Reactive chlorine emissions from cleaning and reactive nitrogen chemistry in an indoor athletic facility

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KEYWORDS

Indoor air, reactive chlorine, reactive nitrogen, nitryl chloride, nitrate radical, photolysis

ABSTRACT

Indoor gas phase radical sources are poorly understood but expected to be much different than outdoors. Several potential radical sources were measured in a windowless, LED-lit room, in a college athletic facility over a two-week period. Alternating measurements between the room air and the supply air of the heating, ventilation, and air-conditioning system allowed an assessment of sources. Use of a chlorine-based cleaner was a source of several photolabile reactive chlorine compounds, including $ClNO_2$, and Cl_2. During cleaning events, photolysis rates for these two compounds were up to 0.0023 pptv min^{-1}, acting as a source of chlorine atoms even in this low-light indoor environment. Unrelated to cleaning events, elevated $ClNO_2$ was often observed during daytime and lost to ventilation. The nitrate radical (NO_3), which is rapidly photolyzed outdoors during daytime, may persist in low-light indoor environments. With negligible photolysis, loss rates of NO_3 indoors were dominated by bimolecular reactions. At times with high NO_2 and O_3 ventilated from outdoors, N_2O_5 was observed. Elevated $ClNO_2$ measured concurrently suggests formation through heterogeneous reactions, acting as an additional source of reactive chlorine within the athletic facility and outdoors.

SYNOPSIS

Gaseous chlorine chemicals were observed in an athletic facility as a result of cleaning, as well as through heterogeneous reactions of nitrogen oxides formed from reactions of outdoor pollutants indoors.

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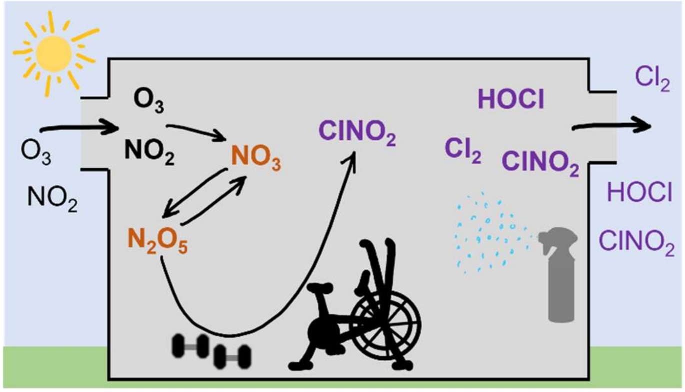

Introduction

People spend much of their time indoors, with Americans typically spending about 90 % of their time inside.[1] Thus, chemical processes altering indoor air quality could impact human health. Despite this, air chemistry occurring indoors is not as well understood as outdoors. Chemistry indoors is expected to differ from that occurring outdoors for several reasons, including lower abundance of short-wave light indoors,[2–4] higher surface-to-volume ratio indoors,[2,4] indoor activities that result in large emissions (e.g., cooking[5] and cleaning[6]), and considerable heterogeneities within[7] and between[8] indoor environments.

Radicals drive gas phase chemistry, but their occurrence and abundance indoors remain a source of uncertainty. Outdoor radical production is driven by photolysis and dominated by hydroxyl radicals (OH), for which the dominant formation pathways typically require abundant high energy light. Since light levels and energies are reduced indoors, OH concentrations are expected to be much lower.[3,7] The result is an increased relative importance of radical formation processes driven by lower-energy photons or by chemical reactions, such as formation of chlorine atoms and nitrate radicals (NO_3), respectively. Chlorine atoms and NO_3 can react with organics by abstracting a hydrogen atom or adding to a carbon-carbon double bond, with abstraction dominating for Cl and addition dominating for NO_3.[9,10] High levels of reactive chlorine species (Cl*), such as HOCl, Cl_2, $ClNO_2$, and chloramines, have been measured indoors, following surface cleaning with chlorine bleach.[6,11] Chemicals classified as Cl* are those that can readily react to form the chlorine atom. Some Cl* observed from use of chlorine bleach can be photolyzed by indoor light sources[11,12] to produce the chlorine atom:[13]

$$HOCl + h\nu \rightarrow OH + Cl \ (\lambda < 480 \text{ nm}) \qquad \text{(R1)}$$

$Cl_2 + h\nu \rightarrow 2Cl$ ($\lambda < 550$ nm) (R2)

$ClNO_2 + h\nu \rightarrow Cl + NO_2$ ($\lambda < 350$ nm) (R3)

During cleaning with bleach, elevated levels of Cl from the photolysis of HOCl and Cl_2 have been calculated, exceeding levels found outdoors.[11]

Nitrogen oxide chemistry is similarly amenable to radical and oxidant generation indoors. Accumulation of NO_3 can occur in spaces with low light levels, formed by reaction of NO_2 and O_3 and lost rapidly through reaction with NO, photolysis, or reaction with organics:[13]

$NO_2 + O_3 \rightarrow NO_3 + O_2$ (R4)

$NO_3 + NO \rightarrow 2NO_2$ (R5)

$NO_3 + h\nu \rightarrow NO_2 + O$ (585 nm $< \lambda < 640$ nm) (R6a)

$\rightarrow NO + O_2$ (400 nm $< \lambda < 640$ nm) (R6b)

$NO_3 + RH{=}CH_2 \rightarrow RH\text{-}CH_2NO_3$ (R7)

NO_3 exists in equilibrium with N_2O_5:

$NO_3 + NO_2 \rightleftharpoons N_2O_5$ (R8)

with N_2O_5 formation becoming more favorable as temperature decreases. Outdoors, detectable levels of N_2O_5 and NO_3 occur mainly at night with N_2O_5 levels typically exceeding NO_3 by more than an order of magnitude (e.g. [14]). Because many indoor environments have low light levels and ozone levels sufficiently high for R4 to proceed, the potential formation of NO_3 and N_2O_5 indoors has been discussed (e.g.,[15–20]). However, only two indoor measurements of NO_3 and N_2O_5 have been made. In the first, the sum of NO_3 and N_2O_5 was measured using an offline technique in an unoccupied office conference room in Denmark, with levels of 1 to 58 pptv observed.[21] In situ measurements of NO_3 and N_2O_5 made in a residence during use of a gas stove were both below the limit of detection (1.5 pptv), except in instances when O_3 was added, leading to NO_3 and N_2O_5 levels of a few pptv and up to 190 pptv, respectively.[22] While NO_3 could act as an important oxidant on its own,[19,20] it may also contribute to the formation of Cl*, as N_2O_5 can react heterogeneously to form $ClNO_2$:

$$N_2O_5 + Cl^-_{(surf)} \rightarrow ClNO_2 + NO_3^- \qquad \text{(R9)}$$

This process is the dominant source of $ClNO_2$ outdoors (e.g., [23,24]) but, to our knowledge, has not been observed as a source of $ClNO_2$ indoors.

Athletic facilities have been the subject of few studies (e.g., [25,26]) motivated by the impacts of air quality on exercising individuals. During November 2018, the ATHLETic center study of Indoor Chemistry (ATHLETIC) campaign collected high time-resolution atmospheric measurements in a university athletic facility.[27–29] Comprehensive measurements collected during ATHLETIC allowed a detailed examination of Cl* and radical formation in an indoor environment with a high air exchange rate that is subject to routine chlorine-based cleaning. The objectives of this work were to: (i) determine levels and temporal variation of Cl*, NO_3, and N_2O_5 in an athletic facility; (ii) assess the impact of cleaning events on Cl*; and (iii) determine the potential for formation of NO_3, N_2O_5, and $ClNO_2$ in the facility.

2. Methods

2.1. Athletics facility and ventilation system

The ATHLETIC study is described in detail in Finewax et al.[28] Briefly, measurements were made from Nov 1 – 20, 2018, in the weight room of the Dal Ward Athletic Center of the University of Colorado in Boulder, CO, USA. Data considered in this study were collected between Nov 7 – 16, 2018. The 1700 m^3 room was used by university varsity athletes and equipped with strength and cardiovascular training equipment. The windowless room was illuminated solely by light emitting diodes (LEDs). The air exchange in the room was regulated by a heating, ventilation, and air-conditioning (HVAC) system, which controlled the room air temperature to 19.5 ± 0.2 °C. Outside air was drawn into the HVAC system and mixed with return air from the weight room and other rooms in the building (Figure S1). Mixed air was then filtered and humidified at the building's main air handler before passing over a heating unit (at 60 °C) and entering the weight room at a constant flow (~ 195 m^3 min^{-1}) through 14 supply air vents installed in the ceiling, where the return air vents were also situated. The residence time of air in the weight room was 8.5 min, which is equivalent to an air exchange rate (AER) of 7 hr^{-1}. The outdoor air fraction of the supply air was determined by using the HVAC air temperatures and/or damper-based flow rates measured by building operations in the outdoor supply air duct, the return air duct, and the mixed air. Although the athletic facility has a pool, it is served by a separate air handler, so there is no air exchange between the pool and the weight room considered here.

2.2. Instrumentation and measurements

Instrumentation and sampling are described in detail in Finewax et al.[28] Gas phase instruments were placed on a balcony in the weight room (Figure S1). A sampling inlet was installed in the room (at the height of the balcony railing) and another sampling inlet was inside the supply air vent (30 cm upstream of the outlet). For this, 0.47 cm ID PFA tubing (1.34 m length for the room air and 4.27 m for the supply air inlet) were connected to a PTFE solenoid valve manifold (with sample flow only contacting PFA/PTFE surfaces), which alternated between the room and supply air every 5 mins and served as a manifold to supply different trace gas instruments. Makeup flow was applied to room and supply air inlets, when not sampled by instruments, to ensure that they were always sampling at a constant flow rate.

An iodide chemical ionization mass spectrometer (I-CIMS, TOFWERK, Thun, Switzerland) was used to measure Cl_2, HOCl, $ClNO_2$, chloramines (NCl_3, $NHCl_2$, NH_2Cl), N_2O_5, as well as NO_3^- as a proxy for NO_3/N_2O_5 chemistry (Text S1, Figure S2),[30–33] and other species not considered in this study, at 0.2 Hz. The I-CIMS was connected to the manifold by an additional 1.0 m of PFA tubing at flow rate of 1.9 L min^{-1}, leading to total residence times of 0.7 and 1.0 sec for room and supply air, respectively. Due to the short residence times, differences in inlet lengths did not cause bias between room and supply air measurements, which is supported by nearly identical values of room and supply air measurements of HCl as discussed below. Calibration of Cl_2 was performed using a permeation source at 35 °C, the output of which was verified by titration with potassium iodide. Other gases were not calibrated directly. For $ClNO_2$ and N_2O_5, concentrations were approximated using I-CIMS calibration factors previously reported,[34] scaled to the measured calibration factor of Cl_2.[35] Remaining gases are reported as the signal from the I-CIMS normalized to the sum of I^- and $I{\cdot}H_2O^-$ reagent ions, multiplied by 10^6, and reported as normalized counts per second (ncps). These signals are likely to scale linearly with concentration at levels expected in indoor air, especially as no reagent ion signal depletion was observed during the campaign. Measurements of HCl were performed using a cavity ring down spectrometer (CRDS, model SI2108, Picarro, Santa Clara, CA, USA),[36] sampling at 2 L min^{-1}. The CRDS was connected to the manifold by 3.5 m of 0.47 cm ID PFA tubing, yielding total residence times of 0.7 and 1.0 s for room and supply air, respectively. HCl was measured at 0.5 Hz yielding a 2-sec precision of <2 pptv (<0.05 pptv for 5 min averages) and 3 σ limit of detection of <5 pptv (<0.2 pptv for 5 min averages). Measurements of NO and NO_2 were made using chemiluminescence (42i-TL) at 1 Hz and O_3 using UV-absorption (49i) at 0.25 Hz, by Thermo Scientific Inc (Waltham, Massachusetts, USA). A spectrometer (USB 2000+, Ocean Optics, Dunedin, Florida, USA) was installed at balcony level to measure spectral irradiances from 350 to 750 nm every 20 sec.[37] Measurements of monoterpenes and several other species were made at 1 Hz using a Vocus proton transfer reaction mass spectrometer (PTR-MS, TOFWERK, Thun, Switzerland), as described previously.[27,28] The limonene response was calibrated using a standard mixture; limonene was found to be the dominant monoterpene in this study using gas chromatographic measurements.[27] Timeseries were time matched by interpolation to 1 sec time resolution. For statistical analysis, data were averaged in 5 min room and supply air blocks after removing sample line flushing periods due to valve switching. Specifications of the measurements, including their uncertainties, are listed in Table S1.

2.3. Disinfection and cleaning events

Exercise equipment was disinfected six times during the campaign, four times from Nov 7 – 16, using a dichlor cleaning solution, which consists of sodium dichloro-s-triazinetrione tablets that form HOCl once dissolved in water. The cleaning solution was applied with a nebulizing device that electrostatically charged the cleaning liquid aerosols to increase their deposition on equipment surfaces and thereby reducing dispersion of cleaning liquid aerosols in room air.

2.4. Photolysis, production, and loss calculations

Production rates of Cl from photolysis of Cl* were calculated using measured concentrations of Cl* and photolysis rate coefficients. Rate coefficients were calculated using measured photon fluxes, along with reported absorption cross-sections and quantum yields (Text

S2).[13,38–41] Although the spectrometer fiber optics collect light from multiple angles, we do not account for any spatial differences in photon fluxes, which have been shown to occur indoors.[42,43] Loss and production rates of NO_3 were also determined. For NO_3, formation by R4 and R8, along with losses by R5, R6, R7 (as limonene, one of the most abundant organics measured in the room and among the most reactive with NO_3),[19,27,28] and R8. Measured levels of O_3, NO, NO_2, and limonene were used, along with temperature dependent rate coefficients (R4 and R5)[13] and rate coefficients reported at 298 K for the reaction of NO_3 with limonene (R7).[44] Photolysis rate coefficients were calculated as described above.[45] Reactions with organics other than limonene were excluded, so the NO_3 loss rate represents a lower limit (uncertainty discussed in Text S3). For N_2O_5, formation and loss through R8 were considered. Because of the high AER as a competing sink, steady-state concentrations of NO_3 and N_2O_5 cannot be reached and were therefore not determined.

3. Results and Discussion

3.1. Variability of reactive nitrogen and chlorine compounds

Indoor air chemistry in the athletic center room was governed by: (1) the emission, deposition, and reactions occurring indoors; (2) the filtering of indoor air and introduction of outdoor air through the HVAC system; and (3) the properties and chemical composition of the outdoor air introduced. Since simultaneous measurements of outdoor and indoor components would have required another set of instrumentation (due to lack of outdoor sampling access from the sampling location), we instead performed alternating measurements of the room and supply air. Investigating their difference helps us to elucidate chemical sinks and sources indoors, the circulation of air in the HVAC system and the influence from outdoor air. Maintaining constant weight room temperature led to lower outdoor air fraction during cold periods and a higher fraction during warmer periods (Figures 1, S3). Over the campaign, the air delivered to the room was comprised of 5 – 80 % outdoor air, with a distinct diurnal cycle (median outdoor air fractions were 0.1 at night and 0.3 during the day). The diurnal boxplot statistics of the outdoor air fraction, supply air flow rate, the room and outdoor temperatures are shown in Figure S3.

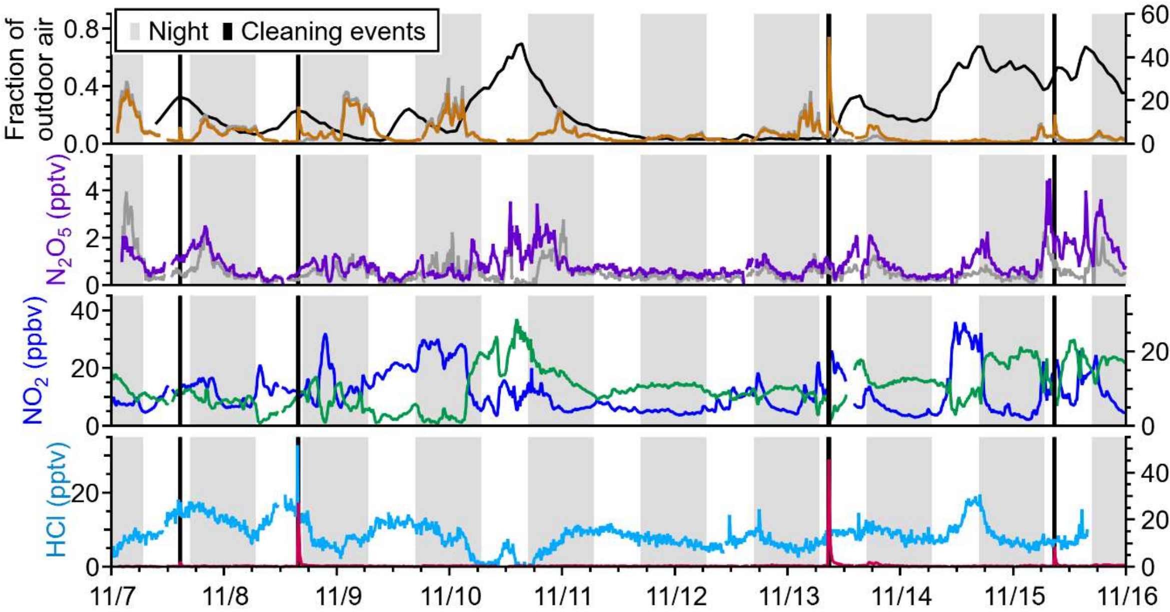

Figure 1. Mixing ratios of $ClNO_2$, N_2O_5, NO_2, O_3, HCl, and Cl_2 observed in the room (colored traces) and $ClNO_2$, and N_2O_5 in the supply air (dark grey traces) along with the calculated fraction of outdoor air in the supply air (black trace, top panel). All species are averaged over 5-minute intervals. Shaded regions on all panels indicate nighttime (grey) and dichlor cleaning events (black).

Mixing ratios of Cl_2, $ClNO_2$, HCl, and N_2O_5 were measured during the campaign (Figure 1). During periods of dichlor cleaning, elevated Cl_2 and $ClNO_2$ were observed in the athletic facility room, up to 130 pptv (46 pptv in 5-min averaged data) and 1143 pptv (494 pptv in 5-min averaged data), respectively. Mixing ratios of HCl and N_2O_5 were not elevated during these times, although elevated HCl was observed immediately prior to one of the events. Dichlor cleaning events will be discussed further in Section 3.2.

Observed levels of HCl were below 35 pptv and were similar between the room air and supply air (Figure S4). The comparable room and supply air mixing ratios, showing little variation with the fraction of outdoor air, indicates that there were no major sources or sinks of HCl in the athletic facility. During the same campaign, Finewax et al.[28] observed volatile products of reaction between HOCl and amino acids that generate HCl as a product. We observed no evidence of that HCl source affecting overall HCl levels in the facility. In the absence of dichlor cleaning, relatively stable levels of Cl_2 less than 1 pptv were observed (Figure S4), suggesting that dichlor cleaning was the major source of Cl_2 in the facility. Slightly higher (~0.1 pptv) levels of Cl_2 were consistently observed in the room compared to the supply air, which may indicate another small source of Cl_2 in the room.

In the absence of cleaning, levels of $ClNO_2$ often exceeded 50 pptv at night and were below 50 pptv during the day (Figure 2). Levels of N_2O_5 were always below 5 pptv and were generally highest in the late afternoon/early evening. Differences between the supply and room air indicate that $ClNO_2$ was higher in the supply air during the night, implying transport from outdoors. Similarly, N_2O_5 was often higher in the supply air at night. This is consistent with the diurnal variation of N_2O_5 and $ClNO_2$ typically observed outdoors, with elevated levels during the night (e.g., [14,46]). During the day, levels of N_2O_5 and $ClNO_2$ were frequently higher in the room than the supply air. Although short-lived differences of this nature could occur as outdoor levels of N_2O_5 and $ClNO_2$ dropped in the morning and the facility was flushed of nighttime accumulated N_2O_5 and $ClNO_2$, the sustained difference during daytime implies formation chemistry within the athletic facility (discussed further in Section 3.3).

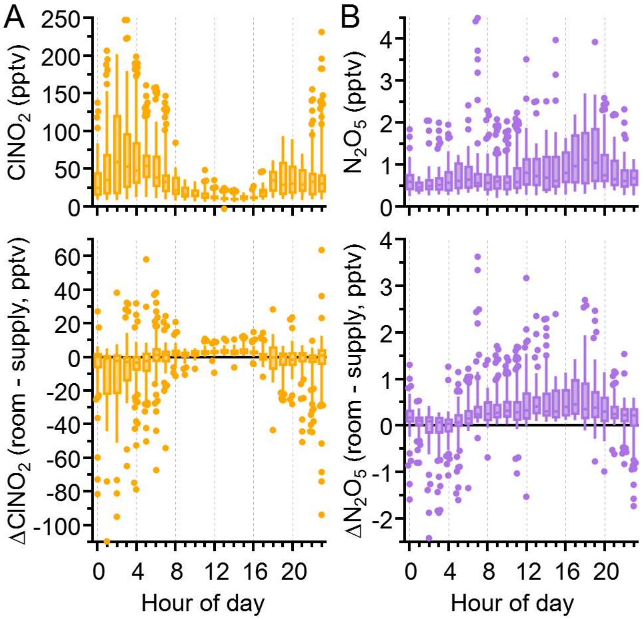

Figure 2: Diurnal boxplot statistics of 5-minute data for a) $ClNO_2$ (excluding cleaning events) and b) N_2O_5. Box represents 25th to 75th percentiles, with line indicating the median. Whiskers represent 9th to 91st percentile. Colored points are outliers. Shown are values for the room air (top panels) and the difference between room air and the supply air (bottom panels).

3.2. Dichlor cleaning events

During the four dichlor cleaning events, we observed rapid increases of gaseous inorganic reactive chlorine (Figure 3a).[28] Consistent with previous studies on surface cleaning with chlorine bleach, we observed elevated HOCl, Cl_2, $ClNO_2$, NCl_3, and $NHCl_2$.[6,11] Mixing ratios increased during the events up to 130 pptv for Cl_2 and 1142 pptv for $ClNO_2$ (Table S2). Observed mixing ratios in this study were lower—by several times to orders of magnitude—than those previously measured from surface chlorine bleach application.[6,11] In addition, surface cleaning with chlorine bleach in a previous study led to much higher mixing ratios of Cl_2 compared to $ClNO_2$,[6] while we observed the opposite, with $ClNO_2$ consistently higher in our measurements. In contrast to previous studies that measured[12] or proposed[6] increased HCl mixing ratios following floor cleaning with chlorine bleach, we did not observe elevated HCl following dichlor cleaning. While differences between our study and previous works may be caused by chemical differences between the nature of the chemicals applied, they may also be related to differences in quantities of cleaning agent applied, the nature of the surfaces cleaned, proximity of gas instrumentation to cleaned surface, ventilation rates and room size, and/or other differences between the indoor spaces in which measurements were made. Further work is needed to better understand the surface emissions related to use of chlorine-containing cleaners.

Several Cl* species are highly photolabile and may photolyze under indoor light conditions, leading to production of the chlorine atom.[11,12] In the athletic facility, LED lights provided the only source of photons. Photon flux of LEDs is low compared to other indoor light wsources and is negligible below 400 nm.[42] Under these conditions, photolysis of some Cl* may proceed. Photolysis rate coefficients for Cl_2, $ClNO_2$, and HOCl were calculated from the measured light intensity and were 1.1×10^{-7} s^{-1}, 2.1×10^{-9} s^{-1}, and 1.6×10^{-9} s^{-1}, respectively (Figure S5, Table S2). These are comparable to those that have been previously determined for LED-lit indoor environments (Table S2)[12] and lower than those estimated or measured in locations with higher-energy light sources.[6,11] We estimated the photolysis rates for Cl_2 and $ClNO_2$ for the maximum levels observed during cleaning events (Table S2). The maximum photolysis loss rate for Cl_2 was 8.3×10^{-4} pptv min^{-1} and for $ClNO_2$ was 1.5×10^{-4} pptv min^{-1}, which corresponded to a maximum chlorine atom production rate of 1.8×10^{-3} pptv min^{-1} (~ 10^4 atoms cm^{-3} min^{-1}). Most Cl atoms react with volatile organic compounds, which were abundant in the athletic facility,[27,28] to form HCl. We might expect to observe an impact on measured HCl levels from the photolysis of reactive chlorine. However, the photolysis rate coefficients (on the order of 10^{-7} to 10^{-9} s^{-1}, see above) for reactions that would produce Cl atoms and lead to HCl production were much too small compared to the air exchange rate (~1.9×10^{-3} s^{-1}) to generate a detectable difference between room and supply air in our measurement.

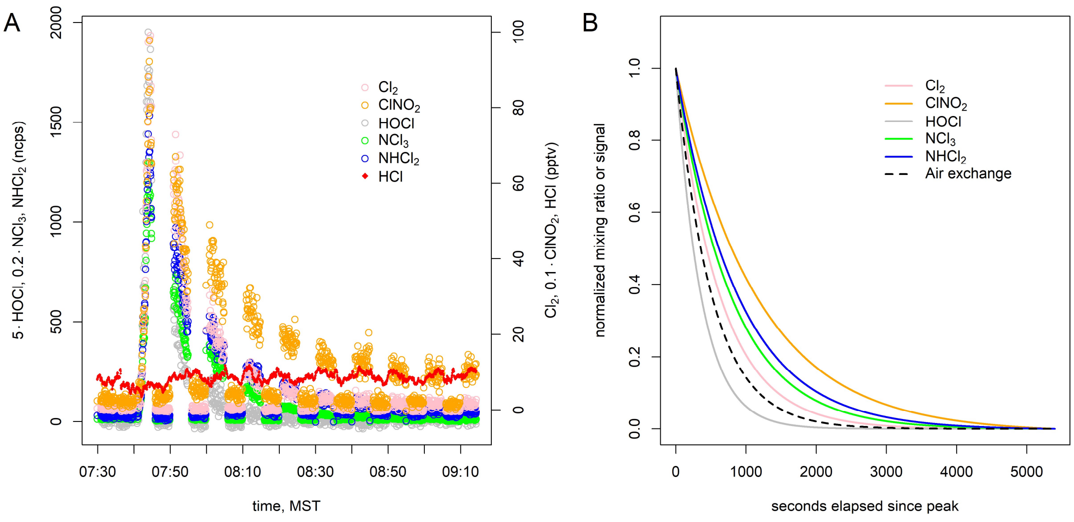

Figure 3: (a) Increases and subsequent decay of selected Cl species observed during a dichlor cleaning event on Nov 13. Measurement time series alternate between room (higher levels) and supply air (lower levels). To compare the decay rates between species (b) the exponential decay functions were normalized by the respective peak values and background subtracted.*

From the peak levels following cleaning with dichlor, reactive chlorine decayed exponentially (Figure 3b). Levels of HOCl were observed to decay faster than air exchange (~1.9 x 10^{-3} s^{-1}, Table S3), consistent with previous observations following surface cleaning with chlorine bleach.[6,11] Photolysis was not an important sink for HOCl in this environment (1.6 x 10^{-9} s^{-1}), as described above. Reaction with gas-phase terpenes is another possible loss process for HOCl.[47] Measurements of 0.05 - 0.5 ppbv of limonene—the dominant terpene—throughout the campaign,[27,28] which corresponds to HOCl losses of up to 2.3 x 10^{-6} s^{-1},[47] indicate this was likely a minor sink. Heterogeneous reactions of HOCl with unsaturated skin oils could also be a loss process for HOCl.[48] Assuming a conservative skin-oil-covered-surface to volume ratio of 0.33 m^2 m^{-3},[49] this results in a loss rate of ~7 x 10^{-3} s^{-1},[48] which suggests this is an important sink of HOCl (Table S3). Additional reactions of HOCl are also possible. For example, expected products for the reaction between amino acids and HOCl were observed, but not quantified, during the ATHLETIC campaign,[28] indicating this also contributed to HOCl losses. All other Cl* species generated during cleaning events decayed slower than the AER. The AER includes some recycling of room air, though the negligible increases in duct levels (Figure 3a) suggest that Cl* species were either vented to outdoors or lost through other means in the HVAC system and were not recirculated into the room. Although there is some uncertainty in the calculation of AER, and thus, in the decay by air exchange, this suggests continued production of these species following the initial application of the cleaning solution. This contrasts with previous measurements after surface cleaning with chlorine bleach, where Cl* were observed to decay faster than the AER (test home at 0.6 h^{-1})[6] or equivalent to the AER, within experimental uncertainties (laboratory at 12.74 h^{-1}).[11] As described above, the only Cl* that was measured at elevated levels in the athletic facility outside of dichlor cleaning events was $ClNO_2$, which suggests other sources may contribute to its presence.

3.3. Evidence for indoor NO_3, N_2O_5, and $ClNO_2$ chemistry

On some days, we observed evidence of formation of $ClNO_2$ indoors from N_2O_5, which, to our knowledge, has not before been reported indoors. As described above, on most days – including those on which no dichlor cleaning was performed – daytime $ClNO_2$ was higher in the room than the supply air (Figures 1, 2, S6). We also observed the presence of N_2O_5, with highest levels observed in late afternoon to early evening (Figure 2). During daytime, N_2O_5 was often higher in the room than the supply air. Because the supply air was heated before entering the room, increased thermal dissociation of N_2O_5 would be expected. We observed the diurnal variation of the uncalibrated NO_3^- signal also maximized in the afternoon (Figure S7). The presence of NO_3 and N_2O_5 at appreciable levels outdoors is not expected during daytime due to rapid photolysis of NO_3 (R6, e.g., [46,50]). Thus, we assume that any daytime N_2O_5 indoors was not of outdoor origin, implying an indoor source. The presence of high O_3 and NO_2 favors the formation of NO_3 through R4. In the athletic facility, NO_2 was generally higher in the room than supply air, while O_3 and NO were higher in the supply air (Figure S8). In the absence of major indoor sources of O_3 (e.g.

photocopiers,[51] indoor air purifiers[52]), the dominant source of indoor O_3 is most likely to be transport of outdoor air.[53] Similarly, in the absence of indoor combustion sources (e.g., gas stoves), the dominant source of indoor NO_x was also likely outdoor air.[17,18,54] The observation of higher NO_2, lower NO, and lower O_3 in the athletic facility presumably results in part from the reaction between NO and O_3 to form NO_2 continuously, while the rate of photolysis decreases substantially for NO_2 indoors. At the same time, lower light and NO levels indoors reduced NO_3 losses (via R5 and R6) compared to those expected outdoors. Although these may be countered somewhat by increased NO_3 losses to organics (R7), which have been observed to be greater indoors than outdoors,[19] overall losses of NO_3 are likely much lower indoors during daytime. Thus, we infer that NO_3 formed because of abundant NO_2 and O_3 in the athletic facility and persisted because of reduced loss processes. Accumulated NO_3 indoors could then form N_2O_5 via R8. In the presence of surface chloride, $ClNO_2$ could form heterogeneously via R9. Chloride is commonly found on indoor surfaces through transfer of skin salts from human contact, deposition of gaseous or particulate chlorine,[55–57] or chlorine-based cleaners.[6]

As a case study to explore the formation of N_2O_5 and $ClNO_2$ in the athletic facility, we consider Nov 14, which was a sunny day with a high fraction of outdoor air delivered into the room. Higher N_2O_5 and $ClNO_2$ were observed during daylight hours in room compared to supply air (Figure 4). A simultaneous increase of N_2O_5 and $ClNO_2$ was observed in the room during the afternoon, which coincided with a decrease in NO transported from outdoors. Calculated loss processes for NO_3 for the same day (room: Figure 5, supply air: Figure S9) demonstrate that loss through photolysis (R6) was negligible ($<5.2 \times 10^{-4}$ s^{-1}), while loss through reaction with NO (R5) varied in importance (up to 6.5 s^{-1}) as result of changing indoor mixing ratios. A decrease in total NO_3 reactivity through daylight hours was observed, along with an increase in the fraction of reactivity attributed to reaction with NO_2 (i.e., N_2O_5 formation (R8), Figure S10). Calculated production of NO_3 (Figures 5, S8) demonstrates the importance of formation from the reaction of O_3 and NO_2 (R4), as well as dissociation of N_2O_5 (R8). Maximum calculated NO_3 production (0.30 pptv s^{-1}) as well as the highest fraction of daytime NO_3 loss to reaction with NO_2 (60 %) occurred in the afternoon. Levels of N_2O_5 and $ClNO_2$, as well as NO_3^- signal in the room increased through the afternoon, reaching their maxima in late afternoon or early evening (Figure 4). These observations are consistent with heterogeneous reaction of N_2O_5 and surface chloride as the source of observed $ClNO_2$ in the absence of cleaning activities.

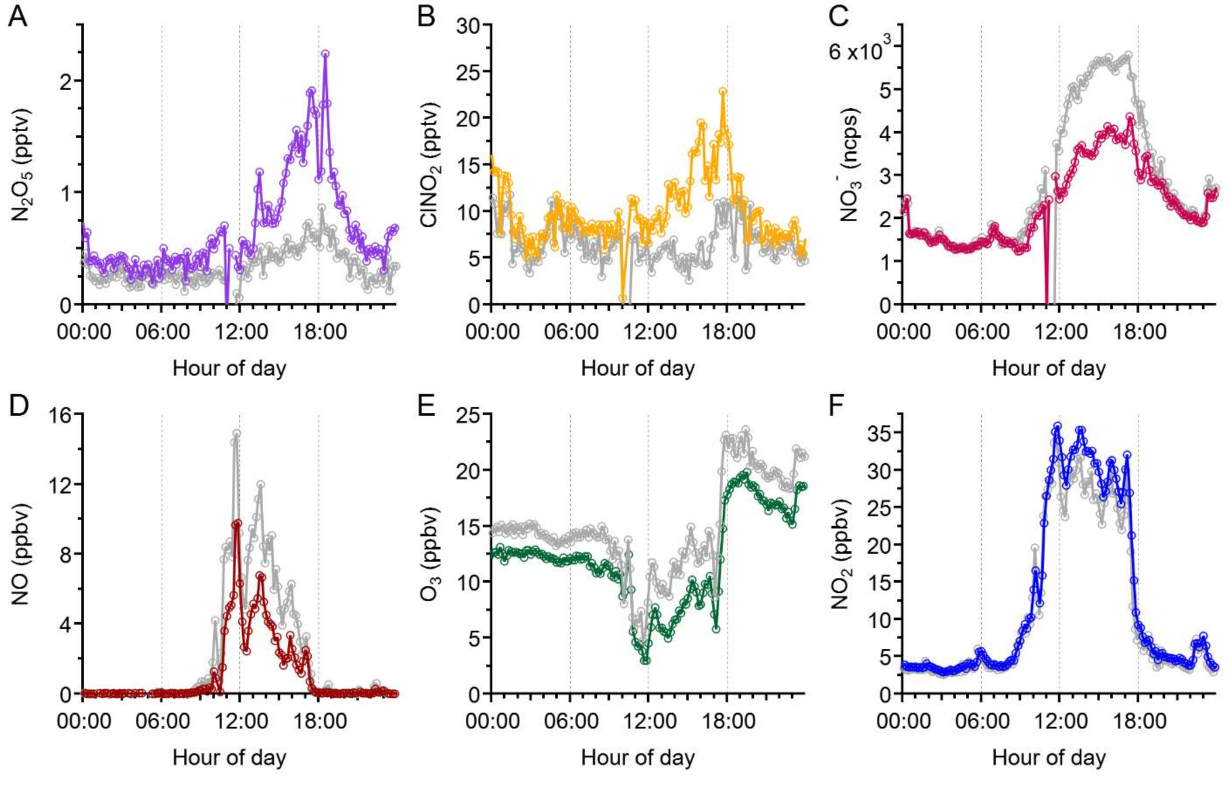

Figure 4: Diurnal variations of 5-minute average measurements in room air (colored traces) and supply air (grey traces) for (a) N_2O_5, (b) $ClNO_2$, (c) NO_3^-, (d) NO, (e) O_3, and (f) NO_2 on Nov 14.

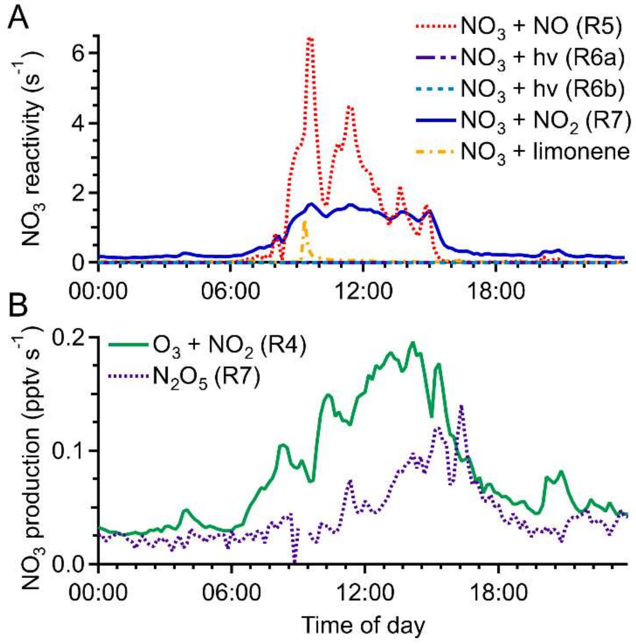

Figure 5: Calculated (a) NO_3 loss and (b) production rates for different reaction pathways in the room for Nov 14.

4. Implications

Cleaning with an electrostatically sprayed chlorine-based cleaner leads to increased levels of Cl*, though levels were lower and relative quantities of individual Cl* were different than surface cleaning with chlorine bleach. This indicates that further work is needed to understand the impacts and chemistry of different chlorine-containing cleaners. Even in low-light LED-illuminated conditions, some formation of chlorine atoms from photolysis of cleaning-emitted Cl* will occur. Losses of most Cl* were driven primarily by AER, apart from HOCl, which has several known indoor loss processes. This emphasizes that indoor environments with high AER could act as sources of Cl* to outdoors.

We observed elevated daytime $ClNO_2$ in the absence of cleaning, suggesting formation indoors from heterogeneous reaction of N_2O_5. Accumulation of NO_3 was possible in the athletic facility because of i) abundant precursors to NO_3 (NO_2 and O_3); and ii) negligible loss of NO_3 through photolysis. A high ventilation rate with air from outdoors - enabled by a high AER and high outdoor air fraction - was necessary to facilitate sufficiently high O_3 and NO_2 levels for the production of NO_3 and N_2O_5. In the presence of surface chloride, N_2O_5 formed from the NO_3 was observed to react to form $ClNO_2$. Since most indoor surfaces contain chloride, this chemistry would be expected to occur in other indoor environments that have high O_3 and NO_2, as well as low light and NO levels. This illustrates a new pathway for outdoor pollutants to affect chemistry indoors when AER is high.

The chemistry demonstrated here emphasizes the potential interplay between indoor and outdoor Cl* chemistry under high AER conditions. This is of emerging concern because one solution to minimize the potential for disease transmission indoors is an increase in AER.[58] Many individual Cl* chemicals are known to be toxic and/or reactive, so this may result in negative impacts on both indoor and outdoor air quality.

SUPORTING INFORMATION

Calculation of maximum Cl* production from Cl_2, $ClNO_2$, HOCl photolysis during cleaning events and measured photon flux. Estimation of alternative HOCl loss processes. Discussion of NO_3/N_2O_5 chemistry detection, NO_3 reactions with organics. Supporting figures on layout and performance of the ventilation system. Effect of duct air heating on NO_3 production rate. Fractional NO_3 loss attributed to non-photolytic reactions. Additional figures on HCl, Cl_2, $ClNO_2$, NO_3, NO, NO_2 and O_3 mixing ratios in supply and duct air. Supporting information on experiment setup and applied methods.

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