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Elevated levels of chloramines and chlorine detected near an indoor sports complex

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Abstract

Chloramines (NH_2Cl, $NHCl_2$, and NCl_3) are toxic compounds that can be created during the use of bleach-based disinfectants that contain hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) as their active ingredients. Chloramines can then readily transfer from the aqueous-phase to the gas-phase. Atmospheric chemical ionisation mass spectrometry using iodide adduct chemistry (I-CIMS) made observations across two periods (2014 and 2016) at an urban background site on the University of Leicester campus (Leicester, UK). Both monochloramine (NH_2Cl) and molecular chlorine (Cl_2) were detected and positively identified from calibrated mass spectra during both sampling periods and to our knowledge, these are the first detection of NH_2Cl outdoors. Mixing ratios of NH_2Cl reached up to 2.2 and 4.0 parts per billion by volume (ppbv), with median mixing ratios of 30 and 120 parts per trillion by volume (pptv) during the 2014 and 2016 sampling periods, respectively. Levels of Cl_2 were observed to reach up to 220 and 320 pptv. Analysis of the NH_2Cl and Cl_2 data pointed to the same local source, a nearby indoor sports complex with a swimming pool and a cleaning product storage shed. No appreciable levels of $NHCl_2$ and NCl_3 were observed outdoors, suggesting the indoor pool was not likely to be the primary source of the observed ambient chloramines, as prior measurements made in indoor pool atmospheres indicate that NCl_3 would be expected to dominate. Instead, these observations point to indoor cleaning and/or cleaning product emissions as the probable source of NH_2Cl and Cl_2 where the measured levels provide indirect

evidence for substantial amounts transported from indoors to outdoors. Our upper estimate for total NH_2Cl emissions from the University of Leicester indoor sports complexes scaled for similar sports complexes across the UK is $3.4\times10^5 \pm 1.1\times10^5$ µg hr^{-1} and 0.0017±0.00034 Gg yr^{-1}, respectively. The Cl-equivalent emissions in HCl are only an order of magnitude less to those from hazardous waste incineration and iron and steel sinter production in the UK National Atmospheric Emissions Inventory (NAEI).

Environmental Significance Statement

Chloramines (NH_2Cl, $NHCl_2$, and NCl_3) are toxic pollutants generated during use of chlorinated cleaning products that contain hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) as their active ingredients upon reaction with reduced nitrogen species (e.g. NH_3, amino acids). Chloramines have been linked to negative long-term effects on respiratory health even at low levels. Limited data exist on gas-phase chloramines both indoors and outdoors. Ambient measurements made near a sports complex found elevated levels of NH_2Cl and Cl_2 likely originating from cleaning product emissions and reaction products of cleaning activities. These findings imply that indoor cleaning events act as sources of chloramines and atmospheric oxidant precursors (i.e. Cl_2); which can impact outdoor air quality.

Introduction

Atmospheric chlorine containing species, such as molecular chlorine (Cl_2), chlorine dioxide (ClO_2), and nitryl chloride ($ClNO_2$) are highly reactive and readily undergo photolysis to yield Cl atoms. Reservoir species for the Cl atom are increasingly being recognized as important to atmospheric oxidative budgets and are prevalent in both indoor and outdoor atmospheres.[1–6] The formation and fate of atmospheric chloramines (NH_xCl_y), which include monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3) are not yet well-described, but substantial knowledge on their formation in aqueous media has been described. Major chemical or direct sources of chloramines to the outdoor atmosphere are not known.

The source of chloramines formed in aqueous solutions occurs via the reaction of HOCl with reduced nitrogen, which reactions R1-3 demonstrate for NH_3.[7,8]

$$\mathbf{NH_3 + HOCl \rightarrow NH_2Cl + H_2O} \qquad \textbf{(R1)}$$

$$\mathbf{NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O} \qquad \textbf{(R2)}$$

$$\mathbf{NHCl_2 + HOCl \rightarrow NCl_3 + H_2O} \qquad \textbf{(R3)}$$

Hypochlorite-based disinfectants are frequently used in aqueous systems and exist in a pH-dependent equilibrium with Cl_2 (R4). The aqueous reaction of NH_3 with HOCl has a known temperature-dependant rate constant of 3.1×10^6 M^{-1} s^{-1} at 298 K.[9]

$$\mathbf{Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl} \qquad \mathbf{(R4)}$$

As a result, chloramines can be formed in swimming pools *via* reactions analogous to R1-3 with compounds containing amino groups such as uric acid, urea, creatine, alkyl amines, and several amino acids, which typically originate from the human body.

Subsequent surface disturbances in pool water, for example from swimming, have been shown to accelerate the transfer of produced chloramines – predominantly NCl_3 – to the gas-phase.[10,11] Recent real-time measurements by Wu *et al.* observed indoor NCl_3 levels increasing with the number of active swimmers, reaching peak concentrations up to 116 and 226 ppbv during swimming activities.[10] A median mixing ratio of 80 ppbv of NCl_3 was measured by Weng *et al.* in an indoor swimming pool facility, despite a high outdoor to indoor air exchange rate (AER) of 9 hr^{-1}.[12] The observed high levels of NCl_3 highlights how even with proper ventilation chloramines can reach levels that are hazardous to human health indoors (see below). Other studies have observed median or mean mixing ratios of NCl_3 in pool areas to range from 21-110 ppbv.[12,13]

Elevated levels of the other chloramines have been observed in other indoor spaces through the application of novel atmospheric chemistry instrumentation, during use of chlorinated cleaning products, such as bleach-based disinfectants that contain HOCl and OCl^- as their active ingredients. Wong *et al.* demonstrated that Cl_2, HOCl, $ClNO_2$, Cl_2O, and chloramines increase in the gas-phase following floor washing with a commercial bleach solution, where emitted reactive chlorine levels were in the ppbv range for Cl_2 and HOCl.[14] Indoor measurements of chloramines during bleach cleaning activities have estimated upper limits on the mixing ratios of NH_2Cl, $NHCl_2$, and NCl_3 to be 60, 0.5, and 6.8 ppbv, respectively.[15] Finewax *et al.*[16] and Moravek *et al.*[6] observed increased concentrations of chloramines, HOCl, $ClNO_2$, and Cl_2 after a solution of dichloro-s-triazinetrione (dichlor) was used to clean an indoor weight room. Increases in these species were attributed to reactions involving HOCl on the surfaces – where the solution was applied using charged droplets – as opposed to direct emissions from the application of spray solution. It was shown that for the majority of indoor reactive chlorine species, apart from HOCl which has several indoor loss processes, removal of chloramines and other reaction products was driven primarily by AER.

Taken together, indoor environments with elevated AER are likely direct sources of reactive chlorine species (i.e., Cl^*) to the outdoor atmosphere. [6,10,12–16]

The need for high AER is because elevated levels of gas-phase chloramines in indoor areas are a health concern, with exposure linked to eye irritation, rashes, and respiratory difficulty.[17] The World Health Organization (WHO) recommends levels of gaseous chloramines (measured as NCl_3) to be below 90 ppbv; while a study by Parrat *et al.* argues that this limit should be 60 ppbv.[18,19] Even at lower levels, long term chronic chloramine exposure can have health impacts; including irritation of the lungs, as well as bronchitis with the development of phlegm, shortness of breath, and/or cough.[17] With increasing recognition that chloramines may be ubiquitous at elevated levels indoors, mitigated with high AER, this compound class has potential to impact outdoor chemistry upon transport.

Atmospheric loss processes for chloramines may occur in the aqueous or gas phases. More is known regarding condensed phase fate of chloramines and contrasting these against the fate of other reduced nitrogen species such as ammonia (NH_3) is instructive. In aqueous solution, all three chloramines been observed to photolyze readily under UVC light ($\lambda < 298$ nm), with NCl_3 also reported to absorb readily in the condensed phase from 300-400 nm.[20–22] The measured loss rate of NH_3 to hydroxyl radical (OH) in the condensed phase is $1x10^8$ M^{-1} s^{-1};[23] while a slow loss of 20 M^{-1} s^{-1} has been reported for reaction with ozone (O_3) under neutral pH conditions.[24] Replacement of hydrogen atoms on NH_3 with electron withdrawing chlorine is expected to reduce the reactivity of chloramines in the condensed phase relative to NH_3.[25] Comparing condensed-phase rate constants at 298 K for reaction with OH shows that chloramines are less reactive with increasing chlorination ($k = 6.06x10^8$, $2.57x10^8$, $1.67x10^8$ M^{-1} s^{-1} for NH_2Cl, $NHCl_2$, and NCl_3, respectively).[26] Comparing the reactivity series with O_3 at 298 K for condensed-phase chloramines (26.0 and 1.30 M^{-1} s^{-1} for NH_2Cl and $NHCl_2$, respectively) also shows decreased reactivity with increasing chlorination.[27] The above comparisons point to chloramines having a similar to lower reactivity than other reduced nitrogen species in the condensed phase. The resulting lifetimes could allow chloramines to have differing impacts and fates compared to NH_3 and alkylamines, upon transfer to the gas phase.[28–31]

The air-water partition coefficients (K_{aw}) for NH_3, NH_2Cl, $NHCl_2$, and NCl_3 are 0.71, 0.45, 1.5, and 440 at 20°C, respectively[32] indicating that NCl_3 and $NHCl_2$ are more volatile than NH_2Cl and NH_3. The lower volatilities of NH_2Cl and NH_3 are driven by their greater capacity for hydrogen bonding interactions or ionization in aqueous solution. It would also be expected that greater loss of NH_2Cl from the gas phase onto environmental surfaces would result from this lower volatility and hydrogen bonding interactions relative to other chloramines since interfacial water is ubiquitous. Chloramines are also suspected to be reactive on surfaces, as they form $ClNO_2$ (K_{aw} = 0.96)[33] *via* reaction with nitrite in the condensed-phase.[34] In aqueous solutions chloramines have also been observed to transfer a chlorine atom to yield N-chloro derivatives of amino acids, peptides, and methylamine.[35] Once transferred to the gas phase, limited data exists on the reactivity of chloramines under atmospheric condistions, generally because they can be difficult and hazardous to handle in the gas-phase.[36]

Photolysis of NCl_3 is known to take place readily through a strong absorption feature from 300-400 nm, which yields a lifetime on the order of minutes (photon flux spectrum estimated from the NCAR TUF model for 40° N, June 30, 2015).[37,38] The capacity of NH_2Cl and $NHCl_2$ to undergo gas phase photolysis at wavelengths relevant to tropospheric chemistry is not known. Reaction with OH may also impact the atmospheric fate of chloramines. Atmospheric NH_3 has a lifetime that is on the order of a month against gaseous reaction with OH ($k = 1.6\text{x}10^{-13}$ cm^3 $molecule^{-1}$ s^{-1})[39] and using the same rationale as in the condensed phase, the chloramines should react on similar to longer timescales. In a similar vein, the chloramine rate constants with OH are also likely substantially slower than alkylamines such as methyl- ($1.9\text{x}10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}) and ethylamine ($2.5\text{x}10^{-11}$ cm^3 $molecule^{-1}$ s^{-1})[40], as well as with O_3 than gaseous organic amines (e.g. $7.4 \text{ x } 10^{-21}$ for methyl- and $1.7\text{x}10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} for dimethylamine).[41]

The knowledge of atmospheric chloramines is improving, yet the sources, transformations, and concentrations of outdoor gas-phase chloramines remain limited, in part owing to the difficulty in their quantification.[10,15] In this work we present a new set of ambient outdoor measurements made with an iodide-adduct (I^-) Chemical Ionization Mass Spectrometer (CIMS) at an urban background site located near University of Leicester Indoor Sports Complex (UL ISC), where chloramines were found at measurable levels. We use laboratory calibrations to estimate detection limits and accuracy, along with resulting ambient mixing ratios. Observations from two periods near the UL ISC are used to identify potential sources for the chloramines. Plumes are then transformed with a simple gaussian diffusion model to estimate indoor mixing ratios in the identified locations. The plume emission rates are then scaled to estimate the mass of chloramines as a reactive chlorine source emitted across

UK recreational facilities and then compared to the National Atmospheric Emissions Inventory (NAEI) for known HCl sources.

2.0 Method

2.1 Site description

Measurements were made at the University of Leicester campus, located in central England (UK). The campus hosts a site of the UK Automatic Urban and Rural Network (AURN) and is classed as an "urban background" site. The AURN site is located near (~20 m) the UL ISC, which includes an indoor swimming pool (see Section 3.3).

The measurements described here were part of a larger measurement campaign described in more detail previously.[1,42] In this work we focus on two measurements periods (4-28 August 2014 and 1-26 February 2016) during which the Leicester Chemical Ionisation Mass Spectrometer (CIMS) was located at the AURN site. Concurrent meteorological data were obtained from the AURN station instruments (https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00573).

2.2 CIMS measurements

The Leicester CIMS instrument (THS Instruments LLC, GA, USA) was operated with a configuration similar to Liao *et al.* using iodide (I^-) as the reagent ion.[43] The instrument includes a Collisional Dissociation Chamber (CDC), which consists of an octopole with an applied voltage of -0.046V, kept at a pressure of 0.35 torr. The inlet sampling flow was ~1 slpm and the sample enters the CDC via a pinhole (diameter = 0.343 mm) with a voltage of -0.25V. The CIMS instrument was configured to primarily measure $ClNO_2$ and Cl_2. The latter was measured at m/z 197 and 199, corresponding to two of the three isotopic combinations of the $[I{\cdot}Cl_2]$- ion cluster. The third isotopomer at m/z = 201 amu could not be used because of interference from another unidentified species. The background signal of the CIMS instrument for the analytes was determined regularly by diverting the sample flow through a stainless-steel coil heated at 175 °C via a Teflon coated 3-way solenoid valve. This background signal was subtracted from collected data. The Cl_2 signal was calibrated using a certified standard of 5 ppmv in N_2 from BOC, diluted in N_2 over the range 2-210 ppbv. Limits of detection (LOD) were determined by overflowing the inlet with pure nitrogen for 10 minutes, then using 1 minute of data towards the end of the interval to determine the signal to noise. The LOD for Cl_2 was calculated to be 8.5 pptv (3σ, 1 minute), with an uncertainty of 18.8% (2σ), respectively. Here the counts reported for all species have been normalized to 10^6 counts of the water cluster with the reagent ion ($[H_2O{\cdot}I]^-$).

2.3 Identification and calibration of chloramine

During the period of measurements at the AURN site NH_2Cl was observed at m/z 178 and 180, corresponding to the ^{35}Cl and ^{37}Cl isotopic forms of the ion cluster $[I{\cdot}NH_2Cl]^-$. Like other chlorine containing compounds, the $[I{\cdot}NH_2Cl]^-$ adduct can fragment inside the instrument flow tube and produce $[I{\cdot}Cl]^-$ fragments at m/z 162 and 164. The bulk of the $[I{\cdot}Cl]^-$ signal in our measurements was initially entirely attributed to $ClNO_2$ which is known to produce signals both at m/z 208, 210 ($[I{\cdot}ClNO2]^-$) and at m/z 162, 164. However, a more in-depth analysis provided evidence of contribution from an 'unknown' Cl-containing molecule: First, the signals at m/z 162 and 164 did not increase when HCl was deliberately sampled and the signals were also not detected in the absence of $ClNO_2$ signals at m/z 208 and 210 (Equations SE1-2 and Figures S1-2). Second, after removing the contribution of $ClNO_2$, the "Unknown" signal at m/z 162, 164 (Section S1) was found to be correlated to m/z 178 (i.e., $[I{\cdot}NH_2Cl]^-$, Figures S2-3). Finally, the signals at m/z 178 and 180 showed a ratio reasonably close to that expected by the presence of one Cl atom (i.e. 3.13, Table S1, Figures S3-4). The regressed ratios of 178 to 180 were 2.79±0.02 (1σ) and 3.20±0.02 (1σ) for the 2014 and 2016 measurement periods, respectively (Table S1). Uncertainty in these isotopic ratios can come in part from increased interference from noise when analyte signal is low. A prime candidate for the identity of these masses is NH_2Cl, which was confirmed by the periodically conducted mass scans (Figure S5).

In order to calibrate the CIMS instrument, gas-phase chloramines were generated by flowing of mixture of humidified zero air and Cl_2 through a glass reaction tube filled with $(NH_4)_2SO_4$ coated glass beads, with the Cl_2 mixing ratio increased in a step-wise manner. The Cl_2 and NH_2Cl signals were monitored continuously using $[I{\cdot}Cl_2]$- at m/z 197 and 199, as well as $[I{\cdot}NH_2Cl]$- at m/z 178 and 180, respectively. Full range mass scans were also taken periodically during the calibration experiments, which indicated that in addition to NH_2Cl, $NHCl_2$ ($[I{\cdot}NHCl_2]$- at m/z 212 and 214) and NCl_3 ($[I{\cdot}NHCl_2]$- at m/z 246 and 248) were also produced in appreciable quantities. Quantitative determination of chloramine sensitivities were then estimated from the measured loss of Cl_2 exiting the reactor tube, considering the reaction stoichiometry between Cl_2 and $(NH_4)_2SO_4$ to produce NH_2Cl, $NHCl_2$, and NCl_3 sequentially (SI, SR1-3). The limit of detection (LOD) for NH_2Cl was estimated to be 55 pptv, with an overall uncertainty (σ) of 43%. The same sensitivity value for NH_2Cl was applied to both the 2014 and 2016 datasets, as the calibration was performed afterwards, and we do not know if the sensitivity changed over time. Variance in Cl_2 sensitivity between 2014 and 2016 was at most 26%, lower than the estimated overall uncertainty for NH_2Cl (43%). The sensitivity for NH_2Cl was not scaled relative to the changes in Cl_2, as we cannot be sure that they are impacted by the same factors. Similarly, dependence on relative humidity (RH) likely varied minimally as RH values for August 2014 (72±17%) and February 2016 (82±12%) were similar. As a result, the reported levels of NH_2Cl are likely within a factor of 2 of the real value. An in-depth description of the calibration and sensitivity calculations can be found in Section S3 of the Supplemental Information.

3.0 Results and Discussion

3.1 Detection of ambient NH_2Cl and Cl_2

During the ambient measurements on the University of Leicester campus, enhancements in ion signal were observed at m/z 197, 199 and 178, 180 (Figure 1). The signals for the former pair correspond to the iodide clusters of Cl_2 ($^{35}Cl^{35}Cl$ and $^{35}Cl^{37}Cl$, respectively), positively confirmed by the mass scans (Figure S1). The signals at m/z 178 and 180 were identified as NH_2Cl, as discussed in Section 2.3. Higher chloramines, such as $NHCl_2$ and NCl_3, have previously been speculated to be present outdoors by Mattila *et al.*, but with mixing ratios typically below their reported detection limits of 1 and 0.2 pptv.[15] Signals on the masses corresponding to $NHCl_2$ and NCl_3 were not detected in the spectra collected at the Leicester AURN site. To our knowledge, the results presented here represent the first positive detection of NH_2Cl outdoors.

3.2 Quantification of ambient NH_2Cl and Cl_2

The ambient mixing ratios of NH_2Cl and Cl_2 were quantified using the determined calibration sensitivities for NH_2Cl (232 ncps/ppbv with an estimated uncertainty of 43%, see Sections 2.3 and S3, and Table S2) and Cl_2 (Section 2.2). Generally, both NH_2Cl and Cl_2 were higher during the 2016 sampling period compared to levels seen in 2014 (Table 1), however some of the difference in NH_2Cl may be due to changes in instrument sensitivity over that time period, which is likely within measurement uncertainty (43 %). Maximum mixing ratios of NH_2Cl were measured to be 2.2 and 3.9 ppbv in 2014 and 2016, respectively. These maxima were typically short in duration – of the order of minutes. During the 2014 sampling period, measured NH_2Cl was close to the detection limit, with 67% of the data being below the LOD (n=19,073 1-minute data points).

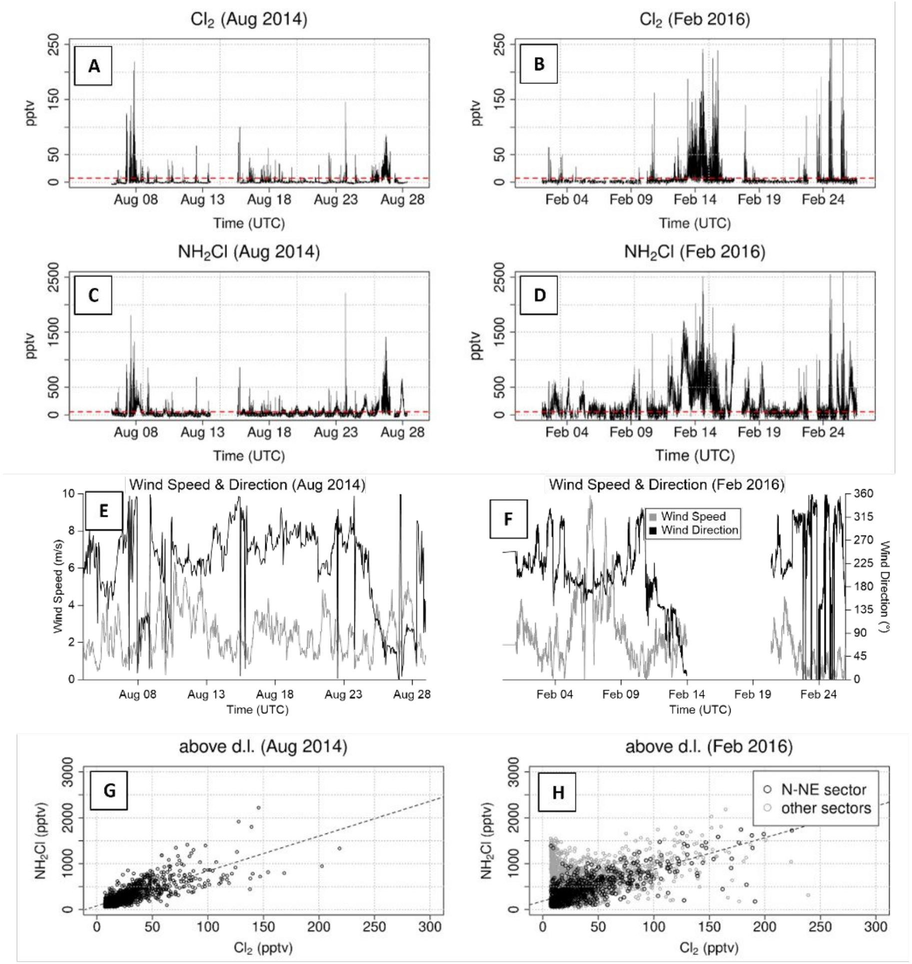

Figure 1: Ambient Cl_2 and NH_2Cl data for August 2014 (A, C) and February 2016 (B, D). Wind speed and wind direction are displayed for 2014 (E) and 2016 (F) as well. NH_2Cl mixing ratios are also plotted against Cl_2 mixing ratios for 2014 (G) and 2016 (H) where the observations are filtered for Cl_2 data above LOD. The horizontal red-dashed lines represent analyte detection limits in the time series. The presented r^2 values in Panel H are for N-NE sector.

In contrast, during the 2016 sampling period, only 28% of the NH_2Cl signal was below the LOD (n=19,283 1-minute data points). There were no clear diurnal trends during the periods in which NH_2Cl was measured above LOD (Figure S15), though peak mixing ratios were typically observed in the afternoon, perhaps owing to increased activities in and/or ventilation of the sports centre (Section 3.3). When considering only periods when the wind direction was from the N-NE, measured levels of Cl_2 and NH_2Cl were weakly to moderately correlated during both campaigns (r^2= 0.63 and 0.59, respectively, Figure 1). The observed correlation points to a similar source(s) for both species and is explored further in the next section. The outdoor levels of NH_2Cl measured in the current work are lower than the suggested exposure limits of 90 ppbv by the WHO[25] and 60 ppbv by Parrat *et al.* [19] Owing to the lack of constraint on the atmospheric fate for NH_2Cl, its impacts on local and regional tropospheric chemistry as a reactive chlorine carrier are largely unknown. Further investigation into the dominant loss processes for NH_2Cl are warranted because while there may not be significant acute effects at the measured mixing ratios of NH_2Cl, there may still be chronic effects at the observed levels if NH_2Cl for local exposure or if it persists in the atmosphere over long periods of time in regions of high emissions.

Since $NHCl_2$ or NCl_3 were not observed, and the estimated LODs for $NHCl_2$ and NCl_3 were 20 and 16 pptv from our calibration experiments with uncertainties of 72% and 140%, respectively (Table S2), a potential upper limit on $NHCl_2$ and NCl_3 mixing ratios is up to tens of pptv outdoors. This is despite the close proximity of a potential emission source with detectable levels of NH_2Cl (Table 1). The low $NHCl_2$ and NCl_3 abundance outdoors is consistent with previous measurements of these two chloramine species being below LOD of a ToF-CIMS.[15]

Table 1: Summary statistics of the measured NH_2Cl and Cl_2 levels during both sampling periods. Variability shown is one standard deviation (σ) of the mean. The limit of detection (LOD) is determined from calibrations as 3σ in the respective ion signal obtained when overflowing the inlet with zero air.

		Mean (pptv)	**Median (pptv)**	**Maximum (pptv)**	**Minimum (pptv)**	**LOD (pptv)**
AURN 2014	**NH_2Cl**	68±110	<LOD	2200	<LOD	55
	Cl_2	5.7±13	<LOD	220	<LOD	8.5
AURN 2016	**NH_2Cl**	240±290	120	4000	<LOD	55
	Cl_2	7.3±18	<LOD	320	<LOD	8.5

3.3 Identification of the chloramine source

Figure 2A presents polar plots from the August 2014 and February 2016 measurements of Cl_2 and NH_2Cl. The polar plots were generated with the openair package (Version 2.10)[44] in R (Version 4.1), using the non-parametric Wind Regression approach of Henry *et al.*[45] It is important to note that in the 2014 dataset a more evenly distributed wind direction was observed over the course of the campaign. In particular, north-easterly winds were more frequent than those found in the 2016 campaign, wherein most of the wind originated from the South (Figure S16). In this sense, the 2016 dataset is useful corroborating evidence, but the

2014 dataset gives us a clearer picture of the local point sources of Cl_2 and NH_2Cl. The 2014 polar plots point to sources for NH_2Cl originating Northeast and East of the sampling site at relatively low wind speeds (<4 m/s). Cl_2 data from 2014 also shows a distinct source originating Northeast of the sampling site at low wind speeds (Figure 2A). Data from 2016 show the same distinct sources of NH_2Cl and Cl_2 lying to the Northeast and East of the sampling point, respectively, as observed in 2014 (Figure 2A). These results suggest a direct source of both Cl_2 and NH_2Cl close to the sampling point in a Northeast/Easterly direction, but they could, for example, originate from different exhaust vents on the same building. When comparing an aerial view of the sampling area (Figure 2B), a chemical and cleaning product storage shed as well as the UL ISC (with an indoor swimming pool) both lie Northeast of the AURN site. The storage shed contained both sodium hypochlorite and hydrochloric acid used as disinfectants in the sports centre. The storage shed contained both concentrates of sodium hypochlorite and hydrochloric acid used as disinfectants for surface cleaning or water treatment in the sports centre. These compounds could react with each other to from Cl_2 during solution preparations and dispensing in the shed, some of which is handled continuously and automatically. Gaseous emissions of HOCl from the headspace of the storage containers could also occur through these activities, followed by its reaction with ambient NH_3 (~50 pptv – 5 ppbv)[46] on the shed surfaces to form gas-phase NH_2Cl.Therefore, both locations are potential sources of the observed NH_2Cl and Cl_2, based on prior reports of these molecules from their use indoors.[6,14–16,47] Cooling towers and water treatment facilities are potential sources of chloramines outdoors.[32] Treated water contains chloramines that can partition into the air when converted to a fine mist. There are no such towers or facilities nearby the sampling site that could contribute to our observed levels of NH_2Cl. Our ambient data provide no indication that said phenomena were observed.

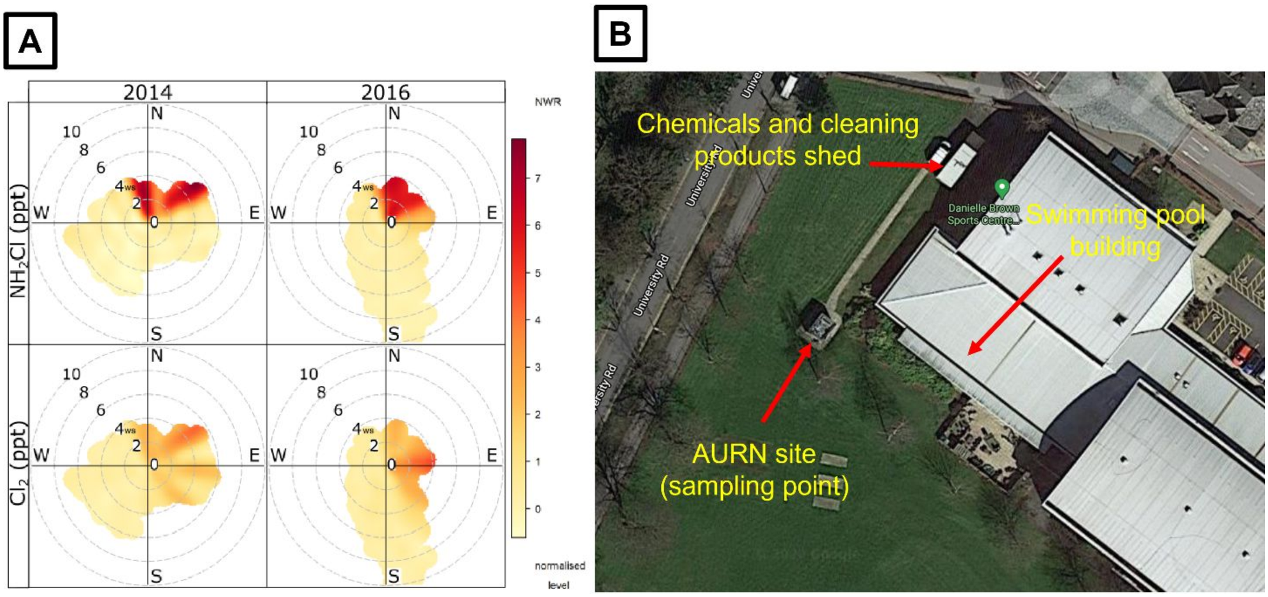

Figure 2: Polar plots of Cl_2 and NH_2Cl for August 2014 and February 2016 (Panel A). An aerial view of the sampling site is also shown (Panel B). Data included in the analysis has been restricted to Cl_2 and NH_2Cl above LOD.

3.4 Conclusions & Atmospheric Implications

The findings presented here positively detect NH_2Cl across two different sampling periods for the first time in the outdoor atmosphere near the UL ISC with an athletic facility, pool, and a shed containing hypochlorite-based cleaning products (Figure 2). Previous work has observed significant levels of gas-phase NCl_3 in indoor swimming pool areas, with mixing ratios up to several hundred ppbv. The lower capacity of NCl_3 to act as an H-bond acceptor and absence of H-bond donor capacity, relative to NH_2Cl and $NHCl_2$, drives its favourable partitioning from the aqueous to the gas-phase, as reflected by their air-water partitioning coefficients (K_{aw}). In the current work, we observed appreciable levels of NH_2Cl (up to 2 ppbv), while $NHCl_2$ and NCl_3 were consistently below LOD (tens of ppt) in outdoor air. We would expect NCl_3 to be the dominant ambient chloramine if the source was pool air. These results suggest that the observed chloramines were not formed in swimming pool water. In such a circumstance, their formation would be followed by exchange of this air from the pool area outdoors. If that was the case, $NHCl_2$ and NCl_3 would readily partition, compared to NH_2Cl. The NCl_3 and $NHCl_2$ would also not be preferentially lost, relative to NH_2Cl, prior to detection (e.g. ventilation systems surfaces, or losses in the gas-phase by photolysis or oxidative degradation) as these losses are all likely negligible over the small timescales (<1 minute) between point source and sampling here. In fact, the opposite would be expected based on K_{aw}; that is NH_2Cl would be preferentially lost on surfaces over the other chloramines, subject to lesser photolysis, and comparable oxidative degradation.

Instead of pool air, the observed similarities in source locations for Cl_2 and NH_2Cl point to cleaning and/or cleaning product emissions as the source of NH_2Cl to the outdoor air sampled. Significant levels of Cl_2 (tens of ppbv), $ClNO_2$, and NH_2Cl have been observed during cleaning indoors previously.[14,15] Rapid increases in chloramines, particularly NH_2Cl, were observed in another university athletic centre after cleaning activities with a dichlor solution, which generates OCl^- and HOCl.[16] Given the similar facility present here, it is reasonable to speculate that the NH_2Cl observed outdoors may have originated from regular cleaning activities in the nearby indoor sports complex. As notable levels of Cl_2 were correlated with NH_2Cl (Figure 2), the observed NH_2Cl may have formed via reaction of HOCl with NH_3 on surfaces as NH_3 is ubiquitous in urban and indoor atmospheres.[48–51] Fugitive emissions from cleaning products in the storage shed may also account for some of the observed ambient Cl_2 and NH_2Cl. Thus, the elevated levels outdoors point to potentially significantly higher levels indoors if the emission or transformation source(s) was(were) within the UL ISC. No additional NH_2Cl from known potential sources are near the sampling site, with the closest a water treatment plant about 6 km to the south. As high levels of NH_2Cl were not observed at high wind speeds (Figure 2), this suggests little to no influence of longer-range transport from other local to regional sources, such as the water treatment plant. Instead, peak levels of NH_2Cl and Cl_2 were observed at low wind speeds originating from northeast and east; the direction of the sports centre. This evidence suggests that the measured NH_2Cl are arriving in plumes originating from this facility.

The outdoor observations in the current work point to cleaning activities/emissions in an indoor sports complex as a persistent point source for gaseous Cl-containing compounds outdoors. This closes the loop with previous work that suggested these molecules can be effectively removed from indoor environments with sufficient AER,[6,16] and our observations confirm that they reach the outdoor atmosphere. Previous measurements in Leicester observed median levels of 15.4 and 139 pptv for $ClNO_2$, with maxima of 74.2 and 733 pptv during 2014 and 2016, respectively[42], comparable to NH_2Cl levels presented in the current work (Table 1). $ClNO_2$ was only observed at night and not concurrent with elevated levels of NH_2Cl during daytime.[42] While NH_2Cl may not photolyze at tropospheric wavelengths like NCl_3,[37] it could partition to the condensed-phase like NH_3, as NH_2Cl was not detected during ambient measurements at the Chemistry building on the University of Leicester campus (located ca. 350 m from the sports complex) in 2014 and 2015.[42] Though, atmospheric dilution of plumes from the sports complex (estimated to be by a factor of 17) may have also contributed to drive the NH_2Cl mixing ratios below the LOD by the time an emitted plume arrived at the Chemistry building. Other losses could include NH_2Cl reacting homogeneously with OH, O_3, or Cl; or heterogeneously on surfaces to form $ClNO_2$, followed by photolysis.[34]

Indoor sports complexes, fitness centres, and gyms are common and as such, NH_2Cl production arising from cleaning in such facilities may act as an important yet unrecognized source of reactive chlorine species in urban areas. Cleaning in any routinely occupied commercial/public indoor space may also be potential sources but are beyond the scope of this work. To estimate the potential impact of emissions from indoor sports complexes on urban air quality, we calculated an average NH_2Cl emission rate of $3.4 \times 10^5 \pm 1.2 \times 10^5 (1\sigma)$ µg hr^{-1} over the two periods from the UL ISC using a modelled plume dilution calculation.[52] This was estimated by first selecting five large NH_2Cl plumes for each year that are likely due to direct emissions from the UL ISC and taking the maximum measured mixing ratio from each. The maximum mixing ratios provide an upper estimate of NH_2Cl emission rates from the UL ISC via the plume dilution from emission to sampling location (See Section S6, Table S3, and ES13).

To estimate the mixing ratio of NH_2Cl from inside the building, the rate of ventilation from building exhaust vent is needed.[6] We were unable to obtain the ventilation rate for the UL ISC, and so we made two assumptions about its ventilation rate: first to be like that of another sports centre by volume, at 12 000 m^3 hr^{-1},[6] and second by using the total volume of the building operated at an air exchange rate (AER) of 6 hr^{-1} typical of such facilities operating under modern guidelines.[53–55] The resultant indoor mixing ratio of NH_2Cl was calculated to be 19±8 ppbv under the lower ventilation conditions and 1.7±0.7 ppbv under high AER. This mixing ratio range is comparable in magnitude to maxima in NH_2Cl measured during bleach cleaning events in a residence (60 ppbv) as well as NCl_3 measured inside swimming pool facilities (80 ppbv)[12,15], suggesting that the calculated emission rate of NH_2Cl under reasonable air exchange conditions from the UL ISC results in a suitable approximation. We further assumed, based on the hours of operation, that the ventilation system ran for 12 hours a day at the UL ISC. Combining emission rates with operation hours for active ventilation, we were able to estimate the annual emission of NH_2Cl from the UL ISC assuming a constant emission rate during the 12 hours of operations per day. This gave a total emission of $2.5 \times 10^{-7} \pm 5.0 \times 10^{-8}$ Gg yr^{-1} (250±50 g yr^{-1}) of NH_2Cl from the UL ISC. Upper and lower limits of vent distance and height were used to estimate the uncertainty in the plume analysis.

Across the UK there are ca. 7200 indoor sports complexes, fitness centres, and gyms.[56] To estimate the emission from indoor sports centres and gyms to the outdoor air across the UK, we have assumed that similar equipment and cleaning practices are employed across all these facilities and therefore all have the same emission rate of NH_2Cl as the UL ISC. We note that this approach is likely subject to significant uncertainty, as the UL ISC may be larger than most fitness centres or gyms, but note that other indoor environments subject to similar cleaning procedures could also contribute (e.g. commercial and residential buildings, hospitals, etc.), such that this initial assessment is useful for comparing to other urban source strengths.

The annual NH_2Cl emission rate from all indoor sports centres was therefore estimated to be 0.0017 ± 0.00034 Gg yr^{-1}. To compare to other emission sources of reactive chlorine, we explored the reported emission factors of HCl from sources in the UK National Atmospheric Emissions Inventory (NAEI). Using HCl is a suitable comparator as it is the dominant atmospheric reservoir for gas-phase chlorine.[57] According to the UK NAEI, the largest source of HCl emissions across the UK in 2019 was from incineration, such as sewage sludge (0.24 Gg yr^{-1}) and clinical waste (0.11 Gg yr^{-1}). The estimated yearly emission of NH_2Cl from all indoor sports complexes across the UK is two orders of magnitude lower, but only one order of magnitude lower than yearly HCl emissions from hazardous waste incineration and iron and steel sinter production (0.042 and 0.029 Gg yr^{-1}, respectively); which are the fourth and fifth largest sources of HCl in the UK, respectively.[58] The estimated emissions from UK-wide indoor sports centres is several orders of magnitude higher than other sources reported by the NAEI, such as stationary combustion in manufacturing industries and construction from non-ferrous metals (9.9×10^{-5} Gg yr^{-1}).[58] The emissions from indoor gyms/sports centres to these sources suggests that they can be potentially important point sources of chlorinated species affecting outdoor air quality in urban areas. However additional ambient measurements, using instruments with varying detection schemes, are required to confirm if ambient chloramines are ubiquitous in urban areas.

We conclude that chloramines may be an important Cl reservoir that could impact the formation of reactive chlorine species in urban areas which is not typically included in current atmospheric chemical models. Future work should include laboratory studies to better parameterise the chemical fate and physical properties of chloramines in the gas-phase under typical atmospheric conditions. This would allow chloramine chemistry to be incorporated into models and the understanding tested in future field observations. Improved calibration procedures are also highly desirable. This would lead to an improved understanding of the reactive chlorine budget, and contributors to urban oxidative radical budgets.

Conflicts of Interest

There are no conflicts of interest to declare.

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