

Observations of organic and inorganic chlorinated compounds and their contribution to chlorine radical concentrations in an urban environment in Northern Europe during the wintertime

5 Michael Priestley¹, Michael le Breton^{1†}, Thomas J. Bannan¹, Stephen D. Worrall^{1^}, Asan Bacak¹, Andrew R. D. Smedley^{1*}, Ernesto Reyes-Villegas¹, Archit Mehra¹, James Allan^{1,2}, Ann R. Webb¹, Dudley E. Shallcross³, Hugh Coe¹, Carl J. Percival^{1l}.

¹Centre for Atmospheric Science, School of Earth and Environmental Sciences, University of Manchester, Manchester, M13 9PL, UK

10 ²National Centre for Atmospheric Science, University of Manchester, Manchester, M13 9PL, UK

³School of Chemistry, The University of Bristol, Cantock's Close BS8 1TS, UK

[†]Now at Department of Chemistry and Molecular Biology, University of Gothenburg, 412 96 Göteborg, Sweden

[^]Now at School of Materials, University of Manchester, Manchester, M13 9PL, UK

15 ^{*} Now at School of Mathematics, University of Manchester, Manchester, M13 9PL, UK

^lNow at Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109

Correspondence to: Carl Percival (carl.j.percival@jpl.nasa.gov)

Abstract. A number of inorganic (nitryl chloride, ClNO₂; chlorine, Cl₂; and hypochlorous acid, HOCl) and chlorinated, oxygenated volatile organic compounds (CIOVOCs) have been measured in Manchester, UK during October and November 2014 using time of flight chemical ionisation mass spectrometry (ToF-CIMS) with the I⁻ reagent ion. CIOVOCs appear to be mostly photochemical in origin although direct emission from vehicles is also suggested. Peak concentrations of ClNO₂, Cl₂ and HOCl reach 506, 16 and 9 ppt respectively. The concentrations of ClNO₂ are comparable to measurements made in London, but measurements of CIOVOCs, Cl₂ and HOCl by this method are the first reported in the UK. Maximum HOCl and Cl₂ concentrations are found during the day and ClNO₂ concentrations remain elevated into the afternoon if photolysis rates are low. Cl₂ exhibits a strong dependency on shortwave radiation further adding to the growing body of evidence that it is a product of secondary chemistry, however night time emission is also observed. The contribution of ClNO₂, Cl₂ and CIOVOCs to the chlorine radical budget suggests that Cl₂ can be a greater source of Cl than ClNO₂, contributing ~~74-57%~~ of the Cl radicals produced on a high radiant flux day. In contrast, on a low radiant flux day, this drops to ~~47-14%~~ as both Cl₂ production and loss pathways are inhibited by reduced photolysis rates. This results in ClNO₂ making up the dominant fraction (~~68-83%~~) on low radiant flux days as its concentrations are still high. As most CIOVOCs appear to be formed photochemically, they exhibit a similar dependence on photolysis, contributing ~~between 15-3%~~ ~~-24%~~ of the Cl radical budget observed here.

35 1. Introduction

Oxidation controls the fate of many atmospheric trace gases. For example, increasing the oxidation state of a given species may increase its deposition velocity (Nguyen et al. 2015) or solubility (Carlton et al. 2006) and

reduce its volatility (Carlton et al. 2006), all of which act to reduce the atmospheric lifetime of that species and can lead to the formation of secondary material such as secondary organic aerosol (SOA) or ozone (O₃). As the
 40 identity of the chemical species change with oxidation, intrinsic and diverse properties of the chemical species are altered; influencing their toxicity (Borduas et al. 2015) and their impact on the environment e.g. cloud particle nucleating efficiency (Ma et al. 2013) or global warming potential (Boucher et al. 2009).

The hydroxyl radical (OH) is considered the most important daytime atmospheric oxidant due to its ubiquity and high reactivity with an average tropospheric concentration of 10⁶ molecules cm⁻³ (Heal et al. 1995). However,
 45 rate coefficients for the reaction of the chlorine radical (Cl) can be two orders of magnitude larger than those for OH (Spicer et al. 1998) indicating that lower Cl concentrations of 1x10⁴ atoms cm⁻³ that are estimated to exist in urban areas (e.g. Bannan et al., 2015), can be just as significant in their contribution to oxidation.

Cl initiated oxidation of volatile organic compounds (VOCs) forms chlorinated analogues of the OH initiated oxidation products, via addition (1) or hydrogen abstraction (2) forming HCl that may react with OH to
 50 regenerate Cl. Subsequent peroxy-radicals formed through Cl oxidation can take part in the HO_x cycle and contribute to the enhanced formation of O₃ and SOA (Wang & Ruiz 2017).



where X is OH or Cl.

55 Nitryl chloride (ClNO₂) is a major reservoir of Cl that is produced by aqueous reactions between particulate chloride (Cl⁻) and nitrogen pentoxide (N₂O₅) (4, 5). Gaseous ClNO₂ is produced throughout the night and is typically photolysed at dawn before OH concentrations reach their peak (6). This early morning release of Cl induces oxidation earlier in the day and has been shown to increase maximum 8 hour mean O₃ concentrations by up to 7 ppb under moderately elevated NO_x levels (Sarwar et al. 2014). Typical ClNO₂ concentrations measured
 60 in urban regions range from 10s of ppt to 1000s of ppt. Mielke et al. (2013) measured a maximum of 3.6 ppb (0.04Hz) during summer time in L.A. with maximum sunrise concentrations of 800 ppt. Bannan et al. (2015) measured a maximum concentration of 724 ppt (1Hz) at an urban background site in London during summer. They state that in some instances, ClNO₂ concentrations increase after sunrise and attribute this to the influx of air masses with higher ClNO₂ concentrations by either advection or from the collapse of the residual mixing
 65 layer. In urban environments where NO_x emission and subsequent N₂O₅ production is likely, Cl⁻ may be the limiting reagent in the formation of ClNO₂ if excess NO does not reduce NO₃ (3) before N₂O₅ is produced (e.g. Bannan et al., 2015). Whilst distance from a marine source of Cl⁻ may explain low, inland concentrations (Faxon et al. 2015), long range transport of marine air can elevate inland ClNO₂ concentrations (Phillips et al. 2012) and long range transport of polluted plumes to a marine location can also elevate ClNO₂ concentrations (e.g. Bannan
 70 et al. 2017).





75 Anthropogenic emission of molecular chlorine is identified as another inland source of Cl⁻ in the U.S. (e.g. Thornton et al. 2010; Riedel et al. 2012) and in China (e.g. Wang et al. 2017, Liu et al. 2017) where some of the highest concentrations 3.0 - 4.7 ppb have been recorded. As well as industrial processes, the suspension of road salt used to melt ice on roads during the winter has been suggested as a large source of anthropogenic Cl⁻ (Mielke et al. 2016). This winter time only source, combined with reduced nitrate radical photolysis, is expected
80 to yield greater ClNO₂ concentrations at this time of the year (Mielke et al. 2016).

The photolysis of molecular chlorine (Cl₂) is another potential source of Cl. Numerous heterogeneous formation mechanisms leading to Cl₂ from Cl⁻ containing particles are known. These include the reaction of Cl⁻ and OH (Vogt et al. 1996), which may originate from the photolysis of O_{3(aq)} (Oum 1998) or reactive uptake of ClNO₂ (Leu et al. 1995), ClONO₂ (Deiber et al. 2004) or HOCl (Eigen & Kustin 1962) to acidic Cl⁻ containing
85 particles. Thornton et al. (2010) also suggest that inorganic Cl reservoirs such as HOCl and ClONO₂ may also enhance the Cl concentration, potentially accounting for the short fall in the global burden (8-22 Tg yr⁻¹ source from ClNO₂ and 25-35 Tg yr⁻¹ as calculated from methane isotopes). These may be directly through photolysis or indirectly through heterogenous reactions with Cl⁻ on acidic aerosol.

Globally, Cl₂ concentrations are highly variable. In the marine atmosphere, concentrations up to 35 ppt have
90 been recorded (Lawler et al. 2011) whereas at urban coastal sites in the US, concentrations on the order of 100s ppt have been measured (Keene et al. 1993, Spicer et al. 1998). Sampling urban outflow, Riedel et al. (2012) measure a maximum of 200 ppt Cl₂ from plumes and mean concentrations of 10 ppt on a ship in the LA basin. Maximum mixing ratios of up to 65 ppt have also been observed in the continental US (Mielke et al. 2011).

More interestingly, these studies (Keene et al. 1993; Spicer et al. 1998; Lawler et al. 2011; Mielke et al. 2011),
95 report maximum Cl₂ concentrations at night and minima during the day. However, there is a growing body of evidence suggesting day time Cl₂ may also be observed. Although primary emission may be one source of daytime Cl₂ (Mielke et al. 2011), others demonstrate the diurnal characteristics of the Cl₂ time series has a broader signal suggestive of continuous processes rather than intermittent signals typically associated with sampling emission sources under turbulent conditions.

100 In a clean marine environment Liao et al. (2014) observe maximum Cl₂ concentrations of 400 ppt attributed to emission from a local snow pack source. A maxima was measured during the morning and evening with a local minimum during mid-day caused by photolysis. They also describe negligible night time concentrations, with significant loss attributed to deposition. Faxon et al. (2015) measured Cl₂ with a ToF-CIMS recording a maximum during the afternoon of 4.8 ppt (0.0016 Hz) and suggest a local precursor primary source of Cl₂,
105 potentially soil emission, with further heterogeneous chemistry producing Cl₂. At a rural site in north China, Liu et al. (2017) measured mean concentrations of Cl₂ of 100 ppt and a maximum of 450 ppt, peaking during the day; they also report 480 ppt observed in an urban environment in the US during summer. They attribute power generation facilities burning coal as the source.

Another potential source of Cl to the atmosphere is the photolysis of chlorinated organic compounds (ClVOCs, chlorocarbons, organochlorides) that are emitted from both natural (biomass burning, oceanic and biogenic
110 emission) (e.g. Yokouchi et al. 2000) and anthropogenic sources (e.g. Butler 2000). Whilst many ClVOCs are

only considered chemically important in the stratosphere, those that are photochemically labile in the troposphere e.g. methyl hypochlorite (CH_3OCl) whose absorption cross section is non-negligible at wavelengths as long as 460 nm (Crowley et al. 1994), can act as a source of Cl and take part in oxidative chemistry.

115 Photolysis of ClVOCs have been postulated to contribute $0.1 - 0.5 \times 10^3$ atoms cm^{-3} globally to the Cl budget of the boundary layer (Hossaini et al. 2016), although on much smaller spatial and temporal scales, the variance in this estimate is likely to be large. Very little data exists on the concentrations, sources and spatial extent of oxygenated ClVOCs (ClOVOCs) and their contribution to the Cl budget.

120 The ToF-CIMS is a highly selective and sensitive instrument with a high mass accuracy and resolution (m/dm ~4000) that is capable of detecting a suite of chlorinated compounds including HOCl, ClONO_2 and organic chlorines (Le Breton et al. 2018), as well as other oxygenated chlorine species and chloroamines (Wong et al. 2017). Here we use the ToF-CIMS with the I reagent ion to characterise the sources of chlorine and estimate their contribution to Cl concentrations in winter time Manchester, UK.

2. Methodology / experimental

125 Full experimental details and description of meteorological and air quality measurements can be found in Priestley et al. (2018). A time of flight chemical ionisation mass spectrometer (ToF-CIMS) (Lee, Lopez-Hilfiker, Mohr, Kurtén, Worsnop, Thornton, et al. 2014) using iodide reagent ions was used to sample ambient air between 2014-10-29 and 2014-11-11 at the University of Manchester's south campus, approximately 1.5 km south of Manchester City Centre, UK (N53.467, W2.232) and 55 km east of the Irish Sea. Sample loss to the 1m long $\frac{3}{4}$ " PFA inlet was minimised by using a fast inlet pump inducing a flow rate of 15 standard litres per minute (slm) which was subsampled by the ToF-CIMS. Backgrounds were taken every 6 hours for 20 minutes by overflowing dry N_2 and were applied consecutively. The overflowing of dry N_2 will have a small effect on the sensitivity of the instrument to those compounds whose detection is water dependent, here we find that due to the low instrumental backgrounds, the absolute error remains small and is an acceptable limitation in order to measure a vast suite of different compounds for which no best practice backgrounding method has been established. Whilst backgrounds were taken infrequently, they are of a comparable frequency to those used in previous studies where similar species are measured (Osthoff et al. 2008; Lawler et al. 2011; Phillips et al. 2012). The stability of the background responses (i.e. for Cl_2 0.16 ± 0.07 (1σ) ppt) and the stability of the instrument diagnostics with respect to the measured species suggest that they effectively capture the true instrumental background.

135
140

Formic acid was calibrated throughout the campaign and post campaign. Very little deviation in the formic acid calibrations was observed. The mean average sensitivity was 30.66 ± 1.90 (1σ) Hz/ppt. A number of chlorinated species were calibrated post campaign using a variety of different methods and relative calibration factors were applied based on measured instrument sensitivity to formic acid as has been performed previously (e.g. le Breton et al. 2014; le Breton et al. 2017; Bannan et al. 2015). A summary of calibration procedures and species calibrated are described below. All data from between 16:30 on the 5th of November to midnight on the 7th of November has been removed to prevent the interference of a large scale anthropogenic biomass burning event (Guy Fawkes Night) on these analyses.

145

2.1. Calibrations

150 We calibrate a number of species by overflowing the inlet with various known concentrations of gas mixtures (Le Breton et al. 2012), including molecular chlorine (Cl_2 , 99.5% purity, Aldrich), formic acid (98/100%, Fisher) and acetic acid (glacial, Fisher) by making known mixtures (in N_2) and flowing 0-20 standard cubic centimetres per minute (sccm) into a 3 slm N_2 dilution flow that is subsampled. As all chlorinated VOCs we observe are oxygenated we assume the same sensitivity found for 3-Chloropropionic acid for the rest of the organic chlorine species detected. Chloropropionic acid (Aldrich) was calibrated following the methodology of Lee et al. (2014). A known quantity of chloropropionic acid was dissolved in methanol (Aldrich) and a known volume doped onto a filter. The filter was slowly heated to 200°C to ensure total desorption of the calibrant whilst 3 slm N_2 flowed over it. This was repeated several times. A blank filter was first used to determine the background.

160 ~~As all chlorinated VOCs we observe are oxygenated, we assume the same sensitivity found for acetic acid for the rest of the organic chlorine species detected. The instrument sensitivity to dichloromethane (DCM, VWR) and chloroform (CHCl_3 , 99.8%, Aldrich) were also quantified, but these species were not detected during ambient sampling. Methyl chloride (CH_3Cl) and chloroacetic acid were also detected in the laboratory but not quantified.~~

165 ClNO_2 was calibrated by the method described by Kercher et al. (2009) with N_2O_5 synthesised following the methodology described by Le Breton et al. (2014). Excess O_3 is generated by flowing 200 sccm O_2 (BOC) through an ozone generator (BMT, 802N) and into a 5 litre glass volume containing NO_2 (sigma, >99.5%). The outflow from this reaction vessel is cooled in a cold trap held at -78°C (195 K) by a dry ice/glycerol mixture where N_2O_5 is condensed and frozen. The trap is allowed to reach room temperature and the flow is reversed where it is then condensed in a second trap held at 195 K. This process is repeated several times to purify the mixture. The system is first purged by flowing O_3 for ten minutes before use. To ascertain the N_2O_5 concentration on the line, the flow is diverted through heated line to decompose the N_2O_5 and into to a Thermo Scientific 42i NO_x analyser where it is detected as NO_2 . It is known that the Thermo Scientific 42i NO_x analyser suffers from interferences from NO_y species, indicating that this method could cause an underestimation of the ClNO_2 concentrations reported here. Based on previous studies (e.g. Le Breton et al. 2014; Bannan et al. 2017) where comparisons with a broad beam cavity enhancement absorption spectrometer (BBCEAS) have been made, good agreement has been found between co-located N_2O_5 measurements. We feel that this calibration method works well, likely in part due to the high purity of N_2O_5 synthesised and the possible interference of NO_y on the NO_x analyser during this calibration is considered negligible. The N_2O_5 is passed over a salt slurry where excess chloride may react to produce ClNO_2 . The drop in N_2O_5 signal is equated to the rise in ClNO_2 as the stoichiometry of the reaction is 1:1. The conversion efficiency of N_2O_5 to ClNO_2 over wet NaCl is known to vary by between 60-100% (Hoffman et al. 2003; Roberts et al. 2008). Here we follow the methodology of Osthoff et al. (2008) and Kercher et al. (2009) that ensure conversion is 100% efficient and so we assume 100% yield in this study.

~~We utilise a second method to verify our first ClNO_2 calibration by cross calibration with a turbulent flow tube chemical ionisation mass spectrometer (TF-CIMS) (Leather et al. 2012). We flow a known concentration of 0-20 sccm Cl_2 (99.5% purity Cl_2 cylinder, Aldrich) from a diluted (in N_2) gas mix into an excess constant flow of~~

190 20 sccm NO₂ (99.5% purity NO₂ cylinder, Aldrich) from a diluted (in N₂) gas mix, to which the TF-CIMS has been calibrated. This flow is carried in 52 slm N₂ that is purified by flowing through two heated molecular sieve traps. This flow is subsampled by the ToF-CIMS where the I.CINO₂⁻ adduct is measured. The TF-CIMS is able to quantify the concentration of CINO₂ generated in the flow tube as the equivalent drop in NO₂⁻ signal. This indirect measurement of CINO₂ is similar in its methodology to CINO₂ calibration by quantifying the loss of N₂O₅ reacted with Cl⁻ (e.g. Kercher et al. 2009). We assume the same sensitivity for CIONO₂ as CINO₂. We do not detect an increase in I.Cl₂ signal from this calibration and so rule out the formation of Cl₂ from inorganic species in our inlet due to unknown chemistry occurring in the IMR. The TF-CIMS method gives a calibration factor 58% greater than that of the N₂O₅ synthesis method therefore this is taken as our measurement uncertainty. “We developed a secondary novel method to quantify CINO₂ by cross calibration with a turbulent flow tube chemical ionisation mass spectrometer (TF-CIMS) (Leather et al. 2012). Chlorine atoms were produced by combining a 2.0 SLM flow of He with a 0 — 20 SCCM flow of 1% Cl₂, which was then passed through a microwave discharge produced by a Surfatron (Sairem) cavity operating at 100 W. The Cl atoms were titrated via constant flow of 20 sccm NO₂ (99.5% purity NO₂ cylinder, Aldrich) from a diluted (in N₂) gas mix, to which the TF-CIMS has been calibrated. This flow is carried in 52 slm N₂ that is purified by flowing through two heated molecular sieve traps. This flow is subsampled by the ToF-CIMS where the I.CINO₂⁻ adduct is measured. The TF-CIMS is able to quantify the concentration of CINO₂ generated in the flow tube as the equivalent drop in NO₂⁻ signal. This indirect measurement of CINO₂ is similar in its methodology to CINO₂ calibration by quantifying the loss of N₂O₅ reacted with Cl⁻ (e.g. Kercher et al. 2009). We do not detect an increase in I.Cl₂ signal from this calibration and so rule out the formation of Cl₂ from inorganic species in our inlet due to unknown chemistry occurring in the IMR. The TF-CIMS method gives a calibration factor 58% greater than that of the N₂O₅ synthesis method. The Cl atom titration method and assumes a 100% conversion to CINO₂ and does not take into account any Cl atom loss, which will lead to a reduced CINO₂ concentration and thus greater calibration factor. Also, the method assumes a 100% sampling efficiency between the TF-CIMS and ToF-CIMS, again this could possibly lead to an increased calibration factor. Whilst the new method of calibration is promising, we assume that the proven method developed by Kercher et al. (2009) is the correct calibration factor and assign an error of 50% to that calibration factor. We feel that the difference between the two methods is taken into account by our measurement uncertainty.”

220 We calibrate HOCl using the methodology described by Foster et al. (1999). 100 sccm N₂ is flowed through a fritted bubbler filled with NaOCl solution (min 8% chlorine, Fisher) that meets a dry 1.5 slm N₂ flow, with the remaining flow made up of humidified ambient air, generating the HOCl and Cl₂ signal measured on the ToF-CIMS. The flow from the bubbler is diverted through a condensed HCl (sigma) scrubber (condensed HCl on the wall of 20cm PFA tubing) where HOCl is titrated to form Cl₂. The increase in Cl₂ concentration when the flow is sent through the scrubber is equal to the loss of HOCl signal and as the calibration factor for Cl₂ is known, the relative calibration factor for HOCl to Cl₂ is found.

225 Additionally, several atmospherically relevant CIVOCs were sampled in the laboratory to assess their detectability by the ToF-CIMS with I. The instrument was able to detect dichloromethane (DCM, VWR), chloroform (CHCl₃, 99.8%, Aldrich) and methyl chloride (CH₃Cl, synthesised) although the instrument response was poor. The response to 3-chloropropionic acid was orders of magnitude greater than for the

CIVOCs suggesting the role of the chlorine atom is negligible compared with the carboxylic acid group in determining the I⁻ sensitivity in this case.

230 2.2. Cl radical budget calculations

Within this system, we designate ~~CINO₂~~, CINO₂, HOCl and organic chlorine as sources of Cl. As HCl ~~measurements were not made~~ was not detected, it is not possible to quantify the contribution of Cl from the reaction of HCl + OH. Loss processes of Cl are Cl + O₃ and Cl + CH₄ (7). Photolysis rates for the Cl sources are taken from the NCAR Tropospheric Ultraviolet and Visible TUV radiation model (Mandronich 1987) assuming
235 100% quantum yield at our latitude and longitude with column overhead O₃ measured by Brewer spectrophotometer #172 (Smedley et al. 2012) and assuming zero optical depth. To account for the effective optical depth of the atmosphere including clouds and other optical components, we scale our idealised photolysis rate coefficient (*J*) by the observed transmittance values in the UV-A waveband (325 to 400 nm). These transmittance values are calculated from UV spectral scans of global irradiance, measured at half-hourly
240 intervals by Brewer spectrophotometer and provided as an output of the shicRIVM analysis routine (Slaper et al. 1995). The Cl rate coefficient for the reaction with O₃ is $k_{\text{Cl}+\text{O}_3} = 1.20 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al. 2007) and CH₄ is $k_{\text{Cl}+\text{CH}_4} = 1.03 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al. 2006). The individual $k_{\text{Cl}+\text{VOC}}$ are taken from the NIST chemical kinetics database.

$$245 \quad [Cl]_{ss} = \frac{2J_{Cl_2}[Cl_2] + J_{ClNO_2}[ClNO_2] + J_{HOCl}[HOCl] + J_{ClOvoc}\Sigma[CIVOCs] + J_{ClONO_2}[ClONO_2]}{k_{O_3+Cl}[O_3] + k_{CH_4+Cl}[CH_4] + \Sigma_i^n k_{Cl+VOC_i}[VOC]_i} \quad (7)$$

As methane ~~and VOCs were~~ was not measured, an average CH₄ concentration was taken from ECMWF Copernicus atmosphere monitoring service (CAMS) ~~was used~~. VOC concentrations were approximated by applying representative VOC:benzene ratios for the UK urban environment (Derwent et al. 2000) and applying those to a typical urban UK benzene:CO ratio (Derwent et al. 1995) where CO was measured at the Whitworth
250 observatory. The VOC:benzene ratios are scaled to the year of this study to best approximate ambient levels (Derwent et al. 2014). The calculated benzene:CO ratio is in good agreement with a Non-Automatic Hydrocarbon Network monitoring site (Manchester Piccadilly) approximately 1.5 km from the measurement location indicating that the approximation made here is reasonably accurate. The ratios assume traffic emissions are the dominant source of the VOCs as is assumed here.

255 The photosensitivity of the ClOVOCs to wavelengths longer than 280 nm dictates their ability to contribute to the Cl budget in the troposphere. As many of the identified species here do not have known photolysis rates, we approximate the photolysis of methyl hypochlorite $J_{\text{CH}_3\text{OCl}}$ for all ClOVOCs as it is the only available photolysis rate for an oxygenated organic compound containing a chlorine atom provided by the TUV model and no other
260 more suitable photolysis rate could be found elsewhere e.g. the JPL kinetics database. The same quantum yield and actinic flux assumptions are made.

2.3. Identification by mass defect

Whilst looking for signal in the spectra with high mass defects, indicative of compounds containing multiple Cl atoms, various signals with the I₂ cluster as a reagent ion were detected. ToF CIMS reagent ions such as HNO₃/NO₃⁻ and H₂SO₄/HSO₄⁻ are known to form dimer, trimer and tetramer clusters which serve as additional

265 ionisers (e.g. Sipilä et al. 2015; Simon et al. 2016). It is also known that ionisation with I^- forms I_2^- and I_3^- clusters, which are often used as mass calibrants. Many of the I_2^- adducts measured here are formed with fragments such as O and CN that are likely a consequence of IMR chemistry, however in this instance, we find $I_2^-NO_2^-$ a useful measurement of NO_2/NO_y .

270 Fig 1. demonstrates the strong agreement ($R^2 = 0.93$) between the $I_2^-NO_2^-$ adduct as measured on the ToF-CIMS and the NO_2 measurement of a Thermo Scientific 42i NO_x analyser at the Whitworth Observatory. Chemiluminescence techniques used for the detection of NO_x species, like that employed by the Thermo Scientific 42i NO_x analyser, are known to overestimate NO_2 concentrations through the additional contribution of NO_y (e.g. Reed et al. 2016). Here we observe a non-linear increase in signal from the ToF-CIMS, indicating its susceptibility to interference at higher concentrations is greater than that of the NO_x analyser. The cause is unclear but is likely fragmentation of NO_y in the IMR. This diagnosis is consistent with the largest discrepancy between the measurements being found during bonfire night (5th Nov) which is a large source of organic nitrates (Reyes-Villegas et al. 2017). When the $(NO_y - NO_2):NO_2$ ratio is low, more typical in cleaner environments, the $I_2^-NO_2^-$ adduct may be useful as a measurement for NO_2 .

3. Results

280 Concentrations of all chlorinated species are higher at the beginning of the measurement campaign when air masses originating from continental Europe were sampled (Reyes-Villegas et al. 2017). Toward the end of the measurement campaign $ClONO_2$ and $ClOVOCs$ concentrations were low which is consistent with the pollution during this period having a high fraction of primary components (Reyes-Villegas et al. 2017), see Fig 1.

3.1. Inorganic chlorine

285 We detect a range of inorganic chlorine species and fragments including $I.Cl^-$, $I.ClO^-$, $I.HOCl^-$, $I.Cl_2^-$, $I.ClNO_2^-$ and $I.ClONO_2^-$ however we do not detect $I.ClO_2^-$, $I.Cl_2O^-$, $I.Cl_2O_2^-$, $I.ClNO^-$ or $I.HCl^-$. Laboratory studies have shown that the ToF-CIMS is sensitive to detection of $I.HCl^-$, however under this configuration, the $I.HCl^-$ adduct was not observed. ~~N_2O_5 was measured during the campaign however a strong daytime interference at 235 m/z identified as $C_2H_4O_5$ (tentatively assigned as hydroperoxy(hydroxy)acetic acid, hydroxy acetic hydroperoxide, HAHP), means this signal cannot be utilised during the day.~~ The statistics of the concentrations reported below do not take into account the limits of detection (LOD) and so for some of the measurements, values may be reported below the LOD.

3.1.1. $ClNO_2$ and $ClONO_2$

295 $ClNO_2$ (m/z 208) was detected every night of the campaign with a LOD (3x standard deviation of the background) of 3.8 ppt. ~~The night time N_2O_5 signal anti-correlates with NO as expected, whereas the $ClNO_2$ signal shows no correlation with NO which is also expected if $ClNO_2$ is not being produced in the inlet.~~ The 1Hz mean night time concentration of $ClNO_2$ was 58 ppt (not accounting for the LOD) and a maximum of 506 ppt (not accounting for the LOD) was measured as a large spike on the evening of the 30th Oct. These concentrations are comparable to other urban U.K. measured values although the maximum concentration reported here is 30% lower than that measured in London (Bannan et al. 2015) but is consistent with high concentrations expected during the winter as discussed in the introduction.

The diurnal profile of ClNO₂ increases through the evening to a local morning maximum with rapid loss after sunrise. Although we observe a rapid build-up after sunset (ca. 16:30) and loss after sunrise (ca. 07:30), the maximum concentration measured within a given 24 hour period typically peaks at around 22:00 and halves by 03:00 where it is maintained. The reasons for the early onset in peak concentration and loss throughout the night is unclear although on 1th Nov, a sharp decrease in ClNO₂ is a consequence of a change in wind direction, indicating the source of ClNO₂ is directional. A minimum concentration of <LOD is reached by 15:00 indicating concentrations can persist for much of the day. On 7th Nov ClNO₂ concentrations grow throughout the morning even after photolysis begins until 11:00. Correlated high wind speeds suggest long range transport and downward mixing is a likely cause for this daytime increase.

Typically, elevated concentrations of ClNO₂ are measured when the wind direction is easterly and wind speeds are low (2-4 ms⁻¹) and also during periods of southerly winds between 3-9 ms⁻¹. The potential sources of Cl⁻ precursor from these directions are industrial sites, including waste water treatment facilities (8.5 km east and 7.0 km south) that may use salt water as part of the chemical disinfection process (Ghernaout & Ghernaout 2010). Another source of ClNO₂ precursor is found from the south west at wind speeds of 9 ms⁻¹ indicating a more distant source which is also likely to be industrial/marine. The correlation between ClNO₂ and Cl₂ is poor at most times apart from the night of the 30th where a strong linear relationship is observed. This is consistent with polluted continental air masses advecting a variety of trace gases. Throughout the measurement campaign the relationship between ClNO₂ and Cl₂ is poor and so it is unlikely they share the same source. ~~Maximum ClONO₂ concentrations reach 20.3 ppt. The average concentration is 2.0 ppt (not accounting for the LOD) and LOD of 0.9 ppt. The behaviours of ClONO₂ and ClNO₂ are extremely similar (R²=0.97).~~

3.1.2. HOCl

HOCl concentrations average 2.18 ppt (not accounting for the LOD) and reach a daytime maximum of 9.28 ppt with an LOD of 3.8 ppt. Concentrations peak in the early afternoon similarly to Cl₂ but remain elevated for longer, dropping after sunset. The diurnal profile is similar to that for O₃ with a maximum during the day and minima during morning and evening rush hours when NO_x is emitted locally. The strong correlation with O₃ (R² = 0.67) is expected as the route to formation of HOCl is the oxidation of Cl with O₃ to form ClO and then oxidation by HO₂ to form HOCl. Non negligible night time concentrations of a maximum 8.1 ppt are only measured when concentrations of other inorganic Cl containing species are high. The HOCl signal is artificially elevated after the night of the 5th due to a persistent interference from a large scale biomass burning event ([Guy Fawkes Night, Priestley et al., 2018](#)); that cannot be deconvolved from the dataset ~~due to the small difference in their mass to charge ratios and insufficient instrument resolution. (Guy Fawkes Night, Priestley et al., 2018).~~ For this reason HOCl data after this date are discounted from the analysis.

3.1.3. ClO

We detect the I.ClO⁻ adduct at *m/z* 178 which strongly correlates with I.ClNO₂⁻, ~~I.ClONO₂⁻~~ and I.Cl⁻ signals, all of which show night time maxima. This is inconsistent with the ClO photochemical production pathway of Cl + O₃ suggesting its maximum concentration should be measured during the day as was observed for HOCl. It is not possible to confirm if the I.ClO⁻ is a fragment of a larger ClO containing molecule, however, as the fragmentation of multiple larger molecules are detected as a single adduct e.g. the I.Cl⁻ cluster is a known fragment from ClNO₂ and HOCl, it is reasonable to suspect I.ClO⁻ may be a fragment as well.

3.1.4. Cl₂

We observe concentrations of Cl₂ during the day ranging from 0 – 16.6 ppt with a mean value of 2.3 ppt (not accounting for the LOD) and night time concentrations of 0 – 4.7 ppt with mean concentrations of 0.4 ppt (not accounting for the LOD), see Fig 1. The LOD is 0.5 ppt. These concentrations are of the same order of magnitude as measured at an urban site in the U.S. but up to 2 orders of magnitude smaller than at U.S urban coastal sites (Keene et al. 1993, Spicer et al. 1998) and a megacity impacted rural site in north China (Liu et al. 2017). Although the maximum measured value here is an order of magnitude greater than that measured in Houston (Faxon et al. 2015), the photolysis rate of Cl₂ here is two orders of magnitude smaller compared with Houston at that time.

The diurnal profile of Cl₂ exhibits a maximum at midday and a minimum at night (early morning) consistent with other studies (Liao et al. 2014; Faxon et al. 2015; Liu et al. 2017). The days with the greatest concentration are those where direct shortwave radiation is at its highest. On the 5th of November, the incidence of direct shortwave radiation is unhindered throughout the day and a similarly uniform profile for Cl₂ is also observed. On the 1st of November, Cl₂ concentrations increase unhindered as direct radiation increases but when cloud cover reduces radiation transmission efficiency, a corresponding drop in Cl₂ is also observed (Fig 3). Equally when global radiation is low throughout the day e.g. 7th November, we observe very low concentrations of Cl₂.

There is the potential that the Cl₂ signal detected is an instrumental artefact generated either by chemistry in the IMR or from displacement reactions or degassing on the inlet walls. We believe none of these to be the case. First, the correlation between the signal used for labile chlorine in the IMR ³⁵Cl (*m/z* 35) is high with ClNO₂ (R²=0.98) yet is non-existent with Cl₂ (R²=0.01) indicating Cl₂ concentration is independent of ³⁵Cl concentrations. Second, there is no correlation between HNO₃ and Cl₂ (R²=0.07) which suggests that acid displacement reactions are not occurring on the inlet walls. Third, there is no correlation between temperature and Cl₂ (R²=0.08) indicating that localised ambient inlet heating is also not a contributing factor to increased Cl₂ concentrations. Fourth, we observe a similar direct radiation dependency for other photochemical species as we observe for Cl₂. For example, the temporal behaviour of C₂H₄O₅ (potentially hydroxy acetonehydroxy peroxide, HAHP, a photochemical marker and known product of aqueous ozone chemistry (Leitzke et al. 2001)) exhibits a similar diurnal profile and radiation dependency (Fig 3). Also, the production of O₃ increases and decreases with direct solar radiation at the same times we observe the enhancements in concentrations of Cl₂ and C₂H₄O₅ (Fig 3). The changes in O₃ production are observed when NO concentrations are near zero indicating O₃ production is VOC limited. Finally, other large organic molecules e.g. C₁₀H₁₄O₄ do not exhibit this strong coupling with direct solar radiation. This evidence suggests a local photolytic daytime mechanism is responsible for the increase in daytime concentrations as has previously been suggested (e.g. Finley & Saltzman 2006).

Although peak concentrations of Cl₂ are observed in the daytime, high levels of Cl₂ are also observed during the night. At the beginning of the measurement period, which has previously been characterised using an aerosol mass spectrometer (AMS) as a period of high secondary activity (Reyes-Villegas et al. 2017), there are persistent, non-zero concentrations of Cl₂ (≤ 4 ppt) after sunset. On the 4th November, after the period of high secondary activity, intermittent elevations in night time Cl₂ concentrations, when the wind is northerly, suggest a local emission source, with concentrations reaching a maximum of 4.6 ppt. Two more distinct night time

sources, ranging from the south west through to the east of the measurement site indicate a likely origin of industrial areas, some of which contain chemical production and water treatment facilities.

3.2. Organic chlorine

We detected seven C₂-C₆ ClOVOCs of the forms C_nH_{2n+1}O₁Cl, C_nH_{2n+1}O₂Cl, C_nH_{2n+1}O₃Cl, C_nH_{2n-1}O₂Cl, C_nH_{2n-1}O₃Cl, C_nH_{2n-3}O₂Cl (Fig 4) of which only C₂H₃O₂Cl has been reported before (Le Breton et al. 2018). We find no evidence for the detection of small chlorohydrocarbons e.g. poly-chloromethanes, such as methyl chloride, dimethyl chloride and chloroform, or poly-chloroethanes such as those described by Huang et al. (2014) in the ambient data, but qualitative testing and our laboratory calibrations show that the iodide reagent ion is sensitive can detect to CH₃Cl (not calibrated), CH₂Cl₂ (LOD = 143 ppb) and CHCl₃ (LOD = 11 ppb) albeit with a high LOD. We find no discernable evidence for the detection of 4-chlorocrotonaldehyde, the Cl oxidation product of 1,3-butadiene and unique marker of chlorine chemistry (Wang & Finlayson-Pitts 2001) due to interferences from other CHO compounds. We do not believe these species are products of inlet reactions as there is a poor correlation (R² = -0.039) with labile chlorine ³⁵Cl.

The maximum hourly averaged total ClOVOCs concentration is 140-28 ppt at midday-12:00 and at a minimum of 80-5 ppt at 07:00 when NO_x concentrations are highest at ~30 ppb. Concentrations of C₂H₃O₂Cl (tentatively identified as chloroacetic acid) and C₆H₁₃OCl (tentatively identified as chloro-hexanol) are the highest of any ClOVOCs, accounting for between 20% and 30% respectively of total ClOVOCs concentrations measured. All concentrations rise towards midday with C₃H₇O₂Cl and C₂H₃O₂Cl rising the most by a factor of 1.84 and returning to nominal levels by the early evening (red in Fig 4). C₃H₇O₂Cl and C₂H₃O₂Cl correlate well with Cl₂ (R² 0.7677, 0.62-75 respectively) which is consistent with a photochemical formation mechanism identifying these species as secondary products, potentially, chloro-propanediol and chloro-acetic acid.

Whilst the diurnal profiles of C₆H₁₃OCl, ~~C₃H₅O₃Cl~~ and C₅H₇O₂Cl (blue in Fig 4) are similar to those of C₃H₇O₂Cl and C₂H₃O₂Cl, they do not enhance as much as those photochemical species or return to nominal levels after the solar maximum, instead they increase again during the night, with C₃H₅O₃Cl reaching a maximum concentration of 8 ppt at 20:00. This trend suggests concentration changes could be a function of boundary layer height.

~~C₃H₅O₃Cl~~ C₃H₇O₂Cl and C₄H₇O₂Cl (yellow in Fig 4) are the only ClOVOCs that show a positive correlation with NO_x (R² -0.470.42, R² -0.260.41) and negative correlation with O₃ (R² -0.58, R² -0.340.53). Their correlation is stronger with NO₂ (R² 0.5755, R² 0.3448), a product of traffic emission. This suggests that at least some of the time, they accumulate at low wind speeds, indicating their origins as local, primary emissions, or as thermal degradation products that have a traffic source e.g. polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/F) and their oxidation products (Fuentes et al. 2007; Heeb et al. 2013). The diurnal profile shows maxima during mid-day consistent with other photochemical species which is expected of secondary formation. It is possible that these compounds are isobaric or isomeric with other compounds that interfere with the perceived signals recorded here.

The diurnal profile of C₃H₅O₃Cl (green in Fig 4) exhibits a similar shape to the bimodal distribution observed for NO_x. Cross-correlation indicates that a time lag of -3 hours provides the best correlation with NO₂ of

$R^2=0.80$. This is suggestive of local oxidation chemistry taking place over long periods of the day that is sensitive to traffic emission is the source of this CIOVOC.

4. Discussion

4.1. Effect of global radiation transmission efficiency on Cl radical production

420 Three days are selected based on their different solar short wave transmission efficiencies to quantify the variation in Cl_2 formation and photolysis and so the influence of Cl_2 on producing Cl. The average transmission of global radiation on the 5th of November was high, $84 \pm 14\%$ (1σ), whereas on the 7th of November it was very low $21 \pm 14\%$, sometimes dropping below 10% in the middle of the day. The 1st of November serves as a middle case where the transmission efficiency in the morning was high, $88 \pm 11\%$ but in the afternoon was highly variable and dropped to $55\% \pm 20\%$ see Fig 5. These three days provide good case studies to investigate the effect of global radiation on molecular chlorine concentrations and therefore the production of Cl.

The reduced transmission efficiency inhibits Cl_2 formation thereby reducing the contribution of Cl_2 to Cl production. The lower transmission efficiency also reduces the photolysis of Cl_2 and so reduces the production of Cl even further. Fig 6. shows the divergence between the ideal J_{Cl_2} without transmission efficiency correction (a) and the J_{Cl_2} value scaled by transmission efficiency (b) and subsequent Cl formation. Cl production rates are similar until 11am when the scaled production then becomes on average 47% lower. This is most prominent at 13:00 when the difference between ideal and scaled production is 8.4×10^4 Cl radicals $\text{cm}^{-3} \text{s}^{-1}$.

4.2. Contribution of inorganic chlorine to Cl radical production

435 The contribution of HOCl and ~~CIOVOCs-CINO₂~~ to Cl formation is negligible due to low photolysis rates and low concentrations whereas the contributions from Cl_2 and CINO_2 ~~and CIOVOCs is are~~ much greater (Fig 7). During the morning of the ~~1th and 5th~~ Nov, CINO_2 is the dominant source of Cl contributing 95% of total Cl concentration, a maximum of ~~1.33.0~~ $\times 10^3$ Cl radicals cm^{-3} to the steady state concentration which is approximately a factor of ~~ten-three~~ lower than the estimated maximum concentration of 9.5×10^3 Cl radicals cm^{-3} produced by CINO_2 photolysis in London during the summer (Bannan et al. 2015) and a factor of ~~65-22~~ lower than the maximum concentration of 85.0×10^3 Cl radicals cm^{-3} calculated from measurements of CINO_2 in Houston (Faxon et al. 2015). In both instances this is due to a combination of lower J_{CINO_2} and lower CINO_2 concentrations.

445 As the day progresses, concentrations of Cl_2 increase and it becomes the dominant and more sustained source of Cl contributing 95% of Cl (~~46.812.5~~ $\times 10^3$ Cl radicals cm^{-3}) by the early afternoon, which is approximately ~~12-4~~ times that of CINO_2 measured in the early morning and ~~-68%~~ 1.3 times higher than the maximum estimated concentration calculated from CINO_2 photolysis in London (Bannan et al. 2015). The maximum Cl concentration produced from Cl_2 and CINO_2 photolysis on the 5th reached ~~22.514.2~~ $\times 10^3$ Cl radicals cm^{-3} at 11:30 am which is approximately ~~2616%~~ of the 85.0×10^3 Cl radicals cm^{-3} maximum calculated value from the photolysis of these two species in Houston in summer (Faxon et al. 2015). This is dominated by the contribution of Cl_2 , indicating Cl_2 can be a much more significant source of Cl than CINO_2 . On this high flux day, when

hourly mean Cl₂ concentrations range between 0 – 7 ppt, the source term is calculated to be between 4 - 21 ppt Cl₂ hr⁻¹, which is slightly lower although consistent with previous studies (Spicer et al. 1998; Finley & Saltzman 2006; Faxon et al. 2015).

The 7th Nov has been highlighted as a day with low photolysis rates and high day time ClNO₂ concentrations.

455 On this day, ClNO₂ is the dominant Cl source (95%) reaching a maximum of ~~8.33.4~~ 8.33.4 x 10³ Cl radicals cm⁻³ at 9:30 which is ~87% of that calculated for London (Bannan et al. 2015). A mean Cl₂ concentration of 0.3 ppt (less than the LOD of 0.5 ppt) on this day is very low as production of Cl₂ at its maximum, calculated as 0.6 ppt hr⁻¹, is also low. This combined with a low maximum J_{Cl₂} = 1.13x10⁻⁴ hr⁻¹ means maximum Cl production from Cl₂ photolysis on this day is very low, generating ~~2.40.9~~ 2.40.9 x 10³ Cl radicals cm⁻³ at 10:00 or a quarter of the maximum contributed by ClNO₂ on this day, see Fig 7.



The dependency of Cl formation on Cl₂ production and loss highlights the sensitivity of this reaction channel to photolysis is demonstrated on these two days. The production of Cl from ClNO₂ is relatively speaking, less sensitive to the solar flux as the production of ClNO₂ does not rely on photochemistry but chemical composition cf. (6) and (8). This further highlights the role of photolytic mechanisms in the re-activation of particulate chloride to gaseous chlorine radicals.

4.3. Organic vs inorganic contribution to Cl radical production

470 Summing the concentrations of the ClOVOCs ~~described in the section above~~ and assuming a uniform photolysis rate J_{CH₃OCl} as detailed in the above section, we derive the contribution of total measured ClOVOC to the Cl budget and compare it to the contribution from inorganic Cl measured here (Fig 7). On the high flux day, the Cl concentration reaches ~~4.0 x 10² 6.9 x 10³~~ 4.0 x 10² 6.9 x 10³ Cl radicals cm⁻³ at midday, which is ~~2030%~~ 2030% ~~greater than of~~ the contribution by ClNO₂ ~~and, 603.6% less than of~~ the contribution ~~of from~~ Cl₂ ~~and *2% of the HOCl contribution~~ for the same day. On the low flux day, the ClOVOC contribution is ~~1.8 x 10³ 11.0 x 10²~~ 1.8 x 10³ 11.0 x 10² Cl radicals cm⁻³, which is ~~~202.8%~~ ~202.8% of the ClNO₂ contribution on that day and ~~~8557%~~ ~8557% of the Cl₂ contribution. Like Cl₂, the production of most ClOVOC requires a photolytic step to generate concentrations that can then go on to decompose providing the Cl. Here it is suggested that the organic contribution to Cl production is ~~negligible at~~ negligible at 15% on the low radiant flux day and ~~243%~~ 243% on the high flux day.

5. Conclusion

480 A large suite of inorganic and organic, oxygenated, chlorinated compounds has been identified in ambient, urban air during the wintertime in the UK. Of the 7 organic chlorinated compounds (ClOVOCs) identified here only C₂H₃O₂ClO (tentatively assigned as chloroacetic acid) has previously been reported. No aliphatic or polychlorinated species were detected, although the ToF-CIMS with I is sensitive towards them e.g. methyl chloride (CH₃Cl) dimethyl chloride (CH₂Cl₂) and chloroform (CHCl₃). The sources of ClOVOCs are mostly photochemical with maxima of up to ~~140-28~~ 140-28 ppt observed at midday, although C₃H₇O₃Cl and C₄H₇O₂Cl concentrations correlate with NO_x accumulating at low wind speeds, indicating they are produced locally, potentially as the thermal breakdown products of higher mass chlorinated species such as polychlorinated

dibenzo-*p*-dioxins/dibenzofurans (PCDD/F) from car exhausts or the oxidation products thereof. C₃H₅O₃Cl shows a good diurnal cross-correlation with NO₂ with a time lag of three hours, suggesting its production is sensitive to NO_x concentrations on that time scale.

490 Alongside CIOVOCs, daytime concentrations of Cl₂ and ClNO₂ are measured reaching maxima of 17 ppt and 506 ppt respectively. ClNO₂ is a source of Cl throughout every day time period measured. Cl₂ shows strong evidence of a daytime production pathway limited by photolysis as well as emission sources evident during the evening and night time.

On a day of high radiant flux (84±14% of idealised values), Cl₂ is the dominant source of Cl, generating a
495 maximum steady state concentration of 12.5x10³ 16.8x10³-Cl radicals cm⁻³ or 5774% of the total Cl produced by the photolysis of Cl₂, ClNO₂, HOCl and CIOVOC with the latter two-three contributing 1919%, 4% and 243% respectively. This contrasts with a share of 1714% for Cl₂, 6883% for ClNO₂ and 153% for CIOVOCs on a low radiant flux day (21±14% of idealised values). On the low radiance day not only is the photolysis of all Cl species inhibited, reducing Cl concentrations, but also the formation of Cl₂ and some CIOVOCs by
500 photochemical mechanisms is inhibited thus the variability in contribution between days is highly sensitive to the incidence of sunlight. This further highlights the importance of photochemistry in the re-activation of particulate chloride to gaseous chlorine radicals. Similarly to Cl₂, CIOVOCs can be an important source of Cl although the behaviour of their contribution is similar to Cl₂ relying on high rates of photolysis, rather than high concentrations as is the case for ClNO₂.

505 The contribution of the CIOVOCs to the Cl budget would be better determined if more specific photolysis rates for each compound were available and so would further improve the accuracy of the contribution they make to the Cl budget. In addition, future work should aim to identify the processes leading to the formation of these compounds to better constrain the Cl budget in the urban atmosphere. Further ambient measurements of a broader suite of chlorinated species, as shown here, in different chemical environments would help to better
510 constrain the contribution that chlorine-initiated chemistry has on a global scale.

References

- Atkinson, R. et al., 2007. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III -- gas phase reactions of inorganic halogens. *Atmospheric Chemistry and Physics*, 7, pp.981–1191.
- 515 Atkinson, R. et al., 2006. Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, Web Version, February 2006. *IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry*, pp.1–60.
- Bannan, T.J. et al., 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(20), p.11,154-11,165.
- 520 Bannan, T.J. et al., 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*, 120(11), pp.5638–5657.
- Borduas, N. et al., 2015. Experimental and theoretical understanding of the gas phase oxidation of atmospheric amides with OH radicals: Kinetics, products, and mechanisms. *Journal of Physical Chemistry A*, 119(19),
525 pp.4298–4308.
- Boucher, O. et al., 2009. The indirect global warming potential and global temperature change potential due to

- methane oxidation. *Environmental Research Letters*, 4(4), p.044007.
- Le Breton, M. et al., 2012. Airborne observations of formic acid using a chemical ionization mass spectrometer. *Atmospheric Measurement Techniques*, 5(12), pp.3029–3039.
- 530 Le Breton, M. et al., 2018. Chlorine oxidation of VOCs at a semi-rural site in Beijing: Significant chlorine liberation from ClNO₂ and subsequent gas and particle phase Cl-VOC production. *Atmospheric Chemistry and Physics Discussions*, (January), pp.1–25.
- Le Breton, M. et al., 2017. Enhanced ozone loss by active inorganic bromine chemistry in the tropical troposphere. *Atmospheric Environment*, 155, pp.21–28.
- 535 Le Breton, M. et al., 2014. Simultaneous airborne nitric acid and formic acid measurements using a chemical ionization mass spectrometer around the UK: Analysis of primary and secondary production pathways. *Atmospheric Environment*, 83(3), pp.166–175.
- Le Breton, M. et al., 2014. The first airborne comparison of N₂O₅ measurements over the UK using a CIMS and BBCEAS during the RONOCO campaign. *Anal. Methods*, 6(24), pp.9731–9743.
- 540 Butler, J., 2000. Better budgets for methyl halides? *Nature*, 403(6767), pp.260–1.
- Carlton, A.G. et al., 2006. Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds. *Geophysical Research Letters*, 33(6), pp.2–5.
- Crowley, N. et al., 1994. CH₃OCl: UV/visible absorption cross sections, J values and atmospheric significance. *Journal of Geophysical Research*, 99(D10), p.20,683–20,688.
- 545 Deiber, G. et al., 2004. Uptake study of ClONO₂ and BrONO₂ by Halide containing droplets. *Atmospheric Chemistry and Physics*, 4(5), pp.1291–1299.
- Derwent, R.G. et al., 1995. Analysis and interpretation of air quality data from an urban roadside location in Central London over the period from July 1991 to July 1992. *Atmospheric Environment*, 29(8), pp.923–946.
- 550 Derwent, R.G. et al., 2000. Analysis and interpretation of the continuous hourly monitoring data for 26 C₂–C₈ hydrocarbons at 12 United Kingdom sites during. 1996. *Atmospheric Environment*, 34, pp.297–312.
- Derwent, R.G. et al., 2014. Twenty years of continuous high time resolution volatile organic compound monitoring in the United Kingdom from 1993 to 2012. *Atmospheric Environment*, 99, pp.239–247. Available at: <http://dx.doi.org/10.1016/j.atmosenv.2014.10.001>.
- 555 Eigen, M. & Kustin, K., 1962. The Kinetics of Halogen Hydrolysis. *Journal of the American Chemical Society*, 84(8), pp.1355–1361.
- Faxon, C., Bean, J. & Ruiz, L., 2015. Inland Concentrations of Cl₂ and ClNO₂ in Southeast Texas Suggest Chlorine Chemistry Significantly Contributes to Atmospheric Reactivity. *Atmosphere*, 6(10), pp.1487–1506.
- 560 Finley, B.D. & Saltzman, E.S., 2006. Measurement of Cl₂ in coastal urban air. *Geophysical Research Letters*, 33(11), pp.6–9.
- Foster, K.L. et al., 1999. Techniques for quantifying gaseous HOCl using atmospheric pressure ionization mass spectrometry. *Physical Chemistry Chemical Physics*, 1(24), pp.5615–5621.
- Fuentes, M.J. et al., 2007. Pyrolysis and combustion of waste lubricant oil from diesel cars: Decomposition and pollutants. *Journal of Analytical and Applied Pyrolysis*, 79(1–2 SPEC. ISS.), pp.215–226.
- 565 Ghernaout, D. & Ghernaout, B., 2010. From chemical disinfection to electrodisinfection: The obligatory itinerary? *Desalination and Water Treatment*, 16(1–3), pp.156–175.
- Heal, M. et al., 1995. On the Development and Validation of FAGE for Local Measurement of Tropospheric OH and HO₂. *Journal of the Atmospheric Sciences*, 52(19), pp.3428–3441.

- 570 Heeb, N. V. et al., 2013. PCDD/F formation in an iron/potassium-catalyzed diesel particle filter. *Environmental Science and Technology*, 47(12), pp.6510–6517.
- Hoffman, R.C. et al., 2003. Knudsen cell studies of the reactions of N₂O₅ and ClONO₂ with NaCl: development and application of a model for estimating available surface areas and corrected uptake coefficients. *Physical Chemistry Chemical Physics*, 5(9), pp.1780–1789.
- 575 Hossaini, R. et al., 2016. A global model of tropospheric chlorine chemistry: Organic versus inorganic sources and impact on methane oxidation. *Journal of Geophysical Research: Atmospheres*, 121(23), p.14,271-14,297.
- Huang, B. et al., 2014. Chlorinated volatile organic compounds (Cl-VOCs) in environment - sources, potential human health impacts, and current remediation technologies. *Environment International*, 71, pp.118–138.
- 580 Keene, W.C. et al., 1993. Measurement Technique for Inorganic Chlorine Gases in the Marine Boundary Layer. *Environmental Science and Technology*, 27(5), pp.866–874.
- Kercher, J.P., Riedel, T.P. & Thornton, J.A., 2009. Chlorine activation by N₂O₅: simultaneous, in situ detection of ClNO₂ and N₂O₅ by chemical ionization mass spectrometry. *Atmos. Meas. Tech.*, 2(1), pp.193–204.
- 585 Lawler, M.J. et al., 2011. HOCl and Cl₂ observations in marine air. *Atmospheric Chemistry and Physics*, 11(15), pp.7617–7628.
- Leather, K.E. et al., 2012. Temperature and pressure dependence of the rate coefficient for the reaction between ClO and CH₃O₂ in the gas-phase. *Physical Chemistry Chemical Physics*, 14, pp.3425–3434.
- Lee, B.H., Lopez-Hilfiker, F.D., Mohr, C., Kurtén, T., Worsnop, D.R. & Thornton, J.A., 2014. An iodide-adduct high-resolution time-of-flight chemical-ionization mass spectrometer: Application to atmospheric inorganic and organic compounds. *Environmental Science & Technology*, 48(11), pp.6309–6317.
- 590 Lee, B.H., Lopez-Hilfiker, F.D., Mohr, C., Kurtén, T., Worsnop, D.R., Thornton, J.A., et al., 2014. An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds. *Environmental Science & Technology*, 48(11), pp.6309–6317.
- 595 Leu, M.-T. et al., 1995. Heterogeneous Reactions of HNO₃(g) + NaCl(s) .fwdarw. HCl(g) + NaNO₃(s) and N₂O₅(g) + NaCl(s) .fwdarw. ClNO₂(g) + NaNO₃(s). *The Journal of Physical Chemistry*, 99(35), pp.13203–13212.
- Liao, J. et al., 2014. High levels of molecular chlorine in the Arctic atmosphere. *Nature Geoscience*, 7(2), pp.91–94.
- 600 Liu, X. et al., 2017. High levels of daytime molecular chlorine and nitryl chloride at a rural site on the North China Plain. *Environmental Science & Technology*, (2), p.acs.est.7b03039.
- Ma, Y. et al., 2013. Rapid modification of cloud-nucleating ability of aerosols by biogenic emissions. *Geophysical Research Letters*, 40(23), pp.6293–6297.
- 605 Mandronich, S., 1987. Photodissociation in the Atmosphere Actinic Flux and the Effects of Ground Reflections and Clouds. *Journal of Geophysical Research*, 92, pp.9740–9752.
- Mielke, L.H. et al., 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(18), pp.10638–10652.
- 610 Mielke, L.H. et al., 2016. Ubiquity of ClNO₂ in the urban boundary layer of Calgary, Alberta, Canada. *Canadian Journal of Chemistry*, 94(4), pp.414–423.
- Mielke, L.H., Furgeson, A. & Osthoff, H.D., 2011. Observation of ClNO₂ in a mid-continental urban environment. *Environmental science & technology*, 45, pp.8889–96.
- Nguyen, T.B. et al., 2015. Rapid deposition of oxidized biogenic compounds to a temperate forest. *Proceedings of the National Academy of Sciences*, 112(5), pp.E392–E401.

- 615 Osthoff, H.D. et al., 2008. High levels of nitryl chloride in the polluted subtropical marine boundary layer. *Nature Geoscience*, 1(5), pp.324–328.
- Oum, K.W., 1998. Formation of Molecular Chlorine from the Photolysis of Ozone and Aqueous Sea-Salt Particles. *Science*, 279(5347), pp.74–76.
- 620 Phillips, G.J. et al., 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(10), pp.1–5.
- Reyes-Villegas, E. et al., 2017. Simultaneous Aerosol Mass Spectrometry and Chemical Ionisation Mass Spectrometry measurements during a biomass burning event in the UK: Insights into nitrate chemistry. *Atmospheric Chemistry and Physics Discussions*, (July), pp.1–22.
- 625 Riedel, T.P. et al., 2012. Nitryl chloride and molecular chlorine in the coastal marine boundary layer. *Environmental Science and Technology*, 46(19), pp.10463–10470.
- Roberts, J.M. et al., 2008. N₂O₅ oxidizes chloride to Cl₂ in acidic atmospheric aerosol. *Science*, 321(5892), p.1059.
- 630 Sarwar, G. et al., 2014. Importance of tropospheric ClNO₂ chemistry across the Northern Hemisphere. *Geophysical Research Letters*, 41(11), pp.4050–4058.
- Slaper, H. et al., 1995. Comparing ground-level spectrally resolved solar UV measurements using various instruments: A technique resolving effects of wavelength shift and slit width. *Geophysical Research Letters*, 22(20), pp.2721–2724.
- 635 Smedley, A.R.D. et al., 2012. Total ozone and surface UV trends in the United Kingdom: 1979–2008. *International Journal of Climatology*, 32(3), pp.338–346.
- Spicer, C.W. et al., 1998. Unexpectedly high concentrations of molecular chlorine in coastal air. *Nature*, 394(June 1996), pp.353–356.
- Thornton, J.A. et al., 2010. A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature*, 464(7286), pp.271–274.
- 640 Vogt, R., Crutzen, P.J. & Sander, R., 1996. A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer. *Nature*, 383(6598), pp.327–330.
- Wang, D.S. & Ruiz, L.H., 2017. Secondary organic aerosol from chlorine-initiated oxidation of isoprene. , (May), pp.1–25.
- 645 Wang, W.H. & Finlayson-Pitts, B.J., 2001. Unique markers of chlorine atom chemistry in coastal urban areas: The reaction with 1,3-butadiene in air at room temperature. *Journal of Geophysical Research-Atmospheres*, 106(D5), pp.4939–4958.
- Wang, X. et al., 2017. Observations of N₂O₅ and ClNO₂ at a polluted urban surface site in North China: High N₂O₅ uptake coefficients and low ClNO₂ product yields. *Atmospheric Environment*, 156(3), pp.125–134.
- 650 Wong, J.P.S. et al., 2017. Observations and impacts of bleach washing on indoor chlorine chemistry. *Indoor Air*, 27(6), pp.1082–1090.
- Yokouchi, Y. et al., 2000. A strong source of methyl chloride to the atmosphere from tropical coastal land. *Nature*, 403, pp.295–298.

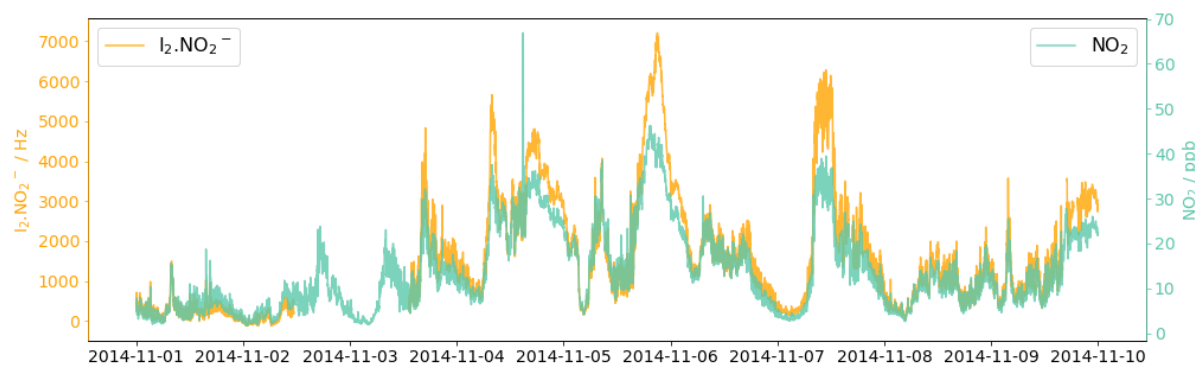
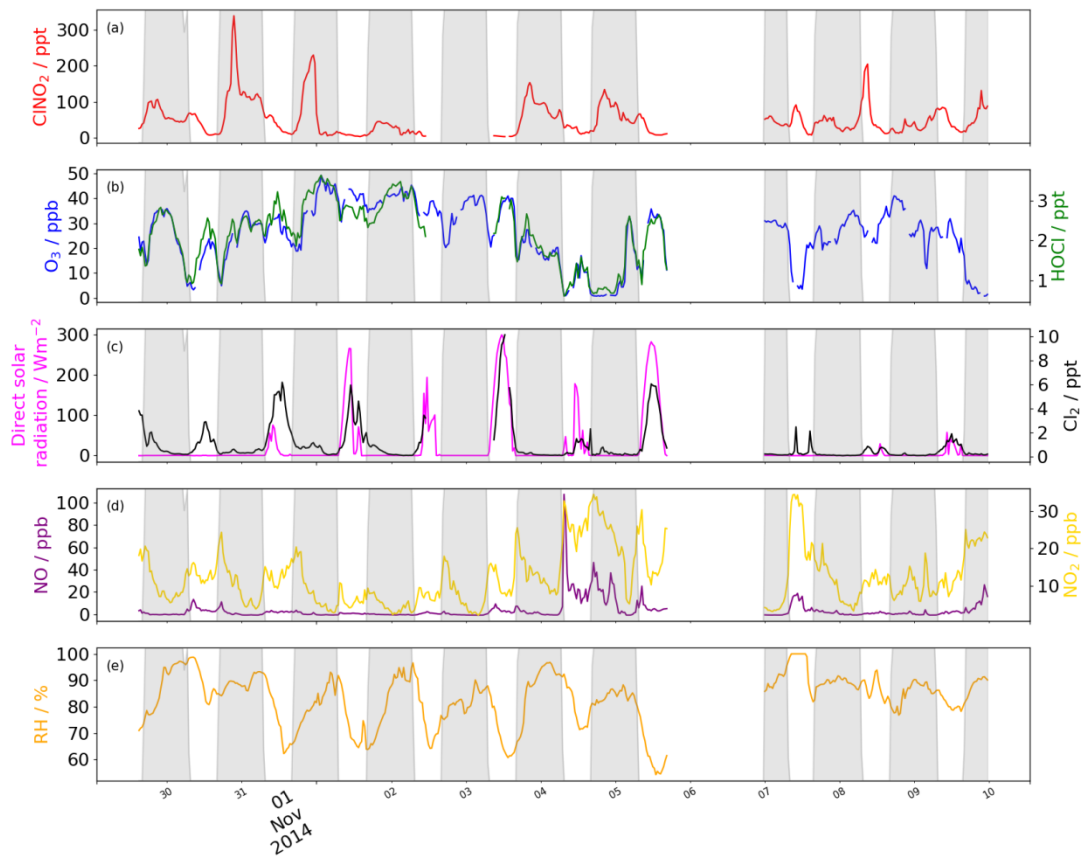
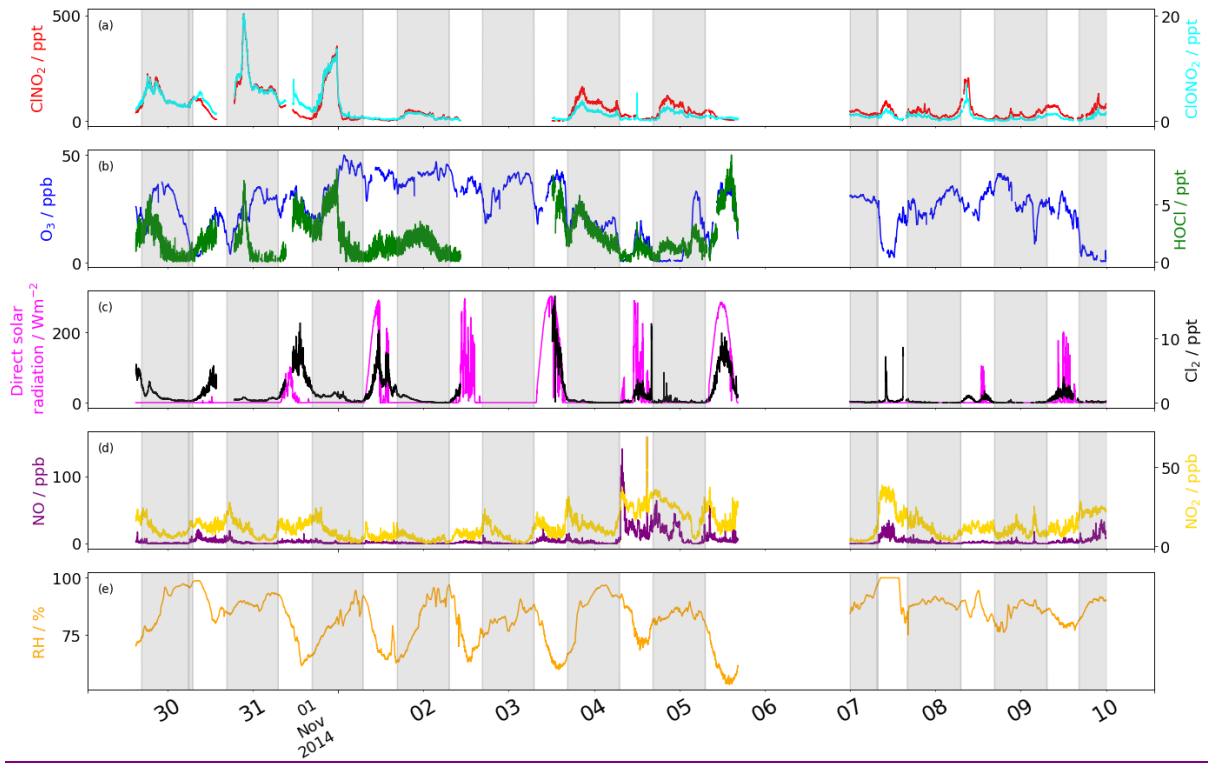
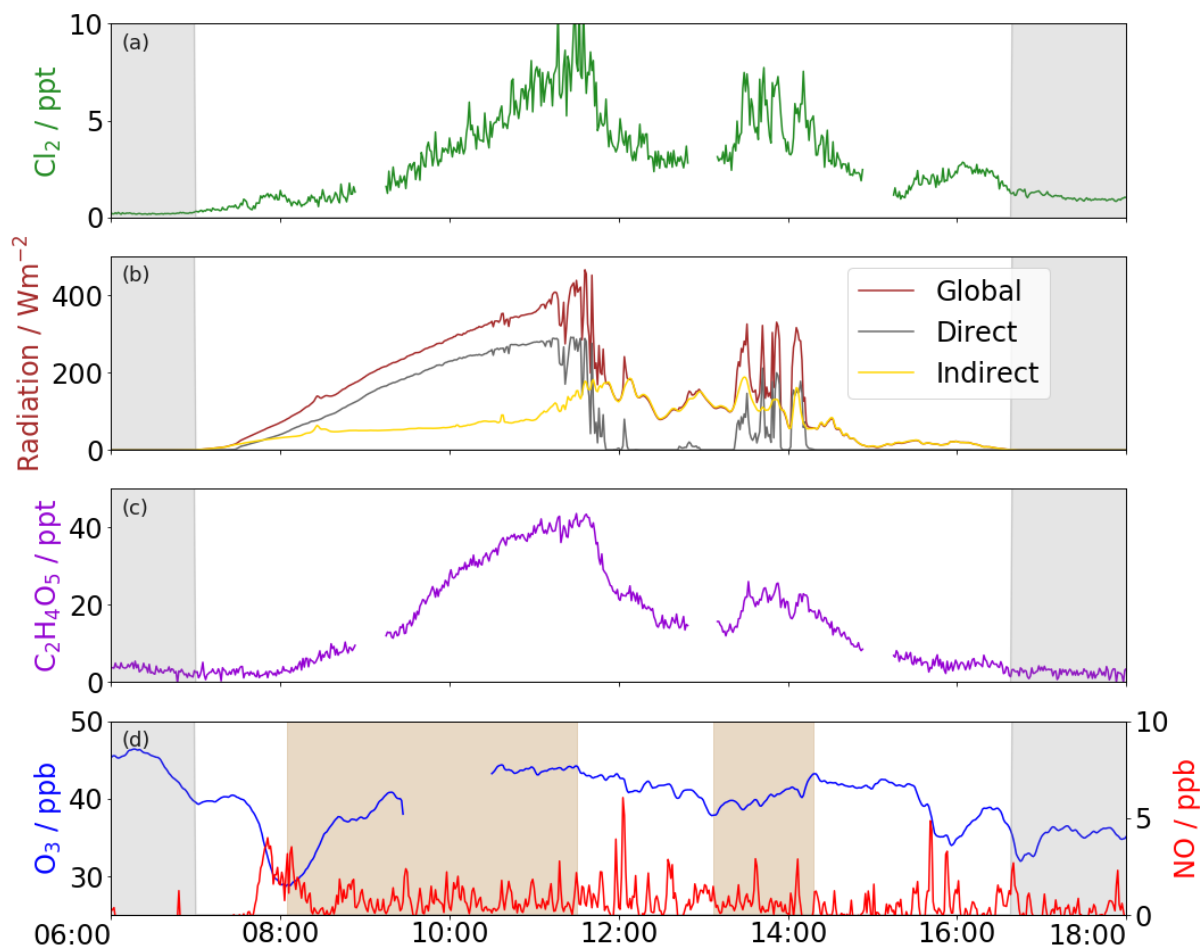


Fig 1. NO_2 measured at the whitworth observatory overlayed with $I_2.NO_2^-$ measured on the ToF CIMS. NO_2 is overestimated by the ToF CIMS at high concentrations. This is potentially due to the degradation of NO_y species in the IMR.

655

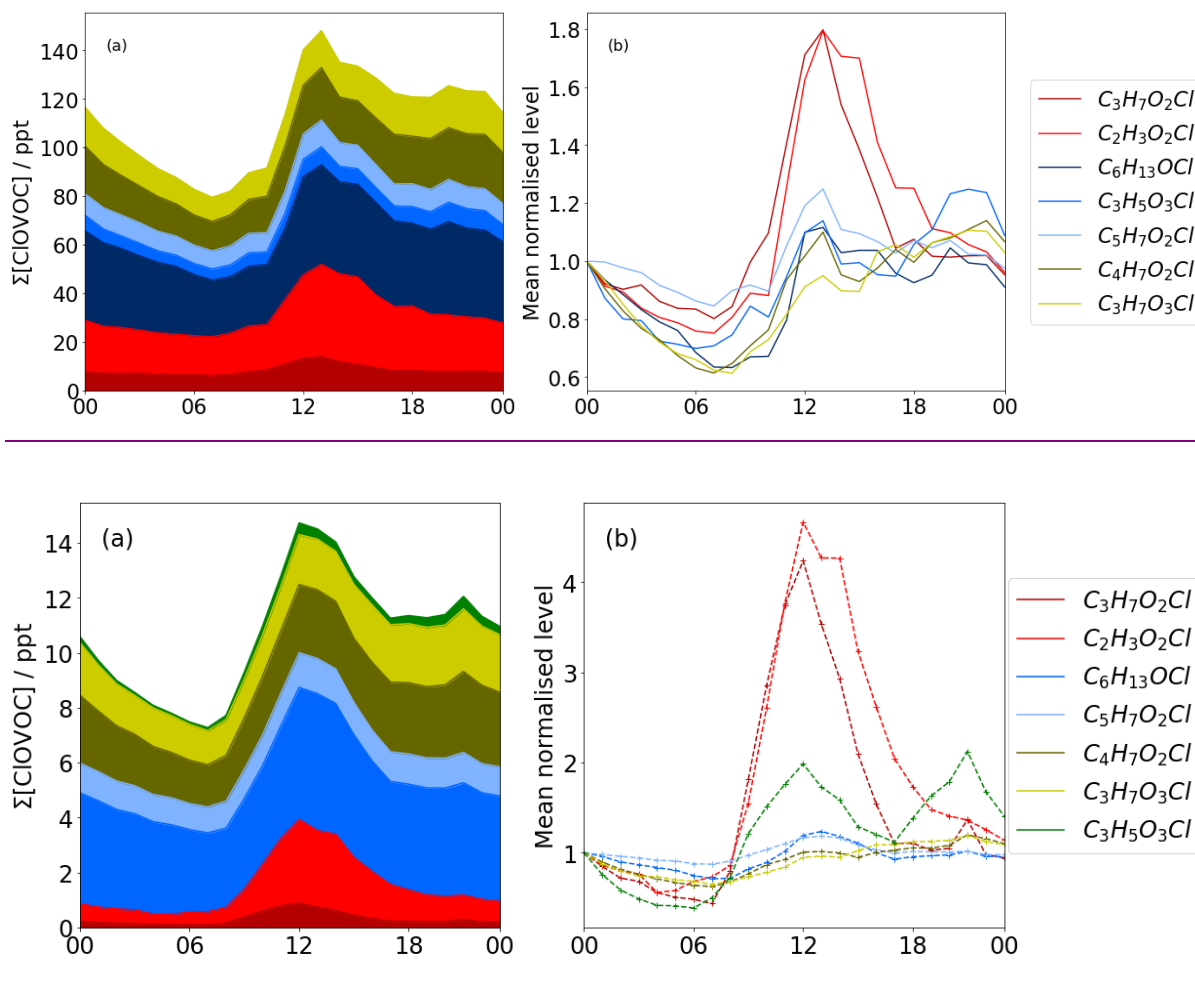


660 | Fig 1. Time series of a. ClNO_2 (ppt), ~~and ClONO_2 (ppt)~~. b. HOCl (ppt) and O_3 (ppb). c. Cl_2 (ppt) and direct solar radiation (Wm^{-2}). d. NO (ppb) and NO_2 (ppb). e. Relative humidity (%). Data is removed during bonfire night (5th-6th) and HOCl data is discounted thereafter due to a persistent interference which was not present earlier.

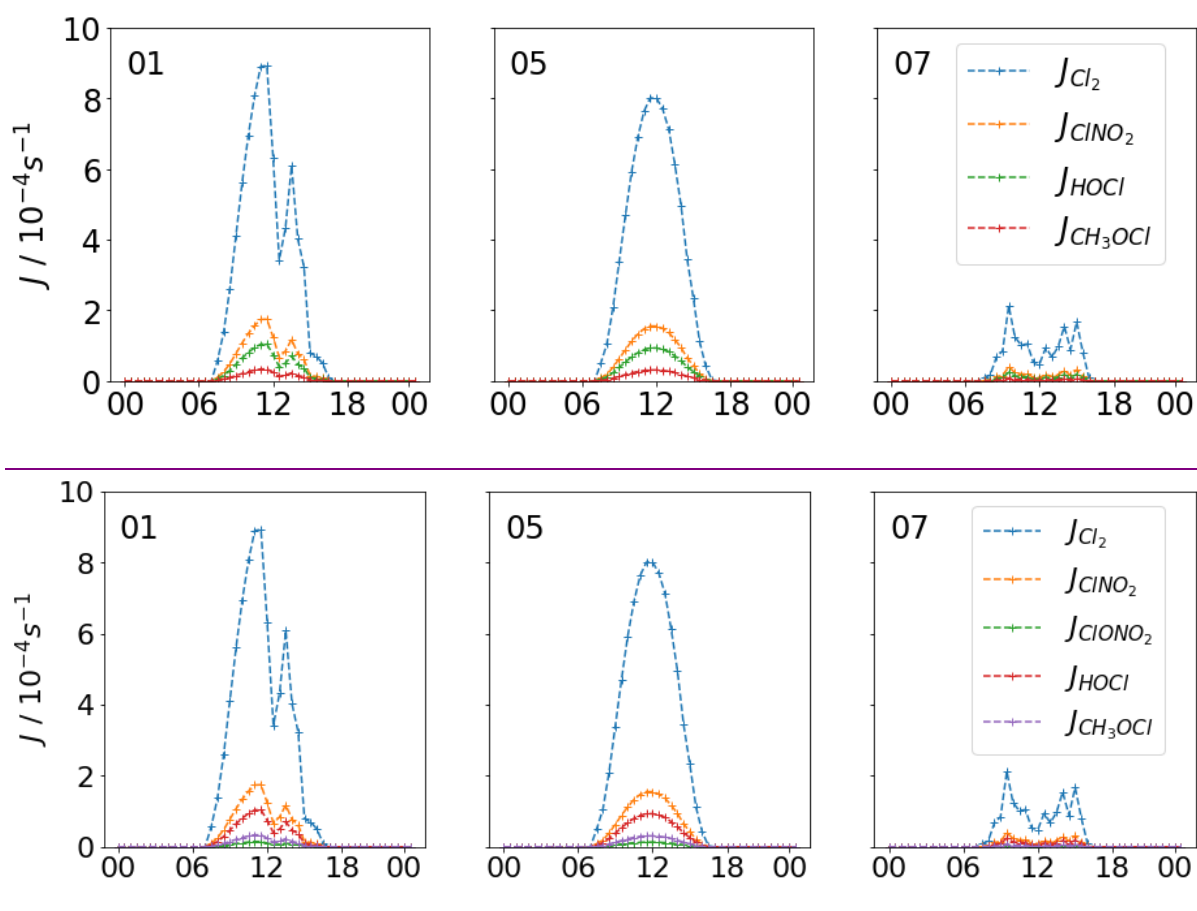


665 | Fig 2. Time series for the day of 1st Nov 2014. a. Cl_2 b. solar radiation (global, direct and indirect) c. photochemical marker $\text{C}_2\text{H}_4\text{O}_5$ d. O_3 and NO_x where highlighted boxes demonstrate $\frac{\Delta[\text{O}_3]}{\Delta t}$ is increasing. The increase in concentration of Cl_2 , $\text{C}_2\text{H}_4\text{O}_5$ and O_3 production when VOC limited are strongly coupled to direct solar radiation. Greyed areas are night time.

670



675 **Fig 4. Diurnal profiles of Cl VOCs. a. Stacked plot showing total Cl VOC concentration. b. The first data point of each diurnal trace is mean normalised to 1.0. Reds show photochemical dominated signals with maxima at midday whereas yellow and blue traces show a more typical diurnal concentration profile associated with changes in boundary layer height indicating these species have longer lifetimes.**



680

Fig 5. Transmission scaled J values for Cl_2 , ClNO_2 , ClONO_2 and HOCl for the 1st, 5th and 7th of Nov. The 1st had high photolysis rates in the morning that were reduced during the afternoon. The 5th is the closest to a full day's ideal photolysis. The 7th shows very weak photolysis.

685

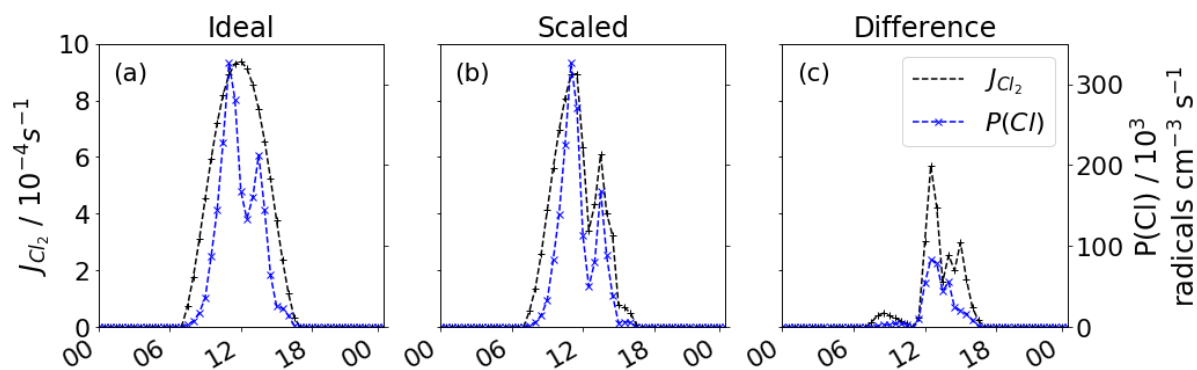


Fig 6. Diurnal profile for 1st Nov of: a. idealised J_{Cl_2} and $P(Cl)$, b. scaled J_{Cl_2} and $P(Cl)$, c. the difference between a and b. Transmission efficiency scaled photolysis reduce $P(Cl)$ from Cl_2 photolysis.

690

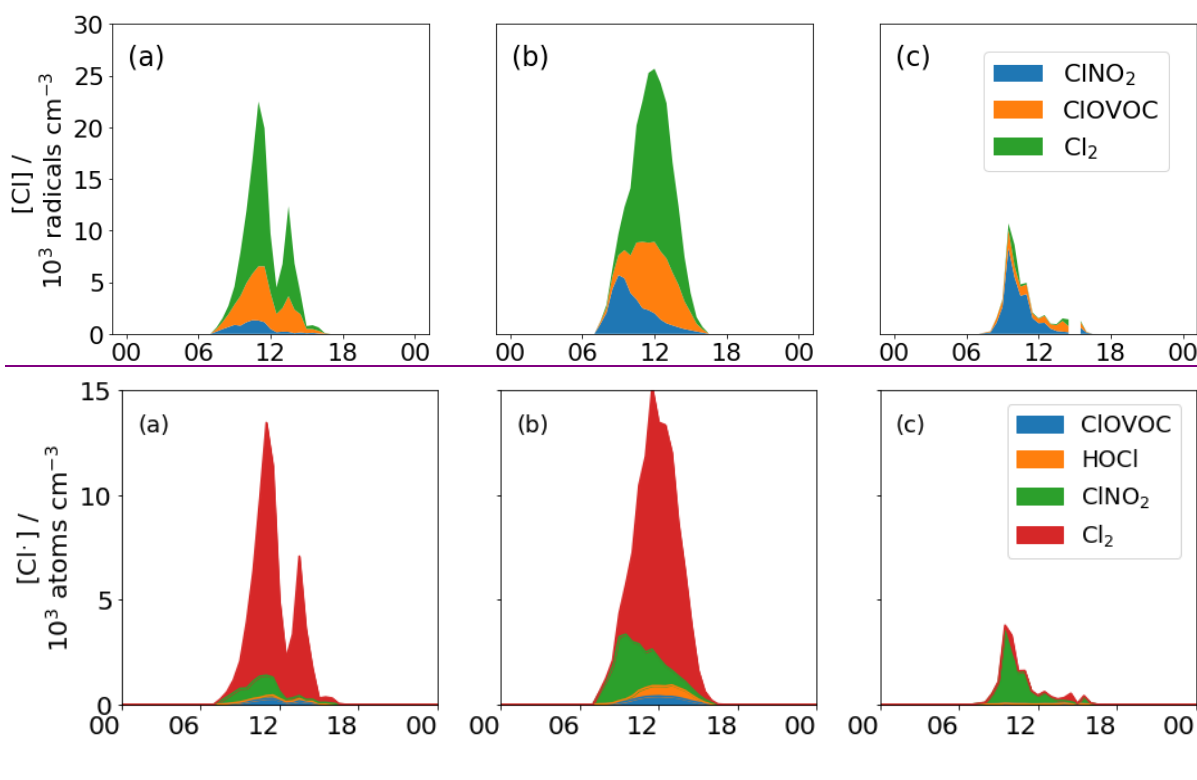


Fig 7. Steady state concentration of Cl from $CINO_2$, Cl_2 , $HOCl$ and total $CIOVOC$ photolysis for a. 1st Nov, b. 5th Nov, and c. 7th Nov. The importance of $CINO_2$ during the morning is most evident on the 5th with a diminishing contribution throughout the day. On the high flux days, Cl_2 and $CIOVOCs$ are the most important source of Cl but on the low flux day $CINO_2$ is most important.

695