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Chlorine oxidation of VOCs at a semi-rural site in Beijing: Significant chlorine liberation from $ClNO_2$ and subsequent gas and particle phase Cl-VOC production

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Abstract. Nitryl Chloride ($ClNO_2$) accumulation at night-time acts as a significant reservoir for active chlorine and impacts the following day´s photochemistry when the chlorine atom is liberated at sunrise. Here, we report simultaneous measurements of N_2O_5, a suite of inorganic halogens including $ClNO_2$ and Cl-VOCs in the gas and particle phase utilizing the FIGAERO-ToF-CIMS during an intensive measurement campaign 40 km Northwest of Beijing in May and June 2016. A maximum concentration of 2900 ppt of $ClNO_2$ was observed with a mean campaign night-time concentration of 487 ppt, appearing to have an anthropogenic source supported by correlation with SO_2, CO and benzene, which often persisted at high levels after sunrise until midday. This was attributed to such high concentrations persisting after numerous e-folding times of the photolytic lifetime enabling the chlorine atom production to reach 2.3 x 10^5 molecules cm^{-3} from $ClNO_2$ alone, peaking at 9:30 am and up to 8.4 x 10^5 molecules cm^{-3} when including the supporting inorganic halogen measurements.

Cl-VOCs were measured in the particle and gas phase for the first time at high time resolution and illustrate how the iodide ToF-CIMS can detect unique markers of chlorine atom chemistry in ambient air from both biogenic and anthropogenic sources. Their presence and abundance can be explained via time series of their measured and steady state calculated precursors, enabling the assessment of competing OH and chlorine atom oxidation via measurements of products from both of these mechanisms and their relative contribution to SOA formation.

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1. Introduction

NO and NO_2 (NO_x) are important catalysts in the photochemical production of ozone (O_3) playing a significant role in the oxidation of volatile organic compounds (VOCs) and subsequently have an adverse effect on air quality. In the daytime NO_x is primarily removed by the hydroxyl radical (OH) to form nitric acid (HNO_3), which is subsequently lost by wet deposition, becoming a major component of acid rain. At night-time, the OH radical is not a significant oxidant as photolysis stops, enabling the reaction between NO_2 and O_3 to form significant concentrations of the nitrate radical (NO_3) (Atkinson, 2000). NO_3 can accumulate at night or further react with NO_2 leading to the formation of N_2O_5 (Brown *et al.*, 2003b, Brown and Stutz, 2012). This equilibrium can lead to the reaction of NO_3 with VOCs at night forming organic nitrates or act as an important intermediate for heterogeneous reaction on aerosols as N_2O_5 produces NO_3^- and NO_2^+ in the aqueous phase (Hallquist *et al* 1999, Hallquist *et al*, 2000, Wagner *et al.*, 2013). In the presence of chlorine, which is assumed in models to predominantly come from sea salt (Baker *et al*., 2016), nitryl chloride ($ClNO_2$) can be formed and released into the gas phase from the aerosol surface (Osthoff *et al*., 2008). $ClNO_2$ formation thereafter acts as a night-time radical reservoir due to its stability at night.

At sunrise $ClNO_2$ is rapidly photolysed, liberating the highly reactive chlorine atom subsequently converting it into Cl, ClO, HOCl and $ClONO_2$ depending on the available sunlight, O_3, HO_x and NO_x levels via the following reaction pathways (R1-R9).

R1. $ClNO_2 + h\nu \rightarrow Cl + NO_2$

R2. $Cl + O_3 \rightarrow ClO + O_2$

R3. $ClO + NO_2 \rightarrow ClONO_2$

R4. $ClO + HO_2 \rightarrow HOCl + O_2$

R5. $ClONO_2 + h\nu \rightarrow Cl + NO_3$

R6. $ClONO_2 + h\nu \rightarrow ClO + NO_2$

R7. $HOCl + h\nu \rightarrow Cl + OH$

R8. $ClONO_2 + H^+ + Cl^- \rightarrow Cl_2 + HNO_3$

R9. $HOCl + H^+ + Cl^- \rightarrow Cl_2 + H_2O$

R10. $ClO + NO \rightarrow Cl + NO_2$

The liberated chlorine atom can react with VOCs and contribute to daytime photochemical oxidation, competing with OH and perturbing standard organic peroxy radical abundance ($RO_x = OH + HO_2 + RO_2$), O_3 production rate, NO_x lifetime and partitioning between reactive forms of nitrogen (Riedel *et al*., 2014). The chlorine atom possesses

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rate constants with a number of VOCs 200 times larger than OH (Tanaka *et al*., 2003); therefore, its abundance, fate and cycling can significantly alter standard daytime oxidation pathways. This perturbation is currently thought to only be significant in the early hours of the day while OH concentrations are low and chlorine atom production is high through the photolysis of $ClNO_2$. Additional Cl_2 photolysis and HCl reaction with OH can also produce chlorine atoms throughout the day but at lower rates.

The oxidation mechanism of saturated hydrocarbon (R11-R13) is initiated by reaction with OH or chlorine atom to form an organic peroxy radical (RO_2), and H_2O or HCl depending on the oxidant. In a heavily polluted environment such as Beijing, the RO_2 favours further reactions with NO to form an oxygenated volatile organic compound, HO_2 and NO_2 or an alkyl nitrate $RONO_2$. Specifically, acyl peroxy radicals can also react with NO_2 to form acyl peroxy nitrates (APN) such as peroxy acetyl nitrate (PAN).

R11. $RH + OH \xrightarrow{O_2} RO_2 + H_2O$

R11. $RH + Cl \xrightarrow{O_2} RO_2 + HCl$

R12a. $RO_2 + NO \rightarrow OVOC + HO_2 + NO_2$

R12b. $RO_2 + NO \rightarrow RONO_2$

R13. $RO_2 + NO_2 \leftrightarrow APN$

Addition of the chlorine atom to unsaturated VOC can also occur and then continue on the similar reaction pathway as R11 – R13. These pathways results in the production of unique chlorine atom chemistry markers which have been previously investigated to indicate the extent of chlorine atom oxidation reactions (Riemer *et al*., 2008, Keil and Shepson, 2006). The utilization of these compounds, such as 2-chloroperoxypropionyl nitrate (2-Cl PPN) and 1-chloro-3-methyl-3butene-2-one (CMBO) as chlorine atom chemistry markers relies on the abundance of the chlorine atom, the VOC precursor; HO_x, NO_x and O_3 and competing pathways for chlorine atom reactions. Riedel *et al.* (2014) calculated that up to tens of ppt Cl-VOCs are formed as a result of chlorine atom addition to alkenes and can therefore provide a number of potential periods of dominating active Cl chemistry (Wang *et al*., 2001).

The production of chloroperoxy radicals via chlorine atom addition can lead to the formation of semi volatile oxidation products which have been observed for both biogenic (Cai and Griffin *et al*., 2006) and anthropogenic emissions (Huang *et al*., 2014, Riva *et al.*, 2015) in controlled laboratory studies. Chlorine initiated oxidation of isoprene could also represent a significant oxidation pathway due to its rapid reaction rate compared to OH (Orlando *et al*., 2003) resulting in gas phase products such as chloroacetaldehyde and CMBO, a unique tracer for atmospheric chlorine atom chemistry (Nordmeyer *et al*., 1997). Furthermore, reactions of the chlorine atom with isoprene or its SOA derived products could serve as an atmospheric chlorine sink (Ofner *et al*., 2012). Wang *et al.* (2017) revealed chlorine initiated oxidation of isoprene can produce SOA yields up to 36%, with products similar to that of OH isoprene oxidation. This SOA formation from chlorine initiated oxidation presents a large knowledge gap in the literature, which to date is limited by measurement capabilities.

This complex system results in a large uncertainty in the global budget of chlorine atoms ~ 15– 40 Tg Cl yr^{-1} calculated by indirect means (Allan *et al*., 2007; Platt *et al*., 2004), which is further limited by the ability of

measurement techniques to accurately quantify short lived species at low concentrations. Our knowledge of the Cl budget therefore depends on the accurate measurement of its precursors, namely $ClNO_2$ and major reaction pathways of the chlorine atom upon liberation in the daytime. Measurements to date show that the concentrations of $ClNO_2$ vary geographically from below limits of detection to hundreds of ppt (Mielke *et al*., 2015, Phillips *et al*., 2012, Bannan *et al*., 2015) and up to 3 ppb (Tham *et al*., 2014, Riedel *et al* 2014, Liu *et al*., 2017) in heavily polluted urban areas. To date, the majority of these measurements have been performed in the United States, although research globally and in China have recently been published (Tham *et al*., 2014, T Wang *et al.*, 2016, X. Wang *et al*., 2017, Z. Wang, Liu *et al*. 2017).

Iodide adduct ionization has previously been applied to measure inorganic halogens in ambient air (Osthoff *et al*., 2008, Riedel *et al*., 2012, Thornton *et al*., 2010, Le Breton *et al*., 2017) using mass spectrometers with quadrupole mass analysers. This technique involves periodically changing the tuning of the spectrometer to allow transmission of a particular mass ion to the detector. Several species are therefore often "chosen" for detection in order to achieve high enough time resolution. Recent developments and availabilities of a Time of Flight Chemical Ionisation Mass Spectrometer (ToF-CIMS) have enabled the simultaneous measurement of all detectable ions by an ionization technique via high frequency full mass spectral collection. The high resolution (4000) of this technique also enables much lower limits of detection for species which may have the similar mass to a compound that is much more abundant via multi peak fitting. This technique has previously been applied for the measurement of $ClNO_2$ and Cl_2 (Faxon *et al* 2015) and recently for Cl-VOCs (Wang *et al.*, 2017) in the gas phase. In this study, a ToF-CIMS utilizing the FIGAERO (Filter Inlet for Gas and AEROsols) is deployed at a site in semi-rural Beijing, China to measure the gas and particle phase precursor ($ClNO_2$, N_2O_5) and selective halogen containing species at high time frequency and resolution to further our understanding of the chlorine atom budget in this region and its potential fate.

2. Experimental

2.1 Site description

The data presented here was collected during the inter-collaborative field campaign, within the framework of a Sino-Sweden research project "Photochemical Smog in China" aimed to further our understanding of the episodic pollution events in China through gas and particle phase measurements with numerous analytical instruments. The laboratory setup in the Changping University Campus of PKU was situated at a semi-rural site 40 km North West of Beijing close to Changping town (40.2207° N, 116.2312° E). The general setup has previously been described by Le Breton *et al*., 2017.

All instruments sampled from inlets setup in a laboratory 12 metres high from the 13th May 2016 to 23rd June 2016. The site has a small town within its vicinity and some small factories within 5 kilometers. A High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) was utilized to measure the mass concentrations and size distributions of non-refractory species in submicron aerosols, including organics, sulfate, ammonium and chloride (DeCarlo *et al, 2006*, Hu *et al.*, 2013). The setup of this instrument has been previously described by Hu *et al.*,

(2016). An Ionicon Analytik high sensitivity PTR-MS (Proton TRansfer Mass Spectrometer) as described by de Gouw and Warneke *et al*, (2007) provided supporting precursor VOC measurements.

2.2 ToF-CIMS setup

Gas and particle phase ambient species were measured using an iodide ToF-CIMS coupled to the FIGAERO inlet (Lopez-Hilfiker *et al*., 2014). The setup for this campaign has previously been described by le Breton *et al*. (2017). Briefly, the iodide ionization scheme was utilised to acquire non-fragmented ions of interest by passing UHP N_2 over a permeation tube containing liquid CH_3I (Alfa Aesar, 99%), and through a Tofwerk X-Ray Ion Source type P (operated at 9.5 kV and 150 µA) to produce the iodide reagent ions. The ionized gas was then carried out of the ion source and into the Ion-Molecule Reaction (IMR) chamber through an orifice (Ø = 1 µm). The inlet lines were 2 metres long and composed of copper tubing (12 mm) for the aerosol inlet and Teflon tubing (12 mm) for the gas sample line. Particles were collected onto a Zefluor® PTFE membrane filter at the same rate as the gas inlet line sampling, 2 SLM. The FIGAERO was operated in a cyclic pattern; 25 minutes of gas phase measurement and simultaneous particle collection, followed by a 20 minute period during which the filter was shifted into position over the IMR inlet and the collected particle mass was desorbed.

2.4 Calibration

In the field formic acid calibrations were performed daily utilising a permeation source maintained at 40 ˚C. A dry N2 flow (200 sccm) was passed over the permeation source and joined a 2 SLM N2 flow line directed towards the inlet. The concentration of the flow was determined by mass loss in the laboratory after the campaign. The sensitivity of the ToF-CIMS to formic acid was found to be 3.4 ion counts per ppt Hz^{-1} for $1x10^5$ iodide ion counts.

N_2O_5 was synthesized by mixing 20 ppm O_3 with pure NO_2 (98%, AGA Gas) in a glass vessel and then passing the mixture through a cold trap held at -78.5 ˚C by dry ice. The N_2O_5 was transferred to a diffusion vial fitted with a capillary tube (i.d. 2 mm). The N_2O_5 diffusion source was held at a constant temperature (-23 ˚C), and the mass loss rate was characterized gravimetrically for a flow rate of 100 sccm. The same flow was added to a dry nitrogen inlet dilution flow of 2 SLM to calibrate the CIMS. $ClNO_2$ measurements were quantified by passing the N_2O_5 over a wetted NaCl bed to produce $ClNO_2$. The decrease in N_2O_5 from the reaction with NaCl was assumed to be equal to the concentration of $ClNO_2$ produced (i.e., a 100% yield). Conversion of N_2O_5 to $ClNO_2$ can be as efficient as 100% on sea salt, but it can also be lower, for example if $ClNO_2$ were to convert to Cl2 (Roberts et al., 2008). For NaCl the conversion efficiency has however been as low as 60% (Hoffman et al., 2003). In this calibration we have followed the accepted methods of Osthoff et al., (2008) and Kercher et al., (2009) that show a conversion yield of 100% and have assumed this yield in the calibrations of this study. In this calibration we have followed the accepted methods of Osthoff et al., (2008) and Kercher et al., (2009) that show a conversion yield of 100% and have assumed this yield in the calibrations of this study. The lower detection limit of the CIMS to N_2O_5 and $ClNO_2$ was found to be 9.5 and 1.2 ppt respectively for 1minute averaged data. Using the error in the individual slope of the calibrations results in a total uncertainty of 30% for both N_2O_5 and $ClNO_2$. These sensitivities were applied relatively to that of formic acid.

A post campaign calibration of chloroacetatic acid (99%, Sigma Aldrich) was utilised to apply a sensitivity factor for all Cl-VOCs measured during the campaign. The calibration was performed using the same method as for formic acid and determined a sensitivity of 1.02 ion counts ppt^{-1} Hz when normalized to $1x10^5$ I^- ion counts. Relative sensitivities will increase the error to an unknown range, but is a commonly applied method within the CIMS community, although it is likely that the sensitivity is similar for all inorganic/organic halogens, as shown by Le Breton *et al*. (2017).

3. Results and Discussion

3.1 Peak identification and quantification

Peak fitting was performed utilizing the Tofware peak fitting software for molecular weights up to 620 AMU. The standard peak shape was fitted a peak on the spectra until the residual was less than 5%. Each unknown peak was assigned a chemical formula using the peaks exact mass maxima to 5 decimal places and also isotopic ratios of subsequent minor peaks. An accurate fitting was characterized by a ppm error of less than 5 and subsequent accurate fitting of isotopic peaks. The analysis here focuses on species identified in the mass spectra considered to possibly play important roles with respect to the night-time chlorine reservoir and several other key night-time oxidants; $ClNO_2$, HCl, Cl_2, ClO, HOCl, OClO, $ClONO_2$, N_2O_5 and Cl-VOCs. Figure 1 displays the average mass spectra for the measurement campaign and the peak fitting applied for ClO and $ClNO_2$. All species were a dominant peak with a multi peak fit, although a number of co-existing peaks were present for much of the campaign. This signifies the importance of high resolution fit data and the need for high resolution measurements. A quadrupole CIMS may not be able to resolve the peak adjacent to ClO at mass 178 and the second dominant peak for the $ClNO_2$ fit would result in a 10% over estimation.

3.2 N_2O_5 measurements

The CIMS and a Cavity Enhanced Absorption Spectrometer (CEAS) measured N_2O_5 (Wang *et al*., 2017) simultaneously from the 13th May 2016 to the 6th June 2016. However, given the use of the FIGAERO, the CIMS alternated measurements between gas and particle phases so did not generate a completely continuous gas phase time series. Here, the CEAS is utilised to validate the CIMS N_2O_5 (at m/z 235) measurements and also instrument stability. The CEAS was calibrated for N_2O_5 in the field whereas the CIMS only performed pre and post campaign calibrations. The simultaneous measurements of N_2O_5 can be shown in Figure 2 for one minute averaged data. The time series show a good agreement for both background concentrations during the day (sub 10 ppt) and high night-time concentrations (up to 800 ppt), excluding one night. The highest N_2O_5 levels observed by both the CEAS and CIMS were observed on the 3rd June although the CEAS reports 880 ppt whereas the CIMS reports 580 ppt. If included in the analysis the R^2 is 0.71 and when excluded it is 0.76. To date the reason for this deviation during that night is not known but it should be stressed that N_2O_5 measurements are delicate and highly depending on sampling condition, e.g. the RH. Nevertheless, excluding this night from the comparison, a slope of 0.85 is observed and a y offset of 0.9. The diurnal profile in Figure 2 represented the difference between the two

measurements throughout the campaign. The largest error between the two measurements occurs at night during the higher levels of N_2O_5, although averaging at 4 ppt. Differences could arise from a number of various factors. Inlet differences such as the CIMS heated IMR (to 40 ˚C to reduce wall loss), residence time and ambient NO_2 can all change thermal decomposition and wall loss rates between the instruments, which is determined for the CEAS in Wang *et al*. (2017) but not for the CIMS in this work. Also, the inlets were facing in different directions within the same laboratory, possibly enabling local wind patterns to affect the concentrations reaching each instrument.

The CEAS data was further utilised to assess any sensitivity changes for the CIMS that daily carboxylic acid calibrations did not account for. A time series of hourly factor differences between the CIMS and CEAS was implemented into the data to weight the measurements to a normalised sensitivity. The high level of agreement from low concentration measurements and a species with a short lifetime from different inlets confirms the accuracy and reliability of the CIMS measurements for this campaign.

Generally, N_2O_5 was detected throughout the campaign with a clear diurnal variation peaking at night-time and rapidly falling to below limits of detection in the daytime as a result of photolysis of N_2O_5 and NO_3. The campaign mean night-time mixing ratio was 121 ppt with a standard deviation of 76 ppt. The maximum concentration of N_2O_5 observed was 880 ppt on the 3rd June. This range of concentrations lie within the recently reported values in the literature, but not at the extreme concentrations as observed in Germany (2.5 ppb) (Phillips *et al*., 2016) or Hong Kong (7.7 ppb) by Wang *et al.* (2016) and Brown *et al.* (2017). Although the mean concentrations do not increase significantly during the pollution episodes, the maximum concentrations detected overnight increase by up to a factor of 4.

3.3 Inorganic chlorine abundance and profiles

Mean diurnal profiles of HCl, Cl_2, $ClONO_2$, HOCl, ClO and $ClNO_2$ are displayed in Figure 3 from data between the 23rd May and the 6th June. HCl exhibited a standard diurnal profile increasing in concentration throughout the day and peaking at 4 pm which then fell off slowly at night. The mean HCl campaign concentration was 510 ppt (σ 270 ppt) and the maximum HCl concentration was 1360 ppt on the 30th June. Cl_2 exhibited a diurnal profile peaking at both the night-time and daytime. High concentrations were observed at night followed by a sharp loss at sunrise and a general build-up throughout the day. The campaign mean concentration was 0.65 ppt (σ 0.5 ppt) and the maximum concentration was 4.2 ppt on the 4th June just before midnight. This agrees well with recent urban measurements of Cl_2 in the USA where Faxon *et al*. (2015) observed a maximum of 3.5 ppt and Finley *et al*. (2006) observed up to 20 ppt in California. Up to 500 ppt Cl_2 has recently been reported in the Wangdu County, South West of Beijing (Liu *et al*., 2017). Although the concentrations we report here are significantly lower, as detailed later, their source maybe of similar origin, which is indicated to be from power plant emissions.

The diurnal profile of HOCl peaked during the daytime via its main formation pathways are via reaction of ClO and HO_2 and Cl with OH. Interestingly the ClO in this work exhibits a night-time diurnal peak, contradicting known formation pathways via Cl reaction with O_3 and the photolysis of $ClONO_2$. The complexity continues as $ClONO_2$ also peaks during the night, given that its main known formation pathway is via reaction of ClO (produced at sunrise via $ClNO_2$ photolysis) with NO_2. The misidentification of $ClONO_2$ and ClO is not thought to be a

possible reason for these discrepancies due to the low number of mass spectral peaks that have maxima at night and the mass defect of chlorine making the peak position unique to chlorine containing molecules. IMR chemistry is also not a possible source as these reactions would occur throughout the day, therefore skewing all of the data and not just the night-time levels. It is hypothesized that in extremely high OH and HO_2 concentrations, all ClO is rapidly converted to HOCl, limiting the formation on significant levels of ClO and subsequently $ClONO_2$. Khan *et al* (2008) suggest that Cl atoms of around $2x10^4$ molecules cm^{-3} could be present at night via analysis of alkane relative abundance. Although a formation mechanism is not proposed, it provides further evidence that ClO formation at night-time is possible and may represent an unknown reaction pathway, which would agree with the measurements presented in this work.

$ClNO_2$ exhibited a similar diurnal profile as N_2O_5, peaking at night-time and lost during daylight due to photolysis. The campaign mean night-time mixing ratio was 487 ppt. The maximum concentration observed was 2900 ppt on the 31st May, similar to that previously measured at semi-rural site in Wangdu (up to 1500 ppt) (Liu *et al.*, 2017), Mount Tai (2000 ppt) (Wang *et al*., 2017), but lower than that in Hong Kong (4 ppb) (Wang *et al* 2016).

The high levels of $ClNO_2$ indicate a local significant source of chlorine to support such high yields. The dominant source of chlorine atoms for $ClNO_2$ production within models, such as the Master Chemical Mechanism (MCM), is from sea salt, although the site is situated 200 km from the Yellow Sea and therefore has low probability that the Cl has this origin. The mean AMS chloride mass loading was 0.05 μg m^{-3} for the campaign with a maximum of 1.7 μg m^{-3}. The Cl^- from the AMS appears to be correlated strongly with CO and SO_2, likely to originate from power plants or combustion sources. This suggests the chlorine has an anthropogenic source and not marine, which is also further supported by the wind direction during higher Cl^- concentrations (Figure 4). Tham *et al*., (2016) observed a strong correlation of aerosol chloride with SO_2 and potassium in the same season in 2014 at Wangdu (semi-rural site 160 km south West of Beijing) and suggested contribution to fine chloride from burning of coal and crop residues. The latter was also supported by satellite fire spot count data (Tham *et al*., 2016). Riedel *et al.* (2013) have previously reported high $ClNO_2$ concentrations observed from urban and power plant plumes measuring high concentrations of gas phase Cl_2. The correlation with SO_2 indicates coal burning as a potential source of particulate chlorine which is known to be a significant source of PM in the Beijing region (Ma *et al*., *2017),* and correlation with CO and benzene is an indicator of biomass burning (Wang *et al*., 2002).

In order to test the hypothesis of biomass burning as a source of particulate chlorine, biomass burning emissions and transport were modelled using the EMEP MSC-W chemical transport model (Simpson et al., 2012, Simpson et al., 2017) driven by meteorology from the WRF-ARW model (Skamarock et al., 2008). The model was run on two nested domains (0.5˚ and 0.1667˚ resolution respectively) with biomass burning emissions from the two databases FINN and GFAS, and anthropogenic emissions from the MEIC inventory (http://meicmodel.org/). Two versions of the model, one getting emissions from open biomass burning from the Fire Inventory from NCAR (FINN) (Wiedinmyer et al., 2011) and one getting them from the Global Fire Assimilation System (GFAS) (Kaiser et al., 2012), were run for the entire period of the Changping measurement campaign. Neither of these two biomass burning databases contain data on chlorine emissions, so instead the biomass burning emissions of CO (CO_{bb}) were tracked and compared to the total concentration of CO (CO_t) at the Changping site. CO was chosen since the measurements at Changping had shown strong correlation between CO and $ClNO_2$ and because CO could be expected to be co-emitted with chlorine for both biomass burning and industrial combustion.

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Figure S1 (supplementary) shows time series of the measured $ClNO_2$ concentrations at the Changping site, as well as the modelled concentrations of CO_t and CO_{bb}. CO_{bb} is shown for both the FINN and GFAS model runs, while CO_t is only shown for the FINN run since it looks almost completely the same for the GFAS run. From this figure it is clear that concentrations of CO_{bb} are very low compared to CO_t. The two episodes of increased concentration, May 18-May 23 and May 28-June 5, are to some extent visible in all time series, but for the biomass burning CO series, the second episode is much less pronounced. Night-time averages of the concentrations shown in figure S2 were calculated for each night for the time period 18:00 to 08:00 local time (UTC+8), roughly corresponding to the period when $ClNO_2$ is not destroyed by photolysis. Nights with significant amount of missing data for the measurements were excluded. Figure S2 shows scatter plots of these averages of $ClNO_2$ against the averages of the other species. Figure S2 also shows a straight line fitted for each of these scatter plots. The $R^2$for these lines were 0.48, 0.04, and 0.21 for CO_t, CO_{bb} FINN, and CO_{bb} GFAS respectively. The fact that concentrations of CO_{bb} is so much smaller than CO_t according to the model, combined with the much better correlation for CO_t than for CO_{bb} strongly suggests that industrial emissions are the dominant source of chlorine, rather than biomass burning.

A particle desorption profile was observed in the high resolution data for $ClNO_2$. The count increase at this 1 AMU mass can be attributed to two sources; SO_3 and $ClNO_2$ as shown in Figure 5. The SO_3 peak is predominantly found in the particle phase and is below limit of detection (LOD) in the gas phase. During initial analysis of the data, SO_3 interfered with the $ClNO_2$ peak fitting and attributed its counts to $ClNO_2$ in the particle phase as its ^{33}S ion is only 0.005 AMU away from the $ClNO_2$ peak. Upon its inclusion into the peak list and utilisation of the Tofware feature which constrains isotopes and reallocates the signal appropriately, $ClNO_2$ remains to indicate a strong desorption profile. The diurnal cycle of these desorptions correlate well with the $ClNO_2$ gas phase profile, indicating a correct assignment of the counts to particle phase $ClNO_2$. The desorption profiles with respect to temperature also exhibit a thermogram structure and not e.g. a gas phase leak into the system which could have accounted for the correlation with the gas phase time series. This suggests the possible presence of $ClNO_2$ in the particle phase. Another possible explanation could be the deposition of $ClNO_2$ from the gas phase onto the filter as the ambient air flows through the FIGAERO.

If we assume the analysis and collection technique is correct, we see an average particle to gas phase partitioning of 0.07, with a maximum of 0.33 and a minimum of 0.009. The average concentration of $ClNO_2$ collected onto the filter during desorption is 13 ppt with a maximum of 120 ppt. Previous modelling studies assume all $ClNO_2$ is in the gas phase due to the low Henry's law constant e.g. for the TexAQS II campaign they calculated that 0.1 ppb in the gas phase would yield 0.54 ppt in the particle phase (Simon *et al.*, 2008). However, these data indicates a significant amount of the chlorine associated with $ClNO_2$ is not liberated from the particle phase. The slope of the particle to gas phase CIMS data is calculated to be 0.048, a factor of 96 higher than using the Henry's law coefficient to estimate the particle concentration.

3.4 $ClNO_2$ daytime persistence and Cl liberation

Both $ClNO_2$ and N_2O_5 are photoyltically unstable, with studies reporting lifetimes on the order of hours for $ClNO_2$ depending on the solar strength (e.g. Ganske et al., 1992, Ghosh et al., 2011). Nocturnal $ClNO_2$ removal pathways have generally been reported to be negligible, with $ClNO_2$ being assumed to be relatively inert (Wilkins et al.,

1974; Frenzel et al., 1998; Rossi, 2003; Osthoff et al., 2008), but the work of Roberts et al., (2008) and Kim et al., (2014) would suggest that this may not be strictly true. However, given that the average diurnal profile does not show the importance of nocturnal removal pathways in this study, observed losses are attributed solely to photolysis, with J($ClNO_2$) controlling the lifetime.

Rapid photolysis can be observed for N_2O_5 in Figure 6 showing a near instant drop below LOD, whereas the $ClNO_2$ concentration not only persists for up to 7 hours, but also shows evidence of an increase in concentration at 7 am (Figure 6). This is observed throughout the campaign and has been frequently observed in the previous study at Wangdu (Tham *et al*., 2016). The breakdown of the nocturnal boundary layer and inflow of air masses from above, carrying pollution from nearby industry/ies is a likely cause of this persistence of possible increase of $ClNO_2$. Liu *et al*. (2017) also observed high daytime concentrations of $ClNO_2$ (60 ppt) at the Wangdu site which they attribute to a possible oxidation mechanism due its correlation with O_3 and Cl_2 providing a daytime formation pathway to maintain concentrations against its rapid photolysis.

Consistent with past measurements and the measurements of this study, $ClNO_2$ is expected to provide a significant source of Cl during day time hours, presenting a potentially significant source of the reactive Cl atom during the day. Its rapid photolysis rate and elevated concentrations enables Cl to compete with OH oxidation chemistry, the known dominant daytime radical source. Here, a simple steady state calculation will be used to determine the Cl atom concentration as detailed;

$$Cl_2 + h\nu \rightarrow Cl + Cl \quad (1)$$

$$ClNO_2 + h\nu \rightarrow Br + Cl \quad (2)$$

$$ClONO_2 + h\nu \rightarrow Cl + NO_2 \quad (3)$$

$$HOCl + h\nu \rightarrow OH + Cl \quad (4)$$

$$OClO + h\nu \rightarrow OH + Cl \quad (5)$$

$$Cl + O_3 \rightarrow ClO \quad (6)$$

$$Cl + CH_{4\ equivalent} \rightarrow HCl + products \quad (7)$$

$$[Cl]_{steady\ state} = \{2J_1[Cl_2] + J_2[ClNO_2] + J_3[ClONO_2] + J_4[HOCl] + J_5[OClO]\} / \{k_6[O_3] + k_7[CH_4]_{equivalent}\}$$

Where $[CH_4]_{equivalent}$ represents the reactive VOC present as if it were equivalent CH_4

Steady state calculations reveal a sharp rise of chlorine atoms produced at sunrise peaking at $1.6x10^5$ molecules cm^3 around 7 am which then gradually decreases, contributing to Cl atom production until 2 pm (Figure 7a). Supporting Cl_2, $ClONO_2$, OClO, HOCl and HCl measurements by CIMS report that chlorine atoms can sustain a relatively high production rate until 3 pm as evidenced by the daytime build-up of HCl and Cl_2. $ClNO_2$ on average contributes to 78% of the chlorine atoms produced from inorganic halogens with 13% from Cl_2. $ClNO_2$ also represents over 50% of the chlorine atoms until midday. After ca. 3 pm Cl_2 and HCl becomes the more dominant Cl atom source. On the night where the highest $ClNO_2$ concentrations were measured, 90% of the chlorine atoms originated from $ClNO_2$ photolysis until 2 pm and HCl and Cl_2 then become main contributors sustaining until 4

pm (up to 80%). $ClONO_2$, HOCl and OClO appear to be insignificant contributors to chlorine atom throughout the campaign compared with $ClNO_2$, HCl and Cl_2.

To put these chlorine atom concentrations into a more global perspective, data collected by the University of Manchester from a marine site and an urban European site have been compared in Figure 7b. Bannan et al., (2015) and (2017) previously utilised a box model to calculate Cl atom concentrations during the campaign so that the rate of oxidation of VOCs by Cl atoms could be compared with oxidation by measured OH and measured ozone. The simple steady state calculation described previously will be used to determine the Cl atom concentration for both this measurement study.

The results show that both at the UK marine and urban site max chlorine atom concentrations are more than an order of magnitude lower than the mean of Beijing. It should however be noted that the only source of Cl in the UK studies was $ClNO_2$, but given the dominance of $ClNO_2$ in this study the measurements presented here suggest a high importance of the chlorine chemistry for the Asian air chemistry.

Although this study does not reach the scope of characterising O_3 and RO_x production from chlorine atom chemistry, statistics are often reported with $ClNO_2$ morning chemistry via modelling simulations, we can put into perspective the mean and maximum concentrations relative to other studies. Tham *et al*. (2016) recorded a maximum $ClNO_2$ concentration of 2070 ppt from a plume originating from Tianjin, the closest megacity to Beijing, and report a 30% increase in RO_x production and up to 13% of O_3 production. Liu *et al* (2017) observed peak concentrations up to 3 ppb and similar diurnal concentrations which they calculated contributes to a 15% enhancement of peroxy radicals and 19% O_3 production. Wang *et al*. (2016) report up to 4.7 ppb of $ClNO_2$ in Hong Kong and calculated a maximum increase of 106% of HO_x in the morning and an enhancement of following daytime O_3 production up to 41%. It is therefore evident that this work supports similar studies in Asia that conclude that chlorine atom oxidation significantly contributes to atmospheric oxidation via RO_x and O_3 production. This consistent result in Asia cannot be drawn globally as a number of studies have deemed chlorine atom chemistry to be insignificant with respect to O_3 production and competing VOC oxidation to OH (Bannan *et al*., 2017), implying a significantly different approach is needed to assessing oxidation chemistry and photochemical smog in Asia (Hallquist *et al*. 2016).

3.5 VOC oxidation by chlorine atoms

Steady state calculations of OH (as described by Whalley *et al*., 2010) estimate that campaign average maximum concentration was 7 x 10^6 molecules cm^3 (Figure 7b), 6 times greater than the maximum chlorine atom concentration and 14 times higher than the average chlorine atom concentration. Pszenny *et al*. (2007) report estimated OH to chlorine atom ratios, from VOC lifetime variability relationships, of 45 to 199 along the East Coast of the United States. Although the ratio appears much larger than calculated in this work, here we present not only significantly high concentrations of $ClNO_2$ which are appearing to be a consistent conclusion from measurements in Asia, but also the chlorine within this study appears to originate from an anthropogenic origin rather than marine, possessing the ability to supply a much larger reservoir of halogens to be liberated through photolysis.

The relative oxidation rate of the chlorine atom and OH to VOCs can vary greatly. Rate coefficients for reaction of Cl atoms with some volatile organic compounds have been shown to be up to 200 times faster than the comparable reaction with OH. The ratio reported here is significantly less than this each day, Cl can subsequently dominate VOC oxidation for some fraction of the day. Here, the diurnal maxima of the chlorine atom and OH differs by 5 hours, enabling chlorine atoms to clearly dominate VOC oxidation earlier in the day before OH concentrations have built up. The relative oxidation rate of VOCs to OH and the chlorine atom also varies greatly, creating a difference for various VOCs. If an average reaction rate for alkenes and alkanes to Cl and OH is calculated, it is possible to generalise the significance of each oxidation pathway to qualitatively asses the contribution chlorine atoms have on oxidation chemistry. It can be seen in Figure 8 that alkenes are much more likely to be oxidised by OH than Cl, although a significant contribution (15%) is attributed to chlorine chemistry. Although significant if evaluated on a global level, Liu *et al*., (2017) estimated that Cl atoms oxidize slightly more alkanes than OH radicals in a similar region of China, implying the increased scale of chlorine oxidation in China. Alkanes are known to have a much higher Cl to OH relative reaction rate than alkenes and Cl contribution to oxidation is higher than OH until midday. The contribution to oxidation remains almost equal for the remainder of the day due to the persistence of $ClNO_2$ and also relatively high levels of Cl_2 and HCl. This analysis is representative of that by Bannan *et al.* (2015) who report contributions of alkene and alkane oxidation by Cl up to 3 and 15% respectively from $ClNO_2$ concentrations peaking at 724 ppt.

This significant oxidation of VOCs by chlorine atoms will result in different products to that of OH oxidation as illustrated that neglecting the contributions made by Cl atoms will significantly underestimate the degree of chemical processing of VOCs in this study, and other evinomrnets where there is a source of Cl atoms. Evidence of the proposed Cl oxidation of VOCs is validated through detection of selected Cl induced oxidation products by the ToF-CIMS, all of which are displayed in Table 1.

3.5.1 Isoprene oxidation by the chlorine atom

1-Chloro-3-methyl-3-butene-2-one (CMBO, C_5H_6ClO), a unique marker of chlorine-isoprene reactions, has previously been measured at concentrations up to 9 ppt by offline gas chromatography in Houston Texas (Tanaka *et al*., 2003) and in laboratory studies of chlorine-isoprene oxidation (Wang *et al*. (2017)). CMBO exhibited a campaign maximum of 13.2 ppt and mean of 5.16 ppt exhibiting a near typical diurnal profile with concentrations rising sharply after sunrise, at the same rate as the chlorine atom production but maintaining concentrations past noon longer than that of isoprene and the chlorine atom, due to its longer atmospheric lifetime.

The daily maxima of CMBO varied throughout the campaign and can be explained by the relative concentrations of its precursors; the chlorine atom and isoprene. Its concentration throughout the campaign followed similar intensities to its precursors and figure 9 highlights its dependence on both Cl atom and isoprene concentrations. The concentrations of Cl and isoprene were relatively low form the 24th to the 27th of May, which resulted in relatively low CMBO concentrations. An increase in isoprene and Cl on the 28th to the 30th May was subsequently mirrored by the CMBO levels as qualitatively expected. On closer inspection of the 30th and 31st May, the concentration of CMBO was lower than expected on the 30th due to higher chlorine atom and isoprene concentrations compared to the 31th. This could be explained by anticipated higher OH concentration as calculated

by the steady state model, which is also further represented by higher concentrations of IEPOX (isoprene epoxydiols, i.e. OH oxidation products) on the 30th. This illustrates how the ToF-CIMS can identify isoprene oxidation products of two competing oxidation pathways. The high levels of IEPOX on the 28th May can also possibly describe the relatively high levels of CMBO in the particle phase due to an already well oxidised air mass.

Further daily oxidation rates can be probed via analysis of the related isoprene oxidation products observed by the CIMS. Figure 10 depicts the diurnal time series of the precursor itself and several Cl-VOC products and IEPOX. CMBO concentrations rise rapidly after sunrise due to the low concentration of OH and high production rate of the chlorine atom. The secondary and tertiary products, $C_5H_9ClO_2$ and $C_5H_9ClO_3$ (also measured in the laboratory by Wang *et al*., 2017) increased in concentration at a much slower rate, but appear to peak later in the day (4 pm) whereas CMBO peaked around 10 am (similar to the $ClNO_2$ peak time) and fall off, due to its further oxidation to form the secondary and tertiary products. IEPOX concentrations increased slowly after sunrise and peaked later in the day, as expected due to the availability of OH and competition from the chlorine atom chemistry. The similar time series of the secondary and tertiary products to IEPOX was also reported by Wang *et al.*, (2017) and were suggested to be ideal tracers of SOA production.

3.5.2 Anthropogenic Cl-VOC production

A similar unique chlorine oxidation marker in urban coastal areas, has been reported in the literature for 1, 3 butadiene; 4-chlorocrotonaldehyde (CCA) (Wang *et al*., 2000). No measurements of 1, 3 butadiene were made during this field campaign, although due to its common source to benzene (automobile exhausts (Ye *et al*., 1998), we present a comparison of the CCA measured by CIMS and benzene measurements made by the PTR-MS. The intensity of CCA in both the gas and particle phase with concentration in the gas phase up to 13 ppt reflect well the concentrations of its precursors. The maximum concentration of the chlorine atom coincides with a high concentration of benzene and subsequently CCA on the 30th May whereas very low levels of CCA were observed for the beginning of the campaign (Figure 11).

The diurnal time series of benzene (Figure 12) indicates high concentrations in the early hours of the day, possibly associated with high anthropogenic activity or an inflow of urban air masses from downtown Beijing. The concentration falls off throughout the day and almost perfectly anti correlates with the CCA gas phase diurnal profile which increases from sunrise and peaks at 3 pm. The particle phase CCA diurnal time series steadily builds up throughout the day and do not peak until late in the evening, providing evidence of SOA production from the chlorine oxidation of anthropogenic pollutants.

4. Conclusions

A FIGAERO ToF-CIMS was utilised in Beijing to assess the liberation of chlorine atoms via inorganic halogen photolysis. A suite of inorganic halogens were detected, namely $ClNO_2$ reaching concentrations up to 2900 ppt, which is suggested to have an anthropogenic origin due to the particulate chlorine correlation with SO_2, benzene and CO. $ClNO_2$ was potentially identified in the particle phase, which may only prove to be significant at such

elevated concentrations as observed in East Asia. $ClNO_2$ concentrations above LOD persisted up to 7 hours past sunrise, attributed to the lifetime of $ClNO_2$ at these high concentrations and a possible in-flow of heavily polluted air masses from the downtown urban area. Supporting Cl_2 and HCl concentrations proved to be significant contributors to chlorine atom production via steady state calculations enabling an average daytime peak concentration of chlorine atoms of 1.6 $x10^5$ molecules cm^{-3}. Compared with data attained from European based campaigns, these concentrations exceed marine and urban environments by at least an order of magnitude.

This high concentration of chlorine atoms resulted in a steady state calculated OH:Cl ratios down to a factor of 6, enabling Cl chemistry to not only dominate alkane oxidation until midday but contribute significantly to alkene oxidation throughout the day (15% on average). This enabled significant concentrations of Cl-VOCs to be formed providing the first ambient high time resolution measurements of specific Cl-VOC species simultaneously measured in the gas and particle phase. The measured unique markers of chlorine chemistry for both biogenic and anthropogenic precursors provides quantitative and qualitative data to probe the extent of chlorine atom chemistry and how they compete with OH. Simultaneous measurements of the VOC precursors via PTR-MS, and IEPOX, Cl-VOCs with the CIMS provides rich information on SOA formation pathways via both OH and chlorine atom oxidation. Multistep oxidation products of Cl-VOCs were also identified and can provide partitioning information and SOA formation rates and lifetimes.

The results highlight how chlorine atom chemistry may be under represented within models due to the lack of quantification and identification of particulate Cl-VOC products. This work provides instrumental capability to probe the competition between OH and Cl oxidation chemistry and quantify the SOA yields as a result of both pathways.

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Table 1. Identified Cl-VOC reaction products, nomenclature of Cl-VOC and precursor compound.

Cl-VOC	Potential nomenclature	Precursor
CHClO	formyl chloride	formaldehyde
C_2H_3ClO	chloroacetaldehyde	acetaldehyde
$C_3H_5ClNO_5$	Chloro PPN	PPN
$C_2H_3ClNO_5$	chloro PAN	PAN
C_3H_5ClO	chloroacetone	acetone
$C_2H_3ClO_2$	chloroacetic acid	acetic acid
$CHClO_2$	chloroformic acid	formic acid
C_4H_7ClO	chloro MEK or butanal	isoprene
C_5H_6ClO	CMBO - chloro 3-methyl-3-butene-2-one	isoprene
$C_5H_9ClO_2$	-	isoprene
$C_5H_9ClO_3$	-	isoprene
C_3H_5ClO	propanoyl chloride	1, 3 butadiene
C_8H_9Cl	chloroethyl benzene	aromatic

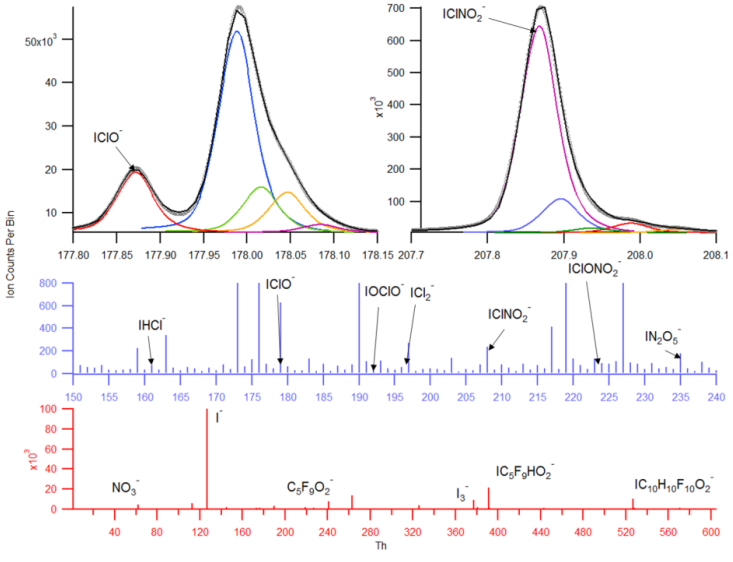

Figure 1. Average high resolution mass spectrum for the whole measured range (red) and for the region that contains all gas phase night time species utilised in this work (blue). A high resolution spectral fit for ClO and $ClNO_2$ are displayed with corresponding multi peaks with 0.5 AMU. The black line represents the total fit from all peaks. The grey line represents the mass spectral raw data.

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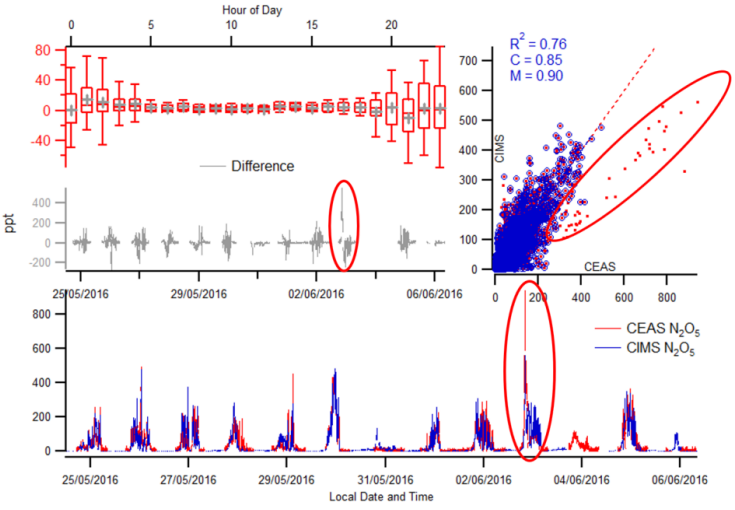

Figure 2. CIMS and CEAS one minute averaged data of N_2O_5 with corresponding correlation plot, campaign and diurnal deviation. The red highlighted periods represent data collected on the 3rd June where a different correlation gradient was observed between CIMS and CEAS. The box and whisker plot represents the diurnal difference for the campaign between the CEAS and CIMS measurements.

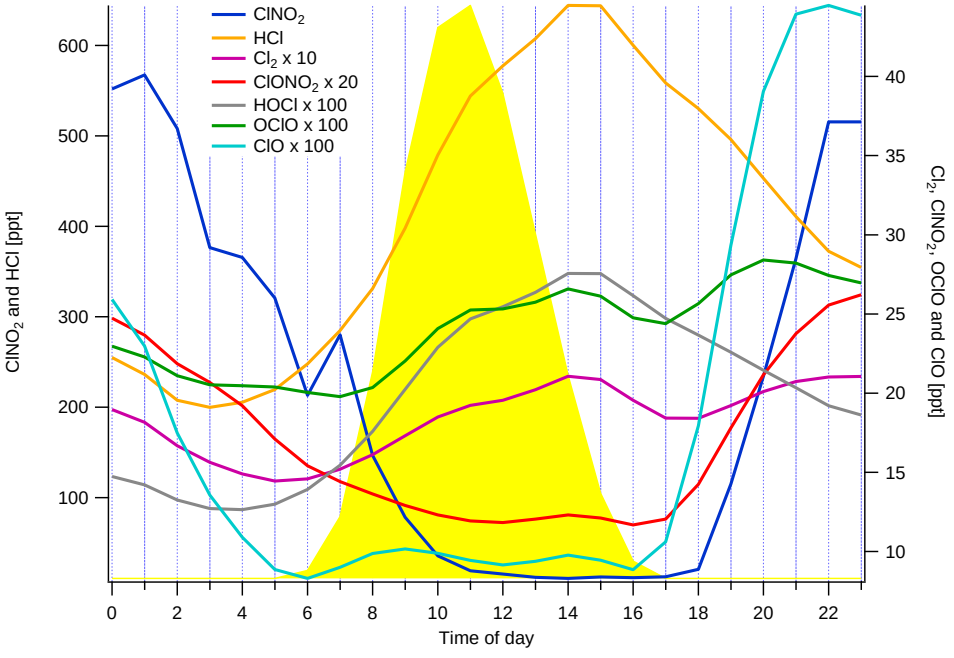

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Figure 3. Mean diurnal profiles of the inorganic halogens detected by the CIMS from the 23rd May to 6th June with average J rate for $ClNO_2$ as guide for photolysis. $ClNO_2$ and HCl concentrations are on the left y-axis and the other inorganic halogens on the right y-axis

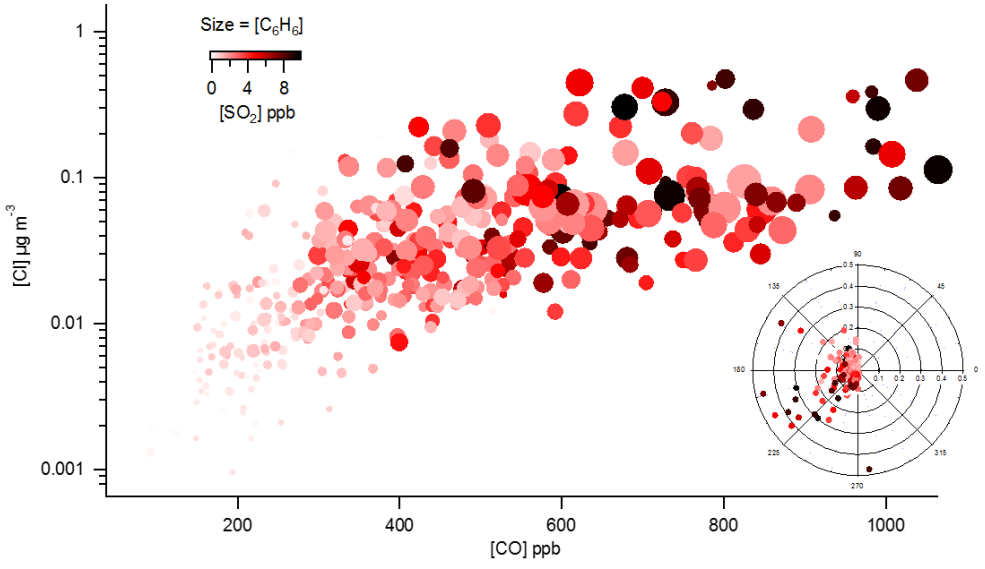

Figure 4. Correlation of particulate Cl^- from the AMS measurements and CO colour coded by SO_2 concentration and size binned by increasing benzene concentration. A wind rose plot illustrates the wind direction and particulate Cl^- concentration colour coded by SO_2 concentration.

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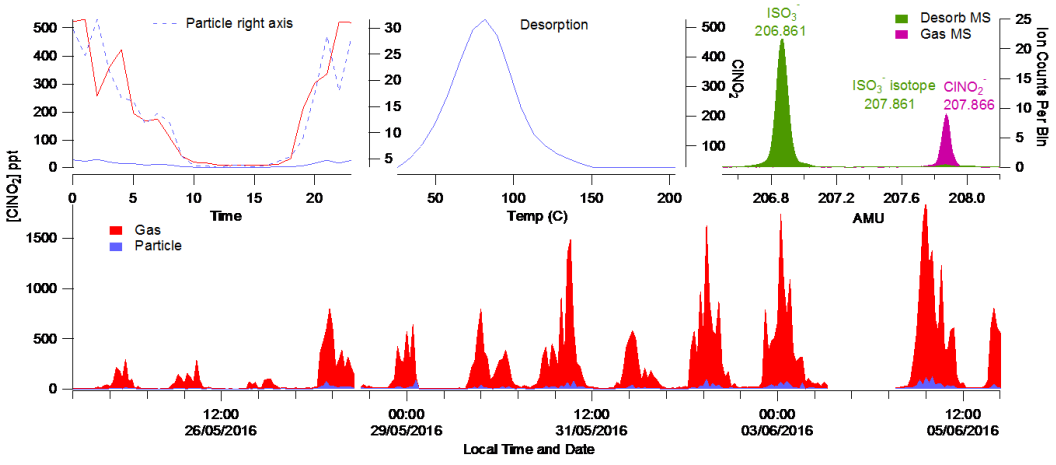

Figure 5. $ClNO_2$ gas and particle phase campaign time series (1 hour averaged) and average diurnal profiles. The peak fitting for $ClNO_2$ and the SO_3 interfering mass at 207-208 AMU is shown and the desorption profile for the counts attributed to the high resolution $ClNO_2$ peak.

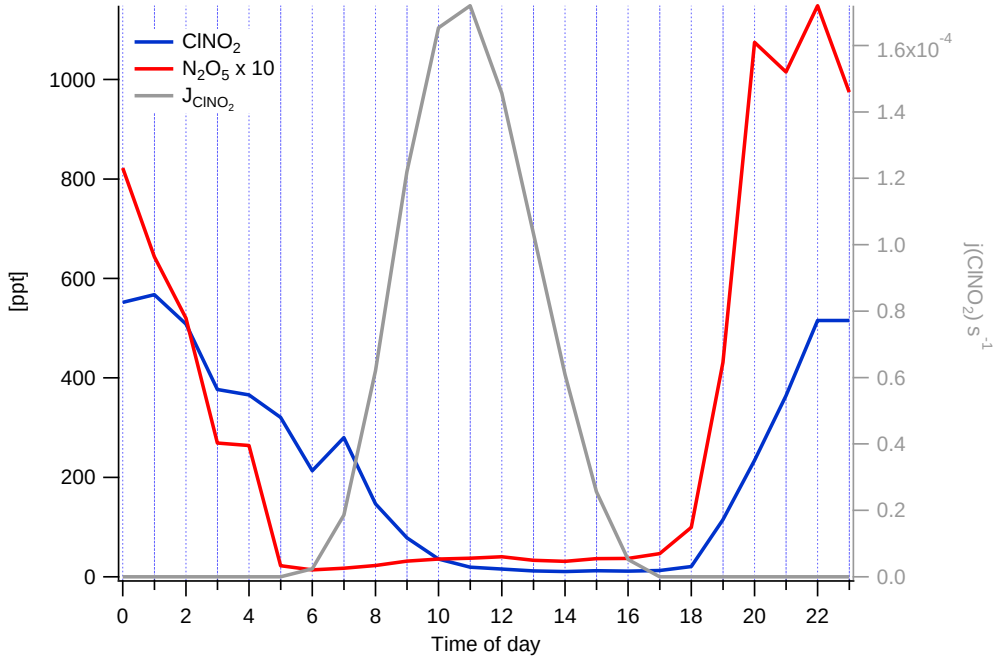

Figure 6. Diurnal profile of N_2O_5, $ClNO_2$ and j($ClNO_2$) for the campaign highlighting the persistence of $ClNO_2$ passed sunrise and the expected rapid photolysis of N_2O_5.

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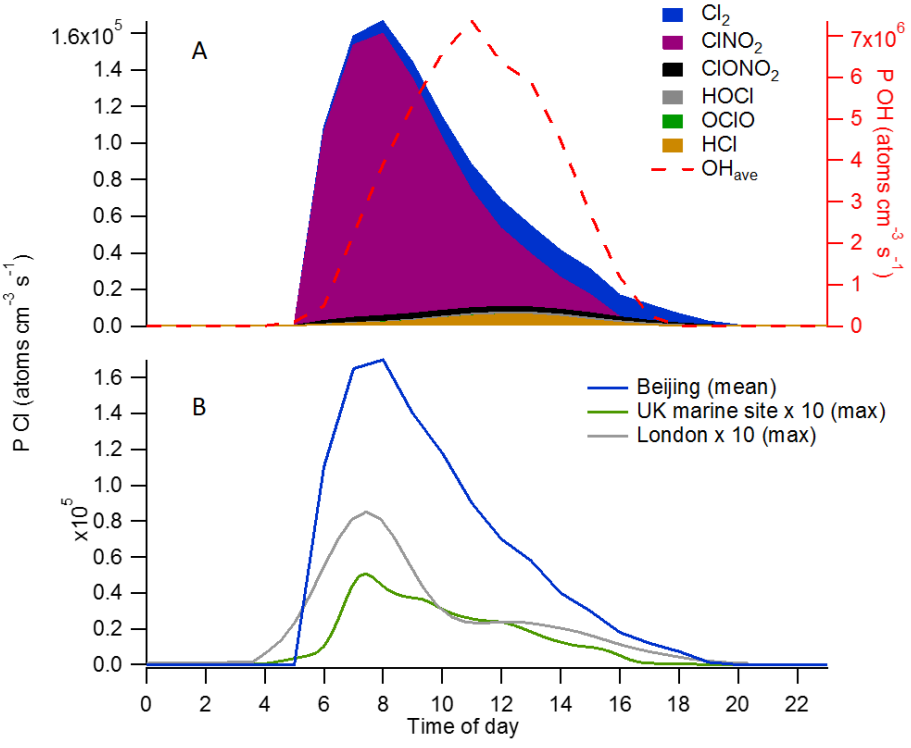

Figure 7. A) Contribution of inorganic halogens to chlorine atom production. B) Relative mean diurnal profiles of calculated chlorine atom concentrations from this work (Beijing) and measurements in the UK (London (Bannan et al., 2015) and a marine site (Weybourne Atmospheric Observatory-Bannan et al., (2017)). The steady state OH production rate from Beijing is also displayed to illustrate relative concentrations of oxidants.

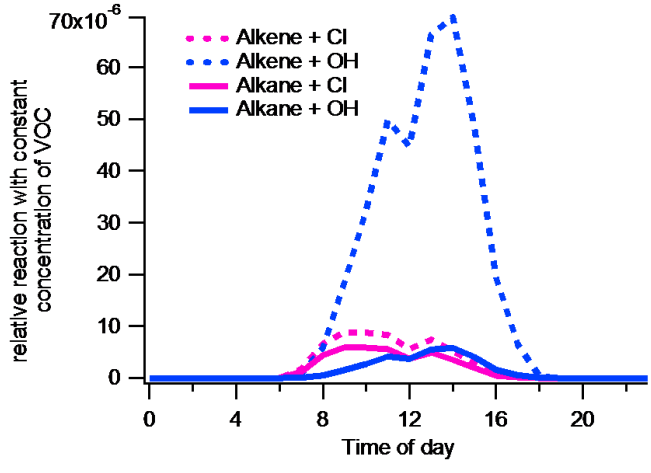

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Figure 8. Mean diurnal time series of alkene (pink) and alkane (blue) relative reaction rate (arbitrary value) with the chlorine atom (dashed) and OH (solid).

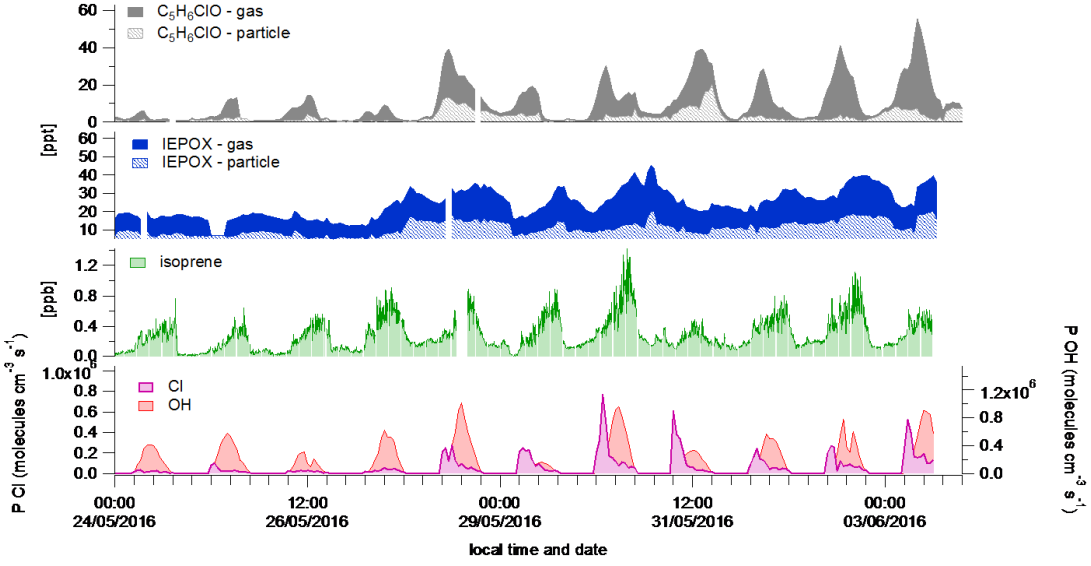

Figure 9. Campaign time series of isoprene, IEPOX, CMBO and steady state production rate of chlorine atoms and OH

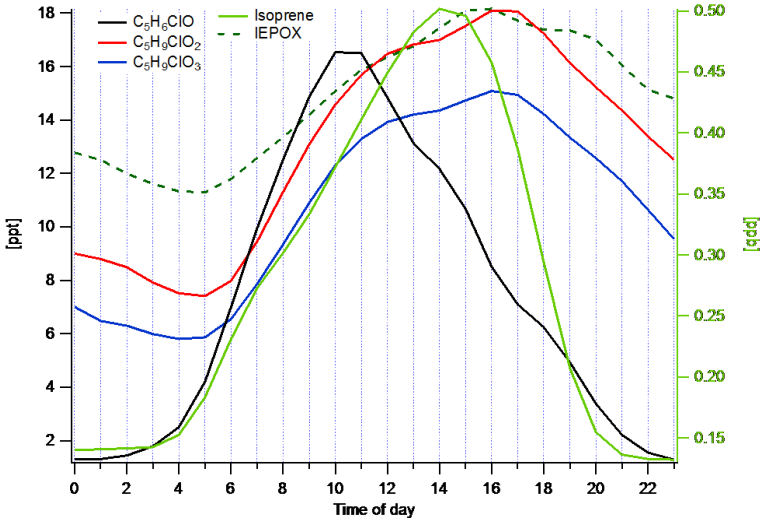

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Figure 10. Mean diurnal profiles of isoprene (right y-axis) and its OH oxidation product (IEPOX) and chlorine atom oxidation products CMBO, $C_5H_9ClO_2$ and $C_5H_9ClO_3$ (left y-axis

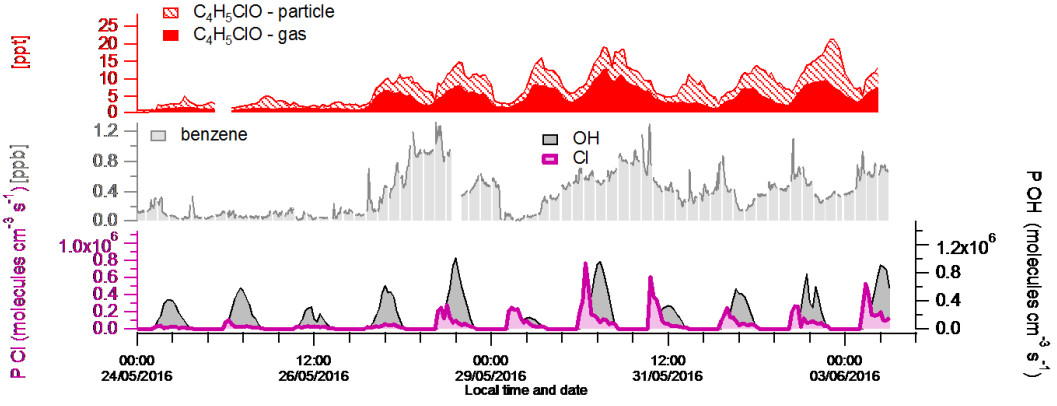

Figure 11. Campaign time series of benzene and CCA with supporting calcualations of OH and the chlorine atom production rates

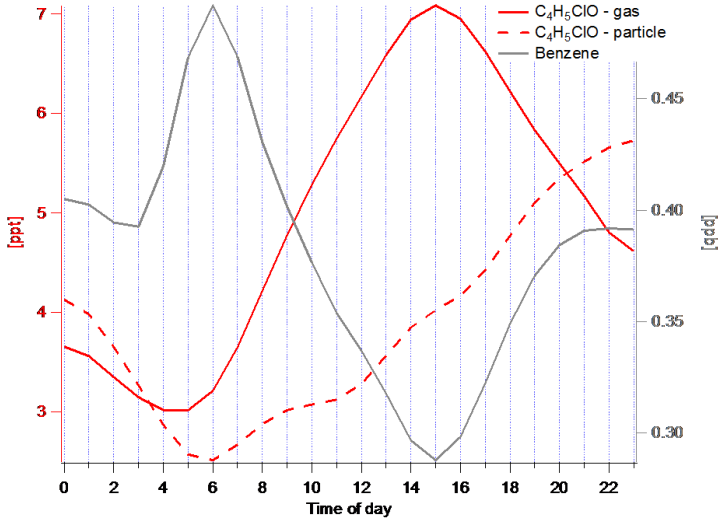

Figure 12. Mean campaign diurnal profiles of benzene (grey) and CCA in the particle (dashed red) and gas phase (solid red).