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Enhanced wintertime oxidation of VOCs via sustained radical sources in the urban atmosphere

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Abstract

Daytime atmospheric oxidation chemistry is conventionally considered to be driven primarily by the OH radical, formed via photolytic sources. In this paper we examine how, during winter when photolytic processes are slow, chlorine chemistry can have a significant impact on oxidative processes in the urban boundary layer. Photolysis of nitryl chloride ($CINO_2$) provides a significant source of chlorine atoms, which enhances the oxidation of volatile organic compounds (VOCs) and the production of atmospheric pollutants.

We present a set of observations of CINO_2 and HONO made at urban locations in central England in December 2014 and February 2016. While direct emissions and insitu chemical formation of HONO continue throughout the day, CINO_2 is only formed at night and is usually completely photolyzed by midday. Our data show that, during winter, CINO_2 often persists through the daylight hours at mixing ratios above 10-20 ppt (on average). In addition, relatively high mixing ratios of daytime HONO (>65 ppt) provide a strong source of OH radicals throughout the day.

The combined effects of ClNO_2 and HONO result in sustained sources of Cl and OH radicals from sunrise to sunset, which form additional ozone, PAN, oxygenated VOCs, and secondary organic aerosol. We show that radical sources such as ClNO_2 and HONO can lead to a surprisingly photoactive urban atmosphere during winter and

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should therefore be included in atmospheric chemical models.

Keywords: nitryl chloride; nitrous acid; chlorine; OH radical; tropospheric ozone

1 Highlights

2	• High CINO ₂ concentrations at sunrise cause it to persist until sunset above 10-20
3	ppt
4	- Daytime HONO accounts for over 90% of OH formation in the winter urban
5	atmosphere
6	• Sustained sources of Cl and OH throughout the day enhance the oxidation of
7	VOCs
8	- Production of O_3 and secondary pollutants increases and continues into the af-
9	ternoon

10 1. Introduction

The oxidation of volatile organic compounds (VOCs) in the lower atmosphere leads 11 to the formation of ozone (O₃), secondary organic aerosol (SOA) and other harmful 12 pollutants (e.g. aldehydes, PAN) via a complex series of chemical reactions initiated 13 by reactive radical species. The current understanding of oxidative processes in the tro-14 posphere is that the most important daytime oxidant is the hydroxyl radical (OH). How-15 ever, chlorine atoms (Cl) are being increasingly recognized as important tropospheric 16 oxidants (Simpson et al., 2015; Sherwen et al., 2017; Wang et al., 2019), although 17 chlorine chemistry is often not included in the air quality models used for regulatory 18 purposes. Because of their high reactivity, Cl atoms can considerably accelerate the ox-19 idation rate of VOCs above that of OH chemistry alone, thus increasing the formation 20 of secondary atmospheric pollutants. 21

The dominant source of the OH radical across the troposphere is the photolysis 22 of ozone, followed by the reaction of excited state oxygen atoms (O¹D) with water 23 vapour (Figure 1). Ambient studies have shown that the reactions of ozone with unsat-24 urated VOCs (alkenes, dialkenes, terpenes) and the photolysis of nitrous acid (HONO) 25 can be more important primary sources of OH than ozone photolysis, especially in the 26 urban boundary layer (Emmerson et al., 2005; Ren et al., 2006; Kanaya et al., 2007; 27 Elshorbany et al., 2009; Lee et al., 2016; Tan et al., 2018; Slater et al., 2020). Because 28 of its relatively short photolysis lifetime (in the order of tens of minutes), HONO has 29 long been considered as a significant OH source, mainly during the morning. However, 30 more recent field studies have found non-negligible HONO concentrations in urban 31 environments during the day, which suggest that there are significant daytime sources 32 of HONO (Kleffmann, 2007; Villena et al., 2011; Michoud et al., 2014) and, there-33 fore, that the influence of HONO on radical production may be more extensive than 34 previously thought. Besides the gas-phase reaction OH + NO, important sources of 35 HONO are direct emissions, e.g. from vehicles (Kurtenbach et al., 2001; Kramer et al., 36 2020) and from microbial activity in the soil (Su et al., 2011). In addition, HONO is 37 known to be formed via heterogeneous reactions of NO2 on humid surfaces both during 38 the night and during the day (Finlayson-Pitts et al., 2002; Vogel et al., 2003; Spataro 39

and Ianniello, 2014). Photo-enhanced conversion of NO₂ into HONO has been observed in laboratory studies on several surfaces, with organic films the most productive (Ammann et al., 1998; George et al., 2005; Stemmler et al., 2006), and has also been observed on "urban grime" on building surfaces (Baergen and Donaldson, 2016) and on snow in urban environments (Chen et al., 2019; Michoud et al., 2015). The relative contribution of urban daytime sources of HONO is an active area of research, with models still largely unable to account for measured daytime concentrations (e.g. Michoud et al. (2014); Lee et al. (2016)).

Cl atoms are released into the gas phase via a number of different mechanisms 48 (Simpson et al., 2015): for example, acid displacement of HCl from aerosol and var-49 ious multi-phase chemical processes that form gas-phase BrCl and Cl₂, followed by 50 photolysis and/or reaction with OH. One mechanism that has recently gathered much 51 attention is the nocturnal formation of nitryl chloride (CINO₂) via reaction of dinitro-52 gen pentoxide (N2O5) on chloride-containing aerosol (Figure 1). The photolysis of 53 ClNO₂ after sunrise forms Cl atoms and nitrogen dioxide (NO₂), thus increasing the 54 oxidation of VOCs and reducing the loss of NOx via the nocturnal formation of HNO3 55 (Figure 1). The combination of Cl reactivity and higher NO₂ concentrations results 56 in enhanced ozone production - up to 10 ppb of additional O3 compared to scenarios 57 without CINO₂ chemistry (Osthoff et al., 2008; Sarwar et al., 2014; Tham et al., 2016). 58 Several studies have reported CINO₂ nocturnal mixing ratios ranging from a few tens 59 of ppt to several ppb (e.g. Osthoff et al. (2008); Mielke et al. (2011); Phillips et al. 60 (2012); Riedel et al. (2012); Bannan et al. (2015); Wang et al. (2016)). Depending on 61 the season and meteorological conditions, the photolysis lifetime of CINO2 at midday 62 in the mid-latitudes can vary between 50 minutes and 3 hours. This means that, typ-63 ically, over 95% of the nitryl chloride present at sunrise is photolyzed before 11:30 64 (summer) or 13:00 (spring/autumn), and that most of the direct effect of chlorine reac-65 tivity on the formation of atmospheric pollutants takes place during the first few hours 66 of the morning (Thornton et al., 2010; Phillips et al., 2012; Haskins et al., 2019). 67

In general, the chemical processes that form pollutants in the boundary layer during winter have received less attention than during other seasons, especially under polluted urban conditions. Wintertime chemistry is characterized by lower temperatures, less

intense sunlight and shorter daylight hours, all of which affect the main sources of 71 oxidants, most of which are photolytic. Therefore, the formation of secondary atmo-72 spheric pollutants is slower during winter, and any additional source of oxidants, such 73 as Cl atoms, can have a significant impact on urban air quality. Only a few studies have 74 reported ClNO₂ observations in wintertime, with nocturnal mixing ratios of the order 75 of several hundreds of ppt (Thornton et al., 2010; Mielke et al., 2016; Priestley et al., 76 2018; Sommariva et al., 2018; Haskins et al., 2019; McNamara et al., 2020). In these 77 studies, CINO₂ mixing ratios usually fell below the respective instrumental detection 78 limits (in the order of a few ppt) around midday, with the exception of Priestley et al. 79 (2018) who observed ClNO₂ mixing ratios >4 ppt up until \sim 15:00 in November in 80 Manchester (UK). 81

In this paper, we present a dataset of CINO2 and HONO observations made during 82 winter in an urban environment in central England (UK). On approximately half of 83 the days, ClNO₂ remained above the instrument detection limit (4.2 ppt) for the entire 84 daylight period. With the help of a box-model, we show how the persistence of $CINO_2$ 85 through the daylight hours of winter, combined with the daytime formation of HONO, 86 leads to significantly higher concentrations of radical species (OH and Cl) in the urban 87 boundary layer, and thereby enhances the oxidation of VOCs and the production of 88 secondary pollutants, such as ozone, oxygenated VOCs, PAN and SOA. 89

90 2. Materials and Methods

91 2.1. Instruments

Nitryl chloride (ClNO₂) was measured using a Chemical Ionization Mass Spec-92 trometer (CIMS). The instrument (THS Instruments LLC, USA) was operated in neg-93 ative ion mode using iodide ions (I^-) as the reagent ion, and CINO₂ was detected at 94 m/z = 208, 210 amu, corresponding to the $[I \cdot CINO_2]^-$ ion cluster (Sommariva et al., 95 2018). Molecular chlorine (Cl₂) was also measured by CIMS at m/z = 197, 199, 201 96 amu, which correspond to the $[I \cdot Cl_2]^-$ ion cluster. The inlet line, a 5 m long PFA tube 97 (OD = 3/8"), was regularly washed with deionized water during the measurements to 98 avoid formation of CINO₂ from particles deposited inside the inlet: there was no signif-99 icant difference in the CIMS signals before and after the line was washed. To calibrate 100

the CIMS, nitryl chloride was synthetized using a humidified flow of Cl_2 (5 ppm in N₂) over a bed of sodium nitrite (NaNO₂) and sodium chloride (NaCl) as described in Thaler et al. (2011): CINO₂ was then quantified via thermal decomposition to Cl and NO₂ (at ~350 °C) followed by measurement of NO₂ by Broadband Cavity Enhanced Spectroscopy (Thalman et al., 2015). Molecular chlorine was calibrated by known dilutions of a 5 ppm certified gas standard (BOC plc, UK). The ClNO₂ and Cl₂ detection limits were 4.2 and 7.1 ppt, respectively (2 σ , 1 minute).

The CIMS instrument was deployed at the University of Leicester campus, together with a O_3 monitor, a NO_x monitor (T400 and T200, Teledyne Technologies Inc, USA) and a spectral radiometer (MetCon GmbH, Germany) to measure the photolysis rates of over 40 species, including O_3 , HONO and ClNO₂. Meteorological information (wind speed and direction, temperature, pressure, humidity) was available from the Automatic Urban and Rural Monitoring Network (AURN). The AURN site is located on the University campus and is classed as "urban background".

Nitrous acid (HONO) was measured using a Long Path Absorption Photometer 115 (LOPAP-03, QUMA Elektronik & Analytik GmbH, Germany). As described in He-116 land et al. (2001), the LOPAP is a wet chemical technique where gas-phase HONO is 117 sampled within a stripping coil into an acidic solution where it is derivatized into an 118 azo dye. Absorption of light at 550 nm by the azo dye is measured with a spectrometer 119 (Ocean Optics Inc, USA) with an optical path length of 2.4 m. The LOPAP sampling 120 unit is a temperature controlled (15-20 $^{\circ}$ C) box containing a quartz inlet (length <5 121 cm) connected to the main instrument via a 3 m umbilical line that carries the reagents 122 and the azo-dye. The instrument was operated and calibrated according to the standard 123 procedures described in Kleffmann and Wiesen (2008). The HONO detection limit 124 was 0.2 ppt (2σ , 30 seconds). 125

The LOPAP instrument was deployed at the University of Birmingham campus; Leicester and Birmingham are two cities in central England ~80 kilometers apart. In both locations, the sampling points on the respective University campuses are comparable "urban background sites".

130 2.2. Box-model

A simple box-model was used to investigate the formation of radicals (OH and Cl), the oxidation of VOCs and the production of secondary pollutants. The model was built using AtChem2 v1.2 (Sommariva et al., 2020) with a chemical mechanism taken from the Master Chemical Mechanism (MCM v3.3.1, Saunders et al. (2003); Jenkin et al. (2003)). The chemical mechanism includes a complete inorganic chemistry scheme plus the oxidation mechanism of the 31 VOCs, including methane, that are routinely measured at the AURN sites (Table 1).

Production of HCl from chlorine reactions with VOCs, and production of Cl from 138 the HCl + OH reaction and from ClNO2 photolysis, are not included in the MCM and 139 were added to the mechanism. The chlorine gas-phase mechanism in the model is very 140 simple and does not include inorganic reactions such as $Cl+O_3$, $Cl+HO_2$ and $Cl+O_2$. 141 For the mixture of CH₄ and VOCs listed in Table 1, calculations show that the dominant 142 reaction of Cl atoms is with organics (over 85%), and thus we do not expect the model's 143 omission of Cl inorganic reactions to significantly affect the conclusions of this work 144 The uptake of N₂O₅ on aerosol and the heterogeneous formation of ClNO₂ were not 145 included in the mechanism, because the model was only run from sunrise to sunset, 146 when CINO₂ formation is not active. Heterogeneous formation of HONO was also not 147 included, because the model was constrained to the average diurnal profile of measured 148 HONO. The model was constrained to the average diurnal profiles of measured jNO₂, 149 jHONO and jClNO₂, while the photolysis rates of the other species in the mechanism 150 were calculated by AtChem2 and scaled to jNO₂. 151

The model was initialized with the average values observed at sunrise in Leicester during winter 2014 and 2016 (Sommariva et al., 2018) for ClNO₂ and other inorganic species (O_3 , NO, NO₂, CO) as well as for temperature, relative humidity and pressure. Since measurements of VOCs were not available in either Leicester or Birmingham, the model was initialized with the average VOC concentrations measured during winter at the nearest suburban background AURN site, London Eltham. The initial conditions of all chemical species and physical parameters in the box-model are listed in Table 1.

3. Results and Discussion

160 3.1. Observations of daytime ClNO₂: sources and sinks

The nitryl chloride measurements presented here were part of a larger project aimed 161 at assessing the spatial and temporal variability of CINO₂ in the UK (Sommariva et al., 162 2018). In this paper, we focus on two wintertime measurement periods in Leicester 163 $(52^{\circ}38' \text{ N}, 01^{\circ}08' \text{ W})$, a city in central England $\sim 200 \text{ km}$ from the ocean – the major 164 source of Cl-containing aerosol (sea-salt). CINO2 was observed above the instrument 165 detection limit every night between 11 and 19 December 2014, and on 19 out of 26 166 nights between 1 and 26 February 2016. Since the measurements were taken in dif-167 ferent years, they are shown in this paper as monthly diurnal averages (Figure 2); the 168 whole dataset and timeseries of the observations are shown and discussed in Som-169 mariva et al. (2018). 170

During both measurement periods, the peak ClNO₂ concentrations were observed 171 at night between 00:00 and 04:00. The mean and median peak mixing ratios were 76 172 ppt and 50.5 ppt, respectively, in December 2014, and 162 ppt and 139 ppt, in Febru-173 ary 2016 (Sommariva et al., 2018). These mixing ratios are consistent with previous 174 wintertime observations of CINO2 (Thornton et al., 2010; Mielke et al., 2016; Priestley 175 et al., 2018; Haskins et al., 2019). Closer inspection of the dataset revealed two cases, 176 hereafter referred to as highCL and lowCL (Figure 2). On 63% of the days in December 177 2014 and on 38% of the days in February 2016, CINO₂ concentrations persisted above 178 the instrument detection limit throughout the daylight hours (case highCL), increasing 179 again after sunset (\sim 16:00 in December, \sim 17:00 in February). The lowest diurnal con-180 centrations during these days were observed around 14:00 (in December) and 15:00 181 (in February), with mean mixing ratios of 10.1 ppt and 20.5 ppt, respectively. On the 182 rest of the days, CINO₂ mixing ratios dropped below the instrument detection limit of 183 4.2 ppt between 11:00 and 13:00 (case lowCL), similar to what has been observed in 184 prior wintertime studies (Thornton et al., 2010; Mielke et al., 2016). During October-185 November 2014, Priestley et al. (2018) observed CINO₂ persisting into the afternoon 186 in Manchester, ~ 120 km northwest of Leicester. However, in that study ClNO₂ de-187 creased below the instrument detection limit (3.8 ppt) around 15:00, approximately 2 188 hours before sunset. 189

The conventional route for the formation of CINO₂ requires the presence of N₂O₅ 190 (Figure 1), which is formed by the reaction $NO_3 + NO_2$ and is mostly a nocturnal 191 species. While N₂O₅ can sometimes be present during the day (Geyer et al., 2003; 192 Brown et al., 2005; Osthoff et al., 2006), this is highly unlikely under the typical urban 193 conditions of Europe. NO₃ photolyzes rapidly (with a lifetime of the order of 7-20 194 seconds at midday in winter) and reacts readily with NO: daytime urban mixing ratios 195 of NO_x are in the order of tens of ppb (Bigi and Harrison, 2010), so the lifetime of NO_3 196 with respect to reaction with NO is ≤ 0.1 seconds (at the average winter temperature of 197 5 °C), about an order of magnitude faster than the reaction of NO₃ with NO₂ to form 198 N_2O_5 . Therefore, NO_3 is effectively removed from the atmosphere before it can form 199 N₂O₅, thus preventing formation of ClNO₂ during the day. There has been one prior 200 report of daytime ClNO₂, with mixing ratios of ~ 60 ppt observed in the afternoon in 201 central China during summer (Liu et al., 2017). In order to explain their observations, 202 Liu et al. (2017) proposed a photochemical mechanism involving very high mixing 203 ratios of Cl₂ during the day (up to 450 ppt). However, such a mechanism cannot explain 204 our observations of daytime ClNO2 in Leicester, because Cl2 was always below the 205 instrument detection limit of 7.1 ppt. 206

Daytime production of CINO₂ in Leicester can thus be ruled out, which might sug-207 gest that the observed daytime concentrations were instead caused by slower removal 208 of ClNO₂ on the days when it persisted until sunset. However, this is not the case: the 209 photolysis rates of ClNO₂ were similar in both cases (Figure 2), and actually slightly 210 faster in the highCL case than in the lowCL case (by 5-7%, on average). If there was no 21 CINO₂ formation during the day and if the photolytic loss of CINO₂ did not vary sig-212 nificantly, the only difference between the two cases was the amount of ClNO2 present 213 at sunrise (between 7:00 and 8:00 during winter). In fact, CINO₂ concentrations at 214 sunrise in the highCL case were, on average, 3.5 to 3.9 times higher than in the lowCL 215 case, which, combined with the short days and slow photolysis rates of winter, resulted 216 in the continuous presence of $CINO_2$ throughout the day at mixing ratios of >10-20 217 ppt, i.e. a factor between of 2 and 5 times above the instrument detection limit (Fig-218 ure 2). It must also be noted that the observed decay rate of $CINO_2$ was, on average, 219 within 10% of that calculated from the photolysis rates alone (Figure 4), which sug-220

gests that deposition, heterogenous reactions and/or boundary layer dynamics did not 221 have a significant effect on the variation of the ClNO₂ mixing ratio during the morning. 222 Both chemical and physical factors contribute to high mixing ratios of CINO₂ at 223 sunrise. Some studies (Thornton et al., 2010; McNamara et al., 2020; Wang et al., 224 2020) have suggested that snow and road salt can be sources of chloride during winter. 225 However, this was not the case during this work, and the measurements of particulate 226 chloride in Leicester during December 2014 (median concentration = $1.3 \ \mu g \ m^{-3}$) were 227 strongly correlated with sodium, indicating a marine origin (Sommariva et al., 2018). 228 In fact, the analysis of the entire dataset showed that the chemical conditions for the 220 formation of CINO2 in Leicester tend to be limited by the availability of O3 rather than 230 of NO₂ or chloride, especially during spring and winter (Sommariva et al., 2018). Gen-231 erally, higher concentrations of ozone lead to stronger production of NO3 and hence of 232 N₂O₅, the key precursor of ClNO₂. However, this is not always the case and meteo-233 rological conditions can play a more important role than chemical conditions. Nights 234 with higher ClNO₂ concentrations were usually colder (by 3-6 °C, Figure 2), which 235 favours the thermal stability of N₂O₅; easterly winds (from less polluted areas of the 236 UK) and stagnant meteorological conditions (wind speeds <2 m/s) also contributed to 237 the accumulation of ClNO₂ during the night in the highCL case. 238

Previous studies in Northern Europe (Bannan et al., 2015; Priestley et al., 2018; Sommariva et al., 2018) have observed that ClNO₂ is typically present in urban environments during all seasons. Our measurements further show that, during winter, ClNO₂ often persists at significant mixing ratios (tens of ppt) through the daylight hours and thereby has the potential to provide a continuous source of Cl atoms in the urban boundary layer.

245 3.2. Effects on the production of radicals

The persistence of nitryl chloride from sunrise to sunset during winter days has two major effects on the formation of radicals in the urban atmosphere. First, more Cl atoms overall are released via ClNO₂ photolysis when ClNO₂ persists throughout the day (case highCL) than when it disappears around midday (case lowCL): this is a direct consequence of the higher concentrations of nitryl chloride at sunrise in the highCL case (Figure 2). Figure 3 shows the average production rates and the total production of Cl and OH radicals. The average production rates of Cl peaked between 9:00 and 10:00 in the morning: the maximum Cl production rates were 3 to 10 times higher – and total Cl production was 3 to 8 times higher – in the highCL case compared to the lowCL case. Production of chlorine atoms was always higher in February than in December, because of the higher nocturnal ClNO₂ concentrations and faster diurnal photolysis rates (Figure 2).

Second, diurnal persistence of CINO₂ affects the timing of the release of Cl atoms, 258 and therefore of the production of O₃ and other secondary pollutants. One hour before 259 sunset, which is at 16:00 in December and at 17:00 in February, the Cl production 260 rates in the highCL case were 4 to 6 times higher than in the lowCL case. This means 261 that production of chlorine atoms, and therefore oxidation of VOCs by Cl, remained 262 significant (> 1×10^3 atoms cm⁻³ s⁻¹) for most of the afternoon in the highCL case. 263 While these values may seem small, it must be noted that VOC oxidation in winter is 264 slower than in summer, due to the low concentrations of OH radicals and, therefore, 265 even small increments in the amount of oxidants can impact the rates of formation of 266 secondary pollutants. 267

To assess the impact of Cl on VOC oxidation, it is necessary to evaluate how it 268 compares with the other main daytime oxidant, the OH radical, for which the dominant 269 sources in an urban environment are the photolysis of O_3 and of HONO (Figure 1). 270 HONO was not measured in Leicester, but HONO measurements were made in Birm-271 ingham in February 2014. Although these measurements were not contemporaneous 272 with the ClNO₂ measurements made in Leicester, previous work has shown that HONO 273 concentrations in the two locations are comparable (Crilley et al., 2016; Kramer et al., 274 2020). Therefore, we used the HONO data measured in Birmingham in February 2014 275 (Figure 2) as a proxy for HONO concentrations in Leicester in February 2016. The 276 bimodal diurnal profile observed for HONO in Birmingham, peaking in the morning 277 (07:00) and in the evening (18:00), suggests vehicle emissions are an important source 278 (Kramer et al., 2020); the high nocturnal HONO mixing ratios (~150 ppt) point to 279 nocturnal sources, likely heterogenous reactions of NO2 on humid surfaces. The mini-280 mum HONO mixing ratio was observed at midday, with average mixing ratios of ~ 65 281

ppt, which indicates sustained daytime source(s) that counteract the increased loss byphotolysis.

The production rate of OH was calculated using the HONO measurements taken in 284 Birmingham, together with the O₃ and photolysis rates measurements taken in Leices-285 ter. Figure 3 shows the average production rates and the total production of OH from 286 O₃ and HONO photolysis during winter: OH production was dominated by HONO 287 photolysis, which was 15-20 times larger than O₃ photolysis, consistent with other re-288 cent studies (Ren et al., 2006; Tan et al., 2018; Slater et al., 2020). Earlier studies 289 (Emmerson et al., 2005; Kanaya et al., 2007) found instead that ozonolysis of unsatu-290 rated VOCs was the main primary source of OH in urban environments during winter: 291 this issue will be discussed in the next section with the help of a box-model. The total 292 production of OH and Cl (Figure 3, bottom) is the integrated number of OH molecules 293 and Cl atoms per unit volume formed since sunrise. During the daylight hours, a total 294 of $\sim 7.0 \times 10^{11}$ molecules cm⁻³ of OH radicals were formed from the photolysis of O₃ 295 (5-7%) and of HONO (93-95%). By comparison, the total production of Cl atoms from 296 ClNO₂ photolysis ranged between 1.3×10^9 atoms cm⁻³ (December, case lowCL) and 297 1.4×10^{11} atoms cm⁻³ (February, case highCL). 298

The calculations presented in Figure 3 show that, compared to the days with low 299 concentrations of ClNO₂ at sunrise, the days with high concentrations of ClNO₂ at 300 sunrise - which showed observable mixing ratios (>10-20 ppt) of ClNO₂ throughout 301 the daylight hours - resulted in up to 8 times more Cl atoms activated in the gas phase, 302 with production continuing at a significant rate right up until sunset. Moreover, the data 303 show that substantial amounts of daytime HONO (in the order of a hundred ppt) were 304 the source of almost all the OH radicals. In the following section, we discuss how these 305 diurnal radical sources affect the oxidative processes in the wintertime urban boundary 306 layer. 307

308 3.3. Effects on the oxidative capacity of the atmosphere

We used two approaches to understand the impact of continuous sources of radicals from the photolysis of $CINO_2$ and HONO in winter and, hence, the relative importance of Cl and OH for the oxidation of VOCs. The following analysis focuses on the month of February, for which both $CINO_2$ and HONO measurements were available (Figure 2).

In the first approach, the lifetimes of selected VOCs were calculated for four dif-314 ferent scenarios: with ClNO₂ persisting until sunset (highCL), with ClNO₂ disappear-315 ing by midday (lowCL), without CINO₂ (noCL), without CINO₂ and without day-316 time sources of HONO (noCL-HONO). The concentrations of OH and Cl used in this 317 calculation were the values at 10:00 calculated with the box-model for the month of 318 February, as discussed below. Table 2 shows that chlorine chemistry increases the oxi-319 dation rates of several VOCs, especially alkanes and oxygenated VOCs: comparing the 320 lowCL and noCL scenarios, the lifetimes of VOCs decrease by between 4% (toluene) 321 and 38% (propane). In the highCL scenario, when more Cl atoms overall are released 322 (Figure 3), the lifetimes of VOCs further decrease by an additional 20% (isoprene) to 323 62% (propane) compared to the lowCL scenario. Of particular importance, because 324 of its climate forcing role, is the effect of Cl on the lifetime of methane which de-325 creases by between 7% (lowCL) and 36% (highCL), compared to the scenario where 326 methane only reacts with OH (noCL). Alkenes, such as propene and isoprene, are less 327 affected by the presence of chlorine (22-28% decrease in lifetimes in the highCL sce-328 nario compared to the noCL scenario) because they react with OH faster than alkanes 329 and aromatics (Table 2). 330

The oxidation of the VOC pool is therefore significantly accelerated in the presence 331 of CINO₂. This is true in all seasons, but the effect is particularly pronounced under 332 the unfavorable photochemical conditions of winter when other oxidant sources, such 333 as O_3 photolysis, are weak. Moreover, the presence of daytime HONO sources leads 334 to higher OH concentrations: if these sources were not taken into account (i.e. if 335 HONO is only formed via OH + NO, as in scenario noCL-HONO), the calculated 336 concentration of OH was 84% lower than the noCL scenario, with a corresponding 337 increase in the lifetimes of VOCs (Table 2). Enhanced oxidation of VOCs affects the 338 formation of gas-phase pollutants, such as O₃ (see below), and of secondary organic 339 aerosol (SOA). Depending on the NO_x and humidity levels, SOA yields from isoprene 340 and toluene oxidation vary between 1-5% and 10-30%, respectively (Ng et al., 2007; 341 Carlton et al., 2009), which means that the increased oxidation of these VOCs can 342

result in additional SOA formation of up to $\sim 0.6\%$ (from isoprene) and up to $\sim 9\%$ (from toluene). Because of the differences in the rate coefficients of Cl with different VOCs, the actual impact of chlorine chemistry depends on the composition of the VOC mixture in the urban atmosphere. It must also be noted that chlorine reactivity has the potential to change the composition of the VOC pool, since some classes of compounds react more readily with Cl than with OH (Table 2).

The second approach used a simple box-model to calculate the effect of enhanced 349 VOC oxidation rates on the production of secondary pollutants, particularly of ozone. 350 The model was run for a 24h period under the four scenarios in Table 2: ClNO₂ was ini-351 tialized using the mean observed ClNO₂ at sunrise in each scenario (Table 1). HONO 352 was constrained to the average measured diurnal profiles in scenarios highCL, lowCL 353 and noCL (Figure 2), and calculated by the model in scenario noCL-HONO. The box-354 model underestimated measured O₃ during the day by up to 4 ppb, because it only 355 includes photochemical processes (rather than, e.g. mixing or transport); therefore, the 356 following analysis is focused on the differences between the model scenarios. 357

The model results (Figure 4) show significant enhancements (a factor of \sim 6) in the 358 concentrations of Cl atoms in the highCL scenario compared to the lowCL scenario. 359 Increased oxidation of VOCs by chlorine atoms also led to higher concentrations of 360 OH (up to 30%), HO₂ and RO₂ (up to a factor of 2). The overall impact on the forma-361 tion of secondary pollutants was significant, with increases of up to 22% and 57% in 362 the concentrations of HCHO and CH3CHO, respectively, and of up to 40% in the con-363 centration of PAN compared to the noCL scenario. The increase in OH concentrations 364 was most pronounced in the morning and was a consequence both of the higher con-365 centrations of peroxy radicals and of the increased OH production from the photolysis 366 of the oxygenated VOCs formed by the oxidation of primary VOCs. Figure 5 shows 367 the amount of additional O₃ formed in the scenarios with ClNO₂ (highCL and lowCL) 368 relative to the baseline scenario without ClNO₂ (noCL): between 0.13 ppb and 0.78 369 ppb more ozone was present at sunset due to Cl reactivity. 370

The model was also run for the month of December, but the impact of chlorine reactivity on secondary pollutant formation was more limited than in February: the additional ozone present at sunset in the highCL scenario was only ~50 ppt compared to the baseline scenario without chlorine chemistry (noCL). The main reason for the low impact of Cl is that both the concentrations and the photolysis rates of $ClNO_2$ were lower than in February (Figure 2), which resulted in ~10 times less Cl atoms released across the day in December (Figure 3).

Analysis of the model results indicate that, in February, HONO was the primary 378 source of OH in the urban boundary layer: the total production rate of OH in the middle 379 of the day was 1.8×10^6 molecules cm⁻³ s⁻¹, of which 47% was due to recycling 380 $(HO_2 + NO)$, 45% due to HONO photolysis and only 5.5% due to O₃ photolysis, while 381 the reactions of ozone with alkenes were responsible for less than 1% of the total OH 382 production. These numbers are consistent with what can be directly inferred from 383 our measurements (Figure 3), as well as with the studies by Ren et al. (2006); Tan 384 et al. (2018); Slater et al. (2020). In contrast, early work in urban environments during 385 winter (Emmerson et al., 2005; Kanaya et al., 2007) concluded that the ozonolysis of 386 unsaturated VOCs was a source of OH radicals as large as HONO photolysis. The 387 modelling study by Emmerson et al. (2005) is especially relevant, as it was conducted 388 in Birmingham, the same region as this work: their model was also based on the MCM 389 and included an heterogeneous HONO source in addition to the gas-phase reaction 390 OH + NO, but it was not constrained to measured HONO, which raises the possibility 391 that HONO concentrations were underestimated by the model. In fact, scenario noCL-392 HONO in Figure 4 shows that our model underestimated HONO concentrations by 393 approximately a factor of 10 at 12:00 and a factor of 40 at 16:00, if not constrained 394 to the observations of HONO. This resulted in lower OH concentrations (a factor of 395 4-5), as well as a shift in the peak OH concentration from 10:00 to 12:00 due to the low 396 HONO concentrations in the morning. In the absence of a strong OH source - such as 397 HONO photolysis - the model calculated that the O₃ concentration at sunset was 0.31 398 ppb less than in the baseline scenario noCL (Figure 5). 399

400 **4. Conclusions**

In this work, we discuss how the presence of strong sources of atomic chlorine, such as $CINO_2$, in an urban environment during winter can substantially accelerate the ⁴⁰³ oxidation of VOCs resulting in the formation of additional ozone and other secondary
⁴⁰⁴ pollutants (oxygenated VOCs, PAN and SOA).

Our observations show that, in winter, ClNO2 can persist in significant mixing 405 ratios (>10-20 ppt, on average) until sunset, and HONO can be present during the day 406 at mixing ratios of the order of a hundred ppt. These conditions create sustained sources 407 of Cl and OH radicals during all daylight hours, which enhance the oxidation of VOCs 408 and extend the production of ozone and secondary pollutants in the afternoon. HONO 409 photolysis dominates the formation of the OH radical, meaning that nitrous acid and 410 nitryl chloride - rather than O3 photolysis or ozonolysis of unsaturated VOCs - are the 411 main sources of oxidants in the urban atmosphere during winter and are responsible for 412 initiating most of the oxidative chemistry that forms atmospheric pollutants. 413

Multiple previous studies have shown that both $CINO_2$ and HONO are present in a range of diverse environments and, hence, they are likely to play a fundamental role in wintertime urban photochemistry in other locations around the world. The processes that form $CINO_2$ and HONO, however, are still highly uncertain and it is therefore recommended that future investigations focus on identifying and quantifying their sources, so that this chemistry can be accurately included in chemical models.

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429 **7. Tables**

Table 1: Initial values of relative humidity (%), temperature ($^{\circ}$ C), inorganic species and VOCs (ppb) used in the box-model. HONO was constrained to its average measured diurnal profile in all scenarios, except in the noCL-HONO scenario where it was calculated by the model. (***) scenario noCL-HONO only (**) scenario highCL (*) scenario lowCL

Species	Value	Species	Value
Relative Humidity	90	Temperature	5
O ₃	20	trans-2-pentene	0.01
NO _x	15	cis-2-pentene	0.01
CO	140	1-pentene	0.01
CH ₄	1900	2-methylpentane	0.07
ethane	6.30	isoprene	0.02
ethene	0.67	hexane	0.06
ethyne	0.49	heptane	0.03
propane	2.30	octane	0.02
propene	0.19	benzene	0.20
i-butane	0.59	toluene	0.19
n-butane	0.97	ethylbenzene	0.03
1-butene	0.05	m-xylene	0.05
trans-2-butene	0.02	p-xylene	0.05
cis-2-butene	0.02	o-xylene	0.04
i-pentane	0.30	1,2,3-trimethylbenzene	0.03
n-pentane	0.20	1,2,4-trimethylbenzene	0.05
1,3-butadiene	0.03	1,3,5-trimethylbenzene	0.02
ClNO ₂ (Dec)	$0.07^{(**)} / 0.02^{(*)}$	HONO	0.13 ^(***)
ClNO ₂ (Feb)	$0.31^{(**)}$ / $0.08^{(*)}$		

Table 2: Reaction rate coefficients of OH and Cl radicals with selected VOCs; lifetimes of selected VOCs with respect to reaction with OH and Cl radicals at 10:00 on February 15th. The concentrations of OH and Cl are in molecules or atoms cm⁻³; the rate coefficients (Orlando et al., 2003; Smith et al., 2002; Atkinson et al., 2006) are in cm³ molecule⁻¹ s⁻¹ and are calculated for $5 \,^{\circ}$ C (average winter temperature).

			Methane	Propane	Propene	Isoprene	Toluene	Ethanol
			CH_4	C_3H_8	C_3H_6	C_5H_8	C_7H_8	C_2H_5OH
		k _{OH}	4.2×10^{-15}	9.3×10^{-13}	3.1×10^{-11}	1.1×10^{-10}	6.1×10^{-12}	3.2×10^{-12}
		k_{C1}	7.6×10^{-14}	1.4×10^{-10}	2.3×10^{-10}	4.3×10^{-10}	6.1×10^{-11}	1.0×10^{-10}
scenario	[OH]	[C1]	VOCs lifetime (hours)					
highCL	6×10^5	1×10^4	84051	142	13	3.9	65	93
lowCL	5×10^5	2×10^3	122318	374	18	4.9	87	153
noCL	5×10^5	-	131127	600	18	5.0	91	172
noCL-HONO	8×10^4	-	819542	3747	113	31	568	1077

8. Figures



Figure 1: Scheme of the main chemical processes in the urban boundary layer. The dashed arrows indicate processes that require the presence of chloride-containing aerosol. The circles indicate the target species of this work (ClNO₂ and HONO) and the squares indicate the radical species.



Figure 2: Average profiles of CINO₂, O₃ and photolysis rates (jCINO₂, jO¹D, jHONO) measured in Leicester in December 2014 and February 2016; average profile of HONO measured in Birmingham in February 2014. The CINO₂ and jCINO₂ data are divided into two cases: days when CINO₂ remained above the detection limit all day (highCL) and days when CINO₂ fell below the detection limit by midday (lowCL). The red dashed line shows the CINO₂ detection limit (4.2 ppt) and the shading shows the 95% confidence intervals of the mean.



Figure 3: Average radical production rates (top) and total radical production (bottom) from O₃, HONO and ClNO₂ photolysis during winter.



Figure 4: Results of the MCM box-model for the month of February, under the scenarios in Table 2. The grey shaded areas show the 95% confidence intervals of the mean for the observations of CINO_2 , HONO and O₃ (1-26 February 2016). Sunrise is at 7:30, sunset is at 17:00.



Figure 5: Difference between modelled ozone concentrations in each model scenario compared to the baseline scenario noCL (Table 2). Results are for the month February (unless indicated). Sunrise is at 7:30, sunset is at 17:00.

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