




ORIGINAL ARTICLE

Formation and emission of hydrogen chloride in indoor air

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Abstract

To improve our understanding of chlorine chemistry indoors, reactive chlorine species such as hydrogen chloride (HCl) must be analyzed using fast time-response measurement techniques. Although well studied outdoors, sources of HCl indoors are unknown. In this study, mixing ratios of gaseous HCl were measured at 0.5 Hz in the indoor environment using a cavity ring-down spectroscopy (CRDS) instrument. The CRDS measurement rate provides a major advance in observational capability compared to other established techniques. Measurements of HCl were performed during three types of household activities: (a) floor exposure to bleach, (b) chlorinated and nonchlorinated detergent use in household dishwashers, and (c) cooking events. Surface application of bleach resulted in a reproducible increase of 0.1 ppbv in the affected room. Emissions of HCl from automated dishwashers were observed only when chlorinated detergents were used, with additional HCl emitted during the drying cycle. Increased mixing ratios of HCl were also observed during meal preparation on an electric element stovetop. These observations of HCl derived from household activities indicate either direct emission or secondary production of HCl via chlorine atoms is possible. Calculations of photolysis rate constants of chlorine atom precursors provide evidence that photolysis may contribute to indoor HCl levels.

KEYWORDS

bleach, cavity ring-down spectroscopy, cooking, hydrochloric acid, reactive chlorine, real-time measurements

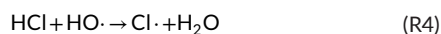
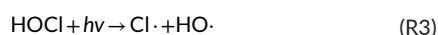
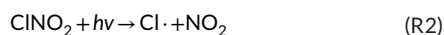
1 | INTRODUCTION

Resulting from direct emission and secondary production, HCl has been known to be present in the atmosphere at detectable levels for the past several decades.^{1–15} Processes such as volcanic eruptions, biomass burning, coal combustion, and waste incineration emit HCl directly.^{7,15} Secondary formation of HCl is facilitated by reactions on chloride-containing aerosols.^{2,15,16} Although the subject of numerous atmospheric measurements and modeling studies, these sources are not well constrained. In indoor environments, sources of HCl are unknown despite knowledge that harmful HCl exposure may occur via inhalation and direct contact.¹⁷ Like other strong acids, HCl exposure causes irritation of respiratory tract, eyes, and skin.¹⁷ While

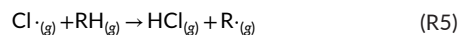
these effects occur when HCl levels reach five parts per million by volume (ppmv), the impact of chronic exposure to low-level HCl (ie, parts per billion to parts per trillion by volume) is not known. In addition, strong acids including HCl can corrode metals such as those in electronic devices¹⁸ and damage works of art.¹⁹

The lifetime of trace atmospheric pollutants is governed by oxidative chemistry in the troposphere.^{20,21} Principal tropospheric oxidants include hydroxyl radicals and chlorine atoms.²⁰ Recent work has shown that chlorine atoms oxidize volatile organic compounds (VOCs) and produce ozone more efficiently than hydroxyl radicals, even in small quantities.²² Chlorine atoms also contribute to destruction of polar boundary layer ozone via a halogen-catalyzed ozone destruction cycle.²³ Both scenarios have significant air quality

and environmental implications; thus, monitoring of chlorine atoms is essential. Yet, due to the highly reactive nature of chlorine atoms, direct measurement techniques do not exist.²⁴ Because of this, chlorine atom precursors are used as proxies to understand chlorine atom chemistry in the troposphere. Precursors include molecular chlorine (Cl_2), nitryl chloride (ClNO_2), hypochlorous acid (HOCl), and HCl (R1-R4).^{2,21,25-28}



Production of chlorine atoms results from photolysis and oxidation reactions of precursor molecules. Chlorine atoms abstract hydrogen rapidly from VOCs:



where RH represents any VOC.^{2,15} Due to the large relative abundance of reactants in polluted coastal regions, the reaction proceeds with ease.¹⁴ It is possible that analogous reactions could occur in the indoor environment.

Emission of reactive chlorine species to indoor air occurs through a wide variety of typical household tasks. Recently, Wong et al²⁹ demonstrated that reactive chlorine in the form of HOCl , Cl_2 , and ClNO_2 is emitted during floor cleaning with chlorine bleach. Cleaning floors with bleach is a method that has been used for decades to disinfect and remove stains and is relatively cost-effective compared to other cleaners. Many recognize bleach by its characteristic scent, which can be overwhelming and lead to side effects such as dizziness and headaches. These reactive chlorine observations, along with the ubiquity of bleach in households globally, demonstrate that further investigation of reactive chlorine emissions indoors is necessary. Unlike the reactive species discussed by Wong et al, sources and human health impacts of traditional water disinfection byproducts (DBPs) indoors have been studied extensively.³⁰⁻³⁴ The most commonly studied DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs), can enter indoor air via washing machines, showers, dishwashers, and taps.^{29,30} This emission is dependent on the concentration of chlorine and DBPs present in municipal drinking water. One region in particular that relies heavily on chlorination for water disinfection is Newfoundland and Labrador. In this

Practical Implications

- Hydrogen chloride (HCl) has not been studied indoors despite extensive research in outdoor environments
- The first real-time measurements of indoor HCl were made in a private, occupied dwelling using a portable, quiet, and fast spectrometric instrument
- Measurements during typical household activities showed that bleach cleaning, chlorinated dishwasher detergent use, and cooking led to increased HCl levels
- The presence of HCl could indicate oxidation chemistry initiated by chlorine atoms

province, many communities have elevated chlorine levels, which sometimes can exceed the national average tenfold.^{35,36} Because of this, it might be expected that exposure to reactive chlorine species is elevated throughout the province. These levels may be further increased when chlorinated detergents are used for washing dishes and clothing. Thus, indoor reactive chlorine exposure may not be limited to only THMs and HAAs from drinking water. Due to the lack of measurements, it is important to begin identifying reactive chlorine species and their sources in private dwellings. In this work, the reactive chlorine species HCl is measured for the first time to enhance understanding of chlorine chemistry and sources indoors. Measurements were collected using a HCl cavity ring-down spectrophotometer (CRDS). Using the CRDS, we provide the following: i) the first high time resolution measurements of indoor HCl ; and ii) preliminary estimates of HCl emissions from typical household activities such as cleaning and cooking.

2 | METHODS

2.1 | Measurements via cavity ring-down spectroscopy

All measurements were performed using a CRDS (G2108 Hydrogen Chloride Analyzer from Picarro, Inc.). This specific model detects trace gaseous HCl , with no interference from other gaseous species such as HOCl , by using a high precision distributed feedback laser centered at $5739.2625 \text{ cm}^{-1}$.³⁷ The Picarro analyzer contains a heated ($70.000 \pm 0.005^\circ\text{C}$), low-pressure ($0.1842 \pm 0.0002 \text{ atm}$) high finesse optical cavity, which has three high reflectivity mirrors, two flat and one curved.³⁸ The total reflectance capability is the magnitude of signal loss in the empty optical cavity, which is less than 50 ppm for this design. This leads to a limit of detection of 84 parts per trillion by volume (pptv) measured over 5 minutes in zero air at 0% relative humidity (RH). Under the same conditions, the precision (1σ) of the instrument was determined to be $\pm 24 \text{ pptv}$ in 5 minutes. The HCl CRDS is an ideal instrument for sampling indoors because it is portable (26.9 kg), quiet (40 dB), does not require consumables (eg, compressed gas cylinders) nor frequent calibration.³⁹

2.2 | Indoor air sampling

Sampling occurred in a private dwelling located in St. John's, Newfoundland and Labrador, from April 17 to May 24, 2017. Mixing ratios of HCl were monitored during the operation of two household appliances: a dishwasher and electrically heated ceramic stovetop. Mixing ratios were also monitored while cleaning the kitchen and dining room floors with bleach. The CRDS was placed on the kitchen counter above the dishwasher for all experimental work, approximately 36 inches above the floor. The inlet, an 8" length of ¼" perfluoroalkoxy (PFA) tubing, was directed toward the stovetop and parallel to the floor and had a 75 ms residence time. Air was sampled at a rate of 2 SLPM. Submicron prefilter and backup filter are present inside the HCl analyzer and remove particles entrained in the sample flow prior to the sample gases entering the optical cavity. We performed laboratory validations of the system using HCl delivered from a permeation tube (see section S1 for more information). By collecting the output of the permeation tube into a bubbler (1 mmol/L KOH) and analyzing the extract by ion chromatography coupled to conductivity detection, the permeation tube output was determined as 140 ± 18 ng/min ($n = 3$). The permeation tube output was measured by the CRDS through an inlet with a 79 ms residence time. Measurements were made at 0, 20, and 50% RH, which encompass typical RH conditions indoors. The CRDS and offline IC measurements agreed within error. Response times ($1/e$) determined from full signal decays under the three RH conditions ranged from 26 to 32 seconds. The room in which the measurements were made had a volume of approximately 71 m³ within a 1.5 story 220 m² home. The doors in the room were left open while measurements were taken, allowing for inter-room air transport. The air exchange rate for the sampling site was not measured for this campaign, but has been estimated to be 0.1 h⁻¹ (see Section S2 in the SI).^{40,41} Background measurements of HCl were taken during a 12-hour period prior to bleach cleaning and cooking experiments. Ambient levels ranged from 0.21 to 0.31 ppbv and remained relatively constant despite changes in solar radiation and temperature (Figure S1).

2.3 | Bleach cleaning experiments

In order to approximate household reactive chlorine emissions while cleaning with bleach, a bottle of commercially available bleach was purchased and diluted as per the manufacturer's instructions. The diluted bleach solution was applied to a 12-m² section of sealed and varnished hardwood flooring over a span of 3-4 minutes. After application, the bleach cleaning solution was moved outdoors to ensure that its emissions did not interfere with the emission measurement from the floor surface. The floor was allowed to dry with minimal disturbance. Two subsequent applications on the same surface were performed using the same technique immediately after the floor had dried and the HCl mixing ratio had decayed to near its initial mixing ratio. All bleach applications were performed after sunset. Lights in the test room were turned on for the duration of the experiment, which was equipped with a

combination of light-emitting diode (LED), halogen-tungsten, and covered fluorescent tube light sources.

2.4 | Dishwashing experiments

The CRDS was placed within 50 cm of the vent from the dishwasher, and various dishwashing scenarios were explored. To investigate detergent composition effects on indoor HCl mixing ratios, organochlorine, bleach, and nonchlorinated detergents were used in the dishwasher. All experiments used the normal wash cycle of a Frigidaire dishwasher. The normal cycle uses 23 L of water over a span of 2 washes and 3 rinses. The drying cycle occurs after the 89-minute-long wash cycle. Dishwasher experiments were performed after sunset or just after sunrise. Lights in the room (LED, halogen-tungsten, and covered fluorescent) were turned on.

2.5 | Cooking experiments

The CRDS inlet was placed 2.5 m away from a stovetop. Mixing ratios of HCl were measured during stovetop cooking using a Frigidaire electric range with ceramic cooktop. The occupants consumed only a plant-based diet during these measurements, and therefore meals included vegetables, seasonings, and oils. Cooking occurred mid-day; thus, the room was illuminated by a combination of ambient sunlight, LED, halogen-tungsten, and covered fluorescent lights during the experiment.

2.6 | Cl Production rate constant calculations

Measurements of wavelength-resolved photon fluxes for common indoor light sources were made by Kowal and Kahan.⁴² Measured photon fluxes were used to calculate photolysis rate constants (J) for chlorine atom precursors Cl₂, HOCl, and ClNO₂ using

$$J = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda) \phi(\lambda) F_{\lambda} d\lambda$$

where λ , σ , and ϕ represent the wavelength, absorption cross-section of the molecule, and photolysis quantum yield, respectively. Absorption cross-sections were taken from Maric et al⁴³ (Cl₂), Barnes et al⁴⁴ (HOCl), and Ghosh et al⁴⁵ (ClNO₂). Quantum yields of 1 were used for Cl₂ and HOCl,⁴⁶ while a quantum yield of 0.93 was used for ClNO₂.⁴⁷ Radical (OH or Cl) production rates were calculated as the product of the photolysis rate constant and the expected concentration of the precursor following bleaching events.

3 | RESULTS/DISCUSSION

3.1 | Cleaning experiments

Elevated HCl mixing ratios relative to background levels were observed following each of three consecutive bleach applications (Figure 1).

All bleach applications showed similar changes in HCl mixing ratios above the background, indicating that the magnitude of the emission is reproducible. With each application, an initial spike of approximately 0.1 ppbv occurred and was followed by a slower decay (Figure 2).

Prior to bleach application, mixing ratios ranged from 0.32 to 0.36 ppbv, and in less than ten minutes, mixing ratios increased to 0.43–0.48 ppbv. Over about thirty minutes, the mixing ratio returned to initial conditions. Figure 2A,B shows that the rise and decay for HCl is reproducible in all three trials. After 30 minutes, HCl mixing ratios had decayed by 52%–62% of peak levels observed during the bleaching event. The emission trends observed for HCl resemble those of gaseous HOCl and Cl₂ reported by Wong et al.²⁹ From these data, we cannot determine whether HCl is emitted directly or formed indirectly. It is possible that photolysis could aid in the indirect formation of HCl. A previous study²⁹ has shown that HOCl, Cl₂, and ClNO₂ are released during floor mopping with bleach. All three are known to photolyze under ambient outdoor light to produce Cl atoms (eg,^{22,24,27}) which react with VOCs to form HCl (Figure 3).^{29,48}

This work was performed under artificial lighting, consisting of LED, halogen-tungsten, and covered fluorescent tubes, which emit at wavelengths longer than 400, 308, and 363 nm, respectively.⁴² Under these light conditions, photolysis reactions shown in Figure 3 could proceed. Calculated Cl photolysis production rates under illumination by various light sources at Cl₂ and HOCl mixing ratios reported after the use of bleach (20 and 200 ppbv), and at an estimated ClNO₂ mixing ratio of 1 ppbv are shown in Table 1 and Table S4.^{29,42} The Cl production rate at the light source represents the maximum production rate, while that at 1 m from the light source is the production expected at approximately human head height. Photolysis rate constants for all three species can be found in the SI. Cl atoms are predicted to be formed from Cl₂ photolysis at rates on the order of $0.1\text{--}1.2 \times 10^8$ molec/cm³/s under illumination by the LED, halogen-tungsten, and covered fluorescent tubes used in the residence, while formation rates from HOCl photolysis will range from 0.2 to 5.9×10^7 molec/cm³/s under the same illumination conditions.

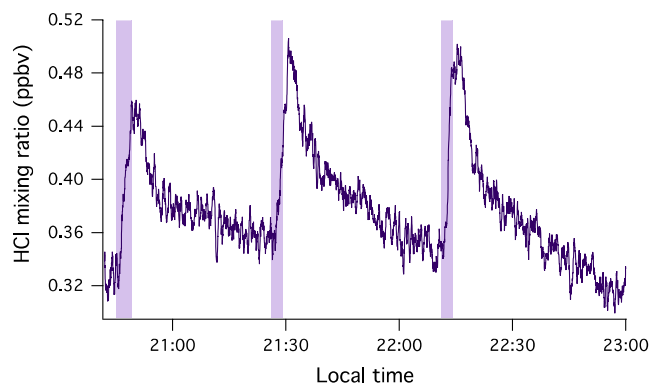


FIGURE 1 HCl mixing ratios measured during three sequential bleach applications. Measurements are presented as the 30-s average of the HCl mixing ratio in parts per billion by volume (ppbv). Bleaching applications spanning 3 ± 1 min periods are represented by the shaded regions and the HCl mixing ratio by the solid line

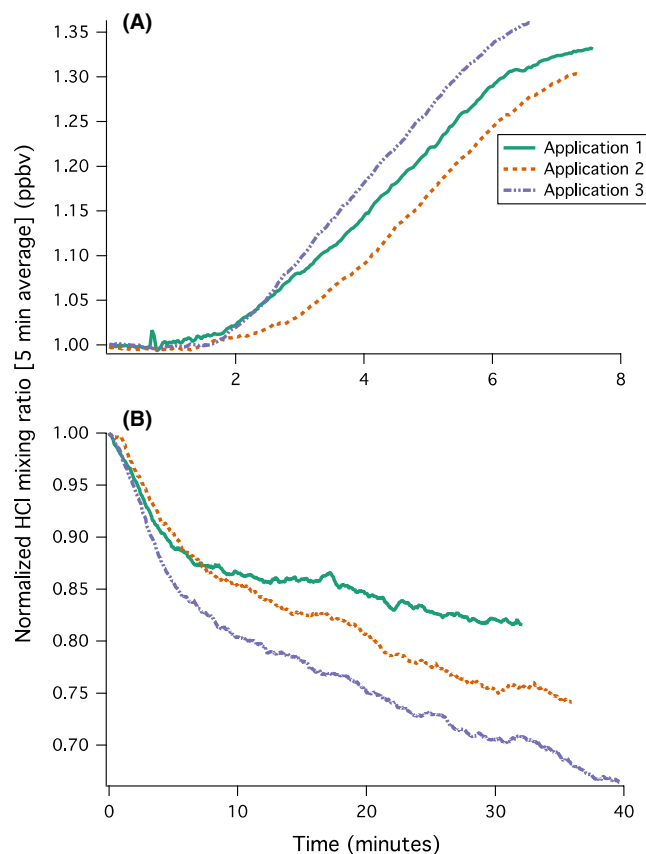


FIGURE 2 A, Rise and (B) decay in HCl mixing ratio after bleach applications. Results from this experiment are presented normalized to the background (A) or maximum (B) concentration. In all cases, the measurements are the 5-min average HCl mixing ratio in parts per billion by volume (ppbv)

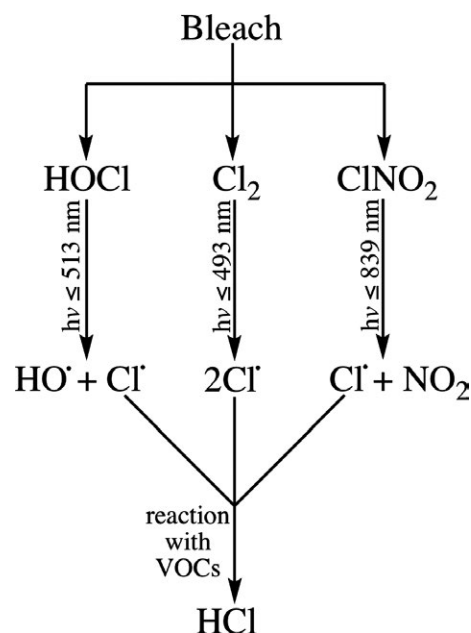


FIGURE 3 Proposed reaction pathway for indirect formation of HCl via photolysis of HOCl, Cl₂, and ClNO₂ emitted from bleach use

TABLE 1 Calculated Cl production rates for light sources in this study for 20 ppbv Cl₂, 200 ppbv HOCl, and 1 ppbv ClNO₂ at 1 m from the light source. Mixing ratios were based on measurements from Wong et al²⁷

Light source	Cl production rate (molecules/cm ³ /s)		
	Cl ₂	HOCl	ClNO ₂
LED	4.62 × 10 ⁵	3.26 × 10 ⁴	2.17 × 10 ²
Halogen	2.56 × 10 ⁶	1.30 × 10 ⁶	6.50 × 10 ³
Office fluorescent (covered)	1.45 × 10 ⁶	4.26 × 10 ⁵	1.20 × 10 ³

Production rates of Cl from ClNO₂ photolysis will not exceed 3 × 10⁵ molec/cm³/s under these conditions. However, it should be reiterated that ClNO₂ mixing ratios after the use of bleach have not been quantified.²⁹ If mixing ratios are significantly larger than the 1 ppbv used in these calculations, it could be an important photochemical Cl source. Assuming the same lamp power, halogen-tungsten lamps will generate the most radicals for each Cl precursor. The Cl production rates listed above were calculated based on photon fluxes measured directly adjacent to the light sources. At a distance of 1 m away from the light sources, the rates will decrease to 0.5–2.6 × 10⁶ molec/cm³/s for Cl₂, 0.3–13 × 10⁵ molec/cm³/s for HOCl, and 0.2–6.5 × 10³ molec/cm³/s for ClNO₂. For context, OH production rates indoors (formed from dark reactions between ozone and alkenes and from HONO photolysis) are expected to be on the order of 10⁷ molec/cm³/s in residences.^{42,49,50} Photochemical Cl production rates during the use of bleach may therefore exceed OH production rates under some conditions. Potential photochemical Cl production rates from light sources not present in the residence during the experiments (including sunlight) are provided in the SI.

The measured HCl production rate during the bleaching experiments was ~1.2 × 10⁷ molec/cm³/s. This is similar to photochemical Cl production rates predicted in Table 1; since Cl reacts at near diffusion-limited rates with many VOCs, photochemical generation of Cl is expected to be the rate-limiting step. This suggests that at least some of the detected HCl may be formed from photolysis of Cl₂ and HOCl, rather than direct emission from the bleach solution. HCl and photolabile chlorine species have not been measured simultaneously indoors after the use of bleach, which would be necessary to determine the source of the HCl with a high degree of certainty.

The double exponential decay observed in Figure 2B is likely attributed to HCl deposition to surfaces and environmental factors (eg, temperature and air exchange rate). Weschler and Nazaroff have recently shown that initially, some semivolatile organic compounds adsorb to surfaces indoors.⁵¹ This adsorption will result in the formation of an organic film on the surface, which can then absorb additional settling species. Since HCl readily deposits to all outdoor surfaces (eg, Crisp et al¹⁵), we expect the same to occur indoors. The abundance of surfaces present in the experimental kitchen participates in the emission and decay of HCl. After emissions cease, these will approach a state of thermodynamic equilibrium that depends on surface properties, temperature, and relative humidity in

the indoor environment. Since the dwelling has radiative heat rather than forced air, the measurement background is not likely affected much by the air exchange rate (~0.1 h⁻¹).^{40,41}

3.2 | Dishwashing experiments

Previous studies have shown that dishwashers emit compounds including chlorinated organics, which are released when chlorinated dishwashing detergents are used.³¹ Emissions from the experimental dishwasher were monitored during four different conditions: (a) no detergent; (b) powdered organochlorine detergent; (c) liquid bleach detergent; and (d) nonchlorinated detergent. All experiments were conducted in the absence of dishes. In condition (1), a dishwasher cycle was started to establish a baseline and determine whether the water alone contributed to HCl emissions. Since Newfoundland is known for elevated chlorination rates, it was essential to determine whether the water itself contributed to indoor HCl levels before assessing the effects of chlorinated detergents.^{35,36} A stable signal was observed before, throughout, and after the cycle, confirming that household HCl emissions did not result from tap water. In conditions (2) and (3) with chlorinated detergents, emission of HCl was observed in all experiments (n = 4) (Table 2, Figure 4).

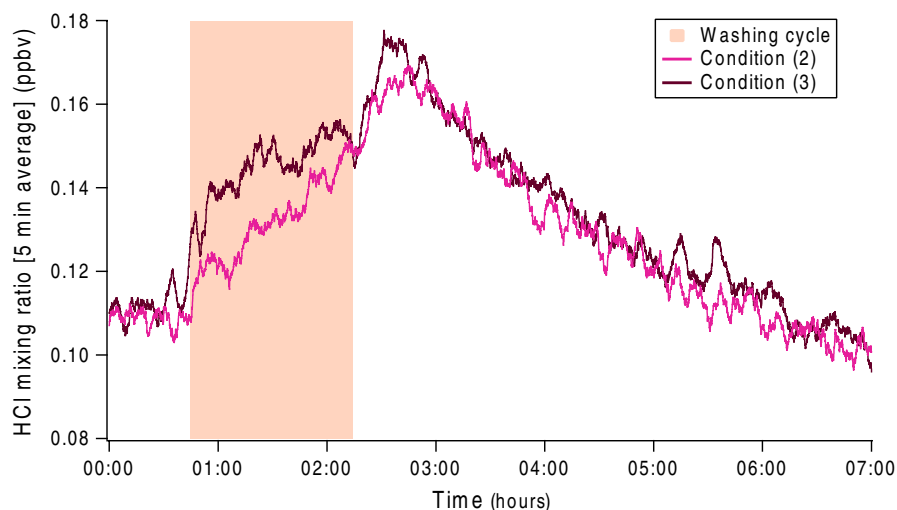
Both organochlorine and bleach detergents showed similar emissions of HCl when used in the empty dishwasher (example shown in Figure 4). There was an initial spike in emissions at the beginning of the cycle, followed by a gradual, yet consistent, increase in HCl mixing ratio. Once the cycle ended, HCl levels increased. This is attributed to the dishwasher drying cycle (mixing ratio increase observed following the shaded area on Figure 4), which evaporates the solution contents of the dishwasher into its headspace and into the kitchen via vents located on the dishwasher door. After the drying cycle ended, the HCl mixing ratio began a slow, constant decay. Similar to cleaning experiments, HCl decayed after dishwashing experiments by double exponential. Comparison between all dishwashing conditions was not possible because of the different environmental factors (eg, temperature) between conditions.

When chlorinated detergents were used, the HCl mixing ratio increased with both washing and drying cycles. The maximum average mixing ratio increase from the beginning of the cycle was 22 and 45 pptv due to conditions 2 and 3, respectively. Emissions from the drying cycle further contribute to mixing ratios, as HCl levels undergo an additional increase of 17–19 pptv. From results of conditions 2 and 3, we observe that detergent choice can influence the extent of HCl release indoors. To further confirm the influence of chlorinated detergents on HCl emissions, the experiment was replicated using detergents free of chlorine. No differences in HCl mixing ratios were observed during dishwashing with this type of detergent. The observed HCl mixing ratio increase as a result of dishwashing using chlorinated detergents was approximately twenty times less than from surface bleach application. There is currently no information regarding emissions of photolabile chlorine species (eg, Cl₂) from dishwashers. If reactive chlorine species

TABLE 2 Mixing ratio increases relative to initial background conditions observed during dishwashing experiments

Condition	Detergent type	HCl mixing ratio (pptv) [5 min avg]		
		Background	Increase with cycle	Increase with drying
2	organochlorine	190	22	33
2	organochlorine	130	23	50
3	Bleach	110	40	59
3	Bleach	100	50	65
4	nonchlorinated	180	0	-9.8
		Average increase condition (2)	22	41
		Average increase condition (3)	45	62

FIGURE 4 HCl mixing ratio during a condition (2) and (3) dishwashing scenario. In both cases, the measurements are the 5-min average HCl mixing ratio in parts per billion by volume (ppbv)



are being emitted from dishwashers, the HCl measured could be formed indirectly in addition to direct emission. In all dishwasher experiments, the HCl signal decays to values less than initial conditions. This can be attributed to the home cooling during the day, as dictated by the temperature program (see Table S1 in the SI). Depletion of HCl can also be a result of household air exchange rates over the course of the experiment, which spanned several hours.⁴¹ Since parameters such as photon flux and ventilation rate were not measured, it is difficult to determine a definitive sink of HCl in this case.

It is likely that food residue in the dishwasher would further affect the emissions. Olson and Corsi analyzed emissions of THMs from dishwashers with soiled dishes, which demonstrated that food residues have an impact on emissions depending on type, storage method, and age.³¹ For example, it was demonstrated that meat protein and acidic fruits and vegetables would increase emissions, whereas food storage techniques such as freezing may impact the integrity of the protein and reduce emissions. In order to determine whether or not food residues contribute to indoor HCl levels, further studies that investigate a wide variety of food types are recommended.

3.3 | Cooking experiments

We observed emissions of HCl from frying pan use on an electric stovetop. Since electric appliances require electricity instead of combustion for heat generation, emissions from the stovetop itself are considered negligible. This indicates that food must be the source of HCl while cooking. This is unsurprising, since smoldering-stage biomass burning, a well-known source of gaseous HCl, is a similar physical transformation to cooking.⁵² An example of cooking, showing two events, is presented in Figure 5.

Cooking event 1 began by adding onions to a pan containing preheated vegetable oil. The kitchen HCl mixing ratio remained relatively constant at 220 pptv. The addition of fresh chopped garlic, followed by the addition of other ingredients 3 minutes later, resulted in a 81 pptv increase over approximately 30 min. Other ingredients in event 1 included water, rice, parsley, vegetable bouillon (no NaCl or KCl added), onions, and lettuce. At 16:15, event 2 began. Again, the addition of fresh chopped garlic coincided with the start of a 28 pptv mixing ratio increase over a period of 30 minutes. Other ingredients used in event 2 included salt, curry powder, rice, vegetable bouillon, shallots, and zucchini.

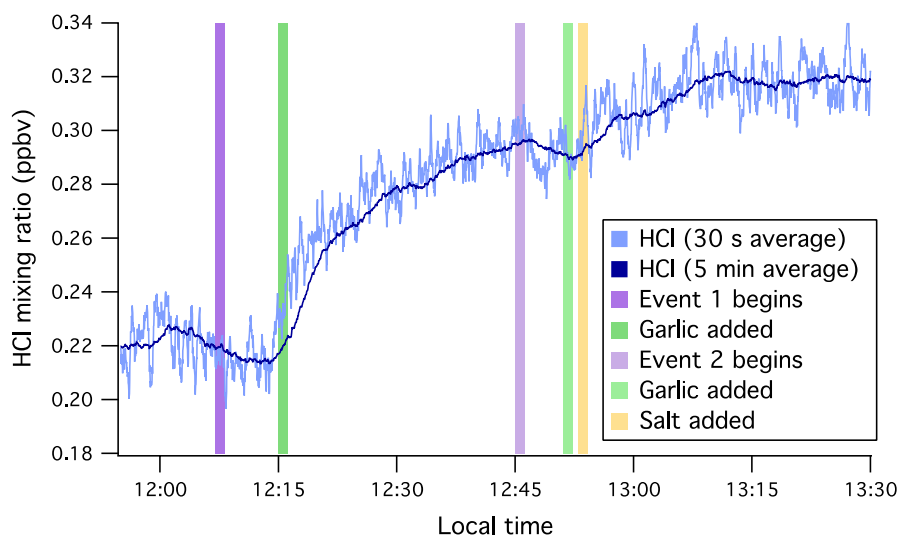


FIGURE 5 HCl mixing ratio during two consecutive cooking experiments. Commencement of cooking, and garlic and salt addition are indicated by shaded regions. HCl mixing ratios are presented by 30-s and 5-min averages in ppbv

Similar to observations of burning vegetation that have experienced sea salt deposition⁵², cooking with table salt will likely increase emissions of HCl. The addition of table salt in cooking may be expected to increase HCl emissions. A slight increase in mixing ratios is coincident with salt addition in event two. In both cooking events, it is interesting to note that the mixing ratio increased as the components in the pan began to brown, and as fresh garlic was added. It is possible that HCl is emitted when these vegetables, among others, cook or burn. Many vegetables and fruits contain chlorine in the form of chloride.^{53,54} On a cellular level, chloride is required for stomatal opening when guard cells cannot synthesize malate.^{54,55} Levels of chloride depend on species, but also on the location and conditions under which the food was grown.^{52,53} For example, food cultivated in close proximity to the ocean may have enhanced chlorine levels because of sea salt deposition and uptake.⁵² Onions and garlic, which belong to the same family (allium) as shallots, have been shown to contain chloride.^{53,54} Thus, it is likely that direct emission via plant species contributes to HCl mixing ratios while cooking. Additional investigation is required to further elucidate HCl sources from cooking, by both accurate measurement of food and cooking food individually.

3.4 | Instrumentation for indoor measurement of HCl

Since regular measurement of HCl has not yet been established for indoor environments, existing techniques must be evaluated for use indoors. The most common technique for HCl measurement outdoors is the annular denuder system (ADS), which is comprised of a sintered glass rod, a backup filter, and a vacuum pump.^{4-6,9,56} Sampling with an ADS occurs over the timescale of hours, providing one collective sample. Since HCl partitions rapidly from the gas to particle phase or deposits on surfaces, accurate measurements in real time are essential.⁵² This requirement is satisfied when high time-response measurements of HCl are acquired with chemical

ionization mass spectrometry (CIMS).^{15,57} While useful for outdoor measurements, CIMS is not ideal for use in private dwellings. It has a large footprint, substantial power draw, and several vacuum pumps, and most require a radioactive ionization source.⁵⁷ Ideal analysis for HCl indoors would provide sensitive, real-time, fast measurements with a safe and easily transportable instrument. This work demonstrates the first use of a compact, quiet, and energy-conservative CRDS instrument suitable for in situ HCl measurements indoors.

4 | CONCLUSIONS

Daily household activities were investigated to determine their contribution to indoor HCl emissions. Measurements were made using an in situ, noninvasive, fast time-response CRDS instrument. These represent the first fast time-response measurements of HCl in an indoor, nonoccupational setting and can be used to identify HCl sources indoors. Surface cleaning and disinfecting using bleach has been found as a source for HCl. Chlorinated dishwasher detergents directly impact household HCl levels, whereas nonchlorinated detergents have no impact. Additionally, the dishwasher drying cycle has a noteworthy impact on already-elevated HCl mixing ratios. Photolysis of photolabile chlorine species (eg, Cl_2), leading to formation of HCl, is possible under indoor conditions, but more work is needed to determine whether bleach cleaning and dishwashing sources of HCl are direct or indirect. Cooking vegetables resulted in emissions of HCl. Sources of HCl in these vegetables can result from chlorine contained within the plant cells, as well as heterogeneous reactions. The findings of this work have enhanced understanding of reactive chlorine chemistry indoors. Despite an advance in knowledge, additional work is required to determine a complete inventory of reactive species and their chemistry to determine how they impact indoor air quality and hence human health.

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REFERENCES

- Rahn KA, Borys RD, Butler EL, Duce RA. Gaseous and particulate halogens in the New York City atmosphere. *Ann N Y Acad Sci*. 1979;322:143-151.
- Graedel TE, Keene WC. Tropospheric budget of reactive chlorine. *Global Biogeochem Cycles*. 1995;9:47-77.
- Gounon J, Milhau A. Analysis of inorganic pollutants emitted by the City of Paris garbage incineration plants. *Waste Manag Res*. 1986;4:95-104.
- Johnson CA, Sigg L, Zobrist J. Case studies on the chemical composition of fogwater: the influence of local gaseous emissions. *Atmos Environ*. 1987;21:2365-2374.
- Keuken MP, Schoonebeek CAM, van Wensveen-Louter A, van Slanina J. Simultaneous sampling of NH₃, HNO₃, HCl, SO₂ and H₂O₂ in ambient air by a wet annular denuder system. *Atmos Environ*. 1988;22:2541-2548.
- Matsumoto M, Okita T. Long term measurements of atmospheric gaseous and aerosol species using an annular denuder system in Nara, Japan. *Atmos Environ*. 1998;32:1419-1425.
- Keene WC, Khalil MAK, Erickson DJ, et al. Composite global emissions of reactive chlorine from anthropogenic and natural sources: reactive chlorine emissions inventory. *J Geophys Res*. 1999;104:8429-8440.
- Jourdain B, Legrand M. Year-round records of bulk and size-segregated aerosol composition and HCl and HNO₃ levels in the Dumont d'Urville (coastal Antarctica) atmosphere: implications for sea-salt aerosol fractionation in the winter and summer. *J Geophys Res Atmos*. 2002;107:1-13.
- Bari A, Ferraro V, Wilson LR, Luttinger D, Husain L. Measurements of gaseous HONO, HNO₃, SO₂, HCl, NH₃, particulate sulfate and PM_{2.5} in New York, NY. *Atmos Environ* 2003;37:2825-2835.
- Keene WC, Pszenny AAP, Maben JR, Stevenson E, Wall A. Closure evaluation of size-resolved aerosol pH in the New England coastal atmosphere during summer. *J Geophys Res D Atmos*. 2004;109:1-16.
- Keene WC, Stutz J, Pszenny AAP, et al. Inorganic chlorine and bromine in coastal New England air during summer. *J Geophys Res Atmos*. 2007;112:1-15.
- Kim S, Huey LG, Stickel RE, et al. Airborne measurements of HCl from the marine boundary layer to the lower stratosphere over the North Pacific Ocean during INTEX-B. *Atmos Chem Phys Discuss*. 2008;8:3563-3595.
- Keene WC, Long MS, Pszenny AAP, et al. Latitudinal variation in the multiphase chemical processing of inorganic halogens and related species over the eastern North and South Atlantic Oceans. *Atmos Chem Phys Discuss*. 2009;9:11889-11950.
- Lawler MJ, Sander R, Carpenter LJ, et al. HOCl and Cl₂ observations in marine air. *Atmos Chem Phys*. 2011;11:7617-7628.
- Crisp TA, Lerner BM, Williams EJ, Quinn PK, Bates TS, Bertram TH. Observations of gas phase hydrochloric acid in the polluted marine boundary layer. *J Geophys Res*. 2014;119:6897-6915. <https://doi.org/10.1002/2013JD020992>.
- Nassar R, Bernath PF, Boone CD, et al. A global inventory of stratospheric chlorine in 2004. *J Geophys Res Atmos*. 2006;111:1-13.
- US Environmental Protection Agency Hydrochloric Acid (Hydrogen Chloride) 7647-01-0. 1992, pp 1-4.
- Franey JP, Graedel TE. Corrosive effects of mixtures of pollutants. *J Air Pollut Control Assoc*. 1985;35:644-648.
- Loupa G, Charpantidou E, Karageorgos E, Rapsomanikis S. The chemistry of gaseous acids in medieval churches in Cyprus. *Atmos Environ*. 2007;41:9018-9029.
- Wingenter OW, Kubo MK, Blake NJ, Smith TW, Blake DR, Rowland FS. Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights. *J Geophys Res*. 1996;101:4331-4340.
- Bannan TJ, Booth AM, Bacak A, et al. The first UK measurements of nitryl chloride using a chemical ionization mass spectrometer in central London in the summer of 2012, and an investigation of the role of Cl atom oxidation. *J Geophys Res Atmos*. 2015;120:5638-5657.
- Osthoff HD, Roberts JM, Ravishankara AR, et al. High levels of nitryl chloride in the polluted subtropical marine boundary layer. *Nat Geosci*. 2008;1:324-328.
- Platt U, Hönninger G. The role of halogen species in the troposphere. *Chemosphere*. 2003;52:325-338.
- Young CJ, Washenfelder RA, Edwards PM, et al. Chlorine as a primary radical: evaluation of methods to understand its role in initiation of oxidative cycles. *Atmos Chem Phys*. 2014;14:3427-3440.
- Pszenny AAP, Keene WC, Jacob DJ, et al. Evidence of inorganic chlorine gases other than hydrogen chloride in marine surface air. *Geophys Res Lett*. 1993;20:699-702.
- Behnke W, George C, Scheer V, Zetzsch C. Production and decay of ClNO₂ from the reaction of gaseous N₂O₅ with NaCl solution: bulk and aerosol experiments. *J Geophys Res Atmos*. 1997;102:3795-3804.
- Thornton JA, Kercher JP, Riedel TP, et al. A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature*. 2010;464:271-274.
- Mielke LH, Furgeson A, Odame-ankrah CA, Osthoff HD. Ubiquity of ClNO₂ in the urban boundary layer of Calgary, Alberta, Canada. *Can J Chem*. 2016;94:1-10.
- Wong JPS, Carslaw N, Zhao R, Zhou S, Abbatt JPD. Observations and impacts of bleach washing on indoor chlorine chemistry. *Indoor Air*. 2017;27:1082-1090.
- Howard C, Corsi RL. Volatilization of chemicals from drinking water to indoor air: the role of residential washing machines. *J Air Waste Manag Assoc*. 1998;48:907-914.
- Olson DA, Corsi RL. In-home formation and emissions of trihaloethanes: the role of residential dishwashers. *J Expo Anal Environ Epidemiol*. 2004;14:109-119.
- Kim E, Little JC, Chiu N. Estimating exposure to chemical contaminants in drinking water. *Environ Sci Technol*. 2004;38:1799-1806.
- Legay C, Rodriguez MJ, Sadiq R, Sérodes JB, Levallois P, Proulx F. Spatial variations of human health risk associated with exposure to chlorination by-products occurring in drinking water. *J Environ Manage*. 2011;92:892-901.
- Guilherme S, Rodriguez MJ. Occurrence of regulated and non-regulated disinfection by-products in small drinking water systems. *Chemosphere*. 2014;117:425-432.
- Newfoundland and Labrador Department of Environment and Climate Change Newfoundland and Labrador Water Resources Portal. Newfoundland and Labrador, Department of Environment and Climate Change. <https://maps.gov.nl.ca/water/>. Accessed May 2, 2017.
- Health Canada Guidelines for Canadian Drinking Water Quality Guideline Technical Document Chlorine. ON, Ottawa; 2009.

37. Rothman LS, Gordon IE, Babikov Y, et al. The HITRAN2012 molecular spectroscopic database. *J Quant Spectrosc Radiat Transf.* 2013;130:4-50.
38. Crosson ERA. Cavity ring-down analyzer for measuring atmospheric levels of methane, carbon dioxide, and water vapor. *Appl Phys B Lasers Opt.* 2008;92:403-408.
39. Picarro. *Picarro G2108 HCl CRDS Analyzer*; Santa Clara, CA, 2016.
40. Isaacs K, Burke J, Smith L, Williams R. Identifying housing and meteorological conditions influencing residential air exchange rates in the DEARS and RIOPA studies: Development of distributions for human exposure modeling. *J Expo Sci Environ Epidemiol.* 2013;23:248-258.
41. Chan WR, Nazaroff WW, Price PN, Sohn MD, Gadgil AJ. Analyzing a database of residential air leakage in the United States. *Atmos Environ.* 2005;39:3445-3455.
42. Kowal SF, Allen SR, Kahan TF. Wavelength-resolved photon fluxes of indoor light sources: implications for HOx production. *Environ Sci Technol.* 2017;51:10423-10430.
43. Maric D, Burrows JP, Meller R, Moortgat GK. A study of the UV-visible chlorine absorption spectrum of molecular. *J Photochem Photobiol A Chem.* 1993;70:205-214.
44. Barnes RJ, Sinha A, Michelson HA. Assessing the contribution of the lowest triplet state to the near-UV absorption spectrum of HOCl. *J Phys Chem A.* 1998;102:8855-8859.
45. Ghosh B, Papanastasiou DK, Talukdar RK, Roberts JM, Burkholder JB. Nitryl chloride (ClNO₂): UV/vis absorption spectrum between 210 and 296 K and O(3P) quantum yield at 193 and 248 nm. *J Phys Chem A.* 2012;116:5796-5805.
46. Burkholder JB, Sander SP, Abbatt J, et al. Chemical kinetics and photochemical data for use in atmospheric studies evaluation No.18. JPL Publication 15-10. Jet Propulsion Laboratory, Pasadena, California 2015, pp 1-153.
47. Nelson HH, Johnston HS. Kinetics of the reaction of Cl with ClNO and ClNO₂ and the photochemistry of ClNO₂. *J Phys Chem.* 1981;85:3891-3896.
48. Burkholder JB, Sander SP, Abbatt J, et al. Chemical kinetics and photochemical data for use in atmospheric studies evaluation number 15. JPL Publ 15-10. 2006;California:1-153.
49. Gomez Alvarez E, Amedro D, Afif C, et al. Unexpectedly high indoor hydroxyl radical concentrations associated with nitrous acid. *Proc Natl Acad Sci.* 2013;110:13294-13299.
50. Weschler CJ, Shields HC. Production of the hydroxyl radical in indoor air. *Environ Sci Technol.* 1996;30:3250-3258.
51. Weschler CJ, Nazaroff WW. Growth of organic films on indoor surfaces. *Indoor Air.* 2017;27:1101-1112.
52. Stockwell CE, Yokelson RJ, Kreidenweis SM, et al. Trace gas emissions from combustion of peat, crop residue, domestic biofuels, grasses, and other fuels: configuration and Fourier transform infrared (FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4). *Atmos Chem Phys.* 2014;14:9727-9754.
53. Souci S, Fachmann W, Kraut H. *Food Composition and Nutrition Tables, Die Zusammensetzung der Lebensmittel - Nährwert-Tabellen, La composition des aliments - Tableaux des valeurs nutritives*, 3rd edn. Stuttgart, Germany: Wissenschaftliche Verlagsgesellschaft; 1989.
54. Schnabl H, Raschke K. Potassium chloride as stomatal osmoticum in *Allium cepa* L., a species devoid of starch in guard cells. *Plant Physiol* 1980;65:88-93.
55. Heckman JR. Chlorine. In: Barker AV, Pilbeam, DJ, eds. *Handbook of Plant Nutrition*. Boca Raton, FL: CRC/Taylor & Francis; 2007; 279-288.
56. Dasgupta PK, Campbell SW, Al-Horr RS, et al. Conversion of sea salt aerosol to NaNO₃ and the production of HCl: analysis of temporal behavior of aerosol chloride/nitrate and gaseous HCl/HNO₃ concentrations with AIM. *Atmos Environ.* 2007;41:4242-4257.
57. Roberts JM, Veres P, Warneke C, et al. Measurement of HONO, HNCO, and other inorganic acids by negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS): application to biomass burning emissions. *Atmos Meas Tech.* 2010;3:981-990.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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