FORMATION AND EMISSION OF REACTIVE CHLORINE IN INDOOR AIR

by

© Kathryn E. R. Dawe

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Abstract

Chlorine atoms are powerful atmospheric oxidants known to degrade air quality. Despite much focus, a direct measurement technique does not exist. Instead, chlorine atom precursors are used as proxies to study chlorine atom chemistry. Reactions of precursors resulting in chlorine atoms studied in outdoor environments are also possible indoors. Daily household activities, especially those involving chlorinated cleaning products, are suspected to contribute to indoor chlorine atom chemistry. Indoor air studies are hindered by sampling techniques, as few appropriate instruments exist. A common atmospheric measurement technique was evaluated while monitoring gas and particulate phase species emitted during indoor bleach use. This instrument collects a non-selective gaseous and a particulate chloride sample. Recent advances in indoor instrumentation allow for selective measurement of chlorine atom precursor, hydrogen chloride (HCl), using a cavity-ring down spectroscopy instrument. Present ubiquitously outdoors, atmospheric HCl is a result of direct emission and secondary production. Previous measurements of HCl indoors are rare and have been limited to non-residential buildings using integrated sampling. This sampling strategy does not provide the source of HCl emissions. In order to better understand sources of HCl indoors, real-time gas-phase mixing ratios of HCl during typical household activities were monitored such as floor exposure to bleach, detergent use in household dishwashers, and cooking events. Based on calculated rates of chlorine atom precursors, both photolysis and direct emission could be contributing to elevated HCl levels indoors. This work presents insights regarding HCl production and the influence of household activities on indoor air quality.

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List of Abbreviations, Nomenclature and Symbols

°	degrees
°C	degrees Celcius
^{31}P	phosphorous-31
ADS	annular denuder system
CH_4	methane
CIMS	chemical ionization mass spectrometry
Cl^-	chloride
Cl_2	molecular chlorine
$ClNO_2$	nitryl chloride
cm^{-1}	wavenumbers
CRDS	cavity ring-down spectroscopy
D_2O	deuterium oxide
DBPs	disinfection byproducts
DFS	denuder-filter system
DOM	dissolved organic matter
EPA	Environmental Protection Agency
g	gram
HAAs	haloacetic acids
HCl	hydrogen chloride
HDPE	high-density polyethylene
HNO_3	nitric acid
HOCl	hypochlorous acid
HONO	nitrous acid
IC	ion chromatography
kg	kilogram
KOH	potassium hydroxide
mA	milliamps
MBL	marine boundary layer
MCHAMAAR	Multichannel Atmospheric Medium Volume Assay for Aerosol Research
MFC	mass flow controller
mg L^{-1}	milligrams per liter
MHz	megaHertz
mL	milliliter
mL min^{-1}	milliters per minute
mm	millimeter
mM	millimolar
N_2	nitrogen
N_2O_5	dinitrogen pentoxide

Na_2CO_3	sodium carbonate
NaCl	sodium chloride
NH_3	ammonia
NMHCs	non-methane hydrocarbons
NMR	nuclear magnetic resonance
NO_2	nitrogen dioxide
NO_3	nitrate radical
NOM	natural organic matter
NOPL	naso-oro-pharyngo-laryngeal
O_3	ozone
OCl^-	hypochlorite
•OH	hydroxyl radical
PBL	planetary boundary layer
pCl	particulate chlorine
PEEK	polyether ether ketone
PFA	perfluoroalkoxy
PM_{10}	aerosol diameter <10 μm
$PM_{2.5}$	aerosol diameter <2.5 μm
ppbv	parts per billion by volume
ppmv	parts per million by volume
ppqv	parts per quadrillion by volume
pptv	parts per trillion by volume
PTFE	polytetrafluoroethylene
SLPM	standard liters per minute
SO_2	sulfur dioxide
h^{-1}	times per hour
TB	tracheobronchial
THMs	trihalomethanes
VOCs	volatile organic compounds
μg	microgram
μg m^{-3}	micrograms per meter cubed
UHP	ultra-high purity
μL	microliter
μm	microns

List of Appendices

Co-authorship Statement

This thesis is comprised of one manuscript that is in preparation for submission to be published in a peer-reviewed scientific journal, and one complementary manuscipt. It should be noted that Chapter 1 comprises the introduction to this thesis, while Chapter 2 is comprised of methodologies in Chapters 3 and 4. All chapters were written by Kathryn E. R. Dawe with critical comments by Cora J. Young, and editorial comments by Chris Rowley and Michael Katz. The contributions of co-authors are detailed below:

Chapter 1 – Introduction □

Contributions – Prepared by Kathryn E. R. Dawe with editorial comments provided by Cora J. Young.

Chapter 2 – Methodology□

Contributions - Prepared by Kathryn E. R. Dawe with editorial comments provided by Cora J. Young. Kathryn E. R. Dawe conducted offline sampling and shipped sample extracts to Toronto, ON where Cora J. Young and Trevor C. VandenBoer performed ion chromatography analysis at the University of Toronto. Online sampling was performed by Cora J. Young, Trevor C. VandenBoer and Teles C. Furlani. Data interpretation was performed by all those involved in sampling. NMR analysis was performed by Kathryn E. R. Dawe with assistance from Michael J. Katz and Mason C. Lawrence.

Chapter 3 – Formation and emission of hydrogen chloride in indoor air

Author List – Kathryn E. R. Dawe, Teles C. Furlani, Shawn F. Kowal, Tara F. Kahan, Trevor C. VandenBoer, and Cora J. Young.

Contributions – See Chapter 2: Methodology Contributions for above Author List. Data analysis was performed by Kathryn E. R. Dawe, with critical contributions from Cora J. Young. Shawn F. Kowal and Tara F. Kahan calculated and tabulated photochemical rate constants for Cl production. Data interpretation and manuscript preparation was completed by Kathryn E. R. Dawe with critical comments provided by Cora J. Young, Trevor C. VandenBoer, Teles C. Furlani, Shawn F. Kowal and Tara F. Kahan.

Chapter 4 – Measurement of reactive chlorine emissions in indoor air

Contributions – See Chapter 2: Methodology Contributions for analysis assistance. Data interpretation and manuscript preparation was performed by Kathryn E. R. Dawe with critical comments provided by Cora J. Young.

1 Introduction

1.1 *Introduction to Atmospheric Chemistry*

1.1.1 Atmospheric Composition

The Earth's atmosphere is comprised of four main layers that vary in temperature with altitude. Due to the temperature variance, mixing between layers does not occur as readily as intra-layer mixing.[1] These four layers can be further subdivided into the upper and lower atmosphere, where the lower atmosphere is comprised of the troposphere and stratosphere, and the upper atmosphere is composed of the thermosphere and mesosphere (Figure 1-1).

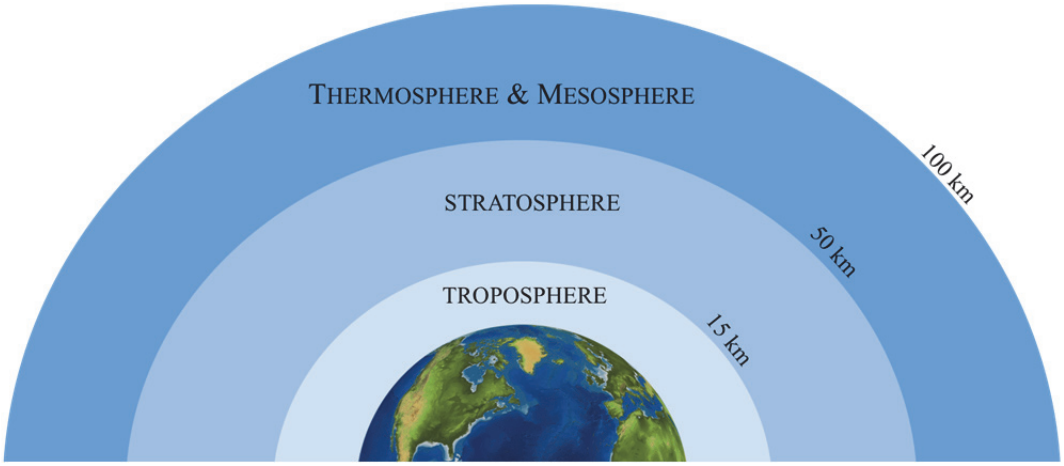

Figure 1-1. Atmospheric structure based on altitude.

Since the bulk of the atmosphere is contained in the lower portion, it has received far more attention from atmospheric scientists than the upper atmosphere. It is essential to highlight a key region located in the troposphere. The planetary boundary layer (PBL) spans 5 vertical km above sea level and is the first point of contact between the atmosphere and emission sources.[2] This region is more complex than the rest of the troposphere due to temperature and topography variations at the Earth's surface. Over time, emissions in the PBL will mix into the troposphere and have the potential to undergo long-range transport.

In general, it is challenging to understand the chemistry of the lower atmosphere, as it requires acknowledgement of contributions of atmospheric, marine and terrestrial sources to chemical, physical and biological processes.[2] The reactions involved in these processes can be divided into two main groups: heterogeneous and homogeneous. Homogeneous reactions occur when species of the same phase interact, whereas heterogeneous reactions involve species of at least two different phases. In the atmosphere, these phases mainly include gases and suspended particulate matter.[3] Since nitrogen and oxygen account for 99% of atmospheric volume, species in the remaining 1% are considered trace gases. Atmospheric gases in the troposphere absorb infrared radiation, which contributes to air quality degradation. These trace gases can be emitted from a variety of anthropogenic and biogenic sources, which complicates identification and constraint. Sources of well-known trace gases such as nitrogen dioxide (NO_2) and ozone (O_3) have been identified, which allowed for agencies such as the World Health Organization (WHO) to adopt air quality standards for such gases.[1] Atmospheric gases are described using mixing ratios, defined by the number of moles of a particular gas in one mole of air and are represented in units of parts-per-million, billion, trillion or quadrillion by volume (ppmv, ppbv, pptv, ppqv).[3] This measurement system is widely used, thus air quality standards are reported in units of ppmv. An important facet of air quality monitoring is the impact on human health. Atmospheric trace gases not only facilitate smog production, but can also cause acute health effects such as cardiovascular and respiratory tract diseases.[4] Other trace atmospheric components, referred to as suspended particulate matter, contribute to reduced air quality and hence hindered human health.

Suspended particulate matter, otherwise known as aerosols, can be solid, liquid, or a combination of both.[5] Aerosols are emitted directly by primary sources and can be formed in the atmosphere via secondary processes. Primary emissions can be anthropogenic or biogenic in nature, and include sources such as volcanic eruptions, ocean wave action and coal combustion. Secondary processes include gas-particle interactions, and evaporation and condensation of aerosols. Collection is commonly performed using impaction and filtration, where aerosols are separated based on their aerodynamic diameter. Traditional sampling techniques separate samples into two size bins – coarse and fine mode. Coarse mode particles include particles with diameters between 2.5 and 10 microns (μm), and are injected directly into the atmosphere via processes such as volcanic eruptions and ocean wave breaking. Fine mode particles include particles with diameters less than 2.5 μm. Typical cut-off points for this size range are instrument-dependent. Fine mode particles are also referred to as accumulation mode particles, which range from 0.1 to 2.5 μm. Said particles are generated via secondary processes including fossil fuel combustion and photolysis reactions. Additionally, Aitken mode particles (< 0.1 μm) fall into the accumulation mode after rapid coagulation. For simplicity, coarse and fine mode particles are classified as PM_{10} and $PM_{2.5}$, respectively (Figure 1-2).[5]

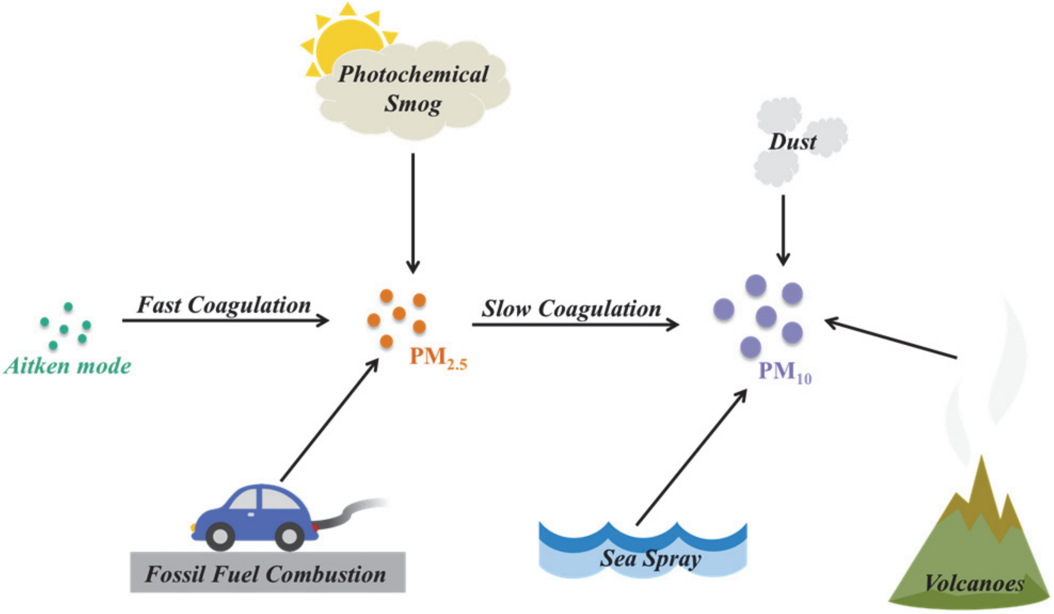

Figure 1-2. Principal emission sources of fine and coarse mode aerosols

In terms of atmospheric lifetimes, coarse particles exist on the span of days, whereas fine mode particles can exist for weeks. The longer lifetime of fine mode particles allows for long-range transport. Fine mode particles are able to travel far (on the order of kilometers) from the source but coarse mode particles only affect local air quality.

Since aerosols are composed of more than one phase, concentrations cannot be expressed using mixing ratios.[5] Instead, ambient aerosol concentrations are reported as number, size or mass distributions. Concentrations are most often reported in mass distributions, or loadings, in units of mass per volume. From an environmental standpoint, aerosols are responsible for absorbing and scattering light, which contributes to the greenhouse effect and reduces visibility, respectively. In addition to this, aerosols contribute to the production of secondary pollutants, as their surfaces act as a reaction sites for atmospheric gases. Similar to gases, constant exposure to suspended particulate matter leads to serious health problems, and has been shown to increase mortality rates in certain regions.[6] Exposure to aerosols is constant, as sources are continuously emitting into the regions where humans live and breathe. The aerodynamic diameter can be used to determine how far aerosols can travel through the respiratory tract. Since the tract is relatively small, aerosols can travel long distances within it before settling occurs. It is important to note that, in this case, health effects are associated with inhalation of fine mode particles through the nose and mouth. Health effects caused by coarse particles are considered negligible, as they are removed in the upper region of the respiratory tract. The regions of the respiratory system affected by fine mode aerosol deposition can be divided into three regions: naso-oro-pharyngo-laryngeal (NOPL), tracheobronchial (TB) and (3) pulmonary regions. Important structures in each region include the nose and mouth (NOPL), the trachea and bronchi (TB), and alveolar ducts and sacks (pulmonary).[7] Adverse human health effects, along with environmental impacts motivate studies in the field of atmospheric chemistry. Such studies include those involving particular processes such as atmospheric oxidation. The analysis of gases and aerosols is an important metric to study oxidation chemistry of the atmosphere, as these species act as sources, reservoirs and sinks for primary atmospheric oxidants.

1.1.2 Atmospheric Oxidation

The oxidative capacity of the atmosphere is governed by radical chemistry. While considered dominant atmospheric oxidants, hydroxyl radicals (·OH) are only present in trace quantities.[8,9] It should be noted that other species such as chlorine atoms and nitrate radicals contribute to atmospheric oxidation. Due to the high reactivity of hydroxyl radicals, measured mixing ratios are unable to depict the importance of this oxidant.

Lifetimes of hydroxyl radicals range from 0.01 to 1 second, which indicates that they are consumed almost immediately after production.[9] Major production pathways of hydroxyl radicals are photolysis of O_3, nitrous acid (HONO) and aldehydes.[1,10] Production of hydroxyl radicals occurs primarily during daytime, as the dominant photolysis production pathways require sunlight to proceed. Because of this, hydroxyl radical reservoirs such as HONO build up from dusk to dawn and hydroxyl radical production peaks mid-day when the sun is at its peak, resulting in a diurnal cycle.[10] While these reactions proceed in both urban and rural areas, it is important to note that air quality degradation such as smog formation is more pronounced in polluted regions. Once produced, hydroxyl radicals readily abstract hydrogen atoms from volatile organic compounds (VOCs) to form further radical species (R1-1):

$$RH_{(g)} + \cdot OH_{(g)} \rightarrow R\cdot_{(g)} + H_2O_{(g)} \qquad \text{(R1-1)}$$

where RH is any VOC. Sources of VOCs are anthropogenic and biogenic, such as fossil fuel combustion or canopy foliage, respectively, and are not well-constrained.[1] The global ubiquity of atmospheric VOCs allows for reactions of this nature to proceed routinely. However, the rate of hydrogen abstraction of VOCs is increased by at least one order of magnitude when the hydroxyl radicals are replaced with chlorine atoms (R1-2).[10–12]

$$RH_{(g)} + Cl\cdot_{(g)} \rightarrow R\cdot_{(g)} + HCl_{(g)} \qquad \text{(R1-2)}$$

The presence of chlorine atoms was originally limited to marine regions, as it was considered a product of heterogeneous reactions involving sea salt aerosols.[10,11,13] As a result, chlorine atom concentrations were not evaluated in inland regions for an extended period of time. Recent studies have demonstrated that anthropogenic emissions also contribute to chlorine atom levels.[11,12,14] These findings indicate that atmospheric chlorine chemistry may have a more significant impact than originally estimated and thus requires more in-depth examination.

1.2 Atmospheric Chlorine Chemistry

1.2.1 Motivations for Monitoring Chlorine Chemistry

Chlorine chemistry plays important roles in both regions of the lower atmosphere. In the stratosphere, chlorine atoms are responsible for ozone destruction, which contribute to ozone layer depletion (R1-3 & R1-4).[15,16]

$$Cl_{(g)} + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)} \qquad \text{(R1-3)}$$

$$ClO_{(g)} + O_{(g)} \rightarrow Cl_{(g)} + O_{2(g)} \qquad \text{(R1-4)}$$

The net reaction demonstrates ozone destruction pathway (R1-5).

$$O_{(g)} + O_{3(g)} \rightarrow 2O_{2(g)} \qquad \text{(R1-5)}$$

Chlorine atom chemistry in this case has been well studied and is widely understood. Sources have been identified and constrained, and reaction pathways are known. In the troposphere, however, chlorine atom chemistry is more complicated as sources and sinks are more plentiful. While much is still unknown about chlorine atom chemistry in the troposphere, it is understood that chlorine atoms destroy[17,18] and produce[11,19] ozone in this region. Ozone destruction in the troposphere is considered a minor loss process and only important under very specific scenarios. A common misconception is that ozone production in the troposphere benefits the atmosphere via reconstruction of the ozone hole, but this is not the case. Elevated ozone mixing ratios result in increased production of hydroxyl radicals, which has the potential to harm human health, degrade air quality and contribute to photochemical smog production.[20] Additionally, chlorine atoms have the potential to control the lifetime of methane (CH_4), a dominant greenhouse gas, as well as non-methane hydrocarbons (NMHCs) with faster reaction rates than hydroxyl radicals.[21] Since chlorine atoms are more reactive oxidants on a per-radical basis than hydroxyl radicals, it is important to improve understanding of chlorine atom chemistry.

1.2.2 Sampling Challenges of Chlorine Atoms

The elevated reactivity and hence short lifetime of chlorine atoms does not allow for direct measurement.[14] At this point in time, a direct measurement technique does not exist. However, the reactivity has been instrumental in the development of indirect measurement techniques. While chlorine atoms are consumed rapidly, the products resulting from these reactions have much longer lifetimes. Because of this, chlorine atom precursors are used as proxies to study chlorine chemistry in the troposphere. Such precursors include molecular chlorine (Cl_2), hypochlorous acid (HOCl), nitryl chloride ($ClNO_2$), and hydrogen chloride (HCl) (R1-6 – R1-9).[22–27]

$$Cl_{2(g)} + h\nu \rightarrow Cl\cdot_{(g)} + Cl\cdot_{(g)} \qquad \text{(R1-6)}$$

$$HOCl_{(g)} + h\nu \rightarrow Cl_{(g)}\cdot + HO\cdot_{(g)} \qquad \text{(R1-7)}$$

$$ClNO_{2(g)} + h\nu \rightarrow Cl\cdot_{(g)} + NO_{2(g)} \qquad \text{(R1-8)}$$

$$HCl_{(g)} + HO\cdot_{(g)} \rightarrow Cl\cdot_{(g)} + H_2O_{(g)} \qquad \text{(R1-9)}$$

Chlorine atom generation is facilitated by photolysis (R6-8) and oxidation by hydroxyl radicals (R9). Both types of reactions typically occur during sunlight hours. For photolysis reactions, precursors build up in the night time, and photolyze when the sun rises. Similarly, hydroxyl radicals are injected to the atmosphere by photolysis of precursors, thus oxidation reactions adopt the same diurnal cycle as chlorine atom precursor photolysis. In order to advance knowledge of chlorine atom chemistry via precursor compounds, production and loss pathways (also referred to as sources and sinks) must be investigated. It should be noted that an investigation of production pathways must involve accounting for potential atmospheric reservoir species. A broadened understanding of these pathways will allow for better estimation of the oxidative capacity of the atmosphere as it relates to chlorine atom chemistry.

1.2.3 Sources, Sinks & Reservoirs

Chlorine atom precursors are formed from direct emission and secondary formation, where sources can be both biogenic and anthropogenic in nature. Direct emission is facilitated via processes such as volcanoes, biomass burning, waste incineration, coal combustion, and manufacturing, whereas indirect formation occurs via reactions with chloride-containing aerosols.[22,28,29] In order to evaluate known sources, precursor compounds will be discussed individually. Emissions from chemical manufacturing, sewage treatment and paper production result in direct tropospheric emission of Cl_2.[22] Indirect sources include free radical reactions in sea salt aerosols, and heterogeneous reactions such as HOCl on sea salt aerosols (R1-10 & 1-11).[22,25]

$$2Cl^{-}{}_{(aq)} + O_{3(g)} \rightarrow Cl_{2(g)} + 2OH^{-}{}_{(aq)} + O_{2(g)} \qquad \text{(R1-10)}$$

$$HOCl_{(g)} + NaCl_{(s)} \rightarrow Cl_{2(g)} + NaOH_{(s)} \qquad \text{(R1-11)}$$

It should be noted that Cl_2 is produced indirectly by another chlorine atom precursor, HOCl. While this is considered a sink of HOCl, it is still a source of chlorine atoms via Cl_2 photolysis. Because of this, it is often quite difficult to differentiate between sources of Cl_2 and HOCl. These precursor compounds are often designated as Cl_2^*.[22,24] Source elucidation has been hindered as a result of the complex nature of HOCl chemistry and the adoption of the Cl_2^* designation.[14,24] While sources are not well studied; HOCl is a known reservoir species for chlorine atoms.[14,22,30] Reservoirs temporarily sequester chlorine atoms until release is favourable. In this case, reservoirs build up at night and are photolyzed to release chlorine atoms during sunlight hours. Though HOCl is a well-known reservoir, all previously mentioned precursors sequester chlorine atoms, and thus should be designated as reservoirs as well. Nitryl chloride has also been identified as a chlorine atom reservoir.[11] The importance of $ClNO_2$ as a chlorine atom precursor was only discovered in the last decade. Upon photolysis, it releases NO_2, which can degrade air quality. A single, indirect source involving sea salt aerosols (SSA) has been studied extensively.[11,14,27,31,32] In this case, a surface reaction of dinitrogen pentoxide (N_2O_5) on sea salt produces $ClNO_2$ (R1-12).

$$N_2O_{5(s)} + NaCl_{(aq)} \rightarrow ClNO_{2(g)} + HNO_{3(aq)} \qquad \text{(R1-12)}$$

It is important to note that these reactions proceed with ease in the polluted marine boundary layer (MBL), where sea salt and nitrogenous anthropogenic emissions are ubiquitous. Since this source is relatively new, only one source has been identified. Unlike $ClNO_2$, HCl has been studied for the past several decades. While extensively studied, regular measurements of HCl are not performed and hence identified sources are not well constrained.[13,21,39–43,22,28,33–38] Direct sources of HCl include biomass burning, coal combustion, waste incineration and volcanic eruptions.[13,28] Heterogeneous reactions on chloride-containing aerosols result in secondary formation of HCl (R1-13).

$$HNO_{3(g)} + Cl^{-}{}_{(aq)} \rightarrow HCl_{(g)} + NO_{3}{}^{-}{}_{(aq)} \qquad \text{(R1-13)}$$

In comparison to chlorine atom sources, the number of sinks is quite small. Main loss processes include dry and wet deposition.[22] The atmospheric lifetime of HCl by dry and wet deposition ranges from 1.2-1.5 days.[22,28] Dry deposition occurs when suspended matter such as gases and particles begin to settle on a surface. Typical surfaces include foliage and buildings. Water-soluble precursors are easily removed via wet deposition, often referred to as 'washout'. This loss process is especially pronounced in regions where precipitation events occur on a regular basis. Thus the wet deposition lifetime is highly dependent on the frequency of these events.

1.2.4 Hydrogen Chloride as a Chlorine Chemistry Precursor

Of the chlorine atom precursors mentioned, HCl is by far the most studied. The indirect formation of HCl via a heterogeneous reaction with sea salt has made it an ideal proxy for chlorine atom studies in marine environments. Since HCl has been studied extensively, there are a number of established measurement techniques. Such techniques can be separated into two main groups – offline and online. Many traditional atmospheric measurement techniques are considered offline, where a collective sample is taken over a specific time period. The most common offline measurement technique for HCl is the Annular Denuder System (ADS).[35–37,39,44] The main component of the ADS is the annular denuder, a sintered glass rod surrounded by sintered glass tubes coated with a reactive solution to sorb gases. Other components of the ADS include a back-up filter and a vacuum pump. The pump allows for an air sample to be drawn into the ADS via an inlet. Inside the ADS, the reactively coated denuders are used to remove gases from the sample via sorption. The flow is then directed towards the back-up filter, where aerosol impaction occurs. It is important to note that denuders are placed up-stream from the back-up filter to avoid any possible gas-aerosol interactions. These interactions can skew collected mass-loadings by generating false-positive results. Offline techniques provide insight in terms of analyte concentration during the sampling period, but cannot capture characteristics such as atmospheric lifetimes and emission sources of highly reactive species. Because of this, online techniques have become increasingly popular for atmospheric studies.

Online techniques provide measurements in real-time, thus advancing sampling capabilities and atmospheric knowledge. Such techniques include Chemical Ionization Mass Spectrometry (CIMS) and Cavity Ring-Down Spectroscopy (CRDS) instruments.[28,45,46] CIMS instruments provide sensitive and selective measurements of species of interest in the gas and aerosol phase in the presence of interfering species.[47] The sensitivity and selectivity of CIMS is tuneable by the selection of the reagent ion, which allows for ionization of atmospheric pollutants of interest. Briefly, ion production occurs as a result of passing volatilized reagent over a radioactive source. These ions are then available to form adducts with species of interest entering through the inlet and then detected by the mass spectrometer. It is important to note that these instruments are quite large, require consumables in the form of gas cylinders and contain a sealed radioactive source, rendering their transportation logistically difficult. Recent developments in CRDS, on the other hand, have resulted in a more portable instrument. A more in depth discussion of the CRDS will be discussed in Chapter 2. With consistent advances in technology, the use of online techniques is becoming increasingly popular.

1.3 Indoor Chlorine Chemistry

1.3.1 Indoor Air Quality

Much like outdoor environments, indoor air can be degraded by the presence of atmospheric pollutants.[48] Indoor air pollution is invisible, and has thus received far less attention than outdoor air studies. Since humans spend approximately 90% of their lives indoors, focus has shifted towards indoor studies.[49] Compared to outdoor air, it is unknown whether exposure to indoor pollution will result in more adverse health effects.[48] Enhancements made to household insulation in modern homes to increase efficiency may have, in turn, enabled enhanced build-up of indoor emissions. If this is the case, human exposure to indoor pollutants is likely higher than those encountered outdoors. Indoor air pollutants have a vast number of sources and vary on a per-building basis. Typical sources include household dust, pets, chores, building materials, cleaning activities, and occupants.[48,50–54] Sources emit pollutants that include, but are not limited to ozone, water disinfection by-products (DBPs), suspended particulate matter, chlorine atom precursors, and flame retardants. Concentrations of these pollutants are governed by the volume of air in the enclosed space, production rate and rate of removal.[48] Removal in indoor environments occurs via reactions (e.g. photolysis), settling and air exchange rate. It is important to note that air does transfer between outdoor and indoor environments, but in modern homes with adequate insulation and low air exchange rates the extent of transfer is low. The diversity of indoor air quality and the lack of regular sampling hinder the estimation of pollutant exposure to humans indoors.

1.3.2 Sampling Considerations

The lack of regular indoor sampling is a partially a result of inadequate measurement techniques. Numerous atmospheric sampling techniques exist for outdoor environments, but they are not suitable for use indoors.[48] It is important to note that requirements for measurement techniques vary depending on the type of indoor environment. Laboratories, arguably the most accessible type of indoor environment, have far fewer sampling restrictions than private, occupied dwellings. Studies in laboratories proceed with ease, as increased power consumption is not a concern, and any necessary permits are easily obtained. Since laboratories have faster air exchange rates than modern homes, they are not representative for indoor air quality studies. Additionally, it is difficult to mimic conditions and provide insight into household air quality when studies are performed elsewhere. In order to mimic indoor emissions as accurately as possible, it is essential to perform all experimental work in a typical dwelling such as a residential home. Ideally, an instrument would be placed in an occupied home and left to measure emissions from daily tasks. The instrument should not impede daily life for occupants, so it must have a small footprint. Fast-response instruments are useful for this, as occupants and investigators alike are able to observe changes in pollutant levels, hence allowing for source determination. This is especially important when the indoor species of interest are highly reactive. Since occupants are present during sampling, it is important that the instrument is safe. For example, CIMS requires a radioactive source for ionization, which is unrealistic for private dwellings, as occupants would require radiation-specific safety training. Power consumption of the instrument must also be considered. To ensure the instrument can run constantly to maximize data collection and hence advance understanding of indoor air emissions, power consumption must be comparable to a typical household appliance. Furthermore, it is important to engage the occupant in the sampling campaign. If the instrument is user-friendly, occupants will have a greater understanding of their contribution to degraded indoor air quality. An additional hindrance of indoor air studies is the difference in considerations required in comparison to outdoor environments. Emission sources and sinks have a much more profound effect in indoor environments and require extra attention. Studies of indoor air quality must account for the effects of lighting conditions,[55] air exchange rates.[56,57] and surface deposition and reactions.[58–61] In addition to these considerations, drinking water quality[50,51,62,63] and cleaning product use[53,64] are especially important for studies of chlorine atom chemistry.

1.3.3 Previous Studies of Indoor Chlorine Chemistry

Though the lack of measurement techniques has hindered routine indoor air studies, a small number of previous studies have been successful in quantifying chlorinated emissions. These studies, performed in laboratories and test homes, focus on emissions from drinking water use in various household appliances and floor exposure to bleach via mopping.

Drinking water is considered potable after it has been disinfected by chlorination or irradiated using ultra-violet light.[65] This process protects human health by eradicating any water-borne illnesses. Chlorination becomes a concern when the water source is rich in natural organic matter (NOM). The reaction between chlorine and NOM results in the production of DBPs. Governing bodies such as Health Canada and the Environmental Protection Agency (EPA) monitor and regulate levels of two identified classes of DBPs, haloacetic acids (HAAs) and trihalomethanes (THMs).[66] Structures of typical HAAs and THMs are presented in Figure 1-3.

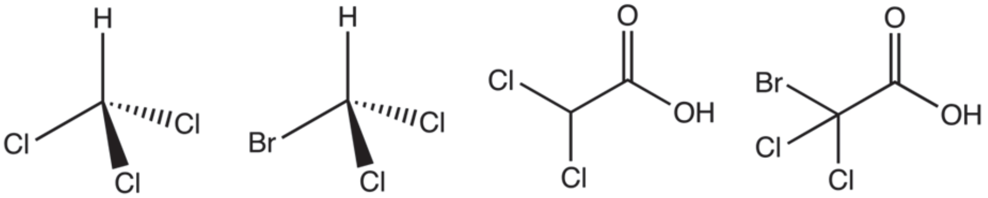

Figure 1-3. Common THMs and HAAs detected in drinking water as DBPs. From left to right: chloroform and bromodichloromethane (THMs), and dichloroacetic acid and bromodichloroacetic acid (HAAs).

The exposure route of typical concern for Health Canada and the EPA is ingestion, even though studies have shown that gaseous emissions are possible.[50,51,63] Extensive modelling, and offline gaseous and aqueous sampling has demonstrated that household emissions of DBPs occur while using dishwashers and washing machines.[50,51] A particularly compelling study demonstrated that levels of DBPs in the form of HAAs and haloketones were observed at detectable levels in blood after showering.[63] Inhalation levels were estimated on the scale of micrograms (μg) per day. This confirmed that DBP exposure is not limited to ingestion alone. While principal DBPs have been identified and are regularly monitored, production is not limited to HAAs and THMs alone.[67] Since these are not regulated, it is impossible to determine exposure rates and associated side effects. Drinking water quality in Newfoundland and Labrador is of particular concern. In some communities, typically rural in nature, chlorine levels exceed the national average tenfold.[66,68] While exposure levels via inhalation and dermal absorption are widely unknown, we expect them to be greater in communities with elevated chlorine levels. Findings from previous work provide proof of indoor emission and human exposure to DBPs, but this class of compounds is only one component of the indoor chlorine inventory. Since chlorine atoms could potentially have a profound impact on indoor air chemistry, indoor sources and sinks of chlorine atom precursors are of the utmost concern for this study.

A recent study performed by Wong et al.[53] detected emissions of HOCl and Cl_2 from floor exposure to commercial bleach. This is the first confirmed indoor emission of chlorine atom precursors from household activities. Results from bleach headspace studies showed that Cl_2 is present as an impurity, but bulk emissions of Cl_2 and HOCl arise when the floor is exposed to bleach. The action of mopping resulted in the formation of HOCl and Cl_2 on the order of 100's and 10's of ppbv, respectively. Results also indicated formation of $ClNO_2$ is possible, but this was not confirmed since an accepted standard for gaseous $ClNO_2$ does not yet exist. As expected for indoor air studies, primary loss pathways include air exchange rate and photolysis. Since this particular study was performed in a laboratory, the air exchange rate (12.7 times per hour (h^{-1})) was much higher than typical residential homes ($0.1 – 3.0\ h^{-1}$).[53,56,57] With a reduced air exchange rate it is possible the lifetime of chlorine atom precursors will be greater in residential homes or other loss pathways will dominate. In addition to experimental work, modelling studies were also performed to determine decay rate constants under different lighting conditions.[53] Modelling indicates that both production and photolysis of other chlorine atom precursors such as HCl and particulate chlorine (pCl) is possible. Despite this, indoor measurements of HCl and pCl are limited to commercial buildings using integrated sampling.[69,70] The emission of pCl plays an important role in the production of chlorine atom precursors (Figure 1-4).[31,53]

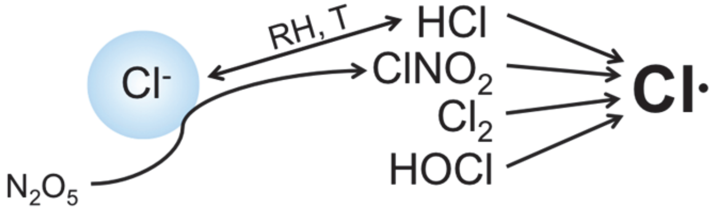

Figure 1-4. Chlorine atom production via precursors emitted from bleach mopping.

Where RH is any VOC, and T is temperature.[28] It should be noted that N_2O_5 is produced via the reaction of the nitrate radical (NO_3) and NO_2.[53] The nitrate radical is produced by the reaction of NO_2 with O_3. The quantification of HCl in indoor air is essential as it may cause a risk to human health. Confirmed acute side effects of HCl exposure include coughing, hoarseness, and inflammation and ulceration of the respiratory tract.[71]

1.3.4 Suspected Sources of Hydrogen Chloride Indoors

Based on modelling studies by Wong et al.[53], it is likely floor exposure to bleach will result in elevated indoor mixing ratios of HCl, as well as greater mass loadings of pCl. Other chlorinated detergents, especially those containing bleach, will presumably emit HCl indoors. Such detergents are typically used in dishwashers and washing machines; thus these household activities are potential sources. An additional source of indoor HCl is cooking. If cooking is compared to the smouldering stage of biomass burning, we expect to observe HCl emissions based on previous biomass burning studies.[72] In particular, if the addition of salt to food is compared to sea-salt deposition to grasses, HCl emission is likely. The influence of cooking in conventional ovens on HCl levels is directly related to the oven-opening frequency. Because of this, it is likely that stovetop cooking emissions will have a more profound effect on indoor HCl mixing ratios. In general, indoor HCl emissions are expected from routine household activities requiring chlorinated detergents, as well as cooking. Because studies of this kind have not been performed indoors, it is difficult to determine whether these suggested sources are a comprehensive inventory of all sources of HCl indoors.

1.4 Thesis Objectives

This work aims to achieve four main goals in order to enhance current understanding of the reactive chlorine inventory in indoor environments. First, the suitability of two atmospheric measurement techniques will be assessed for indoor use (Chapter 2). The results gathered from the deployment of these techniques will be discussed in Chapters 3 and 4. Second, a state-of-science, fast-response measurement technique will be used to monitor and measure indoor HCl emissions (Chapter 3). This technique will allow us to determine sources of HCl indoors. It must be noted that there are countless possible sources of indoor HCl, but this study aims to elucidate those that we expect to have the most profound effect on indoor air. Third, a traditional atmospheric measurement technique will be evaluated for indoor use (Chapter 4). Since these instruments are more accessible for atmospheric chemistry researchers, it is important to assess their feasibility for indoor air studies. Results of this may increase the frequency of indoor air studies if researchers can use existing atmospheric measurement techniques. The fourth and final objective was to assess the impact of household bleach use indoors (Chapters 3 & 4). In particular, the source of emissions will be probed via headspace and mopping experiments. The overall goal of this work is to solve a piece of the complex puzzle that is indoor air quality, in hopes of remediation and thus reduced human health side effects.

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2 Methodology

2.1 Introduction

The highly reactive nature of chlorine atoms leads to very low atmospheric levels and does not allow for direct measurement. Thus, chlorine atom precursors are used as proxies to study chlorine atoms indirectly. While measurement techniques exist for these precursors, few are appropriate for indoor applications. The field of indoor chemistry is relatively new, thus few accepted measurement techniques exist. Because of this, established atmospheric measurement techniques must be evaluated for use indoors. Said techniques, however, are not appropriate for every indoor environment. These techniques are typically cumbersome, which inhibits portability between dwellings. Additionally, many traditional techniques collect one sample over the sampling period, which is inappropriate for indoor source determination. Other than existing techniques, low-footprint state-of-science measurement techniques must be evaluated for indoor use. With advances in technology, these techniques are becoming increasingly popular. It is important to note that, while indoor measurements of any kind are beneficial in advancing knowledge, those mimicking real conditions are especially beneficial. Ideally, measurements would be taken in a residential home, office building or vehicle using an instrument that does not impede daily life, since human occupants and activities are known to impact indoor chemistry.[1–4] Considering this, the ideal measurement technique should be user-friendly, low power, portable, have a small footprint, and not require consumables. Since these measurements will be taken in private homes, it is important that lives of occupants are not disturbed by these measurements. An additional facet of this is that occupants will be immersed in the sampling campaign and able to visualize how their daily activities affect their indoor air quality. Studies of this manner have the potential to ignite interest and curiosity of indoor air quality. In order to achieve this, we must first establish an appropriate measurement technique for indoor studies.

2.2 Offline Sampling

2.2.1 MCHAMMAR

The URG Corp-3000 ABC (URG Corporation – Chapel Hill, NC, USA), otherwise known as the Multichannel Atmospheric Medium Volume Assay for Aerosol Research (MCHAMAAR), was used to sample emissions from floor exposure to bleach. The MCHAMAAR is equipped with three inlets, one PM_{10} downtube and two $PM_{2.5}$ cyclones, and a vacuum manifold containing eight critical orifices. The PM_{10} downtube collects coarse mode particles, which have diameters of 2.5 to 10 microns. Each $PM_{2.5}$ cyclone collects fine mode particles, which have diameters less than 2.5 microns. The critical orifices allow for regulation of flow of 8.25 litres per minute (Lpm) per channel, resulting in an overall flow of 66 Lpm. This permits collection of eight simultaneous samples – four fine and four coarse mode. Collection media for the MCHAMAAR is completely customizable to suit the analyte of interest. In this case, the MCHAMAAR is equipped with annular denuders and filter packs. Annular denuders are composed of a sintered glass rod surrounded by two sintered glass tubes. The inside walls of the denuder are coated with a reactive solution to facilitate the sorption of gaseous acids and bases.

Once gaseous species of interest have been removed from the sample flow, only aerosols remain and are collected via impaction on a solid substrate (Figure 2-1).

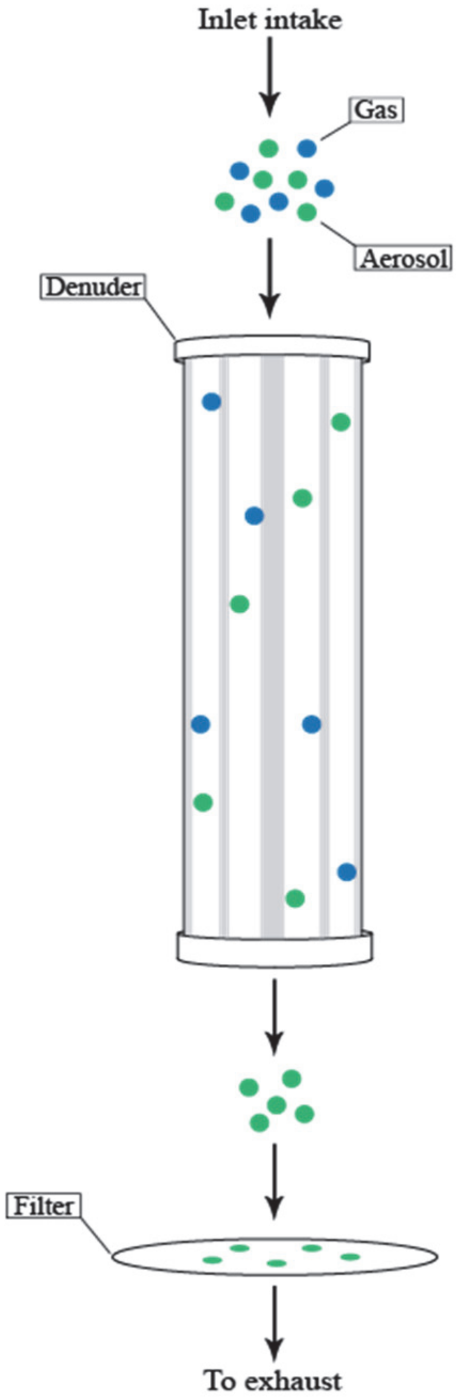

Figure 2-1. Denuder-filter system separation of atmospheric gases and aerosols.

It is important to note that denuders are placed upstream from filters to eliminate gas-particle interactions. The MCHAMAAR is a useful technique to study atmospheric composition in the gaseous and aerosol form. However, the instrument is cumbersome (61.4 kg) and is equipped with a loud vacuum pump, hindering its use in private dwellings.

2.2.2 Denuder Preparation, Sampling & Extraction

Before sampling, each denuder required preparation via a reactive coating and drying. As per the EPA Compendium Method IO-4.2[5], the denuders were coated in a sodium carbonate (Na_2CO_3)-alkali solution. This coating solution in particular is selective for acidic atmospheric constituents such as HCl and HOCl. To make the solution, 50 mL of anhydrous ethyl alcohol (95%, Commercial Alcohol) was combined with 50 mL of 18.2 MΩ cm nanopure water (Barnstead Nanopure Infinity, Thermo Scientific, Waltham, MA, USA) in a 125 mL high-density polyethylene (HDPE) bottle. The HDPE bottle was placed on a top-loading balance where 1 gram (g) of glycerol and 1 g of Na_2CO_3 (ACS grade, ACP Chemicals) were delivered using a 9-inch disposable borosilicate glass Pasteur pipette (**Fisher**brand®) and a metal scoopula, respectively. In order to encourage complete dissolution, the HDPE bottle was labelled, capped and placed in a warm water bath, and shaken intermittently. Once all solid dissolved, the solution was sealed and stored until use.

The denuder, sealed on each end with a Teflon cap, was opened at one end and placed closed-side down. A 10 millilitre (mL) aliquot was delivered to the denuder at a

45-degree (°) angle using a 10 mL borosilicate glass pipette (Grade A, Corning). The open end was capped and the denuder was rotated to ensure all walls were coated uniformly. After coating, one end of the denuder was opened to drain 9 mL of excess solution. To dry the walls, the denuder was uncapped and attached to a Teflon drying manifold that delivered a steady flow of N_2 gas (Ultra-High Purity, Praxair) for 10 to 15 minutes. If the glass walls appeared frosted rather than shiny, they were considered dry and ready for use. If sampling did not begin immediately after the drying procedure, denuders were capped and stored until use.

Unlike preparation, denuder installation is not labour intensive. Before sampling, denuders were uncapped and threaded into couplers. One end of the denuder has a flow-straightener, which is designated as the entry point. The other end of the denuder, where the glass is flush with the end of the tube, was threaded into a Teflon filter pack. Hoses from the vacuum manifold were then connected to the bottom of the filter pack. The setup was then turned on and sampling began. After a pre-determined sampling period, the MCHAMAAR was turned off and denuders were removed in the order opposite of installation – removal of hose from manifold, filter pack from denuder and denuder from coupler. The denuders were then capped and samples stored in the fridge until extraction.

Denuders were extracted by opening one end and placing it cap-side down. A 5 mL aliquot of nano-UV water was delivered to the denuder at a 45° angle using a 5 mL borosilicate glass pipette (Grade A, Corning). The denuder was capped and rotated to ensure efficient extraction, then uncapped to transfer the extract into a 15 mL conical Falcon® tube (High-clarity polypropylene, Corning). The extraction procedure was repeated with an additional 5 mL aliquot. Both extracts were combined in the same tube. The tube was then sealed with Parafilm M and refrigerated until analysis.

2.2.3 Filter Preparation, Sampling & Extraction

Quartz fibre sheets (Tissuquartz™ 2500QAT-UP, PALL Life Sciences) were cut into small rounds with diameters of 4.7 centimeters (cm). To remove impurities, filters were baked (500 degrees Celsius (°C), 4 hours) and stored in baked (500 °C, 4 hours) aluminum foil envelopes used to avoid contamination prior to sampling. Once cooled to room temperature, filters were placed in Teflon filter packs (URG-2000-30FG, URG Corporation-Chapel Hill, NC, USA). For sampling, filter packs were screwed into the bottom end of the denuder and connected to the vacuum manifold. When the sampling period ended, the filter packs were disconnected and unscrewed from the denuder. A Teflon cap was screwed into the top of the filter pack to protect the filter from contamination during transportation. Filters were removed from the filter packs using stainless steel tweezers and placed in pre-labelled sterile, polystyrene petri dishes (60 mm × 15 mm, Fisherbrand®) for refrigeration.

The filter extraction procedure is designed to ensure efficient extraction. Using two pairs of clean stainless steel tweezers, filters were rolled to fit into 15 mL Falcon® tubes. A 10 mL glass pipette (Grade A, Corning) was used to transfer an aliquot of nanopure water to the tube. It is important to note that filters were extracted individually, thus each tube contained a single filter. To ensure the filter was completely submerged in nanopure water, the tube was spun using a Vortex-Genie (Cat # 12-812, Fisher Scientific) for 10-15 seconds. Tubes were then placed in a sonication bath (FS140H, Fisher

Scientific) at 25°C for 30 minutes. At this point, the filters had degraded and filter matter was suspended in the extract. In order to expedite the filtration process, the samples were spun for 30 minutes in a centrifuge (Model 5430, Eppendorf) to force the filter paper to the bottom of the tube. After extraction, the tubes were sealed using Parafilm M and chilled until analysis.

2.2.4 Ion Chromatography Analysis

All analyses were performed by ion chromatography (IC) equipped with a conductivity detector at the University of Toronto. For shipment, samples were taken from the fridge, packed in a Styrofoam cooler with ice packs and expedited to York University in Toronto, Ontario. Samples were shipped through FedEx within one day. The shipping process agitated the samples, resulting in suspension of filter fragments so they were centrifuged for an additional 10 minutes while holding the relative centrifugal force at 9000. Since the introduction of suspended particulate matter could be detrimental to the IC, a 5 mL subsample of each sample was transferred to a cleaned syringe assembly using polyether ether ketone (PEEK) tubing and a luer adapter. The adapter was removed to allow for filtration through a 0.45 μm polytetrafluoroethylene (PTFE) syringe filter. Since only a third of the sample was required for analysis, the remainder was archived for future analyses.

The ion chromatography system at the University of Toronto uses an AS-DV autosampler (ThermoScientific) and an Integrion IC system. An IC method developed by Place et al.[6] was used for all analyses. Briefly, separations were achieved using AG and AS-19 guard (4 × 50 mm) and analytical (4 × 250 mm) columns, respectively. An isocratic solvent program with 18 millimolar (mM) potassium hydroxide was used at a flow rate of 1.5 millilitres per minute (mL min^{-1}) spanning a total run time of 30 minutes. The temperature of the conductivity detector and analytical column was maintained at 35°C for the duration of the run. Before detection, analytes passed through an AERS-500 suppressor to remove the mobile phase. This was performed with a current of 42 milliamps (mA).

While the AS-DV performed all injections, requirements differed for denuder and filter extracts. The solution used to coat denuders for gas sorption contains carbonate, which can become troublesome in IC separations. The heightened level of carbonate can compete with the mobile phase and compromise analyte elution order. To remedy this, a 1000 microliter (μL) sample loop was connected upstream from the analytical system. This diluted the carbonate interference and thus reduced its impact on the separation. For filter extracts, a 1000 μL aliquot was delivered to an anion preconcentration column (TAC-ULP1) before introduction to the IC system.

2.2.5 Quality Assurance & Control

Because of the carbonate interference, preparation of standards for calibration curves required alteration to account for the sample loop. Calibration curves were prepared using a mixed 7-anion standard solution (Dionex). This specific standard solution contains 30 milligrams per liter (mg L^{-1}) of sodium chloride (NaCl) for chloride (Cl^-) analysis. It should be noted that Cl^- analysis via IC does not allow for differentiation between HCl and HOCl. Standards for calibration curves were prepared by serial dilution of a 1:100 stock solution prepared from the 7-anion mix. For filter standards, a 15 mL aliquot of nanopure water was added to 50 mL perfluoroalkoxy (PFA) volumetric flasks before addition of the stock solution. To account for the presence of carbonate in denuder extracts, standards were matrix-matched using a 10 mg mL^{-1} Na_2CO_3 solution instead of water. After addition of the stock solution, calibration standards were diluted to the calibrated mark with the appropriate solvent, inverted eight times and transferred to clean, labelled HDPE bottles (Nalgene).

Many measures were taken to reduce interference and hence mitigate errors throughout sampling and analysis. First, all Falcon® tubes used in extractions underwent an extensive cleaning procedure before use. Since IC measures analytes at trace concentrations, residue from manufacturing could introduce error to analysis. To abate this, tubes were filled with 15 mL of nanopure water, capped and placed in a sonication bath at 35°C for 30 minutes. After sonication, contents of tubes were discarded, caps were rinsed with nanopure water and the washing procedure was repeated twice more. The tubes and caps were inverted and left to dry. To confirm this washing procedure was successful, the IC at Memorial University was used to analyze three samples from the third washing step. Results indicated that this washing procedure efficiently removed any contamination from the Falcon® tubes.

Similarly, filtered samples at York were placed in 15 mL tubes and caps rinsed three times with nanopure water. The water bottle used to wash tubes was also washed in the same manner. In order to determine the relative magnitude of contamination from the water used in washing steps, four reagent blanks were collected and analyzed:

1. Nanopure water from wash bottle to determine the extent of trace Cl^- exposure to the tubes from the wash bottle

2. Nanopure water from wash bottle and syringe to track exposure to Cl^- from the syringes used to transfer and filter samples
3. 5 mL of filtered nanopure water collected after syringe filter was washed three times with nanopure water
4. 5 mL of filtered nanopure water collected after syringe filter without pre-washing

Results from reagent blanks were used to determine potential sources of contamination from the experimental apparatus during sample handling steps (Table 1).

Table 2-1. Results from IC analysis of reagent blanks used to track Cl^- contamination from experimental apparatus

Reagent blank	Cl^- (μg injected)
1	0.0150
2	0.0083
3	0.0044
4	0.0048

It is important to note that the syringe, luer adapter and PEEK tubing were cleaned after handling each reagent blank and sample, as this portion of the apparatus is reused. The cleaning procedure involved rinsing the inside of the syringe, luer adapter and PEEK tubing six times with deionized water. Since the PEEK tubing was immersed in sample and blank solutions, the outside was rinsed with copious amounts of nanopure water prior to interior washing. Additionally, the syringe filters were rinsed three times with nanopure water prior to sample filtrations, and were discarded after use. Unfortunately this portion of this apparatus cannot be reused, as it is impossible to guarantee removal of every filter segment. The disposal of used syringe filters completely eliminates the possibility of contamination in this step.

Blanks were also required during the sampling campaign. To determine error associated with the denuder coating and drying procedure, a denuder blank was analyzed. Briefly, a prepared denuder was extracted as per the aforementioned denuder extraction procedure. The extract was analyzed and results were subtracted from denuder sample results to mitigate any associated error. For filter samples, a prebaked filter was extracted and filtered at York. Results from IC analysis of the blank were subtracted from those of the sample. Additionally, a blank experiment was performed. In other words, the MCHAMAAR, with the same denuder and filter pack configuration used in experimental work, was turned on in the sampling location for 8 hours. This blank provided pre-existing levels of anions in the sampling location. These results were compared with those from the experiment to elucidate the actual impact on indoor air.

2.2.6 Data Handling & Analysis

The method formulated by Place et al.[6] allows for clear separation of anions in the 7-anion mix (Figure 2-2).

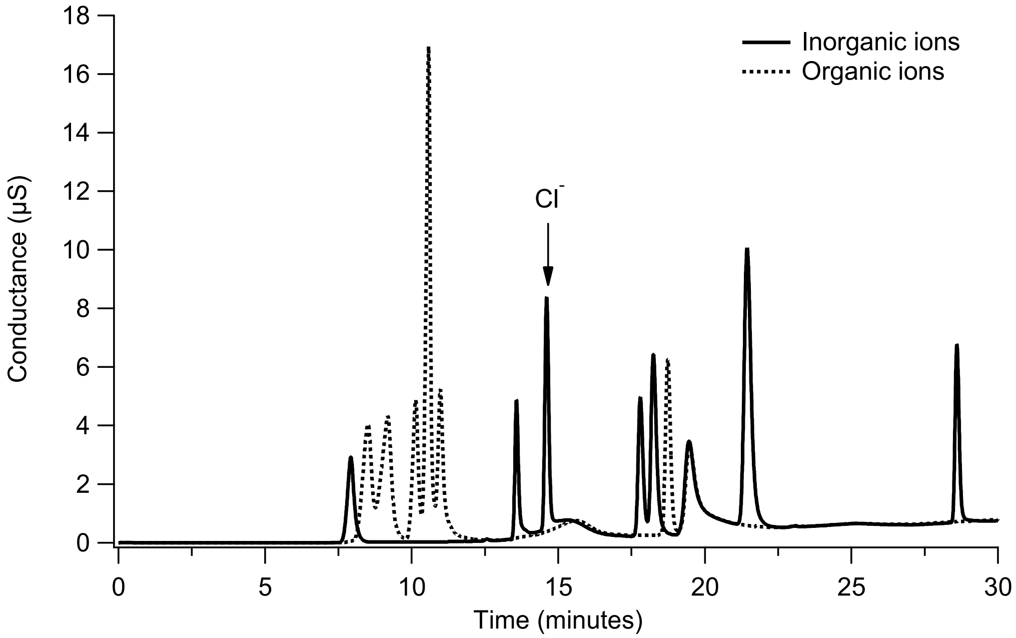

Figure 2-2. IC chromatogram of inorganic and organic separation. The chloride peak is well resolved and free from interference.

With the integrated software, Chromeleon™, the area under the peak was selected and used with known concentrations to generate a calibration curve (Figure 2-3).

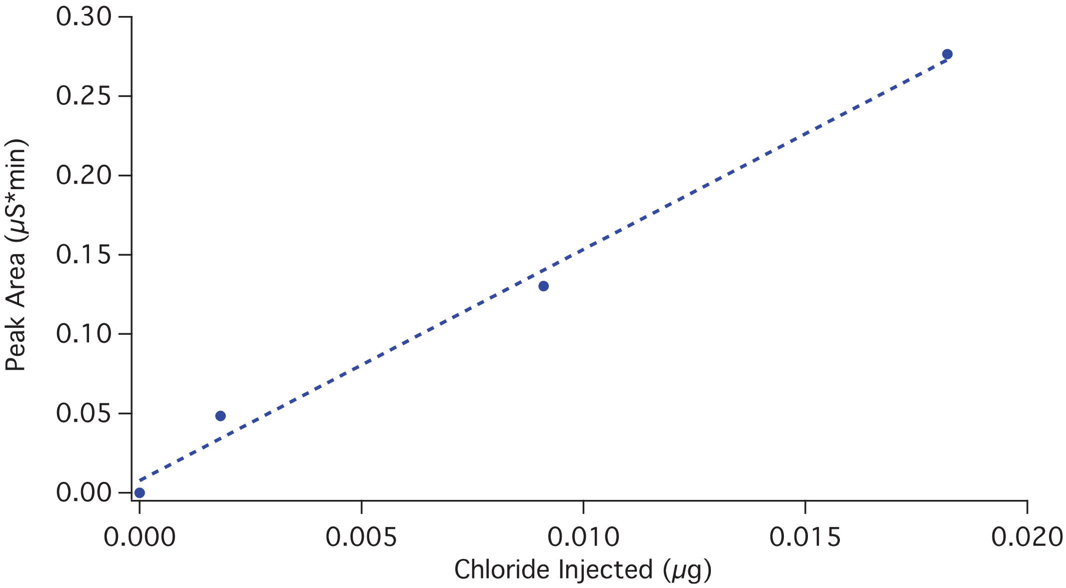

Figure 2-3. Calibration curve for chloride (R^2=0.9915) analysis of filter extracts.

Regression analysis of calibration curves was used to quantify chloride levels in filter and denuder extracts by solving the regression equation for mass of chloride injected. The mass was then used to calculate the mixing ratio or mass loading based on the known sampling time. Results were then analyzed and compared to draw conclusions from experiments.

2.3 Online Sampling

2.3.1 Cavity Ring-Down Spectroscopy

Cavity Ring-Down Spectroscopy (CRDS) is a long path direct absorption measurement technique for gas phase species.[7,8] In particular, this measurement is used for atmospheric trace gases.[8] While instrument specifics vary, a typical CRDS consists of three main components: a laser, a high finesse optical cavity and a photodetector.[7] The laser is used to direct light into the optical cavity, which contains at least two highly reflective mirrors. These mirrors enhance the path length of the cavity, and the sensitivity of the CRDS.[7,8] The photodetector monitors the build-up of the optical activity over time by light that leaks through the back mirror. When optical activity reaches a maximum, the laser is quickly turned off and optical decay is monitored by the photodetector. This is referred to as the ring-down time. An example of typical CRDS operation is shown in Figure 2-4.

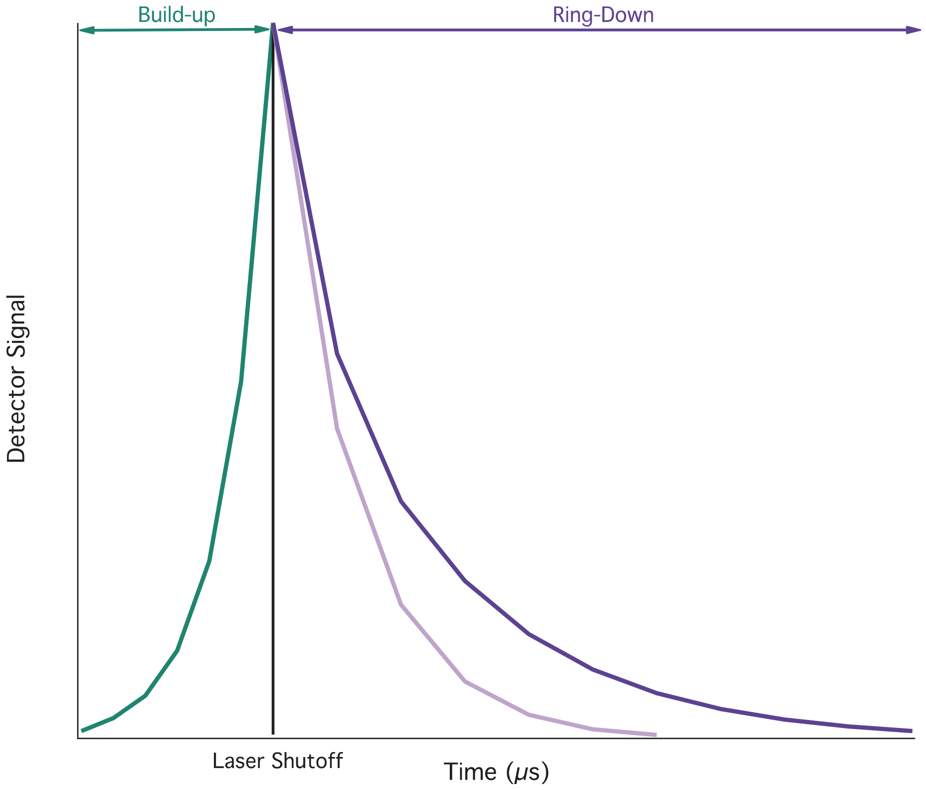

Figure 2-4. Typical operation of a CRDS instrument. Detector signal builds up (green) when laser is turned on. Ring-down time varies depending on whether the cavity is empty (dark purple) or contains an absorber (light purple**).**

Optical activity decays exponentially, resulting in a exponential decay constant.[8] When an absorber is present, the exponential decay time constant is reduced. Exponential decay time constants for a cavity with and without the presence of an absorber can be used to determine an absolute measurement of optical extinction, α (Equation 2-1).

$$\sigma[A] = \alpha = \frac{R_l}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \qquad \text{(R2-1)}$$

Where σ and [*A*] are the absorption cross-section and the concentration of the absorber, respectively. R_l is the ratio of total length of the cavity to the length of the cavity in the presence of an absorber. The speed of light is denoted by *c*, and τ and τ_0 represent the exponential time constants with and without an absorber in the cavity, respectively. It should be noted that this equation is rearranged to solve for concentration of the absorber of interest. State-of-science instruments perform this rearrangement automatically when accompanying software reports measurements in terms of gas mixing ratios, which uses air pressure measurements to perform this calculation. Such instruments are valuable for *in situ* measurements in indoor and outdoor environments alike.

2.3.2 Picarro HCl CRDS

Indoor HCl emissions from daily activities were monitored using a CRDS. The HCl CRDS (G2108 Hydrogen Chloride Analyzer, Picarro, Inc.) was used to detect trace gaseous HCl. This measurement is possible even in the presence of interfering gaseous species. The reduction of interfering gaseous species is possible by using a high precision distributed feedback laser centered at 5739.2625 wavenumbers (cm^{-1}).[9] For example, species such as HOCl from floor exposure to bleach will not interfere with HCl measurements (Figure 2-5).

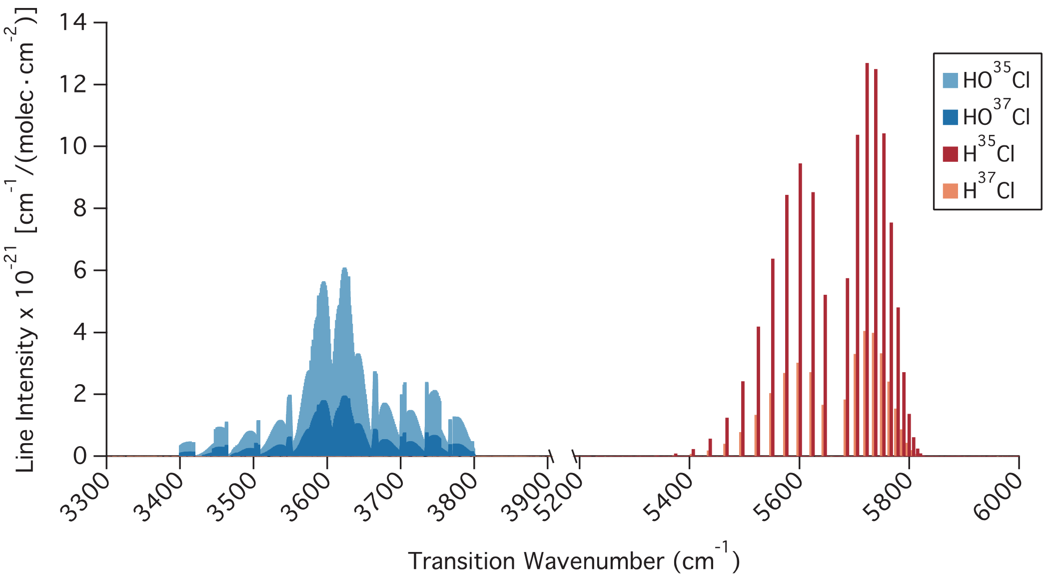

Figure 2-5. Line data for HOCl and HCl

Unlike traditional CRDS instruments, the high-finesse cavity of the Picarro CRDS contains three mirrors, two flat and one curved. The magnitude of signal loss in the empty optical cavity, otherwise known as the total reflectance capability is less than 50 ppm for this instrument.[7] This allows for a precise measurement of HCl.

The HCl CRDS is an excellent measurement technique for indoor environments. It is particularly attractive for private dwellings as it is user-friendly and has a measurement interval of approximately 5 seconds.[10] Fast-response measurements are essential for highly reactive species like HCl. Additionally; the high sensitivity (lower detection limit <120 ppt) is an important asset for trace gas measurement. Other than the analyzer itself, requirements include a small vacuum pump, a computer monitor, mouse and keyboard, and a small inlet. Considering this, no consumables (e.g. gas cylinders) are required for this instrument. The HCl CRDS is portable (31.75 kg) and quiet (40 dB), allowing for instrument placement in dwellings with minimal disruption to occupants. During sampling campaigns, intervention is only required for data retrieval and technical fixes.

2.3.3 Data Handling & Analysis

Data was retrieved from the HCl CRDS and imported into Igor Pro (Version 6.37, WaveMetrics, Inc). Since the instrument measures in the Greenwich Mean Time (UTC+0) zone, time values were converted to the local time zone, Newfoundland Day Time (UTC-2:30). Time conversion allowed for comparison between sampling notes and increased mixing ratios, thus facilitating source elucidation. The HCl CRDS reports HCl mixing ratios in 2 second intervals, and averages of 2, 5 and 10 minutes in units of ppbv. Since the instrument calculates mixing ratios, data handling included cutting data to remove redundant background measurements and determining the extent of mixing ratio increase as a result of household activities.

2.3.4 Quality Assurance & Control

While frequent calibration is not required, it is important to perform an initial calibration to determine the precision of the instrument. A HCl permeation source was used at 0% humidity to determine the precision of the HCl CRDS was ± 28 pptv over a span of 5 minutes.

2.4 Conclusions

Both methods presented can be used in indoor environments to measure reactive chlorine species. However, the MCHAMAAR is only appropriate for measurements of Cl^- and particulate chlorine. It is impossible to determine whether Cl^- detected in denuder extracts was a result of HCl or HOCl. Furthermore, the MCHAMAAR is large and loud, which inhibits its portability significantly. This offline instrument is best suited for to enhance knowledge of total anionic content in the aerosol and gas phase. The advent of HCl CRDS, however, has enhanced measurement capabilities in occupied dwellings. Boasting perks such as portability, minimal calibrations and high sensitivity, the HCl CRDS is an ideal technique for indoor studies.

2.5 References

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3 Formation and emission of hydrogen chloride in indoor air

3.1 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, fast measurements (0.5 Hz) of HCl mixing ratios were made in an 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.

3.2 Practical Implications

Despite extensive research in outdoor atmospheres, hydrogen chloride (HCl) has not been studied by fast-response intstruments 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.

3.3 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.[7,12] Secondary formation of HCl is facilitated by reactions on chloride-containing aerosols.[2,7,16] 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 dermal contact.[17] While these side 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. Due to the highly soluble nature of HCl, it can dissolve in water in indoor air and on surfaces, which can corrode metals such as those in electronic devices.[18]

The lifetime of trace atmospheric pollutants is governed by oxidative chemistry in the troposphere.[19,20] Principal tropospheric oxidants include hydroxyl radicals and chlorine atoms.[19] Recent work has shown that chlorine atoms oxidize volatile organic compounds (VOCs) and produce ozone more efficiently than hydroxyl radicals, even in small quantities.[21] Chlorine atoms also contribute to destruction of polar boundary layer ozone via a halogen catalyzed ozone destruction cycle.[22] 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.[23] 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 (R3-1 – R3-4).[2,20,24–27]

$$Cl_{2(g)} + hv \rightarrow Cl\cdot_{(g)} + Cl\cdot_{(g)} \qquad \text{(R3-1)}$$

$$ClNO_{2(g)} + hv \rightarrow Cl\cdot_{(g)} + NO_{2(g)} \qquad \text{(R3-2)}$$

$$HOCl_{(g)} + hv \rightarrow Cl\cdot_{(g)} + HO\cdot_{(g)} \qquad \text{(R3-3)}$$

$$HCl_{(g)} + HO\cdot_{(g)} \rightarrow Cl\cdot_{(g)} + H_2O_{(g)} \qquad \text{(R3-4)}$$

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

$$Cl\cdot_{(g)} + RH_{(g)} \rightarrow HCl_{(g)} + R\cdot_{(g)} \qquad \text{(R3-5)}$$

where RH represents any VOC. [2,7] Due to the large relative abundance of reactants in polluted coastal regions, the reaction proceeds with ease.[6] 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.[28] 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.[29–33] The most commonly studied DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs), can enter indoor air via washing machines, showers, dishwashers and taps.[28,29] 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.[34,35] 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 in real-time for the first time to enhance understanding of chlorine chemistry and sources indoors. Fast-response 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.

3.4 Methods

3.4.1 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 cm^{-1}.[36] The Picarro analyzer contains a heated (70.000 ± 0.005 °C), low-pressure (0.1842 ± 0.0002 atm) high finesse optical cavity, which has three high reflectivity mirrors, two flat and one curved.[37] 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 120 parts-per-trillion by volume (pptv). The precision (1 σ) of the instrument when measuring zero air at 0% relative humidity (RH) was determined to be ± 24 pptv in 5 minutes. The HCl CRDS is an ideal instrument for sampling indoors because it is portable (31.75 kg), quiet (40 dB), has high sensitivity (< 120 ppt), does not require consumables (e.g. compressed gas cylinders) nor frequent calibration.[38]

3.4.2 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 and 2.5 m away from the stovetop. The inlet, an 8" length of ¼" 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. A submicron pre-filter and back-up filter are present inside the HCl analyzer to 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 Appendix A1 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 ± 18 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 m^3 within a 1.5 story 220 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 h^{-1} (see Section A2).[39,40] 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 provided in Appendix A).

3.4.3 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 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.

3.4.4 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, 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.

3.4.5 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.

3.4.6 Cl Production Rate Constant Calculations

Measurements of wavelength-resolved photon fluxes for common indoor light sources were made by Kowal and Kahan.[41] Measured photon fluxes were used to calculate photolysis rate constants (*J*) for chlorine atom precursors Cl_2, HOCl, and $ClNO_2$ using

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

where λ, σ, φ represent the wavelength, absorption cross-section of the molecule, and photolysis quantum yield, respectively. Absorption cross sections were taken from Maric et al.[42] (Cl_2), Barnes et al.[43] (HOCl), and Ghosh et al.[44] ($ClNO_2$). Quantum yields of 1 were used for Cl_2 and HOCl,[45] while a quantum yield of 0.93 was used for $ClNO_2$.[46] 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.

3.5 Results/Discussion

3.5.1 Cleaning Experiments

Elevated HCl mixing ratios relative to background levels were observed following each of three consecutive bleach applications (Figure 3-1).

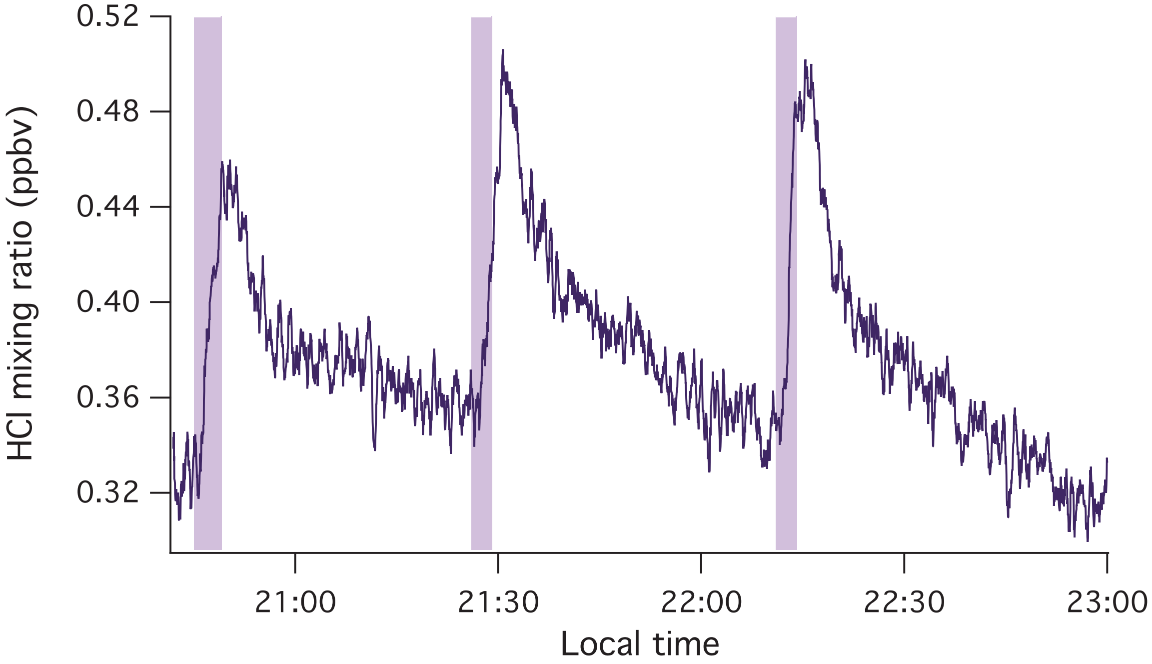

Figure 3-1. HCl mixing ratios measured during three sequential bleach applications. Measurements are presented as the 30-second average of the HCl mixing ratio in parts-per-billion by volume (ppbv). Bleaching applications spanning 3±1 minute periods are represented by the shaded regions, and the HCl 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 3-2).

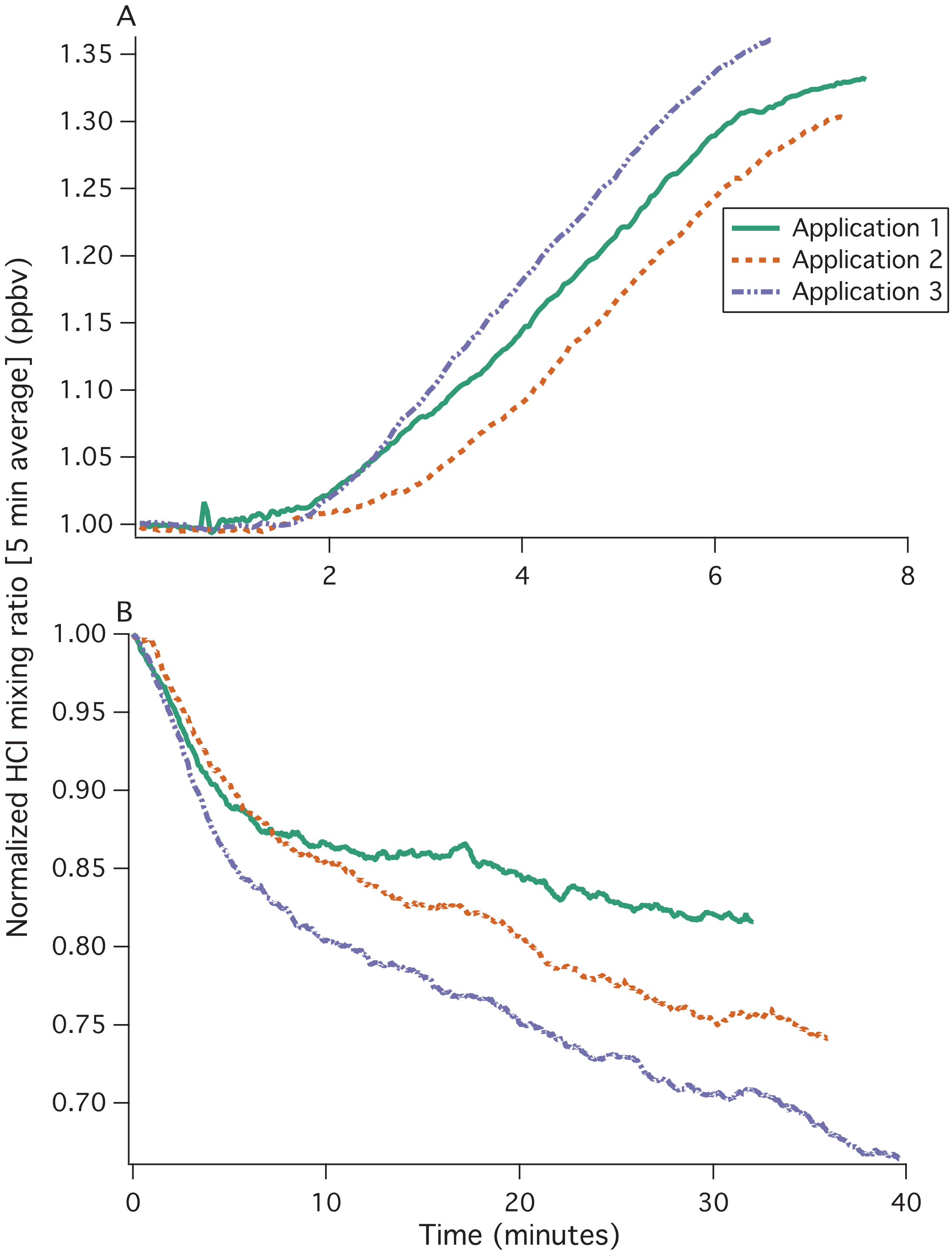

Figure 3-2. (A) Rise and **(B)** decay in HCl mixing ratio after bleach applications. Results from this experiment are presented normalized to the background (A) or maximum (B) concentration. In all cases, the measurements are the 5-minute average HCl mixing ratio in parts-per-billion by volume (ppbv).

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 3-2A 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_2 reported by Wong et al.[28] 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[28] has shown that HOCl, Cl_2 and $ClNO_2$ are released during floor mopping with bleach. All three are known to photolyze under ambient outdoor light to produce Cl atoms[21,23,26] which react with VOCs to form HCl (Figure 3-3).[28,45]

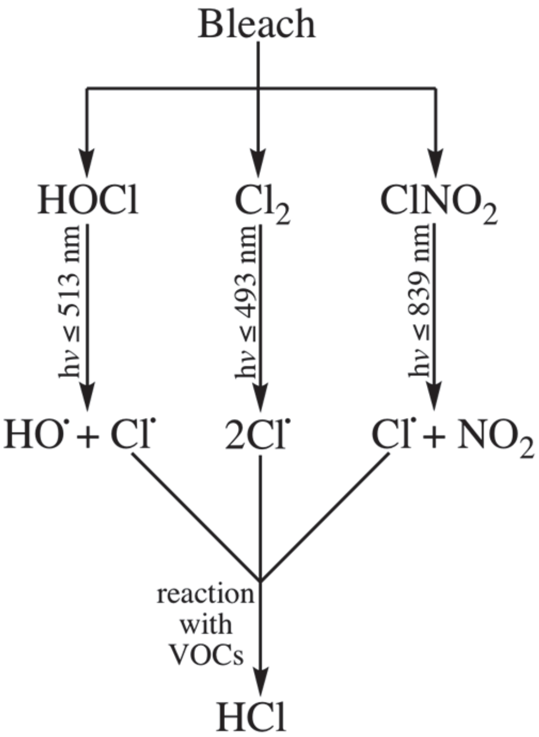

Figure 3-3. Proposed reaction pathway for indirect formation of HCl via photolysis of HOCl, Cl_2, and $ClNO_2$ emitted from bleach use.

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.[41] Under these light conditions, photolysis reactions shown in Figure 3-3 could proceed. Calculated Cl photolysis production rates under illumination by various light sources at Cl_2 and HOCl mixing ratios reported after the use of bleach (20 ppbv and 200 ppbv), and at an estimated $ClNO_2$ mixing ratio of 1 ppbv are shown in Table 3-1.[28,41] 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 Appendix. Cl atoms are predicted to be formed from Cl_2 photolysis at rates on the order of $0.1 - 1.2 \times 10^8$ molec cm^{-3} 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 $0.2 - 5.9 \times 10^7$ molecules cm^{-3} s^{-1} under the same illumination conditions. Production rates of Cl from $ClNO_2$ photolysis will not exceed 3×10^5 molecules cm^{-3} s^{-1} under these conditions. However, it should be reiterated that $ClNO_2$ mixing ratios after the use of bleach have not been quantified.[28] 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 $0.5 - 2.6 \times 10^6$ molecules cm^{-3} s^{-1} for Cl_2, $0.3 - 13 \times 10^5$ molecules cm^{-3} s^{-1} for HOCl, and $0.2 - 6.5 \times 10^3$ molecules cm^{-3} s^{-1} for $ClNO_2$. 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 molecules cm^{-3} s^{-1} in residences.[41,47,48] 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 Appendix.

The measured HCl production rate during the bleaching experiments was ~1.2×10^7 molecules cm^{-3} s^{-1}. This is similar to the photochemical Cl production rates predicted in Table 3-1; 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_2 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 3-1. Calculated Cl production rates for light sources in this study for 20 ppbv Cl_2, 200 ppbv HOCl, and 1 ppbv $ClNO_2$. Mixing ratios were based on measurements from Wong et al.[28]

Light source	Cl Production Rate (molecules cm^{-3} s^{-1})					
	At light source			1 m from light source		
	Cl_2	HOCl	$ClNO_2$	Cl_2	HOCl	$ClNO_2$
LED	2.57×10^7	1.81×10^6	1.20×10^4	4.62×10^5	3.26×10^4	2.17×10^2
Halogen	1.16×10^8	5.89×10^7	2.96×10^5	2.56×10^6	1.30×10^6	6.50×10^3
Office fluorescent (covered)	9.93×10^6	2.91×10^6	8.22×10^3	1.45×10^6	4.26×10^5	1.20×10^3

The bimodal decay observed in Figure 3-2B 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.[49] 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.[7]), 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}).[39,40]

3.5.2 Dishwashing Experiments

Previous studies have shown that dishwashers emit compounds including chlorinated organics, which are released when chlorinated dishwashing detergents are used.[30] 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.[34,35] 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 3-2, Figure 3-4).

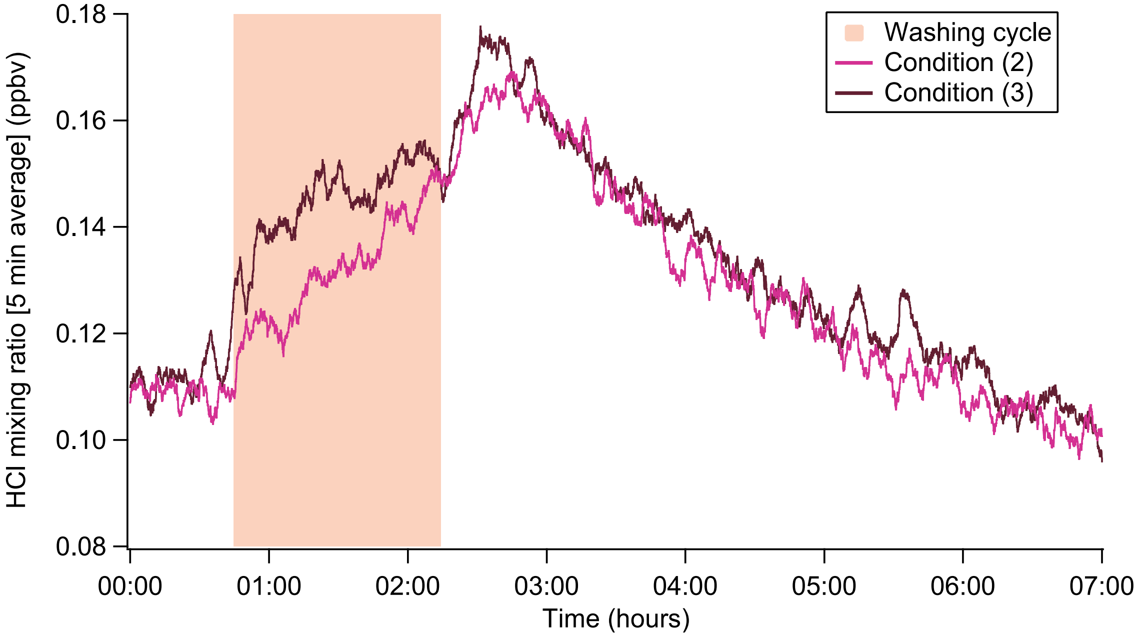

Figure 3-4. HCl mixing ratio during a condition (2) and (3) dishwashing scenario. In both cases, the measurements are the 5-minute average HCl mixing ratio in parts-per-billion by volume (ppbv).

Both organo-chlorine and bleach detergents showed similar emissions of HCl when used in the empty dishwasher (example shown in Figure 3-4). 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. The decay of HCl signal after dishwashing experiments was similar to the bimodal decay observed after cooking experiments. Comparison between all dishwashing conditions was not possible because of the different environmental factors (e.g. temperature) between conditions.

Table 3-2. Mixing ratio increases relative to initial background conditions observed during dishwashing experiments.

		HCl mixing ratio (pptv) [5 min avg]		
Condition	Detergent Type	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. 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.[40] 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.[30] 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.

3.5.3 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.[50] An example of cooking, showing two events, is presented in Figure 3-5.

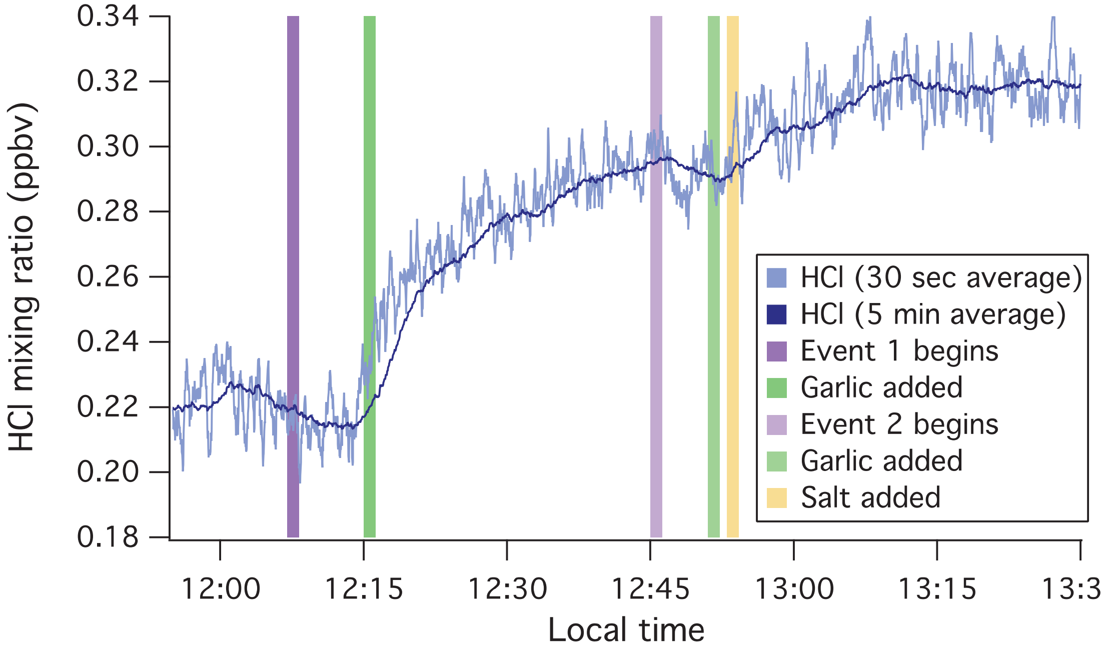

Figure 3-5. HCl mixing ratio during two consecutive cooking experiments. Commencement of cooking, and garlic and salt addition are indicated by shaded regions. HCl mixing ratios are presented by 30-second and 5-minute averages in ppbv.

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,[50] 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. Onions, which belong to the same family (allium) as shallots and garlic, are known to contain chlorine.[51] On a cellular level chloride is required for stomatal opening when guard cells cannot synthesize malate.[51,52] Since chlorine is very water soluble and present ubiquitously in water, it is likely that all plants and vegetables contain chlorine in one form or another. Furthermore, if food is cultivated in close proximity to the ocean, sea salt deposition may enhance chlorine levels.[50] Thus it is likely that direct emission via allium species chlorine content 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.

3.5.4 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 back-up filter and a vacuum pump.[9–11,14,53] 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.[50] This requirement is satisfied when high time-response measurements of HCl are acquired with chemical ionization mass spectrometry

(CIMS).[7,54] 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 requires a radioactive ionization source.[54] 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.

3.6 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_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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4 Measurement of reactive chlorine emissions in indoor air

4.1 Abstract

Chlorinated detergent use is known to contribute to the reactive chlorine inventory indoors. While commonly studied in the aqueous phase, gaseous and aerosol emissions of chlorinated cleaning products are unknown. Since few appropriate measurement techniques exist, traditional atmospheric measurement techniques were evaluated for use indoors. In this work, reactive chlorine was measured in the gaseous and aerosol phase using a medium volume air sampler equipped with coated annular denuders and filters. Emissions from bleach were measured from the headspace of the bulk solution and during surface application. Results indicated that chlorinated emissions arise when bleach is used as intended in cleaning processes, such as floor mopping. Measurements of reactive chlorine were performed while manipulating two variables: (1) number of bleach applications, and (2) drying time. A single floor application of bleach yielded higher levels of aerosolized chlorine compared to three consecutive applications. Elevated chloride aerosol mass loadings were observed in the coarse mode after 30 minutes of drying, but diminished after 60 minutes, indicative of aerosol settling. Observed reactive chlorine levels provide evidence of indoor formation and emission of HCl, HOCl, or a combination of both species.

4.2 Introduction

In order to assess human exposure to poor indoor air quality, emissions from daily household activities must be monitored. It is important to note that exposure is not limited to consumption, but also includes inhalation and dermal adsorption. Since humans spend approximately 90% of their lives indoors, everyday activities are potentially harmful to human health.[1] A major area of concern is exposure from chemically treated tap water. Water must meet an extensive list of criterion set by the federal government to be considered potable.[2–4] In order to meet these criteria, water is often disinfected via chlorination, UV-light irradiation treatment, or ozonolysis.[5] Chlorination of water sources rich in natural organic matter (NOM) is of particular concern due to the production of disinfection by-products (DBPs).[6–8] Principal by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) have been studied extensively and are hence regulated by government agencies.[6,7,9–12] While these DBPs are closely monitored, other non-regulated species exist that have the potential to further degrade indoor air quality.[7] As of late, indoor reactive chlorine studies have been limited to DBPs from drinking water disinfection.

Previous research has demonstrated that reactive chlorine species are emitted during floor exposure to bleach.[13,14] Such species include molecular chlorine (Cl_2), nitryl chloride ($ClNO_2$), hypochlorous acid (HOCl), and hydrogen chloride (HCl).[13,14] These compounds are considered chlorine atom precursors, and are commonly used as proxies to study chlorine atoms. Proxies are required for chlorine atom investigations due to their high reactivity and thus short atmospheric lifetime.[15,16] Chlorine atoms act as oxidants in the atmosphere, and facilitate tropospheric ozone production and stratospheric ozone destruction.[17,18] Furthermore, chlorine atoms can react with volatile organic compounds (VOCs) to produce HCl.[19,20] While this reaction is often observed in polluted coastal regions, there is potential for analogous reactions indoors. To date, few studies have shown the impact of daily household activities on HCl production and indoor air quality. This may be due to lack of appropriate instrumentation for indoor measurements. In order to address this, established atmospheric measurement techniques can be evaluated for use indoors.

For the past several decades, denuder-filter systems (DFS) have been used to measure atmospheric chlorine in trace gases and aerosols (Figure 4-1A).[21–27] Since the DFS collects both gaseous and aerosol forms, two different sampling methods within the system are required. For gaseous species, the annular denuder is used. The annular denuder is comprised of a series of sintered glass tubes spaced with small Teflon spacers and centered about a sintered glass rod. To protect the glass tubes and rods, the denuder is encased in a steel tube. In order to facilitate gas sorption, denuders are coated with a reactive solution and dried under inert gas before use. It should be noted that the reactive solution is determined for each analyte to maximize selectivity. For example, carbonate solutions are used to trap species such as HCl, sulfur dioxide (SO_2) and nitric acid (HNO_3), whereas citric acid solutions are used to trap ammonia (NH_3). Aerosols are collected using a filter held in a Teflon filter pack. The filter media is dependent on the analyte of interest, and is commonly quartz or Nylon. In order to avoid gas-aerosol interactions, the annular denuder is placed before the filter pack (Figure 4-1B).

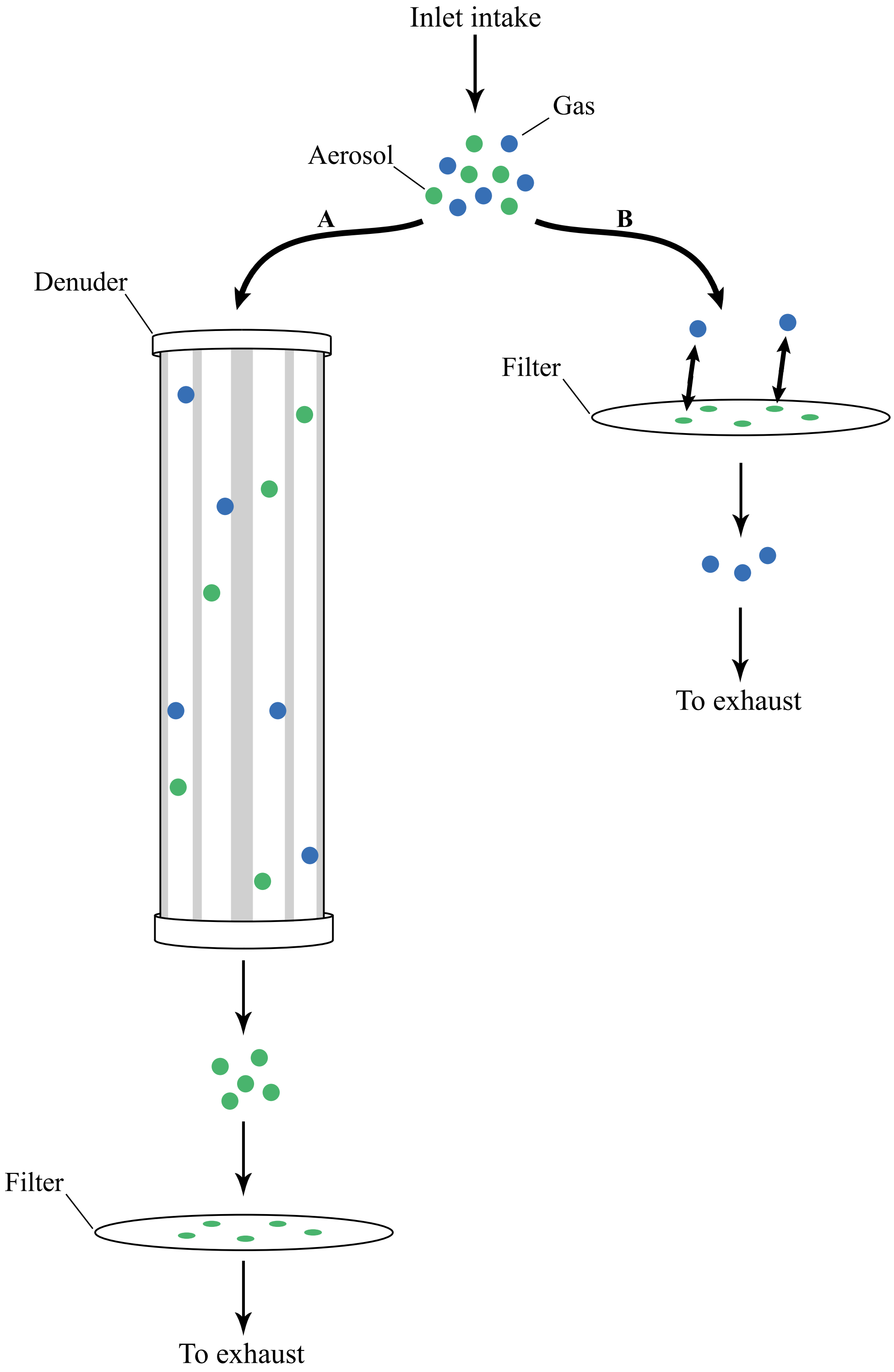

Figure 4-1. **(A)** Denuder filter system for gas and particle collection; (**B**) collection without an annular denuder.

This configuration allows for gaseous species removal from the sample flow and hence only aerosols impact the filter. For sampling to occur, the DFS must be connected to an appropriate inlet and a vacuum pump. The inlet will restrict the sampled particle size, and the vacuum pump will promote a controlled airflow through the DFS. Typically a critical orifice, which aids in constricting flow and hence controlling sampling rate, is used in these systems. Unlike real-time high-response instruments, the DFS provides an integrated sample. Sampling periods are at the user's discretion and samples require extraction and analysis before results are known. Collected samples are typically analyzed via ion chromatography, which gives the speciated ion content. These techniques are potentially useful for proof-of-principle laboratory studies and determination of total chloride content from household activities. However, based on findings in Chapter 3, such techniques are impractical for source determination in private dwellings. This study provides: (i) a comparison of instrumentation techniques for indoor applications, and (ii) the first measurement of chloride-containing aerosols indoors.

4.3 Methods

4.3.1 Denuder Preparation

Denuders were prepared as per EPA Compendium Method IO-4.2.[28] All denuders were coated with a Na_2CO_3 solution. This coating solution collects reactive acids such as HCl, HF, HNO_2, SO_2, and HNO_3. Details of reactive coating solution preparation and coating process can be found in Chapter 2 (Section 2.2.2).

4.3.2 Filter Preparation

Quartz fibre filter paper (Tissuquartz™ 2500QAT-UP, PALL Life Sciences) was punched to size using a hollow arc punch. Filter preparation and storage procedures are provided in Chapter 2 (Section 2.2.3).

4.3.3 Bleach Bubbling Experiments

Commercially available concentrated bleach (Old Dutch) was purchased and diluted as per manufacturer's instructions. A 20 mL aliquot was added to a 25 mL midget impinger equipped with a sintered glass frit (Ace Glass, Incorporated). Ultra-high purity nitrogen gas (UHP N_2, Praxair) was flowed into the impinger at 10 standard litres per minute (SLPM) to achieve a steady bubbling rate. Flow was controlled using a mass flow controller (MFC) and a control box. The output of the impinger was directed into a multi-channel annular denuder followed by a filter pack containing a quartz fibre filter (Figure 4-2). All tubing and fittings past the MFC were gas-tight and made of perfluoroalkoxy (PFA). Experiments were performed in the absence of both natural and artificial light.

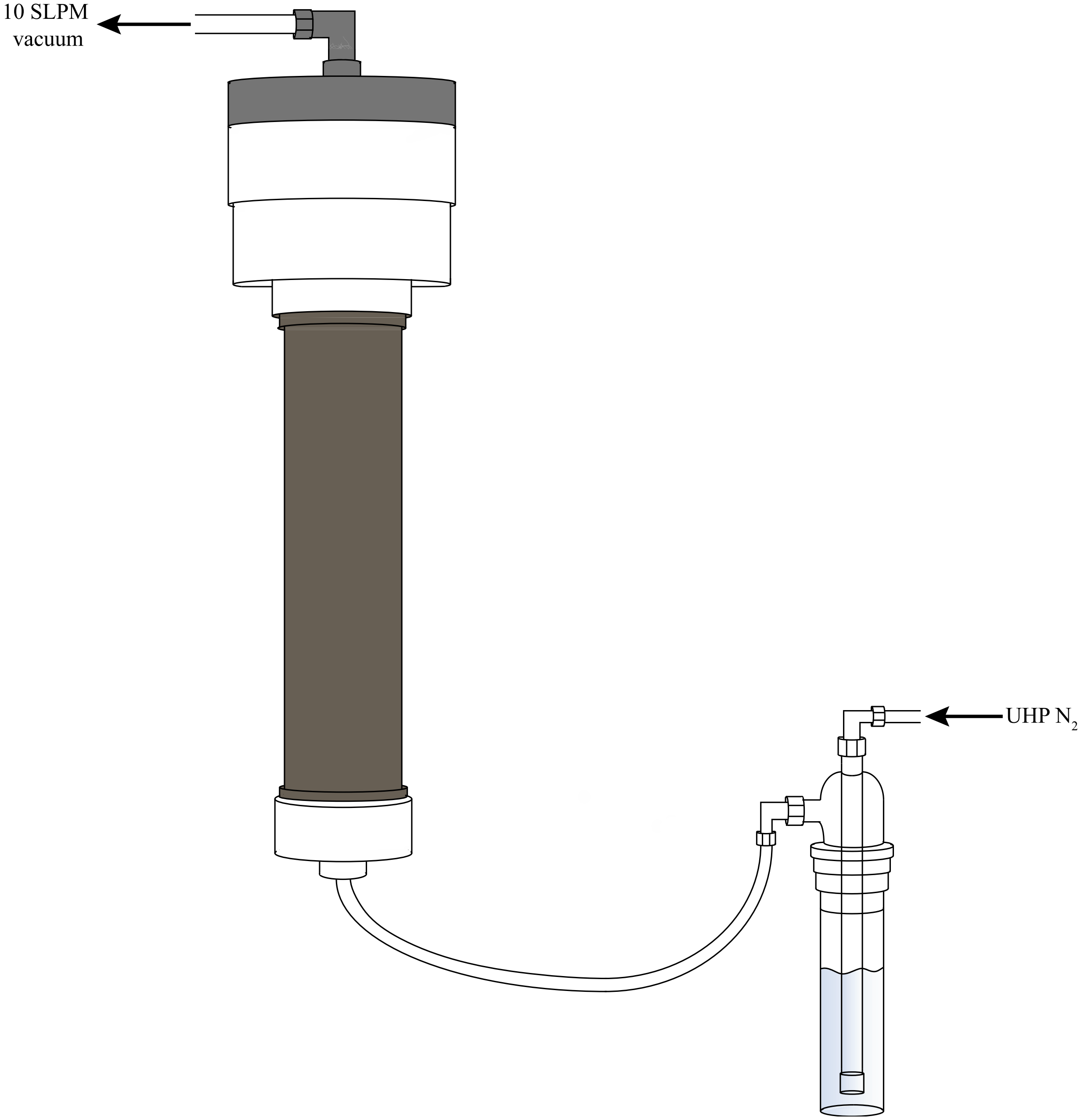

Figure 4-2. Sampling apparatus for bleach bubbling experiments. A flow of ultra-high purity nitrogen is directed into the glass impinger (filled with either dilute bleach or tap water) to a coated denuder and filter pack. A mass flow controller is used to maintain a flow rate of 10 SLPM.

4.3.4 Bleaching Experiments

Commercially available bleach (Old Dutch) was purchased and diluted as per manufacturer's instructions prior to floor application. Bleach was applied to a 3.5 m^2 section of painted concrete floor for 3 – 4 minutes and left undisturbed to dry for 30 – 60 minutes. After floor exposure, excess bleach was removed from the room and disposed of once the sampling period ended. A fresh 1 L portion of bleach was prepared for every bleaching experiment.

4.3.5 Indoor Air Sampling

All indoor air samples were collected using a Medium Volume Particulate Sampler (URG-3000ABC from URG Corp.). The URG-3000ABC (Figure 4-3) is equipped with three Teflon coated inlets: one coarse mode (aerosol diameter less than 10 µm (PM_{10})) and two fine mode (aerosol diameter less than 2.5 µm ($PM_{2.5}$)), which have maximum flow rates of 32 and 16.7 SLPM, respectively. Eight critical orifices along with a 15" Hg vacuum control the overall flow rate of 66 SLPM.

4.3.6 Sample Collection

After denuders were prepared, three were installed in the $PM_{2.5}$ channels using Teflon couplers (Figure 4-3). A fourth denuder was used as a blank. The denuder blank was opened at one end and remained open until all denuders were installed.

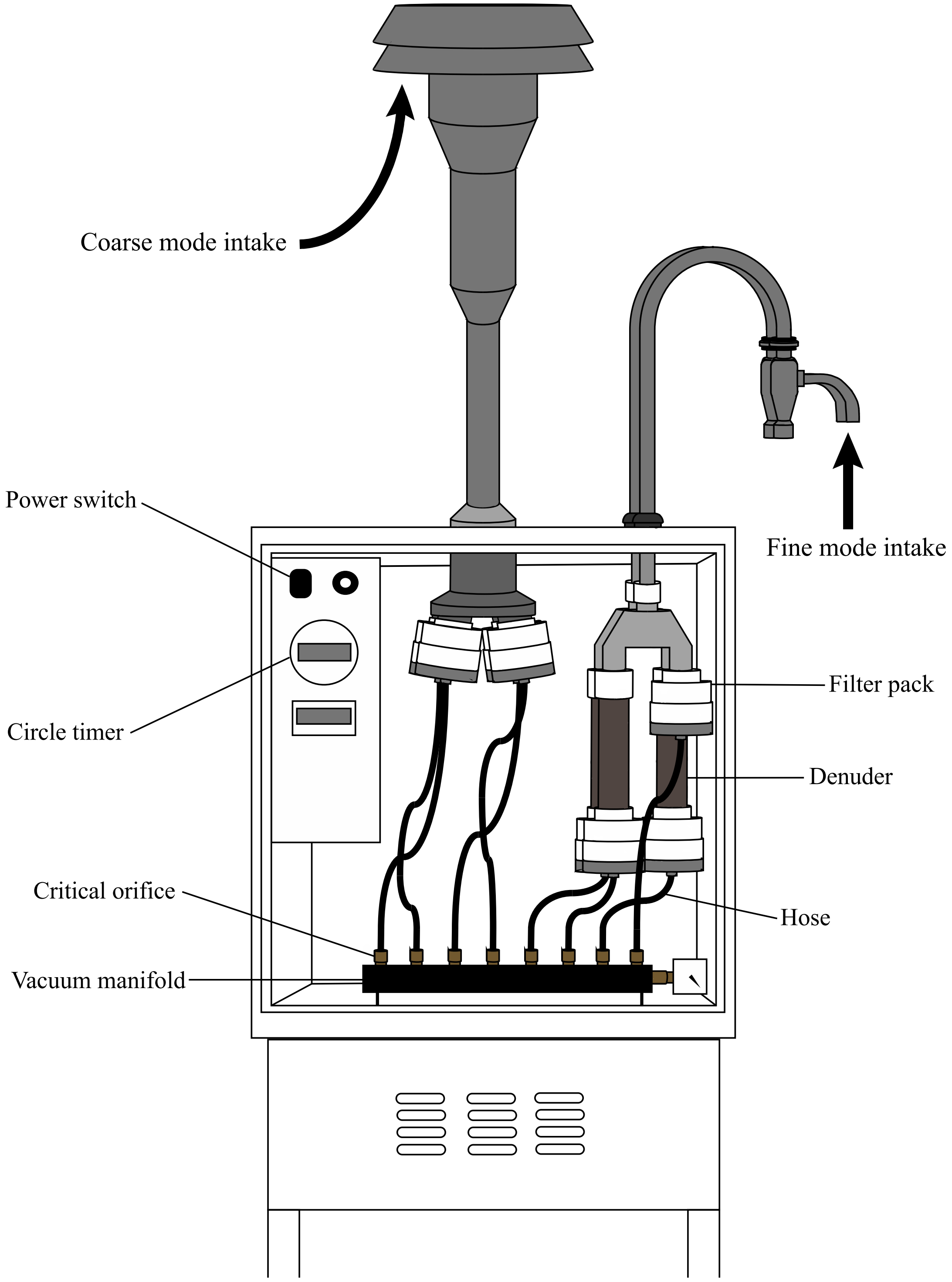

Figure 4-3. Schematic of the URG-3000ABC instrument and sampling configuration for all experiments.

Quartz filters were removed from storage using stainless steel tweezers and placed in filter packs. A Teflon cap was used to protect the filter media from contamination before installation. Upon installation, eight filter packs were divided for installation in the $PM_{2.5}$ and PM_{10} channels (Figure 4-3). Three filter packs were screwed into the open end of the three $PM_{2.5}$ denuders and one was installed into the remaining $PM_{2.5}$ port without a denuder. The remaining four filter packs were installed in PM_{10} channels. An additional filter, stored in a Petri dish, served as a filter blank. The Petri dish remained open during installation and was closed once all filter packs were installed.

When all denuders and filter packs were installed, hoses from the vacuum manifold were attached to the end of the filter packs. Once the URG-3000ABC was plugged in and the power switch was turned on, sampling began. The duration of the sampling period is at the user's discretion. Sampling occurred in the absence of both natural and artificial light, with the exception of a single desk lamp. The lamp, equipped with an incandescent light, was directed towards the wall as a safety precaution. Human activity in the room was minimal and limited to a single operator for essential experimental requirements (i.e. turning the instrument on and off).

At the end of the sampling period, hoses were unplugged from the bottom of the filter packs. Filter packs were then unscrewed, capped and refrigerated until extraction. Similarly, denuders were unscrewed, capped on both ends and refrigerated.

4.3.7 Denuder Extraction

After sample collection, capped denuders were removed from the fridge to equilibrate to room temperature. Denuders were extracted as per the procedure outlined in Chapter 2 (Section 2.2.2).

4.3.8 Filter Extraction

Filters were removed from labelled Petri dishes using stainless steel tweezers. An additional set of tweezers was used to roll the filter for placement in a 15 mL Falcon™ tube. Filters were extracted as per the procedure outlined in Chapter 2 (Section 2.2.3).

4.3.9 Sample Shipment

Falcon™ tubes containing denuder and filter extracts were sealed using Parafilm M to ensure sample preservation during shipment. Tubes were placed in Styrofoam racks and placed in a box containing a Styrofoam cooler. Ice packs were added to the box to ensure samples were kept cool in transit. Samples were sent via FedEx express shipping from Memorial University in St. John's, Newfoundland to York University in Toronto, Ontario. When samples arrived in Ontario, they were refrigerated and stored until analysis was performed at University of Toronto.

4.3.10 Ion Chromatography

In order to avoid injection of particulate matter, filter extracts were spun using a centrifuge at 9000g for 10 minutes to remove suspended filter paper. Approximately 5 mL of each sample solution was transferred to a pre-cleaned syringe assembly using polyether ether ketone (PEEK) tubing and a luer adapter. Once the appropriate volume was acquired, the adapter was removed and the sample solution was passed through a pre-cleaned polytetrafluoroethylene (PTFE) syringe filter and into a clean Falcon™ tube. Denuder extracts did not require filtration as there was not any visible suspended particulate matter in the samples.

A calibration curve was prepared using a mixed 7-anion standard solution (Dionex). This particular standard mix contains 30 mg L^{-1} sodium chloride (NaCl) for chloride (Cl^-) analysis. Standards were prepared by serial dilution of a 1:100 stock solution made from the 7-anion mix in 50 mL PFA flasks. For filter analysis, a 15 mL aliquot of deionized water (18.2 MΩ cm) was added to each flask prior to addition of standard. In order to account for the presence of carbonate in denuder extracts, matrix-matched standards were required and hence a 10 mg mL^{-1} carbonate solution was used instead of deionized water. Once the appropriate volume of stock solution was added, volumes were diluted to the calibration mark and inverted 8 times to ensure the standard was well mixed. Standards were transferred to deionized water rinsed high-density polyethylene (HDPE) Nalgene bottles. Standards and samples were transferred to new, clean 5 mL autosampler vials and capped prior to analysis.

Ion chromatography (IC) for filter extract analysis was performed using a method previously developed by Place et al.[29] A ThermoScientific AS-DV autosampler and Integrion IC system, located at the University of Toronto was used for all analyses. The AS-DV delivers a 1000 µL aliquot of sample to an anion preconcentration column (TAC-ULP1) prior to introduction via injection to the analytical system. In order to achieve separation, an AG and AS-19 guard (4 × 50 mm) and analytical (4 × 250 mm) columns were used with an 18 milimolar (mM) potassium hydroxide (KOH) isocratic elution methodology. The column and conductivity detector temperatures were maintained at 35 °C for the duration of the separation. Analytes of interest passed through a suppressor (AERS-500) prior to detection. The suppressor removed the mobile phase using a current of 42 milliamps (mA). The flow rate was maintained at 1.5 mL min^{-1} for the total run time of 30 minutes.

The presence of carbonate in the denuder samples can alter the performance of the IC method by competing with the elution solvent. Because of this, the method used for filter analysis required modification to better suit denuder samples. Instead of using a preconcentration column, a 1000 μL loop was installed in the system. The increased tube length allowed for sample dilution, which reduced carbonate interference. This diminished carbonate-elution solvent competition and hence the method by Place et al.[29] could be used for denuder extracts.

4.3.11 Nuclear Magnetic Resonance

Concentrated bleach was analyzed by phosphorous-31 nuclear magnetic resonance (^{31}P NMR) using a benchtop NMR unit (NMReady-60PRO, Nanalysis Corp). The benchtop NMR has an operating frequency of 60 megahertz (MHz) for proton measurement and is tuned to 25 MHz for ^{31}P analysis.

4.4 Results & Discussion

4.4.1 Bleach Bubbling Experiments

In order to determine whether reactive chlorine species are directly emitted from bleach, bleach bubbling experiments were performed. The bleach used in all bubbling experiments was diluted using municipal tap water obtained immediately before sampling started. Tap water was used rather than deionized water to mimic typical household use. Because of this, a sample of bubbled tap water was collected to serve as a background measurement. This measurement was essential to avoid a false positive as a result of chlorine levels in tap water. In order to ensure all reactive chlorine was captured during the sampling period, two different sampling periods were probed: (1) tap water bubbling for 20 minutes followed by bleach bubbling for 30 minutes, and (2) tap water bubbling followed by bleach bubbling for 60 minutes each. Both experiments followed the same procedure. First, 20 mL of tap water was bubbled for the pre-determined time period, then the impinger was rinsed with deionized water, dried and filled with 20 mL of dilute bleach. The dilute bleach was then bubbled for the allotted time period. In total, ten samples were obtained: four denuder samples, four filter samples, one denuder blank and one filter blank. The denuder and filter blanks were used to track contamination from the sampling media themselves. In other words, analysis of the denuder blank would determine if coating solution or the ultra-high purity nitrogen flow were contaminated. Since these are systematic errors, the results from the blanks can be subtracted from the sample results to account for the error. Similarly, any filter contamination will be detected in the blank and hence subtracted from filter extract results.

After accounting for levels in the blanks, the denuder samples did not contain chloride. The presence of denuder chloride is a result of gaseous HCl and HOCl collection (R4-1 & 4-2).

$$HCl_{(g)} \xrightarrow{Denuder} Cl^{-} + H^{+} \qquad \text{(R4-1)}$$

$$HOCl_{(g)} \xrightarrow{Denuder} OCl^{-} + H^{+} \qquad \text{(R4-2)}$$

The conjugate base of HOCl, hypochlorite (OCl^-) can be collected using the same method as chloride but it cannot be analyzed by IC.[30] Since OCl^- degrades to Cl^- at the suppressor, observed Cl^- could be from HCl, HOCl or a combination of the two.

Because of this, we can deduce that gaseous reactive chlorine is not emitted from bleach headspace. Our results in Chapter 3 showed HCl emitted after bleach application. This suggests emission of HCl facilitated when bleach comes in contact with the floor and hence indoor air. These results are consistent with previous work by Wong et al.[13]. Since the pH of bleach is approximately 11, it is unlikely that the acidic reactive chlorine components will be liberated from the solution to the headspace. Wong et al.[13] suggest that the solution is acidified after mopping, which results in emission of acidic chlorine species such as HOCl (R4-3).

$$H_3O^{+}{}_{(aq)} + ClO^{-}{}_{(aq)} \rightleftharpoons HOCl_{(g)} + H_2O_{(aq)} \qquad \text{(R4-3)}$$

By the same rationale, HCl could also be released (R4-4).

$$H_3O^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \rightleftharpoons HCl_{(g)} + H_2O_{(aq)} \qquad \text{(R4-4)}$$

It should be noted that the acidified surface provides protons, allowing for the entropically favourable release of HCl (R4-4). Considering this, it is likely that emissions of bleach are different in the bulk (observed in this experiment) and when exposed to surfaces (Chapter 3).

While bleach headspace does not contain gaseous reactive chlorine species, results indicate that chloride-containing aerosols are produced with bubbling (Figure 4-4).

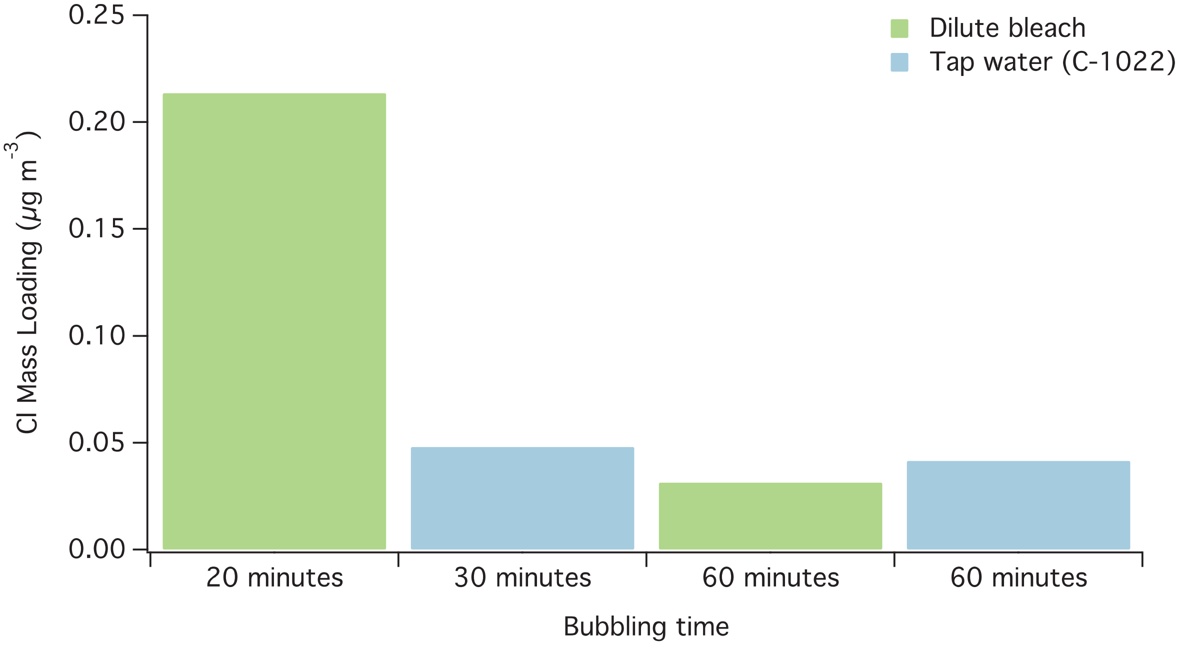

Figure 4-4. Aerosol chloride mass loading results from bleach bubbling experiment (1) (20-30 minutes) and (2) (60 minutes). Mass loading is reported in terms of the mass of aerosol chloride injected per volume of air sampled in units of micrograms per meters cubed (μg m^{-3}).

Mass loadings resulting from chloride-containing aerosols ranged from 0.0415 to 0.2135 μg m^{-3}. In the first bubbling experiment, the aerosol chloride produced by dilute bleach was approximately 0.17 μg m^{-3} higher than tap water, suggesting that most aerosol chlorine was derived from bleach rather than tap water. However, it appears bubbling for less time has a greater impact on chloride-containing aerosol formation. Since tap water emissions remained consistent regardless of time spent bubbling, it is unlikely that water chlorination is contributing to observed differences. A possible explanation for the inverse relationship with time is total chloride concentration. In other words, dilute bleach contains a limited amount of chloride that can be aerosolized. This aerosolized chloride can contribute to indoor chlorine chemistry by acting as a reaction surface to indirectly form HCl.

4.4.2 Floor Bleaching Experiments

In order to enhance understanding of air quality impacts from floor exposure to bleach, the URG-3000ABC was set up to sample emissions from three different bleaching experiments: (1) one application with drying time of 30 minutes, (2) one application with drying time of 60 minutes, and (3) three sequential applications with combined drying time of 120 minutes. All experiments were designed to mimic bleaching experiments conducted in Chapter 3. In (1), bleach was applied and left to dry for 30 minutes. After 30 minutes, parts of the floor still appeared wet. This inspired (2), where bleach was left to dry for 60 minutes after one application. For (3), bleach was applied once and left to dry for 30 minutes. After 30 minutes, a new portion of bleach was diluted and the floor was washed for a second time and left to dry for 30 minutes. A third application was performed after 30 minutes and left to dry for 60 minutes. The additional drying time was added to account for the additional bleach applications and hence reduced evaporation rates. It is important to note that the URG-3000ABC was started immediately before the floor was exposed to the initial bleach application, allowing sampling of both mopping and drying emissions.

The expectation, when increasing the number of bleach applications from one in (2) to three in (3), was that chloride mixing ratios would increase three-fold. However, the opposite occurred (Figure 4-5).

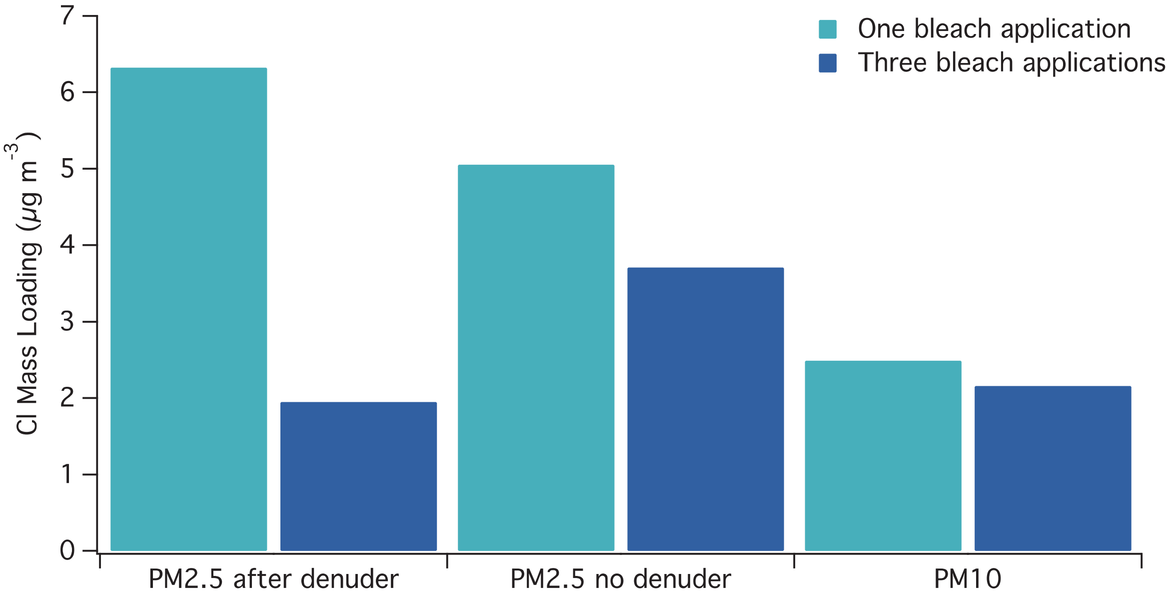

Figure 4-5. Chloride mass loading results from bleaching experiments (2) and (3), where number of applications was varied from one to three, respectively. All mass loading values are presented in units of µg m^{-3}.

Mass loadings of chloride-containing aerosols observed after one application were higher than those after three applications. While it is difficult to study temporal trends with an integrated sample, we attributed this to dilution effects. Each application introduces more dilute bleach and thus more water to the bleaching surface. The introduction of more water inhibits bleach from the previous application from drying and hence evaporation of chloride. After three applications, this effect becomes cumulative. It is possible that additional applications restrict the amount of chloride liberated from the bleach on the floor. The degree of floor cleanliness could also contribute to the reduced mass loadings in (3). In Table 4-1, the total chloride mass loading resulting from bleaching is reduced with sequential experiments. With increasingly clean floors, less chloride is liberated. When the number of applications of bleach is increased, the floor becomes cleaner, but the surface chemistry of the floor has also been altered significantly. The degree of cleanliness hence dictates chlorine emissions, which in this case are reduced with increased applications.

Table 4-1. Total chloride mass loadings for bleach mopping experiments.

Experiment	Chloride mass loading (μg m^{-3})			Total chloride mass loading (μg m^{-3})
	PM$_{2.5}$ after denuder	PM$_{2.5}$ no denuder	PM$_{10}$	
1	4.067	2.783	9.117	15.97
2	6.327	5.055	2.491	13.87
3	1.950	3.709	2.159	7.818

While emission of HCl in Chapter 3 was immediate and only lasted 30 minutes, it is likely that chloride-containing aerosols do not follow the same emission process. Additionally, a single application of bleach yields more fine mode aerosols. Since fine mode aerosols mainly result from secondary production, it is likely that the dominant emission pathway of chloride-containing aerosols is indirect. Indirect formation of aerosols occurs when emitted gases condense onto the surface of existing aerosols. This further supports the argument that increasing the number of applications will decrease production via dilution. In order to determine whether or not dilution is playing a role in emission pathways, the effect of drying time required further investigation.

While the indoor sampling method used for these bleaching experiments is not ideal for source determination, it does allow for exploration of certain variables such as drying time with respect to particle size (Figure 4-6).

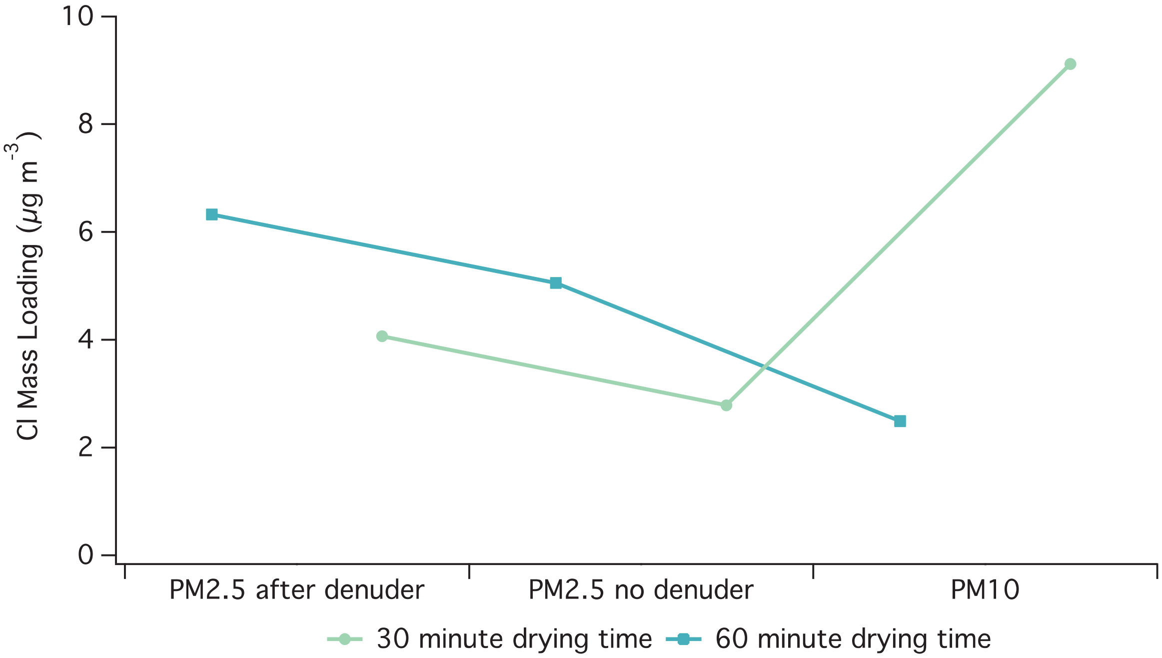

Figure 4-6. Aerosol chloride mass loadings as a result of extending drying time 30 minutes. Mass loadings are reported in units of μg m^{-3}.

The truly intriguing results emerge from the coarse mode size fraction. After 30 minutes of drying time, the aerosol chloride mass loading was 9.117 μg m^{-3}. When drying time was doubled, coarse mode aerosol chloride mass loading decreased to 2.491 μg m^{-3}. Since coarse mode particles are emitted directly rather than a result of chemical processes, it is possible that elevated chloride levels after 30 minutes is a result of mopping. This, however, does not explain the reduction in mass loading with increased drying time. The significant difference observed with the coarse mode particles suggests deposition to indoor surfaces. Particle deposition, which occurs when a particle adheres to a surface, has been studied in test homes, residential homes and office buildings.[31–33] Predominant factors affecting particle deposition include air exchange rates and surface-to-volume ratios.[32,33] Studies have consistently observed that large particles (PM_{10}) have higher deposition rates than smaller particles ($PM_{2.5}$), as dictated by their atmospheric lifetimes.[31–33] Coarse mode particles have atmospheric lifetimes on the scale of hours to days, whereas fine mode particles have lifetimes of days to weeks.[34] Considering this, it is likely that a drying time of 30 minutes captures the maximum loading of coarse mode particles. Once coarse mode aerosols settle, the room air is mainly composed of fine mode particles. In the $PM_{2.5}$ size range chloride mixing ratios varied by a factor of 1.5 – 1.8, but did not experience significant change with increased drying time. Temporal analysis of fine mode particle behaviour was limited by the collection of an integrated sample. This limitation could be resolved if an *in situ* measurement technique was available. It is important to note that laboratories in the Chemistry-Physics building at Memorial University have an elevated air exchange rate compared to the private dwelling studied in Chapter 3. However, these factors do not change the observed trend for particle diameter. It should also be noted that the presence of the denuder did not alter the fine mode composition, indicating that the occurrence of any gas-aerosol interactions did not impact aerosol chloride measurement. If the denuder was protecting the filter from interfering species, chloride levels would be elevated in the filter without a denuder in line.

Unlike the CRDS method used in Chapter 3, base-coated DFS is selective for acidic gases, where speciation is limited by the selectivity of the offline extraction and analysis. Since HOCl and HCl cannot be distinguished by IC, this method cannot determine the levels of gaseous HCl. However, it is a useful metric to collect total reactive chlorine. The DFS can be used to determine phase composition. In other words, results from denuder and filter extracts are able to provide insight on whether bulk emissions are in the form of a gas or aerosol. In Figure 4-7, it is clear the majority of emitted chlorinated species are gaseous. As for the efficacy of the denuder placed before one of the filters, it appears to have no discernable effect on collection of chloride-containing aerosols. Because of this, we suggest that denuders are not required for protection of filters in future bleaching studies.

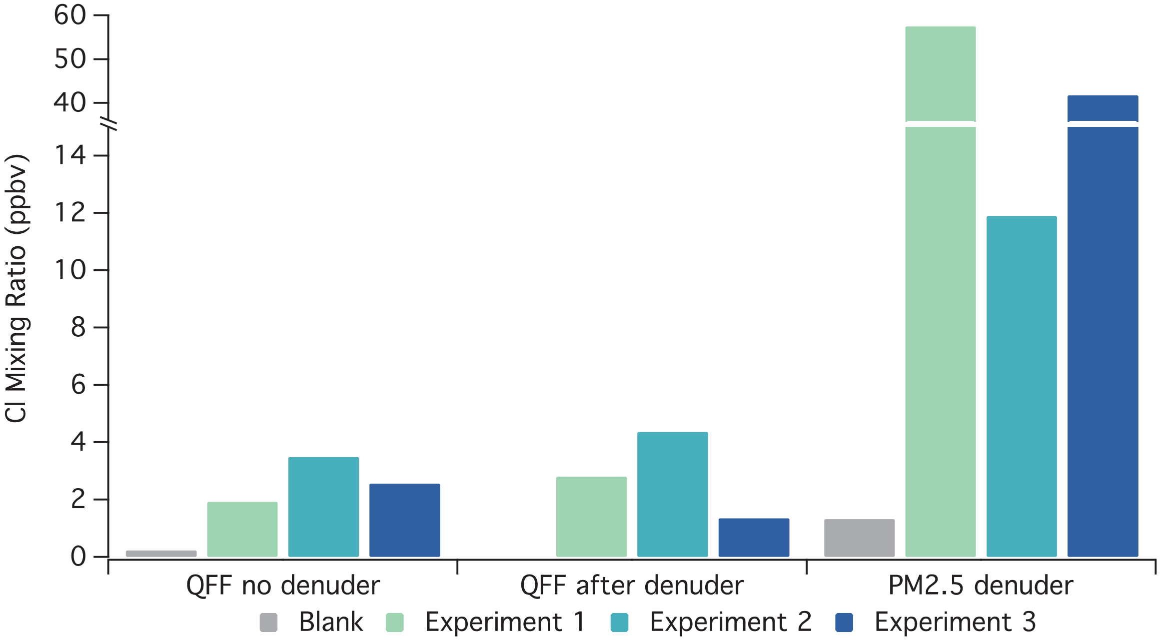

Figure 4-7. Fine mode aerosol analysis after three different types of bleaching experiments.

Using knowledge gained from bleaching experiments in Chapter 3, elevated levels of gaseous chlorinated species were expected. However, mixing ratios observed in denuder extracts are at least 2 orders of magnitude higher than those using the CRDS in Chapter 3. Since the CRDS is selective for HCl, it is likely that mixing ratios are elevated by other species, and thus gaseous bleaching emissions are not limited to HCl. Previous work by Wong et al.[13] showed that HOCl, $ClNO_2$ and Cl_2 are emitted during bleach floor exposure experiments. Of these chlorinated species, it is likely that the basic denuder coating is collecting HOCl in addition to HCl, as the pKa of HOCl is 7.4.[13] However, without further investigation and speciation of bleaching emissions, we cannot conclusively identify these chlorinated species. While the DFS does not provide a selective detection of chlorinated species of interest, it has been proven useful for estimating the total chloride mixing ratio from floor exposure to bleach.

4.4.3 Other Anions from Bleaching Experiments

The IC method used to analyze the filter samples was originally developed for atmospheric measurements. In order to quantify atmospheric anions, the 7-anion mixed standard was chosen. This allows for quantification of 7 anions using a single set of calibration standards. When applied to indoor applications where the anion of interest is chloride, little attention is focused on the other anions. However, other anions may provide auxiliary information that could be used to elucidate mechanisms of chlorine emissions. In this case, elevated levels of a species that eluted at the same time as a phosphate standard in the denuder data during bleaching experiments was of particular interest (Figure 4-8). Mixing ratios of this species in (1) and (2) exceeded those observed for chloride. It should be noted that the capture of phosphate by the denuder is rare in both indoor and outdoor environments, because phosphate-forming species such as phosphoric acid are not present in the gas phase. Because of this, it is likely that this peak is an interfering species rather than phosphate.

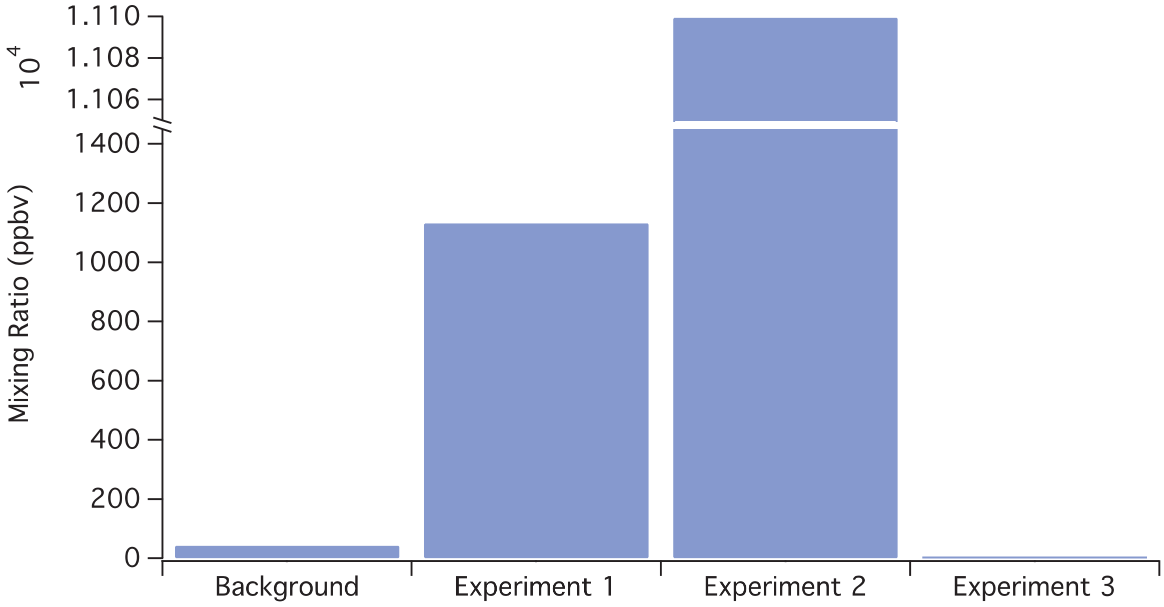

Figure 4-8. Phosphate denuder results from bleaching experiments

Since the safety data sheet for the commercial bleach stated that it contained only NaOCl and NaOH, the source is unknown. To further investigate this, concentrated bleach was analyzed via ^{31}P NMR. Three samples were analyzed: (A) H_3PO_4 standard in deuterium oxide (D_2O), (B) concentrated bleach with internal standard, and (C) concentrated bleach (Figure 4-8). The standard provided by the company was used as a reference point to show the chemical shift of phosphate. In order to analyze bleach via ^{31}P NMR, solvent locking was required, thus a few drops of D_2O were added with shaking. An internal standard, potassium phosphate (K_2HPO_4; ≥ 98%, Sigma-Aldrich) was added to one of the bleach samples in the event that phosphate was not present. The internal standard was added to a bleach sample and inverted until all solid dissolved.

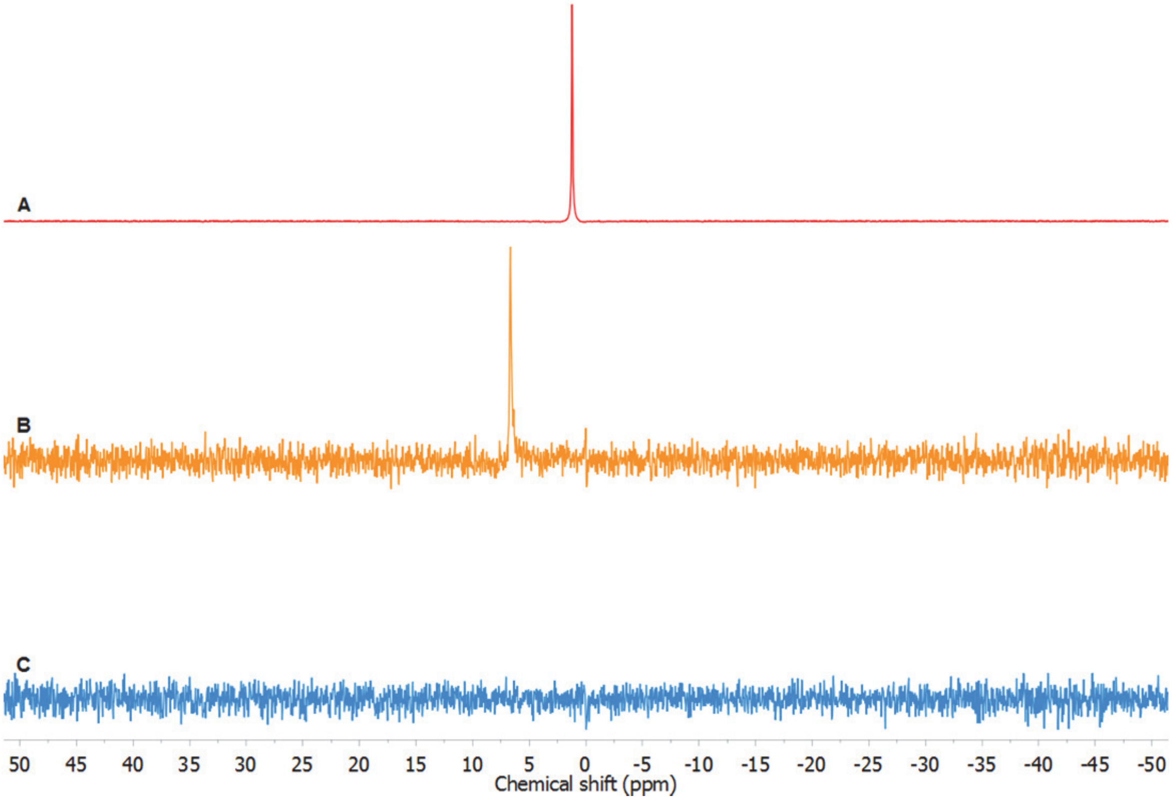

Figure 4-9. Phosphorous-31 NMR analysis of (**A**) H_3PO_4 in D_2O, (**B**) K_2PO_4 in bleach and D_2O, and (**C**) bleach and D_2O.

The spectrum obtained from (A) has one sharp, distinct peak centered at 0 ppm (Figure 4-9A). Results obtained from (C), however, indicate that bleach does not contain detectable levels of phosphate (Figure 4-9C). This is further confirmed by analysis of (B), which produced a clear, distinct peak at ~0.1 ppm (Figure 4-9B).

This confirms that concentrated bleach does not contain detectable levels of phosphate or any phosphorus-containing species. Thus, phosphate is not being emitted when the floor is exposed to bleach. When raw data is analyzed using IC software, analytes are identified based exclusively on matching retention times with authentic standards. This highlights the hindered selectivity of the conductivity detection used by

IC. While this method is widely used and commonly accepted, it does not make it immune to errors. Since all ions will produce a signal, it is possible that an interfering species with similar size and ionic properties is eluting at the retention time typically assigned to phosphate. This would lead to a false positive reading of phosphate. Seeing that phosphate is triply charged, common singly charged chlorinated species can be eliminated, as retention time interference is unlikely. For example, perchlorate is a singly charged chlorinated species likely present in bleach.[35] Further investigation is required to determine what the interference with phosphate could be since knowledge of indoor air impacts of bleach is limited.

4.5 Conclusions

The influence of indoor bleach use was probed for generation of reactive chlorine species. Bleach bubbling experiments proved that HCl emissions from floor bleaching observed in Chapter 3 were a result of secondary production rather than direct emission. It is possible that production is facilitated via acidification upon room exposure. Using an indirect measurement technique, chloride-containing aerosols were measured indoors for the first time. Maximum aerosol chloride levels were reached after one bleach application, contrary to initial expectations. Three consecutive bleach applications introduced too much water to the bleaching area, which hindered evaporation rates. Altering drying time allowed for observation of coarse mode particle deposition. Occurring between 30 and 60 minutes, deposition appears to be the primary loss pathway for coarse mode aerosols. For fine mode constituents, gaseous chlorinated species were dominant. The DFS coupled to the URG-3000ABC is not as selective as the method used in Chapter 3 and presents issues for understanding speciated reactive chlorine, but it can be used as a metric for studying trends in total reactive chlorine. It should be noted that integrated sampling is problematic when interpreting temporal trends, as well as sources and sinks of species of interest. An *in situ* measurement technique is required to gain more definitive speciation and temporal information. The ^{31}P NMR analysis resolved the confusion of phosphate presence in concentrated bleach. Elevated phosphate mixing ratios as a result of floor exposure to bleach are likely due to incorrect peak assignment, resulting in a false positive phosphate measurement. Further analysis is required to identify this unknown atmospheric constituent. This work has demonstrated that typical atmospheric measurement techniques can be deployed for indoor laboratory studies, however the major limitation is lack of speciation. While this study has enhanced knowledge on indoor air impacts caused by floor exposure to bleach, future work must include speciation of gaseous products.

4.6 References

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5 Conclusions & Future Work

This work has demonstrated four main points: the utility of fast-response, *in situ* measurement techniques for indoor environments, the impracticality of traditional atmospheric measurement techniques indoors, the influence of daily household tasks on indoor air quality, and the requirement for routine measurements indoors.

The CRDS instrument provided the first indoor measurement of HCl in real-time, allowing for identification of indoor sources. Identified indoor sources of HCl include surface application of bleach, chlorinated dishwasher detergent use, and cooking allium species. While sources have been elucidated, we were unable to determine whether sources were emitting HCl directly, or if HCl was formed via a secondary pathway. If HCl was formed indirectly, photolysis is a likely pathway. Photolabile chlorine species, emitted when bleach is used, could photolyzed in the test home to form HCl.

While non-invasive *in situ* measurement techniques are ideal for private dwellings, existing atmospheric measurement techniques can be used in laboratory settings. In terms of the medium volume sampler, the lack of speciation and temporal information are the main disadvantages for indoor studies. Nevertheless, we have demonstrated that atmospheric techniques can be deployed indoors to measure chloride-containing aerosols. This measurement is the first of its kind. By varying sampling time, coarse mode particle deposition was observed. Additionally, bleach headspace studies indicated that the chemistry of the bulk bleach solution differs from surface application chemistry.

Overall, results of this study indicate that household tasks performed by occupants enhance indoor chlorine chemistry and hence degrade air quality indoors. Despite these findings, further work is required to establish a more complete reactive chlorine inventory in indoor environments, especially those in non-commercial, occupied dwellings. In particular, future experiments should focus on gas-phase chlorine emissions from cooking experiments, allowing for better understanding of chlorine content of a variety of foods. Additionally, a more selective measurement technique is required for denuder and filter extract analyses. If the IC conductivity detector was replaced with a mass spectrometer, the "mystery" anion could be identified.

Enhanced knowledge of indoor chlorine chemistry will allow for a more accurate determination of associated health side effects. From a health aspect, it is important to establish appropriate measurement techniques for indoor environments, allowing for routine monitoring of indoor pollutants. Since humans spend approximately 90% of their lives indoors, indoor air quality monitoring and remediation is essential to maintain human health. It is important to note that to ameliorate indoor air quality, identification of the sources and sinks of all indoor pollutants is essential.

Appendix A – Supporting Information for Chapter 3

Section A1. Laboratory validation of HCl analyzer

A custom-built permeation tube containing concentrated HCl was kept at 60 °C in a thermostated aluminum block. The output of the permeation tube was collected in a 49.7 standard cubic centimetres per minute (sccm) flow of N_2 into a glass bubbler containing 1 mM KOH. Three separate samples were collected; with sampling times from 120 to 147 min. Bubbler contents were analyzed using ion chromatography (ICS-2100, ThermoScientific, Sunnyvale, CA, USA) coupled to suppressed (AERS 500) conductivity detection (DS6 heated conductivity cell). Calibration standards were prepared by dilution of a mixed anion standard (ThermoScientific, Dionex Seven-Anion II). Anions were separated according to the method of Place et al.[1] Briefly, the separation used ThermoScientific AG11 guard and analytical columns, as well as a KOH gradient mobile phase with a fixed flow rate of 1.5 mL min^{-1}. Volumes of 1.0 mL were injected and pre-concentrated using a concentrator column (TAC-ULP1, 5 x 23 mm).

The output of the permeation tube was diluted into a 2100 sccm flow of N_2 and directed through perfluoroalkoxy tubing and fittings (total residence time of 79 ms) into the cavity ring-down spectrometer (CRDS). A portion of the flow was directed through a bubbler to obtain relative humidity (RH) values of 0, 20, and 50 %. Measurements from the CRDS agreed with the offline IC measurement within acceptable error for all three RH conditions (Table A-1).

Table A-1. Results of laboratory validation of HCl CRDS analyzer using HCl permeation tube.

Permeation tube measurement type	HCl (pptv)	Standard deviation (pptv)	Decay response time (1/e, sec)
IC-quantified output	45	6	
CRDS (0 % RH)	45.900	0.008	25.6
CRDS (20 % RH)	45.51	0.02	28.3
CRDS (50 % RH)	41.082	0.007	31.9

A2. Experimental Setup

All experiments were performed in a room measuring approximately 71 m^3. Light sources inside the dwelling included light emitting diodes (LED), halogen-tungsten, and covered fluorescent. Air circulation and heating patterns were pre-set, allowing for any changes in data collection caused by heating to be properly elucidated. When the house warmed in the morning (7:30 am NDT), dramatic partitioning was observed. The temperature program is presented in Table A-2 below.

Table A-2. Experimental dwelling weekly temperature program

Weekdays	
Time (NDT)	Temperature (°C)
07:15 - 08:45	18.5
08:45 - 17:45	15.5
17:45 - 20:00	19.5
20:00 - 07:15	16.0

Weekends	
Time (NDT)	Temperature (°C)
07:30 - 20:30	19.5
20:30 - 07:30	16.0

It is important to note that the dwelling has radiative heating. Based on work by Isaacs et al., and typical normalize air leakage rates for homes in the United States, the air exchange rate (AER) was estimated to be 0.1 h^{-1} using the equation below:[2,3]

$$AER = 48\left(\frac{2.5}{H}\right)^{0.3}\frac{NL}{HF} \qquad (\mathbf{A1})$$

where H is ceiling height (8 ft), NL is normalized air leakage (0.49) and F is a scaling factor (when $F = 16$ is used, distributions fit US AER data).

A3. Ambient HCl Measurements

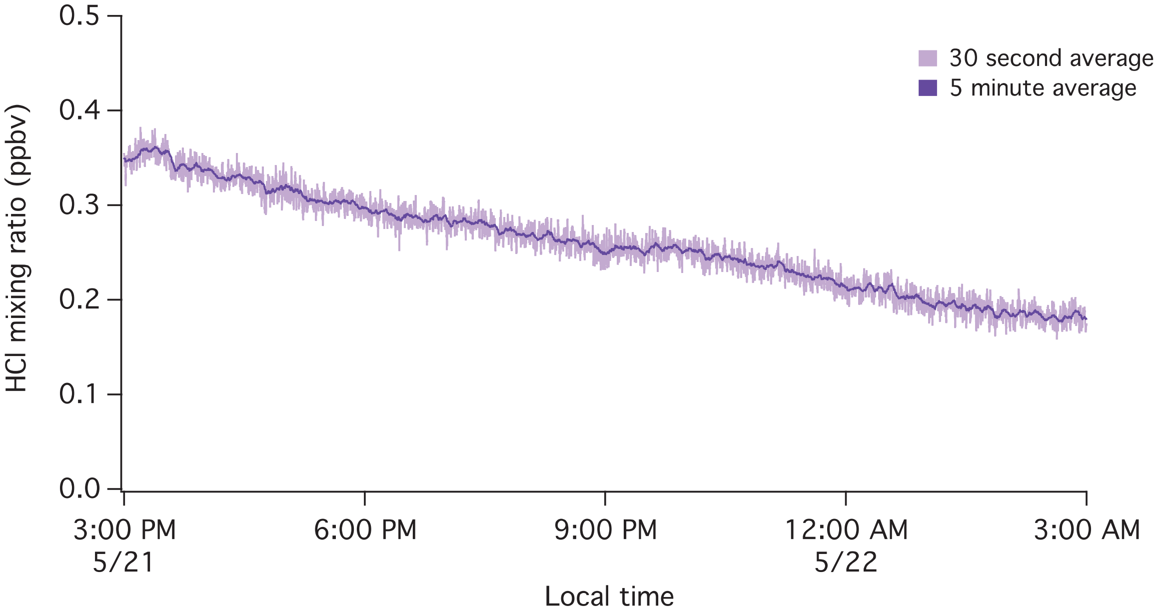

Figure A-1. Ambient measurement of HCl during a 12-hour period prior to bleach cleaning and cooking experiments. HCl mixing ratios are reported in units of parts per billion by volume.

A4. Radical Production Rate

Table A-3. Calculated Cl production rate constants for light sources in this study (top) and commonly found indoors (bottom).

	Rate constant (s^{-1})					
	At light source			1 m from light source		
Light source	Cl_2	HOCl	$ClNO_2$	Cl_2	HOCl	$ClNO_2$
LED	2.39×10^{-5}	3.36×10^{-7}	4.48×10^{-7}	4.29×10^{-7}	6.05×10^{-9}	8.06×10^{-9}
Halogen	1.08×10^{-4}	1.10×10^{-5}	1.10×10^{-5}	2.38×10^{-6}	2.41×10^{-7}	2.42×10^{-7}
Office fluorescent (covered)	9.23×10^{-6}	5.42×10^{-7}	3.06×10^{-7}	1.35×10^{-6}	7.91×10^{-8}	4.46×10^{-8}
Incandescent	9.24×10^{-5}	9.74×10^{-6}	1.04×10^{-5}	2.03×10^{-6}	2.14×10^{-7}	2.29×10^{-7}
Compact fluorescent	4.09×10^{-4}	3.86×10^{-5}	4.15×10^{-5}	6.13×10^{-6}	5.79×10^{-7}	6.22×10^{-7}
Fluorescent tube	2.03×10^{-4}	2.87×10^{-5}	4.36×10^{-5}	1.96×10^{-5}	2.78×10^{-6}	4.23×10^{-6}
Office fluorescence (uncovered)	1.68×10^{-4}	2.48×10^{-5}	3.85×10^{-5}	2.46×10^{-5}	3.64×10^{-6}	5.66×10^{-6}
Sunlight	1.83×10^{-4}	1.74×10^{-5}	1.06×10^{-5}	1.65×10^{-4}	1.57×10^{-5}	9.55×10^{-6}

Table A-4. Calculated Cl production rates from light sources commonly used in residences and businesses

	Cl Production Rate (molecules cm^{-3} s^{-1})[a]					
	At light source			1 m from light source		
Light source	Cl_2	HOCl	$ClNO_2$	Cl_2	HOCl	$ClNO_2$
LED	2.57×10^7	1.81×10^6	1.20×10^4	4.62×10^5	3.26×10^4	2.17×10^2
Halogen	1.16×10^8	5.89×10^7	2.96×10^5	2.56×10^6	1.30×10^6	6.50×10^3
Office fluorescent (covered)	9.93×10^6	2.91×10^6	8.22×10^3	1.45×10^6	4.26×10^5	1.20×10^3
Incandescent	9.94×10^7	5.24×10^7	2.80×10^5	2.19×10^6	1.15×10^6	6.17×10^3
Compact fluorescent	4.40×10^8	2.08×10^8	1.12×10^6	6.59×10^6	3.12×10^6	1.67×10^4
Office fluorescence (uncovered)	1.80×10^8	1.33×10^8	1.04×10^6	2.65×10^7	1.96×10^7	1.52×10^5
Sunlight	1.97×10^8	9.37×10^7	2.86×10^5	1.77×10^8	8.44×10^7	2.57×10^5

a) Cl precursor concentrations were chosen based on measured (Cl_2 and HOCl) and estimated ($ClNO_2$) mixing ratios from Wong et al.[4]

A5. References

(1) Place, B. K.; Young, C. J.; Ziegler, S. E.; Edwards, K. A.; VandenBoer, T. C. Passive sampling capabilities for ultra-trace quantitation of atmospheric nitric acid (HNO_3) in remote environments. *Submitted to Atmos. Environ.* **2018**.

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(3) Chan, W. R.; Nazaroff, W. W.; Price, P. N.; Sohn, M. D.; Gadgil, A. J. Analyzing a database of residential air leakage in the United States. *Atmos. Environ.* **2005**, *39*, 3445–3455 DOI: 10.1016/j.atmosenv.2005.01.062.

(4) Wong, J. P. S.; Carslaw, N.; Zhao, R.; Zhou, S.; Abbatt, J. P. D. Observations and impacts of bleach washing on indoor chlorine chemistry. *Indoor Air* **2017**, *27*, 1–23 DOI: 10.1111/ina.12402.