# Winter CINO<sub>2</sub> formation in the region of fresh anthropogenic emissions: Seasonal variability and insights into daytime peaks in northern China

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## 21 Abstract

22 Nitryl chloride (ClNO<sub>2</sub>) is an important chlorine reservoir in the atmosphere that affects the oxidation of volatile organic compounds (VOCs) and the production of RO<sub>x</sub> radicals 23 and ozone (O<sub>3</sub>). This study presents measurements of ClNO<sub>2</sub> and related compounds at 24 urban, polluted rural, and polluted lower tropospheric (mountaintop) sites in the winter 25 of 2017-2018 over the North China Plain (NCP). The nocturnal concentrations of 26 ClNO<sub>2</sub> were lower at the urban and polluted rural sites but higher at the polluted lower 27 tropospheric site. The winter concentrations of ClNO<sub>2</sub> were generally lower than the 28 summer concentrations that were previously observed at these sites, which was due to 29 the lower nitrate radical (NO<sub>3</sub>) production rate ( $P(NO_3)$ ) and the smaller N<sub>2</sub>O<sub>5</sub> uptake 30 coefficients ( $\gamma$ (N<sub>2</sub>O<sub>5</sub>)) in winter, despite the higher dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) to NO<sub>3</sub> 31 ratios in winter. Significant daytime peaks of ClNO<sub>2</sub> were observed at all the sites 32 during the winter campaigns, with ClNO<sub>2</sub> mixing ratios of up to 1.3 ppbv. Vertical 33 transport of ClNO<sub>2</sub> from the residual layers and prolonged photochemical lifetime of 34 ClNO<sub>2</sub> in winter may explain the elevated daytime concentrations. The daytime-35 averaged chlorine radical (Cl) production rates (P(Cl)) from the daytime ClNO<sub>2</sub> were 36 0.17, 0.11, and 0.12 ppbv  $h^{-1}$  at the polluted rural, urban, and polluted lower 37 tropospheric sites, respectively, which were approximately 3 - 4 times higher than the 38 campaign-averaged conditions. Box model calculations showed that the Cl atoms 39 liberated during the daytime peaks of ClNO<sub>2</sub> increased the RO<sub>x</sub> levels by up to 27 - 37 % 40 and increased the daily  $O_3$  productions by up to 13 - 18 %. Our results provide new 41 insights into the ClNO<sub>2</sub> processes in the lower troposphere impacted by fresh and 42 intense anthropogenic emissions and reveal that ClNO<sub>2</sub> can be an important daytime 43

- 44 source of Cl radicals under certain conditions in winter.
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#### 46 Key points:

47 1. Winter measurements of ClNO<sub>2</sub> concentrations were made at rural, urban, and
48 mountain sites in northern China.

- 49 2. The elevated daytime mixing ratios of ClNO<sub>2</sub> were up to 1.3 ppbv.
- 3. The daytime peaks of ClNO<sub>2</sub> increased the concentration of RO<sub>x</sub> radicals by up to 27
- 51 37 % and the net O<sub>3</sub> production by 13 18 %.
- 52

## 53 **1. Introduction**

54 Cl is a potent atmospheric oxidant that reacts analogously to hydroxyl radicals (OH) with hydrocarbons (Simpson et al., 2015). Cl is highly reactive toward alkanes, with 55 the rate constants of its reactions with alkanes being approximately 10-200 times 56 greater than some of the OH + VOCs reactions (Atkinson and Arey, 2003; Young et al., 57 2014; Burkholder et al., 2015). Consequently, Cl enhances the production of  $RO_x$  (= 58  $OH + HO_2 + RO_2$ ) via Reactions R1-R4, which promotes O<sub>3</sub> formation by converting 59 60 nitric oxide (NO) to nitrogen dioxide (NO<sub>2</sub>) (Reactions R3 and R5). Cl also consumes O<sub>3</sub> via Reaction R8. The net effect of the Cl chemistry is typically the depletion of O<sub>3</sub> 61 in the remote atmosphere, such as the stratosphere (Molina and Rowland, 1974) and 62 remote oceans (Simpson et al., 2015; Wang et al., 2019b), and an increase in O<sub>3</sub> 63 production in the polluted troposphere (Riedel et al., 2014; Xue et al., 2015). 64

65 (R1)  $\operatorname{RH}(g) + \operatorname{Cl}(g) \rightarrow \operatorname{R}(g) + \operatorname{HCl}(g)$ 

66 (R2)  $R(g) + O_2(g) + M \rightarrow RO_2(g) + M$ 

- 67 (R3)  $\operatorname{RO}_2(g) + \operatorname{NO}(g) \to \operatorname{RO}(g) + \operatorname{NO}_2(g)$
- 68 (R4)  $\operatorname{RO}(g) + \operatorname{O}_2(g) \to \operatorname{HO}_2(g) + \operatorname{products}$
- 69 (R5)  $HO_2(g) + NO(g) \rightarrow OH(g) + NO_2(g)$
- 70 (R6) NO<sub>2</sub>(g) +  $hv \rightarrow$  NO(g) + O(<sup>3</sup>P)
- 71 (R7)  $O_2(g) + O({}^{3}P) + M \rightarrow O_3(g) + M$

72 (R8) 
$$\operatorname{Cl}(g) + \operatorname{O}_3(g) \to \operatorname{ClO}(g) + \operatorname{O}_2(g)$$

- 73 where M denotes the third body in ambient air.
- 74

75 The production of Cl is determined by the formation and decomposition of Cl precursors such as ClNO<sub>2</sub> (Chang et al., 2011; Simpson et al., 2015). ClNO<sub>2</sub> is produced 76 77 mostly in dark conditions by the heterogeneous uptake of  $N_2O_5$  on chloride (Cl<sup>-</sup>)-laden aerosols (Reactions R9-R13) and undergoes photolysis during the day (Reaction R14) 78 79 (Finlayson-Pitts et al., 1989). ClNO<sub>2</sub> formation is constrained by the NO<sub>3</sub> production rate ( $P(NO_3)$ ), Reaction R9). NO<sub>3</sub> is in thermal equilibrium with N<sub>2</sub>O<sub>5</sub> (Reaction R10), 80 and the equilibrium constant (Keq) depends on temperature and NO<sub>2</sub> concentrations. 81 N<sub>2</sub>O<sub>5</sub> formation is suppressed by NO and VOCs as they consume NO<sub>3</sub> (Reactions R11– 82 12). The N<sub>2</sub>O<sub>5</sub> uptake probability ( $\gamma$ (N<sub>2</sub>O<sub>5</sub>)) and ClNO<sub>2</sub> production yield ( $\varphi$ (ClNO<sub>2</sub>)) 83 are kinetic parameters with values between 0 and 1, which can be derived from the 84 85 observation data of N<sub>2</sub>O<sub>5</sub>, ClNO<sub>2</sub>, and related species (Brown et al., 2006; Phillips et al., 2016). Previous laboratory studies have demonstrated that  $\gamma(N_2O_5)$  is enhanced by 86 higher relative humidity (RH) and particulate Cl<sup>-</sup> concentrations but suppressed by 87

higher temperature and concentrations of aerosol nitrate (NO<sub>3</sub><sup>-</sup>) and organic species
(Behnke et al., 1997; Hallquist et al., 2003; Bertram et al., 2009; Griffiths and Anthony
Cox, 2009).

- 91 (R9) 92 (R10)  $NO_2(g) + O_3(g) \rightarrow NO_3(g) + O_2(g)$  $NO_3(g) + NO_2(g) \leftrightarrow N_2O_5(g)$
- 93 (R11)  $NO_3(g) + NO(g) \leftrightarrow 2NO_2(g)$
- 94 (R12)  $NO_3(g) + VOC_3(g) \rightarrow products$
- 95 (R13)  $N_2O_5(g) + Cl^{-}(aq) \rightarrow ClNO_2(g) + NO_3^{-}(aq)$
- 96 (R14)  $\operatorname{ClNO}_2(g) + hv \to \operatorname{Cl}(g) + \operatorname{NO}_2(g)$
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98 Field observations of CINO<sub>2</sub> were first reported in the marine boundary layer off the coast of the Houston-Galveston area in the USA (Osthoff et al., 2008). Subsequent 99 100 studies demonstrated the worldwide ubiquity of ClNO2 and confirmed its significant role in photochemistry (Thornton et al., 2010; Mielke et al., 2011; Phillips et al., 2012; 101 Edwards et al., 2013; Bannan et al., 2015; Wild et al., 2016; Wang et al., 2016; Bannan 102 et al., 2019; Eger et al., 2019). The role of ClNO<sub>2</sub> in the radical budget could be more 103 104 important than that of OH in winter, because OH production is reduced in winter owing to lower concentrations of O3 and H2O vapor in this season. A limited number of winter 105 observations of ClNO<sub>2</sub> have been conducted on various platforms, including on 106 aircrafts over northern Europe (Priestley et al., 2018) and the eastern US (Haskins et al., 107 2018, 2019), on a tall tower in Boulder, USA (Riedel et al., 2013), on a mountain top 108 in Hong Kong (Wang et al., 2016), and at ground sites in Alberta, Canada (Mielke et 109 al., 2016) and Heshan, China (Yun et al., 2018). These studies found high ClNO2 mixing 110 ratios of up to 7.7 ppbv (Yun et al., 2018) in winter and a contribution of ClNO<sub>2</sub> to Cl 111 liberation of up to 83 % (Priestley et al., 2018) in urban Manchester, and that CINO<sub>2</sub> 112 was a more dominant radical source than OH both in the early morning and the whole 113 114 day in the polluted marine boundary layer downwind of the northeast US (Haskins et al., 2019). ClNO<sub>2</sub> usually exhibits higher concentrations in aged and polluted air masses 115 116 than in clean air and in regions subject to significant fresh NO emissions (Wang et al., 117 2016; Wang et al., 2017c; Osthoff et al., 2018).

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The chemical production of ClNO<sub>2</sub> in winter has some unique features compared 119 with that in warmer seasons. Long winter nights provide more time for CINO2 120 production and accumulation. Lower temperatures in winter shift the N2O5-NO3 121 equilibrium to the N<sub>2</sub>O<sub>5</sub> side (Brown et al., 2003) and increase the  $\gamma$ (N<sub>2</sub>O<sub>5</sub>) on aerosols 122 (Bertram and Thornton, 2009). Besides, NOx has longer lifetimes in winter compared 123 with summer due to less abundant OH radicals in winter and its slower reaction rate 124 with OH (Kenagy et al., 2018). However, P(NO<sub>3</sub>) might be lower in winter due to 125 reduced O<sub>3</sub> concentrations. The availability of aerosol Cl<sup>-</sup> also varies in winter and 126 summer. More Cl<sup>-</sup> is emitted due to coal burning in winter (McCulloch et al., 1999; Fu 127 et al., 2018). In places like East Asia, the winter monsoon brings air masses from the 128 129 interior of the continent, thereby suppressing the transport of sea salt to inland areas. Because of the contrasts in the availability of aerosol chloride and the variability in 130 meteorology and NO<sub>x</sub> emissions that affect the N<sub>2</sub>O<sub>5</sub> chemistry, it is not clear whether 131

- 132 ClNO<sub>2</sub> formation is more prevalent in winter.
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The North China Plain (NCP) – home to Beijing and several other megacities – is 134 one of the most industrialized and populous regions of China, and frequently suffers 135 from severe haze pollution in winter (An et al., 2019; Fu et al., 2020). CINO2 136 concentrations have been measured over the NCP (Breton et al., 2018; Zhou et al., 137 2018), but only one study was conducted in winter (Breton et al., 2018). The present 138 study presents recent field observations of CINO2 concentrations from three campaigns 139 conducted in winter and early spring at three sites in the NCP. The results were 140 compared with those obtained in the previous summer campaigns at the same locations. 141 We examined the factors controlling  $ClNO_2$  formation, i.e.,  $P(NO_3)$ , the nocturnal 142 reactivity of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>,  $\gamma$ (N<sub>2</sub>O<sub>5</sub>), and  $\varphi$ (ClNO<sub>2</sub>). We then focused on the 143 unexpected daytime peaks of ClNO<sub>2</sub> concentrations that were observed at the sites and 144 evaluated their impact on the daytime atmospheric oxidative capacity using a chemical 145 box model. 146

#### 148 **2. Methods**

149 2.1 Observation sites

Field campaigns were performed in Wangdu, Beijing, and Mt. Tai in sequence during 150 the winter-early spring of 2017 - 2018 (Table 1). The locations of the three sites are 151 shown in Fig. S1. The sites were selected for investigation of ClNO<sub>2</sub> in urban, rural, 152 and mountain areas of the NCP. The winter indoor-heating period lasts from early 153 November to 15 March of the following year (Ran et al., 2016), and thus the 154 155 observations were made mostly during the heating period during which coal is intensively used. Detailed descriptions of the measurement sites are available in 156 previous studies (Tham et al., 2016; Wang et al., 2017c; Xia et al., 2019), and a brief 157 158 introduction is given here.

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Location/ Coordinate	Site category	Season	Observation period	NO <sub>x</sub> (ppbv)	O <sub>3</sub> (ppbv)
Wangdu (38.66 °N, 115.25 °E)	polluted rural	Winter <sup>1</sup>	9-31 December 2017	83.2 ± 81.3	$4.7\pm4.5$
		Summer <sup>2</sup>	21 June to 9 July 2014	$18.3 \pm 11.8$	$37.8\pm26.2$
Beijing (40.04 °N, 116.42 °E)	Urban	Winter <sup>1</sup>	6 January to 1 February 2018	$35.6\pm37.4$	$14.5 \pm 11.5$
		Early summer <sup>3</sup>	24 April to 31 May 2017	$22.4\pm18.3$	$27.2\pm20.6$
Mt. Tai (36.25 °N, 117.10 °E)	Polluted lower troposphere	Winter to early spring <sup>1</sup>	7 March to 8 April 2018	$2.4 \pm 2.0$	65.1 ± 14.1
		Summer <sup>4</sup>	24 July to 27 August 2014	$3.1 \pm 3.0$	$77.8\pm20.1$

160 Table 1. Locations and periods of the field campaigns relevant to this study.

<sup>1</sup>Observations from this study.

<sup>2-4</sup>Observations from previous studies, i.e., Tham et al. (2016), Xia et al. (2019), and
Wang et al. (2017c), respectively.

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Our observations at the Wangdu site were part of the Campaign of Oxidation 165 Potential Research for air Pollution in winter (COPPER). The Wangdu site is located in 166 Dongbaituo Village, Hebei Province. Local villagers use coal stoves for cooking and 167 heating during winter. National road G4 and provincial road S335 are 1 km and 3 km 168 to the west of the sampling site, respectively. Many heavy-duty trucks passed through 169 G4 and S335 every night during the study period, emitting a large amount of NO<sub>x</sub> and 170 particulate matters. Therefore, the site experienced heavy pollution from coal burning 171 172 and road traffic (Peng et al., 2020).

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The Beijing site is located at the Chinese Research Academy of Environmental Science (CRAES), which is 15 km northeast of the city center. The sampling site is surrounded by intra-city roads, commercial buildings, and residential buildings with few industrial facilities. When the prevailing wind originates from the north (i.e., remote mountainous regions), the site is upwind from the Beijing downtown area and thus is less polluted. However, when the wind originates from the south, the site receives pollutants from Beijing's urban areas in the NCP (Xia et al., 2019).

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182 Mt. Tai is located approximately 40 km south of Jinan City (population: 8.9 million) 183 and 15 km north of Tai'an City (population: 5.6 million) (Wen et al., 2018). 184 Measurements were taken at Mt. Tai meteorological station (1534 m a.s.l.). The site is 185 isolated from the anthropogenic emissions of tourist areas and is not affected by local 186 emissions. The observation period, i.e., March to April, was in early spring in the NCP. 187 However, considering the low temperature ( $4.6 \pm 6.3$  °C) observed on top of Mt. Tai, 188 this study considered the observation period as winter to early spring.

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190 2.2 Measurements of N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> concentrations

N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> were simultaneously measured by a chemical ionization mass 191 spectrometer with a quadrupole mass analyzer (Q-CIMS; THS Instruments). The 192 principles and calibrations of the Q-CIMS measurements are available in previous 193 studies (Wang et al., 2016; Tham et al., 2016; Wang et al., 2017c; Xia et al., 2019). 194 195 Briefly, the primary ions used in the Q-CIMS were iodide (I<sup>-</sup>) and its water clusters, which were generated using CH<sub>3</sub>I with an inline ionizer (<sup>210</sup>Po). The iodide adducts, 196 namely  $IN_2O_5^-$  and  $ICINO_2^-$ , were then detected by the mass spectrometer. An example 197 of the mass spectrum is shown in Fig. S2. The integration time of the signals recorded 198 by the Q-CIMS is shown in Table S1. The isotopic ratios of I<sup>35</sup>ClNO<sub>2</sub><sup>-</sup> and I<sup>37</sup>ClNO<sub>2</sub><sup>-</sup> in 199 the ambient data were used to confirm the identity of ClNO<sub>2</sub> (Fig. S3). Gas-phase 200 mixtures of NO<sub>2</sub> and O<sub>3</sub> produced N<sub>2</sub>O<sub>5</sub> for N<sub>2</sub>O<sub>5</sub> calibration. The synthetic N<sub>2</sub>O<sub>5</sub> was 201 converted to ClNO<sub>2</sub> by passage through a humidified NaCl slurry for ClNO<sub>2</sub> calibration. 202 The dependence of the N<sub>2</sub>O<sub>5</sub> sensitivities on ambient RH was tested once in each 203 campaign and used to calibrate the N2O5 data (Fig. S4a). ClNO2 sensitivities were found 204

not affected by RH (Fig. S4b). Single-concentration calibrations of N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> 205 were performed every 1 - 2 days, which showed stable sensitivities of N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> 206 (Text S1 and Fig. S5). And the linearity of the N2O5 and ClNO2 signals to concentrations 207 was checked via multi-concentration calibrations in the Mt. Tai campaign (Fig. S6). 208 Backgrounds of N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> were determined by passing the ambient air through 209 210 glass wool once a day at different time. The background signals of  $N_2O_5$  (3.3 – 7.7 pptv) and  $CINO_2$  (1.0 – 7.5 pptv) were stable and independent of the time of the day (Fig. S7). 211 The detection limits of N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> were 6.9 - 7.3 pptv and 3.8 - 5.3 pptv, which 212 is defined here as three times of the standard deviation of the background signals in 5 213 minutes (Table S2). A virtual-impactor design (Peng et al., 2020) was adopted, and the 214 sampling tube was replaced daily to minimize inlet artifacts. 215

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217 2.3 Other measurements

The trace gases, particle number size distribution (PNSD), ionic composition of 218 aerosols and other species were simultaneously measured (Table S3). Online non-219 methane hydrocarbons were measured by gas chromatography-flame-ionization 220 detection/mass spectrometry (GC-FID/MS; Chromatotec Group) at the Beijing site 221 222 (Zhang et al., 2017) and Wangdu site (Zhang et al., 2020). At Mt. Tai, we used canisters to collect air samples, which were analyzed using GC-FID/MS. In Wangdu and Mt. Tai, 223 224 oxygenated volatile organic compounds (OVOCs) samples were collected on DNPHcoated sorbent cartridges followed by post-campaign analysis using high performance 225 liquid chromatography. The ionic compositions of PM<sub>2.5</sub> (e.g., NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and 226 Cl<sup>-</sup>) were quantified by the Monitor for AeRosols and GAses in ambient air (MARGA, 227 228 Metrohm) at the Beijing and Mt. Tai sites (Wen et al., 2018). An aerosol chemical speciation monitor (ACSM, Aerodyne Research Inc.) was utilized at the Wangdu site 229 to monitor the non-refractory components of these ions in PM2.5. The concentrations of 230 the  $NO_3^-$ ,  $SO_4^{2-}$ , and  $NH_4^+$  measured simultaneously by the MARGA and ACSM were 231 in good agreement, whereas the concentration of Cl<sup>-</sup> measured by the ACSM was 232 slightly lower than that measured by the MARGA, which was possibly due to the 233 significant proportion of refractory chloride, e.g., NaCl, present in the aerosols (Xia et 234 al., 2020). We assumed that the particles sampled by a wide-range particle spectrometer 235 (WPS) were spherical in shape and calculated the aerosol surface area density (S<sub>a</sub>) and 236 volume density (Va). A parameterization was adopted to consider the hygroscopic 237

growth factor (GF) of aerosol sizes, as follows:  $GF = a \times \left(b + \frac{1}{1-RH}\right)^{1/3}$  (Lewis, 2008),

where the parameters a and b were derived as 0.582 and 8.460, respectively in a
previous field study over the NCP (Achtert et al., 2009).

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242 2.4 Calculation of N<sub>2</sub>O<sub>5</sub> loss and ClNO<sub>2</sub> production

Some analytical metrics were calculated from the observation data.  $P(NO_3)$  was calculated using Eq. (1), where  $k_1$  represents the rate constant of Reaction R9 (Atkinson and Lloyd, 1984).

246 (Eq. 1)  $P(NO_3) = k_1 \times [O_3] \times [NO_2]$ 

247  $k(NO_3)$  during the night was calculated using the measured mixing ratios of NO and

- non-methane hydrocarbons that were measured by GC (section 2.3). As most OVOCs
  react with NO<sub>3</sub> at much slower rates compared to those with hydrocarbons especially
  alkenes (Atkinson and Arey, 2003), the OVOCs were not included in the calculation of
- 251  $k(NO_3)$ . Nonetheless, the  $k(NO_3)$  might be slightly underestimated here.

252 (Eq. 2) 
$$k(NO_3) = \sum k_i [VOC_i] + k_{NO+NO_3} [NO]$$

253 where  $k_i$  is the rate constant for a specific VOC + NO<sub>3</sub> reaction and is adopted from

Atkinson and Arey (2003) and  $k_{\rm NO+NO_3}$  represents the rate constant for Reaction R11

(DeMore et al., 1997). The ambient concentrations of NO<sub>3</sub> were estimated by assuming
 that NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> were in dynamic equilibrium (DeMore et al., 1997).

257 (Eq. 3) 
$$[NO_3] = \frac{[N_2O_5]}{[NO_2]K_{eq}}$$

- 258 The loss rates of NO<sub>3</sub> due to NO and VOCs were then calculated by  $k_{\text{NO+NO}_3}$ [NO][NO<sub>3</sub>]
- and  $\sum k_i$  [VOC<sub>i</sub>][NO<sub>3</sub>], respectively.
- 260 The loss rate coefficient of N<sub>2</sub>O<sub>5</sub> on the aerosol surface  $(k(N_2O_5))$  is expressed as 261 follows.
- 262 (Eq. 4)  $k(N_2O_5) = 0.25 \times c(N_2O_5) \times S_a \times \gamma(N_2O_5)$
- 263 where  $c(N_2O_5)$  represents the average molecular velocity of N<sub>2</sub>O<sub>5</sub>. The rate constants
- 264  $(k_1, k_i, and k_{NO+NO_3})$  and equilibrium constant  $(K_{eq})$  are calculated as temperature-
- 265 dependent parameters.
- 266

 $\gamma(N_2O_5)$  and  $\varphi(CINO_2)$  were estimated using steady-state analysis in applicable cases 267 (Brown et al., 2006). This method assumes a steady state of N<sub>2</sub>O<sub>5</sub>, which means that 268 the production rate of N<sub>2</sub>O<sub>5</sub> is equal to its loss rate. We adopted the criteria described 269 by Xia et al. (2020) to select the cases, namely low concentrations of NO, an increasing 270 trend of CINO<sub>2</sub> concentrations, and stable air masses. Equation (5) was then established 271 by plotting  $\tau(N_2O_5)^{-1} \times [NO_2] \times K_{eq}$  against  $0.25 \times S_a \times C_{N_2O_5} \times [NO_2] \times K_{eq}$ , with 272  $\gamma(N_2O_5)$  as the slope and  $k(NO_3)$  as the intercept in the linear regression (Brown et al., 273 2003). Here, the derived  $\gamma(N_2O_5)$  was accepted when the regression had  $R^2 > 0.5$  and 274  $k(NO_3) > 0.$ 275

276 (Eq. 5) 
$$\tau(N_2O_5)^{-1} \times K_{eq} \times [NO_2] \approx 0.25 \times C_{N_2O_5} \times S_a \times K_{eq} \times [NO_2] \times \gamma(N_2O_5) + k(NO_3)$$

 $\phi(CINO_2)$  was then calculated using the following equation:

278 (Eq. 6)  $\varphi(\text{ClNO}_2) = \frac{d[\text{ClNO}_2]/dt}{k(N_2O_5)[N_2O_5]}$ 

- where  $d[CINO_2]/dt$  and  $[N_2O_5]$  represent the increasing rate of CINO\_2 production and the average concentration of  $N_2O_5$ , respectively within the selected cases.
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282 2.5 Box model

An observation-based chemical box model was utilized to simulate the concentrations of Cl and RO<sub>x</sub> radicals and the production and loss pathways of O<sub>3</sub>. The

detailed model description is available in Peng et al. (2020). Based on Master Chemical 285 Mechanism (MCM) v3.3.1 (Jenkin et al., 2015), Peng et al. (2020) modified the 286 chemical mechanisms to include up-to-date gas-phase chlorine and bromine chemistry. 287 The observed N<sub>2</sub>O<sub>5</sub>, ClNO<sub>2</sub>, NO<sub>x</sub>, HONO, O<sub>3</sub>, *j*NO<sub>2</sub>, and related species were 288 constrained in the model for every 10 minutes of model time, after interpolating or 289 290 averaging the data (Table S4). The mixing ratios of NMHCs and OVOCs (Section 2.3) were constrained every hour. As OVOCs were not measured in Beijing in this study, we 291 adopted the concentrations of OVOCs measured in previous studies in winter Beijing 292 (Gu et al., 2019; Qian et al., 2019). We also assumed the CH<sub>4</sub> mixing ratio to be 2000 293 ppbv, which was the mean value in summer at Wangdu (Tan et al., 2017), for our 294 Wangdu and Beijing sites. We acknowledge that the adoption of the summer CH<sub>4</sub> 295 concentrations for our winter studies may underestimate the CH4 level, but the effect 296 297 on the RO<sub>x</sub> budget is expected to be insignificant due to much smaller contribution of CH<sub>4</sub> to RO<sub>x</sub> than NMHCs and OVOCs in polluted environments. The photolysis 298 frequencies of ClNO<sub>2</sub>, O<sub>3</sub>, and other species were simulated according to the solar 299 zenith angle using the Tropospheric Ultraviolet and Visible (TUV) Radiation model and 300 scaled by the observed jNO2 values. Numerical experiments were conducted by 301 constraining (Case 1) and not constraining ClNO<sub>2</sub> data (Case 2) at each site. The 302 differences in the radical concentrations and O<sub>3</sub> budgets between Cases 1 and 2 303 304 represented the effect of ClNO<sub>2</sub>. For example, the increase in RO<sub>x</sub> (%) due to ClNO<sub>2</sub> was calculated by  $(RO_x w - RO_x wo) / RO_x wo$ , where  $RO_x w$  represents the 305 concentration of ROx in Case 1 with ClNO2 constrained in the model and ROx wo 306 represents the concentration of ROx in Case 2 without ClNO<sub>2</sub> constrained. 307

#### 309 **3. Results**

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310 3.1 Overall measurements, diurnal patterns and comparison with other studies

The time series of N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> levels in the three campaigns are displayed in Fig. 311 1. Overall, elevated levels of N2O5 and ClNO2 were observed with different patterns at 312 each site. The ground sites (Wangdu and Beijing) were characterized by high NO<sub>x</sub> levels 313  $(83.2 \pm 81.3 \text{ ppbv and } 35.6 \pm 27.3 \text{ ppbv}$ , respectively) and low O<sub>3</sub> levels  $(8.5 \pm 8.8 \text{ ppbv})$ 314 and  $17.3 \pm 11.4$  ppbv, respectively), whereas the mountain site, Mt. Tai, was marked by 315 relatively lower NO<sub>x</sub> levels ( $2.4 \pm 2.0$  ppbv) and higher O<sub>3</sub> levels ( $64.6 \pm 14.7$  ppbv) 316 (Fig. S8). The campaign-averaged mixing ratios of ClNO<sub>2</sub> were similar at the ground 317 sites  $(71 \pm 132 \text{ pptv} \text{ and } 76 \pm 103 \text{ pptv} \text{ in Wangdu and Beijing, respectively)}$ , and were 318 significantly lower than that at Mt. Tai (179  $\pm$  247 pptv). The nocturnal ratio of 319 320 ClNO<sub>2</sub>/N<sub>2</sub>O<sub>5</sub> at each site displayed large day-to-day variability, which was positively dependent on the ambient RH (Fig. S9) and, to a lesser extent, positively correlated 321 with S<sub>a</sub> (figure not shown). 322



323

Figure 1. Overall observations of N<sub>2</sub>O<sub>5</sub>, ClNO<sub>2</sub> and related species at the (a) Wangdu,
(b) Beijing, and (c) Mt. Tai sites.

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The campaign-averaged diurnal patterns of the mixing ratios of N<sub>2</sub>O<sub>5</sub>, ClNO<sub>2</sub>, and related species are depicted in Fig. 2. ClNO<sub>2</sub> levels typically exhibited a daily cycle, peaking at night and decreasing during the day. The diurnal pattern of ClNO<sub>2</sub> at the Wangdu site in winter was an exception, with elevated concentrations (10 - 90percentiles) around midday (12:00 - 14:00 local time; LT), which resulted from a noontime peak in ClNO<sub>2</sub> concentrations during a few days at Wangdu. The detailed observation results from each site are separately introduced as follows.





Figure 2. Diurnal average levels of N<sub>2</sub>O<sub>5</sub>, ClNO<sub>2</sub>, O<sub>3</sub>, and jNO<sub>2</sub> observed at the Wangdu,
Beijing, and Mt. Tai sites throughout the campaign in winter (this study) and previous
summer field studies (Table 1). The shaded areas indicate the 10th and 90th percentiles.

The nocturnal production of ClNO<sub>2</sub> was insignificant in Wangdu despite the presence 339 of abundant Cl  $(3.3 \pm 3.2 \ \mu g \ m^{-3}$  throughout the observation), which likely originated 340 from the intensive residential coal combustion in the area (Peng et al., 2020). The 341 Wangdu site experienced high mass concentrations of PM2.5 (a maximum of 342 approximately 450 µg m<sup>-3</sup>) and very large mixing ratios of NO (a maximum of 343 approximately 350 ppbv). The wind rose analysis showed that the high concentrations 344 of NO originated from the west of the sampling site where two major roads were located. 345 Numerous heavy-duty trucks on these roads were responsible for high NO 346 concentrations. The presence of abundant NO inhibited N2O5 formation by consuming 347 O<sub>3</sub> and NO<sub>3</sub> at the Wangdu site. When the ambient concentrations of NO substantially 348 decreased, e.g., on 10 December, the N<sub>2</sub>O<sub>5</sub> mixing ratios increased to 1 ppbv. The 349 mixing ratios of ClNO<sub>2</sub> were mostly low (< 200 pptv) during the night. The relationship 350 between nighttime levels of ClNO<sub>2</sub> and grouped NO and NO<sub>x</sub> concentrations is shown 351 in Fig. 3. ClNO<sub>2</sub> showed higher levels when the NO mixing ratios were below 10 ppbv 352 and NO<sub>x</sub> mixing ratios ranged  $10 \sim 20$  ppbv (Fig. 3a, d). However, significant daytime 353 peaks in ClNO<sub>2</sub> mixing ratios were observed on 14 and 28 December, reaching 354 approximately 0.8 ppbv and 1.3 ppbv, respectively. The daytime peaks in ClNO<sub>2</sub> 355 concentrations at the three sites are discussed in detail in Section 3.3. For comparison, 356 the ambient mixing ratios of NO in the summer campaign at Wangdu were much lower 357

(mostly 0-10 ppbv) and O<sub>3</sub> mixing ratios were much higher (i.e., exceeded 90 ppbv on
 most days), which favored the production of N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> (Tham et al., 2016).



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Figure 3. The relationship between nighttime levels of ClNO<sub>2</sub> and grouped NO (a, b, and c) and NO<sub>x</sub> (d, e, and f) mixing ratios in the winter (green color) and summer (purple color) campaigns. The difference in the scale of ClNO<sub>2</sub> in Fig. 3c and Fig. 3f is caused by statistic factors, since only  $10^{th}$  to  $90^{th}$  percentile of ClNO<sub>2</sub> data is shown here.

The winter Beijing observations showed that there was significant production of 367 N<sub>2</sub>O<sub>5</sub> but limited conversion of N<sub>2</sub>O<sub>5</sub> to ClNO<sub>2</sub> in dry conditions. The observation 368 period in Beijing was divided into polluted days (24-h  $PM_{2.5} > 75 \mu g m^{-3}$ ; China's Grade 369 II air quality standard for PM<sub>2.5</sub>) and clean days (24-h PM<sub>2.5</sub>  $< 35 \ \mu g \ m^{-3}$ ; Grade I 370 standard). The polluted periods were characterized by simultaneous high levels of PM<sub>2.5</sub> 371 and NO, e.g., on 19 January. The clean periods were marked by relatively high mixing 372 ratios of O<sub>3</sub>, low levels of PM<sub>2.5</sub> and NO<sub>x</sub>, e.g., from 8 to 11 January. Both polluted and 373 clean conditions were unfavorable for ClNO2 formation owing to the high 374 concentrations of NO on the polluted days and the low concentrations of NO2 and 375 aerosols on the clean days. Moreover, the RH observed in Beijing was typically below 376 40 %, which indicated relatively slow heterogeneous loss of N<sub>2</sub>O<sub>5</sub> and slow ClNO<sub>2</sub> 377

formation. Consequently, N<sub>2</sub>O<sub>5</sub> mixing ratios frequently accumulated to elevated levels, 378 exceeding 0.4 ppbv on 10 of the 26 observation nights, and the mixing ratio of ClNO<sub>2</sub> 379 was mostly below 0.4 ppby. Nighttime levels of ClNO<sub>2</sub> in winter Beijing were higher 380 when NO mixing ratios ranged  $0 \sim 10$  ppbv and NO<sub>x</sub> mixing ratios ranged  $20 \sim 50$  ppbv 381 (Fig. 3b, d). The highest mixing ratios of ClNO<sub>2</sub> were observed (up to approximately 382 383 0.8 ppbv) when the site occasionally intercepted air masses with a higher RH (approximately 75 %), e.g., on the night of 22 January. This result is similar to the 384 previous observation in Beijing (Xia et al., 2019), in which the ratio of ClNO<sub>2</sub> to N<sub>2</sub>O<sub>5</sub> 385 increased significantly from late spring with a low RH (10 - 30 %) to early summer 386 with a higher RH (20 - 80 %). The overall mixing ratios of ClNO<sub>2</sub> in the present Beijing 387 study in winter were also significantly lower than those reported in summer (maximum 388 389 of 1.4 ppbv to 2.9 ppbv) in other studies (Breton et al., 2018; Zhou et al., 2018).

390

Elevated mixing ratios of ClNO<sub>2</sub> (i.e., above 0.5 ppbv) were frequently recorded at 391 the Mt. Tai station in winter. Nighttime levels of ClNO<sub>2</sub> were slightly higher when NO 392 levels were below 0.5 ppbv (Fig. 3c) and showed a positive correlation with NO<sub>x</sub> levels 393 (Fig. 3f). High concentrations of PM<sub>2.5</sub> ( $34.5 \pm 27.3 \ \mu g \ m^{-3}$ ) and high RH ( $63.6 \pm 27.1 \ \%$ ) 394 favored the ClNO<sub>2</sub> formation at Mt. Tai. The maximum level of ClNO<sub>2</sub> (approximately 395 1.7 ppbv) was observed just before midnight on 18 March, which was slightly lower 396 397 than the highest concentration observed at Mt. Tai in the summer of 2014 (Wang et al., 2017c). The elevated concentrations of ClNO<sub>2</sub> observed in the previous summer study 398 at Mt. Tai were due to emissions from distinct coal-fired power plants, whereas this 399 winter study found that coal burning had less effect on concentrations of ClNO<sub>2</sub>. The 400 campaign-averaged levels of SO<sub>2</sub> and particulate SO<sub>4</sub><sup>2-</sup> were  $1.6 \pm 1.6$  ppbv and  $3.6 \pm$ 401 2.9 µg m<sup>-3</sup>, respectively, during the winter observations, which were significantly lower 402 than those observed in the summer campaigns  $(2.9 \pm 3.7 \text{ ppbv and } 14.8 \pm 9.0 \text{ }\mu\text{g m}^{-3}$ , 403 respectively). The decreases in SO<sub>2</sub> and sulfate were attributed to strengthened emission 404 control for coal-fired power generation during 2014 – 2018 and also less transport of 405 emissions from the ground to the Mt. Tai site (1534 m a.s.l.) in late winter and early 406 407 spring compared with that in summer.

408

We compared the observed winter concentrations of ClNO<sub>2</sub> with those reported in 409 previous studies in Asia, North America, and Europe (Fig. 4). The highest winter 410 concentrations of ClNO<sub>2</sub> to date were observed in southern China, with a maximum 411 level of 4.7 ppbv at a mountain top in Hong Kong in aged urban/industrial plumes from 412 the Pearl River Delta (PRD) (Wang et al., 2016) and 8.3 ppbv during a severe pollution 413 episode within the PRD (Yun et al., 2018). The high-concentration ClNO<sub>2</sub> events in 414 southern China were due to concurrent high levels of PM<sub>2.5</sub> and O<sub>3</sub> (e.g., 400 µg m<sup>-3</sup> 415 and 160 ppbv found by Yun et al., 2018), which contrasts the high concentrations of 416 PM<sub>2.5</sub> and low concentrations of O<sub>3</sub> over northern China during the cold winter. The 417 winter mixing ratios of ClNO<sub>2</sub> in the US and Europe range from approximately 0.3 ppbv 418 in urban California (Mielke et al., 2016) and urban Manchester (Priestley et al., 2018), 419 respectively, to 1.3 ppbv in the outflow of coastal urban areas (Riedel et al., 2013; 420 Haskins et al., 2019). In general, the winter concentrations of ClNO<sub>2</sub> over northern 421



422 China were comparable to or slightly higher than those observed in the US and Europe.

Figure 4. Previous observations of ClNO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> levels worldwide. Observation 424 sites in this study are shown in bold. The CINO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> levels shown are the highest 425 that were measured at these sites. Footnotes associated with the locations refer to the 426 references as follows. 1. (Mielke et al., 2011; Mielke et al., 2016; Osthoff et al., 2018). 427 2. (Osthoff et al., 2008; Faxon et al., 2015). 3. (Phillips et al., 2012). 4. (Tham et al., 428 2016; Liu et al., 2017). 5. (Wang et al., 2017a; Breton et al., 2018; Wang et al., 2018; 429 Zhou et al., 2018; Xia et al., 2019). 6. (Nakayama et al., 2008). 7. (Wang et al., 2017c). 430 8. (Xia et al., 2020). 9. (Wang et al., 2019a). 10. (Wang et al., 2017b). 11. (Wang et al., 431 2016; Yun et al., 2017; Yan et al., 2019). 12. (Yun et al., 2018). 13. (Eger et al., 2019). 432 14. (Apodaca et al., 2008; McNamara et al., 2019). 15. (Thornton et al., 2010; Riedel 433 et al., 2013). 16. (Riedel et al., 2012; Mielke et al., 2013). 17. (Brown et al., 2006; 434 Brown et al., 2007; Haskins et al., 2018). 18. (Crowley et al., 2011). 19. (Bannan et al., 435 2015; Sommariva et al., 2018). 20. (Bannan et al., 2019). 21. (Edwards et al., 2013; 436 Wild et al., 2016; McDuffie et al., 2019). 22. (Jeong et al., 2019). 437

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#### 439 3.2 NO<sub>3</sub> production and loss pathways

To gain insight into the processes controlling the variability in concentrations of 440 ClNO<sub>2</sub>, nocturnal  $P(NO_3)$  and NO<sub>3</sub> loss pathways were compared using Eqs. (1-5) in 441 Section 2.4. The average  $P(NO_3)$  was comparable at the three sites in winter, ranging 442 from 0.15 ppbv h<sup>-1</sup> to 0.25 ppbv h<sup>-1</sup>, and these rates were significantly lower than the 443 respective summer values (Fig. 5a). The lower  $P(NO_3)$  in winter was caused by both 444 lower  $k_1$  and lower [NO<sub>2</sub>] × [O<sub>3</sub>] in winter (see Eq. 1). The lower  $k_1$  in winter is caused 445 by lower temperature in winter, while the lower  $[NO_2] \times [O_3]$  in winter is mainly caused 446 by less photochemical production of O3 and more NO that consumes the available O3 447 in winter (Table S5). Nighttime NO<sub>3</sub> removal through NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> was estimated by 448 comparing  $k(NO_3) \times [NO_3]$  (Eqs. 2–3) and  $k(N_2O_5) \times [N_2O_5]$  (Eqs. 4–5). The average 449  $\gamma$ (N<sub>2</sub>O<sub>5</sub>) values derived from each campaign (Table S6 and Fig. S10) were used in Eq. 450

451 (4). The nighttime NO<sub>3</sub> loss via NO titration and VOC oxidation was greater than the 452 N<sub>2</sub>O<sub>5</sub> heterogeneous loss in all the winter and summer campaigns (Fig. 5b). These were 453 the campaign average results. In contrast, the N<sub>2</sub>O<sub>5</sub> loss was greater than the NO<sub>3</sub> loss 454 in selected cases in summer at Mt. Tai (Wang et al., 2017c). To determine the nocturnal 455 loss of NO<sub>3</sub>, we further compared the N<sub>2</sub>O<sub>5</sub>/NO<sub>3</sub> ratio and  $\gamma$ (N<sub>2</sub>O<sub>5</sub>) at the three sites.



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Figure 5. Comparison of  $P(NO_3)$  and loss pathways of NO<sub>3</sub> during the winter and summer observations over the NCP. W and S are abbreviations for winter and summer, respectively.

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The thermal decomposition of N<sub>2</sub>O<sub>5</sub> was suppressed in winter and resulted in high 461 ratios of N<sub>2</sub>O<sub>5</sub>/NO<sub>3</sub> (Fig. 6a; up to approximately 1000), which favored N<sub>2</sub>O<sub>5</sub> loss over 462 NO<sub>3</sub> loss. However, the  $\gamma(N_2O_5)$  in winter was systematically lower than that in summer 463 (Fig. 6b), which indicated slower N<sub>2</sub>O<sub>5</sub> loss in winter. A previous field study in winter 464 Beijing also reported small values of  $\gamma(N_2O_5)$ , ranging < 0.001 to 0.02 (Wang et al., 465 2020). This result differs from previous laboratory studies, which reported larger 466  $\gamma$ (N<sub>2</sub>O<sub>5</sub>) on (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosols at lower temperatures (Hallquist et al., 2003; Griffiths 467 and Anthony Cox, 2009). It is possible that other factors, such as RH and aerosol 468 composition (aside from  $(NH_4)_2SO_4$ ), had a large influence on  $\gamma(N_2O_5)$ . The limited 469 number (2 - 4) of  $\gamma(N_2O_5)$  values obtained in each winter campaign (Table S6) may 470 have also caused a bias in the estimation of the overall  $\gamma(N_2O_5)$ . The opposite effects – 471 a higher N<sub>2</sub>O<sub>5</sub>/NO<sub>3</sub> ratio and lower  $\gamma$ (N<sub>2</sub>O<sub>5</sub>) in winter – offset each other in Wangdu 472 (Fig. 6b) but favored N<sub>2</sub>O<sub>5</sub> loss in Beijing and NO<sub>3</sub> loss at Mt. Tai compared with those 473 in the respective summer campaigns. The higher concentrations of ClNO2 at Mt. Tai 474 during the winter campaigns may be attributable to higher  $\varphi(ClNO_2)$  values in Mt. Tai 475 (Fig. 6c). 476

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478

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Figure 6. Comparison of the (a)  $N_2O_5/NO_3$  ratio, (b)  $\gamma(N_2O_5)$ , and (c)  $\varphi(CINO_2)$  during the winter and summer campaigns. Square dots and error bars indicate the average values and standard deviations, respectively.

## 483 3.3 Daytime peaks in ClNO<sub>2</sub> concentrations

In the winter campaigns, high concentrations of ClNO<sub>2</sub> were sustained after sunrise. 484 Distinct peaks in ClNO<sub>2</sub> concentrations were observed on 3 - 4 days in each campaign, 485 as shown in Fig. 7 displaying one case at each site. Other daytime cases from the three 486 sites are shown in Fig. S11-13. The validity of the daytime peaks was checked by 487 performing isotopic analysis of ClNO<sub>2</sub>, background detection, and onsite calibration. 488 The signals of  $I^{35}CINO_2^-$  and  $I^{37}CINO_2^-$  were well correlated ( $R^2 > 0.99$ ) during daytime 489 peaks in ClNO<sub>2</sub> concentrations (Fig. S3a-c) and calibrations (Fig. S3d-f). The ratio of 490  $I^{37}CINO_2^{-1}$  to  $I^{35}CINO_2^{-1}$  (0.32 – 0.35) was consistent with the natural isotopic ratio of 491 <sup>37</sup>Cl to <sup>35</sup>Cl. The background signals of ClNO<sub>2</sub> were checked when its daytime peaks in 492 concentrations were observed, and no increase in the background was found. We also 493 checked the signal of primary ions (IH2O<sup>-</sup>) and found no abnormal changes when 494 ClNO<sub>2</sub> concentrations showed daytime peaks. These results confirmed that the daytime 495 peaks in ClNO<sub>2</sub> concentrations were real atmospheric phenomena. 496

497

The daytime-ClNO<sub>2</sub> episodes usually occurred from 10:00 to 11:00 LT at each site. 498 The highest daytime mixing ratio of ClNO<sub>2</sub> was 1.3 ppbv (5-minute average) observed 499 at 11:30 on 28 December 2017 in Wangdu. In comparison, the daytime CINO<sub>2</sub> 500 501 concentration observed in the previous summer study at Wangdu (Tham et al., 2016) reached a maximum in the early morning (08:00 LT) and declined to several pptv at 502 11:00 am. Attenuated solar radiation was observed during the days with daytime peaks 503 in ClNO<sub>2</sub> concentrations. For example, the daily maximum rates of *j*NO<sub>2</sub> (1-minute 504 average) for the Wangdu case shown in Fig. 7a  $(2.5 \times 10^{-3} \text{ s}^{-1})$  was significantly lower 505 than the highest rate observed during this campaign  $(6.0 \times 10^{-3} \text{ s}^{-1})$ . The attenuated solar 506 radiation reduced the photolysis of ClNO<sub>2</sub>, which allowed it to persist for a longer 507 period during the day. The chemical data showed contrasting features during the 508 daytime peaks in CINO<sub>2</sub> concentrations at the three sites. At Wangdu, CINO<sub>2</sub> 509

concentrations showed a sharp peak while the concentrations of other pollutants
decreased (Fig. 7a); in Beijing, the daytime peak in ClNO<sub>2</sub> concentrations appeared
with little simultaneous change in the NO<sub>3</sub><sup>-</sup>, NO<sub>x</sub>, and O<sub>3</sub> levels after sunrise (Fig. S12a).
In two cases, daytime peaks of ClNO<sub>2</sub> concentrations at Mt. Tai (Fig. 7c and Fig. S13c)
occurred together with significant increases in NO<sub>3</sub><sup>-</sup>, NO<sub>x</sub>, and PM<sub>2.5</sub> levels, whereas
O<sub>3</sub> concentrations decreased after sunrise and resumed its previous levels.

The daytime peaks in ClNO<sub>2</sub> concentrations were likely caused by the transport of 516 air masses to the respective sites. In situ production of ClNO<sub>2</sub> was limited during the 517 days on which significant daytime ClNO<sub>2</sub> occurred, because the mixing ratios of N<sub>2</sub>O<sub>5</sub> 518 were near the detection limit of the instrument (several pptv). The photochemical 519 lifetime of ClNO<sub>2</sub> at 10:00 am LT was estimated to be 1 - 2 h, based on the inverse of 520 *j*ClNO<sub>2</sub>, which allowed the transport of ClNO<sub>2</sub> produced elsewhere to the observation 521 sites. As daytime peaks in ClNO2 concentrations appeared at both the ground and 522 mountain sites, the high-ClNO2 region may exist in the residual layer above the 523 nocturnal mixing layers. At sunrise, ClNO2-rich air masses may be transported 524 downward to the ground sites (Wangdu and Beijing) and upward to the mountain-top 525 site (Mt. Tai). The downward transport of ClNO2 at Wangdu in summer has been 526 illustrated by Tham et al. (2016), and the upward transport to the top of Mt. Tai has also 527 been implicated by the increasing daytime concentrations of O<sub>3</sub> and other pollutants 528 (e.g., Gao et al., 2005; Zhou et al., 2009; Jiang et al., 2020). Measurements in the 529 residual layers are needed to further investigate the transport of ClNO<sub>2</sub> within the entire 530 boundary layer. 531





532

**Figure 7.** Examples of daytime peaks of ClNO<sub>2</sub> levels observed at (a) Wangdu, (b) Beijing, and (c) Mt. Tai in the winter campaigns. These examples show the highest levels of daytime ClNO<sub>2</sub> at each site. The ionic composition of aerosols was not available on 14 January 2018, owing to an instrument problem.

538

539 3.4 Impact of daytime ClNO<sub>2</sub> on atmospheric oxidation capacity

540 We used the box model (Section 2.5) to show the impact of ClNO<sub>2</sub> on photochemical

541 oxidation at the three sites (Fig. 7a–c). In campaign-averaged conditions, the impact of 542 ClNO<sub>2</sub> was minor, owing to the low daytime concentrations of ClNO<sub>2</sub>. The daytime-543 averaged P(Cl) (06:00 – 18:00 LT) from ClNO<sub>2</sub> photolysis was in the range of 0.03 – 544 0.06 ppbv h<sup>-1</sup>, with the peak values of 0.07 – 0.12 ppbv h<sup>-1</sup>, and the photolysis of ClNO<sub>2</sub> 545 enhanced the daytime RO<sub>x</sub> concentrations by 1.3 – 3.8 % and net O<sub>3</sub> production by 1.3 546 – 6.2 % at the three sites (figures not shown). Such impacts were lower than those 547 during summer at Wangdu (Tham et al., 2016).

548

However, the impact of ClNO<sub>2</sub> increased considerably in the cases of daytime-peak 549 concentrations, as shown in Fig. 8. The daytime-averaged P(Cl) values from ClNO<sub>2</sub> 550 photolysis were  $0.15 \pm 0.13$  (maximum of 0.46),  $0.11 \pm 0.09$  (maximum of 0.32), and 551  $0.19 \pm 0.20$  (maximum of 0.74) ppbv h<sup>-1</sup> at Wangdu, Beijing, and Mt. Tai, respectively 552 (Fig. 8a-c). The winter P(Cl) peak in Wangdu (Fig. 8a, 0.46 ppbv h<sup>-1</sup>) was twice the 553 summer average value (0.24 ppbv h<sup>-1</sup>) (Tham et al., 2016). The P(Cl) during the daytime 554 peaks of ClNO<sub>2</sub> in this study is significantly higher than that in Riedel et al. (2012) 555 (maximum ~0.08 ppbv  $h^{-1}$ ) but slightly lower than that in Haskins et al. (2019) 556 (maximum ~1.3 ppbv h<sup>-1</sup>). P(Cl) from other sources (e.g., the HCl + OH reaction) was 557 minor (8.8 - 14.5 %) during these cases. The relative importance of ClNO<sub>2</sub> in primary 558 radical production varied among these sites. CINO<sub>2</sub> had a minor contribution in Beijing 559 560 but became increasingly important in Wangdu and Mt. Tai (Fig. 8b, c). HONO photolysis was the most important source of OH at the two ground sites, whereas O3 561 was also important at Mt. Tai. 562

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564 The liberated Cl (mostly from ClNO<sub>2</sub> photolysis) accounted for 28.5 - 57.7 % of the daytime (06:00 - 18:00 LT) oxidation of alkanes, 6.1 - 13.7 % of that of alkenes, 5.3 - 13.7565 14.2 % of that of aromatics, and 4.6 - 6.0 % of that of aldehydes in the cases of high 566 levels of daytime ClNO<sub>2</sub>. The Cl + VOCs reactions enhanced the production of OH, 567 HO<sub>2</sub>, and RO<sub>2</sub> by up to 15 - 22 %, 24 - 31 %, and 36 - 52 %, respectively (Fig. 8d–f). 568 The photolysis of ClNO<sub>2</sub> increased the daytime net O<sub>3</sub> production by 5.4 ppbv (18 %), 569 2.8 ppbv (17 %), and 2.6 ppbv (13 %) at Wangdu, Beijing, and Mt. Tai, respectively 570 (Fig. 8g-i). These results indicate the considerable impact of daytime ClNO<sub>2</sub> on the 571 atmospheric oxidative capacity and production of secondary pollutants. 572

573

574 The impact of Cl in the NCP is likely larger than the result shown above. Our model calculations considered photolysis of ClNO<sub>2</sub> (and HCl + OH) as the source of Cl, but 575 not other photolabile Cl-containing gases. However, in the Wangdu field campaign, we 576 577 frequently observed elevated daytime concentrations of bromine chloride (BrCl) and molecular chlorine (Cl<sub>2</sub>), which dominated the Cl production (Peng et al., 2020). In 578 addition, our ClNO<sub>2</sub> measurements were conducted at polluted ground-level sites and 579 at a high mountain site (1534 m a.s.l.), which are not in the nocturnal residual layer 580 where strong ClNO<sub>2</sub> production is expected to occur (Zhang et al., 2017). It is thus 581 highly desirable to measure ClNO<sub>2</sub> in the residual layer in future studies to 582 comprehensively assess the role of ClNO<sub>2</sub> in the lower part of the atmosphere. 583



584

Figure 8. The impact of ClNO<sub>2</sub> photolysis on atmospheric oxidation during daytimeClNO<sub>2</sub> episodes: (a) primary radical production from the photolysis of O<sub>3</sub>, ClNO<sub>2</sub>, and
HONO; (b) percentage increase in OH, HO<sub>2</sub>, and RO<sub>2</sub> due to ClNO<sub>2</sub> photolysis (Section
2.5); and (c) enhancement of net O<sub>3</sub> production rates due to ClNO<sub>2</sub> photolysis.

589

## 590 **4. Summary and conclusions**

Observations of ClNO<sub>2</sub> and related species were conducted at urban, polluted rural, 591 and polluted lower tropospheric sites in the winter of 2017 - 2018 in the NCP, which 592 suffers from severe winter haze pollution. The winter measurements showed lower 593 concentrations of ClNO<sub>2</sub> compared with those in previous summer observations. The 594 campaign averaged NO<sub>3</sub> loss via reaction with NO at night dominated over the N<sub>2</sub>O<sub>5</sub> 595 loss at all the sites due to high NO concentrations, and in situ ClNO<sub>2</sub> formation was 596 generally insignificant. However, high levels of daytime ClNO<sub>2</sub> (exceeding 1 ppbv) 597 were observed at the three sites. We suggest that CINO<sub>2</sub> was efficiently produced in the 598 nocturnal residual layer and was transported to ground-level and high-elevation sites. 599 The daytime concentrations of ClNO<sub>2</sub> had great effects on the production of Cl, RO<sub>x</sub>, 600 and O<sub>3</sub>. Vertical measurements of the concentrations of ClNO<sub>2</sub> and related compounds 601 are needed to better understand the distribution and impact of these species in the lower 602 troposphere. Compared to the previous studies in the clean troposphere or in more aged 603 air masses, our results provide new insights into ClNO2 formation in the region affected 604 by fresh and intense anthropogenic emissions. 605

606

607 Data availability.

The datasets described in this study is available by contacting the corresponding author (cetwang@polyu.edu.hk).

610

611 *Author contributions*.

TW designed this study. JC, YM, LX, JG, and HL provided field measurement sites. MX, XP, and WW conducted the CIMS measurements. CY, ZW, YJT, HC, CZ, PL, and XW provided supporting data. XP and WW performed the box model simulation. MX analyzed and virtualized the research data. MX and TW wrote the manuscript with discussions and comments from all co-authors.

- 617
- 618 *Competing interests.*
- 619 The authors declare that they have no conflict of interest.
- 620

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626

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