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Sommariva, Roberto, Hollis, Lloyd D. J., Sherwen, Tomás orcid.org/0000-0002-3006-3876 et al. (13 more authors) (2018) Seasonal and geographical variability of nitryl chloride and its precursors in Northern Europe. ATMOSPHERIC SCIENCE LETTERS. e844. ISSN 1530-261X

https://doi.org/10.1002/asl.844

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Seasonal and geographical variability of nitryl chloride and its precursors in Northern Europe

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INTRODUCTION

Chlorine atoms (Cl) are highly reactive in the atmosphere and affect several atmospheric chemical processes: the oxidation of organic compounds (including methane, a key climate forcer), the formation of tropospheric ozone and the cycling of sulphur and nitrogen (Saiz-Lopez and von Glasow, 2012).

One of the mechanisms by which unreactive particulate chloride ($\text{Cl}^-$) can be converted into reactive gas-phase chlorine is via the nocturnal formation of nitryl chloride (ClNO$_2$), followed by its photolysis at sunrise to yield Cl and NO$_2$ (1). ClNO$_2$ is formed from the reaction of N$_2$O$_5$ on chloride-containing particles (5) (Finlayson-Pitts et al., 1989; Behnke et al., 1994; Finlayson-Pitts, 2003; Roberts et al., 2008; 2009):

\[
\text{ClNO}_2 \xrightarrow{h^+} \text{Cl} + \text{NO}_2 \tag{1}
\]

\[
\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2 \tag{2}
\]
\[
\text{NO}_3^+ + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5 \quad (3)
\]
\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O}_{(aq)} \rightarrow 2\text{HNO}_3 \quad (4)
\]
\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O}_{(aq)} + \text{Cl}^-_{(aq)} \rightarrow \text{HNO}_3 + \text{ClNO}_2 + \text{OH}^-_{(aq)} \quad (5)
\]

The chemical equilibrium between $\text{NO}_3^-$ and $\text{N}_2\text{O}_5$ (Brown et al., 2003) and the short lifetime of $\text{NO}_3^-$ during the day, due to its rapid photolysis rate and reaction with $\text{NO}$, dictates that reactions 3–5 are important only during the night. Except for slow dry deposition, ClNO$_2$ losses are thought to be insignificant at night (Roberts et al., 2008; Kim et al., 2014). During the day, ClNO$_2$ photolyses, with a lifetime of ~40 min (at midday, 52°N), resulting in a diel pattern with night-time maxima and daytime minima. The conversion of $\text{N}_2\text{O}_5$ to ClNO$_2$ (5) has been shown to occur even at low concentrations of particulate chloride (Roberts et al., 2009). The main source of chloride in the troposphere is sea salt aerosol, although sub-micron particles can also contain $\text{Cl}^-$ following, for example, uptake of HCl from anthropogenic sources (Thornton et al., 2010; Mielke et al., 2011). In addition, saline soils and road salt can be locally important sources of chloride (Jordan et al., 2015).

The formation of ClNO$_2$ reduces the formation of HNO$_3$ (due to the competition between 4 and 5) and therefore slows the overall loss of nitrogen oxides via HNO$_3$ deposition (Brown et al., 2006), leaving more NO$_2$ available for ozone formation in the morning; the photolysis of ClNO$_2$ releases Cl atoms (1), enhancing the oxidation of organic compounds and ozone production (Osthoff et al., 2008; Simon et al., 2009; Sarwar et al., 2012; Riedel et al., 2014; Young et al., 2014; Wang et al., 2016).

Observations of ClNO$_2$ in the troposphere have been reported over the last decade by several research groups, mostly in North America (Osthoff et al., 2008; Kercher et al., 2009; Thornton et al., 2010; Mielke et al., 2011; 2013; Riedel et al., 2012; 2013; Young et al., 2012; Kim et al., 2014; Mielke et al., 2016), with only a few in Europe (Phillips et al., 2012; Bannan et al., 2015; 2017) and in Asia (Tham et al., 2014; Tham et al., 2016; Wang et al., 2016). These studies have shown that ClNO$_2$ is widely distributed in the troposphere, even away from the coast, at concentrations ranging from a few hundred ppt to several ppb.

This paper presents the first seasonally complete set of ClNO$_2$ measurements in Europe, drawn from three sites across the United Kingdom. The observations were used, together with modelling tools, to investigate the spatial and temporal variability of ClNO$_2$ in the United Kingdom and, by extension, Northern Europe.

2 METHODS

2.1 Fieldwork

Measurements of ClNO$_2$, O$_3$, NO$_2$ and aerosol composition were taken during seven periods between 2014 and 2016 at three locations in the United Kingdom:

1. Leicester (52°38′N, 01°08′W) is a middle-sized city (pop: ~330,000) in central England, ~200 km from the ocean. The measurements were made at two sites on the University campus: the Department of Chemistry and the local AURN station (Automatic Urban and Rural Network, http://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00573), which is classified as an urban background site (Hama et al., 2017). The two sites are ~400 m apart and, for this work, were analysed together.

2. Penlee Point (50°19′N, 04°11′W) is on the southwestern coast of the United Kingdom, ~6 km southwest of the city of Plymouth (pop: ~250,000). The Penlee Point Atmospheric Observatory (PPAO, http://www.westernchannelobservatory.org.uk/penlee/) is located ~11 m above mean sea level and ~30 m from the shoreline. The site receives unpolluted air from the Atlantic Ocean during prevailing southwesterly conditions (~50% of the time, Yang et al., 2016).

3. Weybourne (52°57′N, 01°07′E) is on the eastern coast of the United Kingdom, ~180 km northeast of London. The Weybourne Atmospheric Observatory (WAO, http://weybourne.uea.ac.uk/) is located ~150 m from the shoreline and receives clean air masses from the North Sea, as well as continental outflow from the United Kingdom and/or Northern Europe (Penkett et al., 1999).

The locations and dates of the measurements periods cover a variety of chemical conditions and geographical areas, from unpolluted coastal to urban environments. A map of the study region is given in the Supplementary Information (SI. 1, Supporting Information), and a summary of the dataset is shown in Table 1.

2.2 Instruments

ClNO$_2$ was measured by Chemical Ionisation Mass Spectrometry (CIMS). The Leicester CIMS instrument (THS Instruments LLC, GA) was operated in negative ion mode, with a configuration similar to Liao et al. (2011), using iodide (I$^-$) as the reagent ion. ClNO$_2$ was detected as the cluster ion [LCINO$_3$]$^-$ at m/z = 208 and 210 amu, as in Osthoff et al. (2008) and Thaler et al. (2011). The instrument was calibrated by generating ClNO$_2$ with a flow of Cl$_2$ (5 ppm in N$_2$) over a bed of sodium nitrite (NaNO$_2$) and NaCl, similar to Thaler et al. (2011). Quantitative determination of the amount of ClNO$_2$ produced was obtained by thermally decomposing ClNO$_2$ to NO$_2$ at ~350 °C and measuring NO$_2$ by broadband cavity-enhanced spectroscopy (Thalman et al., 2015). During fieldwork, the CIMS instrument’s background signal was determined every hour by diverting the sample flow through a heated (~175 °C) stainless steel coil, which destroys all ClNO$_2$ in the sample. The
1-min detection limit for CINO₂ was 4.2 ppt at 2σ (5.1 ppt at 3σ), with 18% accuracy and 14% precision.

O₃ was measured by UV absorption in Leicester (Model T400, Teledyne Technologies Inc., City of Industry, CA, Hama et al., 2017), in Penlee Point (Model 205, 2B Technologies, Boulder, CO, Yang et al., 2016) and in Weybourne (Model 49i, Thermo Fisher Scientific Inc., Franklin, MA). NO₂ was measured at Leicester and in Penlee Point with a Teledyne Model T200 NO/NO₃/NO₄ analyser, using chemiluminescence detection with a molybdenum converter (Hama et al., 2017). This type of instrument is known to be subject to interference from PAN and other NOₓ species (Reed et al., 2016): although this is unlikely to be an issue for Leicester, where fresh NOₓ emissions dominate, it may be significant for Penlee Point. Concentrations of PAN in clean oceanic air masses are typically lower than 300–400 ppt (Roberts et al., 1996; Heard et al., 2006); with a conversion factor of PAN on a molybdenum converter of 80–95% (Williams et al., 1998; Steinbacher et al., 2007), it can be estimated that the interference was of the order of ~300 ppt. In Weybourne, NO₂ was measured with a dual-channel chemiluminescent instrument using a UV-LED photolytic converter (Air Quality Design Inc., Golden, CO, Reed et al., 2016).

Aerosol composition was measured in 2014 in Leicester and in 2015 at Weybourne but not during the other periods. A PM10 Leckel SEQ47/50 sequential sampler was used in Leicester (Hama et al., 2017), and a multistage Sierra-type cascade impactor was used in Weybourne. Soluble ionic components of the filters from both sites were extracted and analysed by ion chromatography, as described in Baker et al. (2007). Details of the aerosol samplers and analytical procedures are given in the Supplementary Information (SI. 2). All measurements were made at ~5 m above ground; the data were processed and analysed using R and the open air package (Carslaw and Ropkins, 2012).

3 | RESULTS

3.1 | Overview

The highest concentrations of CINO₂ were typically observed between 00:00 and 04:00 GMT. The median CINO₂ concentration at the different sites during this period varied between the detection limit (4.2 ppt) and 139 ppt (15-min averages, Table 1); the maximum concentration was 1,100 ppt, measured in Weybourne in July 2015. These observations are consistent with previous reports (e.g., Osthoff et al., 2008; Mielke et al., 2011; Riedel et al., 2012). In Europe, peak concentrations between 50 and 800 ppt were observed in Kleiner Feldberg (Germany) and in London (United Kingdom) by Phillips et al. (2012) and Bannan et al. (2015). More recently, Bannan et al. (2017) reported peak concentrations of up to 65 ppt in Weybourne (United Kingdom).

Median particulate chloride concentrations of up to 1.3 µg/m³ and 2.3 µg/m³ were measured in Leicester and Weybourne, respectively. Chloride was well correlated (r² = 0.81–0.99) with Na⁺ at both sites (Figure 1, left). In Weybourne, the measured Cl⁻/Na⁺ mass ratio was 1.87, very close to the average seawater ratio of 1.8 (Stumm and Morgan, 1995). The size-resolved measurements of aerosol composition at Weybourne showed that the percentage of total Cl⁻ in sub-micron aerosol was 5–19% (median = 12%), indicating that most Cl⁻ was in the coarse fraction (e.g., sea

---

**TABLE 1** Date, season and location of the measurement periods. Median, interquartile range and maximum measured concentrations of CINO₂, NO₂, O₃ (15-min average between 00:00–04:00 GMT) and particulate Cl⁻ (24 h average) during each measurement period

<table>
<thead>
<tr>
<th>Date</th>
<th>Season</th>
<th>Location</th>
<th>Year</th>
<th>Median Concentration (µg/m³)</th>
<th>Interquartile Range (µg/m³)</th>
<th>Maximum Concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3–11 Mar 2014</td>
<td>Spring</td>
<td>Leicester</td>
<td>2014</td>
<td>CINO₂ 110</td>
<td>15.4–50.5</td>
<td>&gt;139</td>
</tr>
<tr>
<td>4–28 Aug 2015</td>
<td>Summer</td>
<td>Leicester</td>
<td>2014</td>
<td>NO₂ 9.0</td>
<td>6.8–8.6</td>
<td>13.1</td>
</tr>
<tr>
<td>11–19 Dec 2014</td>
<td>Winter</td>
<td>Leicester</td>
<td>2014</td>
<td>O₃ 24.2</td>
<td>17.0–38.3</td>
<td>22.1</td>
</tr>
<tr>
<td>20 Apr–8 May 2015</td>
<td>Penlle Point</td>
<td>2015</td>
<td>CINO₂ &lt;DL a</td>
<td>&lt;DL b</td>
<td>21.5</td>
<td>139</td>
</tr>
<tr>
<td>26 Jun–3 Aug 2015</td>
<td>Weybourne</td>
<td>2016</td>
<td>NO₂ 9.0</td>
<td>6.8</td>
<td>13.1</td>
<td>7.9</td>
</tr>
<tr>
<td>22–29 Sep 2015</td>
<td>Autumn</td>
<td>Leicester</td>
<td>2015</td>
<td>O₃ 24.2</td>
<td>17.0–38.3</td>
<td>22.1</td>
</tr>
<tr>
<td>1–26 Feb 2016</td>
<td>Winter</td>
<td>Leicester</td>
<td>2016</td>
<td>CINO₂ 110</td>
<td>15.4–50.5</td>
<td>&gt;139</td>
</tr>
</tbody>
</table>

* a Detection limit (DL) = 4.2 ppt.
  b Detection limit (DL) = 0.2 µg/m³.
  c Particle diameter <10 µm (PM10) for the Leicester data and >0.01 µm for the Weybourne data.
salt). In Leicester, the measured Cl\textsuperscript−/Na\textsuperscript+ mass ratio was 1.32, consistent with the dechlorination of aerosol during transport from the ocean (Yang et al., 2011; Saiz-Lopez and von Glasow, 2012). In both Weybourne and Leicester, the measured Mg\textsuperscript2+/Na\textsuperscript+ mass ratio was 0.12–0.13, equal to the average seawater ratio (Jordan et al., 2015). Aerosol composition was not measured in Penlee Point, but the observatory is on a headland ~30 m from the water's edge, and sea spray is always abundant. These data strongly suggest that sea salt aerosol was the main source of Cl\textsuperscript− not only at the two coastal sites but also in Leicester (~200 km from the ocean), providing enough surface area for reaction 5 to occur.

The mean ClNO\textsubscript2 nocturnal maxima in Leicester and Weybourne were not correlated with particulate Cl\textsuperscript− not only in the same season. The aim is to investigate the seasonal and geographical patterns of ClNO\textsubscript2 and of its precursors, rather than the short term (e.g., day-to-day) variability.

3.2 Seasonal variability

Observations in Leicester were made in all seasons and provide information on the seasonal variability of ClNO\textsubscript2. A seasonal cycle is apparent (Figure 2), consistent with the observations made by Mielke et al. (2016) in Calgary (Canada). The highest median ClNO\textsubscript2 concentrations were observed in spring (110 ppt) and in winter (50.5–139 ppt) and the lowest in summer (15.4 ppt) (Table 1).

The nocturnal levels of NO\textsubscript2 were similar in all seasons, with median concentrations of 6.8–9.0 ppb in spring/winter and 8.6–13.1 ppb in summer/autumn. The median nocturnal O\textsubscript3 concentrations showed a larger seasonal range and were higher during spring/winter (22.1–24.2 ppb), compared to summer/autumn (8.4–17.0 ppb). This suggests that, on average, the variability of O\textsubscript3 was more influential than that of NO\textsubscript2 in driving the seasonal changes of ClNO\textsubscript2 in Leicester. Furthermore, the NO\textsubscript3 production rate (k\textsubscript1[NO\textsubscript2][O\textsubscript3]) showed a weak but positive correlation with ClNO\textsubscript2 (Figure 2, right), which points to reaction 2 as the rate-limiting step for ClNO\textsubscript2 formation.

The duration of the daylight period, which changes with the season, can have an effect on the concentration of ClNO\textsubscript2 as its formation occurs in the dark. Autumn and spring have similar daylight periods but different levels of ClNO\textsubscript2, O\textsubscript3 and NO\textsubscript2 (Figure 2), suggesting that changes in the chemical precursors are more important. Several processes involved in the production of ClNO\textsubscript2 have temperature dependencies. The mean temperature in Leicester was 6 °C in winter and 15 °C in summer; simulations with a simple box model (section 3.4 and SI. 4) showed that the temperature difference impacts ClNO\textsubscript2 concentrations by 12% or less, which suggests a limited impact of temperature on the seasonal variability of ClNO\textsubscript2.

3.3 Geographical variability

Observations were made in two different locations in spring (Leicester and Penlee Point) and in summer (Leicester and Weybourne), thus providing information on the geographical variability of ClNO\textsubscript2 in the same season.

The interquartile range of ClNO\textsubscript2 concentrations during spring was 50.1–150 ppt in Leicester and <DL-6.3 ppt in Penlee Point. It must be noted that the observations made in Penlee Point were highly skewed: the mean concentration was 66.1 ppt (Figure 2), and the median was 1.7 ppt (i.e., below the detection limit). This was mostly due to a single night (April 30, 2015) characterized by northeasterly winds, when the concentration of ClNO\textsubscript2 reached 922 ppt. For most of the measurement period, southwesterly winds transported clean air masses from the Atlantic Ocean to Penlee Point, and the concentration of ClNO\textsubscript2 was below 6.3 ppt. Although the median O\textsubscript3 concentrations were ~40% lower in Leicester than in Penlee Point, the median NO\textsubscript2...
concentrations were a factor of 10 higher, leading to higher ClNO$_2$ concentrations in Leicester (Table 1). This result is consistent with the spring observations previously made by Bannan et al. (2017) in Weybourne: although O$_3$ concentrations were higher (45–50 ppb) than in Leicester, the mean ClNO$_2$ concentration was about a factor of 6 lower (4–15 ppt) due to lower NO$_x$ levels in Weybourne.

During summer, the median O$_3$ concentrations were ~40% lower and the median NO$_2$ concentrations a factor of 3 higher in Leicester, compared to Weybourne. Contrary to springtime, lower O$_3$ and higher NO$_2$ resulted in lower ClNO$_2$ concentrations in Leicester (15.4 ppt) than in Weybourne (21.5 ppt). This suggests that the concentration of ClNO$_2$ in the two locations was, on average, controlled by different mechanisms, with NO$_2$ being the more influential parameter in Weybourne and O$_3$ in Leicester.

The Leicester and Weybourne data can be compared to the other European measurements, which were obtained during summer (Phillips et al., 2012; Bannan et al., 2015). In London, O$_3$ concentrations (~20 ppb, Bohnenstengel et al., 2015) were similar to those observed in Leicester and lower than those observed in Weybourne, while NO$_2$ concentrations were generally higher (10–15 ppb), which resulted in higher mean concentrations of ClNO$_2$ (~150 ppt, Bannan et al., 2015). The pattern was less clear for Kleiner Feldberg, likely because air masses of continental origin were also sampled (Phillips et al., 2012), and under those conditions, it cannot be assumed that particulate chloride was not a limiting factor.

### 3.4 Discussion

The measurements presented here, and those by Bannan et al. (2015; 2017), suggest that ClNO$_2$ levels in the United Kingdom are controlled by the gas-phase precursors (O$_3$ and NO$_2$), rather than by the uptake and reaction of N$_2$O$_5$ with particulate chloride. To investigate the relationship between ClNO$_2$, O$_3$ and NO$_2$ in more detail, a simple box model was developed. The model includes reactions 2–5, plus:

\[
\begin{align*}
    \text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
    \text{NO} + \text{NO}_3 & \rightarrow 2\text{NO}_2 \\
    \text{RH} + \text{NO}_3 & \rightarrow \text{RO}_2
\end{align*}
\]

where RH represent a generic hydrocarbon (with the rate coefficient of NO$_3$ + propene and initial concentration of 1 ppb) and RO$_2$ the corresponding peroxy radical. The model was run 96 times, each time with a different initial concentration of NO$_2$ (0.1–50 ppb) or O$_3$ (1–100 ppb). The uptake coefficient of N$_2$O$_5$ was set to 0.01 (Bertram and Thornton, 2009) and the ClNO$_2$ yield to 0.5 (Roberts et al., 2009). The model was run for 4 hr at constant temperature.
(285 K, mean of all measurement periods) to simulate the formation of ClNO₂ during the night.

The measured and modelled concentrations of ClNO₂ are plotted in Figure 3 (middle and right) as a function of O₃ and NO₂. Although the model is very simple, it is able to capture the main features of the observations. Running the model with different temperature (278 K), N₂O₅ uptake coefficient (0.005) or ClNO₂ yield (0.2) does not substantially alter the shape of the envelope of model results (see Supplementary Information, SI. 4). Two distinct regions with lower ClNO₂ concentrations can be identified (Figure 3, right): one is NO₂-limited, and the other is O₃-limited. The observations at Penlee Point and Weybourne fall predominantly in the regime where ClNO₂ concentrations are constrained by the availability of NO₂, while those in Leicester fall mainly in the O₃-limited regime (Figure 3, left). The highest ClNO₂ concentrations are obtained when the chemical conditions fall between these two regimes, which is the case for some of the observations from Leicester and Weybourne.

This is consistent with the analysis presented above (sections 3.2 and 3.3). As Leicester is largely O₃-limited, the seasonal variability of ClNO₂ is controlled by the variability of O₃ concentrations, and the variability of NO₂ has less impact. Lower O₃ concentrations also explain why the ClNO₂ concentrations observed in Leicester during summer were, on average, lower than in Weybourne, even though NO₂ levels were a factor of 3 higher (Figure 2). On the other hand, ClNO₂ concentrations in Penlee Point and Weybourne were mostly constrained by the availability of NO₂, rather than of O₃. Although the two locations cannot be directly compared as the measurements were made in different seasons, Weybourne usually experienced higher NO₂ concentrations than Penlee Point, resulting in higher ClNO₂ concentrations even under similar O₃ levels (Figure 3).

As shown previously (Figure 1, right), both the Leicester and the Weybourne data suggest that NO₃ production (2) was the rate-limiting step in the sequence of reactions leading to ClNO₂ formation (2–5), which is consistent with the existence of O₃-limited and NO₂-limited chemical regimes. Extrapolating the results of this simple box model, it can be concluded that, under conditions of abundant sea salt aerosol, the formation of ClNO₂ can be either O₃-limited or NO₂-limited. These conditions are likely to occur in most of the United Kingdom and Northern Europe, as well as in other regions across the world.

4 | CHEMICAL TRANSPORT MODELLING

The chemical transport model GEOS-Chem (v10-01, http://www.geos-chem.org, Bey et al., 2001) was run for the period of the observations driven by offline GEOS-FP meteorology with 72 levels, extending to 0.01 hPa. The model includes HOₓ-NOₓ-VOC-O₃-BrO chemistry and has been recently updated to include Cl, Br, I chemistry (Schmidt et al., 2016; Sherwen et al., 2016a; 2016b), as described in detail by Sherwen et al. (2017). The chlorine chemical mechanism in the model includes further reactions of chlorine and bromine with organics compounds, ClNO₂ formation following N₂O₅ uptake on sea salt, and heterogeneous iodine cycling to produce ICl, IBr. Reaction probabilities for N₂O₅ uptake follow Evans and Jacob (2005) for sea salt aerosol (producing ClNO₂) and non-sea salt aerosol (producing HNO₃).

The model was run at a medium global resolution (2° × 2.5°) for 2 years for the seasonal comparisons, following a 1-year “spin up”. A higher-resolution “nested” simulation (0.25° × 0.3125°, Sherwen et al., 2017) was also run for two contrasting observational periods—spring and summer—following a 2-week “spin-up” for each analysis period. The average surface concentrations for the grid box closest to the measurements sites are compared with the measured average diel profiles of ClNO₂, NO₂ and O₃ in
The medium-resolution version of GEOS-Chem (2° × 2.5°/C14 × 2.5°/C14) was able to reproduce the diel ClNO2 cycle but failed to reproduce the seasonal cycle as observed in Leicester. The model showed good agreement with the measurements during spring and winter but overestimated ClNO2 during summer and autumn (Figure 4, top). However, the model showed good agreement with the summertime measurements of ClNO2 at Weybourne (Figure 4, bottom), as previously reported by (Sherwen et al., 2017). The high-resolution version of GEOS-Chem (0.25°/C14 × 0.3125°/C14) calculated roughly the same concentrations of ClNO2 as the medium-resolution version for spring in Leicester and summer in Weybourne, thereby agreeing reasonably well with the observations. Although the high-resolution model showed improved agreement for summer in Leicester, it still overestimated the measurements of ClNO2 by a factor of ~2 (Figure 4). The comparison between modelled and measured O3 and NO2 suggests that the improved performance of the higher-resolution model was due to a better representation of nocturnal O3 during summer (ClNO2 being mostly O3-limited in Leicester, section 3.4).

The GEOS-Chem results complement the work by (Sherwen et al., 2017), which focused on the observations at Weybourne in summer 2015 and explored the regional effects of halogen chemistry. The expanded set of model results and measurements discussed here, covering a larger temporal and geographical range, highlight the challenges and possible future directions for chemical transport models. A key issue is the high bias in modelled surface ozone, a known problem for GEOS-Chem (e.g., Travis et al., 2016). The simulation of the seasonal cycle of ClNO2 is a significant challenge for chemical transport models. The models need to be able to accurately simulate the nocturnal concentrations of O3, NO2, NO3, N2O5 and effective Cl− surface area. It is likely that significant uncertainties in nocturnal chemical and physical processes lead to resolution dependencies in current chemical transport models. The results presented here suggest that there is a tendency for lower-resolution models to overestimate ClNO2 concentrations, which may not be apparent in higher-resolution models.

5 | CONCLUSIONS

Measurements of ClNO2 and its precursors (O3, NO2, particulate chloride) were taken in 2014–2016 at Leicester, Penlee Point and Weybourne, three sites in different parts of the United Kingdom. The measurements covered all seasons, and ClNO2 was observed at all locations and in all seasons. The median nocturnal concentrations of ClNO2 ranged from below the detection limit (4.2 ppt) to 139 ppt. The highest concentration (1,100 ppt) was observed in Weybourne in July 2015.
CINO₂ displayed a clear seasonal cycle, with maxima in spring and winter. Significant differences were observed between different locations during the same season. Analysis of the dataset indicates that sea salt aerosol was the main source of particulate chloride (Cl⁻). Observational evidence suggests that production of NO₃ (2) was the rate-limiting step in the formation of CINO₂, rather than the aerosol uptake of N₂O₅ and its reaction with Cl⁻. In general, the data indicate that the observed variability of CINO₂ was driven by the availability of either O₃ or NO₂, depending on the season and the location. The seasonal and geographical variability of CINO₂ can be explained in terms of O₃-limited and NO₂-limited chemical regimes, broadly reproducible with a simple chemical box model.

The GEOS-Chem chemical transport model at medium resolution (2° × 2.5°) could reproduce the diel cycle of CINO₂, but not the observed seasonal cycle and geographical distribution. The likely reason is that GEOS-Chem overestimated the concentrations of CINO₂ precursors, particularly of O₃. Simulations at higher resolution (0.25° × 0.3125°) improved the fidelity of the simulation, although CINO₂ was still overestimated in Leicester during summer. Future work is clearly necessary to improve the representation of night-time chemistry and dynamics in models.

This work, as well as Phillips et al. (2012) and Bannan et al. (2015; 2017), shows that the presence of CINO₂ is widespread across Northern Europe: where there is sufficient particulate chloride and the total aerosol surface area is large enough (e.g., where sea salt aerosol is abundant), CINO₂ chemistry is expected to occur. These conditions are typical of the United Kingdom and large areas of Northern Europe; they are also likely to be encountered in other parts of the world and are particularly relevant for coastal urbanized regions and megacities.

ACKNOWLEDGEMENTS

We thank D. Tanner, G. Huey (Georgia Institute of Technology); T.C. Brown, D. Diec, R. Leigh (University of Leicester); and G. Bustin, P. Chauhan, G. Nicholson, C. Schieferstein (University of Leicester Chemistry Workshop) for continuing help and support. We also thank W.J. Bloss and the ICOZA team for collaboration during fieldwork at Weybourne. Special thanks are due to Roland von Glasow for many useful discussions and for inspiring this project. This is contribution no. 4 from the Penlee Point Atmospheric Observatory. Photo credit (Graphical ToC): Jacques Descloires, MODIS Land Rapid Response Team, NASA/GSFC.

Conflict of interests

The authors declare no conflicts of interest.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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