

















## RESEARCH ARTICLE

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

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## Funding information

Natural Environment Research Council (NERC), Grant/Award Number: NE/K004069/1, NE/N018044/1, NE/K012169/1, NE/L01291X/1; National Oceanic and Atmospheric Administration (NOAA), Climate and Health of the Atmosphere Initiatives. The Weybourne Atmospheric Observatory is supported by the National Centre for Atmospheric Science

Measurements of nitryl chloride (ClNO<sub>2</sub>) and its precursors (O<sub>3</sub>, NO<sub>2</sub>, particulate chloride) were made in 2014–2016 at three contrasting locations in the United Kingdom: Leicester, Penlee Point and Weybourne. ClNO<sub>2</sub> was observed at all sites and in every season, with the highest concentrations between 00:00 and 04:00 GMT. The median nocturnal concentration of ClNO<sub>2</sub> ranged between the detection limit (4.2 ppt) and 139 ppt. A clear seasonal cycle, with maxima in spring and winter, and significant differences between locations in the same season were observed. The main source of particulate chloride was sea salt aerosol (including at Leicester, ~200 km from the coast). In general, ClNO<sub>2</sub> levels were controlled by the concentrations of O<sub>3</sub> and NO<sub>2</sub>, rather than by the uptake and reaction of N<sub>2</sub>O<sub>5</sub> with particulate chloride. Under these conditions, the seasonality and geographical distribution of ClNO<sub>2</sub> can be explained in terms of O<sub>3</sub>-limited and NO<sub>2</sub>-limited regimes affecting the formation of the N<sub>2</sub>O<sub>5</sub> precursor. A global version of the GEOS-Chem model at medium resolution (2° × 2.5°) was not able to fully capture the observed seasonality of ClNO<sub>2</sub>, mostly because the model overestimated the concentrations of the precursors, particularly of nocturnal O<sub>3</sub>. A higher-resolution (0.25° × 0.3125°) version of GEOS-Chem showed better agreement with the observations, although it still overestimated ClNO<sub>2</sub> concentrations during summer.

## KEYWORDS

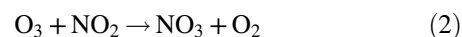
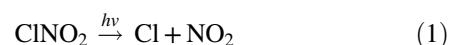
chlorine, ClNO<sub>2</sub>, nitryl chloride, ozone, seasonality, variability

## 1 | 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).

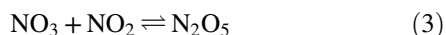
One of the mechanisms by which unreactive particulate chloride (Cl<sup>-</sup>) can be converted into reactive gas-phase

chlorine is via the nocturnal formation of nitryl chloride (ClNO<sub>2</sub>), followed by its photolysis at sunrise to yield Cl and NO<sub>2</sub> (1). ClNO<sub>2</sub> is formed from the reaction of N<sub>2</sub>O<sub>5</sub> on chloride-containing particles (5) (Finlayson-Pitts *et al.*, 1989; Behnke *et al.*, 1994; Finlayson-Pitts, 2003; Roberts *et al.*, 2008; 2009):



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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  $\text{NO}$ , dictate that reactions 3–5 are important only during the night. Except for slow dry deposition,  $\text{ClNO}_2$  losses are thought to be insignificant at night (Roberts *et al.*, 2008; Kim *et al.*, 2014). During the day,  $\text{ClNO}_2$  photolyses, with a lifetime of  $\sim 40$  min (at midday,  $52^\circ\text{N}$ ), resulting in a diel pattern with night-time maxima and daytime minima. The conversion of  $\text{N}_2\text{O}_5$  to  $\text{ClNO}_2$  (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  $\text{HCl}$  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  $\text{ClNO}_2$  reduces the formation of  $\text{HNO}_3$  (due to the competition between 4 and 5) and therefore slows the overall loss of nitrogen oxides via  $\text{HNO}_3$  deposition (Brown *et al.*, 2006), leaving more  $\text{NO}_2$  available for ozone formation in the morning; the photolysis of  $\text{ClNO}_2$  releases  $\text{Cl}$  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  $\text{ClNO}_2$  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  $\text{ClNO}_2$  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  $\text{ClNO}_2$  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  $\text{ClNO}_2$  in the United Kingdom and, by extension, Northern Europe.

## 2 | METHODS

### 2.1 | Fieldwork

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

1. Leicester ( $52^\circ 38'\text{N}$ ,  $01^\circ 08'\text{W}$ ) is a middle-sized city (pop:  $\sim 330,000$ ) in central England,  $\sim 200$  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](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  $\sim 400$  m apart and, for this work, were analysed together.
2. Penlee Point ( $50^\circ 19'\text{N}$ ,  $04^\circ 11'\text{W}$ ) is on the southwestern coast of the United Kingdom,  $\sim 6$  km southwest of the city of Plymouth (pop:  $\sim 250,000$ ). The Penlee Point Atmospheric Observatory (PPAO, <http://www.westernchannelobservatory.org.uk/penlee/>) is located  $\sim 11$  m above mean sea level and  $\sim 30$  m from the shoreline. The site receives unpolluted air from the Atlantic Ocean during prevailing southwesterly conditions ( $\sim 50\%$  of the time, Yang *et al.*, 2016).
3. Weybourne ( $52^\circ 57'\text{N}$ ,  $01^\circ 07'\text{E}$ ) is on the eastern coast of the United Kingdom,  $\sim 180$  km northeast of London. The Weybourne Atmospheric Observatory (WAO, <http://weybourne.uea.ac.uk/>) is located  $\sim 150$  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

$\text{ClNO}_2$  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 ( $\text{I}^-$ ) as the reagent ion.  $\text{ClNO}_2$  was detected as the cluster ion  $[\text{I} \cdot \text{ClNO}_2]^-$  at  $m/z = 208$  and  $210$  amu, as in Osthoff *et al.* (2008) and Thaler *et al.* (2011). The instrument was calibrated by generating  $\text{ClNO}_2$  with a flow of  $\text{Cl}_2$  (5 ppm in  $\text{N}_2$ ) over a bed of sodium nitrite ( $\text{NaNO}_2$ ) and  $\text{NaCl}$ , similar to Thaler *et al.* (2011). Quantitative determination of the amount of  $\text{ClNO}_2$  produced was obtained by thermally decomposing  $\text{ClNO}_2$  to  $\text{NO}_2$  at  $\sim 350^\circ\text{C}$  and measuring  $\text{NO}_2$  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 ( $\sim 175^\circ\text{C}$ ) stainless steel coil, which destroys all  $\text{ClNO}_2$  in the sample. The

**TABLE 1** Date, season and location of the measurement periods. Median, interquartile range and maximum measured concentrations of ClNO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub> (15-min average between 00:00–04:00 GMT) and particulate Cl<sup>−</sup> (24 h average) during each measurement period

Date	3–11 Mar	4–28 Aug	11–19 Dec	20 Apr–8 May	26 Jun–3 Aug	22–29 Sep	1–26 Feb
Year	2014	2014	2014	2015	2015	2015	2016
Season	Spring	Summer	Winter	Spring	Summer	Autumn	Winter
Location	Leicester	Leicester	Leicester	Penlee Point	Weybourne	Leicester	Leicester
ClNO <sub>2</sub>	110	15.4	50.5	<DL <sup>a</sup>	21.5	27.7	139
(ppt)	50.1–150	<DL–31.2 <sup>a</sup>	23.4–100	<DL–6.3 <sup>a</sup>	9.1–67.4	18.7–41.5	5.5–281
	274	74.2	248	922	1,100	75.6	733
NO <sub>2</sub>	9.0	8.6	6.8	0.9	2.7	13.1	7.9
(ppb)	5.8–21.6	4.4–14.1	5.3–11.4	0.4–1.9	1.6–3.8	6.0–19.6	5.1–20.5
	33.5	26.4	38.3	6.3	9.4	32.9	43.4
O <sub>3</sub>	24.2	17.0	23.2	39.0	26.7	8.4	22.1
(ppb)	15.7–28.9	11.4–21.3	18.6–29.0	32.5–42.8	22.3–32.3	3.3–15.7	11.3–29.6
	35.7	30.3	34.9	50.3	82.7	26.7	39.8
Cl <sup>−c</sup>	0.7	<DL <sup>b</sup>	1.3	—	2.3	—	—
(µg/m <sup>3</sup> )	0.4–1.2	<DL–0.6 <sup>b</sup>	1.1–1.5	—	1.5–4.8	—	—
	2.6	2.0	1.6	—	22.2	—	—

<sup>a</sup> Detection limit (DL) = 4.2 ppt.

<sup>b</sup> Detection limit (DL) = 0.2 µg/m<sup>3</sup>.

<sup>c</sup> Particle diameter <10 µm (PM10) for the Leicester data and >0.01 µm for the Weybourne data.

1-min detection limit for ClNO<sub>2</sub> was 4.2 ppt at 2σ (5.1 ppt at 3σ), with 18% accuracy and 14% precision.

O<sub>3</sub> 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). NO<sub>2</sub> was measured at Leicester and in Penlee Point with a Teledyne Model T200 NO/NO<sub>2</sub>/NO<sub>x</sub> 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 NO<sub>y</sub> species (Reed *et al.*, 2016): although this is unlikely to be an issue for Leicester, where fresh NO<sub>x</sub> 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, NO<sub>2</sub> 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

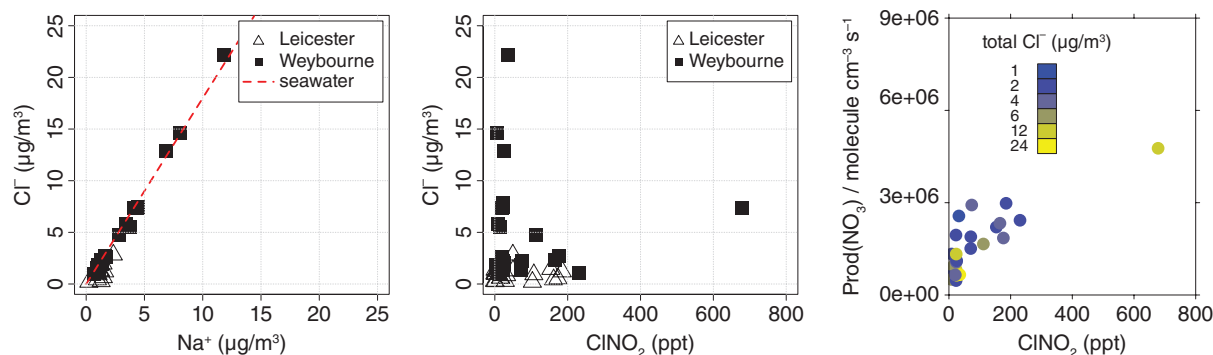
(SI. 2). All measurements were made at ~5 m above ground; the data were processed and analysed using R and the open air package (Carslaw and Ropkins, 2012).

### 3 | RESULTS

#### 3.1 | Overview

The highest concentrations of ClNO<sub>2</sub> were typically observed between 00:00 and 04:00 GMT. The median ClNO<sub>2</sub> 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/m<sup>3</sup> and 2.3 µg/m<sup>3</sup> were measured in Leicester and Weybourne, respectively. Chloride was well correlated ( $r^2 = 0.81–0.99$ ) with Na<sup>+</sup> at both sites (Figure 1, left). In Weybourne, the measured Cl<sup>−</sup>/Na<sup>+</sup> 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<sup>−</sup> in sub-micron aerosol was 5–19% (median = 12%), indicating that most Cl<sup>−</sup> was in the coarse fraction (e.g., sea



**FIGURE 1** Measured particulate  $\text{Cl}^-$  versus  $\text{Na}^+$  (left) and  $\text{ClNO}_2$  (middle); the red dashed line in the left panel is the average chloride/sodium mass ratio in seawater (1.8).  $\text{NO}_3$  production rate (from measured  $\text{O}_3$  and  $\text{NO}_2$ ) versus  $\text{ClNO}_2$ , coloured by measured particulate chloride (right). Data from Leicester and Weybourne, averaged to the sampling intervals of the aerosol impactors

salt). In Leicester, the measured  $\text{Cl}^-/\text{Na}^+$  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  $\text{Mg}^{2+}/\text{Na}^+$  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  $\sim 30$  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  $\text{Cl}^-$  not only at the two coastal sites but also in Leicester ( $\sim 200$  km from the ocean), providing enough surface area for reaction 5 to occur.

The mean  $\text{ClNO}_2$  nocturnal maxima in Leicester and Weybourne were not correlated with particulate  $\text{Cl}^-$  (Figure 1, middle and right), which suggests that the concentration of chloride was not, in general, a limiting factor for the formation of  $\text{ClNO}_2$ .

The complete time series of the measured species are given in the Supplementary Information (SI. 3). In this paper, the observational dataset was aggregated and analysed in two ways: (a) data collected in the same place but in different seasons and (b) data collected in different places and in the same season. The aim is to investigate the seasonal and geographical patterns of  $\text{ClNO}_2$  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  $\text{ClNO}_2$ . A seasonal cycle is apparent (Figure 2), consistent with the observations made by Mielke *et al.* (2016) in Calgary (Canada). The highest median  $\text{ClNO}_2$  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  $\text{NO}_2$  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  $\text{O}_3$  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  $\text{O}_3$  was more influential than that of  $\text{NO}_2$  in driving the seasonal changes of  $\text{ClNO}_2$  in Leicester. Furthermore, the  $\text{NO}_3$  production rate ( $k_1[\text{NO}_2][\text{O}_3]$ ) showed a weak but positive correlation with  $\text{ClNO}_2$  (Figure 1, right), which points to reaction 2 as the rate-limiting step for  $\text{ClNO}_2$  formation.

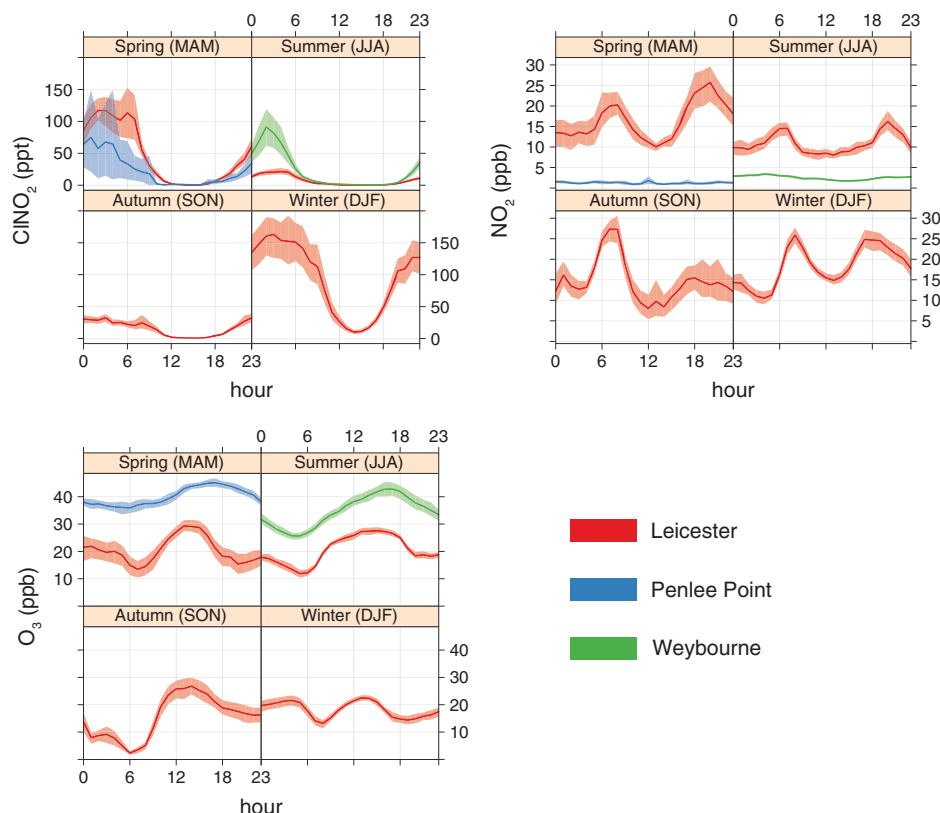
The duration of the daylight period, which changes with the season, can have an effect on the concentration of  $\text{ClNO}_2$  as its formation occurs in the dark. Autumn and spring have similar daylight periods but different levels of  $\text{ClNO}_2$ ,  $\text{O}_3$  and  $\text{NO}_2$  (Figure 2), suggesting that changes in the chemical precursors are more important. Several processes involved in the production of  $\text{ClNO}_2$  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  $\text{ClNO}_2$  concentrations by 12% or less, which suggests a limited impact of temperature on the seasonal variability of  $\text{ClNO}_2$ .

### 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  $\text{ClNO}_2$  in the same season.

The interquartile range of  $\text{ClNO}_2$  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  $\text{ClNO}_2$  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  $\text{ClNO}_2$  was below 6.3 ppt. Although the median  $\text{O}_3$  concentrations were  $\sim 40\%$  lower in Leicester than in Penlee Point, the median  $\text{NO}_2$





**FIGURE 2** Average diel profiles of  $\text{ClNO}_2$ ,  $\text{NO}_2$  and  $\text{O}_3$  in different seasons and locations. The shaded areas are the 95% confidence intervals of the mean. The median and quartile concentrations are given in Table 1

concentrations were a factor of 10 higher, leading to higher  $\text{ClNO}_2$  concentrations in Leicester (Table 1). This result is consistent with the spring observations previously made by Bannan *et al.* (2017) in Weybourne: although  $\text{O}_3$  concentrations were higher (45–50 ppb) than in Leicester, the mean  $\text{ClNO}_2$  concentration was about a factor of 6 lower ( $\sim 15$  ppt) due to lower  $\text{NO}_x$  levels in Weybourne.

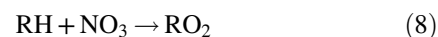
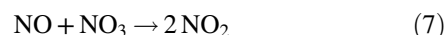
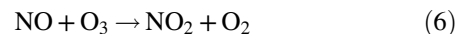
During summer, the median  $\text{O}_3$  concentrations were  $\sim 40\%$  lower and the median  $\text{NO}_2$  concentrations a factor of 3 higher in Leicester, compared to Weybourne. Contrary to springtime, lower  $\text{O}_3$  and higher  $\text{NO}_2$  resulted in lower  $\text{ClNO}_2$  concentrations in Leicester (15.4 ppt) than in Weybourne (21.5 ppt). This suggests that the concentration of  $\text{ClNO}_2$  in the two locations was, on average, controlled by different mechanisms, with  $\text{NO}_2$  being the more influential parameter in Weybourne and  $\text{O}_3$  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,  $\text{O}_3$  concentrations ( $\sim 20$  ppb, Bohnenstengel *et al.*, 2015) were similar to those observed in Leicester and lower than those observed in Weybourne, while  $\text{NO}_2$  concentrations were generally higher (10–15 ppb), which resulted in higher mean concentrations of  $\text{ClNO}_2$  ( $\sim 150$  ppt, Bannan *et al.*, 2015). The pattern was less clear for Kleiner Feldberg, likely because air masses of continental origin were also

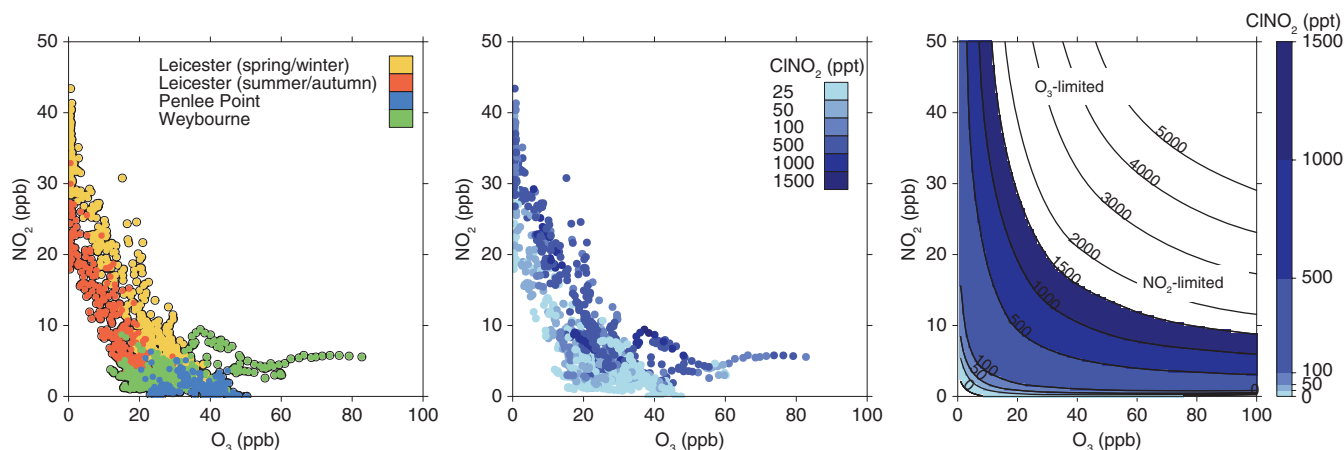
sampled (Phillips *et al.*, 2012), and under those conditions, it cannot be assumed that particulate chloride was not a limiting factor.

### 3.4 | Discussion

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



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



**FIGURE 3** Measured  $O_3$  and  $NO_2$  coloured by measurement period and site (left). Measured  $O_3$  and  $NO_2$  coloured by measured  $ClNO_2$  (middle). Modelled  $ClNO_2$  versus initial  $O_3$  and  $NO_2$  concentrations, as calculated with the simple box model (right)

(285 K, mean of all measurement periods) to simulate the formation of  $ClNO_2$  during the night.

The measured and modelled concentrations of  $ClNO_2$  are plotted in Figure 3 (middle and right) as a function of  $O_3$  and  $NO_2$ . 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),  $N_2O_5$  uptake coefficient (0.005) or  $ClNO_2$  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  $ClNO_2$  concentrations can be identified (Figure 3, right): one is  $NO_2$ -limited, and the other is  $O_3$ -limited. The observations at Penlee Point and Weybourne fall predominantly in the regime where  $ClNO_2$  concentrations are constrained by the availability of  $NO_2$ , while those in Leicester fall mainly in the  $O_3$ -limited regime (Figure 3, left). The highest  $ClNO_2$  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  $O_3$ -limited, the seasonal variability of  $ClNO_2$  is controlled by the variability of  $O_3$  concentrations, and the variability of  $NO_2$  has less impact. Lower  $O_3$  concentrations also explain why the  $ClNO_2$  concentrations observed in Leicester during summer were, on average, lower than in Weybourne, even though  $NO_2$  levels were a factor of 3 higher (Figure 2). On the other hand,  $ClNO_2$  concentrations in Penlee Point and Weybourne were mostly constrained by the availability of  $NO_2$ , rather than of  $O_3$ . Although the two locations cannot be directly compared as the measurements were made in different seasons, Weybourne usually experienced higher  $NO_2$  concentrations than Penlee Point, resulting in higher  $ClNO_2$  concentrations even under similar  $O_3$  levels (Figure 3).

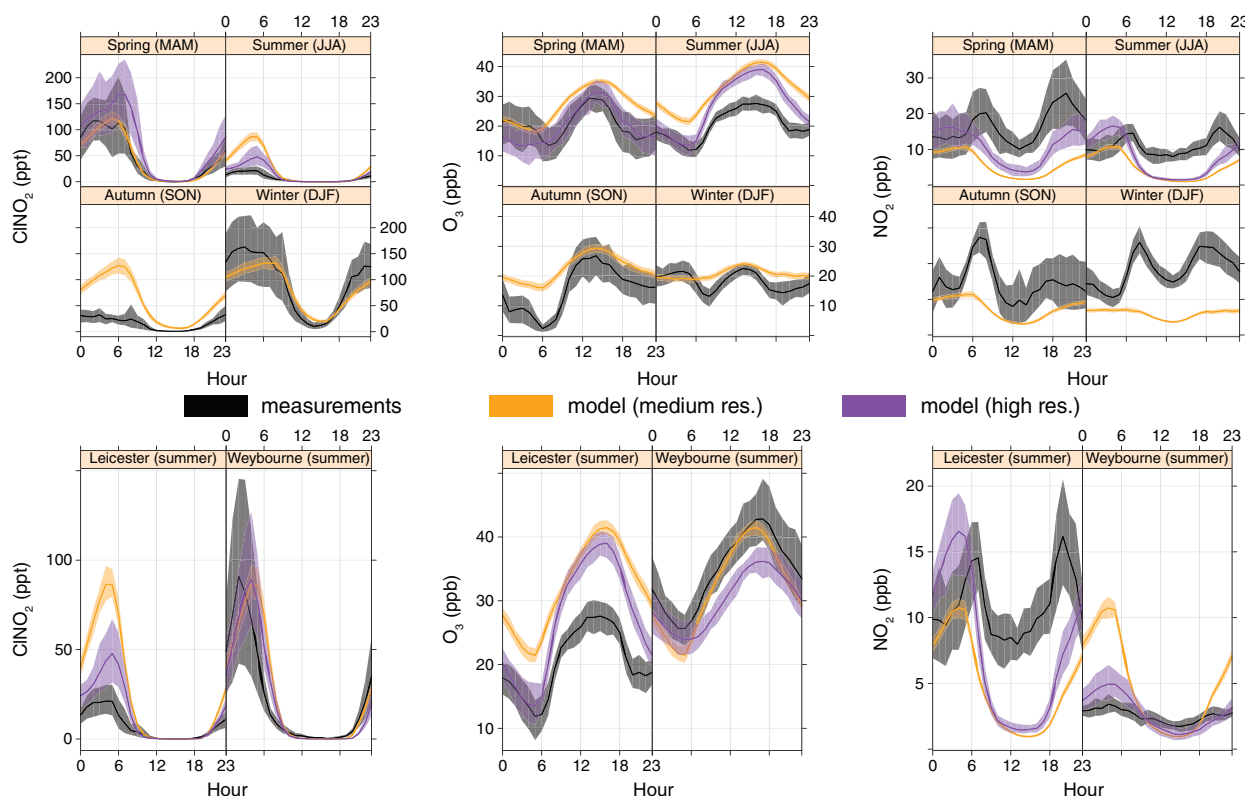
As shown previously (Figure 1, right), both the Leicester and the Weybourne data suggest that  $NO_3$  production (2)

was the rate-limiting step in the sequence of reactions leading to  $ClNO_2$  formation (2–5), which is consistent with the existence of  $O_3$ -limited and  $NO_2$ -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  $ClNO_2$  can be either  $O_3$ -limited or  $NO_2$ -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  $HO_x$ - $NO_x$ -VOC- $O_3$ -Br $O_x$  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,  $ClNO_2$  formation following  $N_2O_5$  uptake on sea salt, and heterogeneous iodine cycling to produce ICl, IBr. Reaction probabilities for  $N_2O_5$  uptake follow Evans and Jacob (2005) for sea salt aerosol (producing  $ClNO_2$ ) and non-sea salt aerosol (producing  $HNO_3$ ).

The model was run at a medium global resolution ( $2^\circ \times 2.5^\circ$ ) for 2 years for the seasonal comparisons, following a 1-year “spin up”. A higher-resolution “nested” simulation ( $0.25^\circ \times 0.3125^\circ$ , 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  $ClNO_2$ ,  $NO_2$  and  $O_3$  in



**FIGURE 4** Modelled and measured average diel profiles of  $\text{ClONO}_2$ ,  $\text{NO}_2$  and  $\text{O}_3$ , divided by season (in Leicester, top) and by location (in summer, bottom). The shaded areas are the 95% confidence intervals of the mean

Figure 4. Additional plots are given in the Supplementary Information (SI. 5).

The medium-resolution version of GEOS-Chem ( $2^\circ \times 2.5^\circ$ ) was able to reproduce the diel  $\text{ClONO}_2$  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  $\text{ClONO}_2$  during summer and autumn (Figure 4, top). However, the model showed good agreement with the summertime measurements of  $\text{ClONO}_2$  at Weybourne (Figure 4, bottom), as previously reported by (Sherwen *et al.*, 2017). The high-resolution version of GEOS-Chem ( $0.25^\circ \times 0.3125^\circ$ ) calculated roughly the same concentrations of  $\text{ClONO}_2$  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  $\text{ClONO}_2$  by a factor of  $\sim 2$  (Figure 4). The comparison between modelled and measured  $\text{O}_3$  and  $\text{NO}_2$  suggests that the improved performance of the higher-resolution model was due to a better representation of nocturnal  $\text{O}_3$  during summer ( $\text{ClONO}_2$  being mostly  $\text{O}_3$ -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  $\text{ClONO}_2$  is a significant challenge for chemical transport models. The models need to be able to accurately simulate the nocturnal concentrations of  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$  and effective  $\text{Cl}^-$  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  $\text{ClONO}_2$  concentrations, which may not be apparent in higher-resolution models.

## 5 | CONCLUSIONS

Measurements of  $\text{ClONO}_2$  and its precursors ( $\text{O}_3$ ,  $\text{NO}_2$ , 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  $\text{ClONO}_2$  was observed at all locations and in all seasons. The median nocturnal concentrations of  $\text{ClONO}_2$  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.

CINO<sub>2</sub> 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<sup>-</sup>). Observational evidence suggests that production of NO<sub>3</sub> (2) was the rate-limiting step in the formation of CINO<sub>2</sub>, rather than the aerosol uptake of N<sub>2</sub>O<sub>5</sub> and its reaction with Cl<sup>-</sup>. In general, the data indicate that the observed variability of CINO<sub>2</sub> was driven by the availability of either O<sub>3</sub> or NO<sub>2</sub>, depending on the season and the location. The seasonal and geographical variability of CINO<sub>2</sub> can be explained in terms of O<sub>3</sub>-limited and NO<sub>2</sub>-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 CINO<sub>2</sub>, but not the observed seasonal cycle and geographical distribution. The likely reason is that GEOS-Chem overestimated the concentrations of CINO<sub>2</sub> precursors, particularly of O<sub>3</sub>. Simulations at higher resolution (0.25° × 0.3125°) improved the fidelity of the simulation, although CINO<sub>2</sub> 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 CINO<sub>2</sub> 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), CINO<sub>2</sub> 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 Descloitres, 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.

**How to cite this article:** Sommariva R, Hollis LDJ, Sherwen T, et al. Seasonal and geographical variability of nitryl chloride and its precursors in Northern Europe. *Atmos Sci Lett*. 2018;19:e844. <https://doi.org/10.1002/asl.844>