
Publisher's PDF, also known as Version of record

License (if available):
CC BY

Link to published version (if available):
10.5194/acp-18-13481-2018

Link to publication record in Explore Bristol Research
PDF-document

This is the final published version of the article (version of record). It first appeared online via Copernicus at https://www.atmos-chem-phys.net/18/13481/2018/. Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
http://www.bristol.ac.uk/pure/about/ebr-terms
Observations of organic and inorganic chlorinated compounds and their contribution to chlorine radical concentrations in an urban environment in northern Europe during the wintertime

Michael Priestley\textsuperscript{1}, Michael le Breton\textsuperscript{1,a}, Thomas J. Bannan\textsuperscript{1}, Stephen D. Worrall\textsuperscript{1,b}, Asan Bacak\textsuperscript{1}, Andrew R. D. Smedley\textsuperscript{1,c}, Ernesto Reyes-Villegas\textsuperscript{1}, Archit Mehra\textsuperscript{1}, James Allan\textsuperscript{1,2}, Ann R. Webb\textsuperscript{1}, Dudley E. Shallcross\textsuperscript{3}, Hugh Coe\textsuperscript{1}, and Carl J. Percival\textsuperscript{1,d}

\textsuperscript{1}Centre for Atmospheric Science, School of Earth and Environmental Sciences, University of Manchester, Manchester, M13 9PL, UK
\textsuperscript{2}National Centre for Atmospheric Science, University of Manchester, Manchester, M13 9PL, UK
\textsuperscript{3}School of Chemistry, The University of Bristol, Cantock’s Close BS8 1TS, UK
\textsuperscript{a}now at: Department of Chemistry and Molecular Biology, University of Gothenburg, 412 96 Gothenburg, Sweden
\textsuperscript{b}now at: School of Materials, University of Manchester, Manchester, M13 9PL, UK
\textsuperscript{c}now at: School of Mathematics, University of Manchester, Manchester, M13 9PL, UK
\textsuperscript{d}now at: Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109, USA

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

Received: 6 March 2018 – Discussion started: 7 March 2018
Revised: 27 July 2018 – Accepted: 28 August 2018 – Published: 21 September 2018

Abstract. A number of inorganic (nitryl chloride, ClNO\textsubscript{2}; chlorine, Cl\textsubscript{2}; and hypochlorous acid, HOCl) and chlorinated, oxygenated volatile organic compounds (ClOVOCs) have been measured in Manchester, UK during October and November 2014 using time-of-flight chemical ionisation mass spectrometry (ToF-CIMS) with the I\textsuperscript{−} reagent ion. ClOVOCs appear to be mostly photochemically in origin, although direct emission from vehicles is also suggested. Peak concentrations of ClNO\textsubscript{2}, Cl\textsubscript{2} and HOCl reach 506, 16 and 9 ppt respectively. The concentrations of ClNO\textsubscript{2} are comparable to measurements made in London, but measurements of ClOVOCs, Cl\textsubscript{2} and HOCl by this method are the first reported in the UK. Maximum HOCl and Cl\textsubscript{2} concentrations are found during the day and ClNO\textsubscript{2} concentrations remain elevated into the afternoon if photolysis rates are low. Cl\textsubscript{2} 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 ClNO\textsubscript{2}, Cl\textsubscript{2} and ClOVOCs to the chlorine radical budget suggests that Cl\textsubscript{2} can be a greater source of Cl than ClNO\textsubscript{2}, contributing 74\% of the Cl radicals produced on a high radiant-flux day. In contrast, on a low radiant-flux day, this drops to 14\%, as both Cl\textsubscript{2} production and loss pathways are inhibited by reduced photolysis rates. This results in ClNO\textsubscript{2} making up the dominant fraction (83\%) on low radiant-flux days, as its concentrations are still high. As most ClOVOCs appear to be formed photochemically, they exhibit a similar dependence on photolysis, contributing 3\% of the Cl radical budget observed here.

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 (O\textsubscript{3}). As the 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 10^6 molecules cm^-3 (Heal et al., 1995). However, rate coefficients for the reaction of the chloride radical (Cl) can be 2 orders of magnitude larger than those for OH (Spicer et al., 1998), indicating that lower Cl concentrations of 1 x 10^4 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 Eq. (1) or hydrogen abstraction Eq. (2), forming HCl that may react with OH to regenerate Cl. Subsequent peroxy radicals formed through Cl oxidation can take part in the HO_x cycle and contribute to the enhanced formation of O_3 and SOA (Wang and Ruiz, 2017). This is represented by the following:

\[ R + X \rightarrow R(X)OO, \]  
\[ RH + X \rightarrow ROO^{-} + HX, \]  

where \( X \) is OH or Cl.

Nitryl chloride (ClNO_2) is a major reservoir of Cl that is produced by aqueous reactions between particulate chlorine (Cl^-) and nitrogen pentoxide (N_2O_5), as seen in Eq. (4) and Eq. (6). Gaseous ClNO_2 is produced throughout the night and is typically photolysed at dawn before OH concentrations reach their peak, as in Eq. (6). This early morning release of Cl induces oxidation earlier in the day and has been shown to increase maximum 8 h mean O_3 concentrations by up to 7 ppb under moderately elevated NO_x levels (Sarwar et al., 2014). Typical ClNO_2 concentrations measured in urban regions range from 10 s of ppt to 1000 s of ppt. Mielke et al. (2013) measured a maximum of 3.6 ppb (0.04 Hz) during the summertime in Los Angeles, with maximum sunrise concentrations of 800 ppt. Bannan et al. (2015) measured a maximum concentration of 724 ppt (1 Hz) at an urban background site in London during summer. They state that in some instances, ClNO_2 concentrations increase after sunrise and attribute this to the influx of air masses with higher ClNO_2 concentrations by either advection or from the collapse of the residual mixing layer. In urban environments where NO_x emission and subsequent N_2O_5 production is likely, Cl^- may be the limiting reagent in the formation of ClNO_2 if excess NO does not reduce NO_3 as seen in Eq. (3) before N_2O_5 is produced (e.g. Bannan et al., 2015). Whilst the distance from a marine source of Cl^- may explain low, inland concentrations Faxon et al., 2015), the long-range transport of marine air can elevate inland ClNO_2 concentrations (Phillips et al., 2012) and the long-range transport of polluted plumes to a marine location can also elevate ClNO_2 concentrations (e.g. Bannan et al., 2017). These processes may be represented by the following equations:

\[ NO_3 + NO \rightarrow 2NO_2, \]  
\[ NO_3 + NO_2 \rightarrow N_2O_5(g) \rightarrow N_2O_5(aq). \]  
\[ Cl^- + N_2O_5 \rightarrow ClNO_2 + NO_3^{-}. \]  
\[ ClNO_2(aq) \rightarrow ClNO_2(g) \rightarrow Cl + NO_2. \]  

The anthropogenic emission of molecular chlorine is identified as another inland source of Cl^- in the US (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 wintertime-only source, combined with reduced nitrate radical photolysis, is expected to yield greater ClNO_2 concentrations at this time of the year (Mielke et al., 2016).

The photolysis of molecular chlorine (Cl_2) is another potential source of Cl. Numerous heterogeneous formation mechanisms leading to Cl_2 from particles containing Cl^- 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 from the reactive uptake of ClNO_2 (Leu et al., 2015, ClONO_2 (Deiber et al., 2004) or HOCl (Eigen and Kustin, 1962) to acidic Cl^- containing particles. Thornton et al. (2010) also suggest that inorganic Cl reservoirs such as HCl and ClONO_2 may also enhance the Cl concentration, potentially accounting for the shortfall in the global burden (8–22 Tg yr^-1 source from ClNO_2 and 25–35 Tg yr^-1 as calculated from methane isotopes). This may be direct through photolysis or indirect through heterogeneous reactions with Cl^- on acidic aerosol.

Globally, Cl_2 concentrations are highly variable. In the marine atmosphere, concentrations of up to 35 ppt have 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 Cl_2 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; Lawler et al., 2011; Mielke et al., 2011; Spicer et al., 1998) report maximum Cl_2 concentrations at night and minima during the day. However, there is a growing body of evidence suggesting that daytime Cl_2 may also be observed. Although the primary emission may be one source of daytime Cl_2 (Mielke et al., 2011), others demonstrate that the diurnal characteristics of the Cl_2 time series have a broader signal suggestive of continuous processes rather than intermittent
signals typically associated with sampling emission sources under turbulent conditions.

In a clean marine environment Liao et al. (2014) observe maximum Cl₂ concentrations of 400 ppt attributed to emissions from a local snow pack source. A maximum was measured during the morning and evening with a local minimum during midday caused by photoysis. They also describe negligible night-time concentrations, with significant loss attributed to deposition. Faxon et al. (2015) measured Cl₂ with a time-of-flight chemical ionisation mass spectrometry (ToF-CIMS) recording a maximum during the afternoon of 4.8 ppt (0.0016 Hz) and suggesting a local precursor primary source of Cl₂ that is potentially soil emission, with further heterogeneous chemistry producing Cl₂. At a rural site in northern 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 (CIVOCs, chlorocarbons, organochlorides) that are emitted from both natural (biomass burning, oceanic and biogenic emission) (e.g. Yokouchi et al., 2000) and anthropogenic sources (e.g. Butler, 2000). Whilst many CIVOCs are only considered chemically important in the stratosphere, those that are photochemically labile in the troposphere, e.g. methyl hypochlorite (CH₂OCl), 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.

Photolysis of CIVOCs have been postulated to contribute 0.1 – 0.5 × 10³ 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 few data exist on the concentrations, sources and spatial extent of oxygenated CIVOCs (CIOVOCs) and their contribution to the Cl budget.

The ToF-CIMS is a highly selective and sensitive instrument with high mass accuracy and a resolution (m/dm ~ 4000) that is capable of detecting a suite of chlorinated compounds, including HOCI and organic chlorine (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 the wintertime in Manchester, UK.

2 Methodology/experiment

Full experimental details and a 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 et al., 2014b) using iodide reagent ions was used to sample ambient air between 29 October and 11 November 2014 at the University of Manchester’s southern campus, approximately 1.5 km south of Manchester city centre, UK (53.467° N, 2.232° W) and 55 km east of the Irish Sea. The sample loss to the 1 m long 3/4″ Perfluoroalkoxy alkane (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 6h for 20 min by overflowing dry N₂ and were applied consecutively. The overflowing of dry N₂ 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 (Lawler et al., 2011; Osthoff et al., 2008; Phillips et al., 2012). The stability of the background responses, i.e. for Cl₂ 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.

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⁻¹. 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., 2014a, 2017; Bannan et al., 2015). A summary of calibration procedures and species calibrated are described below. All data from between 16:30 LT on 5 November and 00:00 LT on 7 November have been removed to prevent the interference of a large-scale anthropogenic biomass burning event (Guy Fawkes Night) on these analyses.

2.1 Calibrations

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 (Cl₂, 99.5 % purity, Aldrich), formic acid (98/100 %, Fisher) and acetic acid (glacial, Fisher) by making known mixtures (in N₂) and flowing 0–20 standard cubic centimetres per minute (sccm) into a 3 slm N₂ dilution flow that is subsampled. The Cl₂ calibration factor is 4.6 Hz ppt⁻¹.

As all chlorinated VOCs we observe are oxygenated we assume the same sensitivity found for 3-chloropropionic acid (10.32 Hz ppt⁻¹) 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 was doped onto a filter. The filter was slowly heated to 200 °C to ensure the total desorption of the calibrant whilst 3 slm N₂ flowed over it. This was repeated several times. A blank filter was first used to determine the background.

CINO₂ was calibrated by the method described by Kercher et al. (2009) with N₂O₅ synthesised following the methodology described by Le Breton et al. (2014)⁵, giving a calibration factor of 4.6 Hz ppt⁻¹. Excess O₃ is generated by flowing 200 sccm O₂ (BOC) through an ozone generator (BMT, 802N) and into a 5 L glass volume containing NO₂ (σ, > 99.5 %). The outflow from this reaction vessel is cooled in a cold trap held at −78 °C (195 K) by a dry ice and glycerol mixture where N₂O₅ 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 O₃ for 10 min before use. To ascertain the N₂O₅ concentration on the line, the flow is diverted through heated line to decompose the N₂O₅ and into to a Thermo Scientific 42i NO₃ analyser, where it is detected as NO₂. It is known that the Thermo Scientific 42i NO₃ analyser suffers from interferences from NO₃ species, indicating that this method could cause an underestimation of the CINO₂ 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 N₂O₅ measurements. We feel that this calibration method works well, likely in part due to the high purity of the N₂O₅ synthesised and because the possible interference of NO₃ on the NO₃ analyser during this calibration is considered negligible. The N₂O₅ is passed over a salt slurry where excess chloride may react to produce CINO₂. The drop in the N₂O₅ signal is equated to the rise in CINO₂, as the stoichiometry of the reaction is 1 : 1. The conversion efficiency of N₂O₅ to CINO₂ over wet NaCl is known to vary by 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 ensures that conversion is 100 % efficient, so we assume a 100 % yield in this study.

We developed a secondary novel method to quantify CINO₂ by cross-calibration with a turbulent flow 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 a 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.Cl 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 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 a 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.

We calibrate HOCI using the methodology described by Foster et al. (1999) giving a calibration factor of 9.22 Hz ppt⁻¹. 100 sccm N₂ is flowed through a 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 (σ) scrubber (condensed HCl on the wall of 20 cm 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.

Additionally, several atmospherically relevant ClVOCs were sampled in the laboratory to assess their detectability by the ToF-CIMS with Γ. 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 ClVOCs suggesting that the role of the chlorine atom is negligible compared with the carboxylic acid group in determining the Γ sensitivity in this case.

2.2 Cl radical budget calculations

Within this system, we designate CINO₂, HOCI and organic chlorine as sources of Cl. As HCl 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 US National Center for Atmospheric Research
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., 2018). Toward the end of the measurement campaign, CINO₂ and ClOVCs concentrations were low, which is consistent with the pollution during this period having a high fraction of primary components (Reyes-Villegas et al., 2018), see Fig. 1.

3.1 Inorganic chlorine

We detect a range of inorganic chlorine species and fragments including I.Cl⁻, IClO²⁻, I.HOCl⁻, ICl⁻, IClO₂⁻, and I.CINO₂⁻, however we do not detect IClO₃⁻, ICl₂O⁻, ICl₂O²⁻, I.CINO⁻ or LHCl⁻. Laboratory studies have shown that the ToF-CIMS is sensitive to detection of LHCl⁻, however under this configuration, the LHCl⁻ adduct was not observed. The statistics of the concentrations reported below do not take into account the limits of detection (LOD), so for some of the measurements, values may be reported below the LOD.

3.1.1 CINO₂

CINO₂ (m/z 208) was detected every night of the campaign with an LOD (3× standard deviation of the background) of 3.8 ppt. The 1 Hz mean night-time concentration of CINO₂ 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 30 October. These concentrations are comparable to other urban UK 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 CINO₂ 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 LT) and loss after sunrise (ca. 07:30 LT), the maximum concentration measured within a given 24 h period typically peaks at around 22:00 LT and halves by 03:00 LT, where it is maintained. The reasons for the early onset in peak concentration and loss throughout the night is unclear, although on 1 November, a sharp decrease in CINO₂ is a consequence of a change in wind direction, indicating that the source of CINO₂ is directional. A minimum concentration of < LOD is reached by 15:00 LT, indicating that concentrations can persist for much of the day. On 7 November CINO₂ concentrations grow throughout the morning, even after photolysis begins, until 11:00 LT. Correlated high wind speeds suggest that the long-range transport and downward mixing is a likely cause for this daytime increase.
Typically, elevated concentrations of ClNO$_2$ are measured when the wind direction is easterly and wind speeds are low (2–4 ms$^{-1}$), 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 and Ghernaout, 2010). Another source of the ClNO$_2$ precursor is found from the southwest at wind speeds of 9 ms$^{-1}$, indicating a more distant source that is also likely to be industrial or marine. The correlation between ClNO$_2$ and Cl$_2$ is poor at most times, apart from the night of the 30 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 ClNO$_2$ and Cl$_2$ is poor, so it is unlikely they share the same source.

### 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 Cl$_2$, but remain elevated for longer, dropping after sunset. The diurnal profile is similar to that for O$_3$, with a maximum during the day and minima during morning and evening rush hours when NO$_x$ is emitted locally. The strong correlation with O$_3$ ($R^2 = 0.67$) is expected, as the route to the formation of HOCl is the oxidation of Cl with O$_3$ to form ClO and then the oxidation by HO$_2$ 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 5 due to a persistent interference from a large-scale biomass burning event (Guy Fawkes Night, Priestley et al., 2018), which cannot be de-convolved from the dataset due to the small difference in their mass-to-charge ratios and insufficient instrument resolution. 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.CINO$_2^-$ and I.CI$^-$ signals, all of which show night-time maxima. This is inconsistent with the ClO photo-
chemical production pathway of Cl + O₃, suggesting that its maximum concentration should be measured during the day, as was observed for HOCl. It is not possible to confirm if the I.CIO⁻ 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.CI⁻ cluster is a known fragment from ClNO₂ and HOCl, it is reasonable to suspect that I.CIO⁻ 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 and a calibration factor of 4.5 Hz ppt⁻¹ was found. These concentrations are of the same order of magnitude as measured at an urban site in the US but up to 2 orders of magnitude smaller than at US urban costal sites (Keene et al., 1993; Spicer et al., 1998) and a megacity impacted rural site in northern 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 2 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 (Faxon et al., 2015; Liao et al., 2014; Liu et al., 2017). The days with the greatest concentration are those where direct shortwave radiation is at its highest. On 5 November, the incidence of direct shortwave radiation is unhindered throughout the day and a similarly uniform profile for Cl₂ is also observed. On 1 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. 2). Also, when global radiation is low throughout the day, e.g. 7 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 ClINO₂ (R² = 0.98) yet is non-existent with Cl₂ (R² = 0.01) indicating Cl₂ concentration is independent of ClINO₂ concentrations. Second, there is no correlation between HONO 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 C₂H₄O₃ exhibits a similar diurnal profile and radiation dependency (Fig. 2). 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 C₂H₄O₃ (Fig. 2). The changes in O₃ production are observed when NO concentrations are near zero, indicating that 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 that a local photolytic daytime mechanism is responsible for the increase in daytime concentrations as has previously been suggested (e.g. Finley and 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., 2018), there are persistent, non-zero concentrations of Cl₂ (≤ 4 ppt) after sunset. On 4 November, after the period of high secondary activity, intermittent elevations in night-time Cl₂ concentrations when the wind is northerly suggest that 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 in 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 CₙH₂ₙ₊₁OCl, CₙH₂ₙ₊₁O₂Cl, CₙH₂ₙ₊₁O₃Cl, CₙH₂ₙ−₁O₂Cl, CₙH₂ₙ−₁O₃Cl and CₙH₂ₙ−₂O₂Cl (Fig. 3), of which only C₂H₂O₂Cl has been previously reported (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 laboratory calibrations show that the iodide reagent ion can detect CH₃Cl (not calibrated), CH₂Cl₂ (LOD = 143 ppb) and CHCl₃ (LOD = 11 ppb). We find no discernible evidence for the detection of 4-chlorocrotonaldehyde, the Cl oxidation product of 1,3-butadiene and unique marker of chlorine chemistry (Wang and Finlayson-Pitts, 2001) due to interferences from other CHO compounds. We do not believe that 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 28 ppt at 12:00 LT and at a minimum of 5 ppt at 07:00 LT, when NOx concentrations are highest at ~ 30 ppb. Concentrations of C₂H₂O₂Cl (tentatively identified as chloroacetic acid) and C₄H₇OCl (tentatively identified as chloro-hexanol) are the highest of any ClOVOCs, ac-
Figure 2. Time series for 1 November 2014, with (a) Cl₂, (b) solar radiation (global, direct and indirect), (c) photochemical marker C₂H₄O₅, and (d) O₃ and NOₓ, where highlighted boxes demonstrate that \( \frac{\Delta [\text{O}_3]}{\Delta t} \) is increasing. The increase in concentration of Cl₂, C₂H₄O₅ and O₃ production when VOC limited are strongly coupled with direct solar radiation. Greyed areas are night time.

Figure 3. 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 that these species have longer lifetimes.

counting for between 20% and 30% of total CIOVOCs concentrations measured. All concentrations rise towards midday, with C₃H₇O₃Cl and C₂H₃O₂Cl rising the most by a factor of 4 and returning to nominal levels by the early evening (red in Fig. 3). C₃H₇O₂Cl and C₂H₃O₂Cl correlate well with Cl₂ (\( R^2 = 0.77 \) and 0.75, respectively), which is consistent with a photochemical formation mechanism identifying these species as secondary products, potentially chloropropanediol and chloro-acetic acid.

Whilst the diurnal profiles of C₆H₁₃OCl and C₃H₇O₂Cl (blue in Fig. 3) are similar to those of C₂H₃O₂Cl 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 C₃H₇O₃Cl reaching a maximum concentration of 8 ppt at 20:00 LT. This trend suggests that concentration changes could be a function of boundary layer height.

C₃H₇O₂Cl and C₄H₇O₂Cl (yellow in Fig. 3) are the only CIOVOCs that show a positive correlation with NOₓ (\( R^2 = 0.42 \), \( R^2 = 0.41 \)) and negative correlation with O₃ (\( R^2 = -0.58 \), \( R^2 = -0.53 \)). Their correlation is stronger with NO₂ (\( R^2 = 0.55 \), \( R^2 = 0.48 \)), 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 midday consistent with other photochemical species, which is expected of secondary formation. It is possible that these compounds are isobaric or isomeric with the other compounds that interfere with the perceived signals recorded here.

The diurnal profile of C₃H₇O₃Cl (green in Fig. 3) exhibits a similar shape to the bimodal distribution observed for NOₓ. Cross-correlation indicates that a time lag of \(-3\) h provides the best correlation with NO₂ of \( R^2 = 0.80 \). This suggests that local oxidation chemistry, which takes place over long
periods in the day and is sensitive to traffic emission, is the source of this ClOVOc.

4 Discussion

4.1 Effect of global radiation transmission efficiency on CI radical production

Three days are selected based on their different solar short wave transmission efficiencies to quantify the variation in Cl₂ formation and photolysis and thus the influence of Cl₂ on producing Cl. The average transmission of global radiation on 5 November was high with 84 ± 14 % (1σ), whereas on 7 November it was very low with 21 ± 14 %, sometimes dropping below 10 % in the middle of the day. The middle case is represented by 1 November, where the transmission efficiency in the morning was high with 88 ± 11 %, but in the afternoon it was highly variable and dropped to 55 ± 20 % (see Fig. 4). These 3 days provide good case studies for the investigation of the effect of global radiation on molecular chlorine concentrations and therefore the production of Cl.

The reduced transmission efficiency inhibits Cl₂ formation, thereby reducing the contribution of Cl₂ to Cl production. The lower transmission efficiency also reduces the photolysis of Cl₂ and so reduces the production of Cl even further. Figure 5 shows the divergence between the ideal $J_{Cl}$ without transmission efficiency correction (a), the $J_{Cl}$ value scaled by transmission efficiency (b) and subsequent Cl formation. Cl production rates are similar until 11:00 LT, when the scaled production then becomes an average 47 % lower. This is most prominent at 13:00 LT, when the difference between ideal and scaled production is 8.4 × 10^{4} Cl radicals cm^{-3} s^{-1}.

4.2 Contribution of inorganic chlorine to CI radical production

The contribution of HOCl and ClOVOcs to Cl formation is negligible due to low photolysis rates and low concentrations, whereas the contributions from Cl₂ and CINO₂ are much greater (Fig. 6). During the morning of 5 November, CINO₂ is the dominant source of Cl, contributing 95 % of the total Cl concentration, a maximum of 3.0 × 10^{3} Cl radicals cm^{-3}, to the steady-state concentration, which is approximately a factor of 3 lower than the estimated maximum concentration of 9.5 × 10^{3} Cl radicals cm^{-3} produced by CINO₂ photolysis in London during the summer (Bannan et al., 2015) and a factor of 22 lower than the maximum concentration of 85.0 × 10^{3} Cl radicals cm^{-3} calculated from measurements of CINO₂ in Houston (Faxon et al., 2015). In both instances, this is due to a combination of lower $J_{CINO₂}$ and lower CINO₂ concentrations.

As the day progresses, concentrations of Cl₂ increase and it becomes the dominant and more sustained source of Cl by contributing 95 % of Cl (12.5 × 10^{3} Cl radicals cm^{-3}) by the early afternoon, which is approximately 4× that of the CINO₂ measured in the early morning and 1.3× higher than the maximum estimated concentration calculated from the CINO₂ photolysis in London (Bannan et al., 2015). The maximum Cl concentration produced from Cl₂ and CINO₂ photolysis on 5 November reached 14.2 × 10^{3} Cl radicals cm^{-3} at 11:30 LT which is approximately 16 % 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 Cl₂, indicating that Cl₂ can be a much more significant source of Cl than CINO₂. On this high-flux day, when hourly mean Cl₂ concentrations range between 0–7 ppt, the source term is calculated between 4–21 ppt Cl₂ h^{-1}, which is slightly lower, although consistent with previous studies (Faxon et al., 2015; Finley and Saltzman, 2006; Spicer et al., 1998).

A day with low photolysis rates and high daytime CINO₂ concentrations has been highlighted as 7 November. On this day, CINO₂ is the dominant Cl source (95 %) reaching a maximum of 3.4 × 10^{3} Cl radicals cm^{-3} at 09:30 LT, 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 h^{-1}, is also low. This combined with a low maximum of $J_{Cl} = 1.13 × 10^{-4} h^{-1}$ means that maximum Cl production from Cl₂ photolysis on this day is very low, generating 0.9 × 10^{3} Cl radicals cm^{-3} at 10:00 LT.
or a quarter of the maximum contributed by ClNO$_2$ on this day (see Fig. 6). This is represented by the following equation;

\[
\text{Cl}_2^{\text{(aq)}} \xrightarrow{J} \frac{1}{2}\text{Cl}_2^{\text{(g)}} \xrightarrow{k_{reac}} \text{Cl}. \tag{8}
\]

The dependency of Cl formation on Cl$_2$ production and loss highlights the sensitivity of this reaction channel to the photolysis that is demonstrated on these 2 days. The production of Cl from ClNO$_2$ is less sensitive, relatively speaking, to the solar flux, as the production of ClNO$_2$ does not rely on photochemistry but chemical composition cf. Eqs. (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

Summing the concentrations of the CIOVOCs and assuming a uniform photolysis rate $J_{\text{Cl}_2\text{OCl}}$ as detailed in the above section, we derive the contribution of total measured CIOVOC to the Cl budget and compare it to the contribution from inorganic Cl measured here (Fig. 6). On the high-flux day, the Cl concentration reaches $4.0 \times 10^2$ Cl radicals cm$^{-3}$ at midday, which is 30% of the contribution by ClNO$_2$, 3.6% of the contribution from Cl$_2$ and 2% of the HOCI contribution for the same day. On the low-flux day, the CIOVOC contribution is $11.0 \times 10^2$ Cl radicals cm$^{-3}$, which is $\sim 2.8$% of the ClNO$_2$ contribution on that day and $\sim 57$% of the Cl$_2$ contribution. Like Cl$_2$, the production of most CIOVOC 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 15% on the low radiant-flux day and 3% on the high-flux day.

5 Conclusions

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 seven organic chlorinated compounds (CIOVOCs) identified here, only C$_2$H$_3$O$_2$ClO (tentatively assigned as chloroacetic acid) has previously been reported. Although the ToF-CIMS with $1^{-}$ is sensitive towards chlorinated and polychlorinated aliphatic compounds, e.g. methyl chloride (CH$_3$Cl), dimethyl chloride (CH$_2$Cl$_2$) and chloroform (CHCl$_3$), their concentrations were below the detection limit. The sources of CIOVOCs are mostly photochemical with maxima of up to 28 ppt observed at midday, although C$_3$H$_7$O$_2$Cl and C$_4$H$_8$O$_2$Cl concentrations correlate with NO$_2$ accumulating at low wind speeds, indicating they are produced locally, potentially as the thermal breakdown products of higher-mass chlorinated species such as polychlorinated dibenzofurans (PCDD/F) from car exhausts or the oxidation products thereof. C$_3$H$_5$O$_3$Cl shows a good diurnal cross-correlation with NO$_2$ with a time lag of 3 h, suggesting that its production is sensitive to NO$_x$ concentrations on that time scale.

Alongside CIOVOCs, daytime concentrations of Cl$_2$ and ClNO$_2$ are measured, reaching maxima of 17 and 506 ppt, respectively. ClNO$_2$ is a source of Cl in every daytime period measured. Cl$_2$ 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 $\pm$ 14 % of idealised values), Cl$_2$ is the dominant source of Cl, generating a maximum steady state concentration of $12.5 \times 10^5$ Cl radicals cm$^{-3}$ or 74% of the total Cl produced by the photolysis of Cl$_2$, CINO$_2$, HOCI and CIOVOC, with the latter three contributing 19%, 4% and 3%, respectively. This contrasts with a share of 14% for Cl$_2$, 83% for ClNO$_2$ and 3% for CIOVOCs on a low radiant-flux day (21 $\pm$ 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 Cl$_2$ and some CIOVOCs by 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 Cl$_2$, CIOVOCs can be an important source of Cl, although the behaviour of their contribution is similar to Cl$_2$, relying on high rates of photolysis rather than high concentrations as is the case for ClNO$_2$.

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 constrain the contribution that chlorine-initiated chemistry has on a global scale.

**Data availability.** The data are to be uploaded to http://catalogue.ceda.ac.uk/ (last access: 20 September 2018).

**Author contributions.** MP, MIB, TJB and AB operated the CIMS during for the measurement period. Data analysis was performed by MP, MIB and TJB. ERV and JA aided with data analysis. The manuscript was written by MP, MP, SDW and AM performed laboratory calibrations. ARDS and AW provided transmittance data and contributed to that section of the manuscript. DES and CJP provided assistance with the steady-state calculation. DES, CJP and HC supported with project management and manuscript refinement.

**Competing interests.** The authors declare that they have no conflict of interest.

**Acknowledgements.** This work was conducted during a PhD study supported by the Natural Environment Research Council (NERC) EAO Doctoral Training Partnership and is fully funded by NERC, whose support is gratefully acknowledged (Grant ref no. NE/L002469/1).

Edited by: Steven Brown
Reviewed by: two anonymous referees

**References**


Leu, M.-T., Timonen, R. S., Keyser, L. F., and Yung, Y. L.: Heterogeneous Reactions of HNO3(g) + NaCl(s) .fwdarw. HCl(g) + NaNO3(s) and N2O5(g) + NaCl(g) .fwdarw. ClONO2(g) + NaNO3(s), J. Phys. Chem., 99, 13203–13212, https://doi.org/10.1021/j10035a026, 1995.


