

## Formation and emission of hydrogen chloride in indoor air

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**This is the peer reviewed version of the following article:**

Dawe, K.E.R., Furlani, T.C., Kowal, S.F., Kahan, T.F., VandenBoer, T.C., Young, C.J. 2019 Formation and emission of hydrogen chloride in indoor air. *Indoor Air* 29:70-78, doi:10.1111/ina.12509,

which has been published in final form at <https://onlinelibrary.wiley.com/doi/10.1111/ina.12509>.

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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: (1) floor exposure to bleach, (2) chlorinated and non-chlorinated detergent use in household dishwashers, and (3) 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.

## ***Key Words***

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

## ***Practical Implications***

Despite extensive research in outdoor atmospheres, hydrogen chloride (HCl) has not been well studied indoors. These are the first real-time measurements of indoor HCl. They were made using a portable, quiet, and fast spectrometric instrument that allowed sampling to occur in a

private, occupied dwelling. The use of this instrument allows for HCl source elucidation during typical household activities. Occupants maintained a detailed activity log, which allowed for sources to be determined. We show that activities such as cleaning with bleach, chlorinated dishwasher detergent use and cooking lead to increased HCl levels, with implications for potential oxidation chemistry in the indoor air environment.

### ***Introduction***

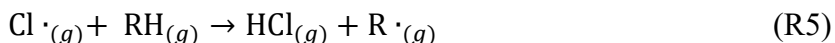
Resulting from direct emission and secondary production, HCl has been known to be present in the atmosphere at detectable levels for the past several decades.<sup>1-15</sup> Processes such as volcanic eruptions, biomass burning, coal combustion and waste incineration emit HCl directly.<sup>7,15</sup> Secondary formation of HCl is facilitated by reactions on chloride-containing aerosols.<sup>2,15,16</sup> Although the subject of numerous atmospheric measurements and modelling 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.<sup>17</sup> Like other strong acids, HCl exposure causes irritation of respiratory tract, eyes, and skin.<sup>17</sup> While these effects occur when HCl levels reach 5 parts per million by volume (ppmv), the impact of chronic exposure to low-level HCl (i.e. parts per billion to parts per trillion by volume) is not known. In addition, strong acids such as HCl can corrode metals such as those in electronic devices<sup>18</sup> and damage works of art.<sup>19</sup>

The lifetime of trace atmospheric pollutants is governed by oxidative chemistry in the troposphere.<sup>20,21</sup> Principal tropospheric oxidants include hydroxyl radicals and chlorine atoms.<sup>20</sup> Recent work has shown that chlorine atoms oxidize volatile organic compounds (VOCs) and produce ozone more efficiently than hydroxyl radicals, even in small quantities.<sup>22</sup> Chlorine atoms

also contribute to destruction of polar boundary layer ozone via a halogen catalyzed ozone destruction cycle.<sup>23</sup> 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.<sup>24</sup> 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).<sup>2,21,25–28</sup>



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



where  $RH$  represents any VOC.<sup>2,15</sup> Due to the large relative abundance of reactants in polluted coastal regions, the reaction proceeds with ease.<sup>14</sup> 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 al.<sup>29</sup> 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, demonstrates 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 has been studied extensively.<sup>30-34</sup> The most commonly studied DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs), can enter indoor air via washing machines, showers, dishwashers and taps.<sup>29,30</sup> 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 province, many communities have elevated chlorine levels, which sometimes can exceed the national average tenfold.<sup>35,36</sup> 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: 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.

## ***Methods***

### *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  $5739.2625\text{ cm}^{-1}$ .<sup>37</sup> The Picarro analyzer contains a heated ( $70.000 \pm 0.005\text{ }^{\circ}\text{C}$ ), low-pressure ( $0.1842 \pm 0.0002\text{ atm}$ ) high finesse optical cavity, which has three high reflectivity mirrors, two flat and one curved.<sup>38</sup> The total reflectance capability is the magnitude of signal loss in the empty optical cavity, which is less than 50 ppm for this design, leads to a limit of detection of 84 parts-per-trillion by volume (pptv) measured over 5 min in zero air at 0% relative humidity (RH). Under the same conditions, the precision ( $1\ \sigma$ ) of the instrument was determined to be  $\pm 24$  pptv in 5 min. The HCl CRDS is an ideal instrument for sampling indoors because it is portable (31.75 kg), quiet (40 dB), does not require consumables (e.g. compressed gas cylinders) nor frequent calibration.<sup>39</sup>

### *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  $\frac{1}{4}$ " perfluoroalkoxy (PFA) tubing, was directed towards the stovetop and parallel to the floor and had a 75 ms residence time. Air was sampled at a rate of 2 SLPM. Submicron pre-filter and back-up 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 mM KOH) and analyzing the extract by ion chromatography coupled to conductivity detection, the permeation tube output was determined as  $140 \pm 18 \text{ ng min}^{-1}$  ( $n = 3$ ). 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 s. The room in which the measurements were made had a volume of approximately  $71 \text{ m}^3$  within a 1.5 story  $220 \text{ m}^2$  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  $0.1 \text{ h}^{-1}$  (see Section S2 in the SI).<sup>40,41</sup> Background measurements of HCl were taken during a 12-hour period prior to bleach cleaning and cooking experiments. Ambient levels ranged from 0.21 – 0.31 ppbv and remained relatively constant despite changes in solar radiation and temperature (Figure S1).

### *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  $12 \text{ m}^2$  section of 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.

### *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, organo-chlorine, bleach, and non-chlorinated 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.

### *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.

### *Cl Production Rate Constant Calculations*

Measurements of wavelength-resolved photon fluxes for common indoor light sources were made by Kowal and Kahan.<sup>42</sup> Measured photon fluxes were used to calculate photolysis rate constants ( $J$ ) for chlorine atom precursors  $\text{Cl}_2$ ,  $\text{HOCl}$ , and  $\text{ClNO}_2$  using

$$J = \int_{\lambda_i}^{\lambda_f} \sigma(\lambda)\varphi(\lambda)F_{\lambda} d\lambda$$

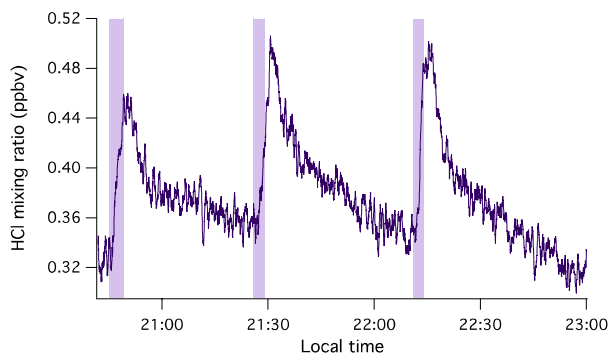


where  $\lambda$ ,  $\sigma$ ,  $\phi$  represent the wavelength, absorption cross-section of the molecule, and photolysis quantum yield, respectively. Absorption cross sections were taken from Maric et al.<sup>43</sup> ( $\text{Cl}_2$ ), Barnes et al.<sup>44</sup> ( $\text{HOCl}$ ), and Ghosh et al.<sup>45</sup> ( $\text{ClNO}_2$ ). Quantum yields of 1 were used for  $\text{Cl}_2$  and  $\text{HOCl}$ ,<sup>46</sup> while a quantum yield of 0.93 was used for  $\text{ClNO}_2$ .<sup>47</sup> Radical ( $\text{OH}$  or  $\text{Cl}$ ) production rates were calculated as the product of the photolysis rate constant and the expected concentration of the precursor following bleaching events.

## ***Results/Discussion***

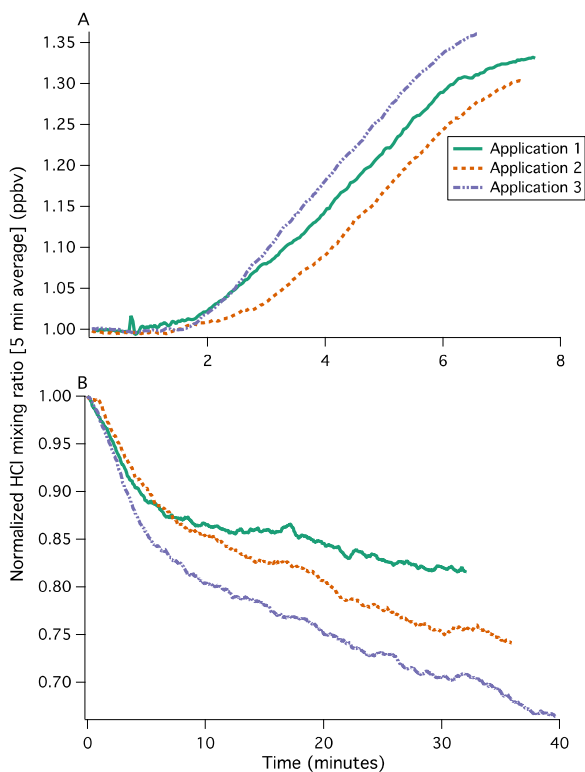
### *Cleaning Experiments*

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



**Figure 1.** HCl mixing ratios measured during three sequential bleach applications. Measurements are presented as the 30-second average of the HCl mixing ratio in parts-per-billion by volume (ppbv). Bleaching applications spanning  $3 \pm 1$  minute periods are represented by the shaded regions, and the HCl mixing ratio by the solid line.

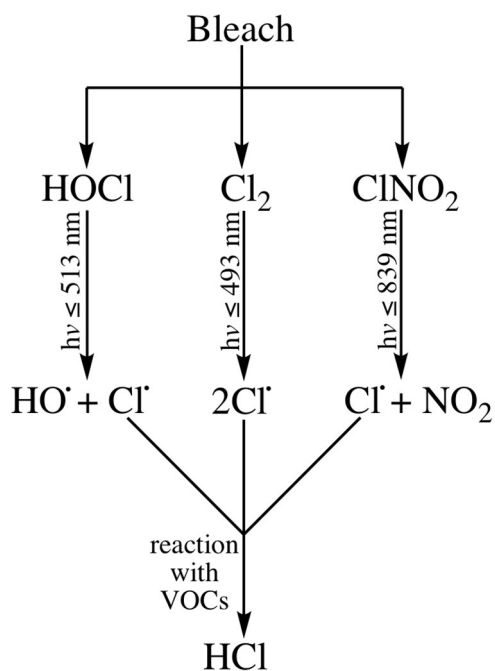
All bleach applications showed similar changes in HCl mixing ratios above the background, indicating that the magnitude of the emission is reproducible. With each application, an initial spike of approximately 0.1 ppbv occurred and was followed by a slower decay (Figure 2).



**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-minute average HCl mixing ratio in parts-per-billion by volume (ppbv).

Prior to bleach application, mixing ratios ranged from 0.32-0.36 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. Both figures 2A and B show 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 Cl<sub>2</sub> reported by Wong et al.<sup>29</sup> From this 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 study<sup>29</sup> has shown that HOCl, Cl<sub>2</sub> and ClNO<sub>2</sub> are released

during floor mopping with bleach. All three are known to photolyze under ambient outdoor light to produce Cl atoms (e.g. <sup>22,24,27</sup>) which react with VOCs to form HCl (Figure 3).<sup>29,48</sup>



**Figure 3.** Proposed reaction pathway for indirect formation of HCl via photolysis of HOCl, Cl<sub>2</sub>, and ClNO<sub>2</sub> emitted from bleach use.

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.<sup>42</sup> Under these light conditions, photolysis reactions shown in Figure 3 could proceed. Calculated Cl photolysis production rates under illumination by various light sources at Cl<sub>2</sub> and HOCl mixing ratios reported after the use of bleach (20 ppbv and 200 ppbv), and at an estimated ClNO<sub>2</sub> mixing ratio of 1 ppbv are shown in Table 1 and Table S4.<sup>29,42</sup> 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 Cl<sub>2</sub> photolysis at rates on the order of  $0.1 - 1.2 \times 10^8 \text{ molec cm}^{-3} \text{ s}^{-1}$  under illumination by

the LED, halogen-tungsten, and covered fluorescent tubes used in the residence, while formation rates from HOCl photolysis will range from  $0.2 - 5.9 \times 10^7$  molec  $\text{cm}^{-3} \text{s}^{-1}$  under the same illumination conditions. Production rates of Cl from ClNO<sub>2</sub> photolysis will not exceed  $3 \times 10^5$  molec  $\text{cm}^{-3} \text{s}^{-1}$  under these conditions. However, it should be reiterated that ClNO<sub>2</sub> mixing ratios after the use of bleach have not been quantified.<sup>29</sup> 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  $0.5 - 2.6 \times 10^6$  molec  $\text{cm}^{-3} \text{s}^{-1}$  for Cl<sub>2</sub>,  $0.3 - 13 \times 10^5$  molec  $\text{cm}^{-3} \text{s}^{-1}$  for HOCl, and  $0.2 - 6.5 \times 10^3$  molec  $\text{cm}^{-3} \text{s}^{-1}$  for ClNO<sub>2</sub>. 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  $10^7$  molec  $\text{cm}^{-3} \text{s}^{-1}$  in residences.<sup>42,49,50</sup> 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  $\sim 1.2 \times 10^7$  molec  $\text{cm}^{-3} \text{s}^{-1}$ . 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 Cl<sub>2</sub> 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; however, this would be necessary to determine the source of the HCl with a high degree of certainty.

**Table 1.** Calculated Cl production rates for light sources in this study for 20 ppbv Cl<sub>2</sub>, 200 ppbv HOCl, and 1 ppbv ClNO<sub>2</sub> at 1 m from the light source. Mixing ratios were based on measurements from Wong et al.<sup>27</sup>

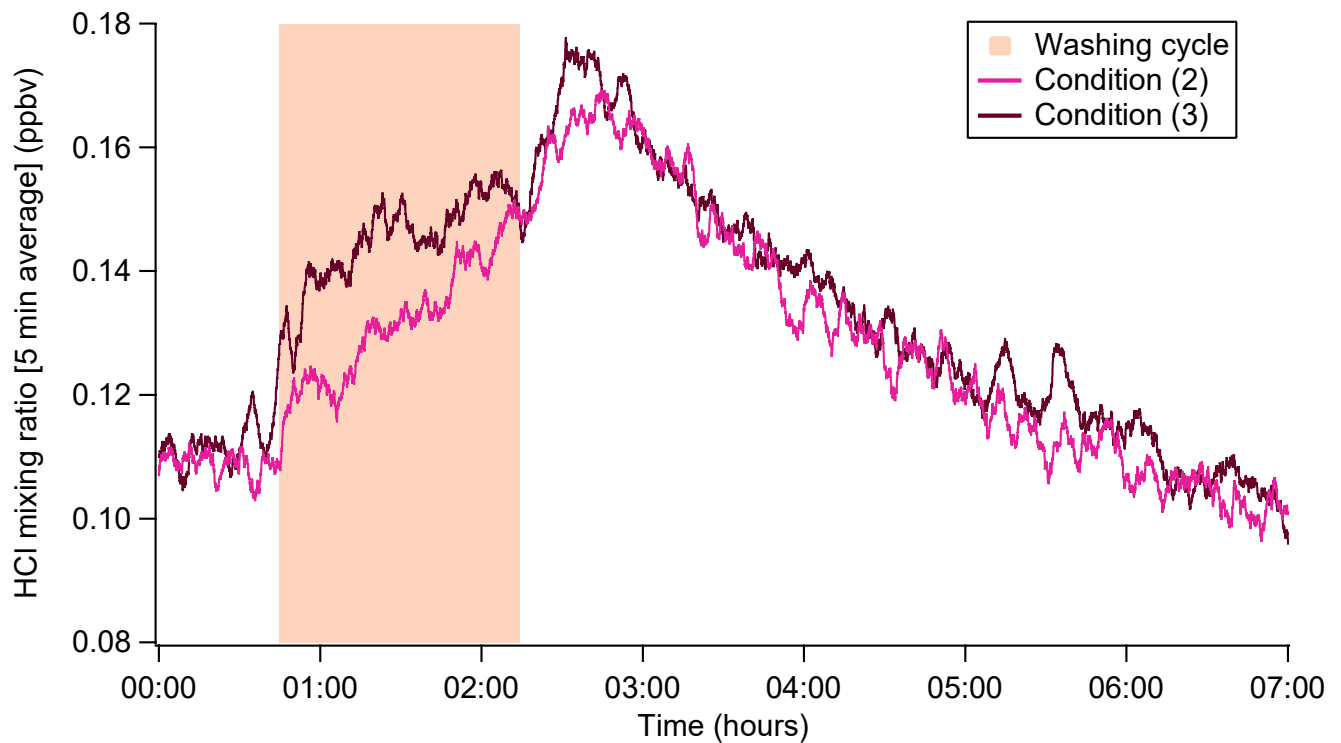
Light source	Cl Production Rate (molecules cm <sup>-3</sup> s <sup>-1</sup> )		
	Cl <sub>2</sub>	HOCl	ClNO <sub>2</sub>
LED	$4.62 \times 10^5$	$3.26 \times 10^4$	$2.17 \times 10^2$
Halogen	$2.56 \times 10^6$	$1.30 \times 10^6$	$6.50 \times 10^3$
Office fluorescent (covered)	$1.45 \times 10^6$	$4.26 \times 10^5$	$1.20 \times 10^3$

The bimodal decay observed in Figure 2B is likely attributed to HCl deposition to surfaces, and environmental factors (e.g. temperature and air-exchange rate). Weschler and Nazaroff have recently shown that initially, some semi-volatile organic compounds adsorb to surfaces indoors.<sup>51</sup> 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 (e.g. Crisp et al.<sup>15</sup>), 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 ( $\sim 0.1 \text{ h}^{-1}$ ).<sup>40,41</sup>

### *Dishwashing Experiments*

Previous studies have shown that dishwashers emit compounds including chlorinated organics, which are released when chlorinated dishwashing detergents are used.<sup>31</sup> Emissions from the experimental dishwasher were monitored during four different conditions: (1) no detergent; (2) powdered organo-chlorine detergent; (3) liquid bleach detergent; and (4) non-chlorinated

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.<sup>35,36</sup> 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).



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

Both organo-chlorine 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 (e.g. temperature) between conditions.

**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	Organo-chlorine	190	22	33
2	Organo-chlorine	130	23	50
3	Bleach	110	40	59
3	Bleach	100	50	65
4	Non-chlorinated	180	0	-9.8
		Average increase (2)	22	41
		Average increase (3)	45	62

When chlorinated detergents are used, the HCl mixing ratio increases 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 to 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

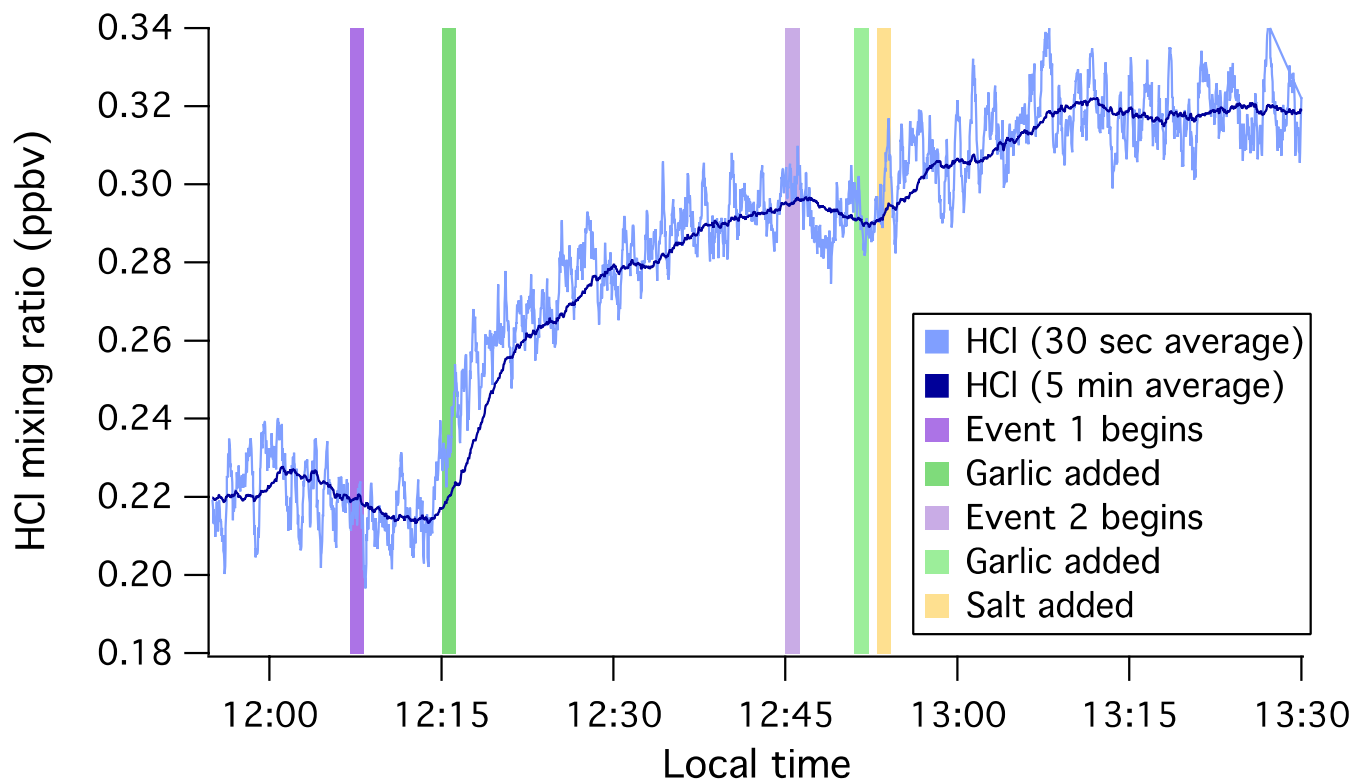
increase as a result of dishwashing using chlorinated detergents was approximately twenty times less than from surface bleach application. There is currently no information regarding emissions of photolabile chlorine species (e.g.  $\text{Cl}_2$ ) from dishwashers. If reactive chlorine species are being 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.<sup>41</sup> 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 has an impact on emissions depending on type, storage method, and age.<sup>31</sup> 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.

### *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.<sup>52</sup> An example of cooking, showing two events, is presented in Figure 5.





**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-second and 5-minute averages in ppbv.

Cooking event 1 began by adding onions to a pan containing pre-heated 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 min 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.

Similar to observations of burning vegetation that have experienced sea salt deposition<sup>52</sup>, 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 2. 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.<sup>53,54</sup> On a cellular level chloride is required for stomatal opening when guard cells cannot synthesize malate.<sup>54,55</sup> Levels of chloride depend on species, but also on the location and conditions under which the food was grown.<sup>52,53</sup> For example, food cultivated in close proximity to the ocean may have enhanced chlorine levels because of sea salt deposition and uptake.<sup>52</sup> Onions and garlic, which belong to the same family (allium) as shallots, have been shown to contain chloride.<sup>53,54</sup> 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.

#### *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 back-up filter and a vacuum pump.<sup>4-6,9,56</sup> 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.<sup>52</sup> This requirement is satisfied when high time-response measurements of HCl are acquired with chemical ionization mass spectrometry (CIMS).<sup>15,57</sup> While useful for outdoor measurements,

CIMS is not ideal for use in private dwellings. It has a large footprint, substantial power draw, several vacuum pumps, and most require a radioactive ionization source.<sup>57</sup> 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.

### ***Conclusions***

Daily household activities were investigated to determine their contribution to indoor HCl emissions. Measurements were made using an in situ, non-invasive, fast time-response CRDS instrument. These represent the first fast-time response measurements of HCl in an indoor, non-occupational 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 non-chlorinated detergents have no impact. Additionally, the dishwasher drying cycle has a noteworthy impact on already-elevated HCl mixing ratios. Photolysis of photolabile chlorine species (e.g. Cl<sub>2</sub>), 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.

### *Acknowledgements*

We thank the Natural Science and Engineering Research Council of Canada, Memorial University, and Syracuse University for funding.

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