The observation (Haslett et al., 2023) in 2019 is included for comparison, where the gaseous HCl measurements are not available. The right axis in (a) indicates solar radiation during the campaign in 2023. The exact sunrise (07:07~07:15) time in 2019 is about 30 min later than that in 2023 (06:55~06:32), while the sunset time in 2019 (17:24~18:03) is about 30 min earlier according to the records from timeanddate website. Gaseous HCl and particulate Cl measured by CIMS are also shown in (d). The upper and lower edge of the box and whisker in (a), (b) and (d) represent the 25th and 75th, and 10th and 90th percentiles, respectively. The dots and squares denote mean values and the lines inside the boxes indicate median levels. The shaded area in (a)-(d) indicates the 10th and 90th percentile range.

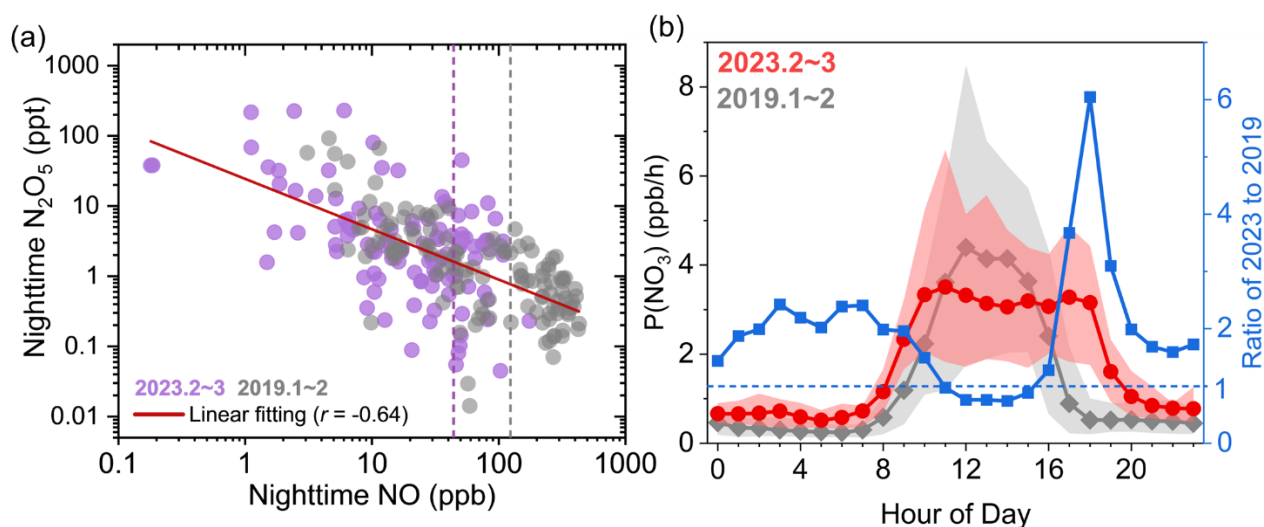
3.2 Influencing factors of N₂O₅-ClNO₂ chemistry

Lower NO concentrations in 2023 relative to 2019 reduce NO₃[•] losses to reactions with NO, resulting in elevated nocturnal N₂O₅ levels. The reaction with NO dominated NO₃[•] losses both in 2019 and 2023 (~99%, Table S2 and Fig. S7a), contributing to the low abundances and short-lived occurrences of N₂O₅ in Delhi (Haslett et al., 2023). The strong anti-correlation between nocturnal N₂O₅ and NO persists in 2023, where the N₂O₅ mixing ratios overlap with those in 2019 when NO concentrations are within the same range (approximately 2–100 ppb) (Fig. 2a). However, in 2023, the frequency of relatively low-NO conditions (<2 ppb) rose from 0 to 8% and extreme NO levels (>100 ppb) nearly disappeared, indicating that NO titration in suppressing N₂O₅ production has diminished (Fig. 2a). With the decline in NO concentrations from 2019 (nighttime averages 124 ± 25 ppb) to 2023 (44 ± 9 ppb) (Fig. 1c), the nighttime NO₃[•] reactivity towards NO dropped by ~66% from 83.7 s⁻¹ to 28.4 s⁻¹, extending NO₃[•] lifetimes approximately two folds during the nighttime in 2023 (0.04 s). The reduced NO₃[•] losses to NO increased the availability of NO₃[•] for reacting with NO₂, thereby enhancing N₂O₅ production. Additionally, no significant correlation between chloride and ClNO₂ was observed in 2019, likely because the chloride increases were accompanied by a substantial elevation in NO, which suppressed N₂O₅ formation (Fig. S11b).

Higher NO₃[•] production rates (P(NO₃)) enhance N₂O₅ formation. Due to the increases in nocturnal O₃ levels (from 3.5 to 6.8 ppb) and the reaction rate constant between NO₂ and O₃ (from 2.36 × 10⁻¹⁷ to 2.93 × 10⁻¹⁷ cm³·molec⁻¹·s⁻¹), the average nocturnal P(NO₃) in 2023 almost doubled (0.75 ppb h⁻¹) compared to 2019 (0.41 ppb h⁻¹) (Fig. 2b). The observed (P(NO₃)) in Delhi 2023 exceeds those reported in the United States (Wang et al., 2023b; Noxon et al., 1980) and Europe (Ljungström and Hallquist, 1996; Wang et al., 2023b), and 1~2 times lower than those observed in China (Wang et al., 2024; Yan et al., 2021; Chen et al., 2023). Consistently, N₂O₅ mixing ratios in 2023 peak after sunset around 18:00~19:00 (Fig. 1a), coinciding with the period of elevated P(NO₃) (Fig. 2b) and relatively low NO levels (Fig. 1c). Other factors, such as the decreased aerosol surface area (2637 ± 152 and 1411 ± 162 μm²/cm³ in 2019 and 2023, respectively) results in reduced first-order heterogeneous loss rate coefficient of N₂O₅ (k_{hete}) from 0.74 ± 0.09 s⁻¹ in 2019 to 0.14 ± 0.02 s⁻¹ in 2023, which also contributes to the elevated nocturnal N₂O₅ mixing ratios observed in 2023. Overall, the enhanced NO₃[•] production and reduced losses to NO led to elevated NO₃[•] and N₂O₅ levels in 2023, aligning with the higher estimated steady-state NO₃[•] mixing ratios (0.25 ppt vs. 0.03 ppt in 2019) (Fig. S7b).

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 (Beig, 2010, 2018; Sahu et al., 2023). 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 O₃ concentrations were observed in spring compared to winter, which facilitates the

363 removal and decrease of NO and P(NO₃). Overall, the seasonal variability in NO concentrations is the
 364 main driver of the differences in NO and P(NO₃) observed between the two campaigns.



365
 366 **Fig. 2 Factors contributing to nocturnal N₂O₅ enhancement.** (a) Scatter plot of nighttime NO versus
 367 N₂O₅. Nighttime is defined as the period from 20:00 to 04:00, excluding the transition period between
 368 day and night when the air mass was unstable. The purple and grey dashed lines indicate the average
 369 NO concentrations during the 2023 and 2019 campaign, respectively. (b) Campaign-averaged diurnal
 370 variations of P(NO₃) in 2023 and 2019, respectively. The right axis in (b) displays the 2023-to-2019
 371 ratio of P(NO₃). The dots and squares denote mean values and the shaded area indicates the 10th and
 372 90th percentile range.

373 High chloride concentrations promote N₂O₅ uptake and ClNO₂ production in Delhi. The field-
 374 derived uptake parameter ($\gamma \times f$) in Delhi is similar with those observed in marine air (~0.02 on
 375 average)¹¹ and several times to an order of magnitude higher than those reported in other continental
 376 regions ($6 \times 10^{-4} \sim 8 \times 10^{-3}$) (Xia et al., 2021; Tham et al., 2018; Xia et al., 2020; Mielke et al., 2013). As
 377 is shown in Fig. 3a, this parameter increases with the chloride level in Delhi, reflecting the combined
 378 effects of chloride in promoting N₂O₅ uptake and ClNO₂ yield observed in prior laboratory studies
 379 (Bertram and Thornton, 2009; Jahl et al., 2021). By contrast, despite comparable high chloride was
 380 observed in Wangdu (Xia et al., 2021) (upper triangle in Fig. 3b), both the uptake parameter ($\sim 6 \times 10^{-4}$
 381 on average) and the nocturnal ClNO₂ level (typically <50 ppt) are significantly lower than those
 382 measured in Delhi. This is likely due to the lower ambient water content (~0.4%) compared to Delhi
 383 (~1.5%), which limits aerosol liquid water content and thereby suppresses N₂O₅ hydrolysis on particles
 384 (Xia et al., 2021; Tham et al., 2018).

385 The high chloride in Delhi is largely in the form of semi-volatile NH₄Cl, originating from gas to
 386 particle partitioning. We observed a concurrent late-evening enrichment of non-refractory chloride
 387 measured by CIMS and Cl element measured by XRF (Fig. 1d), indicating the semi-volatile nature of

particulate Cl (i.e., NH_4Cl) in Delhi. Additionally, direct measurements of both HCl and particulate Cl enabled us to examine the gas–particle partitioning behavior of Cl. As shown in Fig. 3b, the 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 (Acharja et al., 2023; Gunthe et al., 2021). A recent study suggests that increasing RH promotes the migration of chloride from the particle bulk phase to the gas-particle interface (Fauré et al., 2024). This phenomenon helps explain the observed post-midnight accumulation of ClNO_2 and consistently low N_2O_5 levels in Delhi, which are attributed to enhanced heterogeneous conversion of N_2O_5 to ClNO_2 on aerosol surfaces. The observed thermodynamically-driven partitioning behavior of Cl agrees with previous model simulations (Gunthe et al., 2021; Chen et al., 2022b).

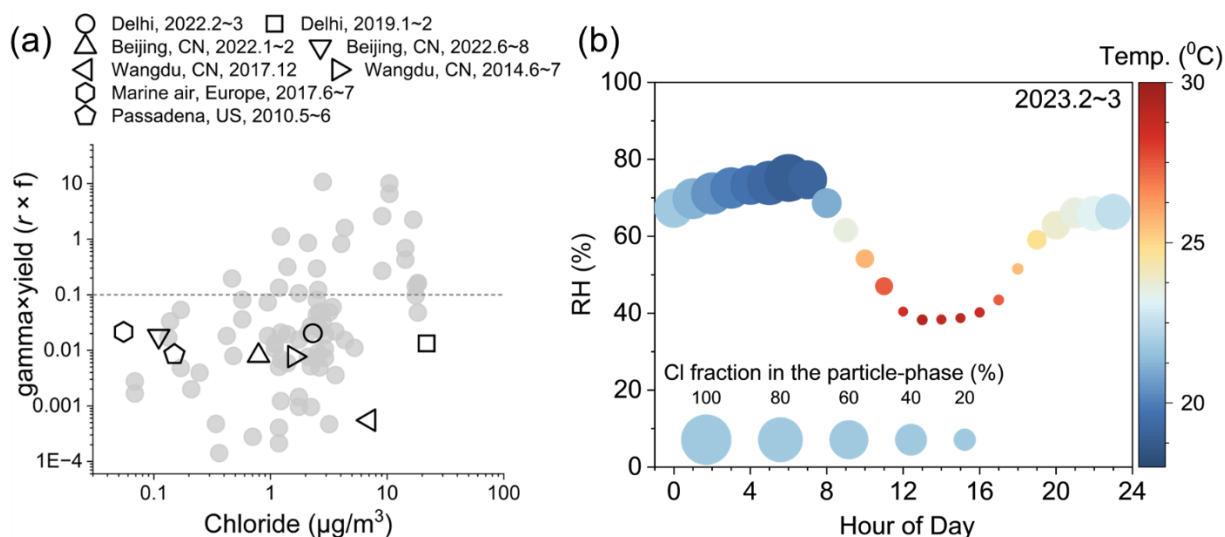


Fig. 3 Factors contributing to nocturnal ClNO_2 enhancement in Delhi. (a) Dependence of the field-observed uptake parameter ($\gamma \times f$) on particulate Cl concentrations in 2023. The campaign-average value for 2023 (excluding unusually high values of $\gamma \times f > 0.1$) is shown as an open circle. The values derived from previous observations in Delhi 2019 (Haslett et al., 2023), Beijing (Chen et al., 2025b), Wangdu (Xia et al., 2021; Tham et al., 2018), Pasadena (Mielke et al., 2013), and marine air in Europe (Eger et al., 2019) are shown as different markers. The reference line of $\gamma \times f$ equals to 0.1 is also plotted. (b) Campaign-averaged diurnal variation of RH in 2023, color-coded by ambient temperature. The size of the datapoints is proportional to the observed Cl fraction in the particle-phase, which is calculated as $\text{Cl}_p/(\text{Cl}_p + \text{HCl}_g)$.

ClNO_2 levels in Delhi were influenced by the transport of ClNO_2 -laden biomass burning plumes from upwind regions, and vertical intrusion initiated by the breakup of the residual layer during the early morning (6:00~8:00). We observed some cases with unusually high $\gamma \times f$ values exceeding 0.1, implying additional ClNO_2 sources beyond the local N_2O_5 uptake. Most of the high values were found

during episodes of easterly ($50\sim130^\circ$) winds with elevated particulate Cl concentrations (Fig. 4a), when the air masses passed over biomass-burning hotspots (Fig. S15). This suggests substantial ClNO₂ production on high chloride containing biomass burning aerosols, as observed in previous laboratory experiments (Ahern et al., 2018; Jahl et al., 2021). A typical case is shown in Fig. S16, where ClNO₂ abruptly increases concurrently with the sharp rise in particulate Cl, biomass-burning tracers (K and HCN), and easterly wind speeds. Additionally, a continued rise in ClNO₂ was observed after sunrise (6:00~8:00; Fig. 1b and Fig. S16), likely due to the downward mixing of ClNO₂-rich air masses aloft, as reported in other locations (Tham et al., 2016; Haslett et al., 2023).

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. The nighttime Cl strongly correlates with K ($r = 0.82$) and HCN ($r = 0.73$) (Fig. 4b-c and Fig. S17), indicating significant Cl emissions from biomass burning in Delhi. The ambient nighttime Cl to K ratio (1.6 ± 0.8) in Delhi is about three-fold higher (0.4 ± 0.2) than those measured from biomass/biofuel emission sources (Table S4), indicating additional sources of Cl potentially from plastic-contained garbage burning, industrial processes, and coal combustion (Gunthe et al., 2021). Consistently, we observed a moderate correlation between Cl and the coal combustion tracer SO₂ ($r = 0.51$). In contrast, the poor correlation of Cl with NO ($r = -0.30$) and CO ($r = -0.08$) indicated limited contributions from vehicle exhaust, consistent with their low Cl emission factors (Table S4).

Since the above discussions are built on two short-term campaigns, we further assess the prevalence of N₂O₅ and ClNO₂ production in Delhi based on the long-term distributions of the identified influencing factors, i.e., NO, P(NO₃), and chloride (Fig. S2). The occurrence distribution of nighttime NO and P(NO₃) during the 2023 campaign largely overlapped with the conditions commonly occurred in Delhi (Fig. S2a-b), indicating comparable N₂O₅ production potential throughout the years in Delhi. In addition, the occurrence frequency distribution of chloride in 2023 campaign is comparable to that observed from January to April of 2022 and much higher than those reported from May to September (Fig. S2c). The seasonal variation of chloride reflects the temperature-driven evaporation of semi-volatile NH₄Cl as discussed previously. Given the critical role of chloride in promoting N₂O₅ uptake and driving ClNO₂ production in Delhi, these results suggest that elevated nighttime N₂O₅ and ClNO₂ levels are most likely observed during the warm and cold seasons, respectively, in Delhi.

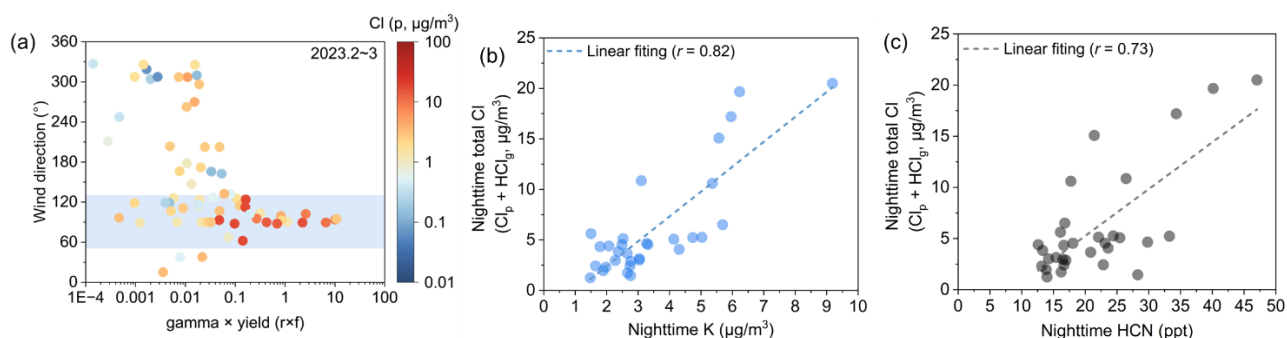


Fig. 4 Potential sources of chlorine in Delhi. (a) Scatter plot of uptake parameter ($\gamma \times f$) and wind direction color-coded by particulate Cl concentrations. The shaded area in (a) indicates the region with wind direction ranging from 50° to 130° . Correlation of nocturnal total Cl (sum of Cl_p and HCl_g) with (b) particulate K and (c) gaseous HCN. The reported HCN mixing ratio can be considered a lower-limit estimate (see Methods 2.1).

3.3 Impacts on atmospheric radical production and VOCs oxidation

Enhanced N_2O_5 - ClNO_2 chemistry at lower NO levels emphasizes the important roles of $\text{Cl}\cdot$ and $\text{NO}_3\cdot$ in initiating the oxidation of VOCs in Delhi. The average daytime $\text{P}(\text{Cl}\cdot)$ (Eq. 5) from ClNO_2 photolysis in 2023 (0.035 ppb/h) is about approximately twice that observed in 2019 (0.015 ppb/h). The maximum daytime-averaged $\text{P}(\text{Cl}\cdot)$ (0.24 ppb/h) from the photolysis of all the detected $\text{Cl}\cdot$ precursors (Cl_2 , ClNO_2 , NHCl_2 , and NCl_3) is up to an order of magnitude higher than values reported for the urban inland areas of Europe and North America (0.02~0.07 ppb/h) (Priestley et al., 2018; McNamara et al., 2020; Faxon et al., 2015), and remains several times lower than those observed during the pollution episodes in China (0.5~1.1 ppb/h) (Chen et al., 2023; Tham et al., 2016; Liu et al., 2017). ClNO_2 photolysis dominates the production of $\text{Cl}\cdot$ around the sunrise hours (7:00~8:00) when the $\text{P}(\text{Cl}\cdot)_{\text{total}}$ to $\text{P}(\text{OH})$ ratio (42 on average) was also the highest (Fig. 5a), suggesting non-negligible Cl -initiated oxidation of VOCs under these conditions in Delhi.

Consistently, we observed specific gaseous organic oxidation products indicative of the prevalence of chlorine chemistry (Fig. 5b). We identified organochlorinated species, i.e., $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ and $\text{C}_3\text{H}_5\text{O}_2\text{Cl}$ (presumably chloroacetic acid and chloropropionic acid), which were previously measured in chamber experiments from $\text{Cl}\cdot$ reacting with ethylbenzene (Jahn et al., 2024) and isoprene (Wang et al., 2022) and used as markers for the occurrence of chlorine chemistry in field studies (Priestley et al., 2018; Li et al., 2025). The daytime concentration fraction of $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ in the total measured gaseous organics increases from ~0.9% in 2019 to ~1.8% in 2023. Additionally, the daytime average peak mixing ratio of $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ (~100 ppt) in 2023 is about 5~30 times higher than those measured in Hong Kong (12~20 ppt) (Li et al., 2025) and Manchester (~3 ppt) (Priestley et al., 2018), indicating significant $\text{C}_2\text{H}_3\text{ClO}_2$ production in Delhi. We also identified a series of hydroxynitrates (HN) homologues, i.e., $\text{C}_8\text{H}_{17}\text{O}_4\text{N}$, $\text{C}_{10}\text{H}_{21}\text{O}_4\text{N}$, and $\text{C}_{12}\text{H}_{25}\text{O}_4\text{N}$, which were potentially early-generation products from the chlorine-initiated oxidation of $\text{C}_{8,10,12}$ -alkanes under high NO_x conditions

474 (Wang and Hildebrandt Ruiz, 2018). Here their sharp increase in the early morning hours (7:00~8:00)
475 when $\text{Cl}\cdot$ was likely the dominant atmospheric oxidant (Fig. 5a-b), together with the positive
476 correlations between these HN and the product of $\text{P}(\text{Cl})$ and NO ($r_{7:00\sim 8:00} = 0.59$, Fig. 5e), underscores
477 the $\text{Cl}\cdot$ initiated alkane oxidation in the presence of NO as an important source of HN in Delhi. It is
478 noted that these HN can also be formed via OH-initiated oxidation processes (Lim and Ziemann, 2009),
479 but would then likely peak later in the day when OH concentrations are higher. Here, a quantitative
480 comparison between the $\text{Cl}\cdot$ - and OH-initiated reaction pathways is missing in current study due to the
481 lack of VOCs precursor measurements and warrants further investigation.

482 The NO_3 -initiated nocturnal oxidation of VOCs was strengthened during the 2023 campaign. The
483 fraction of nitrogen-containing organics (CHON) in the total measured gaseous oxygenated organic
484 compounds in 2023 (~46%) was similar to that observed in 2019 (42%). However, the diurnal pattern
485 of the CHON fraction was inversed, exhibiting a moderate increase (~9%) during the nighttime (Fig.
486 5c), which resembles those found in other locations (Ye et al., 2021; Huang et al., 2019), indicating
487 enhanced nocturnal NO_3 -driven organic oxidation in 2023. We further identified the nighttime gaseous
488 organic species with the criteria of average nighttime (20:00~04:00) to daytime (7:00~16:00) mixing
489 ratio larger than 1. Most of the nighttime species are nitrogen-containing compounds, primarily
490 including $\text{C}_{4,5,6}\text{H}_{3,5,7}\text{O}_5\text{N}$ and $\text{C}_{10}\text{H}_{17}\text{O}_{4,5}\text{N}$ (Fig. 5f), which are typical first-generation oxidation
491 products from NO_3 -induced oxidation of heterocyclics (i.e., furan, methylfuran, and dimethylfuran)
492 (Chen et al., 2022a; Joo et al., 2019; Jiang et al., 2020) and monoterpenes (Jenks et al., 2023; Ayres et
493 al., 2015), respectively. These oxidation products exhibited strong intra-group correlations ($r_{20:00\sim 4:00}$
494 = 0.71 to 0.77), whereas the correlations between the $\text{C}_{4,5,6}\text{H}_{3,5,7}\text{O}_5\text{N}$ and $\text{C}_{10}\text{H}_{17}\text{O}_{4,5}\text{N}$ groups were
495 weak ($r_{20:00\sim 04:00} < 0.2$), confirming their production from distinct precursors. Moreover, their low
496 correlations with CO and NO ($r_{20:00\sim 4:00} < 0.4$) largely exclude direct combustion emissions as the
497 dominant source. Notably, observations of furan-derived $\text{NO}_3\cdot$ oxidation products have currently been
498 limited to laboratory studies (Chen et al., 2022a; Joo et al., 2019; Jiang et al., 2020). Our findings offer
499 direct field evidence of NO_3 -initiated furan oxidation in the atmosphere.

500 Another prominent nighttime compound potentially associated with $\text{NO}_3\cdot$ induced oxidation is
501 $\text{C}_5\text{H}_{11}\text{NO}_5$ (Fig. 5f), which exhibited the largest nocturnal enhancement among all the observed species,
502 increasing by a factor of 3.6. $\text{C}_5\text{H}_{11}\text{NO}_5$ correlates well with $\text{C}_{10}\text{H}_{17}\text{O}_5\text{N}$ ($r_{20:00\sim 4:00} = 0.71$) and shows
503 a marked increase between 18:00 and 19:00 (Fig. 5d), coinciding with the peak of the estimated
504 $\text{NO}_3\cdot$ levels (~2.3 ppt) (Fig. S7b). It is thus likely a co-product from the reaction of $\text{NO}_3\cdot$ with
505 monoterpenes. However, this compound has not been reported from any NO_3 -initiated oxidation
506 processes (Jenks et al., 2023; Ayres et al., 2015; Xu et al., 2025). Further investigation is required to
507 elucidate the formation mechanisms of $\text{C}_5\text{H}_{11}\text{NO}_5$ in Delhi's atmosphere.

508 In addition to the specific organic products discussed above, the overall oxidation state of the
509 measured organic aerosols (OA) is elevated in 2023 compared to 2019. The bulk oxygen-to-carbon

(O/C) ratio of OA (0.76 on average) was higher than the value (0.66) reported in the 2019 campaign (Huang et al., 2024), indicating an increased contribution from more oxidized or aged secondary organic aerosols (SOA) (Jimenez et al., 2009). A clear negative dependence of the O/C ratio on NO was observed at night when NO exceeded about 10 ppb (Fig. S18), agreeing with the suppression effect of NO on organic oxidation by increasing the competitive $\text{RO}_2 + \text{NO}$ channel under the radical-limited regime commonly found in Delhi (Nelson et al., 2021; Kenagy et al., 2024). Taken together, the characteristics of the bulk organics provide additional field evidence for the enhanced atmospheric organics oxidation in 2023.

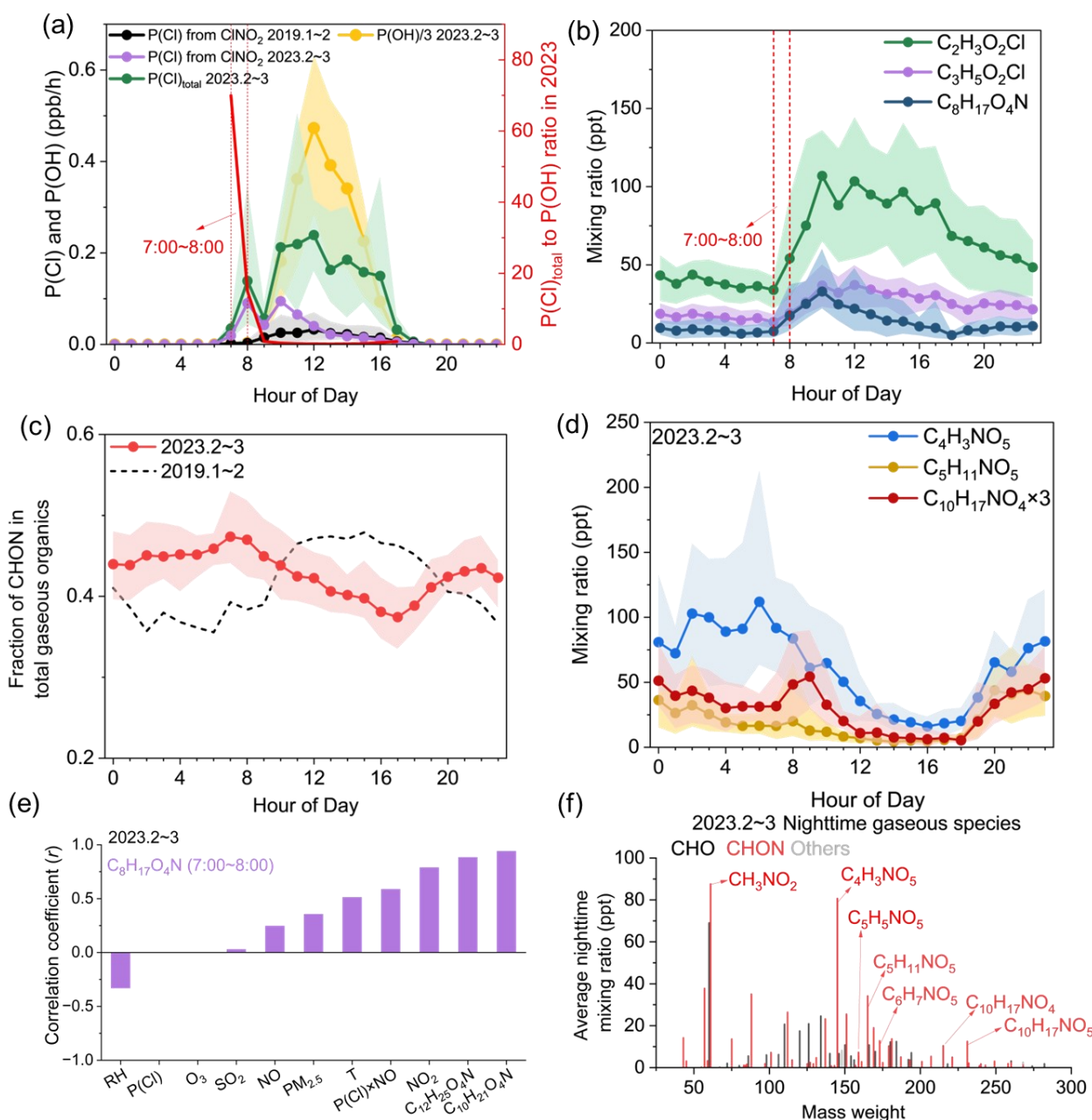


Fig. 5 Enhanced daytime $\text{Cl}\cdot$ and nocturnal $\text{NO}_3\cdot$ initiated oxidation of organics in Delhi. (a) P(Cl) in 2023 and 2019, and P(OH) from the photolysis of O_3 in 2023. The P(Cl)_{total} 2023 includes

Cl $\cdot$ production from the sum of ClNO $_2$, Cl $_2$, NHCl $_2$, and NCl $_3$ photolysis. The P(Cl) $_{\text{total}}$ to P(OH) ratio in 2023 is shown in the right axis. The value of P(OH) is divided by a factor of 3 to place it on the same scale as P(Cl). Average diurnal variations of tracer compounds indicating (b) Cl $\cdot$ and (d) NO $_3\cdot$ initiated oxidation, respectively. (c) Comparison of the diurnal variations of CHON compounds fraction in total detected gaseous organics in 2019 and 2023. (e) Correlation coefficients, using observations between 7:00 and 8:00 of C $_8$ H $_{17}$ NO $_4$ with P(Cl) $_{\text{total}}$, meteorological parameters, trace gases, and related homologue species. (f) Molecular composition and average nighttime mixing ratios for the nighttime gaseous species. The shaded area in (a-d) indicates the 10th and 90th percentiles and the dots denote mean values.

4 Conclusions

This study characterized N $_2$ O $_5$ -ClNO $_2$ chemistry in Delhi (Fig. 6). We observed a clear dependency on available nocturnal NO that high NO suppresses N $_2$ O $_5$ production and reduces the formation of ClNO $_2$ while decreased NO promotes nocturnal N $_2$ O $_5$ -ClNO $_2$ chemistry. The former pattern is consistent with the previously reported significant NO suppression in 2019 (Haslett et al., 2023). With moderate NO in 2023, substantial ClNO $_2$ is produced after midnight hours in Delhi, which is driven by the elevated RH and chloride levels that promote efficient conversion of N $_2$ O $_5$ to ClNO $_2$. The abundance of chloride strongly correlates with the biomass burning tracers, indicating emissions from biomass burning as an important source of Cl in Delhi. The increased ClNO $_2$ levels at lower nocturnal NO conditions implies that the atmospheric oxidation of organics is amplified both during the nighttime (via NO $_3\cdot$ pathways) and daytime (via Cl $\cdot$ pathways) in Delhi.

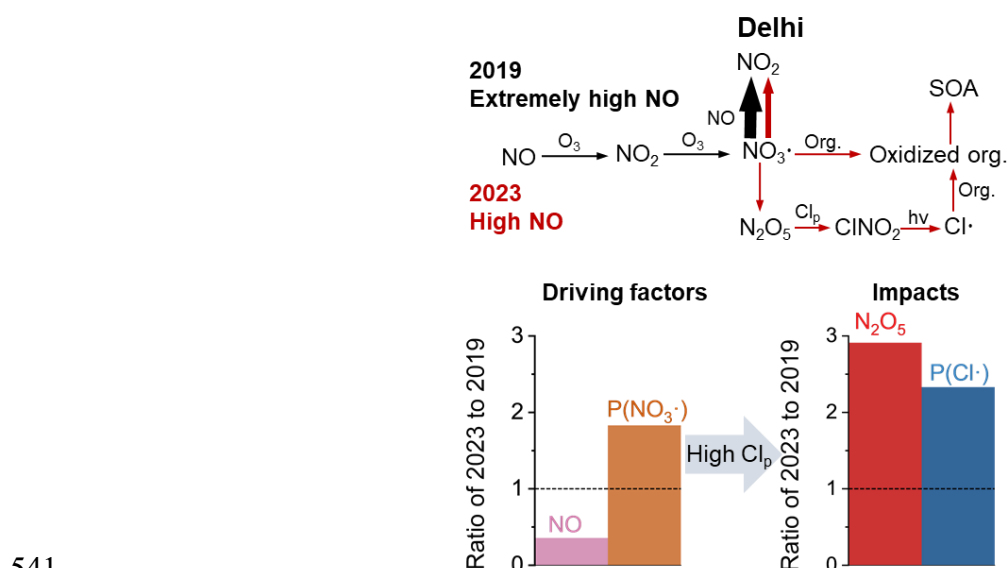


Fig. 6 Amplified N $_2$ O $_5$ and ClNO $_2$ production and impacts on secondary organic aerosol formation in Delhi. A schematic comparing N $_2$ O $_5$ -ClNO $_2$ chemistry between the 2019 and 2023 campaigns. Red arrows indicate reactions that are largely enhanced during the 2023 campaign.

The differing behaviors of N_2O_5 and ClNO_2 depending on the levels of nocturnal NO emphasize the need of continuous monitoring of air pollutants in Delhi, which is essential to understand the evolution of emission sources and atmospheric chemical processes. The complexity of the air pollution situation in Delhi has been further scrutinized where we noted that as chloride levels declined, nitrate has become the leading inorganic component since late 2019 (Fig. S2a-b) and plays an increasingly important role in exacerbating Delhi's $\text{PM}_{2.5}$ pollution (Fig. S2c). Thus, future studies should pay attention to elucidating the dominant production pathways of nitrate in Delhi, especially the contribution from N_2O_5 heterogeneous hydrolysis (Wang et al., 2017; Yan et al., 2023).

The present study suggests that NO_x emission control may intensify atmospheric oxidation of organics and secondary organic aerosol (SOA) formation in Delhi, whereas concurrent chlorine emission regulations may help mitigate the associated negative impacts. Previous studies have revealed the critical role chloride has in exacerbating haze formation in Delhi by enhancing aerosol liquid water content (ALWC) (Chen et al., 2022b; Gunthe et al., 2021), while our study implies that, with the decrease in NO concentrations, chloride can also be readily activated into photolabile gases, contributing to the formation of secondary pollutant, e.g., SOA, through generating radicals and advancing atmospheric organics oxidation. **An updated chlorine emission inventory combined with modelling studies, is necessary to quantitatively evaluate the contribution of chlorine chemistry to $\text{PM}_{2.5}$ formation under different NO_x conditions and inform targeted emission control strategies.** Finally, the interplay between nitrogen and halogen chemistry in India warrants continued investigation in the context of ongoing industrialization, vehicle electrification, and a changing climate.

Supporting Information

Text S1 to **S2**, Table S1 to S4 and Fig. S1 to S20

Acknowledgments

We acknowledge financial support from National Natural Science Foundation of China (grant no. 22188102), Tsinghua Scholarship for Overseas Graduate Studies (contract no. 2023012), Swedish Research Council (grant no. 2023-045209), the Swedish Research Council for Sustainable Development (grant no. 2020-02009 and 2022-01441) and the Swedish Strategic Research Area MERGE (Modelling the Regional and Global Earth System). Nishu Sachdeva and Johan Boman from University of Gothenburg are gratefully acknowledged for their contributions to the EDXRF analyses.

Data Availability

The dataset used for this study is available at <https://cloud.tsinghua.edu.cn/d/cb099983b459474fa1df/>. Measurement data from the Sri Aurobindo Marg monitoring station in Delhi is available at <https://www.dpccairdata.com/dpccairdata/display/AallAdvanceSearchMet.php?stName=U3JpQXVyYmluZG9NYXJn>. The Tropospheric Ultraviolet and Visible Radiation (TUV) Model is accessible at https://www.acom.ucar.edu/Models/TUV/Interactive_TUV. The exact sunrise and sunset time during

the 2023 and 2019 campaign are retrieved from the website
<https://www.timeanddate.com/sun/india/delhi>.

Author Contributions

M.H., Y.C., C.W., and J.J. designed the study. E.T., J.P., C.W., R.P., and M.H. organized and performed the field observations in Delhi. R.P., H.M., G.H., and G.T. provided the measurement space, helped setting up the instruments, and facilitated the measurements. Y.C., E.T. and J.P. calibrated and quantified the data. Y.C. analyzed and visualized the data. Y.C. wrote the original draft with inputs from J.J., M.H., and C.W. All co-authors contributed to scientific discussions and reviewing the manuscript.

Author Information

The authors declare no competing financial interests.

References

- Acharja, P., Ghude, S. D., Sinha, B., Barth, M., Govardhan, G., Kulkarni, R., Sinha, V., Kumar, R., Ali, K., Gultepe, I., Petit, J.-E., and Rajeevan, M. N.: Thermodynamical framework for effective mitigation of high aerosol loading in the Indo-Gangetic Plain during winter, *Scientific Reports*, 13, 13667, <https://doi.org/10.1038/s41598-023-40657-w>, 2023.
- Aggarwal, S., Bansal, P., Wang, Y., Jorga, S., Macgregor, G., Rohner, U., Bannan, T., Salter, M., Zieger, P., Mohr, C., and Lopez-Hilfiker, F.: Identifying key parameters that affect sensitivity of flow tube chemical ionization mass spectrometers, *Atmospheric Measurement Techniques*, 18, 4227-4247, <https://doi.org/10.5194/amt-18-4227-2025>, 2025.
- Ahern, A. T., Goldberger, L., Jahl, L., Thornton, J., and Sullivan, R. C.: Production of N_2O_5 and ClNO_2 through nocturnal processing of biomass-burning aerosol, *Environmental Science & Technology*, 52, 550-559, <https://doi.org/10.1021/acs.est.7b04386>, 2018.
- Ayres, B. R., Allen, H. M., Draper, D. C., Brown, S. S., Wild, R. J., Jimenez, J. L., Day, D. A., Campuzano-Jost, P., Hu, W., de Gouw, J., Koss, A., Cohen, R. C., Duffey, K. C., Romer, P., Baumann, K., Edgerton, E., Takahama, S., Thornton, J. A., Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Wennberg, P. O., Nguyen, T. B., Teng, A., Goldstein, A. H., Olson, K., and Fry, J. L.: Organic nitrate aerosol formation via NO_3 + biogenic volatile organic compounds in the southeastern United States, *Atmospheric Chemistry Physics*, 15, 13377-13392, <https://doi.org/10.5194/acp-15-13377-2015>, 2015.
- Bannan, T. J., Booth, A. M., Bacak, A., Muller, J. B. A., Leather, K. E., Le Breton, M., Jones, B., Young, D., Coe, H., Allan, J., Visser, S., Slowik, J. G., Furger, M., Prévôt, A. S. H., Lee, J., Dunmore, R. E., Hopkins, J. R., Hamilton, J. F., Lewis, A. C., Whalley, L. K., Sharp, T., Stone, D., Heard, D. E., Fleming, Z. L., Leigh, R., Shallcross, D. E., and Percival, C. J.: The first UK measurements of nitryl chloride using a chemical ionization mass spectrometer in central London in the summer of 2012, and an investigation of the role of Cl atom oxidation, *Journal of Geophysical Research: Atmospheres*, 120, 5638-5657, <https://doi.org/10.1002/2014jd022629>, 2015.
- Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO_2 from the reaction

617 of gaseous N_2O_5 with NaCl solution: Bulk and aerosol experiments, *Journal of Geophysical Research:*
618 *Atmospheres*, 102, 3795-3804, <https://doi.org/10.1029/96JD03057>, 1997.

619 Beig, G.: SAFAR-Delhi-2010: Development of High Resolution Emission Inventory for National
620 Capital Region Delhi, Indian Institute of Tropical Meteorology (IITM), 2010.

621 Beig, G.: SAFAR-Delhi-2018: SAFAR-High Resolution Emission Inventory of Megacity Delhi 2018,
622 Indian Institute of Tropical Meteorology (IITM), 2018.

623 Bertram, T. H., and Thornton, J. A.: Toward a general parameterization of N_2O_5 reactivity on aqueous
624 particles: the competing effects of particle liquid water, nitrate and chloride, *Atmospheric Chemistry*
625 *and Physics*, 9, 8351-8363, <https://doi.org/10.5194/acp-9-8351-2009>, 2009.

626 Brown, S. S., and Stutz, J.: Nighttime radical observations and chemistry, *Chemical Society Reviews*,
627 41, 6405-6447, <https://doi.org/10.1039/C2CS35181A>, 2012.

628 Bryant, D. J., Nelson, B. S., Swift, S. J., Budisulistiorini, S. H., Drysdale, W. S., Vaughan, A. R.,
629 Newland, M. J., Hopkins, J. R., Cash, J. M., Langford, B., Nemitz, E., Acton, W. J. F., Hewitt, C. N.,
630 Mandal, T., Gurjar, B. R., Shivani, Gadi, R., Lee, J. D., Rickard, A. R., and Hamilton, J. F.: Biogenic
631 and anthropogenic sources of isoprene and monoterpenes and their secondary organic aerosol in Delhi,
632 India, *Atmospheric Chemistry and Physics*, 23, 61-83, <https://doi.org/10.5194/acp-23-61-2023>, 2023.

633 Burkholder, J., Sander, S., Abbatt, J., Barker, J., Cappa, C., Crounse, J., Dibble, T., Huie, R., Kolb, C.,
634 and Kurylo, M.: Chemical kinetics and photochemical data for use in atmospheric studies, evaluation
635 Number 19 (JPL Publication 19-5), Jet Propulsion Laboratory, Pasadena, 2020.

636 Chen, K., Mayorga, R., Raeofy, N., Lum, M., Woods, M., Bahreini, R., Zhang, H., and Lin, Y.-H.:
637 Effects of Nitrate Radical Levels and Pre-Existing Particles on Secondary Brown Carbon Formation
638 from Nighttime Oxidation of Furan, *ACS Earth and Space Chemistry*, 6, 2709-2721,
639 <https://doi.org/10.1021/acsearthspacechem.2c00244>, 2022a.

640 Chen, X., Xia, M., Wang, W., Yun, H., Yue, D., and Wang, T.: Fast near-surface ClNO_2 production and
641 its impact on O_3 formation during a heavy pollution event in South China, *Science of the Total*
642 *Environment*, 858, 159998, <https://doi.org/10.1016/j.scitotenv.2022.159998>, 2023.

643 Chen, X., Jiang, Y., Zong, Z., Wang, Y., Sun, W., Wang, Y., Xia, M., Guan, L., Liu, P., Zhang, C., Chen,
644 J., Mu, Y., and Wang, T.: Atmospheric reactive halogens reshaped by the clean energy policy and
645 agricultural activity in a rural area of the north China plain, *Environmental Science & Technology*, 59,
646 12775-12785, <https://doi.org/10.1021/acs.est.4c13986>, 2025a.

647 Chen, Y., Wang, Y., Nenes, A., Wild, O., Song, S., Hu, D., Liu, D., He, J., Hildebrandt Ruiz, L., Apte,
648 J. S., Gunthe, S. S., and Liu, P.: Ammonium chloride associated aerosol liquid water enhances haze in
649 Delhi, India, *Environmental Science & Technology*, 56, 7163-7173,
650 <https://doi.org/10.1021/acs.est.2c00650>, 2022b.

651 Chen, Y., Xia, M., Zhang, J., Tsiligiannis, E., Wu, C., Yan, C., Cai, R., Zheng, G., Li, Y., Guo, J., An,
652 Z., Li, Y., Zhao, X., Qu, Q., Hua, C., Wang, Z., Wang, S., Liu, Y., Cao, L., He, K., Kulmala, M.,
653 Hallquist, M., Wang, T., Worsnop, D., and Jiang, J.: Chloramine chemistry as a missing link in
654 atmospheric chlorine cycling, *Science Advances*, 11, eadv4298,
655 <https://doi.org/10.1126/sciadv.adv4298>, 2025b.

656 Dale W. Margerum, L. M. S., JoLynn Hobson, and Elizabeth E. Moore: Water chlorination chemistry:
657 Nonmetal redox kinetics of chloramine and nitrite ion, *Environmental Science & Technology*, 28, 331-

337, 1994.

Dalton, E. Z., Hoffmann, E. H., Schaefer, T., Tilgner, A., Herrmann, H., and Raff, J. D.: Daytime atmospheric halogen cycling through aqueous-phase oxygen atom chemistry, *Journal of the American Chemical Society*, 145, 15652-15657, <https://doi.org/10.1021/jacs.3c03112>, 2023.

Dentener, F. J., and Crutzen, P. J.: Reaction of N_2O_5 on tropospheric aerosols: Impact on the global distributions of NO_x , O_3 , and OH, *Journal of Geophysical Research: Atmospheres*, 98, 7149-7163, <https://doi.org/10.1029/92JD02979>, 1993.

Dunlea, E. J., and Ravishankara, A.: Measurement of the rate coefficient for the reaction of $\text{O}(^1\text{D})$ with H_2O and re-evaluation of the atmospheric OH production rate, *Physical Chemistry Chemical Physics*, 6, 3333-3340, 2004.

Eger, P. G., Friedrich, N., Schuladen, J., Shenolikar, J., Fischer, H., Tadic, I., Harder, H., Martinez, M., Rohloff, R., Tauer, S., Drewnick, F., Fachinger, F., Brooks, J., Darbyshire, E., Sciare, J., Pikridas, M., Lelieveld, J., and Crowley, J. N.: Shipborne measurements of ClNO_2 in the Mediterranean Sea and around the Arabian Peninsula during summer, *Atmospheric Chemistry and Physics*, 19, 12121-12140, <https://doi.org/10.5194/acp-19-12121-2019>, 2019.

Evans, M. J., and Jacob, D. J.: Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, *Geophysical Research Letters*, 32, L09813, <https://doi.org/10.1029/2005GL022469>, 2005.

Fauré, N., Chen, J., Artiglia, L., Ammann, M., Bartels-Rausch, T., Kanji, Z. A., Wang, S., Pettersson, J. B. C., Thomson, E. S., Gladich, I., and Kong, X.: Formation of sodium chloride on the surface of sulfate-rich Gobi desert salt in response to water adsorption, *ACS ES&T Air*, 1, 1373-1382, <https://doi.org/10.1021/acsestair.4c00092>, 2024.

Faxon, C., Bean, J., and Ruiz, L.: Inland Concentrations of Cl_2 and ClNO_2 in Southeast Texas Suggest Chlorine Chemistry Significantly Contributes to Atmospheric Reactivity, *Atmosphere*, 6, 1487-1506, <https://doi.org/10.3390/atmos6101487>, 2015.

Finlayson-Pitts, B. J., Ezell, M. J., and Pitts, J. N.: Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and ClONO_2 , *Nature*, 337, 241-244, <https://doi.org/10.1038/337241a0>, 1989.

Gani, S., Bhandari, S., Patel, K., Seraj, S., Soni, P., Arub, Z., Habib, G., Hildebrandt Ruiz, L., and Apte, J. S.: Particle number concentrations and size distribution in a polluted megacity: the Delhi Aerosol Supersite study, *Atmospheric Chemistry and Physics*, 20, 8533-8549, <https://doi.org/10.5194/acp-20-8533-2020>, 2020.

Gunthe, S. S., Liu, P., Panda, U., Raj, S. S., Sharma, A., Darbyshire, E., Reyes-Villegas, E., Allan, J., Chen, Y., Wang, X., Song, S., Pöhlker, M. L., Shi, L., Wang, Y., Kommula, S. M., Liu, T., Ravikrishna, R., McFiggans, G., Mickley, L. J., Martin, S. T., Pöschl, U., Andreae, M. O., and Coe, H.: Enhanced aerosol particle growth sustained by high continental chlorine emission in India, *Nature Geoscience*, 14, 77-84, <https://doi.org/10.1038/s41561-020-00677-x>, 2021.

Haslett, S. L., Bell, D. M., Kumar, V., Slowik, J. G., Wang, D. S., Mishra, S., Rastogi, N., Singh, A., Ganguly, D., Thornton, J., Zheng, F., Li, Y., Nie, W., Liu, Y., Ma, W., Yan, C., Kulmala, M., Daellenbach, K. R., Hadden, D., Baltensperger, U., Prevot, A. S. H., Tripathi, S. N., and Mohr, C.: Nighttime NO emissions strongly suppress chlorine and nitrate radical formation during the winter in

699 Delhi, Atmospheric Chemistry and Physics, 23, 9023-9036, <https://doi.org/10.5194/acp-23-9023-2023>,
700 2023.

701 Huang, W., Saathoff, H., Shen, X., Ramisetty, R., Leisner, T., and Mohr, C.: Chemical Characterization
702 of Highly Functionalized Organonitrates Contributing to Night-Time Organic Aerosol Mass Loadings
703 and Particle Growth, Environmental Science & Technology, 53, 1165-1174,
704 <https://doi.org/10.1021/acs.est.8b05826>, 2019.

705 Huang, W., Wu, C., Gao, L., Gramlich, Y., Haslett, S. L., Thornton, J., Lopez-Hilfiker, F. D., Lee, B.
706 H., Song, J., Saathoff, H., Shen, X., Ramisetty, R., Tripathi, S. N., Ganguly, D., Jiang, F., Vallon, M.,
707 Schobesberger, S., Yli-Juuti, T., and Mohr, C.: Variation in chemical composition and volatility of
708 oxygenated organic aerosol in different rural, urban, and mountain environments, Atmospheric
709 Chemistry Physics, 24, 2607-2624, <https://doi.org/10.5194/acp-24-2607-2024>, 2024.

710 Jahl, L. G., Bowers, B. B., Jahn, L. G., Thornton, J. A., and Sullivan, R. C.: Response of the reaction
711 probability of N₂O₅ with authentic biomass-burning aerosol to high relative humidity, ACS Earth and
712 Space Chemistry, 5, 2587-2598, <https://doi.org/10.1021/acsearthspacechem.1c00227>, 2021.

713 Jahn, L. G., McPherson, K. N., and Hildebrandt Ruiz, L.: Effects of Relative Humidity and Photoaging
714 on the Formation, Composition, and Aging of Ethylbenzene SOA: Insights from Chamber Experiments
715 on Chlorine Radical-Initiated Oxidation of Ethylbenzene, ACS Earth and Space Chemistry, 8, 675-
716 688, <https://doi.org/10.1021/acsearthspacechem.3c00279>, 2024.

717 Jenks, O. J., DeVault, M. P., Ziola, A. C., Morris, M. A., Schueneman, M. K., Stark, H., Jimenez, J. L.,
718 Ziemann, P. J., and de Gouw, J. A.: Investigation of Gas-Phase Products from the NO₃ Radical
719 Oxidation of Δ-3-Carene, ACS Earth and Space Chemistry, 7, 1097-1106,
720 <https://doi.org/10.1021/acsearthspacechem.3c00020>, 2023.

721 Jiang, J., Carter, W. P. L., Cocker, D. R., III, and Barsanti, K. C.: Development and Evaluation of a
722 Detailed Mechanism for Gas-Phase Atmospheric Reactions of Furans, ACS Earth and Space Chemistry,
723 4, 1254-1268, <https://doi.org/10.1021/acsearthspacechem.0c00058>, 2020.

724 Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo,
725 P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P.,
726 Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J.,
727 Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J.
728 M., Collins, D. R., Cubison, M. J., E., Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R.,
729 Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian,
730 K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun,
731 J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A.
732 M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop,
733 D. R.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525-1529,
734 <https://doi.org/doi:10.1126/science.1180353>, 2009.

735 Joo, T., Rivera-Rios, J. C., Takeuchi, M., Alvarado, M. J., and Ng, N. L.: Secondary Organic Aerosol
736 Formation from Reaction of 3-Methylfuran with Nitrate Radicals, ACS Earth and Space Chemistry, 3,
737 922-934, <https://doi.org/10.1021/acsearthspacechem.9b00068>, 2019.

738 Kashyap, P., Kumar, A., Kumar, R. P., and Kumar, K.: Biogenic and anthropogenic isoprene emissions
739 in the subtropical urban atmosphere of Delhi, Atmospheric Pollution Research, 10, 1691-1698,

740 <https://doi.org/https://doi.org/10.1016/j.apr.2019.07.004>, 2019.

741 Kenagy, H. S., Heald, C. L., Tahsini, N., Goss, M. B., and Kroll, J. H.: Can we achieve atmospheric
 742 chemical environments in the laboratory? An integrated model-measurement approach to chamber
 743 SOA studies, *Science Advances*, 10, eado1482, <https://doi.org/10.1126/sciadv.ado1482>, 2024.

744 Kercher, J. P., Riedel, T. P., and Thornton, J. A.: Chlorine activation by N₂O₅: Simultaneous, in situ
 745 detection of ClNO₂ and N₂O₅ by chemical ionization mass spectrometry, *Atmospheric Measurement*
 746 *Techniques*, 2, 193-204, <https://doi.org/10.5194/amt-2-193-2009>, 2009.

747 Kumar, V., Giannoukos, S., Haslett, S. L., Tong, Y., Singh, A., Bertrand, A., Lee, C. P., Wang, D. S.,
 748 Bhattu, D., Stefenelli, G., Dave, J. S., Puthussery, J. V., Qi, L., Vats, P., Rai, P., Casotto, R., Satish, R.,
 749 Mishra, S., Pospisilova, V., Mohr, C., Bell, D. M., Ganguly, D., Verma, V., Rastogi, N., Baltensperger,
 750 U., Tripathi, S. N., Prévôt, A. S. H., and Slowik, J. G.: Highly time-resolved chemical speciation and
 751 source apportionment of organic aerosol components in Delhi, India, using extractive electrospray
 752 ionization mass spectrometry, *Atmospheric Chemistry and Physics*, 22, 7739-7761,
 753 <https://doi.org/10.5194/acp-22-7739-2022>, 2022.

754 Le Breton, M., Hallquist, Å. M., Pathak, R. K., Simpson, D., Wang, Y., Johansson, J., Zheng, J., Yang,
 755 Y., Shang, D., Wang, H., Liu, Q., Chan, C., Wang, T., Bannan, T. J., Priestley, M., Percival, C. J.,
 756 Shallcross, D. E., Lu, K., Guo, S., Hu, M., and Hallquist, M.: Chlorine oxidation of VOCs at a semi-
 757 rural site in Beijing: Significant chlorine liberation from ClNO₂ and subsequent gas- and particle-phase
 758 Cl-VOC production, *Atmospheric Chemistry and Physics*, 18, 13013-13030,
 759 <https://doi.org/10.5194/acp-18-13013-2018>, 2018a.

760 Le Breton, M., Wang, Y., Hallquist, Å. M., Pathak, R. K., Zheng, J., Yang, Y., Shang, D., Glasius, M.,
 761 Bannan, T. J., Liu, Q., Chan, C. K., Percival, C. J., Zhu, W., Lou, S., Topping, D., Wang, Y., Yu, J., Lu,
 762 K., Guo, S., Hu, M., and Hallquist, M.: Online gas- and particle-phase measurements of organosulfates,
 763 organosulfonates and nitrooxy organosulfates in Beijing utilizing a FIGAERO ToF-CIMS,
 764 *Atmospheric Chemistry and Physics*, 18, 10355-10371, <https://doi.org/10.5194/acp-18-10355-2018>,
 765 2018b.

766 Li, M., Xia, M., Lin, C., Jiang, Y., Sun, W., Wang, Y., Zhang, Y., He, M., and Wang, T.: Mechanistic
 767 insights into chloroacetic acid production from atmospheric multiphase volatile organic compound-
 768 chlorine chemistry, *Atmospheric Chemistry and Physics*, 25, 3753-3764, [https://doi.org/10.5194/acp-](https://doi.org/10.5194/acp-25-3753-2025)
 769 [25-3753-2025](https://doi.org/10.5194/acp-25-3753-2025), 2025.

770 Lim, Y. B., and Ziemann, P. J.: Chemistry of Secondary Organic Aerosol Formation from OH Radical-
 771 Initiated Reactions of Linear, Branched, and Cyclic Alkanes in the Presence of NO_x, *Aerosol Science*
 772 *and Technology*, 43, 604-619, <https://doi.org/10.1080/02786820902802567>, 2009.

773 Liu, X., Qu, H., Huey, L. G., Wang, Y., Sjostedt, S., Zeng, L., Lu, K., Wu, Y., Hu, M., Shao, M., Zhu,
 774 T., and Zhang, Y.: High levels of daytime molecular chlorine and nitryl chloride at a rural site on the
 775 North China Plain, *Environmental Science & Technology*, 51, 9588-9595,
 776 <https://doi.org/10.1021/acs.est.7b03039>, 2017.

777 Ljungström, E., and Hallquist, M.: Nitrate radical formation rates in scandinavia, *Atmospheric*
 778 *Environment*, 30, 2925-2932, [https://doi.org/https://doi.org/10.1016/1352-2310\(96\)00006-4](https://doi.org/https://doi.org/10.1016/1352-2310(96)00006-4), 1996.

779 Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Lutz, A.,
 780 Hallquist, M., Worsnop, D., and Thornton, J. A.: A novel method for online analysis of gas and particle

composition: description and evaluation of a Filter Inlet for Gases and AEROSols (FIGAERO), Atmospheric Measurement Techniques, 7, 983-1001, <https://doi.org/10.5194/amt-7-983-2014>, 2014.

Ma, W., Chen, X., Xia, M., Liu, Y., Wang, Y., Zhang, Y., Zheng, F., Zhan, J., Hua, C., Wang, Z., Wang, W., Fu, P., Kulmala, M., and Liu, Y.: Reactive chlorine species advancing the atmospheric oxidation capacities of inland urban environments, Environmental Science & Technology, 57, 14638-14647, <https://doi.org/10.1021/acs.est.3c05169>, 2023.

McNamara, S. M., AR, W. R., Wang, S., Thanekar, S., Boone, E. J., Kolesar, K. R., Peterson, P. K., Simpson, W. R., Fuentes, J. D., Shepson, P. B., and Pratt, K. A.: Springtime nitrogen oxide-influenced chlorine chemistry in the coastal Arctic, Environmental Science & Technology, 53, 8057-8067, <https://doi.org/10.1021/acs.est.9b01797>, 2019.

McNamara, S. M., Kolesar, K. R., Wang, S., Kirpes, R. M., May, N. W., Gunsch, M. J., Cook, R. D., Fuentes, J. D., Hornbrook, R. S., Apel, E. C., China, S., Laskin, A., and Pratt, K. A.: Observation of road salt aerosol driving inland wintertime atmospheric chlorine chemistry, ACS Central Science, 6, 684-694, <https://doi.org/10.1021/acscentsci.9b00994>, 2020.

Meidan, D., Brown, S. S., Sinha, V., and Rudich, Y.: Nocturnal atmospheric oxidative processes in the Indo-Gangetic plain and their variation during the COVID-19 lockdowns, Geophysical Research Letters, 49, e2021GL097472, <https://doi.org/10.1029/2021GL097472>, 2022.

Mielke, L. H., Stutz, J., Tsai, C., Hurlock, S. C., Roberts, J. M., Veres, P. R., Froyd, K. D., Hayes, P. L., Cubison, M. J., Jimenez, J. L., Washenfelder, R. A., Young, C. J., Gilman, J. B., Gouw, J. A., Flynn, J. H., Grossberg, N., Lefer, B. L., Liu, J., Weber, R. J., and Osthoff, H. D.: Heterogeneous formation of nitryl chloride and its role as a nocturnal NO_x reservoir species during CalNex - LA 2010, Journal of Geophysical Research: Atmospheres, 118, 10638-10652, <https://doi.org/10.1002/jgrd.50783>, 2013.

Mishra, S., Sinha, V., Hakkim, H., Awasthi, A., Ghude, S. D., Soni, V. K., Nigam, N., Sinha, B., and Rajeevan, M. N.: Reactive chlorine-, sulfur-, and nitrogen-containing volatile organic compounds impact atmospheric chemistry in the megacity of Delhi during both clean and extremely polluted seasons, Atmospheric Chemistry and Physics, 24, 13129-13150, <https://doi.org/10.5194/acp-24-13129-2024>, 2024.

Nelson, B. S., Stewart, G. J., Drysdale, W. S., Newland, M. J., Vaughan, A. R., Dunmore, R. E., Edwards, P. M., Lewis, A. C., Hamilton, J. F., Acton, W. J., Hewitt, C. N., Crilley, L. R., Alam, M. S., Şahin, Ü. A., Beddows, D. C. S., Bloss, W. J., Slater, E., Whalley, L. K., Heard, D. E., Cash, J. M., Langford, B., Nemitz, E., Sommariva, R., Cox, S., Shivani, Gadi, R., Gurjar, B. R., Hopkins, J. R., Rickard, A. R., and Lee, J. D.: In situ ozone production is highly sensitive to volatile organic compounds in Delhi, India, Atmospheric Chemistry and Physics, 21, 13609-13630, <https://doi.org/10.5194/acp-21-13609-2021>, 2021.

Noxon, J. F., Norton, R. B., and Marovich, E.: NO₃ in the troposphere, Geophysical Research Letters, 7, 125-128, <https://doi.org/https://doi.org/10.1029/GL007i002p00125>, 1980.

Ogrizek, M., Kroflič, A., and Šala, M.: Critical review on the development of analytical techniques for the elemental analysis of airborne particulate matter, Trends in Environmental Analytical Chemistry, 33, e00155, <https://doi.org/https://doi.org/10.1016/j.teac.2022.e00155>, 2022.

Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., Bates, T. S., Coffman, D., Quinn, P. K., Dibb, J. E., Stark, H., Burkholder, J. B., Talukdar, R. K.,

Meagher, J., Fehsenfeld, F. C., and Brown, S. S.: High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nature Geoscience*, 1, 324-328, <https://doi.org/10.1038/ngeo177>, 2008.

Patel, A., Reddy, M. C., Zhang, B., Swain, B., Pandithurai, G., Andreae, M. O., Martin, S. T., Liu, P., and Gunthe, S. S.: Linking anthropogenic chlorine emissions to regional air quality in India, *npj Clean Air*, 2, 23, <https://doi.org/10.1038/s44407-026-00066-5>, 2026.

Peng, X., Wang, W., Xia, M., Chen, H., Ravishankara, A. R., Li, Q., Saiz-Lopez, A., Liu, P., Zhang, F., Zhang, C., Xue, L., Wang, X., George, C., Wang, J., Mu, Y., Chen, J., and Wang, T.: An unexpected large continental source of reactive bromine and chlorine with significant impact on wintertime air quality, *National Science Review* 8, nwaa304, <https://doi.org/10.1093/nsr/nwaa304>, 2021.

Phillips, G. J., Tang, M. J., Thieser, J., Brickwedde, B., Schuster, G., Bohn, B., Lelieveld, J., and Crowley, J. N.: Significant concentrations of nitryl chloride observed in rural continental Europe associated with the influence of sea salt chloride and anthropogenic emissions, *Geophysical Research Letters*, 39, L10811, <https://doi.org/10.1029/2012gl051912>, 2012.

Priestley, M., le Breton, M., Bannan, T. J., Worrall, S. D., Bacak, A., Smedley, A. R. D., Reyes-Villegas, E., Mehra, A., Allan, J., Webb, A. R., Shallcross, D. E., Coe, H., and Percival, C. J.: Observations of organic and inorganic chlorinated compounds and their contribution to chlorine radical concentrations in an urban environment in northern Europe during the wintertime, *Atmospheric Chemistry and Physics*, 18, 13481-13493, <https://doi.org/10.5194/acp-18-13481-2018>, 2018.

Raff, J. D., Njegic, B., Chang, W. L., Gordon, M. S., Dabdub, D., Gerber, R. B., and Finlayson-Pitts, B. J.: Chlorine activation indoors and outdoors via surface-mediated reactions of nitrogen oxides with hydrogen chloride, *Proceedings of the National Academy of Sciences*, 106, 13647-13654, <https://doi.org/doi:10.1073/pnas.0904195106>, 2009.

Rai, P., Furger, M., El Haddad, I., Kumar, V., Wang, L., Singh, A., Dixit, K., Bhattu, D., Petit, J.-E., Ganguly, D., Rastogi, N., Baltensperger, U., Tripathi, S. N., Slowik, J. G., and Prévôt, A. S. H.: Real-time measurement and source apportionment of elements in Delhi's atmosphere, *Science of the Total Environment*, 742, 140332, <https://doi.org/https://doi.org/10.1016/j.scitotenv.2020.140332>, 2020.

Riedel, T. P., Bertram, T. H., Crisp, T. A., Williams, E. J., Lerner, B. M., Vlasenko, A., Li, S. M., Gilman, J., de Gouw, J., Bon, D. M., Wagner, N. L., Brown, S. S., and Thornton, J. A.: Nitryl chloride and molecular chlorine in the coastal marine boundary layer, *Environmental Science & Technology*, 46, 10463-10470, <https://doi.org/10.1021/es204632r>, 2012.

Sahu, S. K., Mangaraj, P., and Beig, G.: Decadal growth in emission load of major air pollutants in Delhi, *Earth Syst. Sci. Data*, 15, 3183-3202, <https://doi.org/10.5194/essd-15-3183-2023>, 2023.

Simpson, W. R., Brown, S. S., Saiz-Lopez, A., Thornton, J. A., and Glasow, R.: Tropospheric halogen chemistry: Sources, cycling, and impacts, *Chemical Reviews*, 115, 4035-4062, <https://doi.org/10.1021/cr5006638>, 2015.

Soni, M., Sander, R., Sahu, L. K., Taraborrelli, D., Liu, P., Patel, A., Girach, I. A., Pozzer, A., Gunthe, S. S., and Ojha, N.: Comprehensive multiphase chlorine chemistry in the box model CAABA/MECCA: Implications for atmospheric oxidative capacity, *Atmospheric Chemistry and Physics*, 23, 15165-15180, <https://doi.org/10.5194/acp-23-15165-2023>, 2023.

Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X.,

863 Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations
 864 of nitryl chloride sustained in the morning: Investigations of the causes and impacts on ozone
 865 production in a polluted region of northern China, *Atmospheric Chemistry and Physics*, 16, 14959-
 866 14977, <https://doi.org/10.5194/acp-16-14959-2016>, 2016.

867 Tham, Y. J., Wang, Z., Li, Q., Wang, W., Wang, X., Lu, K., Ma, N., Yan, C., Kecorius, S., Wiedensohler,
 868 A., Zhang, Y., and Wang, T.: Heterogeneous N_2O_5 uptake coefficient and production yield of ClNO_2
 869 in polluted northern China: Roles of aerosol water content and chemical composition, *Atmospheric*
 870 *Chemistry and Physics*, 18, 13155-13171, <https://doi.org/10.5194/acp-18-13155-2018>, 2018.

871 Thornton, J. A., Braban, C. F., and Abbatt, J. P. D.: N_2O_5 hydrolysis on sub-micron organic aerosols:
 872 the effect of relative humidity, particle phase, and particle size, *Physical Chemistry Chemical Physics*,
 873 5, 4593-4603, <https://doi.org/10.1039/B307498F>, 2003.

874 Thornton, J. A., and Abbatt, J. P. D.: N_2O_5 reaction on submicron sea salt aerosol: Kinetics, products,
 875 and the effect of surface active organics, *The Journal of Physical Chemistry A*, 109, 10004-10012,
 876 <https://doi.org/10.1021/jp054183t>, 2005.

877 Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dube, W. P.,
 878 Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S.: A large atomic
 879 chlorine source inferred from mid-continental reactive nitrogen chemistry, *Nature*, 464, 271-274,
 880 <https://doi.org/10.1038/nature08905>, 2010.

881 Trebs, I., Bohn, B., Ammann, C., Rummel, U., Blumthaler, M., Königstedt, R., Meixner, F. X., Fan,
 882 S., and Andreae, M. O.: Relationship between the NO_2 photolysis frequency and the solar global
 883 irradiance, *Atmospheric Measurement Techniques*, 2, 725-739, [https://doi.org/10.5194/amt-2-725-](https://doi.org/10.5194/amt-2-725-2009)
 884 [2009](https://doi.org/10.5194/amt-2-725-2009), 2009.

885 Unga, F., Calzolari, G., Chiari, M., Cuccia, E., Colombi, C., Franciosa, M., Dinoi, A., Merico, E.,
 886 Pennetta, A., Gómez-Sánchez, N., Mapelli, C., Pareti, S., Perrino, C., Yubero, E., and Contini, D.:
 887 Determination of aerosol composition by ED-XRF on Teflon and quartz substrates: potentialities and
 888 limits, *Aerosol Research*, 3, 405-415, <https://doi.org/10.5194/ar-3-405-2025>, 2025.

889 Wang, C., Liggio, J., Wentzell, J. J. B., Jorga, S., Folkerson, A., and Abbatt, J. P. D.: Chloramines as
 890 an important photochemical source of chlorine atoms in the urban atmosphere, *Proceedings of the*
 891 *National Academy of Sciences of the United States of America*, 120, e2220889120,
 892 <https://doi.org/doi:10.1073/pnas.2220889120>, 2023a.

893 Wang, D. S., and Hildebrandt Ruiz, L.: Chlorine-initiated oxidation of n-alkanes under high- NO_x
 894 conditions: Insights into secondary organic aerosol composition and volatility using a FIGAERO-
 895 CIMS, *Atmospheric Chemistry and Physics*, 18, 15535-15553, [https://doi.org/10.5194/acp-18-15535-](https://doi.org/10.5194/acp-18-15535-2018)
 896 [2018](https://doi.org/10.5194/acp-18-15535-2018), 2018.

897 Wang, D. S., Masoud, C. G., Modi, M., and Hildebrandt Ruiz, L.: Isoprene-chlorine oxidation in the
 898 presence of NO_x and implications for urban atmospheric chemistry, *Environmental Science &*
 899 *Technology*, 56, 9251-9264, <https://doi.org/10.1021/acs.est.1c07048>, 2022.

900 Wang, H., Lu, K., Chen, X., Zhu, Q., Chen, Q., Guo, S., Jiang, M., Li, X., Shang, D., Tan, Z., Wu, Y.,
 901 Wu, Z., Zou, Q., Zheng, Y., Zeng, L., Zhu, T., Hu, M., and Zhang, Y.: High N_2O_5 concentrations
 902 observed in urban Beijing: Implications of a large nitrate formation pathway, *Environmental Science*
 903 *& Technology Letters*, 4, 416-420, <https://doi.org/10.1021/acs.estlett.7b00341>, 2017.

904 Wang, H., Wang, H., Lu, X., Lu, K., Zhang, L., Tham, Y. J., Shi, Z., Aikin, K., Fan, S., Brown, S. S.,
 905 and Zhang, Y.: Increased night-time oxidation over China despite widespread decrease across the globe,
 906 Nature Geoscience, 16, 217-223, <https://doi.org/10.1038/s41561-022-01122-x>, 2023b.

907 Wang, J., Wang, H., Tham, Y. J., Ming, L., Zheng, Z., Fang, G., Sun, C., Ling, Z., Zhao, J., and Fan,
 908 S.: Measurement report: Atmospheric nitrate radical chemistry in the South China Sea influenced by
 909 the urban outflow of the Pearl River Delta, Atmospheric Chemistry and Physics, 24, 977-992,
 910 <https://doi.org/10.5194/acp-24-977-2024>, 2024.

911 Wang, L., Slowik, J. G., Tripathi, N., Bhattu, D., Rai, P., Kumar, V., Vats, P., Satish, R., Baltensperger,
 912 U., Ganguly, D., Rastogi, N., Sahu, L. K., Tripathi, S. N., and Prévôt, A. S. H.: Source characterization
 913 of volatile organic compounds measured by proton-transfer-reaction time-of-flight mass spectrometers
 914 in Delhi, India, Atmospheric Chemistry and Physics, 20, 9753-9770, <https://doi.org/10.5194/acp-20-9753-2020>, 2020.

916 Wang, T., Brown, S. S., Dubé, W. P., Tham, Y. J., Zha, Q., Xue, L., Poon, S., Wang, Z., Blake, D. R.,
 917 Tsui, W., and Parrish, D. D.: Observations of nitryl chloride and modeling its source and effect on
 918 ozone in the planetary boundary layer of southern China, Journal of Geophysical Research:
 919 Atmospheres, 121, 2457-2475, <https://doi.org/10.1002/2015jd024566>, 2016.

920 Wang, X., Jacob, D. J., Eastham, S. D., Sulprizio, M. P., Zhu, L., Chen, Q., Alexander, B., Sherwen,
 921 T., Evans, M. J., Lee, B. H., Haskins, J. D., Lopez-Hilfiker, F. D., Thornton, J. A., Huey, G. L., and
 922 Liao, H.: The role of chlorine in global tropospheric chemistry, Atmospheric Chemistry and Physics,
 923 19, 3981-4003, <https://doi.org/10.5194/acp-19-3981-2019>, 2019.

924 Wängberg, I., Etzkorn, T., Barnes, I., Platt, U., and Becker, K. H.: Absolute determination of the
 925 temperature behavior of the $\text{NO}_2 + \text{NO}_3 + (\text{M}) \leftrightarrow \text{N}_2\text{O}_5 + (\text{M})$ equilibrium, The Journal of Physical
 926 Chemistry A, 101, 9694-9698, <https://doi.org/10.1021/jp972203o>, 1997.

927 Xia, M., Peng, X., Wang, W., Yu, C., Sun, P., Li, Y., Liu, Y., Xu, Z., Wang, Z., Xu, Z., Nie, W., Ding,
 928 A., and Wang, T.: Significant production of ClNO_2 and possible source of Cl_2 from N_2O_5 uptake at a
 929 suburban site in eastern China, Atmospheric Chemistry and Physics, 20, 6147-6158,
 930 <https://doi.org/10.5194/acp-20-6147-2020>, 2020.

931 Xia, M., Peng, X., Wang, W., Yu, C., Wang, Z., Tham, Y. J., Chen, J., Chen, H., Mu, Y., Zhang, C., Liu,
 932 P., Xue, L., Wang, X., Gao, J., Li, H., and Wang, T.: Winter ClNO_2 formation in the region of fresh
 933 anthropogenic emissions: seasonal variability and insights into daytime peaks in northern China,
 934 Atmospheric Chemistry and Physics, 21, 15985-16000, <https://doi.org/10.5194/acp-21-15985-2021>,
 935 2021.

936 Xia, M., Jiang, Y., Dai, J., Liu, Y., Yan, C., Kulmala, M., and Wang, T.: Chlorine activation in marine
 937 air: Insights from chemical budgets of molecular chlorine and hypochlorous acid, Journal of
 938 Geophysical Research: Atmospheres, 130, e2024JD042568,
 939 <https://doi.org/https://doi.org/10.1029/2024JD042568>, 2025.

940 Xu, T., Takeuchi, M., Rivera-Rios, J. C., and Ng, N. L.: Multigeneration Chemistry in Secondary
 941 Organic Aerosol Formation from Nitrate Radical Oxidation of Isoprene, ACS Earth and Space
 942 Chemistry, 9, 411-423, <https://doi.org/10.1021/acsearthspacechem.4c00417>, 2025.

943 Yan, C., Tham, Y. J., Nie, W., Xia, M., Wang, H., Guo, Y., Ma, W., Zhan, J., Hua, C., Li, Y., Deng, C.,
 944 Li, Y., Zheng, F., Chen, X., Li, Q., Zhang, G., Mahajan, A. S., Cuevas, C. A., Huang, D. D., Wang, Z.,

945 Sun, Y., Saiz-Lopez, A., Bianchi, F., Kerminen, V.-M., Worsnop, D. R., Donahue, N. M., Jiang, J., Liu,
 946 Y., Ding, A., and Kulmala, M.: Increasing contribution of nighttime nitrogen chemistry to wintertime
 947 haze formation in Beijing observed during COVID-19 lockdowns, *Nature Geoscience*,
 948 <https://doi.org/10.1038/s41561-023-01285-1>, 2023.
 949 Yan, Y., Wang, S., Zhu, J., Guo, Y., Tang, G., Liu, B., An, X., Wang, Y., and Zhou, B.: Vertically
 950 increased NO₃ radical in the nocturnal boundary layer, *Science of the Total Environment*, 763, 142969,
 951 <https://doi.org/https://doi.org/10.1016/j.scitotenv.2020.142969>, 2021.
 952 Yang, X., Wang, Q., Ma, N., Hu, W., Gao, Y., Huang, Z., Zheng, J., Yuan, B., Yang, N., Tao, J., Hong,
 953 J., Cheng, Y., and Su, H.: The impact of chlorine chemistry combined with heterogeneous N₂O₅
 954 reactions on air quality in China, *Atmospheric Chemistry and Physics*, 22, 3743-3762,
 955 <https://doi.org/10.5194/acp-22-3743-2022>, 2022.
 956 Ye, C., Yuan, B., Lin, Y., Wang, Z., Hu, W., Li, T., Chen, W., Wu, C., Wang, C., Huang, S., Qi, J., Wang,
 957 B., Wang, C., Song, W., Wang, X., Zheng, E., Krechmer, J. E., Ye, P., Zhang, Z., Wang, X., Worsnop,
 958 D. R., and Shao, M.: Chemical characterization of oxygenated organic compounds in the gas phase
 959 and particle phase using iodide CIMS with FIGAERO in urban air, *Atmospheric Chemistry and*
 960 *Physics*, 21, 8455-8478, <https://doi.org/10.5194/acp-21-8455-2021>, 2021.
 961 Zhang, T., Zuo, P., Chen, Y., Liu, T., Zeng, L., Lin, W., and Ye, C.: Measurement report: Variations and
 962 environmental impacts of atmospheric N₂O₅ concentrations in urban Beijing during the 2022 Winter
 963 Olympics, *Atmospheric Chemistry and Physics*, 25, 16331-16346, [https://doi.org/10.5194/acp-25-](https://doi.org/10.5194/acp-25-16331-2025)
 964 [16331-2025](https://doi.org/10.5194/acp-25-16331-2025), 2025.
 965 Zhou, W., Zhao, J., Ouyang, B., Mehra, A., Xu, W., Wang, Y., Bannan, T. J., Worrall, S. D., Priestley,
 966 M., Bacak, A., Chen, Q., Xie, C., Wang, Q., Wang, J., Du, W., Zhang, Y., Ge, X., Ye, P., Lee, J. D., Fu,
 967 P., Wang, Z., Worsnop, D., Jones, R., Percival, C. J., Coe, H., and Sun, Y.: Production of N₂O₅ and
 968 ClNO₂ in summer in urban Beijing, China, *Atmospheric Chemistry and Physics*, 18, 11581-11597,
 969 <https://doi.org/10.5194/acp-18-11581-2018>, 2018.

970