**N$_2$O$_5$** uptake onto saline mineral dust: a potential missing source of tropospheric ClNO$_2$ in inland China

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**Abstract.** Nitryl chloride (ClNO$_2$), an important precursor of Cl atoms, significantly affects atmospheric oxidation capacity and O$_3$ formation. However, sources of ClNO$_2$ in inland China have not been fully elucidated. In this work, laboratory experiments were conducted to investigate heterogeneous reactions of N$_2$O$_5$ with eight saline mineral dust samples collected from different regions in China, and substantial formation of ClNO$_2$ was observed in these reactions. ClNO$_2$ yields, \( \varphi(\text{ClNO}_2) \), showed large variations (ranging from \(< 0.05\) to \(\sim 0.77\) for different saline mineral dust samples, depending on mass fractions of particulate chloride. In addition, \( \varphi(\text{ClNO}_2) \) could increase, decrease or show insignificant change for different saline mineral dust samples when relative humidity (RH) increased from 18 % to 75 %. We further found that current parameterizations significantly overestimated \( \varphi(\text{ClNO}_2) \) for heterogeneous uptake of N$_2$O$_5$ onto saline mineral dust. In addition, assuming a uniform \( \varphi(\text{ClNO}_2) \) value of 0.10 for N$_2$O$_5$ uptake onto mineral dust, we used a 3-D chemical transport model to assess the impact of this reaction on tropospheric ClNO$_2$ in China and found that weekly mean nighttime maximum ClNO$_2$ mixing ratios could have been increased by up to 85 pptv during a severe dust event in May 2017. Overall, our work showed that heterogeneous reaction of N$_2$O$_5$ with saline mineral dust could be an important source of tropospheric ClNO$_2$ in inland China.
1 Introduction

The formation of O$_3$ and secondary aerosols, two major air pollutants, is closely related to atmospheric oxidation processes (Lu et al., 2019). Primary pollutants emitted by natural and anthropogenic sources are oxidized by various oxidants to produce O$_3$ and secondary aerosols, affecting air quality and climate. Major tropospheric oxidants include OH radicals, NO$_3$ radicals and O$_3$, and in the last 2 decades Cl atoms have been proposed as an important oxidant (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015; Wang et al., 2019). Rate constants for reactions of certain volatile organic compounds (VOCs) with Cl atoms can be a few orders of magnitude larger than those reacting with OH radicals (Atkinson and Arey, 2003; Atkinson et al., 2006); therefore, despite its lower concentrations in the troposphere, Cl can contribute significantly to atmospheric oxidation capacity in some regions (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015; Wang et al., 2019). For example, a modeling study (Sarwar et al., 2014) suggested that including Cl chemistry in the model could enhance oxidative degradation of VOCs by $>20\%$ in some locations.

One major source of tropospheric Cl atoms is daytime photolysis of nitryl chloride (CINO$_2$) (Thornton et al., 2010; Simpson et al., 2015), which is formed in heterogeneous reaction of N$_2$O$_5$ with chloride-containing particles (R1) at nighttime (Osthoff et al., 2008; Thornton et al., 2010):  

$$N_2O_5(g) + Cl^- (aq) \rightarrow \phi CINO_2(g) + (2-\phi)NO_3^-(aq). \quad (R1)$$

The uptake coefficient, $\gamma(N_2O_5)$, and the CINO$_2$ yield, $\psi(CINO_2)$, both depend on relative humidity (RH), aerosol composition and mixing state, etc. (Bertram and Thornton, 2009; Ryder et al., 2014; Mitroo et al., 2019; McNamara et al., 2020; Yu et al., 2020). Cl atoms produced by CINO$_2$ photolysis can effectively enhance atmospheric oxidation (Le Breton et al., 2018; Wang et al., 2019) and thus increase concentrations of O$_3$ and OH radicals during the day (Simon et al., 2009; Riedel et al., 2014; Sarwar et al., 2014; Tham et al., 2016; Wang et al., 2016). In addition, CINO$_2$ is an important temporary reservoir of NO$_x$ at night and releases NO$_2$ during the daytime via photolysis, thereby further affecting daytime photochemistry.

Sea spray aerosol is the most important source of particular chloride (Cl$^-$), and CINO$_2$ is expected to be abundant at marine and coastal regions impacted by anthropogenic emissions. High levels of CINO$_2$ have been observed at various marine and coastal regions across the globe (Simon et al., 2009; Riedel et al., 2012; Tham et al., 2014; Young et al., 2014; Wang et al., 2016; Osthoff et al., 2018; H. Wang et al., 2020; Yu et al., 2020). In addition, many studies (Thornton et al., 2010; Mielke et al., 2011; Phillips et al., 2012; Riedel et al., 2013; Bannan et al., 2015; Faxon et al., 2015; X. Wang et al., 2017; Z. Wang et al., 2017; Tham et al., 2018; Wang et al., 2018) have also reported significant amounts of CINO$_2$ at various continental sites with limited marine influence. For example, CINO$_2$ concentrations reached 4 ppbv in the summer on the North China Plain (Tham et al., 2016). These observations imply the importance of other sources for aerosol chloride, such as coal combustion (Eger et al., 2019), biomass burning (Ahern et al., 2017), waste incineration (Bannan et al., 2019) and snow-melting agent application (Mielke et al., 2016; McNamara et al., 2020).

In addition to insoluble minerals (e.g., quartz, feldspar, clay and carbonate), mineral dust aerosols emitted from saline topsoil in arid and semi-arid regions may contain significant amounts of soluble material such as chloride and sulfate (Gillette et al., 1992; Abduwaili et al., 2008; Zhang et al., 2009; Wang et al., 2012; Jordan et al., 2015; Frie et al., 2017; Gaston et al., 2017; Tang et al., 2019; Gaston, 2020). As elemental and mineralogical compositions are different for conventional and saline mineral dust, they would differ significantly in their physicochemical properties and impacts on atmospheric chemistry and climate. For example, hygroscopicity and cloud condensation nuclei (CCN) activities of saline mineral dust can be much higher than those of conventional mineral dust (Pratt et al., 2010; Gaston et al., 2017; Tang et al., 2019; Zhang et al., 2020). Recent laboratory studies (Mitroo et al., 2019; Royer et al., 2021) have found that heterogeneous reactions of N$_2$O$_5$ with saline mineral dust originating from the western and southwestern USA can be very effective and produce significant amounts of CINO$_2$. Large variations in $\gamma(N_2O_5)$ and $\psi(CINO_2)$ were reported (Mitroo et al., 2019; Royer et al., 2021), depending on RH as well as on the chemical and mineralogical contents of saline mineral dust samples.

A very recent study (Wu et al., 2020) showed that N$_2$O$_5$ uptake onto saline mineral dust contributed significantly to particulate nitrate formation during a dust storm event in Shanghai, China. One may further expect that it may have a profound effect on CINO$_2$, especially considering that vast areas in China are heavily affected by both mineral dust and NO$_x$. Nevertheless, heterogeneous formation of CINO$_2$ from N$_2$O$_5$ uptake onto saline mineral dust in regions other than the USA has not been explored. In order to provide key parameters required to assess the potential of saline mineral dust as a CINO$_2$ source in China, we conducted a series of laboratory experiments to investigate CINO$_2$ formation in heterogeneous reaction of N$_2$O$_5$ with several saline mineral dust samples collected from different regions in China. In addition to differences in source regions, the saline mineral dust samples examined in our work have substantial variations in composition and mineralogy, enabling us to examine the effects of particle composition and water content on CINO$_2$ production. In order to better understand variations in CINO$_2$ yields with RH and samples, we experimentally measured mass hygroscopic growth factors of the eight samples examined, while previous studies (Mitroo et al., 2019; Royer et al., 2021) used the thermodynamic model ISORROPIA II (Fountoukis and Nenes, 2007) to predict particulate water contents. Based on our laboratory results, we further use a
3-D chemical transport model (GEOS-Chem) to assess the impacts of ClNO₂ produced from N₂O₅ uptake onto mineral dust on ClNO₂ and O₃ in China during a major dust event which occurred in May 2017.

2 Methodology

2.1 Characterization of saline mineral dust samples

Eight saline mineral dust samples, originating from five different provinces in northern China (including Ningxia, Xinjiang, Shandong, Inner Mongolia and Shaanxi), were examined in this work, and full information on these samples can be found elsewhere (Tang et al., 2019). Table 1 summarizes key information on these samples. According to their chloride contents, the eight samples were classified into three categories, including two high-chloride samples (H1 and H2), four medium-chloride samples (M1, M2, M3 and M4) and two low-chloride samples (L1 and L2).

Our previous work (Tang et al., 2019; Zhang et al., 2020) measured mass hygroscopic growth factors of the eight samples at 0%–90% RH with a RH resolution of 10%, using a vapor sorption analyzer (Gu et al., 2017). As the highest RH at which heterogeneous reaction of N₂O₅ with saline mineral dust was conducted in our work was ~75%, we further measured mass growth factors of the eight samples at 75%±2% RH, and the results are also included in Table 1.

2.2 Experimental apparatus

Figure 1 shows the experimental apparatus used to study heterogeneous interactions of N₂O₅ with saline mineral dust. It mainly consists of three parts: (1) N₂O₅ generation, (2) gas–particle interaction, and (3) detection of N₂O₅ and ClNO₂.

2.2.1 N₂O₅ generation

In our work, N₂O₅ was generated via oxidation of NO₂ by O₃. As shown in Fig. 1, a synthetic airflow (30 mL min⁻¹) was passed over a Hg lamp to produce O₃ via O₂ photolysis at 184.95 nm. The photolysis module was stabilized at 35±0.2 °C using a Peltier cooler controlled by a proportion integration differentiation (PID) algorithm, in order to give stable O₃ output. The O₃/airflow was then mixed with a NO₂ flow (80 mL min⁻¹, 10 ppmv in synthetic air) in a temperature-stabilized polyfluoroalkoxy (PFA) reactor with a residence time of ~70 s to produce N₂O₅. After exiting the PFA reactor, the flow (110 mL min⁻¹) was then diluted with a humidified nitrogen flow (2500 mL min⁻¹), and the RH of the humidified nitrogen flow was monitored using a hygrometer. The final flow had a total flow rate of 2610 mL min⁻¹.

2.2.2 Heterogeneous interactions

As shown in Fig. 1, the mixed flow (2610 mL min⁻¹) could be directed through a blank polytetrafluoroethylene (PTFE) membrane filter (47 mm, Whatman, USA) housed in a PFA filter holder, and in this case initial N₂O₅ and ClNO₂ concentrations were measured; in our experiments, initial N₂O₅ concentrations were in the range of 0.4–1.0 ppbv. Alternatively, the flow could also be passed through a PTFE filter loaded with saline mineral dust, and thus N₂O₅ and ClNO₂ concentrations after heterogeneous reaction with saline mineral dust loaded on the filter were measured. During our experiments, the flow could be switched back to pass through the blank filter in order to check whether the initial N₂O₅ and ClNO₂ concentrations were stable.

Saline mineral dust particles were loaded onto PTFE filters using the method described in our previous study (Li et al., 2020; Jia et al., 2021). In brief, 10 mL of particle / ethanol mixture was transferred onto a PTFE filter, and after ethanol was evaporated a relatively uniform particle film, as revealed by visual inspection, was formed on the filter. PTFE filters were weighted before and after being loaded with particles in order to determine the mass of particles loaded onto these filters. In our work, the mass of particles on filters was in the range of 0.6–7.3 mg.

2.2.3 Detection of N₂O₅ and ClNO₂

After exiting one of the two filters, a flow of 2200 mL min⁻¹ was sampled into a time-of-flight chemical ionization mass spectrometry (CIMS) instrument to measure N₂O₅ and ClNO₂ concentrations, and the remaining flow (~400 mL min⁻¹) went into the exhaust. The CIMS instrument has been detailed previously (Kercher et al., 2009; Wang et al., 2016). In brief, N₂O₅ and ClNO₂ were detected as I(N₂O₅)⁻ and I(ClNO₂)⁻ clusters at 235 and 208 m/z (R2a, R2b) using I⁻ as the reagent ion, and a soft X-ray device (Hamamatsu, Soft X-Ray 120°) was employed to generate I⁻ from CH₃I/N₂. The CIMS instrument was calibrated before and after our experiments, which lasted for ~1 month, and further details on calibration can be found in the Appendix. The detection limits were 2 pptv for N₂O₅ and 3 pptv for ClNO₂, calculated as 4 times the standard deviation (4σ) when measuring blank samples with a 1 min average, and the accuracy was estimated to be ~25%.

\[ \text{N}_2\text{O}_5 + \text{I}^- \rightarrow \text{I}(\text{N}_2\text{O}_5)^- \quad (\text{R2a}) \]
\[ \text{ClNO}_2 + \text{I}^- \rightarrow \text{I}(\text{ClNO}_2)^- \quad (\text{R2b}) \]

2.3 Model description

We use GEOS-Chem (version 12.9.3) to quantify the effects of ClNO₂ formation due to heterogeneous reaction of N₂O₅ with saline dust in China. The model, which includes a detailed representation of coupled ozone–NOₓ–VOC–aerosol–halogen chemistry (Wang et al., 2021), is driven by MERRA2 (the Modern-Era Retrospective Analysis for Research and Applications, Version 2) assimilated meteorological fields from the NASA Global Modeling and
Table 1. Overview of mass fractions of major soluble ions and mass ratios of particulate water at 75 % ± 2 % RH to dry particles for the eight saline mineral dust samples examined in this work. Mass fractions of major soluble ions were reported previously (Tang et al., 2019), and particulate water contents at 75 % ± 2 % RH were measured by the present work. The abbreviation n.d. denotes not detected.

<table>
<thead>
<tr>
<th>Category</th>
<th>Sample&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Sample&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Na&lt;sup&gt;+&lt;/sup&gt;</th>
<th>Cl&lt;sup&gt;−&lt;/sup&gt;</th>
<th>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2−&lt;/sup&gt;</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O (75 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>H1</td>
<td>NX</td>
<td>0.3537</td>
<td>0.3870</td>
<td>0.0958</td>
<td>1.3093</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>XJ-5</td>
<td>0.2407</td>
<td>0.2145</td>
<td>0.0973</td>
<td>1.7066</td>
</tr>
<tr>
<td>Medium Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>M1</td>
<td>SD</td>
<td>0.0265</td>
<td>0.0508</td>
<td>0.0754</td>
<td>0.3911</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>XJ-4</td>
<td>0.0326</td>
<td>0.0341</td>
<td>0.0071</td>
<td>0.0428</td>
</tr>
<tr>
<td></td>
<td>M3</td>
<td>IM-2</td>
<td>0.0471</td>
<td>0.0229</td>
<td>0.1413</td>
<td>0.2106</td>
</tr>
<tr>
<td></td>
<td>M4</td>
<td>IM-3</td>
<td>0.1343</td>
<td>0.0095</td>
<td>0.3424</td>
<td>0.0174</td>
</tr>
<tr>
<td>Low Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>L1</td>
<td>XJ-3</td>
<td>0.0239</td>
<td>0.0093</td>
<td>0.0497</td>
<td>0.0475</td>
</tr>
<tr>
<td></td>
<td>L2</td>
<td>SX</td>
<td>0.0003</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.0126</td>
</tr>
</tbody>
</table>

<sup>a</sup> Sample names used in the present work.
<sup>b</sup> Corresponding sample names used in our previous work (Tang et al., 2019).

Figure 1. Schematic diagram of the experimental apparatus.

Assimilation Office (GMAO) with a native horizontal resolution of 0.25° x 0.3125° and 72 vertical levels from the surface to the mesosphere. Our simulation was conducted over East Asia (10° S–55° N, 60–150° E) at the native resolution with dynamical boundary conditions from a 4° x 5° global simulation. Anthropogenic emissions in China are based on the Multi-resolution Emission Inventory for China (MEIC) (Zheng et al., 2018) and an inventory of HCl and fine particulate Cl<sup>−</sup> in China (Fu et al., 2018). Natural dust emissions are calculated based on Ridley et al. (2013). A more detailed description of the model and emissions can be found elsewhere (X. Wang et al., 2020).

For N<sub>2</sub>O<sub>5</sub> uptake onto aqueous aerosols, the parameterization in our previous study (X. Wang et al., 2020) for γ(N<sub>2</sub>O<sub>5</sub>) and ϕ(ClNO<sub>2</sub>) is used in this study, and more details can be found in the Supplement. For N<sub>2</sub>O<sub>5</sub> uptake on dust aerosol, γ(N<sub>2</sub>O<sub>5</sub>) is always assumed to be 0.02, as recommended previously (Crowley et al., 2010; Tang et al., 2017), and ϕ(ClNO<sub>2</sub>) is assumed to be 0 in the standard case; i.e., no ClNO<sub>2</sub> is produced in heterogeneous reaction of N<sub>2</sub>O<sub>5</sub> with mineral dust.

3 Results and discussion

Figure 2a shows changes in N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> concentrations during an experiment in which heterogeneous reaction of N<sub>2</sub>O<sub>5</sub> with sample H1 at 37 % RH was studied. As shown in Fig. 2a, when the mixed flow was passed through the blank filter (0–10 min), N<sub>2</sub>O<sub>5</sub> concentrations were measured to be ∼350 pptv and ClNO<sub>2</sub> was below the detection limit. The mixed flow was then passed through the particle-loaded filter at ∼10 min in order to initiate heterogeneous reaction of N<sub>2</sub>O<sub>5</sub> with sample H1, and a significant decrease in N<sub>2</sub>O<sub>5</sub> concentrations (from ∼350 to ∼150 pptv) and a significant increase in ClNO<sub>2</sub> concentrations (from almost 0 to ∼150 pptv) were observed, suggesting that heterogeneous interaction with sample H1 substantially consumed N<sub>2</sub>O<sub>5</sub> and generated ClNO<sub>2</sub>. In order to check if initial N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> concentrations were stable, during our experiments the mixed flow was switched back to pass through the blank filter from time to time (e.g., at around 40, 75 and 105 min for the experiment displayed in Fig. 2a). Indeed, initial N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> concentrations were constant in our experiments, with another two examples shown in Fig. 2b and c.
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Figure 2. Time series for measured N$_2$O$_5$ and ClNO$_2$ concentrations after the mixed flow was passed through the blank filter or the particle-loaded filter: (a) H1, 37 % RH; (b) M3, 55 % RH; (c) L1, 73 % RH. Periods in which the mixed flow was passed through the particle-loaded filter are shaded gray.

Figure 2b and c show time series of measured N$_2$O$_5$ and ClNO$_2$ concentrations in another two experiments, suggesting that heterogeneous reaction with sample M3 and L1 also led to substantial removal of N$_2$O$_5$. However, much less ClNO$_2$ was produced for sample M3 and L1 when compared to sample H1 (Fig. 2a). The decrease in N$_2$O$_5$ concentrations, $\Delta$[N$_2$O$_5$], and the increase in ClNO$_2$ concentrations, $\Delta$[ClNO$_2$], can be used to calculate ClNO$_2$ yields, $\psi$(ClNO$_2$), according to Eq. (1).

$$\psi$(ClNO$_2$) = $\frac{\Delta$[ClNO$_2$]}{\Delta$[N$_2$O$_5$]}$ (1)

In this work we measured $\psi$(ClNO$_2$) for heterogeneous reaction of N$_2$O$_5$ with eight different saline mineral dust samples at four RH levels, and each experiment was repeated at least three times. It should be mentioned that during each experiment the measured $\psi$(ClNO$_2$) did not vary significantly with time, and therefore an average value of $\psi$(ClNO$_2$) was reported for each experiment. Table 2 summarizes measured $\psi$(ClNO$_2$) for the eight samples at different RH levels, and the results are further discussed in the following sections.

3.1 ClNO$_2$ production yields

Figure 3 shows ClNO$_2$ yields as a function of RH for the two samples with high chloride content (H1 and H2), and $\psi$(ClNO$_2$) values were found to be quite high for the two samples. To be more specific, the mass fraction of chloride was 0.3870 for sample H1, and $\psi$(ClNO$_2$) values were found to increase from 0.402 ± 0.138 at 18 % RH to 0.774 ± 0.028 at 56 % RH, and then they slightly decreased to 0.697 ± 0.311 when RH was further increased to 75 %. For sample H2, the mass fraction of chloride (0.2145) was lower than for sample H1, and $\psi$(ClNO$_2$) showed a small decrease (or remained relatively constant) when RH was increased from 18 % to 56 %, ranging from 0.474 ± 0.026 to 0.560 ± 0.046; a further increase in RH to 75 % resulted in a small decrease in $\psi$(ClNO$_2$) to 0.378 ± 0.069.

ClNO$_2$ yields are shown in Fig. 4 as a function of RH for the two low-chloride samples (L1 and L2), and their mass fractions of chloride were < 0.01. As shown in Fig. 4, $\psi$(ClNO$_2$) values were found to be always < 0.05 for the two samples, suggesting that heterogeneous production of ClNO$_2$ was very limited, despite substantial removal of N$_2$O$_5$ due to heterogeneous reaction (with an example shown in Fig. 2c).
The low \( \varphi(\text{CINO}_2) \) values for sample L1 and L2 could be attributed to their low chloride contents. In addition, \( \varphi(\text{CINO}_2) \) appeared to increase with RH for L1 and L2; however, since the uncertainties associated with \( \varphi(\text{CINO}_2) \) were rather large for these two samples, the dependence of \( \varphi(\text{CINO}_2) \) on RH should be treated in caution.

We also investigated CINO\(_2\) production from heterogeneous reaction of \( \text{N}_2\text{O}_5 \) with four samples with medium-chloride contents (M1, M2, M3 and M4), and the results are displayed in Fig. 5. Mass fractions of chloride were determined to be 0.0508 for M1, 0.034 for M2, 0.0229 for M3 and 0.0095 for M4. CINO\(_2\) yields were found to increase significantly with RH for M1 and M2; more specifically, \( \varphi(\text{CINO}_2) \) increased from 0.271 ± 0.038 at 18 % RH to 0.543 ± 0.086 at 75 % RH for sample M1 and increased from 0.166 ± 0.018 at 18 % RH to 0.418 ± 0.0052 at 75 % RH for sample M2. As shown in Fig. 5, the dependence of \( \varphi(\text{CINO}_2) \) on RH for the other two medium-chloride samples (M3 and M4) was rather different from that of M1 and M2. For sample M3, \( \varphi(\text{CINO}_2) \) first increased from 0.223 ± 0.061 at 18 % RH to 0.251 ± 0.050 at 36 % RH, and a further increase in RH to 75 % caused substantial reduction in \( \varphi(\text{CINO}_2) \). Finally, no significant variation in \( \varphi(\text{CINO}_2) \) with RH (18 %–75 %) was observed for sample M4.

### 3.2 The effects of RH

The dependence of \( \varphi(\text{CINO}_2) \) on RH for the eight saline mineral samples we examined, as discussed in Sect. 3.1, exhibited two interesting features. First, when RH was as low as 18 %, large \( \varphi(\text{CINO}_2) \) values (>0.2) were observed for four samples (H1, H2, M1 and M3). As the deliquescence RH of NaCl is ~75 %, one may wonder where aqueous chloride, which is necessary for heterogeneous formation of CINO\(_2\), came from at 18 % RH. As initially suggested by a previous study (Mitroo et al., 2019), the occurrence of aqueous chloride in saline mineral dust particles at low RH could be due to the presence of CaCl\(_2\) and MgCl\(_2\), which were amorphous under dry conditions and could take up water at very low RH (Guo et al., 2019). Our previous study (Tang et al., 2019) measured water-soluble ions contained by the eight saline mineral dust samples, and as shown in Fig. S1 in the Supplement, the amounts of water-soluble Ca\(^{2+}\) in the four samples (H1, H2, M1 and M3) with larger \( \varphi(\text{CINO}_2) \) at 18 % RH were significantly larger than those in the other four samples.
Figure 4. Measured ClNO\(_2\) yields (black symbol) and \(m_w/m_0\) (red line) as a function of RH for (a) L1 and (b) L2. The error bar represents standard deviation, and \(m_w/m_0\) represents the normalized mass of particulate water (normalized to the mass of dry particles), which was measured as the relative increase in particle mass at a given RH compared to < 1 % RH.

Figure 5. Measured ClNO\(_2\) yields (black symbol) and \(m_w/m_0\) (red line) as a function of RH for (a) M1, (b) M2, (c) M3 and (d) M4. The error bar represents standard deviation, and \(m_w/m_0\) represents the normalized mass of particulate water (normalized to the mass of dry particles), which was measured as the relative increase in particle mass at a given RH compared to < 1 % RH.

(M2, M4, L1 and L2). This observation further supported our deduction that the presence of CaCl\(_2\) enabled efficient formation of ClNO\(_2\) at low RH.

The second interesting feature is that as shown in Figs. 3–5, \(\varphi(\text{ClNO}_2)\) could increase, decrease or remain relatively constant with an increase in RH from 18 % to 75 %. This feature can be understood given the complex mechanisms driving heterogeneous uptake of N\(_2\)O\(_5\) onto saline mineral dust (Mitroo et al., 2019; Royer et al., 2021): at a given RH, N\(_2\)O\(_5\) can react with aqueous water, aqueous chloride and insoluble minerals, and only its reaction with aqueous chloride would produce ClNO\(_2\). The possible effects of RH on
\[ \varphi(\text{ClNO}_2) \] are discussed below: (1) as RH increases, heterogeneous reactivity of N\(_2\)O\(_5\) towards insoluble minerals can be enhanced, suppressed or remain largely unchanged (Tang et al., 2012, 2017); (2) an increase in RH would lead to further hygroscopic growth and dilution of aqueous solutions, leading to a decrease in \( \varphi(\text{ClNO}_2) \) in this regard; (3) the increase in particulate water with RH would cause more chloride to be dissolved into aqueous solutions, and in this regard an increase in RH would promote ClNO\(_2\) formation. As a result, it is not surprising to observe different levels of dependence of \( \varphi(\text{ClNO}_2) \) on RH for different saline mineral dust samples.

### 3.3 Discussion

Figure 6 shows the dependence of \( \varphi(\text{ClNO}_2) \) on mass fractions of chloride for the eight samples we examined at four different RH levels. These samples showed significant variation in \( \varphi(\text{ClNO}_2) \), ranging from \(< 0.1\) to \(> 0.7\), and \( \varphi(\text{ClNO}_2) \) values were the largest for the two high-chloride samples (H1 and H2), followed by the medium-chloride samples (M1, M2, M3, and M4) and low-chloride samples (L1 and L2). Overall, a positive dependence of \( \varphi(\text{ClNO}_2) \) on mass fractions of chloride was observed at each RH level. Figure 6 also reveals that the measured \( \varphi(\text{ClNO}_2) \) values were very sensitive to mass fractions of chloride when the mass fractions of chloride were below 10 %. This is because an increase in RH would promote dissolution of chloride to aqueous water and thus enhance ClNO\(_2\) formation. However, as shown in Fig. 6, higher chloride contents did not always mean larger \( \varphi(\text{ClNO}_2) \), and similar observations have also been reported in previous work (Mitroo et al., 2019; Royer et al., 2021).

Two parameterizations have been widely used to predict the dependence of \( \varphi(\text{ClNO}_2) \) on the chemical compositions and water contents of aqueous aerosol particles (Bertram and Thornton, 2009; Yu et al., 2020). Based on laboratory results, Bertram and Thornton (2009) suggested that ClNO\(_2\) yields can be calculated using Eq. (2):

\[
\varphi(\text{ClNO}_2) = \left( 1 + \frac{k(\text{H}_2\text{O}) \cdot [\text{H}_2\text{O}_{(aq)}]}{k(\text{Cl}^-) \cdot [\text{Cl}^-]} \right)^{-1}, \tag{2}
\]

where \([\text{H}_2\text{O}_{(aq)}]/[\text{Cl}^-] \) is the ratio of molar concentration of H\(_2\)O to that of Cl\(^{-}\) in aqueous particles, and the value of \(k(\text{H}_2\text{O})/k(\text{Cl}^-)\) was suggested to be \(1/(483 \pm 175)\) (Bertram and Thornton, 2009). Very recently, Yu et al. (2020) examined uptake coefficients of N\(_2\)O\(_5\) onto ambient aerosol particles at four different sites in China and suggested that using a value of \(1/(105 \pm 37)\) for \(k(\text{H}_2\text{O})/k(\text{Cl}^-)\) would lead to better agreement between the measured and predicted uptake coefficients of N\(_2\)O\(_5\) (Yu et al., 2020).

The two parameterizations were used in our work to calculate \( \varphi(\text{ClNO}_2) \) at 75 % RH for the eight saline mineral dust samples we examined. \([\text{H}_2\text{O}_{(aq)}]/[\text{Cl}^-] \) was calculated from the measured mass growth factors at 75 % RH and the mass fractions of chloride, assuming that all the chloride contained by saline mineral dust samples was dissolved into aqueous solutions at 75 % RH. The comparison between measured and calculated \( \varphi(\text{ClNO}_2) \) is displayed in Fig. 7, suggesting that both parameterizations significantly overestimated the measured \( \varphi(\text{ClNO}_2) \) for all the eight saline mineral dust samples we investigated. A previous study (Mitroo et al., 2019) investigated \( \varphi(\text{ClNO}_2) \) for heterogeneous uptake of N\(_2\)O\(_5\) onto saline mineral dust samples collected in the southwestern USA, and similarly they found that the measured \( \varphi(\text{ClNO}_2) \) values were significantly smaller than those predicted using the parameterization proposed by Bertram and Thornton (2009).

The observed discrepancies between measured and predicted \( \varphi(\text{ClNO}_2) \) can be caused for several reasons. First, even at \( \sim 75\%\) RH (the highest RH at which our experiments were conducted), chloride contained in saline mineral dust may not be fully dissolved, and therefore our calculation may overestimate \([\text{Cl}^-]/[\text{H}_2\text{O}_{(aq)}]\) and also overestimate \( \varphi(\text{ClNO}_2) \). This effect should not be large as significant water uptake was observed at \( \sim 75\%\) RH for the saline mineral dust sample we examined (Figs. 3–5). Second, perhaps more importantly, saline mineral dust samples contain substantial quantities of insoluble minerals, and some of these minerals, such as clays, are very reactive towards N\(_2\)O\(_5\) (Tang et al., 2017), and only nitrate, and no ClNO\(_2\), was formed (Seisel et al., 2005; Karagulian et al., 2006; Tang et al., 2012). However, the two parameterizations did not take into account heterogeneous reaction of N\(_2\)O\(_5\) with insoluble minerals and as a result would inevitably overestimate \( \varphi(\text{ClNO}_2) \). Finally, our calculations assumed internal mixing, but inter- and intra-particle heterogeneity of saline mineral dust particles could also contribute to the observed gap between measured and calculated \( \varphi(\text{ClNO}_2) \). For example, a wintertime field campaign at Ann Arbor (Michigan, USA) (McNamara et al., 2020) showed that due to nonhomogeneous chloride distribution across road salt aerosol particles, observed \( \varphi(\text{ClNO}_2) \) values were significantly smaller than predicted values. The comparison between measured and predicted \( \varphi(\text{ClNO}_2) \) suggests that while heterogeneous uptake of N\(_2\)O\(_5\) onto saline mineral dust could be an important source of inland ClNO\(_2\), underlying mechanisms which affect heterogeneous production of ClNO\(_2\) from saline mineral dust have not been well elucidated.

### 4 Atmospheric implications

We consider ClNO\(_2\) formation in heterogeneous uptake of N\(_2\)O\(_5\) onto dust aerosol in GEOS-Chem to explore its atmospheric implications. Since Cl\(^-\) concentration in mineral dust is not well known and currently we are not able to parameterize \( \varphi(\text{ClNO}_2) \) for mineral dust (as discussed in Sect. 3.3), we use a fixed \( \varphi(\text{ClNO}_2) \) value of 0.1 in our simulation. This
value, which is at the low end of our measured range of \( \varphi(\text{CINO}_2) \) (< 0.05 to ~ 0.77), is higher than those values determined in our work for low-chloride samples but lower than those for medium-chloride samples. The purpose of our modeling work is to preliminarily assess whether \( \text{N}_2\text{O}_5 \) uptake onto saline dust may have important effects on tropospheric chemistry as a potential source of CINO\(_2\). We focus on simulations on 2–7 May 2017, during which a large dust event took place in East Asia. It caused high concentrations of dust aerosols with a maximum hourly concentration higher than 1000 \( \mu \text{g m}^{-3} \) over a wide area in China (Zhang et al., 2018), which are also well captured by our simulations (Fig. S2 in the Supplement).

Figure 8 shows the weekly mean values of the nighttime maximum surface CINO\(_2\) mixing ratios and the contribution of heterogeneous reaction of \( \text{N}_2\text{O}_5 \) with dust aerosol to CINO\(_2\) over 2–7 May 2017. The impact of \( \text{N}_2\text{O}_5 \) uptake onto dust aerosol is calculated as the difference between the standard case in which \( \varphi(\text{CINO}_2) \) is assumed to be 0 for \( \text{N}_2\text{O}_5 \) uptake onto dust aerosol and the case in which \( \varphi(\text{CINO}_2) \) is assumed to be 0.1. Due to large diurnal variations and near-zero mixing ratios of CINO\(_2\) in the daytime, we use the mean nighttime maximum value for CINO\(_2\), following previous standard practice (Wang et al., 2019). The largest impact on CINO\(_2\) is found in central China, where weekly mean nighttime maximum surface CINO\(_2\) mixing ratios are increased by 85 pptv, due to the heavy impact of dust aerosol transported from the north and high NO\(_x\) emissions in this region. Even larger effects (up to a 240 pptv increase in CINO\(_2\)) can be found on some individual days, as shown in Figs. S3 and S4 in the Supplement. These results suggest that \( \text{N}_2\text{O}_5 \) uptake onto dust could be an important source for tropospheric CINO\(_2\) over central and northeast China, where CINO\(_2\) formation is conventionally believed to be limited due to rela-
eral dust samples collected from different regions in China as a function of RH (18 %–75 %). Significant production of CINO2 was observed for some of the saline mineral dust samples examined, and CINO2 yields, \( \phi(\text{CINO}_2) \), were determined to span from \(< 0.05\) to \(0.77\), depending on chemical compositions of saline mineral dust samples and RH. In general a positive dependence of \( \phi(\text{CINO}_2) \) on mass fractions of particulate chloride was observed at each RH level, but higher particulate chloride content did not always result in higher \( \phi(\text{CINO}_2) \). On the other hand, an increase in RH could increase, reduce or have no significant impacts on \( \phi(\text{CINO}_2) \), revealing the complex mechanisms which drive heterogeneous uptake of \( \text{N}_2\text{O}_5 \) on saline mineral dust.

Two widely used parameterizations (Bertram and Thornton, 2009; Yu et al., 2020) were used to estimate \( \phi(\text{CINO}_2) \) at 75 % RH for the eight saline mineral dust samples we investigated. Both parameterizations were found to significantly overestimate the measured \( \phi(\text{CINO}_2) \), and we suggested that the discrepancies between measured and predicted \( \phi(\text{CINO}_2) \) could be due to incomplete dissolution of particulate chloride, heterogeneous reaction of \( \text{N}_2\text{O}_5 \) with insoluble minerals, and/or inter- and intra-particle heterogeneity of saline mineral dust particles.

Assuming a \( \phi(\text{CINO}_2) \) value of 0.1 for heterogeneous reaction of \( \text{N}_2\text{O}_5 \) with mineral dust, we use GEOS-Chem to assess the impact of this reaction on tropospheric CINO2 and \( \text{O}_3 \) in China during a severe dust event which occurred during 2–7 May 2017. It is found that after taking into account CINO2 production due to \( \text{N}_2\text{O}_5 \) uptake onto mineral dust aerosol, weekly mean nighttime maximum CINO2 mixing ratios could be increased by up to 85 pptv during this period and the daily maximum 8 h average \( \text{O}_3 \) mixing ratios were increased by up to 0.32 ppbv.

In summary, our work shows that heterogeneous reaction of \( \text{N}_2\text{O}_5 \) with saline mineral dust can be an important source for tropospheric CINO2 in inland China. This reaction may also be important for tropospheric CINO2 production in many other regions across the world, as the occurrence of saline mineral dust aerosols has been reported in various locations, such as Iran (Gholampour et al., 2015), the United States (Blank et al., 1999; Pratt et al., 2010; Jordan et al., 2015; Frie et al., 2017) and Argentina (Bucher and Stein, 2016). Currently our limited knowledge precludes quantitative prediction of heterogeneous CINO2 production from saline mineral dust, and further investigation is thus warranted.

Appendix A: \( \text{N}_2\text{O}_5 \) and CINO2 calibration

To calibrate CIMS measurements of \( \text{N}_2\text{O}_5 \), a mixed flow containing \( \text{N}_2\text{O}_5 \), which was produced via \( \text{O}_3 \) oxidation of \( \text{NO}_2 \), was sampled into the CIMS instrument, and \( \text{N}_2\text{O}_5 \) was quantified using the normalized intensities of \( \text{I}(\text{N}_2\text{O}_5^-) \) clusters, \( f(\text{N}_2\text{O}_5^-) \), defined as the ratio of the signal intensity

\[ f(\text{N}_2\text{O}_5^-) = \frac{I(\text{N}_2\text{O}_5^-)}{I_{\text{baseline}}} \]

of an unknown sample to that of a standard.

5 Conclusions

It has been widely recognized that nitryl chloride (CINO2), produced by heterogeneous reaction of \( \text{N}_2\text{O}_5 \) with chloride-containing aerosols, could significantly affect atmospheric oxidation capacity. However, heterogeneous formation of tropospheric CINO2 in inland regions in China has not been well elucidated. In this work, we investigated CINO2 formation in heterogeneous reaction of \( \text{N}_2\text{O}_5 \) with eight saline min-

Figure 8. Modeled weekly mean mixing ratios of nighttime maximum CINO2 (a, b) and maximum daily 8 h average (MDA8) ozone (c, d) in surface air over China during 2–7 May 2017. The left panels (a, c) show simulated mixing ratios in our standard case in which \( \phi(\text{CINO}_2) \) is assumed to be 0 for \( \text{N}_2\text{O}_5 \) uptake onto dust aerosol. The right panels (b, d) show impacts of CINO2 formation due to \( \text{N}_2\text{O}_5 \) uptake onto dust, calculated as the difference between the standard case and the case in which \( \phi(\text{CINO}_2) \) is assumed to be 0.1 for \( \text{N}_2\text{O}_5 \) uptake onto dust.

Figure 8 also shows the effect of CINO2 formation due to heterogeneous reaction of \( \text{N}_2\text{O}_5 \) with dust aerosol on the daily maximum 8 h average (MDA8) ozone mixing ratios in the surface air over China during the same period. MDA8 ozone mixing ratios are increased by up to 0.32 ppbv after considering mineral dust as an additional source of CINO2. Our simulation assumes a low value of \( \phi(\text{CINO}_2) \) in our measured range (< 0.05 to ∼ 0.77) and is conducted in summer when it is more difficult for CINO2 to accumulate due to short nights (compared to winter and spring with long nights). We expect that its impacts on CINO2 and ozone could be larger for dust events in winter and spring.
Figure A1. CIMS sensitivities as a function of RH for (a) N$_2$O$_5$ and (b) ClNO$_2$. 

(cps) of I(N$_2$O$_5$)$^-$ to that of the total reagent ions, i.e., I$^-$ and I(H$_2$O)$_2$$^-$, N$_2$O$_5$ concentrations in the mixed flow were quantified using cavity-enhanced absorption spectroscopy (CEAS) (H. Wang et al., 2017), with a detection limit of 2.7 pptv in 5 s and an uncertainty of $\sim$ 25 %. RH of the mixed flow was varied during the calibration in order to determine the CIMS sensitivity for N$_2$O$_5$ at different RH levels, and the results are displayed in Fig. A1. The sensitivity for N$_2$O$_5$ first increased with RH, reaching the maximum value at $\sim$ 40 % RH, and then decreased with further increases in RH.

To calibrate CIMS measurements of ClNO$_2$, a nitrogen flow (6 mL min$^{-1}$) containing 10 ppmv of Cl$_2$ was passed over a slurry containing NaNO$_2$ and NaCl to produce ClNO$_2$ (Thaler et al., 2011), and NaCl was included in the slurry in order to minimize the formation of NO$_2$ as a byproduct. The mixed flow containing ClNO$_2$ was then conditioned to a given RH and sampled into the CIMS instrument; similarly to N$_2$O$_5$, ClNO$_2$ was quantified using the normalized intensities of I(ClNO$_2$)$^-$ clusters, $f$(ClNO$_2$), defined as the ratio of the signal intensity (cps) of I(ClNO$_2$)$^-$ to that of the total reagent ions. To quantify ClNO$_2$, the mixed flow was delivered directly into a cavity attenuated phase shift spectroscopy (CAPS) instrument (Model N500, Teledyne API) to measure background NO$_2$ concentrations; after that, the mixed flow was delivered through a thermal dissociation model at 365 °C to fully decompose ClNO$_2$ to NO$_2$, and the total NO$_2$ concentrations were then determined using CAPS. The differences in the measured NO$_2$ concentrations with and without thermal dissociation were equal to ClNO$_2$ concentrations. The CAPS instrument had a detection limit of 0.2 ppbv in 1 min for NO$_2$ and an uncertainty of $\sim$ 10 %. As shown in Fig. A1, the sensitivity for ClNO$_2$ increased with RH up to 40 % and showed little variation with further increases in RH.

**Code and data availability.** Data used in this paper can be found in the main text or Supplement. The GEOS-Chem model is available at the GEOS-Chem repository (http://www.geos-chem.org, GEOS-Chem, 2020).

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