Formation and impacts of nitryl chloride in Pearl River Delta

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Abstract. Here we present a field measurement of CINO₂ (nitryl chloride) and N₂O₅ (dinitrogen pentoxide) by a time-of-flight chemical ionization mass spectrometer (ToF-CIMS) with the Filter Inlet for Gas and AEROsols (FIGAERO) at a regional site in the Pearl River Delta during a photochemical pollution season from 26 September to 17 November 2019. Three patterns of air masses are sampled during this campaign, including the dominating air masses from the north and northeast urban regions (Type A), the southeast coast (Type B), and the South China Sea (Type C). The concentration of CINO₂ and N₂O₅ was observed to be much higher in Type A and B than in Type C, indicating that the urban nighttime chemistry is more active than the background marine regions. The N₂O₅ uptake coefficient and CINO₂ production yield were estimated based on the field measurement, and the performance of the previously derived parameterizations was assessed. The nighttime CINO₂ correlated with particulate chloride and the mass concentration of fine particles (most likely due to aerosol surface area) suggested that the CINO₂ formation was limited by the N₂O₅ uptake at this site. By examining the relationship between particulate chloride and other species, we implied that anthropogenic emissions (e.g., biomass burning) rather than sea salt particles dominate the origin of particulate chloride, although the site was only about 100 km away from the ocean. A box model with detailed chlorine chemistry is used to investigate the impacts of CINO₂ chemistry on atmospheric oxidation. Model simulations showed that the chlorine radical liberated by CINO₂ photolysis during the next day had a slight increase in concentrations of OH, HO₂, and RO₂ radicals, as well as minor contributions to RO₂ radical and O₃ formation (<5%, on daytime average), in all the three types of air masses. Relatively high contributions were observed in Type A and B. The overall low contributions of CINO₂
to atmospheric oxidation are consistent with those reported recently from wintertime observations in China (including Shanghai, Beijing, Wangdu, and Mt. Tai). This may be attributed to the following: (1) relatively low particle mass concentration limited ClNO₂ formation; (2) other reactions channels, like nitrous acid (HONO), oxygenated volatile organic compounds (OVOCs, including formaldehyde), and ozone photolysis had a more significant radical formation rate during the ozone pollution episodes and weakened the ClNO₂ contribution indirectly. The results provided scientific insights into the role of nighttime chemistry in photochemical pollution under various scenarios in coastal areas.

1 Introduction

Chlorine radical is an important oxidant in the tropospheric besides OH radicals, NO₃ radicals, and ozone (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015; X. Wang et al., 2019), which alters the fate of many atmospheric compositions, including oxidants, reactive nitrogen compounds, volatile organic compounds (VOCs), and other halogens. The Cl radical is much more reactive than OH concerning certain VOCs (e.g., alkanes) by a few orders of magnitude for the reaction rate constant (Atkinson and Arey, 2003; Atkinson et al., 2006). Therefore it contributes to atmospheric oxidation capacity considerably in the troposphere despite low concentrations. For example, the global model showed about 20% of ethane and 14% of propane oxidation are attributed to chlorine chemistry at the global scale (X. Wang et al., 2019). Modeling simulations also demonstrated that chlorine chemistry enhanced oxidative degradation of VOCs by > 20% at some locations (Sarwar et al., 2014).

Photolysis of ClNO₂ (Reaction R1) is a major source of the tropospheric chlorine radical (Thornton et al., 2010; Simpson et al., 2015); other chlorine radical sources include the reaction of HCl with OH (Riedel et al., 2012; Eger et al., 2019) and photolysis of Cl₂ and other halogen compounds like ICl and BrCl (Peng et al., 2021). Tropospheric ClNO₂ is not only a critical chlorine activation precursor but also a nocturnal reservoir of reactive nitrogen, which is mainly formed by N₂O₅ heterogeneous reaction on chlorine-containing particles with a branching ratio at nighttime (Reaction R2).

\[
\text{ClNO}_2 + hv \rightarrow \text{Cl} + \text{NO}_2, \quad \text{(R1)}
\]

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O}/\text{Cl}^- \rightarrow \gamma\text{ClNO}_2 + (2 - \gamma)\text{NO}_3^-, \quad \text{(R2)}
\]

where \(\gamma\) represents the yield of ClNO₂. This mechanism was firstly proposed by Finlayson-Pitts et al. (1989) through detecting the products of N₂O₅ uptake on NaCl particles. Given this reaction, the formation of ClNO₂ can be influenced by the N₂O₅ uptake (such as N₂O₅ uptake probabilities and aerosol surface area) as well as the production yield of ClNO₂.

The N₂O₅ uptake coefficient, \(\gamma\)(N₂O₅), has been reported as highly varied under tropospheric conditions (Brown and Stutz, 2012). Both field and laboratory studies reveal that this process can be affected by ambient temperature, relative humidity (Mozurkewich and Calvert, 1988; Mentel et al., 1999; Hallquist et al., 2003) and chemical compositions (such as the content of nitrate, liquid water, chloride, and organics) (Mentel et al., 1999; Brown et al., 2006; Bertram and Thornton, 2009; Gaston et al., 2014; McDuffie et al., 2018b; Tang et al., 2014; Anttila et al., 2006), as well as particle morphology (Mielke et al., 2013; Zong et al., 2021). Until now, the key factors that control N₂O₅ uptake coefficients in the different environments have not been well understood. ClNO₂ yield is also highly varied subject to the liquid water and chloride content in the aerosol (Behnke et al., 1997; Roberts et al., 2009; Bertram and Thornton, 2009). Several studies have demonstrated that the ClNO₂ yield is also affected by other factors like aerosol sulfate (Staudt et al., 2019) and organics (Rydert et al., 2015; Tham et al., 2018; McDuffie et al., 2018a). However, the comprehensive quantitative relationship of these factors in controlling the yield still has large uncertainties. These gaps in parameterization of N₂O₅ uptake coefficients and ClNO₂ yield result in being challenging to accurately predict ClNO₂ and particulate nitrate production.

Osthoff et al. (2008) and Thornton et al. (2010) directly observed elevated ClNO₂ in the coastal and inland US respectively by chemical ionization mass spectrometers (CIMSs). They have shed light on the significance of ClNO2 photolysis in launching the radical chemistry during the morning time and also affecting halogen chemistry and reactive nitrogen cycling. Large amounts of chlorine radicals are liberated through the photolysis of nocturnal accumulated ClNO₂ (Reaction R1), which oxidizes VOCs and produces peroxy radicals (RO₂) to initiate the daytime radical cycling in the morning, when other radical sources, like ozonolysis and photolysis of O₃, HONO, and HCHO, are still weak (Osthoff et al., 2008). The impacts of ClNO₂ chemistry on the primary source of radicals and ozone formation comprise a critical topic, the answer to which is very helpful to narrow the gap of the missing primary source of RO₂ and improve our knowledge of the current ozone pollution mechanism (Tan et al., 2017; Tham et al., 2016). Model simulation has highlighted ClNO₂ chemistry could increase mean daily maximum 8 h ozone by up to 7.0 ppbv in some areas in the Northern Hemisphere (Sarwar et al., 2014). The large contribution was also confirmed in the southern California region by a box model study (Riedel et al., 2014). In addi-
tion, global model simulation showed ClNO$_2$ chemistry increases wintertime ozone by up to 8 ppb over polluted continents (X. Wang et al., 2019). Particularly, previous modeling results have also highlight the importance of ClNO$_2$ chemistry in enhancing O$_3$ production in China (Li et al., 2016; X. Yang et al., 2022).

Several field studies have reported the measurement of ClNO$_2$ in varied environments in the past decade (Riedel et al., 2012; Young et al., 2012; Mielke et al., 2013; Riedel et al., 2013; Bannan et al., 2015; Faxon et al., 2015; Mielke et al., 2015; Phillips et al., 2016; Bannan et al., 2017; X. F. Wang et al., 2017; Z. Wang et al., 2017; Le Breton et al., 2018; McDuffie et al., 2018a; Yun et al., 2018a; Zhou et al., 2018; Bannan et al., 2019; Eger et al., 2019; Haskins et al., 2019; Jeong et al., 2019; Xia et al., 2020, 2021; Tham et al., 2016, 2014; Wang et al., 2016; Phillips et al., 2012; Lou et al., 2022; Sommariva et al., 2018), in which the maximum ClNO$_2$ up to sub-ppbv (parts per billion by volume) to several ppbv was reported, indicating its ubiquitous presence worldwide and a broad atmospheric impact over various regions. During the CalNex-LA campaign 2010, ClNO$_2$ was measured at a ground site, on a research vessel, and on an aircraft platform, which depicted a full picture of the abundance of ClNO$_2$ and confirmed its large impacts on atmospheric chemistry in both urban and coastal regions in California (Riedel et al., 2012; Young et al., 2012; Mielke et al., 2013). Recently, Wang et al. (2016) used a box model to simulate the chemical evolution of the plume after leaving the observation site in Hong Kong and showed ClNO$_2$ chemistry had a following-day enhancement of the ozone peak and daytime ozone production rate by 5%–16% and 11%–41%, along with a large increase of OH, HO$_2$, and RO$_2$ concentration especially in the morning. While Xia et al. (2021) and Lou et al. (2022) reported winter measurements of ClNO$_2$ in northern and eastern China respectively, they both showed moderate ClNO$_2$ levels and relatively small contributions of ClNO$_2$ chemistry to radical source and ozone enhancement on campaign average. These results are quite different than those of the summertime in China (Tham et al., 2016; Wang et al., 2016; Tan et al., 2017) and highlight the large variation of ClNO$_2$ chemistry influenced by temporal spatial distribution.

Despite its likely importance to the regional atmospheric oxidation and air quality, investigations of ClNO$_2$ chemistry in China remain relatively sparse. There have been several field measurements of ClNO$_2$ conducted in China in recent years, but considering the large diversities of air mass in inland and coastal regions in China, more fieldwork and model works are needed to gain more insights into the ClNO$_2$ chemistry in various atmospheric environments and assess its atmospheric impacts. Until now, only a few field measurements of ClNO$_2$ have been reported in the Pearl River Delta (PRD) region (Tham et al., 2014; Wang et al., 2016; Yun et al., 2018a), and only Wang et al. (2016) reported a comprehensive analysis of the impact of ClNO$_2$ chemistry on radical and ozone formation in 2013 as mentioned before. To understand the increasing O$_3$ problem in recent years (T. Wang et al., 2019) and examine the role of ClNO$_2$ chemistry in O$_3$ formation in PRD, we measured ClNO$_2$, N$_2$O$_5$, and other related parameters at a regional site in PRD during a severe photochemical pollution season in 2019. The abundance, formation, and variation during different air mass patterns are well characterized. The factors impacting its formation are diagnosed. Finally, the contribution of chlorine radicals liberated by ClNO$_2$ photolysis on the daytime radical chemistry, as well as ozone formation, is comprehensively assessed by a box model coupled with detailed chlorine chemistry.

2 Method

2.1 Measurement site

This campaign was conducted at the Guangdong Atmospheric Supersite of China, which is located on the top of a mountain (≈ 60 m a.s.l.) in Heshan (22.728°N, 112.929°E), Jiangmen, Guangdong Province (S. Yang et al., 2022). This site was in the western Pearl River Delta with no major industries in the surroundings but with some farmland and a few residents living at the hill foot. The traffic is far away from this site and is believed to have little influence on the sampling. The anthropogenic activity is much lower than the urban regions like Guangzhou, but the air quality is often influenced by neighboring cities, especially the outflow of air masses from the regions in the north and northeast. Therefore, the air masses sampled at this site are sometimes representative of the urban pollution from the center of PRD. There were once many atmospheric intensive studies conducted on the site to study the air pollution in PRD (Tan et al., 2019; Yun et al., 2018b). In this study, the instruments were located on the top floor of the measurement building with inlets approximately 15 m above the ground. The data presented in the study were collected from 27 September to 17 November 2019, during which photochemical pollution occurred frequently (S. Yang et al., 2022). Time is given as CNST (Chinese national standard time = UTC+8 h). During the campaign, sunrise was approximately at 06:00 and sunset was approximately at 18:00 CNST.

2.2 Instrument setup

A comprehensive suite of instrumentation is overviewed and listed in Table 1. An iodide-adduct time-of-flight chemical ionization mass spectrometer (ToF-CIMS) with the Filter Inlet for Gas and AEROsols (FIGAERO) was applied to measure ClNO$_2$ and N$_2$O$_5$ along with other oxygenated organic species (Ye et al., 2021; Z. Wang et al., 2020). In brief, the gas-phase species were measured via a 2 m long, 6 mm outer-diameter polyfluorooalkoxy (PFA) inlet while the particles were simultaneously collected on a Teflon filter via a separate 2 m long, 10 mm outer-diameter copper tubing in-
let; both had flow rates of 2 L min$^{-1}$ with a drainage flow of 20 L min$^{-1}$. The gas phase was measured for 25 min at 1 Hz, and the FIGAERO instrument was then switched to place the filter in front of the ion molecule region; it was then heated incrementally to 200$^\circ$C to desorb all the mass from the filter to be measured in the gas phase, which resulted in high-resolution thermograms. ClNO$_2$ and N$_2$O$_5$ are measured as the iodide-adduct ions at $m/z$ 207.867 (IClNO$_2^-$) and $m/z$ 234.886 (IN$_2$O$_5^-$) respectively in the ToF-CIMS. The measurement background and sensitivities for detecting ClNO$_2$ and N$_2$O$_5$ with the dependence of water content were quantified (see Appendix). The limit of detection (LOD) for ClNO$_2$ and N$_2$O$_5$ was 4.3 and 6.0 pptv in 1 min time resolution respectively, with an uncertainty of $\sim$30%.

Sub-micron aerosol composition (PM$_1$) was measured by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006). The soluble ions of sodium and potassium were measured by a commercial instrument (GAC-IC) equipped with an aerosol collector and detected by ion chromatography (Dong et al., 2012). The particle number size distribution (PNSD) were measured by a scanning mobility particle sizer (SMPS, TSI 3938). The aerosol surface area was calculated based on the size distribution measurement and corrected to wet-particle state by a hygroscopicity growth factor, with a total uncertainty of determining wet aerosol surface areas of $\sim$30% (Liu et al., 2013). VOCs were measured by proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) (Wu et al., 2020; He et al., 2022) and an automated gas chromatograph equipped with a mass spectrometer or flame ionization detectors (GC-FID/MS). A commercial instrument (Thermo Electron model 42i) was used to monitor NO$_x$. O$_3$ was measured by a commercial instrument using ultraviolet (UV) absorption (Thermo Electron 49i). PM$_{2.5}$ was measured by a tapered element oscillating microbalance (TEOM, 1400A analyzer). SO$_2$ and CO were measured by commercial instruments (Thermo Electron 43i and 48i). In addition, the meteorological parameters were available during the measurement. Photolysis frequencies were determined by a spectroradiometer (Bohn et al., 2008). The aerosol liquid water content (ALWC) is calculated from the ISORROPIA-II thermodynamic equilibrium model (Clegg et al., 1998). We used the reverse mode in ISORROPIA-II with the input of watersoluble ions along with ambient temperature ($T$) and relative humidity (RH). Given the high RH in this campaign, we ran the model by assuming aerosol phases were metastable.

2.3 Box model setup

A zero-dimensional chemical box model constrained by the field campaign data was applied to simulate the ClNO$_2$ chemistry. The box model was based on the Regional Atmospheric Chemical Mechanism version 2 (RACM2) described in Goliff et al. (2013), and a chlorine-related chemical mechanism was added (H. Wang et al., 2017b; Tan et al., 2017).

Briefly, chlorine chemistry was adapted to RACM2 from the modifications to the Master Chemical Mechanism (Xue et al., 2015), and the oxidation products from reactions between lumped VOC species and chlorine radicals were adapted from those of OH oxidation from RACM2. $j$(ClNO$_2$) was calculated according to the NASA Jet Propulsion Laboratory (JPL) recommendation based on the work by Ghosh et al. (2012). The impact of O$_3$ by ClNO$_2$ chemistry was assessed by differencing the results of two scenarios with and without the constraints of the observed ClNO$_2$ in the model simulation. For the reaction rate constant of the lumped species with Cl, the fastest value from different species was used to represent the upper limit of the impact of chlorine chemistry. It should be noted that the setting will lead to over-estimation of the contributions from ClNO$_2$ chemistry. The model was constrained by the observed ClNO$_2$, NO$_2$, O$_3$, CO, VOCs (assignment to RACM2), photolysis frequencies, ambient temperature, and pressure. The model runs were from 29 September to 17 November 2019 with most of the measurement data accounted for and with a 2 d spin-up. The constant lifetime corresponds to a deposition velocity of 1.2 cm s$^{-1}$ with an assumed boundary layer height of 1000 m used for the input trace gases, and the model-generated species were set to a 24 h lifetime due to the loss caused by the dry deposition (Lu et al., 2012). The input data were averaged and interpolated to 1 h resolution.

3 Results and discussions

3.1 Overview of measurement

Figure 1 shows the time series of ClNO$_2$ and relevant trace gases, particles, and meteorological parameters during the measurements. In this campaign, the meteorological condition featured a high temperature (24.7 $\pm$ 3.8 $^\circ$C), high humidity (62.1 % $\pm$ 15.6 %), and low wind speed (1.5 $\pm$ 0.8 m s$^{-1}$), and the dominant airflow was from the north and northwest. Compared to previous measurements at the same site in January 2017 (Yun et al., 2018b), the temperature was higher and relative humidity was lower during the measurements. The average and maximum concentration of particulate matter (PM$_{2.5}$) was 47.6 $\pm$ 19.3 and 138 µg m$^{-3}$ respectively, which is significantly lower than that observed in January 2017, with a maximum up to 400 µg m$^{-3}$. The dominant air pollutant was O$_3$ with an hourly campaign maximum and average mean daily maximum 8 h O$_3$ (MDA8 O$_3$) of 152.8 and 75.2 $\pm$ 20.9 ppbv respectively. There was 27 d out of 53 d with the hourly maximum of O$_3$ exceeding the Chinese national air quality standard (200 µg m$^{-3}$, equivalent to 93 ppbv), suggesting severe ozone pollution during the measurement period in the PRD region. NO$_2$ concentration was also elevated with 21.0 $\pm$ 10.4 ppbv on campaign average. The concurrent high O$_3$ and NO$_2$ made large nitrate radical production rates occur with a daily average of 2.5 $\pm$ 2.1 ppbv h$^{-1}$ (median,
Table 1. Summary of the information about observed gas and particle parameters during the campaign.

| Species          | Limit of detection | Methods                      | Accuracy |
|------------------|--------------------|-------------------------------|----------|
| N$_2$O$_5$       | 6.0 pptv (3σ, 1 min) | FIGAERO-ToF-CIMS              | ±30%     |
| ClNO$_2$         | 4.3 pptv (3σ, 1 min) | FIGAERO-ToF-CIMS              | ±30%     |
| NO               | 60 pptv (2σ, 1 min)  | Chemiluminescence             | ±20%     |
| NO$_2$           | 0.3 ppbv (2σ, 1 min) | Catalytic convert             | ±20%     |
| O$_3$            | 0.5 ppbv (2σ, 1 min) | UV photometry                 | ±5%      |
| VOCs             | 0.1 ppbv (5 min)    | PTR-ToF-MS                    | ±30%     |
| VOCs             | 20–300 pptv (1 h)   | GC-FID/MS                     | ±20%     |
| PM$_{2.5}$       | 0.1 µg m$^{-3}$ (1 min) | TEOM                          | ±5%      |
| CO               | 4 ppbv (5 min)      | IR photometry                 | ±5%      |
| SO$_2$           | 0.1 ppbv (1 min)    | Pulsed UV fluorescence        | ±10%     |
| HCHO             | 25 pptv (2 min)     | Hantzsch fluorimetry          | ±5%      |
| PNSD             | 14–700 nm (4 min)   | SMPS                          | ±20%     |
| Aerosol composition | < 0.16 µg m$^{-3}$ (30 min) | GAC-IC                        | ±30%     |
| PM$_1$ components | 0.15 µg m$^{-3}$ (4 min) | HR-ToF-AMS                   | ±30%     |
| Photolysis frequencies | Varies with species (20 s) | Spectroradiometer   | ±10%     |

The campaign maximum NO$_3$ production rate was observed at up to 18.6 ppbv h$^{-1}$ in the afternoon on 11 November 2019. At night, the nitrate radical production rate was $1.8 \pm 1.5$ ppbv h$^{-1}$ on campaign average (median, 1.4 ppbv h$^{-1}$). However, the high NO$_3$ production rate did not mean high concentrations of NO$_3$, N$_2$O$_5$, and ClNO$_2$ in the atmosphere, as the concentration was affected by both their sources and their sinks.

N$_2$O$_5$ existed at a moderate concentration for most nights, with the daily nocturnal peaks ranging from < 100 to 1180 pptv and a nocturnal average of 64 ± 145 pptv. During the nights from 27–30 September 2019, the N$_2$O$_5$ concentration was significantly higher than other nights. The NO$_3$ lifetime, calculated by steady-state method (Brown et al., 2003), was much longer in those four nights than other nights, implying a relatively weak sink of NO$_3$–N$_2$O$_5$ for the first four nights. The lifetime of NO$_3$ was < 1 min in general (except the first four nights), indicating active NO$_3$ chemistry at this site. The NO$_3$ concentration was calculated assuming the thermal equilibrium of NO$_2$–NO$_3$–N$_2$O$_5$, with a possible lower bias caused by the equilibrium coefficient for reversible reactions of NO$_3$ and N$_2$O$_5$ ($K_{eq}$) (Chen et al., 2022). Figure 1 shows the variation in calculated NO$_3$ coincided with N$_2$O$_5$. Elevated NO$_3$ occurred on the first four nights with a maximum of 90 ppbv (1 h time resolution), which is comparable with the reported NO$_3$ level at other sites in the Pearl River Delta (Wang and Lu, 2019; Brown et al., 2016). ClNO$_2$ showed a clear diurnal variation with high levels during the night. The nocturnal average and hourly maximum were 198 ± 232 and 1497 pptv respectively. The abundances of ClNO$_2$ and N$_2$O$_5$ are lower than those observed at the same site in 2017, with high NO$_3$ and the highest value ever observed of ClNO$_2$ of 3358 and 8324 pptv (1 min time resolution) respectively (Yun et al., 2018b). The difference in ClNO$_2$ levels between the two campaigns conducted in 2017 and 2019 may be caused by the aerosol loading. High particulate chloride ion was observed in the site with 0.74 ± 1.33 µg m$^{-3}$ on nocturnal average, which was higher at night with a peak in the second half of night and decrease in daytime.

3.2 Characterization of pollutants in different air masses

We noticed the air mass is highly varied during the measurements. For example, during the period of 2–5 October, the observed ozone and ClNO$_2$ were much lower than other days; while during the period of 11–13 November, the air masses were much polluted with high O$_3$, PM$_{2.5}$, and ClNO$_2$. We therefore plotted the backward trajectories of the 24 h history of air masses arriving at the measurement site at 500 m a.m.s.l. height at 00:00, 06:00, 12:00, and 18:00 day by day. The measurement period was separated into three patterns meteorologically according to the analysis of backward trajectories. Table 2 lists detailed information about the air mass classification. The air masses from the northeast (and north) were the dominant ones with a total of 37 d, which were characterized with the outflow of the center city clusters of PRD and those from inland through long-distance transport. We checked the pollutants of the air masses from PRD and north out of PRD (e.g., Hunan or Jiangxi Province), and no significant difference was found. Therefore, we merged the two inland air masses as Type A. The second type was coastal or offshore from the east and southeast (Type B), which features the outflow of coastal cities like Shenzhen and Hong Kong occurred on 12 d in total. The third type was clean air mass from the South China Sea (4 d, Type C). Figure 2 shows three cases of each air mass mentioned above.

The mean diurnal profiles of measured NO$_2$, O$_3$, N$_2$O$_5$, and ClNO$_2$; the particle chloride content; and the ratio of chloride to sodium in the three types of air masses are shown.
Figure 1. Time series of $\text{N}_2\text{O}_5$, $\text{ClNO}_2$, and relevant parameters. The dotted grey line in the $\text{O}_3$ panel denotes Chinese national air quality standard for hourly maximum $\text{O}_3$ (200 µg m$^{-3}$, equivalent to 93 ppbv). $\text{NO}_3$ radical is calculated based on a thermal equilibrium with measured $\text{NO}_2$ and $\text{N}_2\text{O}_5$.

Table 2. The detailed information of three air mass types.

| Air mass type           | Periods                                               | Days    |
|-------------------------|-------------------------------------------------------|---------|
| Type A: inland air from northeast | 26 September–1 October; 10 October; 11–20 October; 24 October–10 November; 14–15 November | 37 (69.8 %) |
| Type B: coast air from east | 6–7 October; 9–10 October; 21–23 October; 11–13 November; 16–17 November | 12 (22.6 %) |
| Type C: marine air from south | 2–5 October                                           | 4 (7.5 %) |

in Fig. 3, with a detailed summary of related parameters in nocturnal medians listed in Table 3. High levels of $\text{NO}_2$ and $\text{O}_3$ were observed in Type A and B air masses, with a small difference of $\text{NO}_2$ diurnal variation during the second half of the night. In comparison, the two pollutants in type C were much lower. If we focus on the abundance at night, we find a large difference in the NO$_2$ level with a sequence Type A $>$ Type B $>$ Type C, which results in the same sequence of NO$_3$ productions in different air masses. The nocturnal NO$_2$ seems to be a good indicator of the level of pollution, and nocturnal CO, PM$_{2.5}$, and SO$_2$ also followed this order with highest concentration in Type A. These results indicate that the most polluted air mass came from the inland urban regions of PRD.

Given the particulate chloride precursor of ClNO$_2$, we examined its diurnal variations in the three air mass types. The highest level of Cl$^-$ was found in Type B, followed by Type A and Type C (also at night). Although the diurnal profile of Cl$^-$ in the three types is similar, the increasing rate of Cl$^-$ during the second half of the night in Type A is much slower than those in coastal and offshore air masses. This implies a different source of chloride, which will be further discussed in Sect. 3.4. $\text{N}_2\text{O}_5$ was observed with moderate concentration in the Type A air mass throughout the night, with a nocturnal peak of 152.4 pptv between 20:00–
Figure 2. Three typical cases with air mass from different regions on 29 September, 12 November and 4 October respectively. Backward trajectory of 24 h history of air masses arriving at the measurement site with 500 m height at 00:00, 06:00, 12:00, and 18:00.

Figure 3. Mean diurnal profiles of $\text{N}_2\text{O}_5$, ClNO$_2$, and relevant parameters in the three types of air masses.

Table 3. Statistics results (median ± standard deviation) of the related parameters in the three types of air masses (from 18:00 to 06:00 CNST).

| Air mass | Type A       | Type B       | Type C       |
|----------|--------------|--------------|--------------|
| RH (%)   | 67.0 ± 11.9  | 78.0 ± 10.9  | 79.0 ± 9.1   |
| $T$ ($^\circ$C) | 22.8 ± 3.0  | 23.3 ± 2.2  | 25.6 ± 1.9   |
| ClNO$_2$ (pptv) | 131.0 ± 202.8 | 162.0 ± 310.1 | 16.7 ± 21.2 |
| $\text{N}_2\text{O}_5$ (pptv) | 17.8 ± 164.9 | 6.3 ± 64.6  | 2.8 ± 9.3   |
| Cl$^-$ (µg m$^{-3}$) | 0.41 ± 1.11  | 0.56 ± 1.85  | 0.33 ± 0.51 |
| PM$_{2.5}$ (µg m$^{-3}$) | 53.0 ± 18.8 | 41.0 ± 21.8 | 32.0 ± 10.2 |
| SO$_2$ (ppbv) | 5.0 ± 4.7  | 3.4 ± 11.4  | 3.4 ± 4.7   |
| Na$^+$ (µg m$^{-3}$) | 0.12 ± 0.07  | 0.18 ± 0.09 | 0.09 ± 0.03 |
| $P$(NO$_3$) (ppbv h$^{-1}$) | 1.60 ± 1.49 | 1.39 ± 1.50 | 0.69 ± 0.49 |
| NO$_2$ (ppbv) | 24.8 ± 10.9 | 18.1 ± 6.2 | 11.2 ± 5.8 |
| O$_3$ (ppbv) | 24.4 ± 21.8 | 29.5 ± 23.1 | 22.4 ± 15.2 |
| CO (ppbv) | 540.3 ± 122.3 | 448.4 ± 130.7 | 367.5 ± 89.8 |

21:00, while only a little $\text{N}_2\text{O}_5$ occurred in the first half of the night in Type B and C with a peak of 75.9 and 13.6 pptv respectively. The concentration difference may be attributed to two aspects. Firstly, the difference in $P$(NO$_3$) results in more $\text{N}_2\text{O}_5$ produced in Type A. Secondly, compared with the air mass from coastal or offshore regions, the nocturnal temperature and RH condition from type A is much lower, and the loss of $\text{N}_2\text{O}_5$ may be faster in Type B and C than in Type A. The nocturnal median RH in Type A reached up to 67 %, while it reached 78 % and 79 % in Type B and Type C, suggesting a favorable condition for heterogeneous hydrolysis of $\text{N}_2\text{O}_5$ for all the three air mass types. The elevated ClNO$_2$ was observed in Type A and B with a nocturnal peak of 273.6 and 479.8 pptv respectively. Significantly less ClNO$_2$ was observed in the Type C air mass with a peak of 82.6 pptv. The reason for the different levels of ClNO$_2$ observed in the three air masses types is discussed in Sect. 3.4.
3.3 \( \text{N}_2\text{O}_5 \) uptake coefficient and ClINO\(_2\) yield

In line with previous studies, we estimate the \( \text{N}_2\text{O}_5 \) uptake coefficient and ClINO\(_2\) yield using the measurements of \( \text{N}_2\text{O}_5 \), ClINO\(_2\), and particulate nitrate (Phillips et al., 2016; Wang et al., 2018; Tham et al., 2018). By assuming both the nocturnal enhancement of nitrate and ClINO\(_2\) are mainly attributed to \( \text{N}_2\text{O}_5 \) uptake processes, ClINO\(_2\) yield can be solely derived by the regression analysis of ClINO\(_2\) versus particulate nitrate (Wagner et al., 2012; Riedel et al., 2013). The \( \varphi \text{ClINO}_2 \) can then be obtained by the fitted regression slope (\( S \), Eq. 1) and named as the regression method.

\[
\varphi = \frac{2S}{(S+1)}
\] (1)

Combining the data of \( \text{N}_2\text{O}_5 \) and aerosol surface area, the increase in ClINO\(_2\) and nitrate can be simulated simultaneously by setting the input of the \( \text{N}_2\text{O}_5 \) uptake coefficient and ClINO\(_2\) yield (named as the simulation method). The optimal \( \text{N}_2\text{O}_5 \) uptake coefficient and ClINO\(_2\) yield are obtained simultaneously by adjusting the two parameters until the simulation reproduces the observed increase of ClINO\(_2\) and nitrate (Phillips et al., 2016; Xia et al., 2020; Tham et al., 2018). This analysis assumes only the \( \text{N}_2\text{O}_5 \) uptake process dominates the increase of ClINO\(_2\) and nitrate, and other physicochemical processes like vertical transportation and deposition are less important. This method requires the air mass in the analysis duration time to be relatively stable and less affected by emission and transportation. In addition, it is not valid in the case with negative changes of ClINO\(_2\) and nitrate.

The following selection criteria are set to pick out the suitable plumes to meet the assumptions. Firstly, the consistent increasing trends of ClINO\(_2\) and NO\(_3^-\) and clear correlation between them during the analysis duration should be observed with a regression coefficient threshold of 0.5, which indicates the two products have the same source. Secondly, the increase in nitrate should be accompanied by an equivalent or faster increase in ammonium to ensure insignificant degassing of HNO\(_3\) to the atmosphere. The observational data were averaged to 30 min for the following analysis; the time period of each derivation ranges from 2.5 to 10 h. Figure 4 depicts an example of the derivation on 5 November 2019, the stable \( S_a \) indicating a stable air mass during the analysis period. And the prediction reproduces well the observed increase in ClINO\(_2\) and NO\(_3^-\).

During this campaign, we carefully identified 20 plumes with clear correlations between ClINO\(_2\) and particulate nitrate by the slope method \( (R^2 \geq 0.5) \). As shown in Table 4, the derived ClINO\(_2\) yield varied from 0.13 to 1.00 with a median of 0.45 ± 0.22 (mean value of 0.44). In the 20 plumes, we derived the \( \text{N}_2\text{O}_5 \) uptake coefficient and ClINO\(_2\) for 12 cases in total. The results for the other eight nights were not valid due to the lack of \( S_a \) data (four nights), or unreasonable high results due to the observed low \( \text{N}_2\text{O}_5 \) concentration near the detection limit biased the simulations. We show good consistency of derived ClINO\(_2\) yields by the two different methods. The estimated \( \text{N}_2\text{O}_5 \) uptake coefficient showed a large variation and ranged from 0.0019 to 0.077 with a median of 0.0195 ± 0.0288 (mean value of 0.0317). The estimated \( \gamma \text{N}_2\text{O}_5 \) is within the range determined by previous field studies (Tham et al., 2018). Specifically in China, the average level of \( \gamma \text{N}_2\text{O}_5 \) is comparable with those reported in urban Beijing (H. Wang et al., 2017a, 2018), Wangdu (Tham et al., 2018), and Jinan (X. F. Wang et al., 2017) during the summertime but systematically higher than those determined in China in wintertime (Xia et al., 2021; H. Wang et al., 2020; Brown et al., 2016), except in the case reported on the urban canopy of Beijing (Chen et al., 2020). McDuffie et al. (2018a) summarized the reported \( \varphi \text{ClINO}_2 \) based on the observations, and we showed that the estimated average \( \varphi \text{ClINO}_2 \) in this study is at the middle to upper end of the values reported globally (Xia et al., 2021; McDuffie et al., 2018a). Due to the limited data points, we cannot distinguish the difference of \( \gamma \text{N}_2\text{O}_5 \) between the three air mass patterns. The ClINO\(_2\) yields in Type A are slightly lower than those in Type B with an average of 0.41 and 0.47 respectively.

To gain insight into the factors governing the \( \text{N}_2\text{O}_5 \) uptake and ClINO\(_2\) formation processes, the estimated \( \gamma \text{N}_2\text{O}_5 \) and \( \varphi \text{ClINO}_2 \) were compared with those predicted from complex laboratory-derived and field-derived parameterizations. An aqueous inorganic iconic reaction mechanism was once raised by Bertram and Thornton (2009) and established a volume-limited parameterization by considering the aerosol
The derived $N_2O_5$ uptake coefficient and CINO$_2$ yields at each night. NaN means not a number.

| No. | Period                  | $\gamma_{N_2O_5}$ | $\varphi_{CINO_2}$ | $\varphi_{CINO_2}$ | $r^{2b}$ | Type |
|-----|-------------------------|--------------------|---------------------|---------------------|----------|------|
| 1   | 2 October 01:00–06:00   | NaN                | NaN                 | 0.13                | 0.90     | C    |
| 2   | 2 October 23:00–06:00   | NaN                | NaN                 | 0.25                | 0.90     | C    |
| 3   | 11 October 01:00–04:00  | NaN                | NaN                 | 0.65                | 1.00     | B    |
| 4   | 14 October 23:00–04:00  | 0.017              | 0.28                | 0.23                | 0.56     | A    |
| 5   | 18 October 18:00–21:00  | 0.0059             | 0.42                | 0.40                | 0.90     | A    |
| 6   | 20 October 20:30–23:00  | 0.045              | 0.44                | 0.47                | 0.71     | A    |
| 7   | 21 October 20:30–01:00  | 0.061              | 0.52                | 0.54                | 0.90     | B    |
| 8   | 22 October 22:30–05:00  | 0.066              | 0.58                | 0.61                | 0.62     | B    |
| 9   | 24 October 22:00–06:00  | 0.065              | 0.26                | 0.23                | 0.74     | A    |
| 10  | 25 October 21:00–02:00  | 0.077              | 1.00                | 1.00                | 0.92     | A    |
| 11  | 28 October 21:00–04:00  | NaN                | NaN                 | 0.15                | 0.74     | A    |
| 12  | 1 November 21:00–23:30  | 0.022              | 0.35                | 0.32                | 0.83     | A    |
| 13  | 2 November 22:00–00:30  | NaN                | NaN                 | 0.29                | 1.00     | A    |
| 14  | 3 November 18:00–06:00  | 0.0031             | 0.52                | 0.50                | 0.92     | A    |
| 15  | 4 November 22:00–06:00  | 0.0019             | 0.45                | 0.47                | 0.86     | A    |
| 16  | 8 November 00:00–06:00  | 0.0097             | 0.34                | 0.32                | 0.85     | A    |
| 17  | 10 November 00:00–04:00 | NaN                | NaN                 | 0.59                | 0.80     | A    |
| 18  | 11 November 22:00–04:00 | NaN                | NaN                 | 0.53                | 0.50     | B    |
| 19  | 12 November 22:00–04:00 | NaN                | NaN                 | 0.42                | 0.62     | B    |
| 20  | 13 November 21:00–00:00 | 0.0070             | 0.70                | 0.75                | 0.92     | B    |

$^a$ The values of $\gamma_{N_2O_5}$ and $\varphi_{CINO_2}$ are derived by simulation method. $^b$ The $\varphi_{CINO_2}$ and the correlation coefficient ($r^2$) between CINO$_2$ and particulate nitrate are derived by regression method; the data were filtered with a correlation coefficient obtained from linear fitting threshold of 0.5.

Figure 5b shows that all the predicted CINO$_2$ yield based on the abovementioned parameterizations overestimated the observations. The performance of the parameterization schemes of BK97 and BT09 based on the model aerosol conditions, with an overestimation up to $\sim 100\%$, is expected and consistent with previous studies, which may be caused by the unaccounted for potentially competitive effect of other species like organics and sulfate for the NO$_2^+$ intermediate.
the yields with aerosol organic or sulfate, as well as the RH of chloride to water confirming the dependence found in labeling the mass ratio and fraction in PM only weakly correlated with the content of chloride (including the mass ratio and fraction in PM$_{2.5}$) and the molar ratio of chloride to water confirming the dependence found in laboratory studies. However, we did not find the dependence of the yields with aerosol organic or sulfate, as well as the RH and water alone in the campaign, implying the ClNO$_2$ yield mechanism is much more complicated than the laboratory conditions.

3.4 The factors influencing ClNO$_2$ formation

The ClNO$_2$ formation can be largely affected by the budget of NO$_3$–N$_2$O$_5$ and N$_2$O$_5$ uptake processes. The variation of NO$_3$ loss by VOC and NO activates the NO$_3$ loss distribution by N$_2$O$_5$ uptake and ClNO$_2$ formation indirectly. Figure 7 shows the correlation between the daily median ClNO$_2$ and mass concentration of chloride, PM$_{2.5}$, and the NO$_3$ production rate for the three types of air masses. Due to the limited dataset of Type C, the correlation analysis may not make sense; therefore, we did not take Type C into consideration in detailed discussion. We show that the mass concentration of chloride also showed a correlation coefficient with ClNO$_2$ by 0.66 and 0.31 for Type A and B respectively. Furthermore, the mass concentration of PM$_{2.5}$ correlated reasonably with the ClNO$_2$ formation with the correlation coefficient of 0.39 and 0.62 for Type A and B respectively. However, the levels of ClNO$_2$ demonstrate little relationship with the nitrate production rate. This is quite different from the results observed in the United Kingdom, where the ClNO$_2$ levels are mainly controlled by NO$_2$ and O$_3$, rather than by the N$_2$O$_5$ uptake processes (Sommariva et al., 2018).

The low correlation between the ClNO$_2$ and NO$_3$ production rates is within expectations. In general, the production of nitrate radical controls the budget of N$_2$O$_5$; if N$_2$O$_5$ uptake dominated the sink of NO$_3$, as a result, the N$_2$O$_5$ uptake and its products would show good correlation with NO$_3$ production rate. But in fact, NO$_3$ loss can also be affected by other loss pathways, like the reactions with NO and VOCs. In many cases, the NO$_3$ loss is dominated by VOC or NO, which means the ClNO$_2$ formation is suppressed. If the two loss pathways were highly varied due to irregular emissions, then the relationship between ClNO$_2$ and NO$_3$ production rate would be less correlated. We confirmed large variations of NO and VOC (not shown) on hourly and daily scales, which means the proportion of N$_2$O$_5$ uptake to the total loss of NO$_3$ is highly varied correspondingly. In addition, the variation of the N$_2$O$_5$ uptake coefficient and ClNO$_2$ yield also results in the weak correlation between the NO$_3$ production rate and ClNO$_2$ concentration. The weak correlation reflects the highly variable chemical processes from NO$_3$ production to ClNO$_2$ production in this region.

As the precursor of ClNO$_2$, higher concentrations of particulate chloride result in high ClNO$_2$ yield from N$_2$O$_5$ uptake to some extent, as evidenced by our field observation (Fig. 6) and previous laboratory studies (Bertram and Thornton, 2009; Roberts et al., 2009; Ryder et al., 2015). High PM$_{2.5}$ concentrations usually provide more aerosol surface area to promote N$_2$O$_5$ uptake. The close relationship between ClNO$_2$ and PM$_{2.5}$ indicates that aerosol surface area is most likely a critical factor that limited ClNO$_2$ formation. The pro-
portion of nitrate in the total PM$_{1.0}$ was small with an average of 10.4 %; therefore the correlation of ClNO$_2$ and PM$_{2.5}$ cannot be attributed to the covariance between nitrate and PM$_{2.5}$. In addition, the ClNO$_2$ level in the air mass of Type B shows higher correlation to both Cl$^-$ and PM$_{2.5}$ than Type A, suggesting that the ClNO$_2$ formation in type B is more effectively affected by the levels of chloride and PM$_{2.5}$.

Recent model simulations indicated that the ClNO$_2$ chemistry level is sensitive to the emission of chloride in the PRD (Li et al., 2021). In this study, a question raised is where is the source of chloride? The mass ratio of Cl$^-$/Na$^+$ is often used as an indicator of sea salt or anthropogenic sources to chloride with a threshold of 1.81 (Yang et al., 2018; Wang et al., 2016). A high ratio means the particulate chloride was affected by anthropogenic emission rather than sea salt. We determine that the mean mass ratios of Cl$^-$ to Na$^+$ are 5.3, 6.3, and 3.1 in Type A, B, and C respectively (Fig. 3). This indicated that PM$_{2.5}$ sampled during the campaign was not strongly influenced by fresh sea salt aerosols. In the three types, the Type C air mass had the lowest ratio and may be influenced by both sea salt and anthropogenic emissions, which seems reasonable since it comes from the South China Sea. If we assume that the Type A air mass is free of sea salt and only influenced by anthropogenic activities, the higher ratio implies a more intensive chloride source in Type B. The correlation between particulate chloride and some possible indicators, including K$^+$, benzene, SO$_2$, CO, and acetonitrile (CH$_3$CN) was examined day by day. Figure 8 shows the max correlation coefficient ($R^2$) on each day with a threshold of 0.5. We filtered out 39 out of 46 d during this campaign with a fraction of 85 %. Among the 39 d, a total of 11 d is associated with the strongest correlation between Cl$^-$ and benzene, which typically come from industrial emissions. Cl$^-$ also correlated with K$^+$, CO, and CH$_3$CN in 19 d in total, implying potential contributions from biomass burning emissions. A total of 9 d for the highest correlations of Cl$^-$ with SO$_2$ indicated coal-fired power plant emissions may also have contributed to Cl$^-$ emission. We summarized that the source of chloride may be highly varied from different anthropogenic activities including biomass burning and industrial processes as well as coal-fired power plants. The statistics results in Table 5 suggest that the Cl$^-$ in the air mass of Type A was affected by various sources, especially related to the sources associated with K$^+$, benzene, and CH$_3$CN; the Cl$^-$ in Type B was mainly contributed by the similar source of CO, and type C was only affected by coal-fired power plants emissions. In addition, Fig. 8 showed that there are 2 d that the correlations between Cl$^-$ and Na$^+$ exceeded the max of the selected anthropogenic factor matrix, indicating
that the aerosol is still also impacted by sea salt to some extent.

### 3.5 The impacts of ClNO₂ on atmospheric oxidation

In this section, we focus on the assessment of the impact of ClNO₂ photolysis on the source of radicals and the contribution to the atmospheric oxidation. Figure 9 shows the diurnal accumulation of the RO₅ production rate from model simulations with ClNO₂ chemistry in the three types of air mass. The total RO₅ production rate was higher in Type A followed by Type B and C, in which photolysis of HONO, HCHO, O₃, and OVOCs had large contributions. In addition, we noticed...
the significant role of OVOCs (including photolysis and reaction with O\textsubscript{3}) in producing RO\textsubscript{x} at this site, especially in the Type A and B air mass. This result is consistent with that constrained by observed OVOCs in Guangzhou (W. Wang et al., 2022). The Cl radical, liberated by ClNO\textsubscript{2}, enhanced little RO\textsubscript{x} production, with a morning peak contribution of 1.3\%, 2.2\%, and 1.8\% for Type A, B, and C, respectively (08:00–09:00). The contribution of ClNO\textsubscript{2} photolysis to the production of RO\textsubscript{x} is less than 1\% on daytime average, similar to the results obtained in winter Shanghai (Lou et al., 2022) as well as North China (Xia et al., 2021) and much lower compared to previous studies reported during the summertime in China (Tan et al., 2017; Tham et al., 2016). However, another winter campaign conducted in Hong Kong SAR in winter showed much more significant impacts compared to our observation (Wang et al., 2016), which indicated that the ClNO\textsubscript{2} chemistry can also have a large influence on the radical formation in wintertime.

Figure 10 shows the enhancement of OH, HO\textsubscript{2}, and RO\textsubscript{x} radicals with the consideration of ClNO\textsubscript{2} chemistry. The enhancement of the three radicals peaked in the morning. On average, OH concentration was enhanced by 1.5\% to 2.6\% in different air masses. The percentage of enhancement for the HO\textsubscript{2} radical was 1.9\% to 4.6\%, whereas the enhancement for RO\textsubscript{x} was a little bit higher (3.0\% to 6.8\%). In general, the enhancement of radicals was more significant in Type B than other two types of air masses, which is related to elevated ClNO\textsubscript{2} concentrations for these air masses. Low ClNO\textsubscript{2} and other radical precursors led to an earlier enhancement peak (08:00–09:00) in Type C and lasted a short time period. Although the increased peak occurred later at 09:00–10:00 for the air mass of Type A and Type B, the increase lasted for a longer time and had a longer effect. Overall, daytime OH, HO\textsubscript{2}, and RO\textsubscript{x} enhanced by 1.0\%, 2.0\%, and 3.0\% on campaign average.

Figure 11 depicts the integral enhancement of O\textsubscript{3} production by ClNO\textsubscript{2} photolysis, which varied from less than 0.1 to 4 ppbv day by day, with a percentage of <1\% to 4.9\% with a median of 0.8\%. Our results are comparable to previous studies reported during the winter case in North China (Xia et al., 2021). The next day, O\textsubscript{3} enhancement was highly correlated with the level of ClNO\textsubscript{2} with a correlation coefficient of 0.7 (Fig. 11a). The daily net O\textsubscript{3} production was enhanced by 0.70 ppbv (0.9\%), 1.02 ppbv (1.9\%) and 0.24 ppbv (0.6\%) for daytime accumulation in Type A, B, and C respectively, which is consistent with the nocturnal level of ClNO\textsubscript{2} in the three air masses presented in Table 3.

Table 6 summarized the observation-constrained box model simulation results about the impacts of ClNO\textsubscript{2} chemistry. The average ClNO\textsubscript{2} concentration in the observation is moderate compared with previous observations; other radical precursors (e.g., HCHO) were also elevated at the same time. This leads to a large total radical and ozone production rate and a relatively minor contribution by ClNO\textsubscript{2} chemistry, which indicates that the contribution of ClNO\textsubscript{2} chemistry is

affected by the budget of other radical precursors. In addition, significant contributions by ClNO\textsubscript{2} chemistry to photochemical pollution were also frequently observed in different campaigns (Tham et al., 2016; Wang et al., 2016), in which the receptor site may have aging plumes with higher ClNO\textsubscript{2} and thus larger contributions (Wang et al., 2016), suggesting the large variability of ClNO\textsubscript{2} and its environmental impacts at various air masses. Here, our observations should be representative of the local condition and reflect the chemistry and impacts of ClNO\textsubscript{2} on the air pollution in PRD region.

Previous studies suggest that chlorine radicals from ClNO\textsubscript{2} photolysis may contribute significantly to the oxidation of some VOC species, especially for long-chain alkanes (Shi et al., 2020; K. Wang et al., 2022). The oxidation of long-chain alkanes (C\textsubscript{10–14} n-alkanes) by chlorine and OH radicals during the morning hour (09:00–10:00) was also evaluated based on modeled oxidant concentration. We observed small contributions of the chlorine radical with a percentage of 4.3\%, 4.3\%, and 3.8\% for n-decane, n-dodecane, and n-tetradecane respectively, during the period (16 October to 17 November 2019) when the long-chain alkane measurement was valid. We also checked the role of chlorine radicals in short-chain alkanes oxidation, obtaining a slightly larger contribution than the long-chain alkanes, which is attributed to relatively large reaction rate constants between Cl and OH with respect to the short-chain alkanes. The daytime average contributions of Cl ranged from 1.4\%–1.6\% and varied by the chain length of the alkanes. Therefore, we concluded that chlorine radicals liberated by ClNO\textsubscript{2} photolysis play a role in the oxidation of alkanes in the morning time but are not critical compared to OH oxidation on the daytime average. We note that several studies have reported that other sources produced a large number of halogen radicals like Cl\textsubscript{2} (Liu et al., 2017; Xia et al., 2020) and BrCl (Peng et al., 2021) during the daytime reaction of HCl with OH (Riedel et al., 2012; Eger et al., 2019; Li et al., 2019). These may cause more alkanes oxidized by halogen radicals. However, it is not possible to assess the overall impacts by constraining all precursors of the chlorine radical in this work, which may warrant further investigation by more comprehensive field studies equipped with the instruments for detecting these species.

4 Conclusion

An intensive field study in the Pearl River Delta took place during a photochemical pollution season from 26 September to 17 November 2019, providing a comprehensive observation dataset to understand the ClNO\textsubscript{2} chemistry and its impact on the air quality. We observed a wide variation for determining factors of ClNO\textsubscript{2} formation in different kinds of air masses. Two types of air mass from northern and northeastern inland cities and the eastern coastal regions were polluted with elevated O\textsubscript{3} and related trace gases like NO\textsubscript{x} and CO. Correlation analysis showed that ClNO\textsubscript{2} formation...
Figure 9. The diurnal cycle and distribution of RO\textsubscript{x} production rate in the three types of air masses.

Figure 10. The diurnal cycle on the enhancement of OH (a), HO\textsubscript{2} (b), and RO\textsubscript{2} (c) by ClNO\textsubscript{2} chemistry in the three air mass patterns.

Figure 11. (a) The correlation of daily median ClNO\textsubscript{2} (18:00–06:00) and its impact on next-day net O\textsubscript{3} production enhancement during the campaign; (b) the average contribution of daytime integral O\textsubscript{3} by ClNO\textsubscript{2} mechanism in the three types of air masses.

is limited by chloride availability and PM\textsubscript{2.5} concentrations (mostly due to aerosol surface area) at this site.

We estimated the N\textsubscript{2}O\textsubscript{5} uptake coefficients and ClNO\textsubscript{2} yield during this campaign and assessed the performance of previous parameterizations schemes. The newly developed observation-based empirical parameterization was also checked and showed an overall underestimation. We showed the $\gamma$N\textsubscript{2}O\textsubscript{5} only strongly correlated with RH, and the parameterization proposed by Evans and Jacob (2005) showed a considerable consistency with the observation. The ClNO\textsubscript{2} yield only showed weak correlation with the content of particle chloride, and the existing parameterizations systematically overestimated the yield. The particulate chloride mainly originated from anthropogenic emissions rather than sea salt. However, the specific contributing source of chloride in this region cannot be determined due to the varying correlation relationship with different kinds of anthropogenic emission indicators day by day. This result highlights the ClNO\textsubscript{2} chemistry may be triggered by many kinds of anthropogenic activities in the PRD regions (Wang et al., 2016; Yang et al., 2018).

The observation-constrained box model revealed chlorine radicals liberated by ClNO\textsubscript{2} chemistry had a relatively small contribution to the following daytime level of RO\textsubscript{x} radicals and O\textsubscript{3} in this region. The small contribution of ClNO\textsubscript{2} chemistry in the PRD region may be due to the limited ClNO\textsubscript{2} produced by N\textsubscript{2}O\textsubscript{5} uptake processes, and other strong primary sources of radicals weakened its contribution indirectly. Given the complex source of particulate chloride, we call for more field investigations to address the chlorine chemistry and its roles in air pollution in China.
Table 6. The summary of impacts of ClNO₂ on the next-day enhancement of ozone and radical production based on the box model that was constrained by field observations in previous literature.

| Location            | Duration               | ClNO₂ peak concentration (ppbv) | Daytime average enhancement (O₃) | Daytime average enhancement (ROₓ) | References                |
|---------------------|------------------------|---------------------------------|----------------------------------|----------------------------------|---------------------------|
| Heshan, CN          | September–November 2019 | 1.5                             | 1.0%–4.9%                        | <2.2%                            | this work                 |
| Shanghai, CN        | October–November 2020  | 0.4                             | 1.3%–6.2%                        | <1.0%                            | Lou et al. (2022)         |
| Wangdu/Beijing/Mt. Tai, CN | 2017–2018            | 1.7                             | 1.3%–6.2%                        | 3.0%                             | Xia et al. (2021)         |
| Wangdu, CN          | June–July 2014         | 2.1                             | 3.0%                             | <10.0%                           | Tham et al. (2016)        |
| Seoul, Korea        | May–June 2016          | 2.5                             | 1.0%–2.0%                        | –                                | Jeong et al. (2019)       |
| Hong Kong, CN       | November–December 2013 | 4.7                             | 11.0%–41.0%                      | –                                | Wang et al. (2016)        |
| California, USA     | May–June 2010          | 1.5                             | 15.0%                            | 17.0%                            | Riedel et al. (2014)      |

*Box model used to estimate the following evolution after the plume passing measurement site and the impacts on the next-day air quality. *b Quantified the upper limit to ozone pollution and ROₓ formation.

Appendix A: The measurement background and calibration of CIMS

The background measurement of ClNO₂ and N₂O₅ was performed during the campaign. Figure A1 shows an example of the background check at the beginning of the campaign, which confirmed the negligible background signal in the measurement of ClNO₂ and N₂O₅ in the ambient condition. The calibration of ClNO₂ measurement sensitivity has been introduced in H. Wang et al. (2022). In brief, a nitrogen flow (6 mL min⁻¹) containing 10 ppmv Cl₂ was passed over a slurry containing NaNO₂ and NaCl to produce ClNO₂ (Thaler et al., 2011), and NaCl was included in the slurry in order to minimize the formation of NO₂ as a byproduct. The mixed flow containing ClNO₂ was then conditioned to a given RH and sampled into the CIMS instrument. To quantify ClNO₂, the mixed flow was delivered directly into a cavity attenuated phase shift spectroscopy instrument (CAPS, Model N500, Teledyne API) to measure background NO₂ concentrations or through a thermal dissociation tube at 365 °C to fully decompose ClNO₂ to NO₂, and the total NO₂ concentrations were then determined using CAPS. The differences in the measured NO₂ concentrations with and without thermal dissociation were equivalent to ClNO₂ concentrations. The CAPS instrument had a detection limit of 0.2 ppbv in 1 min for NO₂ and an uncertainty of ~10%. To calibrate CIMS measurements of N₂O₅, a humidity-adjustable mixed flow containing stable N₂O₅, which was produced via O₃ oxidation of NO₂, was sampled into the CIMS instrument to obtain a normalized humidity dependence curve of N₂O₅. While the concentration of the N₂O₅ source is not quantified due to the absence of a N₂O₅ detector, we delivered the N₂O₅ source flow through a supersaturated sodium chloride solution to convert N₂O₂ to ClNO₂ with a unit efficiency at 50% RH, which is a widely used method for the calibration of ClNO₂ by the CIMS technique. The absolute N₂O₅ sensitivity at 50% RH can be realized and then scaled to other humidity conditions by the normalized N₂O₅ sensitivity curve determined before. The sensitivity curves for N₂O₅ and ClNO₂ to water content are shown in Fig. A2. In this study, the sensitivity of the instrument was calibrated after the campaign. The main parameters (pressure, voltages, etc.) of the CIMS were checked every day and were relatively stable, indicating that the CIMS was operating stably during the campaign.

Figure A1 shows the high-resolution peak fitting results of typical mass spectra at m/z 235 and m/z 208 for N₂O₅ and ClNO₂ in three air mass patterns. The peaks of N₂O₅ and ClNO₂ were clearly resolved in the mass spectra. The peak of N₂O₅ can be well retrieved by separating a large adjacent peak of C₂H₄IO₃S⁻ in the air masses affected by marine emissions (Type B and C), which might be hydroperoxymethyl thioformate (HPMTF) from dimethyl sulfide oxidation (Veres et al., 2020). The interference signals including H₃INO₂S⁻ for ClNO₂ measurements can also be well separated in all the three air mass patterns. These results underline the necessity and feasibility in the application of the ToF analyzer in detecting N₂O₅ and ClNO₂ with an iodide CIMS.
Figure A2. CIMS sensitivities as a function of absolute humidity (AH) for (a) \( \text{N}_2\text{O}_5 \) and (b) \( \text{ClNO}_2 \).

Figure A3. Cases of high-resolution spectra fitting for \( \text{N}_2\text{O}_5 \) and \( \text{ClNO}_2 \) by TOF-CIMS under three air mass patterns.
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Code and data availability. The datasets and code used in this study are available from the corresponding author upon request (byuan@jnu.edu.cn).

Author contributions. HW and BY designed the study. EZ, XZ, JW and HW operated and calibrated the CIMS, KL, CY, LY, SH, WH, SY, YP, JQ, SW, WH, YC, TL, WW, YH, XL and MC conducted the field campaign and provided the sampling data. HW analyzed the data. HW and BY wrote the manuscript with inputs from all co-authors. XW and MS supervised the project.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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