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RESEARCH ARTICLE

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

Roberto Sommariva[1] | Lloyd D. J. Hollis[1] | Tomás Sherwen[2,6] | Alex R. Baker[3] | Stephen M. Ball[1] | Brian J. Bandy[3] | Thomas G. Bell[4] | Mohammad N. Chowdhury[5] | Rebecca L. Cordell[1] | Mathew J. Evans[2,6] | James D. Lee[2,6] | Chris Reed[2] | Claire E. Reeves[3] | James M. Roberts[7] | Mingxi Yang[4] | Paul S. Monks[1]

[1]Department of Chemistry, University of Leicester, Leicester, UK

[2]Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, UK

[3]Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, UK

[4]Plymouth Marine Laboratory, Plymouth, UK

[5]Department of Physics and Astronomy, University of Leicester, Leicester, UK

[6]National Centre for Atmospheric Science, York, UK

[7]Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado

Correspondence
Roberto Sommariva, Department of Chemistry, University of Leicester, Leicester, UK.
Email: rs445@le.ac.uk

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Measurements of nitryl chloride ($ClNO_2$) and its precursors (O_3, NO_2, particulate chloride) were made in 2014–2016 at three contrasting locations in the United Kingdom: Leicester, Penlee Point and Weybourne. $ClNO_2$ 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 $ClNO_2$ 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, $ClNO_2$ levels were controlled by the concentrations of O_3 and NO_2, rather than by the uptake and reaction of N_2O_5 with particulate chloride. Under these conditions, the seasonality and geographical distribution of $ClNO_2$ can be explained in terms of O_3-limited and NO_2-limited regimes affecting the formation of the N_2O_5 precursor. A global version of the GEOS-Chem model at medium resolution ($2° \times 2.5°$) was not able to fully capture the observed seasonality of $ClNO_2$, mostly because the model overestimated the concentrations of the precursors, particularly of nocturnal O_3. A higher-resolution ($0.25° \times 0.3125°$) version of GEOS-Chem showed better agreement with the observations, although it still overestimated $ClNO_2$ concentrations during summer.

KEYWORDS
chlorine, $ClNO_2$, 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^-) 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_2O_5 on chloride-containing particles (5) (Finlayson-Pitts *et al.,* 1989; Behnke *et al.,* 1994; Finlayson-Pitts, 2003; Roberts *et al.,* 2008; 2009):

$$ClNO_2 \xrightarrow{h\nu} Cl + NO_2 \quad (1)$$

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \quad (2)$$

$$NO_3 + NO_2 \rightleftharpoons N_2O_5 \quad (3)$$

$$N_2O_5 + H_2O_{(aq)} \rightarrow 2\,HNO_3 \quad (4)$$

$$N_2O_5 + H_2O_{(aq)} + Cl^-_{(aq)} \rightarrow HNO_3 + ClNO_2 + OH^-_{(aq)} \quad (5)$$

The chemical equilibrium between NO_3 and N_2O_5 (Brown *et al.,* 2003) and the short lifetime of NO_3 during the day, due to its rapid photolysis rate and reaction with NO, dictate 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 N_2O_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 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 $[I.ClNO_2]^-$ at m/z = 208 and 210 amu, as in Osthoff *et al.* (2008) and Thaler *et al.* (2011). The instrument was calibrated by generating $ClNO_2$ 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

TABLE 1 Date, season and location of the measurement periods. Median, interquartile range and maximum measured concentrations of $ClNO_2$, NO_2, O_3 (15-min average between 00:00–04:00 GMT) and particulate Cl^- (24 h average) during each measurement period

Date	**3–11 Mar 2014**	**4–28 Aug 2014**	**11–19 Dec 2014**	**20 Apr-8 May 2015**	**26 Jun-3 Aug 2015**	**22–29 Sep 2015**	**1–26 Feb 2016**
Year							
Season	**Spring**	**Summer**	**Winter**	**Spring**	**Summer**	**Autumn**	**Winter**
Location	**Leicester**	**Leicester**	**Leicester**	**Penlee Point**	**Weybourne**	**Leicester**	**Leicester**
$ClNO_2$	110	15.4	50.5	<DL[a]	21.5	27.7	139
(ppt)	50.1–150	<DL-31.2[a]	23.4–100	<DL-6.3[a]	9.1–67.4	18.7–41.5	5.5–281
	274	74.2	248	922	1,100	75.6	733
NO_2	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_3	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^- [c]	0.7	<DL[b]	1.3	—	2.3	—	—
($\mu g/m^3$)	0.4–1.2	<DL-0.6[b]	1.1–1.5	—	1.5–4.8	—	—
	2.6	2.0	1.6	—	22.2	—	—

[a] Detection limit (DL) = 4.2 ppt.
[b] Detection limit (DL) = 0.2 $\mu g/m^3$.
[c] Particle diameter <10 μm (PM10) for the Leicester data and >0.01 μm for the Weybourne data.

1-min detection limit for $ClNO_2$ was 4.2 ppt at 2σ (5.1 ppt at 3σ), with 18% accuracy and 14% precision.

O_3 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_2 was measured at Leicester and in Penlee Point with a Teledyne Model T200 $NO/NO_2/NO_x$ 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_y species (Reed *et al.,* 2016): although this is unlikely to be an issue for Leicester, where fresh NO_x 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_2 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 $ClNO_2$ were typically observed between 00:00 and 04:00 GMT. The median $ClNO_2$ 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 $\mu g/m^3$ and 2.3 $\mu g/m^3$ were measured in Leicester and Weybourne, respectively. Chloride was well correlated (r^2 = 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

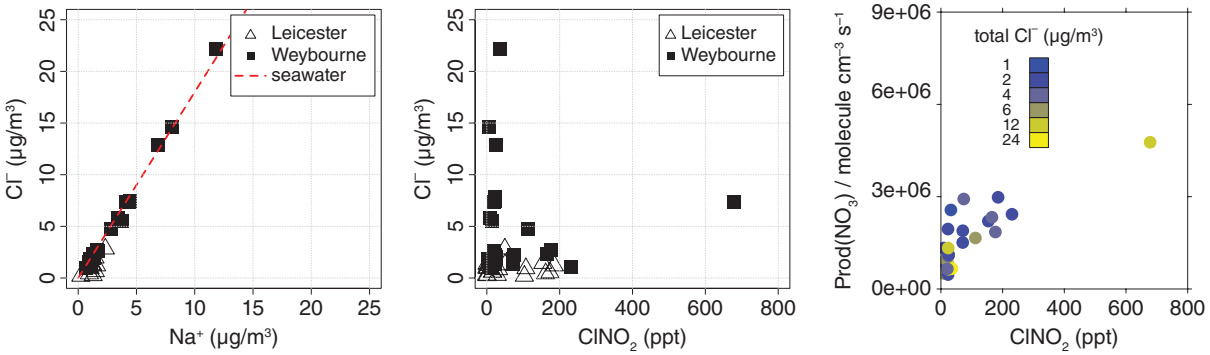

FIGURE 1 Measured particulate Cl^- versus Na^+ (left) and $ClNO_2$ (middle); the red dashed line in the left panel is the average chloride/sodium mass ratio in seawater (1.8). NO_3 production rate (from measured O_3 and NO_2) versus $ClNO_2$, coloured by measured particulate chloride (right). Data from Leicester and Weybourne, averaged to the sampling intervals of the aerosol impactors

salt). In Leicester, the measured Cl^-/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 Mg^{2+}/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 ~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^- 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 $ClNO_2$ nocturnal maxima in Leicester and Weybourne were not correlated with particulate Cl^- (Figure 1, middle and right), which suggests that the concentration of chloride was not, in general, a limiting factor for the formation of $ClNO_2$.

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 $ClNO_2$ 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 $ClNO_2$. A seasonal cycle is apparent (Figure 2), consistent with the observations made by Mielke *et al.* (2016) in Calgary (Canada). The highest median $ClNO_2$ 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 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 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 O_3 was more influential than that of NO_2 in driving the seasonal changes of $ClNO_2$ in Leicester. Furthermore, the NO_3 production rate ($k_1[NO_2][O_3]$) showed a weak but positive correlation with $ClNO_2$ (Figure 1, right), which points to reaction 2 as the rate-limiting step for $ClNO_2$ formation.

The duration of the daylight period, which changes with the season, can have an effect on the concentration of $ClNO_2$ as its formation occurs in the dark. Autumn and spring have similar daylight periods but different levels of $ClNO_2$, O_3 and NO_2 (Figure 2), suggesting that changes in the chemical precursors are more important. Several processes involved in the production of $ClNO_2$ 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 $ClNO_2$ concentrations by 12% or less, which suggests a limited impact of temperature on the seasonal variability of $ClNO_2$.

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 $ClNO_2$ in the same season.

The interquartile range of $ClNO_2$ 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 $ClNO_2$ 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 $ClNO_2$ was below 6.3 ppt. Although the median O_3 concentrations were ~40% lower in Leicester than in Penlee Point, the median NO_2

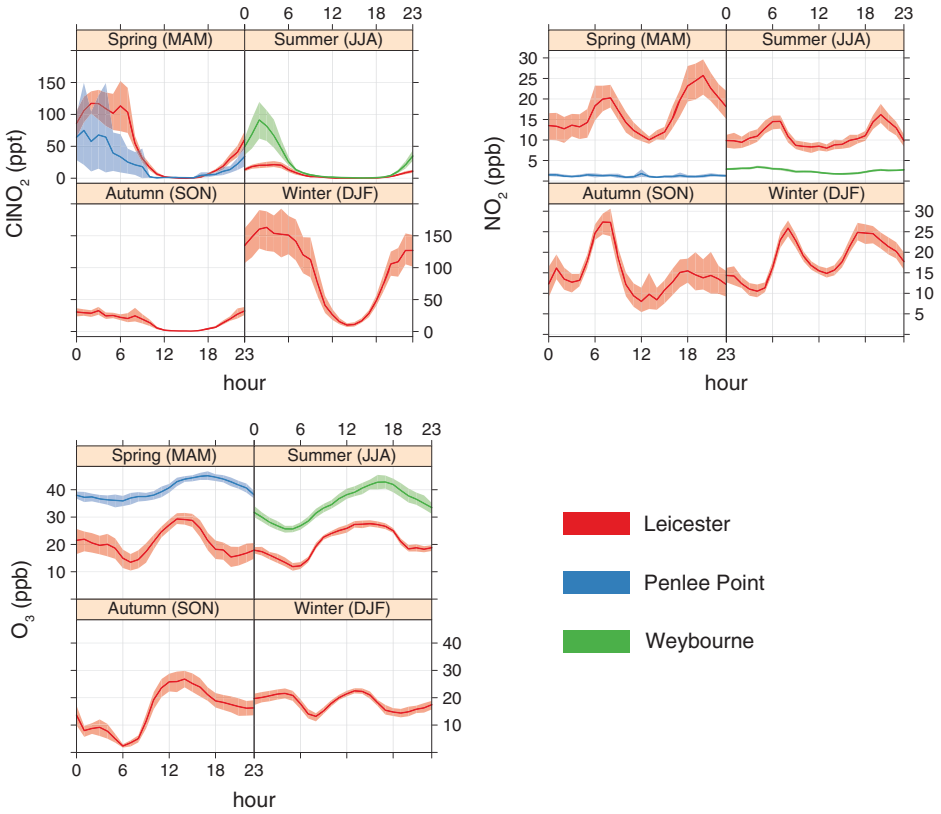

FIGURE 2 Average diel profiles of $ClNO_2$, NO_2 and O_3 in different seasons and locations. The shaded areas are the 95% confidence intervals of the mean. The median and quartile concentrations are given in Table 1

concentrations were a factor of 10 higher, leading to higher $ClNO_2$ 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 (~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_2O_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:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (6)$$

$$NO + NO_3 \rightarrow 2\,NO_2 \quad (7)$$

$$RH + NO_3 \rightarrow RO_2 \quad (8)$$

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_2O_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

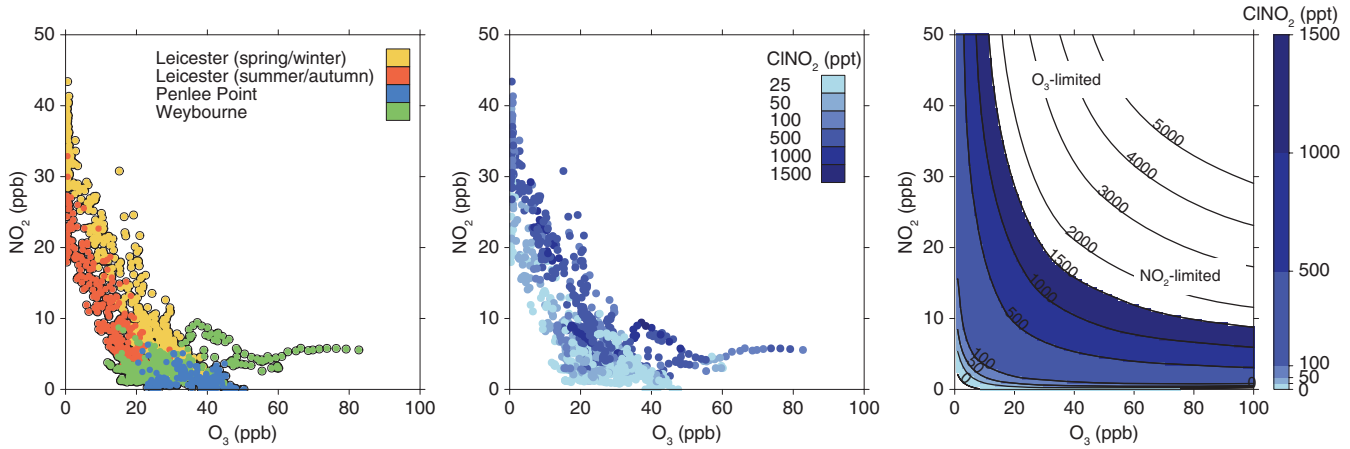

FIGURE 3 Measured O_3 and NO_2 coloured by measurement period and site (left). Measured O_3 and NO_2 coloured by measured $ClNO_2$ (middle). Modelled $ClNO_2$ versus initial O_3 and NO_2 concentrations, as calculated with the simple box model (right)

(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-BrO_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° × 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 $ClNO_2$, NO_2 and O_3 in

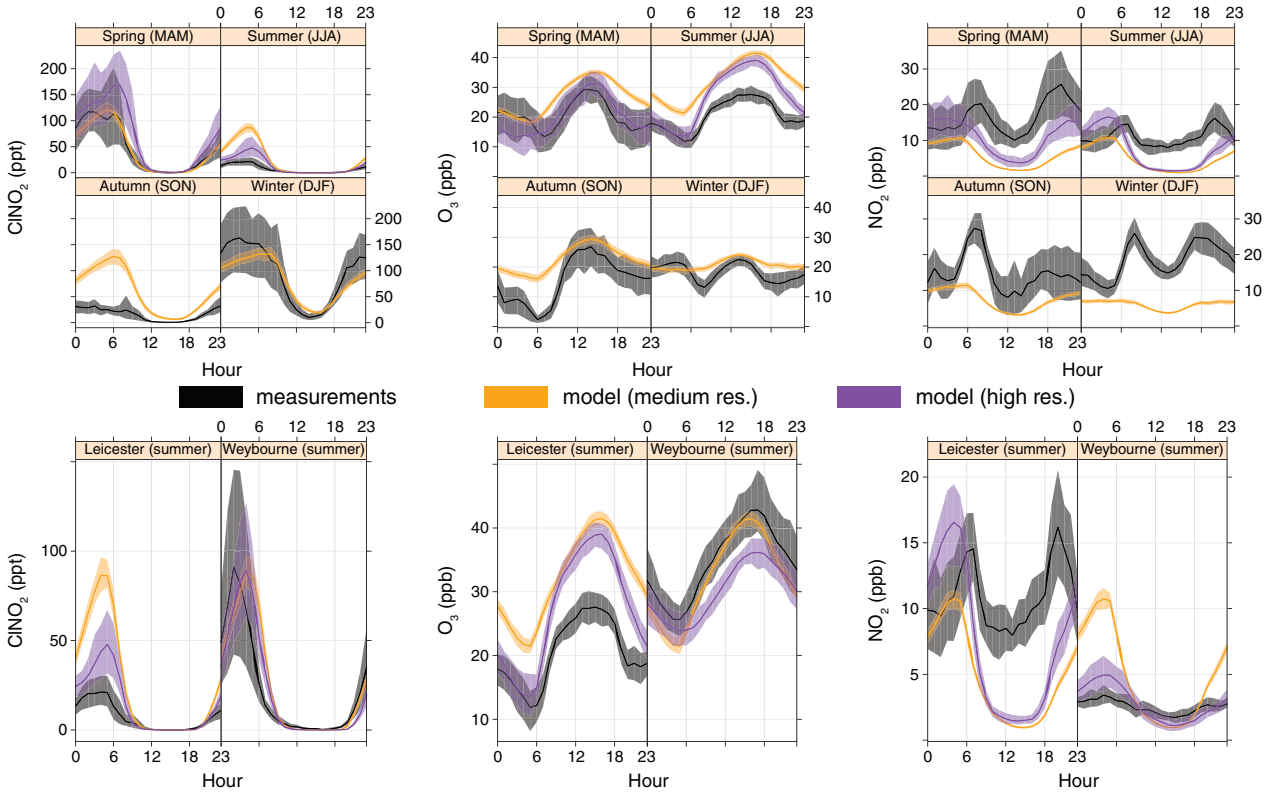

FIGURE 4 Modelled and measured average diel profiles of $ClNO_2$, NO_2 and O_3, divided by season (in Leicester, top) and by location (in summer, bottom). The shaded areas are the 95% confidence intervals of the mean

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

The medium-resolution version of GEOS-Chem ($2° \times 2.5°$) was able to reproduce the diel $ClNO_2$ 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 $ClNO_2$ during summer and autumn (Figure 4, top). However, the model showed good agreement with the summertime measurements of $ClNO_2$ at Weybourne (Figure 4, bottom), as previously reported by (Sherwen *et al.,* 2017). The high-resolution version of GEOS-Chem ($0.25° \times 0.3125°$) calculated roughly the same concentrations of $ClNO_2$ 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 $ClNO_2$ by a factor of $\sim$2 (Figure 4). The comparison between modelled and measured O_3 and NO_2 suggests that the improved performance of the higher-resolution model was due to a better representation of nocturnal O_3 during summer ($ClNO_2$ being mostly 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 $ClNO_2$ is a significant challenge for chemical transport models. The models need to be able to accurately simulate the nocturnal concentrations of O_3, NO_2, NO_3, N_2O_5 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 $ClNO_2$ concentrations, which may not be apparent in higher-resolution models.

5 | CONCLUSIONS

Measurements of $ClNO_2$ and its precursors (O_3, 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 $ClNO_2$ was observed at all locations and in all seasons. The median nocturnal concentrations of $ClNO_2$ 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.

$ClNO_2$ 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 NO_3 (2) was the rate-limiting step in the formation of $ClNO_2$, rather than the aerosol uptake of N_2O_5 and its reaction with Cl^-. In general, the data indicate that the observed variability of $ClNO_2$ was driven by the availability of either O_3 or NO_2, depending on the season and the location. The seasonal and geographical variability of $ClNO_2$ can be explained in terms of O_3-limited and NO_2-limited chemical regimes, broadly reproducible with a simple chemical box model.

The GEOS-Chem chemical transport model at medium resolution ($2° \times 2.5°$) could reproduce the diel cycle of $ClNO_2$, but not the observed seasonal cycle and geographical distribution. The likely reason is that GEOS-Chem overestimated the concentrations of $ClNO_2$ precursors, particularly of O_3. Simulations at higher resolution ($0.25° \times 0.3125°$) improved the fidelity of the simulation, although $ClNO_2$ 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 $ClNO_2$ 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), $ClNO_2$ 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.

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Conflict of interests

The authors declare no conflicts of interest.

ORCID

Roberto Sommariva http://orcid.org/0000-0002-2728-5814
Lloyd D. J. Hollis http://orcid.org/0000-0001-7689-1565
Tomás Sherwen http://orcid.org/0000-0002-3006-3876
Alex R. Baker http://orcid.org/0000-0002-8365-8953
Stephen M. Ball http://orcid.org/0000-0002-5756-4718
Brian J. Bandy http://orcid.org/0000-0002-3736-8162
Thomas G. Bell http://orcid.org/0000-0002-4108-7048
Mohammad N. Chowdhury http://orcid.org/0000-0003-3577-9395
Rebecca L. Cordell http://orcid.org/0000-0002-3775-0193
Mathew J. Evans http://orcid.org/0000-0003-4775-032X
James D. Lee http://orcid.org/0000-0001-5397-2872
Chris Reed http://orcid.org/0000-0002-9886-5875
Claire E. Reeves http://orcid.org/0000-0003-4071-1926
James M. Roberts http://orcid.org/0000-0002-8485-8172
Mingxi Yang http://orcid.org/0000-0002-8321-5984
Paul S. Monks http://orcid.org/0000-0001-9984-4390

REFERENCES

Baker, A.R., Weston, K., Kelly, S.D., Voss, M., Streu, P. and Cape, J.N. (2007) Dry and wet deposition of nutrients from the tropical Atlantic atmosphere: links to primary productivity and nitrogen fixation. *Deep-Sea Research Part I: Oceanographic Research Papers*, 54, 1704–1720.

Bannan, T.J., Booth, A.M., Bacak, A., Muller, J.B.A., Leather, K.E., Le Breton, M., Jones, B., Young, D., Coe, H., Allan, J., Visser, S., Slowik, J.G., Furger, M., Prévôt, A.S.H., Lee, J., Dunmore, R.E., Hopkins, J.R., Hamilton, J.F., Lewis, A.C., Whalley, L.K., Sharp, T., Stone, D., Heard, D. E., Fleming, Z.L., Leigh, R., Shallcross, D.E. and Percival, C.J. (2015) The first UK measurements of nitryl chloride using a chemical ionization mass spectrometer in Central London in the summer of 2012, and an investigation of the role of Cl atom oxidation. *Journal of Geophysical Research: Atmospheres*, 120, 5638–5657. https://doi.org/10.1002/2014JD022629.

Bannan, T.J., Bacak, A., Le Breton, M., Flynn, M., Ouyang, B., McLeod, M., Jones, R., Malkin, T.L., Whalley, L.K., Heard, D.E., Bandy, B., Khan, M.A. H., Shallcross, D.E. and Percival, C.J. (2017) Ground and airborne U.K. measurements of nitryl chloride: an investigation of the role of Cl atom oxidation at Weybourne atmospheric observatory. *Journal of Geophysical Research: Atmospheres*, 122, 11154–11165. https://doi.org/10.1002/2017JD026624.

Behnke, W., Scheer, V. and Zetzsch, C. (1994) Production of $BrNO_2$, $BrNO_2$ and $ClNO_2$ from the reaction between sea spray aerosol and N_2O_5. *Journal of Aerosol Science*, 25, S277–S278.

Bertram, T.H. and Thornton, J.A. (2009) Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride. *Atmospheric Chemistry and Physics*, 9, 8351–8363. http://www.atmos-chem-phys.net/9/8351/2009/.

Bey, I., Jacob, D.J., Yantosca, R.M., Logan, J.A., Field, B.D., Fiore, A.M., Li, Q.-B., Liu, H.Y., Mickley, L.J. and Schultz, M.G. (2001) Global modeling of tropospheric chemistry with assimilated meteorology: model description and evaluation. *Journal of Geophysical Research: Atmospheres*, 106, 23073–23095. https://doi.org/10.1029/2001JD000807.

Bohnenstengel, S.I., Belcher, S.E., Aiken, A.C., Allan, J.D., Allen, G., Bacak, A., Bannan, T.J., Barlow, J.F., Beddows, D.C.S., Bloss, W.J., Booth, A.M., Chemel, C., Coceal, O., Di Marco, C.F., Dubey, M.K., Faloon, K.H., Fleming, Z.L., Furger, M., Gietl, J.K., Graves, R.R., Green, D.C., Grimmond, C.S.B., Halios, C.H., Hamilton, J.F., Harrison, R. M., Heal, M.R., Heard, D.E., Helfter, C., Herndon, S.C., Holmes, R.E., Hopkins, J.R., Jones, A.M., Kelly, F.J., Kotthaus, S., Langford, B., Lee, J.D., Leigh, R.J., Lewis, A.C., Lidster, R.T., Lopez-Hilfiker, F.D., McQuaid, J.B., Mohr, C., Monks, P.S., Nemitz, E., Ng, N.L., Percival, C.J., Prévôt, A.S.H., Ricketts, H.M.A., Sokhi, R., Stone, D., Thornton, J.A., Tremper, A.H., Valach, A.C., Visser, S., Whalley, L.K., Williams, L.R., Xu, L., Young, D. E. and Zotter, P. (2015) Meteorology, air quality, and health in London: the

ClearfLo project. *Bulletin of the American Meteorological Society*, 96, 779–804. https://doi.org/10.1175/BAMS-D-12-00245.1.

Brown, S.S., Stark, H. and Ravishankara, A.R. (2003) Applicability of the steady state approximation to the interpretation of atmospheric observations of NO_3 and N_2O_5. *Journal of Geophysical Research*, 108, 4539. https://doi.org/10.1029/2003JD003407.

Brown, S.S., Neuman, J.A., Ryerson, T.B., Trainer, M., Dubé, W.P., Holloway, J.S., Warneke, C., de Gouw, J.A., Donnelly, S.G., Atlas, E., Matthew, B., Middlebrook, A.M., Peltier, R., Weber, R.J., Stohl, A., Meagher, J.F., Fehsenfeld, F.C. and Ravishankara, A.R. (2006) Nocturnal odd-oxygen budget and its implications for ozone loss in the lower troposphere. *Geophysical Research Letters*, 33, L08801. https://doi.org/10.1029/2006GL025900.

Carslaw, D.C. and Ropkins, K. (2012) Openair – an R package for air quality data analysis. *Environmental Modelling & Software*, 27-28, 52–61. http://linkinghub.elsevier.com/retrieve/pii/S1364815211002064.

Evans, M.J. and Jacob, D.J. (2005) Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH. *Geophysical Research Letters*, 32, L09813. https://doi.org/10.1029/2005GL022469.

Finlayson-Pitts, B.J. (2003) The tropospheric chemistry of sea salt: a molecular-level view of the chemistry of NaCl and NaBr. *Chemical Reviews*, 103, 4801–4822. https://doi.org/10.1021/cr020653t.

Finlayson-Pitts, B.J., Ezell, M.J. and Pitts, J.N. (1989) Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and $ClONO_2$. *Nature*, 337, 241–244. https://doi.org/10.1038/337241a0.

Hama, S.M., Cordell, R.L. and Monks, P.S. (2017) Quantifying primary and secondary source contributions to ultrafine particles in the UK urban background. *Atmospheric Environment*, 166, 62–78. https://doi.org/10.1016/j.atmosenv.2017.07.013.

Heard, D.E., Read, K.A., Methven, J., Al-Haider, S., Bloss, W.J., Johnson, G.P., Pilling, M.J., Seakins, P.W., Smith, S.C., Sommariva, R., Stanton, J.C., Still, T.J., Ingham, T., Brooks, B., De Leeuw, G., Jackson, A.V., McQuaid, J.B., Morgan, R., Smith, M.H., Carpenter, L.J., Carslaw, N., Hamilton, J., Hopkins, J.R., Lee, J.D., Lewis, A.C., Purvis, R.M., Wevill, D.J., Brough, N., Green, T., Mills, G., Penkett, S.A., Plane, J.M.C., Saiz-Lopez, A., Worton, D., Monks, P.S., Fleming, Z., Rickard, A.R., Alfarra, M.R., Allan, J.D., Bower, K., Coe, H., Cubison, M., Flynn, M., McFiggans, G., Gallagher, M., Norton, E.G., O'Dowd, C.D., Shillito, J., Topping, D., Vaughan, G., Williams, P., Bitter, M., Ball, S.M., Jones, R.L., Povey, I.M., O'Doherty, S., Simmonds, P.G., Allen, A., Kinnersley, R.P., Beddows, D.C.S., Dall'Osto, M., Harrison, R.M., Donovan, R.J., Heal, M.R., Jennings, S.G., Noone, C. and Spain, G. (2006) The North Atlantic marine boundary layer experiment (NAMBLEX). Overview of the campaign held at Mace Head, Ireland, in summer 2002. *Atmospheric Chemistry and Physics*, 6, 2241–2272. http://www.atmos-chem-phys.net/6/2241/2006/.

Jordan, C.E., Pszenny, A.A.P., Keene, W.C., Cooper, O.R., Deegan, B., Maben, J., Routhier, M., Sander, R. and Young, A.H. (2015) Origins of aerosol chlorine during winter over north Central Colorado, USA. *Journal of Geophysical Research: Atmospheres*, 120, 678–694. https://doi.org/10.1002/2014JD022294.

Kercher, J.P., Riedel, T.P. and Thornton, J.A. (2009) Chlorine activation by N_2O_5: simultaneous, in situ detection of $ClNO_2$ and N_2O_5 by chemical ionization mass spectrometry. *Atmospheric Measurement Techniques*, 2, 193–204. http://www.atmos-meas-tech.net/2/193/2009/.

Kim, M.J., Farmer, D.K. and Bertram, T.H. (2014) A controlling role for the air-sea interface in the chemical processing of reactive nitrogen in the coastal marine boundary layer. *Proceedings of the National Academy of Sciences*, 111, 3943–3948.

Liao, J., Sihler, H., Huey, L.G., Neuman, J.A., Tanner, D.J., Frieß, U., Platt, U., Flocke, F.M., Orlando, J.J., Shepson, P.B., Beine, H.J., Weinheimer, A.J., Sjostedt, S.J., Nowak, J.B., Knapp, D.J., Staebler, R.M., Zheng, W., Sander, R., Hall, S.R. and Ullmann, K. (2011) A comparison of Arctic BrO measurements by chemical ionization mass spectrometry and long path-differential optical absorption spectroscopy. *Journal of Geophysical Research*, 116, D00R02. https://doi.org/10.1029/2010JD014788.

Mielke, L.H., Furgeson, A. and Osthoff, H.D. (2011) Observation of $ClNO_2$ in a mid-continental urban environment. *Environmental Science & Technology*, 45, 8889–8896. https://doi.org/10.1021/es201955u.

Mielke, L.H., Stutz, J., Tsai, C., Hurlock, S.C., Roberts, J.M., Veres, P.R., Froyd, K.D., Hayes, P.L., Cubison, M.J., Jimenez, J.L., Washenfelder, R.A., Young, C.J., Gilman, J.B., de Gouw, J.A., Flynn, J.H., Grossberg, N., Lefer, B.L., Liu, J., Weber, R.J. and Osthoff, H.D. (2013) Heterogeneous formation of nitryl chloride and its role as a nocturnal NO_x reservoir species during CalNex-LA 2010. *Journal of Geophysical Research: Atmospheres*, 118(10), 638–10,652. https://doi.org/10.1002/jgrd.50783.

Mielke, L.H., Furgeson, A., Odame-Ankrah, C.A. and Osthoff, H.D. (2016) Ubiquity of $ClNO_2$ in the urban boundary layer of Calgary, Alberta, Canada. *Canadian Journal of Chemistry.*, 94, 414–423.

Osthoff, H.D., Roberts, J.M., Ravishankara, A.R., Williams, E.J., Lerner, B.M., Sommariva, R., Bates, T.S., Coffman, D., Quinn, P.K., Dibb, J.E., Stark, H., Burkholder, J.B., Talukdar, R.K., Meagher, J., Fehsenfeld, F.C. and Brown, S.S. (2008) High levels of nitryl chloride in the polluted subtropical marine boundary layer. *Nature Geoscience*, 1, 324–328. https://doi.org/10.1038/ngeo177.

Penkett, S.A., Clemitshaw, K.C., Savage, N.H., Burgess, R.A., Cardenas, L.M., Carpenter, L.J., McFadyen, G.G. and Cape, J.N. (1999) Studies of oxidant production at the Weybourne Atmospheric Observatory in summer and winter conditions. *Journal of Atmospheric Chemistry*, 33, 111–128. https://doi.org/10.1023/A:1005969204215.

Phillips, G.J., Tang, M.J., Thieser, J., Brickwedde, B., Schuster, G., Bohn, B., Lelieveld, J. and Crowley, J.N. (2012) Significant concentrations of nitryl chloride observed in rural continental Europe associated with the influence of sea salt chloride and anthropogenic emissions. *Geophysical Research Letters*, 39, L10811. https://doi.org/10.1029/2012GL051912.

Reed, C., Evans, M.J., Di Carlo, P., Lee, J.D. and Carpenter, L.J. (2016) Interferences in photolytic NO_2 measurements: explanation for an apparent missing oxidant? *Atmospheric Chemistry and Physics*, 16, 4707–4724. http://www.atmos-chem-phys.net/16/4707/2016/.

Riedel, T.P., Bertram, T.H., Crisp, T.A., Williams, E.J., Lerner, B.M., Vlasenko, A., Li, S.-M., Gilman, J., de Gouw, J., Bon, D.M., Wagner, N.L., Brown, S.S. and Thornton, J.A. (2012) Nitryl chloride and molecular chlorine in the coastal marine boundary layer. *Environmental Science & Technology*, 46, 10463–10470. https://doi.org/10.1021/es204632r.

Riedel, T.P., Wagner, N.L., Dubé, W.P., Middlebrook, A.M., Young, C.J., Öztürk, F., Bahreini, R., VandenBoer, T.C., Wolfe, D.E., Williams, E.J., Roberts, J.M., Brown, S.S. and Thornton, J.A. (2013) Chlorine activation within urban or power plant plumes: vertically resolved $ClNO_2$ and Cl_2 measurements from a tall tower in a polluted continental setting. *Journal of Geophysical Research: Atmospheres*, 118, 8702–8715. https://doi.org/10.1002/jgrd.50637.

Riedel, T.P., Wolfe, G.M., Danas, K.T., Gilman, J.B., Kuster, W.C., Bon, D.M., Vlasenko, A., Li, S.-M., Williams, E.J., Lerner, B.M., Veres, P.R., Roberts, J.M., Holloway, J.S., Lefer, B., Brown, S.S. and Thornton, J.A. (2014) An MCM modeling study of nitryl chloride ($ClNO_2$) impacts on oxidation, ozone production and nitrogen oxide partitioning in polluted continental outflow. *Atmospheric Chemistry and Physics*, 14, 3789–3800. http://www.atmos-chem-phys.net/14/3789/2014/.

Roberts, J.M., Parrish, D.D., Norton, R.B., Bertman, S.B., Holloway, J.S., Trainer, M., Fehsenfeld, F.C., Carroll, M.A., Albercook, G.M., Wang, T. and Forbes, G. (1996) Episodic removal of NO_y species from the marine boundary layer over the North Atlantic. *J. Geophys. Res.*, 101, 28947–28960. https://doi.org/10.1029/96JD02632.

Roberts, J.M., Osthoff, H.D., Brown, S.S. and Ravishankara, A.R. (2008) N_2O_5 oxidizes chloride to Cl_2 in acidic atmospheric aerosol. *Science*, 321, 1059–1059. https://doi.org/10.1126/science.1158777.

Roberts, J.M., Osthoff, H.D., Brown, S.S., Ravishankara, A.R., Coffman, D., Quinn, P. and Bates, T. (2009) Laboratory studies of products of N_2O_5 uptake on Cl^- containing substrates. *Geophysical Research Letters*, 36, L20808. https://doi.org/10.1029/2009GL040448.

Saiz-Lopez, A. and von Glasow, R. (2012) Reactive halogen chemistry in the troposphere. *Chemical Society Reviews*, 41, 6448–6472. http://xlink.rsc.org/?DOI=c2cs35208g.

Sarwar, G., Simon, H., Bhave, P. and Yarwood, G. (2012) Examining the impact of heterogeneous nitryl chloride production on air quality across the United States. *Atmospheric Chemistry and Physics*, 12, 6455–6473. http://www.atmos-chem-phys.net/12/6455/2012/.

Schmidt, J.A., Jacob, D.J., Horowitz, H.M., Hu, L., Sherwen, T., Evans, M.J., Liang, Q., Suleiman, R.M., Oram, D.E., Le Breton, M., Percival, C.J., Wang, S., Dix, B. and Volkamer, R. (2016) Modeling the observed

tropospheric BrO background: importance of multiphase chemistry and implications for ozone, OH, and mercury. *Journal of Geophysical Research: Atmospheres*, 121(11), 819–11,835. https://doi.org/10.1002/2015JD024229.

Sherwen, T., Evans, M.J., Carpenter, L.J., Andrews, S.J., Lidster, R.T., Dix, B., Koenig, T.K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A.S. and Ordóñez, C. (2016a) Iodine's impact on tropospheric oxidants: a global model study in GEOS-Chem. *Atmospheric Chemistry and Physics*, 16, 1161–1186. http://www.atmos-chem-phys.net/16/1161/2016/.

Sherwen, T., Schmidt, J.A., Evans, M.J., Carpenter, L.J., Großmann, K., Eastham, S.D., Jacob, D.J., Dix, B., Koenig, T.K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A.S. and Ordóñez, C. (2016b) Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem. *Atmospheric Chemistry and Physics*, 16, 12239–12271. http://www.atmos-chem-phys.net/16/12239/2016/.

Sherwen, T., Evans, M.J., Sommariva, R., Hollis, L.D.J., Ball, S.M., Monks, P.S., Reed, C., Carpenter, L.J., Lee, J.D., Forster, G., Bandy, B., Reeves, C.E. and Bloss, W.J. (2017) Effects of halogens on European air-quality. *Faraday Discussions*, 200, 75–100. http://xlink.rsc.org/?DOI=C7FD00026J.

Simon, H., Kimura, Y., McGaughey, G., Allen, D.T., Brown, S.S., Osthoff, H.D., Roberts, J.M., Byun, D. and Lee, D. (2009) Modeling the impact of $ClNO_2$ on ozone formation in the Houston area. *Journal of Geophysical Research*, 114, D00F03. https://doi.org/10.1029/2008JD010732.

Steinbacher, M., Zellweger, C., Schwarzenbach, B., Bugmann, S., Buchmann, B., Ordóñez, C., Prevot, A.S.H. and Hueglin, C. (2007) Nitrogen oxide measurements at rural sites in Switzerland: bias of conventional measurement techniques. *Journal of Geophysical Research*, 112, D11307. https://doi.org/10.1029/2006JD007971.

Stumm, W. and Morgan, J.J. (1995) *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd edition. Wiley, New York.

Thaler, R.D., Mielke, L.H. and Osthoff, H.D. (2011) Quantification of nitryl chloride at part per trillion mixing ratios by thermal dissociation cavity ring-down spectroscopy. *Analytical Chemistry*, 83, 2761–2766. https://doi.org/10.1021/ac200055z.

Thalman, R., Baeza-Romero, M.T., Ball, S.M., Borrás, E., Daniels, M.J.S., Goodall, I.C.A., Henry, S.B., Karl, T., Keutsch, F.N., Kim, S., Mak, J., Monks, P.S., Muñoz, A., Orlando, J., Peppe, S., Rickard, A.R., Ródenas, M., Sánchez, P., Seco, R., Su, L., Tyndall, G., Vázquez, M., Vera, T., Waxman, E. and Volkamer, R. (2015) Instrument intercomparison of glyoxal, methyl glyoxal and NO_2 under simulated atmospheric conditions. *Atmospheric Measurement Techniques*, 8, 1835–1862.

Tham, Y.J., Yan, C., Xue, L., Zha, Q., Wang, X. and Wang, T. (2014) Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry. *Chinese Science Bulletin*, 59, 356–359. https://doi.org/10.1007/s11434-013-0063-y.

Tham, Y.J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y. and Wang, T. (2016) Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China. *Atmospheric Chemistry and Physics*, 16, 14959–14977. http://www.atmos-chem-phys.net/16/14959/2016/.

Thornton, J.A., Kercher, J.P., Riedel, T.P., Wagner, N.L., Cozic, J., Holloway, J.S., Dubé, W.P., Wolfe, G.M., Quinn, P.K., Middlebrook, A.M., Alexander, B. and Brown, S.S. (2010) A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature*, 464, 271–274. https://doi.org/10.1038/nature08905.

Travis, K.R., Jacob, D.J., Fisher, J.A., Kim, P.S., Marais, E.A., Zhu, L., Yu, K., Miller, C.C., Yantosca, R.M., Sulprizio, M.P., Thompson, A.M., Wennberg, P.O., Crounse, J.D., St. Clair, J.M., Cohen, R.C., Laughner, J.L., Dibb, J.E., Hall, S.R., Ullmann, K., Wolfe, G.M., Pollack, I.B., Peischl, J., Neuman, J.A. and Zhou, X. (2016) Why do models overestimate surface ozone in the Southeast United States? *Atmospheric Chemistry and Physics*, 16, 13561–13577. http://www.atmos-chem-phys.net/16/13561/2016/.

Wang, T., Tham, Y.J., Xue, L., Li, Q., Zha, Q., Wang, Z., Poon, S.C.N., Dubé, W.P., Blake, D.R., Louie, P.K.K., Luk, C.W.Y., Tsui, W. and Brown, S.S. (2016) Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China. *Journal of Geophysical Research: Atmospheres*, 121, 2476–2489. https://doi.org/10.1002/2015JD024556.

Williams, E.J., Baumann, K., Roberts, J.M., Bertman, S.B., Norton, R.B., Fehsenfeld, F.C., Springston, S.R., Nunnermacker, L.J., Newman, L., Olszyna, K., Meagher, J., Hartsell, B., Edgerton, E., Pearson, J.R. and Rodgers, M.O. (1998) Intercomparison of ground-based NO_y measurement techniques. *Journal of Geophysical Research: Atmospheres*, 103, 22261–22280. https://doi.org/10.1029/98JD00074.

Yang, M., Huebert, B.J., Blomquist, B.W., Howell, S.G., Shank, L.M., McNaughton, C.S., Clarke, A.D., Hawkins, L.N., Russell, L.M., Covert, D.S., Coffman, D.J., Bates, T.S., Quinn, P.K., Zagorac, N., Bandy, A.R., de Szoeke, S.P., Zuidema, P.D., Tucker, S.C., Brewer, W.A., Benedict, K.B. and Collett, J.L. (2011) Atmospheric sulfur cycling in the southeastern Pacific – longitudinal distribution, vertical profile, and diel variability observed during VOCALS-REx. *Atmospheric Chemistry and Physics*, 11, 5079–5097. http://www.atmos-chem-phys.net/11/5079/2011/.

Yang, M., Bell, T.G., Hopkins, F.E. and Smyth, T.J. (2016) Attribution of atmospheric sulfur dioxide over the English Channel to dimethyl sulfide and changing ship emissions. *Atmospheric Chemistry and Physics*, 16, 4771–4783. http://www.atmos-chem-phys.net/16/4771/2016/.

Young, C.J., Washenfelder, R.A., Roberts, J.M., Mielke, L.H., Osthoff, H.D., Tsai, C., Pikelnaya, O., Stutz, J., Veres, P.R., Cochran, A.K., VandenBoer, T.C., Flynn, J., Grossberg, N., Haman, C.L., Lefer, B., Stark, H., Graus, M., de Gouw, J., Gilman, J.B., Kuster, W.C. and Brown, S.S. (2012) Vertically resolved measurements of nighttime radical reservoirs in Los Angeles and their contribution to the urban radical budget. *Environmental Science & Technology*, 46, 10965–10973. https://doi.org/10.1021/es302206a.

Young, C.J., Washenfelder, R.A., Edwards, P.M., Parrish, D.D., Gilman, J.B., Kuster, W.C., Mielke, L.H., Osthoff, H.D., Tsai, C., Pikelnaya, O., Stutz, J., Veres, P.R., Roberts, J.M., Griffith, S., Dusanter, S., Stevens, P.S., Flynn, J., Grossberg, N., Lefer, B., Holloway, J.S., Peischl, J., Ryerson, T.B., Atlas, E.L., Blake, D.R. and Brown, S.S. (2014) Chlorine as a primary radical: evaluation of methods to understand its role in initiation of oxidative cycles. *Atmospheric Chemistry and Physics*, 14, 3427–3440. http://www.atmos-chem-phys.net/14/3427/2014/.

SUPPORTING INFORMATION

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

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