



## RESEARCH ARTICLE

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## Key Points:

- Maximum 65 ppt ClNO<sub>2</sub> was recorded during nighttime in the low NO<sub>x</sub> ground-based study, with up to 95 ppt measured on an airborne platform
- Vertical profiles of ClNO<sub>2</sub> showed elevated concentrations at the surface with a reduction after ~600 m in height
- Cl atom oxidation from ClNO<sub>2</sub> photolysis was generally insignificant for total oxidation

## Supporting Information:

- Figure S1

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## Ground and Airborne U.K. Measurements of Nitryl Chloride: An Investigation of the Role of Cl Atom Oxidation at Weybourne Atmospheric Observatory

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**Abstract** Nitryl chloride (ClNO<sub>2</sub>) measurements from the Weybourne Atmospheric Observatory (WAO) are reported from March to April 2013 using a quadruple chemical ionization mass spectrometer with the I<sup>-</sup> ionization scheme. WAO is a rural coastal site with generally low NO<sub>x</sub> concentrations, a type of location poorly studied for ClNO<sub>2</sub> production. Concentrations of ClNO<sub>2</sub> exceeded that of the limit of detection (0.8 ppt) on each night of the campaign, as did concentrations of N<sub>2</sub>O<sub>5</sub>, which was also measured simultaneously with the Cambridge Broadband Cavity Enhanced Absorption Spectrometer. A peak concentration of 65 ppt of ClNO<sub>2</sub> is reported here. Vertical profiles of ClNO<sub>2</sub> from early- to middle-morning flights in close proximity to WAO are also reported, showing elevated concentrations at low altitude. The photolysis of observed ClNO<sub>2</sub> and a box model utilizing the Master Chemical Mechanism modified to include chlorine chemistry was used to calculate Cl atom concentrations. This model utilized numerous VOCs from the second Tropospheric Organic Chemistry project in 2004, at the same location and time of year. From this the relative importance of the oxidation of three groups of measured VOCs (alkanes, alkenes, and alkynes) by OH radicals, Cl atoms, and O<sub>3</sub> is compared. Cl atom oxidation was deemed generally insignificant at this time and location for total oxidation due to the much lower concentration of ClNO<sub>2</sub> observed, even following the night of greatest ClNO<sub>2</sub> production.

### 1. Introduction

Oxidation reactions in the troposphere govern the fate of primary trace gaseous pollutants and have an important influence on air quality and climate (Prinn, 2003). Recent studies have shown that Cl atoms from photolysis of nitryl chloride (ClNO<sub>2</sub>) may contribute significantly to the total oxidizing capacity (Bannan et al., 2015; Osthoff et al., 2008; Phillips et al., 2012; Tham et al., 2014). Cl atoms are highly reactive toward VOCs, and rate coefficients for reactions with alkanes are generally 2 orders of magnitude larger than OH. Calculations show that Cl atoms from ClNO<sub>2</sub> photolysis were an important oxidiser in London during the summer ClearfLo campaign where a maximum value of 724 ppt of ClNO<sub>2</sub> was observed with mean nighttime concentration of 84 ppt (Bannan et al., 2015). In that study calculations showed that Cl was responsible for up to 11% of alkane oxidation, 10% of alkyne oxidation, and was generally insignificant in terms of alkene oxidation. Tham et al. (2014) also showed that Cl production from ClNO<sub>2</sub> photolysis exceeded that of OH production from O<sup>1</sup>(D) by a factor of 3 in the morning, thus having a significant influence on photochemistry during this period. Cl-induced oxidation may have a more significant global influence than initially considered, often enhancing tropospheric ozone production (Sarwar et al., 2012, 2014; Simon et al., 2009).

Heterogeneous reaction of N<sub>2</sub>O<sub>5</sub> and chloride containing aerosol was first shown in laboratory to produce ClNO<sub>2</sub> by Finlayson-Pitts et al. (1989), and recently, field measurements in both continental and polluted coastal sites have reported concentrations ranging between a few ppt and 4 ppb (Bannan et al., 2015; Kercher et al., 2009; Mielke et al., 2013, 2015, 2011; Osthoff et al., 2008; Phillips et al., 2012; Riedel et al., 2012; Tham et al., 2014; Thornton et al., 2010; Wang et al., 2016). Global modeling studies of ClNO<sub>2</sub> have now shown the importance of this species with one area of predicted high production being western Europe, especially in the winter months (Sarwar et al., 2014).

As well as being a source of reactive Cl atoms, ClNO<sub>2</sub> production also alters the lifetime of NO<sub>x</sub> by reducing the production of nitric acid in favor of ClNO<sub>2</sub> production. ClNO<sub>2</sub> acts to recycle the NO<sub>x</sub> in comparison with nitric acid production that is regarded as a terminal sink (Finlayson-Pitts et al., 1989). Therefore, it is important to measure nitric acid in conjunction with N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> so that the efficiency of the production of ClNO<sub>2</sub> can be compared. The release of NO<sub>x</sub> from ClNO<sub>2</sub> has a potentially significant effect on tropospheric ozone production in the early morning (Riedel et al., 2014), with up to 22% of NO<sub>x</sub> cycling coming from this source alone (Osthoff et al., 2008). This may have significant implications in regions where local emissions of NO<sub>x</sub> are minimal, an example being a remote coastal site.

As well as spatially limited ground-based measurements, with only two reported measurements in Europe (Bannan et al., 2015; Phillips et al., 2012), there are also very limited airborne data other than Young et al. (2012). Vertical profiles presented from the Los Angeles Basin show a relatively constant concentration between approximately 1 and 2 ppb within the nocturnal boundary layer (Young et al., 2012). Cl activation is less well understood in low NO<sub>x</sub> conditions (Lawler et al., 2011) such as those that would be expected in a rural marine environment. Hence, measurements in locations including Weybourne are imperative.

In order to assess the impact that ClNO<sub>2</sub> has on tropospheric chemistry around the UK, measurement campaigns were set with the aim of measuring ClNO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, and other species influencing their production using a quadrupole chemical ionization mass spectrometer (CIMS). The first new set of measurements were made during a 3 week deployment at the Weybourne Atmospheric Observatory (WAO), a remote coastal site in Norfolk, and this was made in conjunction with the Cambridge Broadband Cavity Enhanced Absorption Spectrometer (BBCEAS) that measures N<sub>2</sub>O<sub>5</sub> (Kennedy et al., 2011). Nitric acid, among other species, was concurrently measured with CIMS. Aircraft measurements using CIMS on board the BAe-146 research aircraft in fairly close proximity to the WAO were made also in order to provide insight into the vertical profiles of these species around this location. As in Bannan et al. (2015) study the effect that Cl from the photolysis of ClNO<sub>2</sub> has on the total tropospheric oxidizing capacity at WAO is evaluated.

## 2. Measurement Locations and Analytical Techniques

### 2.1. Weybourne Atmospheric Observatory

The Weybourne site is situated on the North Norfolk Coast (52.950490°N, 1.122017°E) around 150 m from the shoreline of the North Sea and more than 1 km away from the nearest small town of Weybourne. The site details are described in detail in Penkett et al. (1999). Plumes of polluted air masses from the UK and continental Europe are common with influence from the Arctic also observed, thus indicating the wide variety of air masses that can be sampled at this site. Between 14 March 2013 and 4 April 2013, an intensive observation period was undertaken where the CIMS and BBCEAS ran an intercomparison study at this site. NO<sub>y</sub> at this site is measured by the Thermo Fisher Model 42i (NO-NO<sub>2</sub>-NO<sub>x</sub>) analyzer and O<sub>3</sub> is measured by the Thermo Fisher Model 49i ozone analyzer.

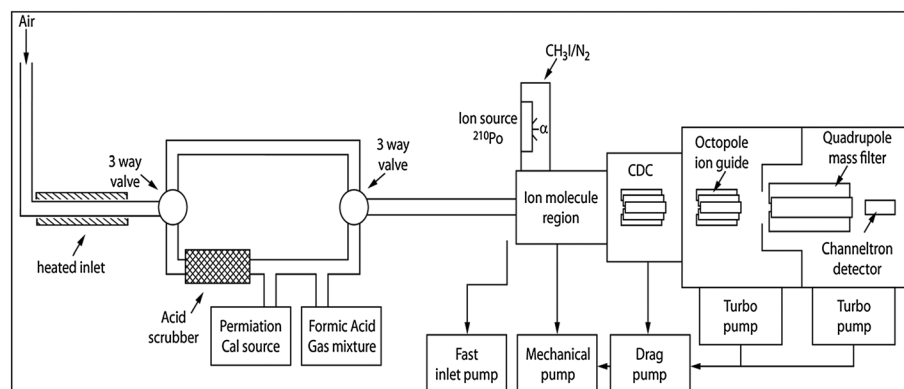
### 2.2. BAe-146 Airborne Measurements

Research flight B822 was undertaken on 1 January 2014, taking off from Cranfield Airport. The flight track took was first to the North Norfolk Coast at an altitude of 3,000 m, and once the coastline was reached low level runs to 30.5 m were made so that altitude profiles could be obtained. All low level runs were over the North Sea in close proximity to the East Anglian coastline.

### 2.3. Chemical Ionization Mass Spectrometry

A chemical ionization mass spectrometer (CIMS) was used to make measurements of ClNO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>, at 1 Hz frequency for all groups of measurements. The Manchester ground CIMS as described by Bannan et al. (2014, 2015) was used for ground-based measurements, and the Manchester flight CIMS as described by Le Breton et al. (2014) and Jones et al. (2014; 2017) was utilized for airborne measurements on board the Facility for Airborne Atmospheric Measurements (FAAM) British Aerospace 146 (BAe-146) research aircraft.

Both CIMS instruments were constructed and designed by the Georgia Institute of Technology and have been described in detail by Nowak et al. (2007), see also the schematic of Figure 1 for the ground CIMS and Figure 2 for the aircraft CIMS. Briefly, the CIMS detects trace gases in the atmosphere by selectively ionizing specific molecules and then detecting ions using mass spectrometry (Nowak et al., 2007).

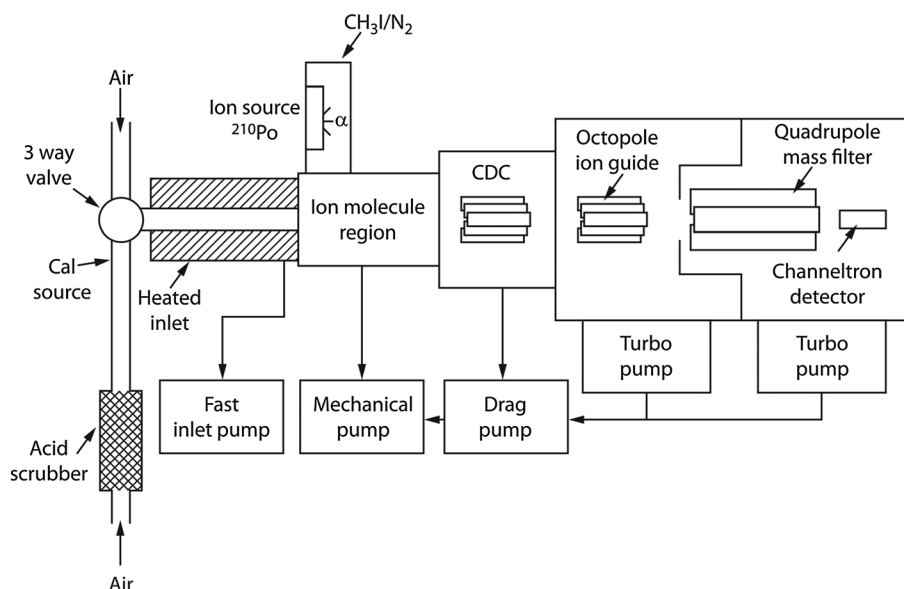


**Figure 1.** Schematic of the Manchester ground CIMS instrument.

The airborne measurements were made with the exact methods as described by Le Breton et al. (2014) and Jones et al. (2014, 2017). The procedures used to make the ground-based measurements with the CIMS are identical to that reported in Bannan et al. (2015) other than the inlet design. At the Weybourne atmospheric observatory there is a permanent 10 m high glass inlet with a diameter of approximately 30 cm. The flow rate within this inlet was in excess of 200 standard liters per minute (slm), from which we subsampled 18 slm by the use of the fast inlet pump illustrated in Figure 1. The glass inlet was chosen to make these measurements due to the high flow rate, and large volume of air sampled to surface area ratio in order to minimize possible surface reactions. The 3/8" PFA connection between the glass inlet and CIMS was heated to 40°C, roughly 30 cm in length and was regularly changed (approximately every 2 days).

### 2.3.1. Calibrations, Sensitivity, and Limit of Detection of the CIMS

The ion molecule chemistry using iodide ions ( $I^-$ ) to detect  $N_2O_5$  as  $NO_3^-$  ( $m/z = 62$ ) has been described in detail by Le Breton et al. (2014) and was also employed for measurements of  $N_2O_5$  in this study.  $ClNO_2$  was measured at the mass  $IClNO_2$  ( $m/z$  207.9) as in Osthoff et al. (2008) and Bannan et al. (2015). Studies such as Wang et al. (2014) and Veres et al. (2015) have noted that measurements of  $N_2O_5$  at  $m/z$  62 are not



**Figure 2.** Schematic of the Manchester flight CIMS instrument.

interference free, with  $\text{HNO}_3$  and  $\text{HO}_2\text{NO}_2$  being identified as key species that could cause interference. Possible interferences from  $\text{HNO}_3$  at both atmospherically relevant and very high concentrations  $m/z$  62 have been extensively studied in the laboratory, and no evidence for this has been observed. Possible interferences from PAN or  $\text{HO}_2\text{NO}_2$  at  $m/z$  62 have not been specifically checked for this work; however, both absolute concentrations and time series against the BBCEAS show a good agreement in  $\text{N}_2\text{O}_5$  measurements in past intercomparisons (Le Breton et al., 2014) and this study. Such interferences are therefore not deemed important in here.

Final calibration of the CIMS was completed post campaign for both  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$ , relative to formic acid, which was calibrated and measured throughout the campaign. This is completed assuming the ratio between formic acid and  $\text{ClNO}_2$  sensitivity remains constant throughout. Procedures for calibrations and determination of backgrounds for  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  are described in detail by Bannan et al. (2015). Calibration of  $\text{N}_2\text{O}_5$  was completed by flowing dry  $\text{N}_2$  over solid purified  $\text{N}_2\text{O}_5$  into the CIMS and a  $\text{NO}_x$  analyzer (Thermo Fisher, model 42i NO- $\text{NO}_2$ - $\text{NO}_x$  Analyzer), with the concentration determined by the stoichiometric ratio of  $\text{NO}_2:\text{N}_2\text{O}_5$ , in R5. There have been reported instances where  $\text{NO}_3$  is sensitive on the  $\text{NO}_x$  analyzer, thus having the potential to influence the concentrations of  $\text{N}_2\text{O}_5$  that are reported in this study. However, numerous intercomparisons with the BBCEAS, including this and the Le Breton et al. (2014) study, show that this calibration method works well, producing very good agreements in total concentrations reported, in part due to the high purity of  $\text{N}_2\text{O}_5$  that was synthesized. The possible interference of  $\text{NO}_y$  on the  $\text{NO}_x$  analyzer is therefore not deemed important in terms of our reported concentrations.  $\text{ClNO}_2$  was produced by flowing a known concentration of  $\text{N}_2\text{O}_5$  in dry  $\text{N}_2$  through a wetted NaCl scrubber. Conversion of  $\text{N}_2\text{O}_5$  to  $\text{ClNO}_2$  can be as efficient as 100% on sea salt, but it can also be lower, for example, if  $\text{ClNO}_2$  were to convert to  $\text{Cl}_2$  (Roberts et al., 2008). For NaCl the conversion efficiency has however been as low as 60% (Hoffman et al., 2003). In this calibration we have followed the accepted methods of Osthoff et al. (2008) and Kercher et al. (2009) that show a conversion yield of 100% and have assumed this yield in the calibrations of this study.

For the Weybourne measurement campaign the sensitivity of  $\text{ClNO}_2$  was determined to be 3.9 counts  $\text{ppt}^{-1}$ , and for  $\text{N}_2\text{O}_5$  15.9 counts  $\text{ppt}^{-1}$  is reported. The  $3\sigma$   $\text{ClNO}_2$  LOD during the summer Weybourne campaign was 0.8 ppt and the  $3\sigma$  LOD of  $\text{N}_2\text{O}_5$  was 1.5 ppt. For the airborne measurements a sensitivity of 33 and 650 counts  $\text{ppt}^{-1}$  is reported with a  $3\sigma$  LOD of 4 and 2 ppt for  $\text{ClNO}_2$  and  $\text{N}_2\text{O}_5$ , respectively. Using the error in the individual slope of the calibrations results in a total uncertainty of 30% for both  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$ .

As described in Bannan et al. (2015) no normalization was required for  $\text{N}_2\text{O}_5$  or  $\text{ClNO}_2$  as the  $\text{I}^-$  (mean =  $1.6 \times 10^6$  cps, standard deviation =  $2.8 \times 10^4$  cps) and  $\text{I.H}_2\text{O}^-$  (mean =  $7.7 \times 10^5$  counts per second (cps), standard deviation =  $3.2 \times 10^4$  cps) cps were well in excess of what is required for  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  to be independent to the small changes (<5%) in the reagent ions that were observed throughout the campaign.

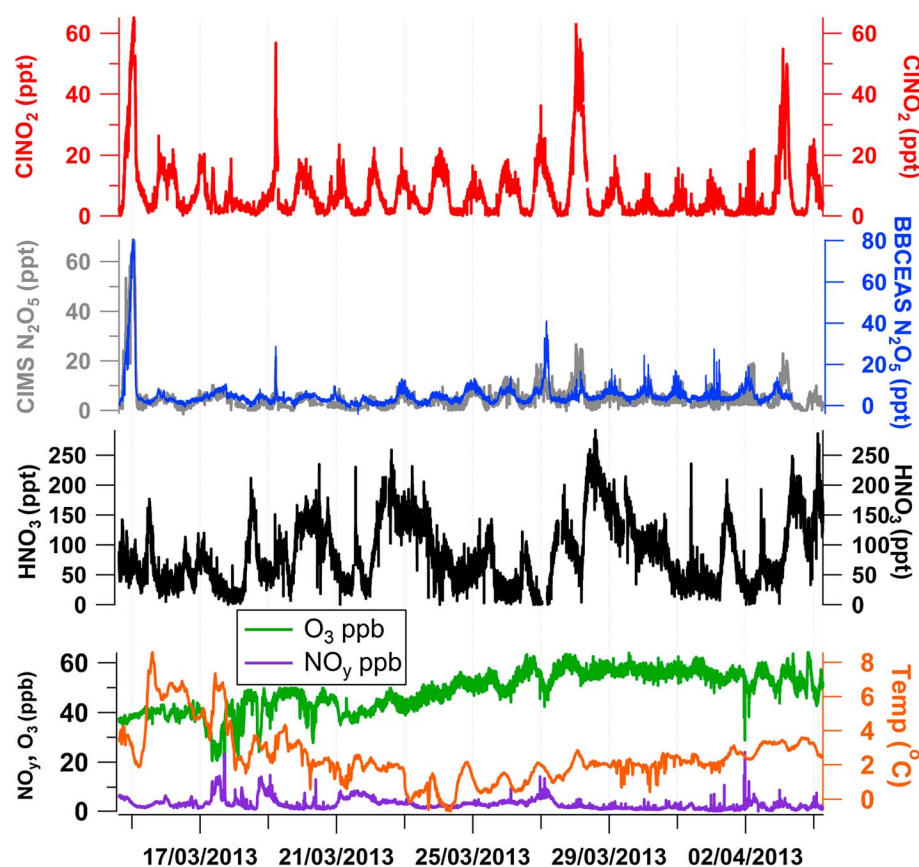
The CIMS produced 1 Hz data from sampling and calibration cycles that were averaged to 30 s. Correlation with meteorological data was completed with 5 min averaged data for the ground-based campaign. Throughout the Weybourne Campaign automatic hourly mass scans were utilized in order to give a complete mass spectrum between 0 and 300 amu.

#### 2.4. Filter Sampling

Filter samples were run at a 24 h time resolution using a high-volume sampler at a flow rate of 1  $\text{m}^3$  per minute. Conductively coupled plasma optical emission spectrometry (ICP-OES) was used to measure the total chloride deposited on the filter over the 24 h period.

#### 2.5. Master Chemical Mechanism Model Runs

A zero-dimensional Facsimile box model was employed to calculate Cl atom concentrations during the campaign so that the rate of oxidation of VOCs by Cl atoms can be compared with oxidation by modeled OH (which compared well to OH observed during second Tropospheric ORganic CHEMistry (TORCH 2)) and measured ozone. The model was constrained to pressure, temperature,  $\text{ClNO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{O}_3$ ,  $\text{SO}_2$ , NO,  $\text{NO}_2$ , and  $\text{HNO}_3$  from the field measurement made in March 2013 combined with VOC data and adapted photolysis rates measured from TORCH 2 (April–May 2004) at the same location (WAO). The TORCH 2 VOC data were representative of the time of year. It was also from an intense measurement campaign and gave measurements



**Figure 3.** Time series of  $\text{ClNO}_2$ ,  $\text{N}_2\text{O}_5$ , and  $\text{HNO}_3$  from the Manchester ground CIMS,  $\text{N}_2\text{O}_5$  from the BBCEAS for the complete Weybourne campaign.  $\text{NO}_y$ ,  $\text{O}_3$ , and temperature are also shown.

of 27 different C2–C10 nonmethane hydrocarbons and C2–C4 oxygenated volatile organic compounds. This allows for a more comprehensive estimate of the oxidation capacity of Cl, OH, and  $\text{O}_3$ . The photolysis rates of key species were first calculated under clear-sky conditions and then compared with those measured in TORCH 2 to obtain a scaling factor for March 2013J( $\text{ClNO}_2$ ) was calculated using the Tropospheric Ultraviolet and Visible Radiation Model, version 4.1, neglecting any upwelling radiation, and then scaled in order to match the measured  $J(\text{NO}_2)$  as has been used in previous studies such as Stone et al. (2010). Measurements of downwelling actinic flux as a function of wavelength across the full actinic range were made using a  $2\text{-}\pi$  solid angle detection spectral radiometer (Edwards & Monks, 2003). The photolysis frequency for  $\text{NO}_2$  was calculated from these measurements using laboratory data for  $\text{NO}_2$  absorption cross sections, and photodissociation quantum yields to generate  $\text{O}(^3\text{P})$  atoms.

The box model used to calculate Cl atom concentrations during the campaign contained a subset of the Master Chemical Mechanism v3.2 (Jenkin et al., 2012), including the Cl atom oxidation of seven measured alkanes (C1–C8). As previously reported in Bannan et al. (2015) the Master Chemical Mechanism (MCM) does not contain a mechanism for the Cl atom initiated oxidation of alkenes (C2–C5) or alkynes (acetylene). Reactions of Cl atoms with these measured species were added to MCM v3.2 mechanism using rate coefficients taken from the National Institute of Standards and Technology (NIST) database (Manion et al., 2014). For H-atom abstraction channels the reported yield was used to generate HCl, but for other channels the reaction was treated as a simple loss for Cl atoms.

The model does not contain an inorganic mechanism for chlorine, so similar chemistry reported by Riedel et al. (2012) and utilized in the box model of Bannan et al. (2015) was included (R1–R9).





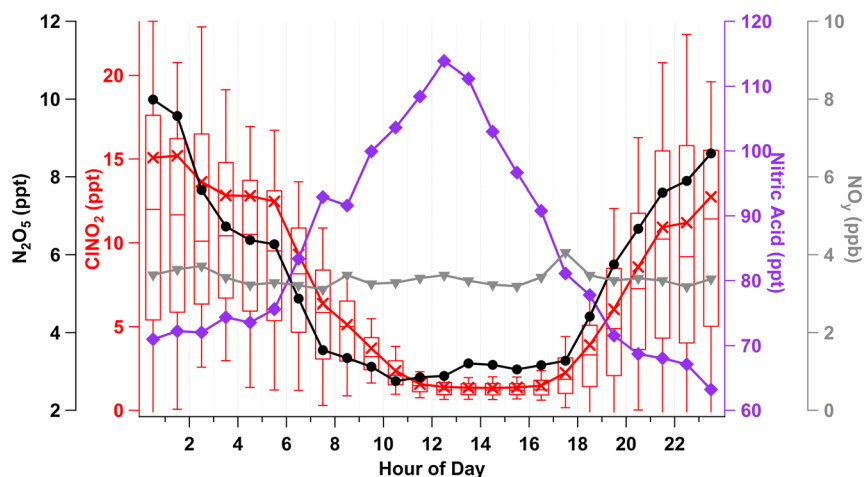


Figure 4. Average diurnal cycle of N<sub>2</sub>O<sub>5</sub>, ClNO<sub>2</sub>, NO<sub>y</sub>, and HNO<sub>3</sub> for the complete Weybourne campaign.



Two models were developed: one constrained to the measured ClNO<sub>2</sub> data with additional chlorine reactions and a chemically identical model without any Cl sources (hence, Cl atom concentrations were zero). This way a comparison was made between the rate of oxidation of VOCs by Cl atoms with the rate of oxidation by modeled OH and measured ozone.

The only source of Cl atoms considered in the model was the initial photolysis of ClNO<sub>2</sub>, and hence, HCl and other gas-phase inorganic Cl species in the reaction mechanism described previously are only generated by

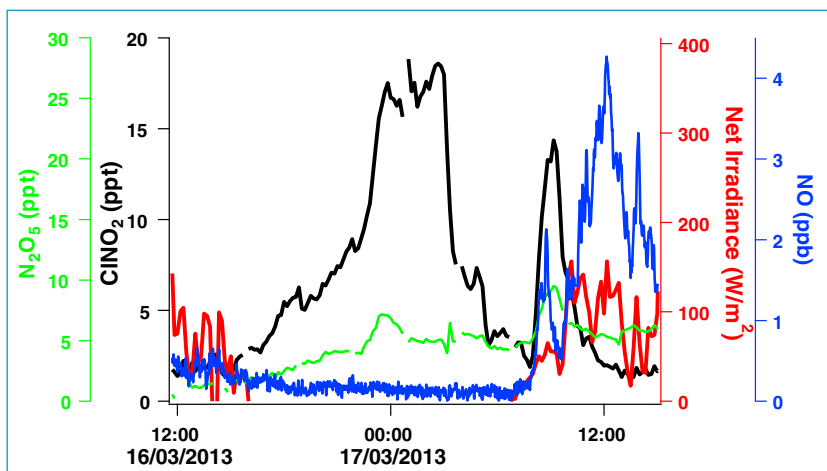
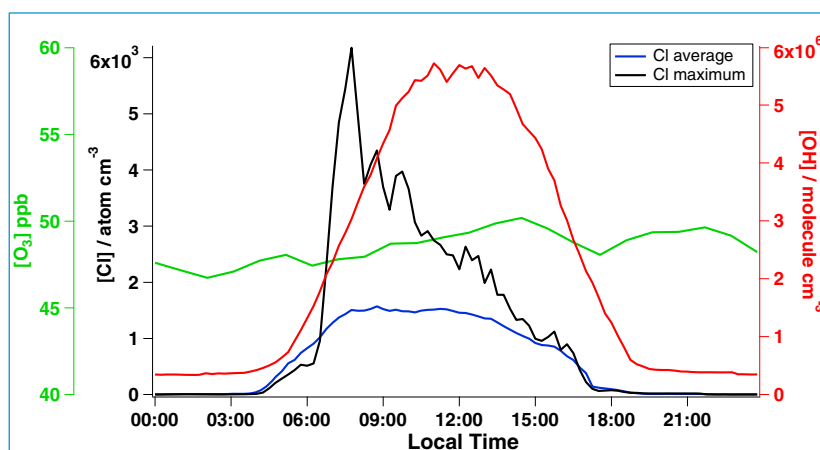


Figure 5. Postsunrise peaks of ClNO<sub>2</sub> on the morning of 17 March. Black trace indicates ClNO<sub>2</sub> concentration, and red shows solar radiation. Green shows N<sub>2</sub>O<sub>5</sub> from the CIMS, and blue shows NO.



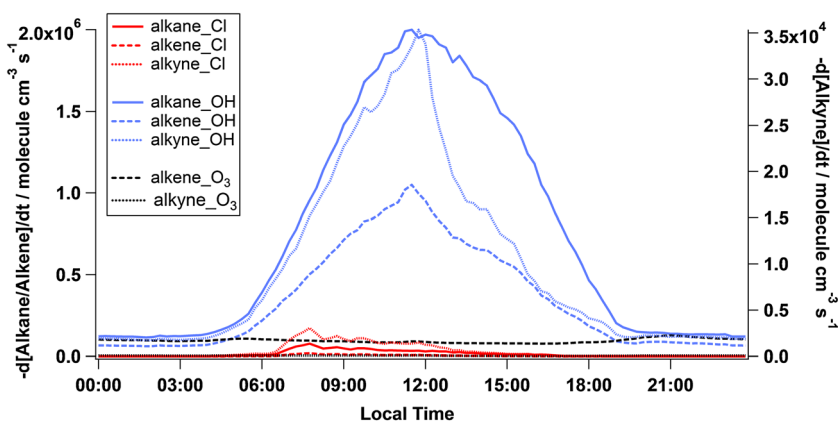
**Figure 6.** Cl atom concentration profile calculated for 15 March 2013 (black), during which the maximum observed concentration of  $\text{ClNO}_2$  was observed, Cl atom concentration profile calculated as an average for the entire campaign (blue), and the modeled OH concentration averaged for the TORCH 2 campaign (red). The 2013 campaign averaged measured  $\text{O}_3$  concentration is also included (green).

the model with an assumed initial concentration of zero. Chlorine atom concentrations were then calculated by the box model using a Facsimile integrator (Curtis & Sweetenham, 1987) and constrained with measured concentrations of VOCs, pressure, temperature,  $\text{ClNO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{O}_3$ ,  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{HNO}_3$ , and photolysis frequencies with a time step of 900 s. Additional details regarding the box model methodology can be found in Whalley et al. (2010). For all unconstrained modeled intermediates a first-order loss rate ( $k$ ) was included. This loss rate varied as a function of the average measured boundary layer height,  $h$ , from TORCH 2 ( $k = V_d/h$ ), where  $V_d$  represents a deposition velocity that was taken to be equal to  $1 \text{ cm s}^{-1}$  for all of the model-generated species. The average measured boundary layer height was varied within the model from 300 m at night increasing to 1,300 m in the morning as the boundary layer collapses and 1,800 m in the afternoon. The boundary layer was measured by vertical wind profile data from the Universities' Facility for Atmospheric Measurement's 1290 Megahertz (MHz) Degreane Mobile Wind Profiler.

### 3. Results and Discussion

#### 3.1. Ground $\text{ClNO}_2$ Measurements

The complete time series of  $\text{ClNO}_2$ ,  $\text{N}_2\text{O}_5$ , and  $\text{HNO}_3$  as measured by CIMS are shown in Figure 3 for the Weybourne Campaign.  $\text{ClNO}_2$  and  $\text{N}_2\text{O}_5$  exceeded the limit of detection on every night of the measurement campaign during nighttime hours. A mean nighttime (sunset-sunrise)  $\text{ClNO}_2$  concentration of 10.5 ppt was observed with a maximum peak of 65 ppt. The peak concentration of  $\text{N}_2\text{O}_5$  is similar to that of  $\text{ClNO}_2$  at



**Figure 7.** Rate of removal of alkanes, alkenes, and alkynes by reaction with the oxidants OH (modeled),  $\text{O}_3$  (measured, campaign average), and Cl atoms calculated for 15 March 2013, when the calculated Cl atom concentration was at its maximum.

**Table 1**

Relative Importance of Cl, OH, and O<sub>3</sub> to the Oxidation of Three Groups of VOCs From Both London Average and Maximum (Bannan et al., 2015) and the Weybourne Average and Maximum

	London (max)	London average	Weybourne (max)	Weybourne average
Alkane Cl%	14.46	3.51	1.85	0.98
Alkane OH%	85.54	96.49	98.15	99.02
Alkane O <sub>3</sub> %	-	-	-	-
Alkene Cl%	2.64	0.62	0.69	0.35
Alkene OH%	76.33	77.92	77.98	78.25
Alkene O <sub>3</sub> %	21.03	21.46	21.32	21.39
Alkyne Cl%	24.95	6.96	4.99	2.58
Alkyne OH%	74.04	91.97	94.28	96.67
Alkyne O <sub>3</sub> %	1.01	1.25	0.73	0.75

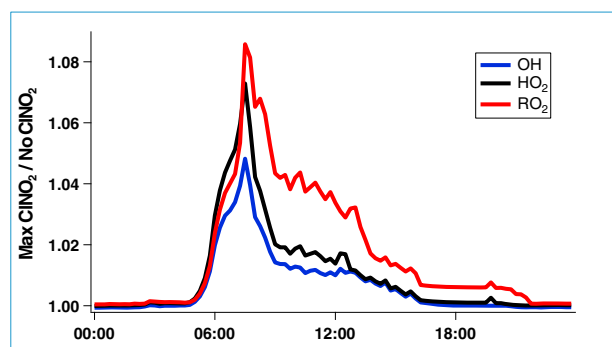
Note. VOC concentrations data used for the calculations for London are included as well as for Weybourne, using measured VOC data.

68.5 ppt, on the same night as the maximum ClNO<sub>2</sub>; but the mean nighttime peak is lower at 6.7 ppt. A time series of measured chloride from filter sampling at a 24 h time resolution is presented in Figure S1.

Measured results are substantially lower than that of other reported U.K. measurements of ClNO<sub>2</sub> in London (Bannan et al., 2015), where a mean nighttime ClNO<sub>2</sub> concentration of 84 ppt was observed, together with a median value of 34 ppt and a maximum peak of 724 ppt. This seems to have been mainly caused by significantly higher NO<sub>3</sub> production rate ( $7.8 \times 10^{-6}$  molecules cm<sup>-3</sup> s<sup>-1</sup>) in London than those in Weybourne ( $3.5 \times 10^{-6}$  molecules cm<sup>-3</sup> s<sup>-1</sup>) because of the higher NO<sub>x</sub> (~13 ppb) levels in London compared with that (~3 ppb) in Weybourne. A campaign high N<sub>2</sub>O<sub>5</sub> concentration in Weybourne was ~67 ppt, as measured by the CIMS, also significantly lower than that reported for London. Intercomparison between the CIMS and BBCEAS for N<sub>2</sub>O<sub>5</sub> measurements is presented in Figure 3. The R<sup>2</sup> of the relation of the CIMS to BBCEAS N<sub>2</sub>O<sub>5</sub> measurements is 0.8 ([N<sub>2</sub>O<sub>5</sub>] CIMS = 1.06 × [N<sub>2</sub>O<sub>5</sub>] BBCEAS + 0.81 pptv), which can be compared with the airborne measurements of Le Breton et al. (2014) showing the reliability of the measurements made.

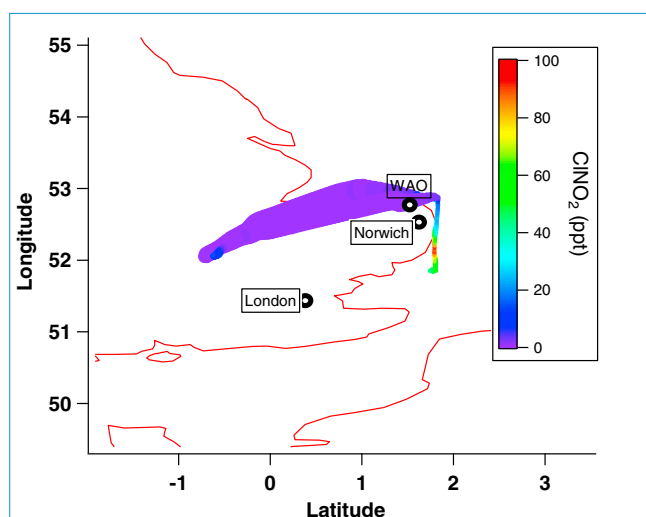
Comparable to the measurements in Bannan et al. (2014), a very obvious diurnal profile was observed in the ClNO<sub>2</sub> throughout that is representative of this species (Kercher et al., 2009; Mielke et al., 2011; Osthoff et al., 2008; Thornton et al., 2010). Concentrations of ClNO<sub>2</sub> above the limit of detection were measured, on average, until 11 A.M. and then built up following sunset. ClNO<sub>2</sub> concentrations peak, on average, at 15.1 ppt and drop below the LOD at approximately midday (Figure 4). As in the Bannan et al. (2015) study, photolysis rates and lifetimes have been calculated for each night of the measurement campaign. During the London campaign an average lifetime of 2.6 h, with respect to photolysis, was calculated. In Weybourne a very similar lifetime of 2.5 h was calculated, despite the seasonal difference. Both lifetimes with respect to photolysis are in range of the values presented by Ganske et al., (1992) (0.73–31 h, depending on solar zenith angle) and Ghosh et al. (2011). The average diurnal profile of N<sub>2</sub>O<sub>5</sub> is similar to that of ClNO<sub>2</sub>. The exception to this trend is seen in the nitric acid average diurnal trend where a daytime maximum is seen. This is as would have been expected based on nitric acid production pathways.

However, there are exceptions to the diurnal trend of ClNO<sub>2</sub> where morning peaks were observed, such as on 17 March (Figure 5). This is analogous to that reported in Bannan et al. (2015) where concentrations rose up to 140 ppt following sunrise. In Weybourne the daytime peak increased to a comparatively lower concentration of 15 ppt but was still significant relative to the concentrations seen at this measurement site. At the time of increased ClNO<sub>2</sub> during the morning of 17 March there was a very slight increase in N<sub>2</sub>O<sub>5</sub>, approximately 2 ppt, which was not observed in the BBCEAS time series, potentially suggesting a sensitivity change in the CIMS at this time. However, other masses such as HCN (*m/z* 154) and nitric acid (*m/z* 189.9) that were simultaneously measured with the CIMS did not show this



**Figure 8.** Enhancement of OH, HO<sub>2</sub>, and RO<sub>2</sub> species observed from addition of the chemical oxidation reactions using the maximum calculated [Cl].





**Figure 9.** The FAAM BAe146 flight track on 8 January 2014 around East Anglia and its surrounding coastline. ClNO<sub>2</sub> mixing ratios are color coded from 0 ppt to 80 ppt.

trend, and we are therefore unsure of the source of discrepancy between BBCEAS and CIMS.

The timing of the enhancement seen in ClNO<sub>2</sub> correlates well with the largest NO concentration observed (up to ~2 ppb) during the measurement period (Figure 5). NO, an indicator of anthropogenic activity, increased significantly at this time indicating that a change in air mass that was being measured at the site was one with a possible urban origin. Enhancement of NO<sub>x</sub> species from an urban environment could enhance N<sub>2</sub>O<sub>5</sub> production and when mixed with chloride containing aerosol produce relatively large concentrations of ClNO<sub>2</sub> at this site.

Given that the average lifetime of ClNO<sub>2</sub> was calculated to be 2.5 h (i.e., a loss rate of  $3.57 \times 10^{-4} \text{ s}^{-1}$ ), should the loss rate be the same as measured at the surface, a concentration of 309 ppt would have been required to see such a peak at 9:20 A.M., over 4 h after sunrise on 17 March. There are other examples, including 23 and 25 March as well as at the final day of sampling on 4 April where there is a small enhancement following sunrise but none as defined at 17 March. Of these exam-

ples it is only 17 March where a correlation with enhancing NO is observed. It is therefore possible that the early-morning enhancements could also be due to mixing down of ClNO<sub>2</sub> from an elevated layer, resulting in a peak in mixing ratios as surface level.

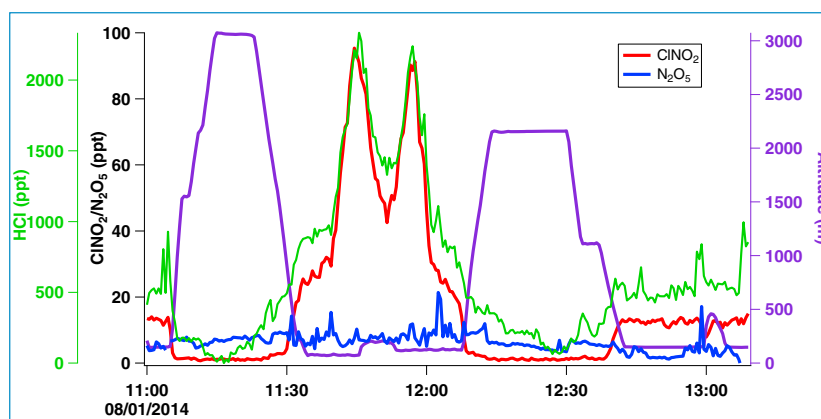
On all days where a ClNO<sub>2</sub> concentration enhancement was observed following sunrise, the wind direction originated from the ocean possibly indicating that production over the ocean, especially on the shore where waves are creating the particulate chloride aerosol, is more efficient. However, there are also days where the wind direction is from the sea and no daytime enhancement is observed. The height of the marine boundary layer is a parameter that was not measured throughout the campaign, but the varying height of this may have had an effect on these daytime increased in ClNO<sub>2</sub> concentrations.

### 3.2. Implications for VOC Oxidation at WAO

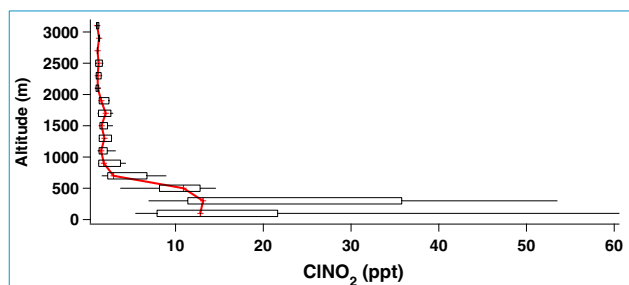
As in the Bannan et al. (2015) study the total rate of removal of alkanes, alkenes, and alkynes by reaction with the oxidants OH, O<sub>3</sub>, or Cl atoms at a given time during the campaign was calculated using

$$-d[\text{alkanes}]/dt = [X] \sum_j k_{X+\text{alkane},j} [\text{alkane}, j] \tag{1}$$

$$-d[\text{alkenes}]/dt = [X] \sum_j k_{X+\text{alkene},j} [\text{alkene}, j] \tag{2}$$



**Figure 10.** Time series of 30 s averaged ClNO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, and HCl observations (left axis) with altitude (right axis) from 8 January 2014 flight.



**Figure 11.** Altitude profile of  $\text{ClNO}_2$  from measurements around East Anglia and its surrounding coastline.

$$-d[\text{alkynes}]/dt = [X] \sum_i k_{X+\text{alkyne},i} [\text{alkyne}, i] \quad (3)$$

where  $[X]$  is the concentration of modeled OH, measured  $\text{O}_3$ , or the calculated one of Cl atoms using the MCM at a given time in the campaign, and  $[\text{alkane}, i]$ ,  $[\text{alkene}, i]$ , and  $[\text{alkyne}, i]$  represent the corresponding measured speciated concentration of each alkane, alkene, and alkyne, and  $k_X$  is the individual bimolecular rate coefficient for the reaction of  $X$  with each species at the measured pressure and temperature. Rate coefficients were taken from those used in the MCM (Jenkin et al., 1997; Saunders et al., 2003) or from the NIST database (Manion et al., 2014). Two model runs were performed using this method, one with the maximum Cl atom production following the greatest night of  $\text{ClNO}_2$  production (65 ppt) and the other using the

average diurnal variation of  $\text{ClNO}_2$ . A baseline model was also run without the Cl chemistry being included in order to show the effect of the inclusion of Cl chemistry has to the  $\text{RO}_2$  production and consequently  $\text{O}_3$  production following a night of  $\text{ClNO}_2$  production.

For both runs the campaign averaged diurnal concentrations for  $\text{O}_3$  at the time of the  $\text{ClNO}_2$  measurements were integrated with modeled OH and VOCs measurements from TORCH 2 to calculate the rates of oxidation. The measured  $\text{O}_3$  concentration from this study, modeled OH concentration, and the average and maximum Cl atom concentration calculated using the MCM from  $\text{ClNO}_2$  photolysis are shown in Figure 6.

Figure 6 shows that, as would have been expected and in agreement with other studies of this type, calculated Cl atom concentrations rise rapidly after sunrise (5 A.M. local time). For 15 March 2013, concentrations reached  $6 \times 10^3$  atoms  $\text{cm}^3$ , which is about 5 times lower than the maximum calculated for London and just under 1,000 times lower than the modeled peak concentration of OH. As in Bannan et al. (2015) study although  $\text{ClNO}_2$  concentrations in this study are very low by noon, Cl atoms are recycled via reactions (R1–R9) and do not reach zero again until later in the afternoon.

The chemical turnover rates for the oxidation of the sum of measured alkanes, alkenes, and alkynes by reaction with OH,  $\text{O}_3$ , or Cl atoms, as calculated by equations (1)–(3), are shown in Figure 7 for 15 March, when Cl atoms peaked. By summing the oxidation rate across this 24 h period shown in Figure 7 (maximum Cl concentration), the total percent removed by reaction with the three oxidants for each type of VOC was calculated (Table 1). The relative importance of Cl from  $\text{ClNO}_2$  in terms of total oxidation at this site is negligible and much less important in comparison with the London study. This is also reflected in the amount of extra  $\text{RO}_2$ , which at maximum is only 9% higher at 7:30 A.M., with only very little increase in  $\text{HO}_2$  (7%) and OH (5%) concentrations, even following the night of greatest  $\text{ClNO}_2$  production (Figure 8). This shows that  $\text{ClNO}_2$  is generally insignificant in terms of the oxidation capacity at this site and time.

### 3.3. Airborne $\text{ClNO}_2$ Measurements

$\text{ClNO}_2$  concentrations and the flight altitude for the FAAM BAe-146 B822 flight around the East Anglian coast are illustrated in Figure 9. Figure 10 shows the flight track, altitude of measurement, and  $\text{ClNO}_2$ ,  $\text{N}_2\text{O}_5$ , and HCl concentrations throughout the complete flight. There are no  $\text{NO}_x$  data available for this flight. The time series shows that a peak concentration of 95 ppt of  $\text{ClNO}_2$  was observed, with Figure 11 showing the vertical profile of these species. Figures 9–11 show much elevated  $\text{ClNO}_2$  concentrations close to the sea surface, reaching very low concentrations above 500 m in altitude. The altitude profile presented here is similar to that of Young et al. (2012), in that the highest concentrations were observed at the surface with a reduction in concentration seen after approximately 600 m in height. Altitude profiles of  $\text{ClNO}_2$  in Young et al. (2012) were only reported between 0–1000 m and did not include measurements of  $\text{N}_2\text{O}_5$  or other species.

The time of measurements for B822 should be noted. Concentrations of  $\text{ClNO}_2$  up to 95 ppt were measured above the sea surface up to midday, suggesting that nighttime concentrations of this species, in a region with a large amount of ship activity and surrounding land emissions, and thus high  $\text{NO}_x$  emissions, would have been significant. Daytime peaks have already been observed in this region as illustrated in Figure 5. Very

small concentrations of  $\text{N}_2\text{O}_5$  were observed during the flight, with only very small spikes being observed throughout, suggesting a shorter lifetime in conjunction with possibly a lower concentration of  $\text{N}_2\text{O}_5$  during the flight.

There are two major peaks in  $\text{ClNO}_2$  observed in this flight, Figure 10, both of which are taken in a very similar location and altitude as the return flight track mirrored the outbound (Figure 10). The first peak is observed at 11:44:30 A.M. where a peak concentration of 95 ppt was measured, and on the second leg at 11:57:30 A.M., 91 ppt was observed. The loss rate of  $\text{ClNO}_2$  calculated, assuming the same parcel of air was sampled, resulted in a lifetime of 4.8 h, about 50% slower than that of the average calculated from the Weybourne campaign.

#### 4. Conclusions

Concentrations of up to approximately 70 ppt of  $\text{ClNO}_2$  have been measured simultaneously with  $\text{N}_2\text{O}_5$  at the Weybourne Atmospheric Observatory between 14 March 2013 and 4 April 2013. An intercomparison with the Cambridge BBCEAS instrument for  $\text{N}_2\text{O}_5$  measurements against the CIMS at  $m/z$  62 reveals very good agreement in both trends and reported concentrations from independent calibrations, again revealing the reliability of this method. The diurnal profile of both measured  $\text{ClNO}_2$  and  $\text{N}_2\text{O}_5$  are similar to previous measurements (e.g., Osthoff et al., 2008), but early-morning elevations of  $\text{ClNO}_2$  are observed in this study. This daytime elevation is consistent with a change in air mass as depicted by a sharp increase in NO at the same time and likely not daytime production of this species. Vertical profiles of  $\text{ClNO}_2$  have also been reported here on board the Bae-146 research aircraft, showing much elevated concentrations at the surface of the East Anglian Coast.

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