Significant production of ClNO$_2$ and possible source of Cl$_2$ from N$_2$O$_5$ uptake at a suburban site in eastern China

Men Xia$^a$, Xiang Peng$^a$, Weihao Wang$^a$, Chuan Yu$^a$, Peng Sun$^b$, Yuanyuan Li$^b$, Yuliang Liu$^b$, Zhengning Xu$^b$, Zhe Wang$^{a,c}$, Zheng Xu$^b$, Wei Nie$^b$, Aijun Ding$^b$, and Tao Wang$^{a,*}$

$^a$Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, China

$^b$Joint International Research Laboratory of Atmospheric and Earth System Sciences, School of Atmospheric Sciences, Nanjing University, Nanjing, 210023, China

$^c$Now at Division of Environment and Sustainability, Hong Kong University of Science and Technology, Hong Kong, China

*Correspondence to: Tao Wang (cetwang@polyu.edu.hk)

Abstract

ClNO$_2$ and Cl$_2$ can affect atmospheric oxidation and thereby the formation of ozone and secondary aerosols, yet their sources and production mechanisms are not well understood or quantified. In this study we present field observations of ClNO$_2$ and Cl$_2$ at a suburban site in eastern China during April 2018. Persistent high levels of ClNO$_2$ (maximum ~3.7 ppbv; 1 min average) were frequently observed at night, due to the high ClNO$_2$ yield ($\phi$(ClNO$_2$), 0.56 ± 0.20) inferred from the measurements. The $\phi$(ClNO$_2$) value showed a positive correlation with the [Cl$^-$]/[H$_2$O] ratio, and its parameterization was improved by the incorporation of [Cl$^-$]/[H$_2$O] and the suppression effect of aerosol organics. ClNO$_2$ and Cl$_2$ showed a significant correlation on most nights. We show that the Cl$_2$ at our site was likely a co-product with ClNO$_2$ from N$_2$O$_5$ uptake on aerosols that contain acidic chloride, rather than being produced by ClNO$_2$ uptake, as previously suggested. The Cl$_2$ yield ($\phi$(Cl$_2$)) derived from the N$_2$O$_5$ uptake hypothesis exhibited significant correlations with [Cl$^-$] and [H$^+$], based on which a parameterization of $\phi$(Cl$_2$) was developed. The derived parameterizations of $\phi$(ClNO$_2$) and $\phi$(Cl$_2$) can be used in models to quantify the nighttime production of ClNO$_2$ and Cl$_2$ and their impact on the next day’s photochemistry.
1. Introduction

Chlorine radicals (Cl·) are potent oxidizers in the atmosphere (Seinfeld and Pandis, 2016). Cl· destroy the O₃ layer in the stratosphere, exposing the biosphere to excess ultraviolet radiation (Molina and Rowland, 1974). In the polluted troposphere, Cl· react with volatile organic compounds (VOCs), especially alkanes, contribute to primary ROₓ (= OH+HO₂+RO₂) production, and affect hydroxyl radical (OH) and O₃ concentrations (Simpson et al., 2015).

Nitryl chloride (ClNO₂) is a major chlorine radical precursor in the troposphere and has been investigated around the globe over the past decade (Osthoff et al., 2008; Thornton et al., 2010; Mielke et al., 2011; Wang et al., 2016). ClNO₂ is an important nocturnal reservoir of chlorine and NOₓ and is produced mostly at night. NOₓ reacts with O₃ to form NO₃ radicals and N₂O₅ (Reactions R1 and R2). When aerosol chloride is present, ClNO₂ and nitrate are produced from the heterogeneous uptake of N₂O₅ on aerosols (Reaction R3) (Finlayson-Pitts et al., 1989). After sunrise, ClNO₂ is photolyzed to return NO₂ and release Cl· (Reaction R4).

\[
\text{NO}_3(g) + \text{O}_3(g) \rightarrow \text{NO}_5(g) + \text{O}_2(g) \quad \text{(R1)}
\]

\[
\text{NO}_3(g) + \text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_5(g) \quad \text{(R2)}
\]
N\textsubscript{2}O\textsubscript{5}(g) + Cl\textsuperscript{-}(aq) \rightarrow \text{ClNO}_2(g) + \text{NO}_3\textsuperscript{-}(aq) \quad (R3)

ClNO\textsubscript{2}(g) + hv \rightarrow \text{Cl}(g) + \text{NO}_2(g) \quad (R4)

Two key kinetic parameters for quantification of ClNO\textsubscript{2} formation are $\gamma$(N\textsubscript{2}O\textsubscript{5}) (i.e., N\textsubscript{2}O\textsubscript{5} uptake probability on aerosols) and $\phi$(ClNO\textsubscript{2}) (i.e., ClNO\textsubscript{2} production yield from N\textsubscript{2}O\textsubscript{5} uptake) (Thornton et al., 2003; Behnke et al., 1997). Laboratory studies have shown that $\phi$(ClNO\textsubscript{2}) is dependent on the [Cl\textsuperscript{-}]/[H\textsubscript{2}O] ratio because aqueous Cl\textsuperscript{-} and H\textsubscript{2}O compete for the NO\textsubscript{2}\textsuperscript{+} intermediate, based upon which a parameterization was developed to predict $\phi$(ClNO\textsubscript{2}) (hereafter denoted as $\phi$(ClNO\textsubscript{2})\textsubscript{BT}) (Bertram and Thornton, 2009). The parameterization was tested in several field studies, and it was found that the parameterized $\phi$(ClNO\textsubscript{2}) values were significantly larger than the field-derived values (Tham et al., 2016; Wang et al., 2017; Tham et al., 2018; McDuffie et al., 2018b; Staudt et al., 2019). The exact causes of these discrepancies are not fully understood. The suppression of $\phi$(ClNO\textsubscript{2}) has been observed in biomass-burning plumes in north China, but the specific species that reduced $\phi$(ClNO\textsubscript{2}) were not identified (Tham et al., 2018). Some inorganic nucleophiles such as sulfate and organic nucleophiles such as acetate were recently proposed to decrease $\phi$(ClNO\textsubscript{2}) by consuming NO\textsubscript{2}\textsuperscript{+} (McDuffie et al., 2018b; Staudt et al., 2019). Such NO\textsubscript{2}\textsuperscript{+}-consuming nucleophiles may generate products from N\textsubscript{2}O\textsubscript{5} uptake other than ClNO\textsubscript{2} and nitrate, and this is deserving of further investigation.

Besides ClNO\textsubscript{2}, Cl\textsubscript{2} is another important chlorine radical precursor that is present in the lower troposphere (Spicer et al., 1998; Custard et al., 2016; Priestley et al., 2018). Elevated levels of Cl\textsubscript{2} (up to ~400 pptv) have been observed during the daytime in polar and continental environments (Liao et al., 2014; Liu et al., 2017), whereas other studies found nocturnal peaks of Cl\textsubscript{2} mixing ratios in polar, coastal, and continental sites (Mielke et al., 2011; Riedel et al., 2012; Riedel et al., 2013; McNamara et al., 2019). Several potential sources of Cl\textsubscript{2} have been proposed, such as direct emissions from power plants (Riedel et al., 2013) and water treatment facilities (Mielke et al., 2011), photochemical formation associated with O\textsubscript{3} (Liao et al., 2014), and heterogeneous conversion from chlorinated compounds (Reactions R5 and R6) (Deiber et al., 2004; Pratte and Rossi, 2006; McNamara et al., 2019).

\begin{align*}
\text{HOCl}(g) + \text{H}^+(aq) + \text{Cl}^{-}(aq) & \rightarrow \text{Cl}_2(g) + \text{H}_2\text{O} \\
\text{(R5)} & 
\end{align*}
ClONO\textsubscript{2}(g) + H\textsuperscript{+}(aq) + Cl\textsuperscript{-}(aq) → Cl\textsubscript{2}(g) + HNO\textsubscript{3}(aq) \hspace{1cm} (R6) 

Cl\textsubscript{2} can also be produced from heterogeneous N\textsubscript{2}O\textsubscript{5} uptake on acidic aerosols laden with chloride, and ClINO\textsubscript{2}(aq) has been proposed as an intermediate in Cl\textsubscript{2} production (Reaction R7) on the basis of laboratory studies (Roberts et al., 2008; Roberts et al., 2009).

CINO\textsubscript{2}(aq) + H\textsuperscript{+}(aq) + Cl\textsuperscript{-}(aq) → Cl\textsubscript{2}(g) + HNO\textsubscript{3}(aq) \hspace{1cm} (R7) 

Significant correlations of CINO\textsubscript{2} and Cl\textsubscript{2} were observed during an airborne campaign in the United States and were interpreted as evidence of Cl\textsubscript{2} production from CINO\textsubscript{2} uptake on acidic aerosols (Haskins et al., 2019). However, this study also found that Cl\textsubscript{2} formation from ClINO\textsubscript{2} uptake was less efficient, because the estimated γ(CINO\textsubscript{2}) value ((2.3 ± 1.8) \times 10\textsuperscript{-5}) was two orders of magnitude lower than that suggested by laboratory studies ((6.0 ± 2.0) \times 10\textsuperscript{-3}) (Roberts et al., 2008; Haskins et al., 2019). It remains unclear whether CINO\textsubscript{2} uptake proceeds more slowly in ambient environments than in laboratory conditions or whether additional pathways are responsible for the formation of Cl\textsubscript{2}. Therefore, the detailed activation process by which inert chlorine (e.g., particulate chloride) is converted to reactive chlorine remains highly uncertain and requires further research.

In April 2018, we conducted field measurements of CINO\textsubscript{2}, Cl\textsubscript{2}, and other trace gases and aerosols in a suburban area of the Yangtze River Delta (YRD), a highly populated and industrialized region in eastern China. High levels of CINO\textsubscript{2} with enhanced Cl\textsubscript{2} were observed at night. In this study, we investigated the activation of chlorine initiated by heterogeneous N\textsubscript{2}O\textsubscript{5} chemistry. We first introduce prominent features of the observation results. The key parameters in CINO\textsubscript{2} formation (i.e., γ(N\textsubscript{2}O\textsubscript{5}) and φ(CINO\textsubscript{2})) are then derived using the ambient data. Factors that influence φ(CINO\textsubscript{2}) are discussed, with a focus on a revision of the parameterization of φ(CINO\textsubscript{2}). We present observational evidence for a possible co-production pathway of Cl\textsubscript{2} with CINO\textsubscript{2} from heterogeneous reactions of N\textsubscript{2}O\textsubscript{5} and propose a new parameterization for nocturnal formation of Cl\textsubscript{2}.

2. Methods

2.1 Observation sites
The field campaign was conducted from 11 to 26 April, 2018 on the Xianlin Campus of Nanjing University, which is situated in a suburban area approximately 20 km northeast of downtown Nanjing (see Fig. 1). The observation sites are surrounded by teaching and residential buildings, sparse roads, and vegetation cover for about 1 to 2 km, with no significant emission sources. Approximately 15 km northwest of the sampling sites are large-scale chemical and steel facilities, which can be sources of gaseous pollutants (CO, SO$_2$, NO$_x$, and VOCs) and particulate matters that may influence the site (Zhou et al., 2017). In addition, Shanghai is approximately 270 km southeast of the measurement site.

The main data reported in this study (i.e., N$_2$O$_5$, ClNO$_2$, and Cl$_2$) and the NO$_x$ and O$_3$ data were obtained at the School of Atmospheric Sciences (SAS) of Nanjing University (sampling site 1). The auxiliary data, including O$_3$, VOCs, aerosol size distribution, and chemical composition, were obtained at the Station for Observing Regional Processes of the Earth System (SORPES, sampling site 2). Fig. 1 shows the locations of the two sampling sites. Interested readers are referred to previous studies for more information about the SORPES site (e.g., Ding et al., 2013; Sun et al., 2018; Ding et al., 2019). A comparison of O$_3$ measurements at the SAS and SORPES sites shows excellent agreement during the observation period (Fig. S1).
Figure 1. Sampling locations. (a) Location of Nanjing city in the YRD region. (b) Location of sampling sites in Nanjing. (c) Sampling sites 1 and 2 on the Xianlin campus of Nanjing University. (© Google Earth)

2.2 N$_2$O$_5$, CINO$_2$, and Cl$_2$ measurements

A chemical ionization mass spectrometer coupled with a quadrupole mass analyzer (Q-CIMS, THS Instruments) was used to detect N$_2$O$_5$, CINO$_2$, Cl$_2$, and HOCl. The Q-CIMS had been used in previous field campaigns to measure N$_2$O$_5$ and CINO$_2$ (Wang et al., 2016; Tham et al., 2016). In this study, we also measured Cl$_2$ and HOCl and tuned the pressure of the drift tube reactor accordingly. The principles and ion chemistry of Q-CIMS were described in detail by Kercher et al. (2009). Briefly, iodide (I$^-$) was adopted as the primary ion for strong affinity with our target species. Charged iodide clusters, such as IN$_2$O$_5^-$, IClNO$_2^-$, ICl$_2^-$, and IHOCl$^-$, are
formed by the ion molecular reactions shown in Reactions (R8) through (R11). Ion clusters with different Cl isotopes (i.e., $^{35}\text{Cl}$ and $^{37}\text{Cl}$) were recorded to examine the identity of $\text{ClNO}_2$ and $\text{Cl}_2$, and this isotopic analysis confirmed that $\text{ClNO}_2$ and $\text{Cl}_2$ had very minor interferences (see Text S1).

N$_2$O$_5$ + I$^-$ → IN$_2$O$_5^-$ (m/z 235) \hspace{1cm} (R8)

CINO$_2$ + I$^-$ → ICINO$_2^-$ (m/z 208, 210) \hspace{1cm} (R9)

Cl$_2$ + I$^-$ → ICl$_2^-$ (m/z 197, 199) \hspace{1cm} (R10)

HOCl + I$^-$ → IHOCI$^-$ (m/z 179, 181) \hspace{1cm} (R11)

The Q-CIMS was housed on the fifth floor of the SAS building. The PFA sampling tube (length, 1.5 m; outer diameter, 0.25 in) extended out through a hole in the side wall. We took precautions to minimize the deposition of particles on the inner wall of the sampling tube and tested the possible formation and loss of N$_2$O$_5$, CINO$_2$, and Cl$_2$ on the sampling tube (see Text S1 for details), which showed a negligible inlet interference on the CIMS measurement. N$_2$O$_5$ and CINO$_2$ were calibrated every two days following established methods (Wang et al., 2016). Briefly, N$_2$O$_5$ was synthesized from the reaction of NO$_2$ and O$_3$, and CINO$_2$ was produced by passing N$_2$O$_5$ through a deliquesced NaCl slurry. The dependence of N$_2$O$_5$ sensitivity on relative humidity (RH) was tested on site (see Fig. S3) and was used to account for changes in ambient RH. A Cl$_2$ permeation tube was used for Cl$_2$ calibration (Liao et al., 2014), and the permeation rate of Cl$_2$ was quantified by chemical titration and ultraviolet spectrophotometry. We assumed the sensitivity of HOCl to be the same as that of ClO, and we used a sensitivity ratio of ClO to Cl$_2$ (0.26) that was experimentally determined by Custard et al. (2016). In this study, the HOCl data were only used qualitatively. In sum, the sensitivities of N$_2$O$_5$, CINO$_2$, Cl$_2$, and HOCl were 0.42 ± 0.11, 0.35 ± 0.13, 0.86 ± 0.37, and 0.22 ± 0.08 Hz/ppbv, respectively. The uncertainties of the N$_2$O$_5$ and CINO$_2$ measurements were estimated to be 19% via error propagation. The Cl$_2$ measurement uncertainty was estimated to be 15%. The details of CIMS calibrations and uncertainty analysis are available in Text S1 and Table S3.

2.3 Auxiliary measurements
In addition to the CIMS measurement at the SAS site, meteorological factors, gaseous and aerosol chemical compositions, particle size distributions, and the NO$_2$ photolysis frequency (jNO$_2$) were simultaneously measured at the SORPES site (Table S1). The ionic compositions of PM$_{2.5}$, including Cl$^-$, NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$, were measured with an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc.) and MARGA (Metrohm, Switzerland). The hourly-averaged ionic compositions from ACSM and MARGA showed good agreement (see Fig. S4). In addition, HNO$_3$ was also measured by MARGA. In this study, the 10-min averaged ACSM data, including total organics, were used for subsequent analysis. The mass concentration of H$^+$ (µg/m$^3$) was estimated to achieve electric charge balance of the cation (NH$_4^+$) and anions (Cl$^-$, NO$_3^-$, and SO$_4^{2-}$) of the ACSM data. The molar concentrations of inorganic ions (i.e., [Cl$^-$], [NO$_3^-$], [SO$_4^{2-}$], [NH$_4^+$], and [H$^+$]) and total organics ([Org]) were estimated using the extended aerosol inorganics model (E-AIM, model III) (Wexler, 2002). The molecular weight of the organic molecules was assumed to be 250 g/mol (McDuffie et al., 2018b). The dry-state submicron particle size distribution was measured with a Scanning Mobility Particle Sizer (SMPS, TSI Inc.), and the data were used to estimate the aerosol surface area density ($S_a$) with the assumption of spherical particles. The hygroscopic growth factor of the particle size was based on an empirical parameterization, $GF = 0.582 \left(8.46 + \frac{1}{1 - RH}\right)^{1/3}$ (Lewis, 2008). The VOCs were measured with a proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS, Ionicon).

### 2.4 Production and loss of NO$_3$ and N$_2$O$_5$

NO$_3$ radicals are primarily produced from NO$_2$ and O$_3$ (Reaction R1). The production rate equation of NO$_3$ ($P$(NO$_3$)) is shown as follows (Eq. (1)):

$$P$(NO$_3$) = $k_1$[NO$_2$][O$_3$] \quad (1)

where $k_1$ is the rate constant of Reaction R1. NO$_3$ is mainly removed by gas-phase reactions with VOCs and NO (Eq. (2)) and heterogeneous loss via N$_2$O$_5$ uptake (Eq. (3)), where $k$(NO$_3$) and $k$(N$_2$O$_5$) are the first-order loss rate coefficients of NO$_3$ and N$_2$O$_5$, respectively.

$$k$(NO$_3$) = $k_{NO} - NO_3$[NO] + $\sum k_i$[VOC] \quad (2)
\[ k(N_2O_5) = \frac{1}{4}c(N_2O_5)S\gamma(N_2O_5) \] \hspace{1cm} (3)

where \( k_{NO_2 + NO_3} \) and \( k_i \) denote the reaction rate constants of \( NO_3 \) with \( NO \) and VOC, respectively, and \( c(N_2O_5) \) is the average velocity of \( N_2O_5 \) molecules. Other minor loss pathways of \( NO_3 \) and \( N_2O_5 \) were not considered (e.g., homogeneous loss of \( N_2O_5 \)).

### 2.5 Estimation of \( \phi(ClNO_2) \) and \( \gamma(N_2O_5) \)

\( \phi(ClNO_2) \) and \( \gamma(N_2O_5) \) were estimated using the observation data and parameterization. We used the observed increasing rates of ClNO\(_2\) and total nitrate (i.e., HNO\(_3\)+NO\(_3\)-) to derive the values for \( \gamma(N_2O_5) \) and \( \phi(ClNO_2) \) in the selected cases (Phillips et al., 2016). Details of the method are described elsewhere (Tham et al., 2016; Phillips et al., 2016). Briefly, the production rate of ClNO\(_2\) \((P(ClNO_2))\) is calculated as follows (Eq. (4)).

\[ P(ClNO_2) = \frac{1}{4}c(N_2O_5)S\gamma(N_2O_5)[N_2O_5]\phi(ClNO_2) \] \hspace{1cm} (4)

The production rate of total nitrate induced by \( N_2O_5 \) uptake during the night \((P(NO_3^{-}))\) is shown by Eq. (5).

\[ P(NO_3^{-}) = \frac{1}{4}c(N_2O_5)S\gamma(N_2O_5)[N_2O_5](2-\phi(ClNO_2)) \] \hspace{1cm} (5)

\( \phi(ClNO_2) \) is obtained by combining Eqs. (4) and (5).

\[ \phi(ClNO_2) = 2(1+\frac{P(NO_3^{-})}{P(ClNO_2)})^{-1} \] \hspace{1cm} (6)

And \( \gamma(N_2O_5) \) is derived as follows (Eq. (7)).

\[ \gamma(N_2O_5) = \frac{2(P(ClNO_2)+P(NO_3^{-}))}{c(N_2O_5)[N_2O_5]} \] \hspace{1cm} (7)

This method assumes that: (1) air masses are relatively stable; and (2) \( N_2O_5 \) uptake dominates \( NO_3^- \) production at night (Tham et al., 2018). Assumption (1) requires careful selection of the cases of interest. Regarding assumption (2), major nocturnal production pathways of total nitrate should be evaluated, such as comparing the reaction rate of \( N_2O_5 \) heterogeneous loss \((k(N_2O_5)[N_2O_5])\) with that of \( NO_3 + VOC \ (k(\{NO_3\})[\{NO_3\}]) \), which may produce HNO\(_3\) via H-abstraction reactions.

\( \phi(ClNO_2) \) was also calculated with the parameterization shown in Eq. (8), in which the \( k_4/k_3 \) ratio was adopted as 483 ± 175 (Bertram and Thornton, 2009).
\[ \phi(\text{ClNO}_2)_{\text{BT}} = \left(1 + \frac{[\text{H}_2\text{O}]}{k_4/k_3[\text{CT}]} \right)^{-1} \]  

When considering the potential competitive effect of other species (denoted as “Y”), such as sulfate or aerosol organics, for the \( \text{NO}_2^- \) intermediate, the following equation (Eq. (9)) was established (McDuffie et al., 2018b). Rearrangement of Eq. (9) yields Eq. (10), in which plotting \( \frac{1}{\phi(\text{ClNO}_2)} - 1 \) to \( \frac{[\text{CT}]}{[\text{H}_2\text{O}]} \) should exhibit a positive correlation. \( k_5 \) represents a constant reaction rate coefficient of “Y” with \( \text{NO}_2^- \).

\[ \phi(\text{ClNO}_2) = \frac{1}{1 + \frac{k_3[\text{H}_2\text{O}]}{k_4[\text{CT}]} + \frac{k_4[\text{Y}]}{k_5[\text{CT}]}} \]  

\[ \left(\frac{1}{\phi(\text{ClNO}_2)} - 1\right) = \frac{k_3}{k_4} \left(\frac{[\text{CT}]}{[\text{H}_2\text{O}]} \right) + \frac{k_4[\text{Y}]}{k_5[\text{CT}]}. \]  

3. Results and Discussions

3.1 Overall observation results

Fig. 2 depicts the time series of \( \text{N}_2\text{O}_5, \text{ClNO}_2, \text{Cl}_2, \) and related species. Overall, the observation sites experienced moderate levels of pollution during the study period (PM\(_{2.5}\), 44.8 ± 18.3 \( \mu \)g/m\(^3\); CO, 0.4 ± 0.2 ppmv; SO\(_2\), 3.1±1.8 ppbv; NO\(_x\), 18.1 ± 16.6 ppbv; O\(_3\), 25.8 ± 18.4 ppbv). The on-site observations indicated mostly stagnant weather with low wind speeds (1 m/s in average). No precipitation was observed except for the evening of 13 April from 22:00 to 22:30 local time. The nocturnal NO mixing ratios were usually near the detection limit of the NO instrument, and the presence of abundant NO\(_2\) and O\(_3\) favored N\(_2\)O\(_5\) formation and subsequent heterogeneous processes.

The most salient features of the observation were the high levels of ClNO\(_2\) and moderate levels of Cl\(_2\) that were present during the night. The ClNO\(_2\) mixing ratios exceeded 1 ppbv on 12 of the 15 nights. The observed ClNO\(_2\) levels were among the highest in the world, with a peak mixing ratio (1-min average, 3.7 ppbv) slightly higher than that of north China (1-min average, 2.1 ppbv) (Tham et al., 2016) but lower than that reported in south China (1 min average, 8.3 ppbv) (Yun et al., 2018). The frequent occurrence of high ClNO\(_2\) levels was favored by several factors, including elevated levels of N\(_2\)O\(_5\) (1 ppbv), humid weather (RH, 67.7 ±...
20.7%), and chloride availability (0.36 ± 0.31 μg/m³) during the field campaign. When high levels of ClNO₂ were observed, elevated concentrations of particulate nitrate as high as 40.8 μg/m³ (10-min average) were also present. We noticed that ClNO₂ and particulate nitrate concentrations both increased more rapidly after midnight than before midnight from 15 to 19 April, which is discussed further below.

Moderate levels of Cl₂ (up to 100 pptv) were also observed during the night. Cl₂ mixing ratios exhibited a clear diurnal pattern, peaking at night and decreasing during the day due to photolysis. The nocturnal peaks of Cl₂ mixing ratios showed discrepancies from some previous observations in which an elevated levels of Cl₂ was found during the day (Liao et al., 2014; Liu et al., 2017). The Cl₂ and ClNO₂ mixing ratios reached peaks synchronously during most nights, and both species decreased in abundance or were absent in NO-rich plumes (e.g., the nights of 13 and 25 April), which suggests that Cl₂ and ClNO₂ were produced from common sources. Similar nighttime correlations of Cl₂ and ClNO₂ were also observed in the United States and in northern China (Qiu et al., 2019; Haskins et al., 2019). A subsequent analysis of the present study aims to elucidate the nighttime formation processes of ClNO₂ and Cl₂.

Figure 2. Time series of ClNO₂, Cl₂, and related measurements during field observations from 11 to 26 April 2018. Data gaps were caused by technical problems or calibrations.

3.2 High ClNO₂ cases

Fig. 3 shows the observation results from 17 and 18 April to further illustrate the ClNO₂ cases.
formation process. This case had the highest ClNO₂ observed during the campaign and shows an example of high ClNO₂ mixing ratios after midnight. As shown in Fig. 3a, the mixing ratio of ClNO₂ began to increase after sunset (18:00 17 April) and decreased after midnight. The period between 22:00 and 24:00 on 17 April was noted as plume 1. After midnight, the ClNO₂ mixing ratios exhibited a more rapid increase from 03:00 to 05:00 on 18 April (plume 3), and the particulate nitrate concentration also synchronously and significantly increased. Plumes 1 and 3 were identified as being different, resulting from an air mass shift between 00:00 and 03:00 on 18 April (plume 2), as indicated by abrupt changes in the RH, temperature, and O₃.

We compared the backward trajectories from plume 1 to plume 3 and found no significant difference (figures not shown here). Thus, the change in the air mass from plume 1 to plume 3 was likely a local phenomenon.

The P(NO₃⁻) and NO₃⁻ loss pathways during plumes 1 and 3 were calculated and compared in Fig. 3b-d using the methods described in Section 2.4. The P(NO₃⁻) was slightly lower during plume 3 than during plume 1, and a larger proportion of NO₃⁻ was lost via the N₂O₅ hydrolysis pathway in plume 3. Thus, the air mass shift, in addition to the higher rate of N₂O₅ hydrolysis, was responsible for the elevated ClNO₂ levels observed after midnight.
Figure 3. Detailed analysis of a high ClNO$_2$ episode observed on 17–18 April. (a) Time series of ClNO$_2$ and related species. (b), (c), and (d) Comparisons of P(NO$_3$) and NO$_3$ loss pathways in plumes 1 and 3.

3.3 ClNO$_2$ production yield from N$_2$O$_5$ uptake

φ(ClNO$_2$) was estimated to investigate its influencing factors and the performance of parameterization in selected cases. The methods described in Section 2.5 were used to estimate the φ(ClNO$_2$) and γ(N$_2$O$_5$) using the observation data. As these methods assume a stable air mass and the dominance of N$_2$O$_5$ uptake in nitrate formation, we applied the following criteria when selecting cases for this analysis. First, the NO mixing ratios must be less than 0.1 ppbv. When significant levels of NO were present, the N$_2$O$_5$ chemistry was suppressed. Second, primary pollutants such as CO, SO$_2$, and meteorological factors (wind, temperature, and RH) were required to exhibit relatively constant levels or stable trends within the cases. Third, the ClNO$_2$ and nitrate levels had to be correlated ($R^2 > 0.6$) and show increasing trends. Fifteen cases that lasted 30 min to 3 hours were selected, and 10-min averaged data were used for calculation. Fig. S5 shows an example of this calculation, which corresponds to plume 1 on 17 April (Fig. 3). We then evaluated the loss pathways of NO$_3$ in the fifteen cases. The results show that the NO$_3$ + VOCs reactions contributed less than one third of the total NO$_3$ + N$_2$O$_5$ loss (e.g., Fig. 3c, d). Nocturnal total nitrate production was thus dominated by N$_2$O$_5$ uptake, and only a small proportion of nitrate was produced by NO$_3$+VOCs reactions.

The derived γ(N$_2$O$_5$) values ranged from 0.004 to 0.014 (mean, 0.008 ± 0.004). The highest γ(N$_2$O$_5$) values (0.0135 and 0.0139) were derived between 03:00 and 05:00 on 18 April (i.e., plume 3 in Fig. 3), which was consistent with the rapid increase in ClNO$_2$ mixing ratios during that period. The variations in the γ(N$_2$O$_5$) value depended mainly on [H$_2$O] ($R^2 = 0.49$) (see Fig. S6) but showed little correlation with other influencing factors, such as [Cl$^-$], [NO$_3$$^-$], and V$_a$/S$_a$ (figures not shown here). The dominant influence of [H$_2$O] on the γ(N$_2$O$_5$) value was also reported in a previous study in north China (Tham et al., 2018).

The φ(ClNO$_2$) value ranged from 0.28 to 0.89 (mean, 0.56 ± 0.15), which was among the
highest values in the world (McDuffie et al., 2018b). The φ(ClNO$_2$) value in this study exhibited
an obvious nonlinear relationship with the [Cl$^-$]/[H$_2$O] ratio ($R^2 = 0.52$) (Fig. 4a), which is
consistent with previous laboratory results (Bertram and Thornton, 2009). However, current
parameterization of φ(ClNO$_2$) based on [Cl$^-$]/[H$_2$O] (φ(ClNO$_2$)$_{BT}$) tended to overestimate the
observed φ(ClNO$_2$) value (Fig. 4b).

Here we give two explanations for the inconsistency between the φ(ClNO$_2$)$_{BT}$ and the field-
derived φ(ClNO$_2$). First, the reactivity of chloride with NO$_2^+$ (i.e., $k_4/k_3$ in Eq. 8) was reduced
in ambient environments due to complicated issues of the mixing state, phase state, and activity
coefficient. As φ(ClNO$_2$) is positively dependent upon [Cl$^-$], a reduction in chloride reactivity
could decrease the φ(ClNO$_2$) value in ambient particles. This explanation is supported by
previous studies of γ(N$_2$O$_5$) (Morgan et al., 2015; McDuffie et al., 2018a), which showed that
when the enhancement effect of chloride on γ(N$_2$O$_5$) was neglected, the parameterized γ(N$_2$O$_5$)
better matched the observed γ(N$_2$O$_5$). The second explanation deals with other unknown factors
that reduce the φ(ClNO$_2$) value. The parameterization φ(ClNO$_2$)$_{BT}$ only considered the
[Cl$^-$]/[H$_2$O] ratio, not other aqueous species that could suppress φ(ClNO$_2$), leading to the
overestimation of φ(ClNO$_2$)$_{BT}$ values.

Regarding the second explanation, we examined the possibility of sulfate and aerosol
organics competing with [Cl$^-$] for the NO$_2^+$ intermediate (see Section 2.4 and Eq. (10)). The
statistical results show that aerosol organics could reduce φ(ClNO$_2$) values ($R^2 = 0.41$; Fig. S7b),
but sulfate did not show such an influence ($R^2 = 0.08$; Fig. S7a). The latter result contrasts with
the finding of a recent laboratory study, which indicated that both sulfate and some organics
(e.g., carboxylate) suppress ClNO$_2$ formation (Staudt et al., 2019).

By incorporating the suppression effect of aerosol organics, we performed regressions of
φ(ClNO$_2$) and obtained an improved parameterization of φ(ClNO$_2$) (noted as φ(ClNO$_2$)$_{BT-Org}$)
that better matched the observed φ(ClNO$_2$) (Fig. 4b). In Eq. (11), the factor 483 ($k_4/k_3$ in Eq. 9)
was adopted from (Bertram and Thornton, 2009), and the factor 235 ($k_4/k_5$ in Eq. 9) was derived
here by iterative algorithms to achieve the least-square errors between the observed and
parameterized φ(ClNO$_2$) values. Given that $k_4/k_3 = 483$ and $k_4/k_5 = 235$, $k_5/k_3$ was calculated as
2.06, which suggests that the reaction rate constant of aerosol organics with NO$_2^+$ was twice that of the H$_2$O + NO$_2^+$ reaction. A recent laboratory study (Staudt et al., 2019) derived $k_5/k_3 = 3.7$ for acetate, which is very similar to our results.

$$\phi(\text{CINO}_2)_{\text{BT+Org}} = \left(1 + \frac{[\text{H}_2\text{O}]}{483[\text{Cl}^-]} + \frac{[\text{Org}]}{235[\text{Cl}^-]}\right)^{-1}$$  \hspace{1cm} (11)  

Figure 4. Influencing factors and parameterizations of $\phi(\text{CINO}_2)$. (a) Dependence of $\phi(\text{CINO}_2)$ on the [Cl$^-$/[H$_2$O] ratio. Dashed red line shows nonlinear fitting of $\phi(\text{CINO}_2)$; “a” represents the $k_4/k_3$ in Eq. (8). (b) Comparison of parameterized $\phi(\text{CINO}_2)$ and observed $\phi(\text{CINO}_2)$, where $\phi(\text{CINO}_2)_{\text{BT}}$ denotes the parameterization proposed by Bertram and Thornton (2009), and $\phi(\text{CINO}_2)_{\text{BT+Org}}$ represents the revised parameterization used in this study (see Eq. (11)).

3.4 Nocturnal Cl$_2$ formation

3.4.1 Cl$_2$ as a co-product of CINO$_2$ from N$_2$O$_5$ uptake

To elucidate the formation pathways of the elevated levels of Cl$_2$ observed during the night, we investigated the correlations of Cl$_2$ with the CINO$_2$, HOCl, and SO$_2$ and the diurnal variations of these (Fig. 5a–5d). Cl$_2$ only exhibited a significant correlation with CINO$_2$ (Fig 5a). The Cl$_2$/CINO$_2$ ratios varied on different nights, which implies that differences exist in the production efficiencies of Cl$_2$ relative to those of CINO$_2$. 

https://doi.org/10.5194/acp-2019-1130
Preprint. Discussion started: 7 January 2020
© Author(s) 2020. CC BY 4.0 License.
Figure 5. Correlations among Cl$_2$, ClNO$_2$, HOCl, and SO$_2$ and their diurnal profiles (a), (b), and (c) show the correlations of Cl$_2$ with ClNO$_2$, HOCl, and SO$_2$ respectively, during the whole campaign. Dots represent 10-min averaged values colored according to campaign days. (d) exhibits the diurnal variation of Cl$_2$, ClNO$_2$, HOCl, and SO$_2$.

The current mainstream interpretation of the observed correlation of ClNO$_2$ and Cl$_2$ is that Cl$_2$ is produced from ClNO$_2$ uptake (Ammann et al., 2013; Qiu et al., 2019; Wang et al., 2019; Haskins et al., 2019). We provide evidence that this interpretation does not apply to measurements from our site. We assessed the ClNO$_2$ uptake hypothesis by examining the magnitude of $\gamma$(ClNO$_2$) needed to explain the nocturnal increase in Cl$_2$ mixing ratios and the dependence of $\gamma$(ClNO$_2$) on its known influencing factors. Assuming a unity yield of Cl$_2$ from ClNO$_2$ uptake, the increasing rate of Cl$_2$ mixing ratios was calculated with Eq. (12). Eq. (13),
which was derived by rearrangement of Eq. (12), was adopted to estimate $\gamma$(ClNO$_2$) via the observed Cl$_2$ and CINO$_2$ levels.

\[ \frac{d[Cl_2]}{dt} = \frac{1}{4}c(ClNO_2)S_a\gamma(ClNO_2)[ClNO_2] \] (12)

\[ \gamma(ClNO_2)_{obs} = \frac{4d[Cl_2]/dt}{c(ClNO_2)S_a[ClNO_2]} \] (13)

where $c(ClNO_2)$ is the mean molecular velocity of CINO$_2$ (m/s), and $[ClNO_2]$ represents the averaged ambient concentration of ClNO$_2$ in the cases of interest.

$\gamma(ClNO_2)_{obs}$ was estimated in the selected cases following criteria 1 and 2 in Section 3.3, and a steady increase in Cl$_2$ mixing ratios was required. The resulting values of $\gamma(ClNO_2)_{obs}$ were compiled according to the local time and are presented in box charts (Fig. 6a). Fig. 6a also shows the potential factors influencing $\gamma(ClNO_2)$: [Cl$^-$], [H$^+$], and particle diameters ($D_p$), derived from the ratio of wet $V_a$ to $S_a$. Here, [Cl$^-$] and $D_p$ were regarded as the factors influencing $\gamma(ClNO_2)$ because a previous field study had found positive correlations of $\gamma(ClNO_2)$ with [Cl$^-$] and $D_p$ (Haskins et al., 2019). [H$^+$] was considered because the previous laboratory study proposed that H$^+$ was as a reactant in Cl$_2$ production (Roberts et al., 2008). Each box represents the $\gamma(ClNO_2)$, [Cl$^-$], [H$^+$], or $D_p$ of 10-min resolutions derived on individual days. For example, the box for 18:00–19:00 contains the $\gamma(ClNO_2)$ estimated at 18:00–19:00 on 11, 12, and 14 April (Fig. 6b–6d). Fig. 6b–6d displays the observed Cl$_2$ levels and the projected trend of Cl$_2$ levels obtained by use of Eq. (12).
Figure 6. $\gamma$(ClNO$_2$) estimated using field observation data. (a) $\gamma$(ClNO$_2$)$_{obs}$, [Cl$^-$], [H$^+$], and $D_p$ estimated at various nighttime periods. (b)–(d) Trends of increasing trends of Cl$_2$ mixing ratios during the early evening hours on 11, 12, and 14 April, respectively. Orange and gray lines represent the projected trend of Cl$_2$ mixing ratios using Eq. (12) with constant $\gamma$(ClNO$_2$) values and observed ClNO$_2$ levels.

As the increasing rate of Cl$_2$ concentrations (d[Cl$_2$]/dt) did not change significantly during the night (Fig. 5d), the $\gamma$(ClNO$_2$) value was constrained by a sharp decreasing trend to compensate for the increasing CINO$_2$ levels after dusk (see Eq. 12). The highest $\gamma$(ClNO$_2$)$_{obs}$ value determined during the early evening hours (18:00–19:00) was similar to the laboratory-derived $\gamma$(ClNO$_2$) value on acidic salt films ($6 \times 10^{-3}$) (Roberts et al., 2008). However, the lowest $\gamma$(ClNO$_2$)$_{obs}$ value estimated during later nighttime hours (22:00–04:00) was two orders of
magnitude lower ($10^{-5}$) and was comparable to that observed during previous field observations (Haskins et al., 2019). The large variations in the $\gamma$(ClNO$_2$) value contrasted with the relatively stable levels of [Cl$^-$], [H$^+$], and D$_p$ at various times of night, which is in opposition to the current understanding of the relationship between the $\gamma$(ClNO$_2$) and these factors. Therefore, the ClNO$_2$ uptake hypothesis cannot explain the nocturnal increase in Cl$_2$ mixing ratios that we observed at our study site. We propose another hypothesis for the ClNO$_2$–Cl$_2$ correlation and suggest that Cl$_2$ is a co-product of ClNO$_2$ produced from N$_2$O$_5$ uptake, in which ClNO$_2$ is not necessarily an intermediate of Cl$_2$. However, further studies are needed to validate this hypothesis.

3.4.2 Parameterizing Cl$_2$ formation from N$_2$O$_5$ uptake

As the nighttime Cl$_2$, ClNO$_2$, and most nitrate ultimately originated from N$_2$O$_5$ uptake, we can derive a relationship between Cl$_2$ and the N$_2$O$_5$ uptake. We assigned a production yield to Cl$_2$ ($\phi$(Cl$_2$)) from the N$_2$O$_5$ uptake analogous to the ClNO$_2$ yield and calculated this using Eq. (14):

$$\phi$(Cl$_2$) = \frac{d[Cl_2]/dt}{k(N_2O_5)[N_2O_5]} \tag{14}$$

$\phi$(Cl$_2$) was estimated in the same cases in which $\gamma$(N$_2$O$_5$) and $\phi$(ClNO$_2$) were derived, because the availability of $\gamma$(N$_2$O$_5$) was a prerequisite of deriving $\phi$(Cl$_2$). The estimated $\phi$(Cl$_2$) value was 0.01–0.04 (Table S2). The dependences of $\phi$(Cl$_2$) on its potential influencing factors (i.e., [Cl$^-$], [H$^+$], and D$_p$) were examined. The results show that $\phi$(Cl$_2$) had positive correlations with both [Cl$^-$] ($R^2 = 0.74$) and [H$^+$] ($R^2 = 0.75$) and that the data had a high $\phi$(Cl$_2$) region and a low $\phi$(Cl$_2$) region (Fig. 7a, b). The low $\phi$(Cl$_2$) values were found in continental air masses with relatively lower chloride concentrations, more alkaline ammonium, less acidic sulfate and nitrate, and thus lower acidity (Fig. 7d), whereas the high $\phi$(Cl$_2$) values were associated with marine air masses with higher loadings of aerosol chloride, less ammonium, and more acidic compounds, and thus higher acidity (Fig. 7c). The higher acidity in the marine air masses may be explained by the passage of this air mass over the industrialized cities in the YRD where large concentrations of SO$_2$ and NO$_x$ are emitted. The dependences of the defined $\phi$(Cl$_2$) on [Cl$^-$] and [H$^+$] indicate that nocturnal Cl$_2$ production requires the presence of highly acidic chloride-rich particles and sufficient levels of N$_2$O$_5$. 
Figure 7. Estimated $\varphi(\text{Cl}_2)$ from $\text{N}_2\text{O}_5$ uptake and the factors influencing $\varphi(\text{Cl}_2)$ (a) and (b) Dependencies of $\varphi(\text{Cl}_2)$ on $[\text{Cl}^-]$ and $[\text{H}^+]$ in selected cases. (c) and (d) are examples of high $\varphi(\text{Cl}_2)$ values in marine air masses (e.g., 13 April) and low $\varphi(\text{Cl}_2)$ values in inland air masses (e.g., 18 April) represented by 24-hour backward trajectories. Inserted pie charts show average aerosol chemical compositions during 21:40 on 12 April to 00:40 on 13 April and from 22:20 to 23:40 17 April, respectively.

A parameterization scheme is derived based on the dependences of $\varphi(\text{Cl}_2)$ on $[\text{Cl}^-]$ and $[\text{H}^+]$ to predict the Cl$_2$ formation involving $\text{N}_2\text{O}_5$ heterogeneous chemistry. Mechanistically, it is assumed that the nocturnal Cl$_2$ is produced from reactions involving NO$_2^+$. The production rates of nitrate, ClNO$_2$, and Cl$_2$ from the loss of NO$_2^+$ are expressed in Eq. (15) through Eq. (17). The loss rate of aerosol organics induced by NO$_2^+$ is expressed in Eq. (18) (noted as $d[\text{Org}]/dt$ here).

\[
\begin{align*}
\frac{d[\text{NO}_3^-]}{dt} &= k_3[\text{NO}_2^+][\text{H}_2\text{O}] \\
\frac{d[\text{ClNO}_2]}{dt} &= k_4[\text{NO}_2^+][\text{Cl}^-] \\
\frac{d[\text{Cl}_2]}{dt} &= k_6[\text{NO}_2^+][\text{Cl}^-][\text{H}^+] \\
\frac{d[\text{Org}]}{dt} &= k_5[\text{NO}_2^+][\text{Org}]
\end{align*}
\]
The symbol $k_6$ represents the rate constant of the reaction involving NO$_2^+$, Cl$,^-$, and H$. $\phi(Cl_2)$ is obtained as follows, by assuming a steady state of the NO$_2^+$ intermediate (Bertram and Thornton, 2009) (Eq. (19)).

$$\phi(Cl_2) = \frac{d[Cl_2]}{dt} = \frac{k_6[Cl^-][H^+]}{k_6[Cl^-][H^+] + k_4[Cl^-] + k_5[H_2O] + k_3[Org]}$$  \hspace{1cm} (19)

To remain consistent with the $\phi(ClNO_2^2)$ parameterizations, the values 483 and 2.05 were adopted for $k_4/k_3$ and $k_5/k_3$, respectively, while $k_6/k_3$ was estimated from the fitting of $\phi(Cl_2)$ using Eq. (19) to achieve the least-squares errors between the observed and parameterized $\phi(Cl_2)$ values. The parameterization of $\phi(Cl_2)$ was then expressed as follows (Eq. (20)):

$$\phi(Cl_2) = \frac{19.38[H^+][Cl^-]}{19.38[H^+][Cl^-] + 483[Cl^-] + [H_2O] + 2.05[Org]}$$ \hspace{1cm} (20)

where the units of [H$^+$], [Cl$^-$], and [Org] are mol/L.

The previous CINO$_2$ uptake method assumed a unity Cl$_2$ yield from CINO$_2$ uptake, but no such assumption is required in the new method for an explicit definition (Eq. 14) and parameterization (Eq. 20) of the $\phi(Cl_2)$. In addition, a quantitative relationship between $\phi(Cl_2)$ and aerosol acidity is established, which was not given in the previous parameterization.

4. Summary and conclusions

This study reports the presence of significant levels of CINO$_2$ and Cl$_2$ at a suburban site in east China. A rapid increase in the CINO$_2$ mixing ratios was found to occur after midnight due to larger rates of N$_2$O$_5$ heterogeneous loss than in early nighttime hours, and a high $\phi(CINO_2)$ value was also responsible for the elevated CINO$_2$ mixing ratios. Improved parameterization of $\phi(CINO_2)$ was achieved by involving the suppression effect of aerosol organics. We suggest that the observed nighttime Cl$_2$ was a co-produced with CINO$_2$ from the heterogeneous N$_2$O$_5$ uptake on acidic aerosols that bear high concentrations of chloride, and we also propose a parameterization for $\phi(Cl_2)$. The combination of $\phi(Cl_2)$, $\phi(CINO_2)$, and $\gamma(N_2O_5)$ can be used to predict the nighttime formation of Cl$_2$ and CINO$_2$ from N$_2$O$_5$ uptake and their effect on the next day’s atmospheric photochemistry.
Acknowledgments. This study was supported by the National Natural Science Foundation of China (NSFC) project (grant number: 91544213 and D0512/41675145), and the Hong Kong Research Grants Council (T24-504/17-N). The authors acknowledge helpful opinions and discussions from Dr. Yee Jun Tham.

Author contributions. TW designed the research. WN and AD managed the sampling sites. MX, XP, and WW performed the CIMS measurements. CY, ZX, PS, YL, YL, ZX provided other data. MX and TW wrote the manuscript with comments from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

Data availability. To request the CIMS, jNO$_2$, and NO$_y$ data described in this study, please contact the corresponding author (cetwang@polyu.edu.hk). Other datasets are available by contacting Dr. Wei Nie (niewei@nju.edu.cn).

References


Bertram, T., and Thornton, J.: Toward a general parameterization of N$_2$O$_5$ reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmospheric Chemistry and Physics, 9, 8351-8363, 2009.


Finlayson-Pitts, B., Ezell, M., and Pitts, J.: Formation of chemically active chlorine compounds...
by reactions of atmospheric NaCl particles with gaseous N$_2$O$_5$ and ClONO$_2$, Nature, 337, 241-244, 1989.


Phillips, G. J., Thieser, J., Tang, M., Sobanski, N., Schuster, G., Fachinger, J., Drewnick, F.,
Borrmann, S., Bingemer, H., and Lelieveld, J.: Estimating N$_2$O$_5$ uptake coefficients using
ambient measurements of NO$_3$, N$_2$O$_5$, CINO$_2$ and particle-phase nitrate, Atmospheric
Chemistry and Physics, 16, 13231-13249, 2016.
Pratte, P., and Rossi, M. J.: The heterogeneous kinetics of HOBr and HOCl on acidified sea salt
and model aerosol at 40–90% relative humidity and ambient temperature, Physical Chemistry
Chemical Physics, 8, 3988-4001, 2006.
Priestley, M., Breton, M. l., Bannan, T. J., Worrall, S. D., Bacak, A., Smedley, A. R., Reyes-
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, 2018.
Qiu, X., Ying, Q., Wang, S., Duan, L., Zhao, J., Xing, J., Ding, D., Sun, Y., Liu, B., and Shi, A.: 
Modeling the impact of heterogeneous reactions of chlorine on summertime nitrate formation
in Beijing, China, Atmospheric Chemistry and Physics, 19, 6737-6747, 2019.
Riedel, T. P., Bertram, T. H., Crisp, T. A., Williams, E. J., Lerner, B. M., Vlasenko, A., Li, S.
Nitril chloride and molecular chlorine in the coastal marine boundary layer, Environ Sci
Riedel, T. P., Wagner, N. L., Dubé, W. P., Middlebrook, A. M., Young, C. J., Öztürk, F., Bahreini,
R., VandenBoer, T. C., Wolfe, D. E., and Williams, E. J.: Chlorine activation within urban or
power plant plumes: Vertically resolved CINO$_2$ and Cl$_2$ measurements from a tall tower in a
polluted continental setting, Journal of Geophysical Research: Atmospheres, 118, 8702-8715,
2013.
Roberts, J. M., Osthoff, H. D., Brown, S. S., Ravishankara, A., Coffman, D., Quinn, P., and
Bates, T.: Laboratory studies of products of N$_2$O$_5$ uptake on Cl$^-$ containing substrates,
Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to
Tropospheric halogen chemistry: Sources, cycling, and impacts, Chemical reviews, 115, 4035-
4062, 2015.
Spicer, C., Chapman, E., Finlayson-Pitts, B., Plastridge, R., Hubbe, J., Fast, J., and Berkowitz,
C.: Unexpectedly high concentrations of molecular chlorine in coastal air, Nature, 394, 353,
1998.
Staudt, S., Gord, J. R., Karimova, N., McDuffie, E. E., Brown, S. S., Gerber, R. B., Nathanson,
G. M., and Bertram, T. H.: Sulfate and Carboxylate Suppress the Formation of CINO$_2$ at
Atmospheric Interfaces, ACS Earth and Space Chemistry, 2019.
Sun, P., Nie, W., Chi, X., Xie, Y., Huang, X., Xu, Z., Qi, X., Xu, Z., Wang, L., and Wang, T.:
Two years of online measurement of fine particulate nitrate in the western Yangtze River Delta: influences of thermodynamics and N$_2$O$_5$ hydrolysis, Atmospheric Chemistry and Physics, 18, 17177-17190, 2018.


