

Geophysical Research Letters



RESEARCH LETTER

10.1029/2019GL083764

Key Points:

- Up to 4 ppb of ClNO₂ is measured at a U.K. landfill site
- Subsequent chlorine chemistry can have a significant impact on ozone formation and VOCs oxidation as shown by WRF-Chem modeling

Supporting Information:

- Supporting Information S1

Correspondence to:

T. J. Bannan,
thomas.bannan@manchester.ac.uk

Citation:

Bannan, T. J., Khan, M. A. H., Le Breton, M., Priestley, M., Worrall, S. D., Bacak, A., et al. (2019). A large source of atomic chlorine from ClNO₂ photolysis at a U.K. landfill site. *Geophysical Research Letters*, 46, 8508–8516. <https://doi.org/10.1029/2019GL083764>

Received 23 MAY 2019

Accepted 10 JUL 2019

Accepted article online 15 JUL 2019

Published online 29 JUL 2019

A Large Source of Atomic Chlorine From ClNO₂ Photolysis at a U.K. Landfill Site

Thomas J. Bannan¹ , M. Anwar H. Khan² , Michael Le Breton³ , Michael Priestley¹ , Stephen D. Worrall^{1,4} , Asan Bacak¹ , Nicholas A. Marsden¹ , Douglas Lowe¹ , Joe Pitt¹ , Grant Allen¹ , David Topping¹ , Hugh Coe¹ , Gordon McFiggans¹ , Dudley E. Shallcross² , and Carl J. Percival^{1,5}

¹Centre for Atmospheric Science, School of Earth and Environmental Science, University of Manchester, Manchester, UK, ²Biogeochemistry Research Centre, School of Chemistry, University of Bristol, Bristol, UK, ³Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden, ⁴Now at School of Materials, University of Manchester, Manchester, UK, ⁵Now at Jet Propulsion Laboratory, Pasadena, CA, USA

Abstract Nitryl chloride (ClNO₂) acts as a source of highly reactive chlorine atoms as well as an important NO_x reservoir. Measurements of ClNO₂ at an operational U.K. landfill site are reported here for the first time. A peak concentration of 4 ppb of ClNO₂ was found with a peak mean nighttime maximum of 0.9 ppb. Using models based upon the photolysis of observed ClNO₂ and atmospheric chlorine chemistry, chlorine atom concentrations reaching in excess of 1.20×10^5 molecules/cm³ in the early morning following sunrise are calculated. These concentrations are approximately 10 times higher than previously reported in the United Kingdom, suggesting a significant impact on the oxidizing capacity around such sites. Given the ubiquity of landfill sites regionally and globally, and the large abundances of Cl atoms from the photolysis of ClNO₂, chlorine chemistry has a significant impact on ozone formation and volatile organic compounds oxidation as shown by WRF-Chem modeling.

Plain Language Summary Landfill sites are a known source of trace gases into the atmosphere, but measurements often focus predominately on methane and carbon dioxide. A small subsection of trace gas measurements at landfill sites have shown, however, that these sites may be important halogen sources that could have subsequent impacts on air quality and climate. Spatially limited field measurements have previously been reported of a halogen species, ClNO₂, showing that this species is consistently formed during nighttime hours, but no such measurements before now have been made at any landfill site. ClNO₂ undergoes photolysis upon sunrise, releasing the extremely reactive Cl as well as NO₂ into the atmosphere and therefore plays an important part in the total budget and distribution of tropospheric oxidants, halogens, and reactive nitrogen species, all of which are important to air quality. Here we present mass spectrometry measurements of ClNO₂ taken at an undisclosed landfill, which show high concentrations in comparison to any other global study of this type. We use predictive modeling techniques to show the importance of this halogen species to air quality, using indicators such as ozone formation. Based on these results we recommend that landfill sources of Cl should be included in future air quality studies.

1. Introduction

Landfill gas is a product of the natural biological decomposition of waste material deposited in landfills, typically characterized by production of methane and carbon dioxide (Farquhar & Rovers, 1973). Emissions of other trace gases from landfill sites are potentially large but often uncharacterized and poorly sampled, with implications for local and regional air quality. Allen et al. (1997) have shown that trace gases other than CO₂ and CH₄ are present in landfill gas and that they are formed from intermediate biochemical reactions associated with degradation processes or directly from the degradation and volatilization of certain materials. The impact of these trace gases on air quality and thus human health may be more significant than that of the bulk gases (Chiriac et al., 2007). Keller (1988) showed that the trace gases found in landfill gas are composed of saturated and unsaturated hydrocarbons, acidic hydrocarbons, sulfur compounds, and halogenated compounds. Allen et al. (1997) and Chiriac et al. (2007) provided information on emissions of halogen-containing compounds from landfill, showing that emissions of such species depend highly on temperature and waste composition as well as the use of compaction vehicles. The principle sources of these volatile

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organic compound (VOC) emissions are due to faults in capping or gas collection, open leachate chambers, faults in the liners and covers of closed cells, and finally open cells (Chiriac et al., 2007). Studies such as Eklund et al. (1998) and Schweigkofler and Niessner (1999) have completed measurements of VOC concentrations at various landfill sites, with these studies suggesting that halogen chemistry may be important in landfill sites. Studies focusing on the emission of precursors to reactive chlorine from Landfill sites are however very limited.

The heterogeneous reaction of N_2O_5 and chloride containing aerosol was first shown in the laboratory to produce ClNO_2 by Finlayson-Pitts et al. (1989) and recently there has been considerable interest in field measurements of ClNO_2 in both continental and polluted coastal sites, with reported concentrations ranging between a few parts per trillion and 4 ppb (Osthoff et al., 2008; Kercher et al., 2009; Thornton et al., 2010; Mielke et al., 2011; Riedel et al., 2012; Phillips et al., 2012; Mielke et al., 2013; Tham et al., 2014; Mielke et al., 2015; Bannan et al., 2015; Wang et al., 2016, 2017; Osthoff et al., 2018; Priestley et al., 2018) as well as modeling the importance of chlorine chemistry (e.g., McFiggans et al., 2012; Sarwar et al., 2012; Sarwar et al., 2014; Sommariva et al., 2018). No such data from locations such as landfill sites as yet exists despite suggestions of a large source of halogens in such environments (Eklund et al., 1998).

Recent studies have shown that Cl atoms from photolysis of ClNO_2 can contribute significantly to the total oxidizing capacity (Bannan et al., 2015; Osthoff et al., 2008; Phillips et al., 2012; Tham et al., 2014). Cl atoms are highly reactive toward VOCs and rate coefficients for their reactions with alkanes are generally 2 orders of magnitude larger than those for OH. As oxidation reactions in the troposphere govern the fate of primary pollutants they have an important influence on air quality, climate, and tropospheric ozone production (Prinn, 2003). ClNO_2 can also have an important influence on NO_x lifetimes (Osthoff et al., 2008). Despite this, such chemistry is sparsely constrained by measurements. As landfill sites are a potential source of gaseous halogens, there is a potentially large source of ClNO_2 as yet unquantified. The highly reactive Cl atoms released from this source are likely to have a significant impact on oxidizing capacity that is as yet unquantified regionally or globally if ClNO_2 is consistently found to be present in significant quantities.

In order to assess the impact that ClNO_2 has on boundary layer chemistry around landfill sites, a measurement campaign with the aim of measuring ClNO_2 using a quadrupole chemical ionization mass spectrometer (CIMS) was completed. The effect that Cl from the photolysis of ClNO_2 has on the total tropospheric oxidizing capacity at this landfill site is evaluated by the method explained in Bannan et al. (2015); Bannan, Bacak, et al. (2017) and also by WRF-Chem regional model.

2. Materials and Methods

2.1. Experimental Site

The landfill site for this measurement campaign, as part of the Greenhouse gAs Uk and Global Emission (Palmer et al., 2018), will remain anonymous. Measurements were made in August 2014. This specific landfill site accepts a typical, wide range of nonhazardous domestic and commercial waste, occupying around 330,000 m^2 , and accepts waste on weekdays and Saturdays. The active waste is covered daily by soil and inert materials and the site is equipped with an active gas control system that is made up of a network of extraction cells connected to four landfill gas engine engines. This landfill site is generally typical of U.K. landfill sites in both size and the waste it accepts and will be assumed to be so in the analysis of this study. The landfill site is in close proximity (<5 km) to the center of a large unnamed town and very close proximity (approximately 500 m) to a busy A road.

The site has an active leachate management system, which treats landfill leachate prior to discharge to sewer. The leachate treatment plant next to the landfill site is a combination of an aeration tank and an ultra-filtration unit and operates continuously. It is likely that the aeration tank is a source of local elevated VOCs as landfill leachate is a complex mixture of trace constituents and water. These trace constituents will be a combination of salts, organic compounds and likely small traces of halogenated compounds based on the use of Cl-base degreasers that is aerated aggressively to reduce the amount of ammonia and organics present before discharge to the sewer. This is a process that potentially volatilizes any Cl-containing species in the mixture. Volatile organic halogenated compounds from this source are however unlikely to contribute to the ClNO_2 production seen at this site.

This site is not permitted to accept hazardous wastes, and as a result, any material containing readily liberated chlorine being accepted in any quantity is unlikely. Chlorine-containing materials that could enter the site would include the following: polyvinyl chloride, nonhazardous materials containing NaCl (wood, food, and consumer products), and certain domestic materials.

Bleaches and other cleaning materials containing free-Cl may be used in small quantities at the site for normal domestic purposes such as cleaning in offices. The wastewater from such activities would be directed to the sewerage system and not to the landfill site. The site is regulated under an Environmental Permit and any large-scale use of Cl-containing bleaches within the permitted boundary is unlikely to occur since this would breach the conditions of the permit. In addition, Cl-containing bleaches are detrimental to the microbiological processes active on site within the waste mass and the leachate treatment process so their use would not be desirable.

The quadrupole CIMS, various methane/CO₂ analyzers, and basic meteorological instrumentation were deployed in this exploratory study. Factors that can affect ClNO₂ production such as O₃, NO_y, aerosol surface area, aerosol composition, and humidity were not measured and are not therefore reported. A process based study to ascertain which specific molecules and pathways contribute to ClNO₂ production at landfills is the next important step but is beyond the scope of the work.

2.2. CIMS

A quadrupole CIMS using iodide reagent ion was used to make measurements of ClNO₂ and was deployed around 200 m from the active filling site, and around 50 m from the nearest closed cell. The measurements presented here have an identical set up, including the inlet, to measurements described in Bannan et al. (2014), Bannan, Bacak, et al. (2017), Bannan, Murray Booth, et al. (2017). ClNO₂ was measured at *m/z* 207.9 (I.ClNO₂). N₂O₅ was measured as a fragment at *m/z* 62 (NO₃⁻) as in Le Breton et al. (2014) and at *m/z* 235 (I.N₂O₅⁻) but a large daytime signal (nonlinear between the two) at this site implied a significant interference at both masses and rendered this measurement unusable.

Final calibration was completed postcampaign for ClNO₂, relative to formic acid, which was calibrated for and measured throughout assuming the ratio between formic acid and ClNO₂ sensitivity remains constant. Procedures for calibrations, determination of backgrounds for ClNO₂ and the associated uncertainties are described by Bannan et al. (2015), Bannan, Bacak, et al. (2017). Sensitivity for N₂O₅ is required first before the sensitivity of the instrument to ClNO₂ can be determined. Calibration of N₂O₅ was completed by flowing dry N₂ over solid, purified N₂O₅ into the CIMS and a NO_x analyzer (Thermo Fisher, model 42i NO-NO₂-NO_x Analyzer), with the concentration determined by the stoichiometric ratio of NO₂:N₂O₅. There have been reported instances where the NO_x analyzer is sensitive to NO₃, thus having the potential to influence the reported concentrations of N₂O₅. However, numerous intercomparisons with the broadband cavity enhanced absorption spectrometer, including Le Breton et al. (2014), Bannan, Bacak, et al. (2017), and Zhou et al. (2018) show that this calibration is robust. The possible interference of NO_y on the NO_x analyzer is therefore not deemed important. ClNO₂ was produced by flowing a known concentration of N₂O₅ in dry N₂ through a wetted NaCl scrubber. Conversion of N₂O₅ to ClNO₂ can be as efficient as 100% on sea salt, but it can also be lower, for example if ClNO₂ were to convert to Cl₂ (Roberts et al., 2008). For NaCl the conversion efficiency has been as low as 60% (Hoffman et al., 2003). In this calibration we have followed the accepted methods of Osthoff et al. (2008) and Kercher et al. (2009) that show a conversion yield of 100% and have assumed this yield here. The sensitivity for ClNO₂ was 4.1 counts per parts per trillion and the 3σ ClNO₂ limit of detection (LOD) was 5 ppt.

2.3. UGGA

CH₄ measurements were made using an Ultra-portable Greenhouse Gas Analyser (UGGA; Los Gatos Research, USA); technical information regarding this spectroscopic technique is given by Paul et al. (2001). Due to its better portability, the UGGA was not colocated with the CIMS but instead was positioned at the edge of a closed landfill cell, adjacent to the active filling area. The noncontinuous CH₄ measurements provide representative values for the on-site landfill environment that enable a loss rate for atomic Cl to be calculated, as described subsequently. Laboratory calibrations using certified references before and after the deployment fell within the 1% absolute uncertainty quoted by the manufacturer.

2.4. Modeling

The potential importance of ClNO₂ acting as a source of Cl atoms can be inspected using a simple model, assuming the following reactions govern the steady state concentration of Cl. It should be noted that this is clearly a simplification as there will inevitably be additional sources and losses of the Cl atom.



$$[\text{Cl}] \text{ steady state} = \{J1[\text{ClNO}_2]\} / \{k2[\text{O}_3] + k3[\text{CH}_4] + k4[\text{C}_6\text{H}_6] + k5[\text{C}_5\text{H}_{10}] + k6[\text{C}_7\text{H}_8] + k7[\text{H}_2\text{S}]\}$$

C₆H₆, C₅H₁₀, C₇H₈, and H₂S were not concurrently measured in this study but have been previously measured as part of local monitoring of this U.K. landfill site. Historical Gas chromatography mass spectrometry (GCMS) measurements used for the calculations of this study were made by sampling the main gas collection line directly before the waste gas goes through the onsite blowers. The concentrations used in the calculations presented here are then scaled to the measured ambient CH₄ concentration during this study. Again this is clearly a simplification with associated unquantifiable errors; however, given the lack of associated measurements concurrent with the CIMS and UGGA measurements, a complete as possible loss term for the Cl is presented here.

The amount of Cl generated from landfill sites is also quantified by incorporating the emissions of ClNO₂ (scaled from the concentrations of ClNO₂ in this study) and landfill sites in England (<https://data.gov.uk/dataset/ad695596-d71d-4cbb-8e32-99108371c0ee/permited-waste-sites-authorized-landfill-site-boundaries>) into the mesoscale nonhydrostatic 3-D meteorological model, WRF-Chem (Archer-Nicholls et al., 2014). By considering the production of Cl from the photolysis of ClNO₂ and the losses of Cl by the reactions with ozone and all modeled VOCs, the concentration of Cl was calculated in the model. The rate coefficients were taken from NIST Chemical Kinetics Database (<https://kinetics.nist.gov/kinetics/index.jsp>). To determine the effect of Cl on tropospheric ozone, we compared the model run that included the emission of ClNO₂ from landfill sites to a base case experiment that omitted this emission. The reactivity comparison between VOCs + Cl and VOCs + OH is also investigated using WRF-Chem model study.

The approximate calculation we present here assumes that the landfill is releasing ClNO₂ at a constant rate to give a 24-hr average level of ClNO₂ consistent with that observed at the site of approximately 350 ppt. We also assume that the emission is from an approximate area of 4 km² into a boundary layer with an approximate height of 0.5 km.

3. Results

The complete time series of ClNO₂ is shown in Figure 1a, with concentrations far exceeding the LOD on every night of the measurement campaign. A mean nighttime peak ClNO₂ concentration of 901 ppt was observed with a maximum peak of 4075 ppt, but only for a very brief period of time. The measured ClNO₂ concentrations are substantially higher than that of other reported U.K. measurements of ClNO₂ in London (Bannan et al., 2015) where a mean nighttime ClNO₂ concentration of 84 ppt was observed and a maximum peak of 724 ppt and considerably higher than those reported in other U.K. measurements (Bannan, Bacak, et al., 2017; Priestley et al., 2018; Sommariva et al., 2018). It is interesting to note that the Sunday (10 August 2014) during the measurement period, on the day there is no waste disposal and active

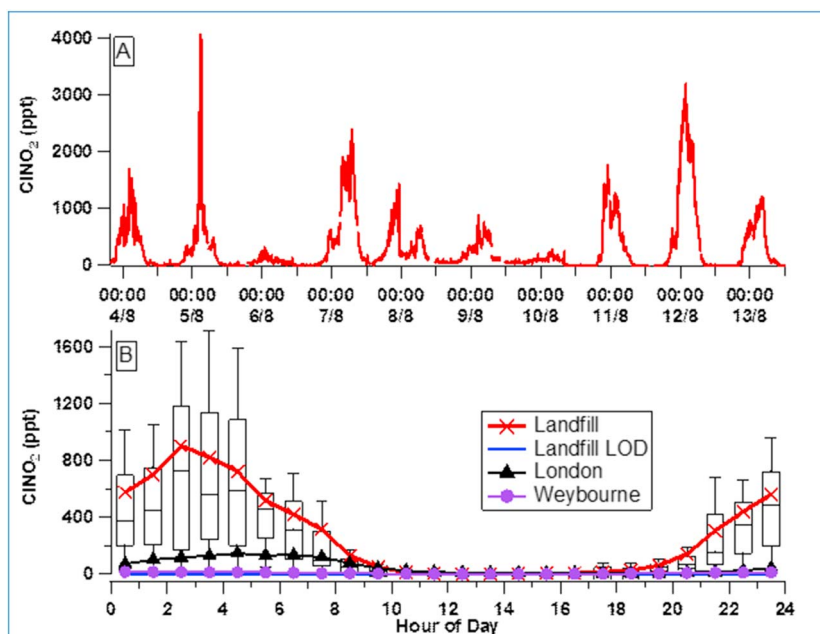


Figure 1. (a) Time series of ClNO_2 from the Manchester ground CIMS. (b) Mean diurnal cycle of ClNO_2 for the complete landfill measurement campaign (red). The box and whisker plots show the, median, 5th and 95th percentiles of ClNO_2 , with the red crosses with connecting lines illustrating the mean values, again for the landfill site. Data between 11 a.m. and 5:30 p.m. whose mean values are below the LOD (signified by the blue line) are excluded from statistical analysis. For comparison the mean ClNO_2 concentration from London (black) and Weybourne are also shown (purple). LOD = limit of detection.

filling, shows the lowest reported measured peak concentrations, but given the relatively short measurement period, a second Sunday measurement was not possible. It is, however, noted that the delivery of waste is only likely to be significant in terms of atmospheric emissions due to the number of vehicle movements as the emissions from the site are thought not to vary significantly day-to-day. Comparable with previously reported measurements of ClNO_2 , a very obvious diurnal profile, linked to production and photolysis was observed in the ClNO_2 (e.g. Kercher et al., 2009; Mielke et al., 2011; Osthoff et al., 2008; Thornton et al., 2010). Concentrations of ClNO_2 above the LOD were measured, on average, until 11 a.m. and then built up again following sunset with a mean peak of 901 ppt (Figure 1b).

Figure 2 illustrates that the vast majority of the high ClNO_2 concentrations arise from the wind sector in which the landfill site is located (active filling site is NW) or during more stagnant winds. There is also a suggestion of elevated concentrations in the sector associated with the sewage treatment works, but this is not correlated with the largest enhancements seen during these measurements. The vast majority of the largest enhancements coming from the landfill site sector enhances our confidence in the conclusion that the landfill site is the source of such elevated ClNO_2 concentrations rather than the nearby large road (SE direction) and the large town also in the SE direction.

While Keller (1988), Allen et al. (1997), and Chiriac et al. (2007) measured a comprehensive suite of halogenated compounds in landfills, the tropospheric lifetimes of the detected species range from 12 to hundreds of years and thus will not contribute to chlorine loading observed here. It is reiterated that a process based study to ascertain which specific molecules and pathways contribute to ClNO_2 production at landfills is the next important step, as is the measurement of such species at other landfill sites.

3.1. Implications for VOC Oxidation

Figure 3a shows that calculated steady state Cl atom concentrations rise rapidly after sunrise, with the peak around 1.24×10^5 atoms cm^{-3} , calculated specifically at the measurement site (R1-7). In Weybourne the Cl atom concentrations reached 6×10^3 atoms cm^{-3} , in comparison with the 1×10^4 atoms cm^{-3} reported in London, using similar methods. The steady state Cl atom concentrations are comparable to the regional

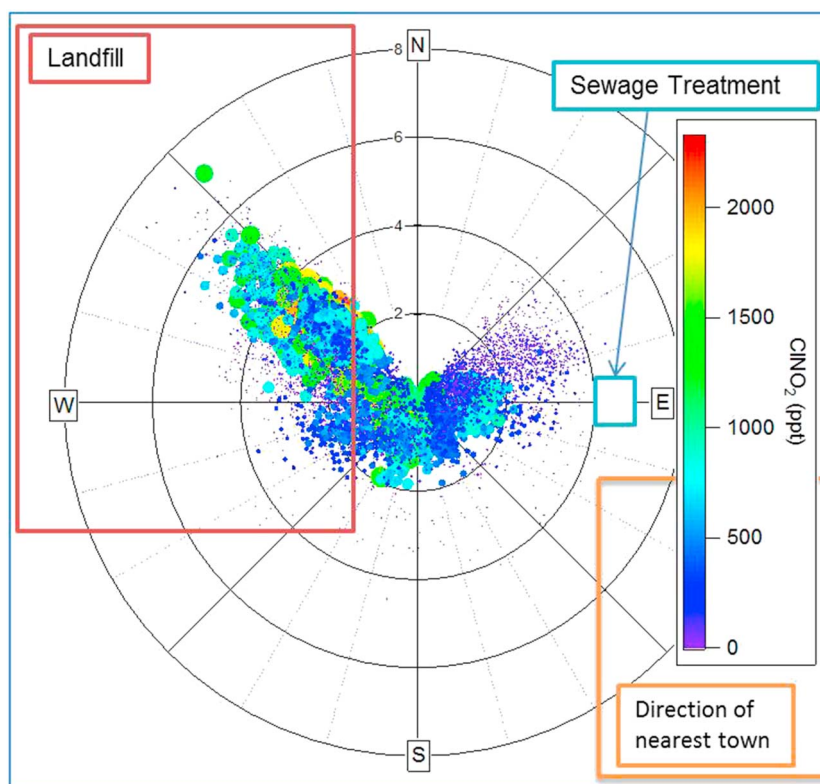


Figure 2. ClNO_2 concentrations as a function of wind speed (m/s) and direction for the complete time period these data are available. Size of the markers also depicts the concentration of ClNO_2 . Boxed areas show general direction but not relative distance of the landfill (Colored red and nearest point 50 m away), sewage treatment (colored blue and situated around 50 m away), and the nearest town (colored orange and 5 mi to the center of the town). The north sector is free of data due to a local obstruction in this direction.

modeling WRF-Chem study that produces $1.25 \times 10^5 \text{ cm}^3$ of Cl in different parts of the United Kingdom (Figures 3b and S1 in the supporting information). The Cl produced from the landfill sites can have a significant impact on ozone levels with increases up to 5 ppb in the polluted cities of the United Kingdom (Figures 3c and S2). The ratio of the loss rates of VOC (e.g., CH_4) by Cl and OH show that VOCs are often removed more effectively by Cl. The removal of CH_4 by Cl can be up to 100 times faster in some parts of the United Kingdom (Figure 3d) than by OH and Cl can also significantly impact ethane, isoprene, 1,3-butadiene and toluene oxidation (Figure S3).

Based on the approximate calculation we present here the annual ClNO_2 production from the landfill is approximately 900 kg/year. There may be uncertainty in the estimates presented here but if our best estimates of emission are correct then landfills are indeed a considerable source of ClNO_2 and should be considered in future studies. Clearly, further work is necessary to establish more accurate emissions estimates and the reproducibility across multiple landfills.

In Bannan et al. (2015), Bannan, Bacak, et al. (2017) chlorine was recycled by a number of chemical pathways, but these reactions are not included in the calculations presented here, meaning that the Cl atoms persisted longer into the day in comparison with the calculations of this study where recycling is not considered. There are also many other species, many of which can be measured by the I^- CIMS, that are not reported here that would have likely increased the concentration of chlorine at this site (e.g., HCl and HOCl). A much increased measurement capability by coupling a time of flight analyzer to the chemical ionization source would also give a more complete chlorine source from this site (e.g., Le Breton et al., 2018; Priestley et al., 2018) as well as other halogen species (e.g., Le Breton et al., 2017). In both regard the simple calculations and incomplete measurement suite presented here represent a lower limit to the total Cl released from this source and more detailed chemistry could enhance the impact of the Cl source from this site. In the steady

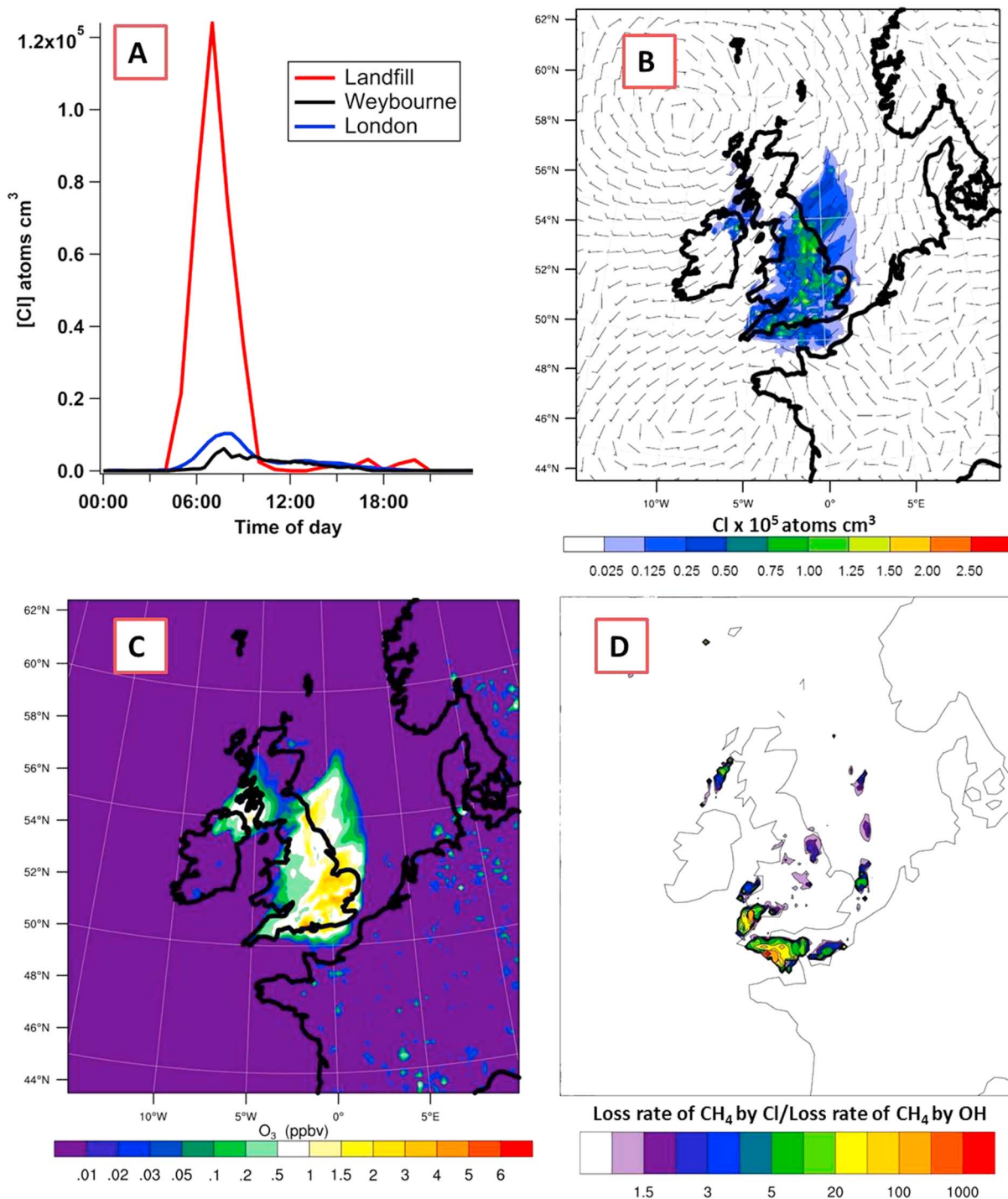


Figure 3. (a) Average calculated diurnal Cl atom concentration profile from the landfill study (red). Cl atom concentration profiles calculated from London (blue) and Weybourne (black) are shown for comparison. (b) WRF-Chem simulations of Cl calculated from incorporating the emissions of ClNO₂ scaled from the concentrations of ClNO₂ in this study to all active U.K. landfill sites at 9 a.m. (c) Enhancement of tropospheric ozone considering the production of Cl from U.K. landfills at 9 a.m. (d) Reactivity comparison between VOCs + Cl and VOCs + OH using WRF-Chem model study at 9 a.m. VOC = volatile organic compound.

state calculation the reaction of Cl with CH₄, among a limited selected others, is used to calculate the loss rate, with the assumption that while other species may be important, the very high methane concentration typical of landfill would be expected to be the dominant reaction pathway for Cl loss. Therefore, a lower limit of Cl loss is also calculated. Despite these acknowledged simplicities in the

chemistry, as a first measurement of this type at a landfill site, it gauges the importance of chlorine chemistry in such locations. Given the measurements and model calculations presented here the importance of chlorine chemistry at sites of this type is significant, especially given the ubiquity of landfill sites.

4. Conclusions

Significant nighttime concentrations of up to 4 ppb of ClNO₂ at a landfill site in the United Kingdom have been measured using a quadrupole CIMS with I-ionization scheme. A mean nighttime peak concentration of 901 ppt suggests that the production of this species is a common occurrence at landfill sites and very simple calculations have shown that this source of Cl alone is significant and much higher than has reported in other measurements of this type in the United Kingdom. This is the first time a measurement of this type has been made at such a site and suggests that chlorine chemistry at landfill sites is important to consider, especially given the ubiquity of landfill sites in the United Kingdom and globally.

Acknowledgments

This work was supported by NERC (NE/H003193/1). The data presented in this paper are stored at <http://data.ceda.ac.uk/badc/gauge/data> website. Alternatively, please email Thomas Bannan at thomas.bannan@manchester.ac.uk for all the data used here.

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