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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 (ClNO₂) 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 ClNO₂ and HONO made at urban locations in central England in December 2014 and February 2016. While direct emissions and in-situ chemical formation of HONO continue throughout the day, ClNO₂ is only formed at night and is usually completely photolyzed by midday. Our data show that, during winter, ClNO₂ 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 ClNO₂ 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 ClNO₂ 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 ClNO₂ 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 O₃ and secondary pollutants increases and continues into the af-
9 ternoon

10 **1. Introduction**

11 The oxidation of volatile organic compounds (VOCs) in the lower atmosphere leads
12 to the formation of ozone (O_3), secondary organic aerosol (SOA) and other harmful
13 pollutants (e.g. aldehydes, PAN) via a complex series of chemical reactions initiated
14 by reactive radical species. The current understanding of oxidative processes in the tro-
15 posphere is that the most important daytime oxidant is the hydroxyl radical (OH). How-
16 ever, chlorine atoms (Cl) are being increasingly recognized as important tropospheric
17 oxidants (Simpson et al., 2015; Sherwen et al., 2017; Wang et al., 2019), although
18 chlorine chemistry is often not included in the air quality models used for regulatory
19 purposes. Because of their high reactivity, Cl atoms can considerably accelerate the ox-
20 idation rate of VOCs above that of OH chemistry alone, thus increasing the formation
21 of secondary atmospheric pollutants.

22 The dominant source of the OH radical across the troposphere is the photolysis
23 of ozone, followed by the reaction of excited state oxygen atoms (O^1D) with water
24 vapour (Figure 1). Ambient studies have shown that the reactions of ozone with unsat-
25 urated VOCs (alkenes, dialkenes, terpenes) and the photolysis of nitrous acid (HONO)
26 can be more important primary sources of OH than ozone photolysis, especially in the
27 urban boundary layer (Emmerson et al., 2005; Ren et al., 2006; Kanaya et al., 2007;
28 Elshorbany et al., 2009; Lee et al., 2016; Tan et al., 2018; Slater et al., 2020). Because
29 of its relatively short photolysis lifetime (in the order of tens of minutes), HONO has
30 long been considered as a significant OH source, mainly during the morning. However,
31 more recent field studies have found non-negligible HONO concentrations in urban
32 environments during the day, which suggest that there are significant daytime sources
33 of HONO (Kleffmann, 2007; Villena et al., 2011; Michoud et al., 2014) and, there-
34 fore, that the influence of HONO on radical production may be more extensive than
35 previously thought. Besides the gas-phase reaction $OH + NO$, important sources of
36 HONO are direct emissions, e.g. from vehicles (Kurtenbach et al., 2001; Kramer et al.,
37 2020) and from microbial activity in the soil (Su et al., 2011). In addition, HONO is
38 known to be formed via heterogeneous reactions of NO_2 on humid surfaces both during
39 the night and during the day (Finlayson-Pitts et al., 2002; Vogel et al., 2003; Spataro

40 and Ianniello, 2014). Photo-enhanced conversion of NO_2 into HONO has been ob-
41 served in laboratory studies on several surfaces, with organic films the most productive
42 (Ammann et al., 1998; George et al., 2005; Stemmler et al., 2006), and has also been
43 observed on “urban grime” on building surfaces (Baergen and Donaldson, 2016) and
44 on snow in urban environments (Chen et al., 2019; Michoud et al., 2015). The rel-
45 ative contribution of urban daytime sources of HONO is an active area of research,
46 with models still largely unable to account for measured daytime concentrations (e.g.
47 Michoud et al. (2014); Lee et al. (2016)).

48 Cl atoms are released into the gas phase via a number of different mechanisms
49 (Simpson et al., 2015): for example, acid displacement of HCl from aerosol and var-
50 ious multi-phase chemical processes that form gas-phase BrCl and Cl_2 , followed by
51 photolysis and/or reaction with OH. One mechanism that has recently gathered much
52 attention is the nocturnal formation of nitryl chloride (ClNO_2) via reaction of dinitro-
53 gen pentoxide (N_2O_5) on chloride-containing aerosol (Figure 1). The photolysis of
54 ClNO_2 after sunrise forms Cl atoms and nitrogen dioxide (NO_2), thus increasing the
55 oxidation of VOCs and reducing the loss of NO_x via the nocturnal formation of HNO_3
56 (Figure 1). The combination of Cl reactivity and higher NO_2 concentrations results
57 in enhanced ozone production – up to 10 ppb of additional O_3 compared to scenarios
58 without ClNO_2 chemistry (Osthoff et al., 2008; Sarwar et al., 2014; Tham et al., 2016).
59 Several studies have reported ClNO_2 nocturnal mixing ratios ranging from a few tens
60 of ppt to several ppb (e.g. Osthoff et al. (2008); Mielke et al. (2011); Phillips et al.
61 (2012); Riedel et al. (2012); Bannan et al. (2015); Wang et al. (2016)). Depending on
62 the season and meteorological conditions, the photolysis lifetime of ClNO_2 at midday
63 in the mid-latitudes can vary between 50 minutes and 3 hours. This means that, typ-
64 ically, over 95% of the nitryl chloride present at sunrise is photolyzed before 11:30
65 (summer) or 13:00 (spring/autumn), and that most of the direct effect of chlorine reac-
66 tivity on the formation of atmospheric pollutants takes place during the first few hours
67 of the morning (Thornton et al., 2010; Phillips et al., 2012; Haskins et al., 2019).

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

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

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

90 **2. Materials and Methods**

91 *2.1. Instruments*

92 Nitryl chloride (ClNO₂) was measured using a Chemical Ionization Mass Spec-
93 trometer (CIMS). The instrument (THS Instruments LLC, USA) was operated in neg-
94 ative ion mode using iodide ions (I⁻) as the reagent ion, and ClNO₂ was detected at
95 $m/z = 208, 210$ amu, corresponding to the $[I \cdot ClNO_2]^-$ ion cluster (Sommariva et al.,
96 2018). Molecular chlorine (Cl₂) was also measured by CIMS at $m/z = 197, 199, 201$
97 amu, which correspond to the $[I \cdot Cl_2]^-$ ion cluster. The inlet line, a 5 m long PFA tube
98 (OD = 3/8"), was regularly washed with deionized water during the measurements to
99 avoid formation of ClNO₂ from particles deposited inside the inlet: there was no signif-
100 icant difference in the CIMS signals before and after the line was washed. To calibrate

101 the CIMS, nitryl chloride was synthesized using a humidified flow of Cl_2 (5 ppm in
102 N_2) over a bed of sodium nitrite (NaNO_2) and sodium chloride (NaCl) as described in
103 Thaler et al. (2011): ClNO_2 was then quantified via thermal decomposition to Cl and
104 NO_2 (at $\sim 350^\circ\text{C}$) followed by measurement of NO_2 by Broadband Cavity Enhanced
105 Spectroscopy (Thalman et al., 2015). Molecular chlorine was calibrated by known di-
106 lutions of a 5 ppm certified gas standard (BOC plc, UK). The ClNO_2 and Cl_2 detection
107 limits were 4.2 and 7.1 ppt, respectively (2σ , 1 minute).

108 The CIMS instrument was deployed at the University of Leicester campus, together
109 with a O_3 monitor, a NO_x monitor (T400 and T200, Teledyne Technologies Inc, USA)
110 and a spectral radiometer (MetCon GmbH, Germany) to measure the photolysis rates
111 of over 40 species, including O_3 , HONO and ClNO_2 . Meteorological information
112 (wind speed and direction, temperature, pressure, humidity) was available from the
113 Automatic Urban and Rural Monitoring Network (AURN). The AURN site is located
114 on the University campus and is classed as “urban background”.

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

126 The LOPAP instrument was deployed at the University of Birmingham campus;
127 Leicester and Birmingham are two cities in central England ~ 80 kilometers apart. In
128 both locations, the sampling points on the respective University campuses are compa-
129 rable “urban background sites”.

130 *2.2. Box-model*

131 A simple box-model was used to investigate the formation of radicals (OH and Cl),
132 the oxidation of VOCs and the production of secondary pollutants. The model was built
133 using AtChem2 v1.2 (Sommariva et al., 2020) with a chemical mechanism taken from
134 the Master Chemical Mechanism (MCM v3.3.1, Saunders et al. (2003); Jenkin et al.
135 (2003)). The chemical mechanism includes a complete inorganic chemistry scheme
136 plus the oxidation mechanism of the 31 VOCs, including methane, that are routinely
137 measured at the AURN sites (Table 1).

138 Production of HCl from chlorine reactions with VOCs, and production of Cl from
139 the $\text{HCl} + \text{OH}$ reaction and from ClNO_2 photolysis, are not included in the MCM and
140 were added to the mechanism. The chlorine gas-phase mechanism in the model is very
141 simple and does not include inorganic reactions such as $\text{Cl} + \text{O}_3$, $\text{Cl} + \text{HO}_2$ and $\text{Cl} + \text{O}_2$.
142 For the mixture of CH_4 and VOCs listed in Table 1, calculations show that the dominant
143 reaction of Cl atoms is with organics (over 85%), and thus we do not expect the model's
144 omission of Cl inorganic reactions to significantly affect the conclusions of this work
145 The uptake of N_2O_5 on aerosol and the heterogeneous formation of ClNO_2 were not
146 included in the mechanism, because the model was only run from sunrise to sunset,
147 when ClNO_2 formation is not active. Heterogeneous formation of HONO was also not
148 included, because the model was constrained to the average diurnal profile of measured
149 HONO. The model was constrained to the average diurnal profiles of measured jNO_2 ,
150 jHONO and jClNO_2 , while the photolysis rates of the other species in the mechanism
151 were calculated by AtChem2 and scaled to jNO_2 .

152 The model was initialized with the average values observed at sunrise in Leicester
153 during winter 2014 and 2016 (Sommariva et al., 2018) for ClNO_2 and other inorganic
154 species (O_3 , NO, NO_2 , CO) as well as for temperature, relative humidity and pressure.
155 Since measurements of VOCs were not available in either Leicester or Birmingham, the
156 model was initialized with the average VOC concentrations measured during winter at
157 the nearest suburban background AURN site, London Eltham. The initial conditions
158 of all chemical species and physical parameters in the box-model are listed in Table 1.

159 **3. Results and Discussion**

160 *3.1. Observations of daytime ClNO₂: sources and sinks*

161 The nitryl chloride measurements presented here were part of a larger project aimed
162 at assessing the spatial and temporal variability of ClNO₂ in the UK (Sommariva et al.,
163 2018). In this paper, we focus on two wintertime measurement periods in Leicester
164 (52°38' N, 01°08' W), a city in central England ~200 km from the ocean – the major
165 source of Cl-containing aerosol (sea-salt). ClNO₂ was observed above the instrument
166 detection limit every night between 11 and 19 December 2014, and on 19 out of 26
167 nights between 1 and 26 February 2016. Since the measurements were taken in dif-
168 ferent years, they are shown in this paper as monthly diurnal averages (Figure 2); the
169 whole dataset and timeseries of the observations are shown and discussed in Som-
170 mariva et al. (2018).

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

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

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

221 gests that deposition, heterogeneous reactions and/or boundary layer dynamics did not
222 have a significant effect on the variation of the ClNO₂ mixing ratio during the morning.

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

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

245 3.2. *Effects on the production of radicals*

246 The persistence of nitryl chloride from sunrise to sunset during winter days has
247 two major effects on the formation of radicals in the urban atmosphere. First, more
248 Cl atoms overall are released via ClNO₂ photolysis when ClNO₂ persists throughout
249 the day (case highCL) than when it disappears around midday (case lowCL): this is
250 a direct consequence of the higher concentrations of nitryl chloride at sunrise in the

251 highCL case (Figure 2). Figure 3 shows the average production rates and the total
252 production of Cl and OH radicals. The average production rates of Cl peaked between
253 9:00 and 10:00 in the morning: the maximum Cl production rates were 3 to 10 times
254 higher – and total Cl production was 3 to 8 times higher – in the highCL case compared
255 to the lowCL case. Production of chlorine atoms was always higher in February than
256 in December, because of the higher nocturnal ClNO₂ concentrations and faster diurnal
257 photolysis rates (Figure 2).

258 Second, diurnal persistence of ClNO₂ affects the timing of the release of Cl atoms,
259 and therefore of the production of O₃ and other secondary pollutants. One hour before
260 sunset, which is at 16:00 in December and at 17:00 in February, the Cl production
261 rates in the highCL case were 4 to 6 times higher than in the lowCL case. This means
262 that production of chlorine atoms, and therefore oxidation of VOCs by Cl, remained
263 significant ($> 1 \times 10^3$ atoms cm⁻³ s⁻¹) for most of the afternoon in the highCL case.
264 While these values may seem small, it must be noted that VOC oxidation in winter is
265 slower than in summer, due to the low concentrations of OH radicals and, therefore,
266 even small increments in the amount of oxidants can impact the rates of formation of
267 secondary pollutants.

268 To assess the impact of Cl on VOC oxidation, it is necessary to evaluate how it
269 compares with the other main daytime oxidant, the OH radical, for which the dominant
270 sources in an urban environment are the photolysis of O₃ and of HONO (Figure 1).
271 HONO was not measured in Leicester, but HONO measurements were made in Birm-
272 ingham in February 2014. Although these measurements were not contemporaneous
273 with the ClNO₂ measurements made in Leicester, previous work has shown that HONO
274 concentrations in the two locations are comparable (Crilley et al., 2016; Kramer et al.,
275 2020). Therefore, we used the HONO data measured in Birmingham in February 2014
276 (Figure 2) as a proxy for HONO concentrations in Leicester in February 2016. The
277 bimodal diurnal profile observed for HONO in Birmingham, peaking in the morning
278 (07:00) and in the evening (18:00), suggests vehicle emissions are an important source
279 (Kramer et al., 2020); the high nocturnal HONO mixing ratios (~150 ppt) point to
280 nocturnal sources, likely heterogeneous reactions of NO₂ on humid surfaces. The mini-
281 mum HONO mixing ratio was observed at midday, with average mixing ratios of ~65

282 ppt, which indicates sustained daytime source(s) that counteract the increased loss by
283 photolysis.

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

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

308 3.3. *Effects on the oxidative capacity of the atmosphere*

309 We used two approaches to understand the impact of continuous sources of radicals
310 from the photolysis of ClNO₂ and HONO in winter and, hence, the relative importance
311 of Cl and OH for the oxidation of VOCs. The following analysis focuses on the month

312 of February, for which both ClNO_2 and HONO measurements were available (Fig-
313 ure 2).

314 In the first approach, the lifetimes of selected VOCs were calculated for four dif-
315 ferent scenarios: with ClNO_2 persisting until sunset (highCL), with ClNO_2 disappear-
316 ing by midday (lowCL), without ClNO_2 (noCL), without ClNO_2 and without day-
317 time sources of HONO (noCL-HONO). The concentrations of OH and Cl used in this
318 calculation were the values at 10:00 calculated with the box-model for the month of
319 February, as discussed below. Table 2 shows that chlorine chemistry increases the oxi-
320 dation rates of several VOCs, especially alkanes and oxygenated VOCs: comparing the
321 lowCL and noCL scenarios, the lifetimes of VOCs decrease by between 4% (toluene)
322 and 38% (propane). In the highCL scenario, when more Cl atoms overall are released
323 (Figure 3), the lifetimes of VOCs further decrease by an additional 20% (isoprene) to
324 62% (propane) compared to the lowCL scenario. Of particular importance, because
325 of its climate forcing role, is the effect of Cl on the lifetime of methane which de-
326 creases by between 7% (lowCL) and 36% (highCL), compared to the scenario where
327 methane only reacts with OH (noCL). Alkenes, such as propene and isoprene, are less
328 affected by the presence of chlorine (22-28% decrease in lifetimes in the highCL sce-
329 nario compared to the noCL scenario) because they react with OH faster than alkanes
330 and aromatics (Table 2).

331 The oxidation of the VOC pool is therefore significantly accelerated in the presence
332 of ClNO_2 . This is true in all seasons, but the effect is particularly pronounced under
333 the unfavorable photochemical conditions of winter when other oxidant sources, such
334 as O_3 photolysis, are weak. Moreover, the presence of daytime HONO sources leads
335 to higher OH concentrations: if these sources were not taken into account (i.e. if
336 HONO is only formed via $\text{OH} + \text{NO}$, as in scenario noCL-HONO), the calculated
337 concentration of OH was 84% lower than the noCL scenario, with a corresponding
338 increase in the lifetimes of VOCs (Table 2). Enhanced oxidation of VOCs affects the
339 formation of gas-phase pollutants, such as O_3 (see below), and of secondary organic
340 aerosol (SOA). Depending on the NO_x and humidity levels, SOA yields from isoprene
341 and toluene oxidation vary between 1-5% and 10-30%, respectively (Ng et al., 2007;
342 Carlton et al., 2009), which means that the increased oxidation of these VOCs can

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

349 The second approach used a simple box-model to calculate the effect of enhanced
350 VOC oxidation rates on the production of secondary pollutants, particularly of ozone.
351 The model was run for a 24h period under the four scenarios in Table 2: ClNO_2 was ini-
352 tialized using the mean observed ClNO_2 at sunrise in each scenario (Table 1). HONO
353 was constrained to the average measured diurnal profiles in scenarios highCL, lowCL
354 and noCL (Figure 2), and calculated by the model in scenario noCL-HONO. The box-
355 model underestimated measured O_3 during the day by up to 4 ppb, because it only
356 includes photochemical processes (rather than, e.g. mixing or transport); therefore, the
357 following analysis is focused on the differences between the model scenarios.

358 The model results (Figure 4) show significant enhancements (a factor of ~ 6) in the
359 concentrations of Cl atoms in the highCL scenario compared to the lowCL scenario.
360 Increased oxidation of VOCs by chlorine atoms also led to higher concentrations of
361 OH (up to 30%), HO_2 and RO_2 (up to a factor of 2). The overall impact on the forma-
362 tion of secondary pollutants was significant, with increases of up to 22% and 57% in
363 the concentrations of HCHO and CH_3CHO , respectively, and of up to 40% in the con-
364 centration of PAN compared to the noCL scenario. The increase in OH concentrations
365 was most pronounced in the morning and was a consequence both of the higher con-
366 centrations of peroxy radicals and of the increased OH production from the photolysis
367 of the oxygenated VOCs formed by the oxidation of primary VOCs. Figure 5 shows
368 the amount of additional O_3 formed in the scenarios with ClNO_2 (highCL and lowCL)
369 relative to the baseline scenario without ClNO_2 (noCL): between 0.13 ppb and 0.78
370 ppb more ozone was present at sunset due to Cl reactivity.

371 The model was also run for the month of December, but the impact of chlorine
372 reactivity on secondary pollutant formation was more limited than in February: the
373 additional ozone present at sunset in the highCL scenario was only ~ 50 ppt compared

374 to the baseline scenario without chlorine chemistry (noCL). The main reason for the
375 low impact of Cl is that both the concentrations and the photolysis rates of ClNO₂ were
376 lower than in February (Figure 2), which resulted in ~10 times less Cl atoms released
377 across the day in December (Figure 3).

378 Analysis of the model results indicate that, in February, HONO was the primary
379 source of OH in the urban boundary layer: the total production rate of OH in the middle
380 of the day was 1.8×10^6 molecules cm⁻³ s⁻¹, of which 47% was due to recycling
381 (HO₂ + NO), 45% due to HONO photolysis and only 5.5% due to O₃ photolysis, while
382 the reactions of ozone with alkenes were responsible for less than 1% of the total OH
383 production. These numbers are consistent with what can be directly inferred from
384 our measurements (Figure 3), as well as with the studies by Ren et al. (2006); Tan
385 et al. (2018); Slater et al. (2020). In contrast, early work in urban environments during
386 winter (Emmerson et al., 2005; Kanaya et al., 2007) concluded that the ozonolysis of
387 unsaturated VOCs was a source of OH radicals as large as HONO photolysis. The
388 modelling study by Emmerson et al. (2005) is especially relevant, as it was conducted
389 in Birmingham, the same region as this work: their model was also based on the MCM
390 and included an heterogeneous HONO source in addition to the gas-phase reaction
391 OH + NO, but it was not constrained to measured HONO, which raises the possibility
392 that HONO concentrations were underestimated by the model. In fact, scenario noCL-
393 HONO in Figure 4 shows that our model underestimated HONO concentrations by
394 approximately a factor of 10 at 12:00 and a factor of 40 at 16:00, if not constrained
395 to the observations of HONO. This resulted in lower OH concentrations (a factor of
396 4-5), as well as a shift in the peak OH concentration from 10:00 to 12:00 due to the low
397 HONO concentrations in the morning. In the absence of a strong OH source – such as
398 HONO photolysis – the model calculated that the O₃ concentration at sunset was 0.31
399 ppb less than in the baseline scenario noCL (Figure 5).

400 **4. Conclusions**

401 In this work, we discuss how the presence of strong sources of atomic chlorine,
402 such as ClNO₂, 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).

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

414 Multiple previous studies have shown that both ClNO₂ and HONO are present in a
415 range of diverse environments and, hence, they are likely to play a fundamental role in
416 wintertime urban photochemistry in other locations around the world. The processes
417 that form ClNO₂ and HONO, however, are still highly uncertain and it is therefore rec-
418 ommended that future investigations focus on identifying and quantifying their sources,
419 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 ($^{\circ}\text{C}$), 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 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and are calculated for 5°C (average winter temperature).

			Methane	Propane	Propene	Isoprene	Toluene	Ethanol
			CH_4	C_3H_8	C_3H_6	C_5H_8	C_7H_8	$\text{C}_2\text{H}_5\text{OH}$
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_{Cl}			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]	[Cl]	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

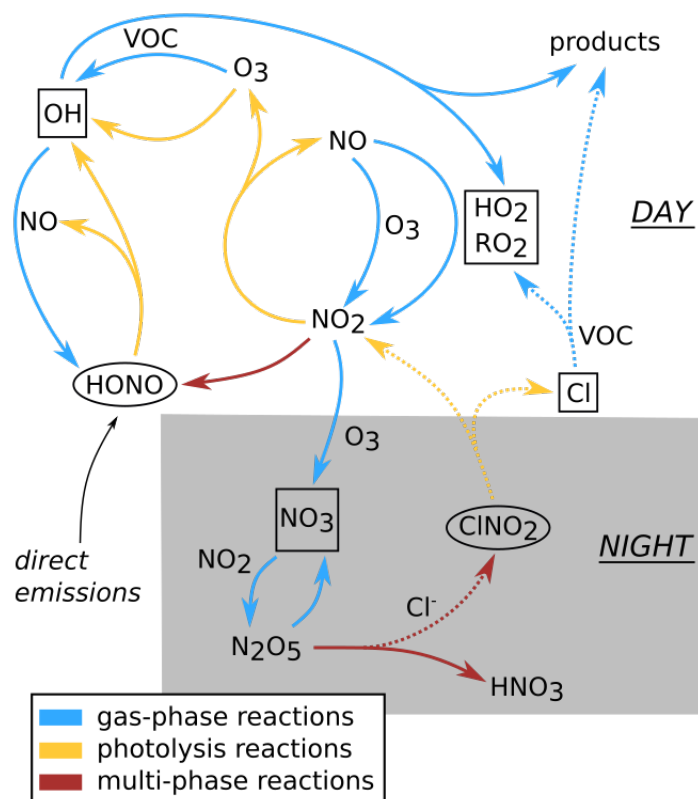


Figure 1: Scheme of the main chemical processes in the urban boundary layer. The dashed arrows indicate processes that require the presence of chloride-containing aerosol. The circles indicate the target species of this work (ClNO₂ and HONO) and the squares indicate the radical species.

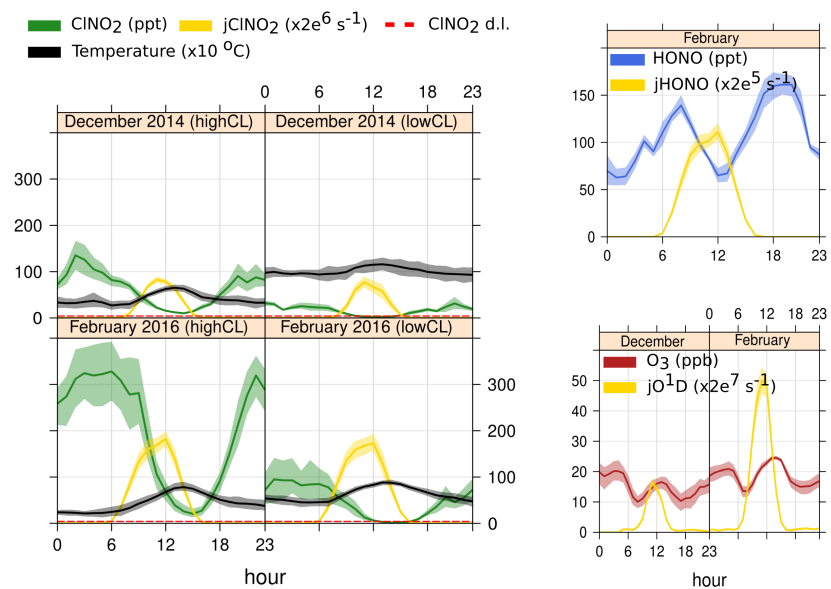


Figure 2: Average profiles of CINO₂, O₃ and photolysis rates (jCINO₂, jO¹D, jHONO) measured in Leicester in December 2014 and February 2016; average profile of HONO measured in Birmingham in February 2014. The CINO₂ and jCINO₂ data are divided into two cases: days when CINO₂ remained above the detection 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.

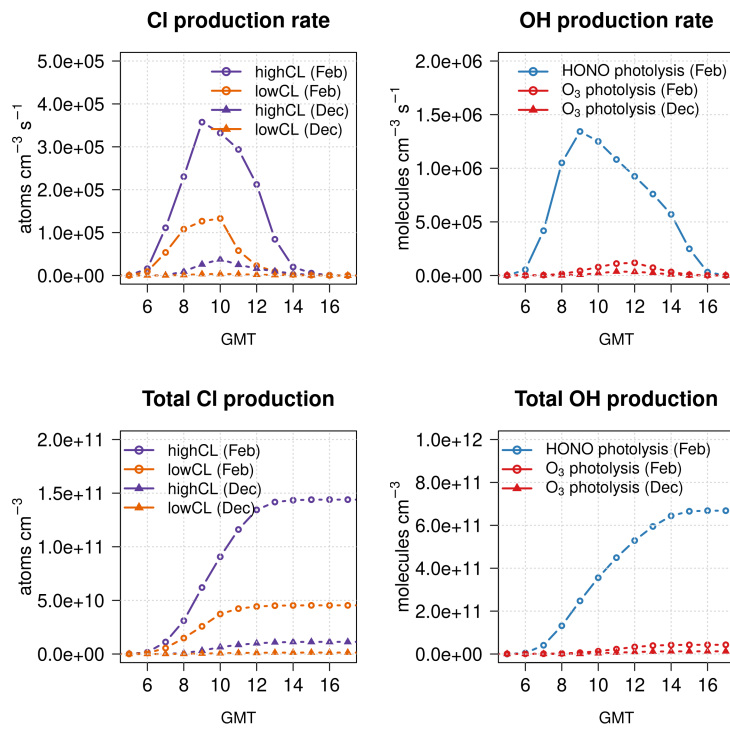


Figure 3: Average radical production rates (top) and total radical production (bottom) from O_3 , HONO and ClNO_2 photolysis during winter.

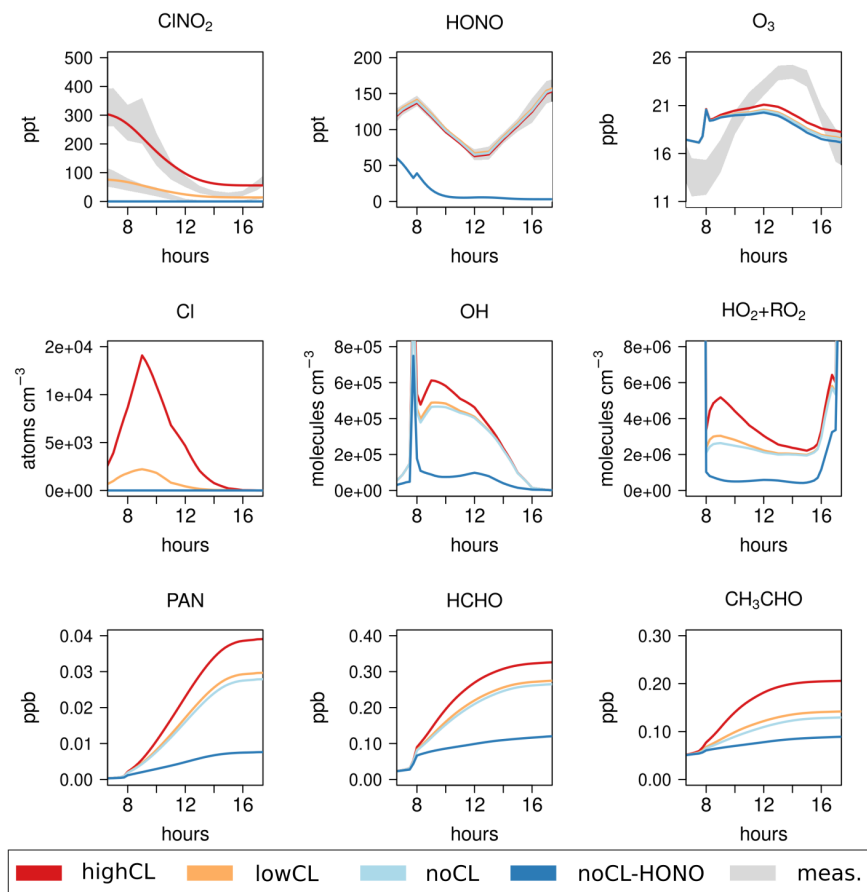


Figure 4: Results of the MCM box-model for the month of February, under the scenarios in Table 2. The grey shaded areas show the 95% confidence intervals of the mean for the observations of CINO₂, HONO and O₃ (1-26 February 2016). Sunrise is at 7:30, sunset is at 17:00.

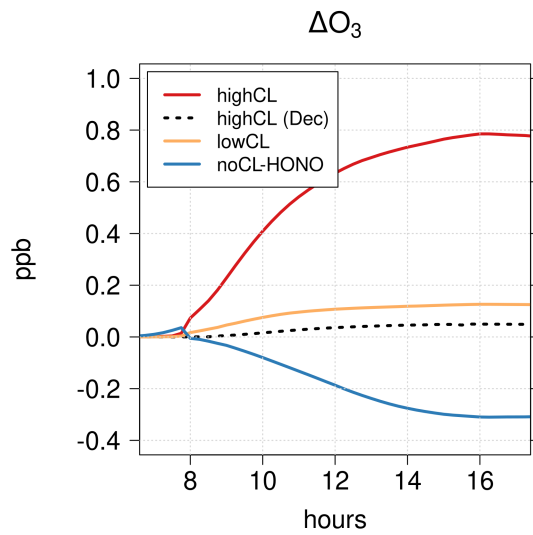


Figure 5: Difference between modelled ozone concentrations in each model scenario compared to the baseline scenario noCL (Table 2). Results are for the month February (unless indicated). Sunrise is at 7:30, sunset is at 17:00.

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