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Development and Validation of a New In-Situ Technique to Measure Total Gaseous Chlorine in Ambient Air

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Abstract

Total gaseous chlorine (TCl_g) measurements can improve our understanding of unknown sources of Cl to the atmosphere. Existing techniques for measuring TCl_g have been limited to offline analysis of extracted filters and do not provide suitable temporal information on fast atmospheric process. We describe high time-resolution in-situ measurements of TCl_g by combusting ambient air over a heated platinum (Pt) substrate coupled to a cavity ring-down spectrometer (CRDS). The method relies on the complete decomposition of TCl_g to release Cl atoms that react to form HCl, for which detection by CRDS has been shown to be fast and reliable. The method was validated using custom organochlorine permeation devices (PDs) that generated gas-phase dichloromethane (DCM), 1-chlorobutane (CB), and 1,3-dichloropropene (DCP). The optimal conversion temperature and residence time through the high-temperature furnace was 825 °C and 1.5 seconds, respectively. Complete conversion was indicated by the near unity orthogonal distance regression analysis slope (±σ) of 0.996 ± 0.012, 1.048 ± 0.006, and 1.027 ± 0.061 for DCM, CB, and DCP, respectively. Breaking these strong C-Cl bonds represents a proof of concept for complete conversion of all similar or weaker bonds that characterize all other TCl_g.

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We applied this technique to both outdoor and indoor environments and found reasonable comparisons in ambient background mixing ratios with the sum of expected HCl from known Cl species. We measured the converted TCl_g in an indoor environment during cleaning activities and observed varying levels of TCl_g comparable to previous studies. The method validated here is capable of measuring in-situ TCl_g and has a broad range of applications to make routine TCl_g measurements in a variety of applications.

1. Introduction

Chlorine (Cl) containing compounds in the atmosphere can impact air quality, climate, and health (Massin et al., 1998; Saiz-Lopez and Von Glasow, 2012; Simpson et al., 2015; White and Martin, 2010). Gaseous chlorinated compounds are either organic (e.g., dichloromethane, chloroform, and carbon tetrachloride) or inorganic (e.g., Cl_2, HCl, and $ClNO_2$), with inorganic chlorine being more reactive under most atmospheric conditions. In this work, total gaseous chlorine (TCl_g) refers to all gas-phase chlorine-containing species, including both inorganic and organic species. Impacts on air quality and climate are due to the high reactivity of atomic Cl produced by common atmospheric reactions (e.g., photolysis and oxidation) of Cl-containing compounds (Haskins et al., 2018; Riedel et al., 2014; Sherwen et al., 2016). The Cl cycle is important to atmospheric composition in the stratosphere and troposphere, affecting species including methane, ozone, and particles (both formation and composition), which influence air quality and climate (Riedel et al., 2014; Sherwen et al., 2016; Solomon, 1999; Young et al., 2014). High levels of some TCl_g species (e.g., Cl_2 and carbon tetrachloride) are known to be toxic (Unsal et al., 2021; White and Martin, 2010). The implications of many TCl_g species on human health are not well understood for low level exposure for extended periods of time. Potential health impacts of organic chlorinated compounds include hepatotoxicity,

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nephrotoxicity, and genotoxicity (Henschler, 1994; Unsal et al., 2021). Impacts of inorganic chlorinated species include the chlorination of squalene, a major part of human skin oils, by HOCl (Schwartz-Narbonne et al., 2019); respiratory irritation and airway obstruction by Cl_2 (White and Martin, 2010); and increased incidence of asthma and other chronic respiratory issues following exposure to chloramines (Massin et al., 1998).

Sources of Cl to the atmosphere are highly variable and depend on both direct emissions and indirect regional Cl activation chemistry (Finlayson-Pitts, 1993; Khalil et al., 1999; Raff et al., 2009). Direct emissions of TCl_g can come from numerous natural and anthropogenic activities such as, but not limited to, ocean and volcanic emissions, biomass burning, disinfection (i.e., household cleaning, pool emission, etc), use of solvents and heat transfer coolants, and incineration of chlorinated wastes (Blankenship et al., 1994; Butz et al., 2017; Fernando et al., 2014; Keene et al., 1999; Lobert et al., 1999; Wong et al., 2017). Activation of Cl is another source, occurring when atmospheric processes transform relatively unreactive chloride (Cl^-) into reactive gaseous chlorine (Cl_y), which will contribute to TCl_g. Understanding global levels of TCl_g is difficult due to complex emissions and chemistry. Our best estimates come from modelling studies combined with collaborative efforts to compose policy reports on halogenated substances, such as the World Meteorological Organization (WMO) Scientific Assessment of Stratospheric Ozone Depletion (WMO, 2018). Mixing ratio estimates of halogenated species from this report are summed from individual measurements (e.g., National Oceanic and Atmospheric Administration (NOAA) and Advanced Global Atmospheric Gases Experiment (AGAGE)). The WMO report includes flask (captured gas from clean air sectors) and in-situ measurements from field campaigns and routine sampling sites (e.g., CONvective Transport of Active Species in the Tropics (CONTRAST)) (Adcock et al., 2018; Andrews et al., 2016;

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72 Montzka et al., 2021; Pan et al., 2017; Prinn et al., 2018). In the most recent WMO report
73 (WMO, 2018), a decrease of 12.7 ± 0.9 pptv Cl yr^{-1} in total tropospheric Cl was determined for
74 Montreal Protocol-controlled substances (e.g., chlorofluorocarbons (CFCs) and
75 hydrochlorofluorocarbons (HCFCs)). The decrease in Montreal Protocol-controlled emissions
76 has been slightly offset by an increase in relatively short-lived substances (e.g., dichloromethane)
77 that are not controlled by the Montreal Protocol (WMO, 2018). Despite the emissions of these
78 regulated chlorinated species being relatively well-constrained, new sources for some of these
79 compounds have appeared in the recent past. For example, unexpected increases observed in
80 CFC-11 emissions suggested new unreported production (WMO, 2018). A new source of
81 chloroform was also recently identified and attributed to halide containing organic matter derived
82 from penguin excrement in the Antarctic tundra (Zhang et al., 2021). Atmospheric levels of TCl_g
83 will additionally be impacted by emission sources that are relatively poorly constrained,
84 including combustion and disinfection. Increasing levels of chlorinated species from known and
85 unknown pathways was observed in a recent ice core study, which estimated an increase of up to
86 170% of Cl_y (= BrCl + HCl + Cl + ClO + HOCl + $ClNO_3$ + $ClNO_2$ + ClOO + OClO + 2·Cl_2 +
87 2·Cl_2O_2 + ICl) from preindustrial times to the 1970s could be attributed to mostly anthropogenic
88 sources (Zhai et al., 2021).

89 Understanding TCl_g source and sink chemistry is not only important for the ambient
90 atmosphere but also for indoor environments. Uncertainty in sources and levels of chemicals,
91 including chlorine-containing compounds, indoors is related to heterogeneity in sources and
92 individual indoor environments, and the fact that relatively few studies have focused on indoor
93 chemistry compared to outdoor. The role of chlorinated species on indoor air quality has been
94 investigated in a few studies (Dawe et al., 2019; Doucette et al., 2018; Giardino and Andelman,

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1996; Mattila et al., 2020; Nuckols et al., 2005; Shepherd et al., 1996; Wong et al., 2017). Most studies have focused on cleaning with chlorine-based cleaners, in which HOCl and other inorganic compounds have been observed in the gas phase at high levels (Mattila et al., 2020; Wang et al., 2019; Wong et al., 2017). Some studies have reported the presence of organic chlorinated species such as chloroform and carbon tetrachloride above bleach cleaning solutions indoors (Odabasi, 2008; Odabasi et al., 2014), and chloroform has been observed during water-based cleaning activities, such as showering and clothing washing (Giardino and Andelman, 1996; Nuckols et al., 2005; Shepherd et al., 1996).

Constraining the Cl budget is critical to better understanding its contributions to climate, air quality, and human health. Robust total Cl measurements are useful because it is not feasible to routinely deploy individual measurements of the large number of Cl-containing compounds (Table S1). As described above, estimates of TCl_g from models and summed measurements have demonstrated gaps in our knowledge. It is therefore essential to have a method capable of measuring true TCl_g to explain discrepancies between model and measured estimates due to unknown species. Measurements of total elemental composition in the condensed phase, including total Cl, have been used for monitoring and managing both known and unknown compounds (Kannan et al., 1999; Kawano et al., 2007; Miyake et al., 2007c, 2007a, 2007b; Xu et al., 2003; Yeung et al., 2008). However, TCl_g methods have been limited to offline analysis of scrubbed sample gas (e.g., flue); these methods rely on multiple extraction steps and the application of condensed-phase total Cl analyses, such as combustion ion chromatography (Kato et al., 2000; Miyake et al., 2007a) or neutron activation analysis (Berg et al., 1980; Xu et al., 2006, 2007). Because offline techniques suffer from extraction uncertainties and do not have the temporal resolution to effectively probe fast source and sink chemistry in the atmosphere, in-situ

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measurements of total elemental gaseous composition have been developed for several elements (Hardy and Knarr, 1982; Maris et al., 2003; Roberts et al., 1998; Veres et al., 2010). For example, total nitrogen has been measured using Pt-catalyzed thermolysis coupled to online chemiluminescence detection (Stockwell et al., 2018). Using a similar approach, we describe here a method for TCl_g, where catalyzed thermolysis is coupled to a high time-resolution HCl cavity ring-down spectrometer (CRDS). This technique relies on the complete thermolysis of TCl_g, which yields chlorine atoms. These Cl atoms readily form HCl via hydrogen abstraction (R1), in this case from propane that is supplied in excess.

$$Cl\ (g) + C_3H_8\ (g) \rightarrow HCl\ (g) + C_3H_7\ (g) \qquad R1$$

The objectives of this paper are to: (i) Develop and validate an instrument capable of in-situ measurement of TCl_g through conversion to HCl and detection by CRDS; and (ii) demonstrate application of the technique to outdoor and indoor TCl_g measurements.

2. Materials and experimental methods

2.1. Chemicals

Commercially available reagents were purchased from Sigma-Aldrich: dichloromethane (DCM, HPLC grade, Oakville, Ontario, Canada), 1-chlorobutane (CB, 99.5%, Milwaukee, Wisconsin, USA), cis-1,3-dichloropropene (DCP, 97%, Milwaukee, Wisconsin, USA), and 52 mesh sized platinum catalyst (99.9 %, Milwaukee, Wisconsin, USA). Nitrogen (grade 4.8) and propane (C_3H_8, 12.7% in nitrogen, v/v) gas was from Praxair (Toronto, Ontario, Canada). Experiments used deionized water generated by a Barnstead Infinity Ultrapure Water System (Thermo Fisher Scientific, Waltham, Massachusetts, USA; 18.2 MΩ cm^{-1}). Clean air was generated by a custom-made zero-air generator.

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2.2. HCl and total chlorine (HCl-TCl) instrument

The main components of the HCl-TCl (Figure 1) are platinum catalyst mesh, a quartz glass flow tube, a split-tube furnace (Protégé Compact, 1100°C max temperature, Thermcraft incorporated, North Carolina, USA), and a CRDS HCl analyzer (Picarro G2108 Hydrogen Chloride Gas Analyzer). The platinum catalyst consisted of ~2 g platinum mesh with a total combined surface area of 134 cm^2. Sample gas was mixed with critical orifice-regulated (Lenox laser, Glen Arm, Maryland, USA, 30 psi; SS-4-VCR-2-50) propane gas (62 ± 6 standard cubic centimetres per minute (sccm)), provided in excess prior to introduction to the furnace to promote (R1). Propane does not fully combust at temperatures < 650 °C, which can lead to spectral interferences in the CRDS analyzer (Figure S1) and should only be added when temperatures exceed 650°C (Furlani et al., 2021). All lines and fittings were made of perfluoroalkoxy (PFA) unless stated otherwise. The mixing line carrying clean air dilution flows was controlled by a 10 L min^{-1} mass flow controller (MFC, GM50A, MKS instruments, Andover, Massachusetts, USA). The length of the sample gas tubing to the furnace was 0.6 m, and the transfer line between the furnace and CRDS was 0.2 m. The coupled CRDS can capture transient fast HCl formation processes on the timescale of a few minutes, limited by inlet effects. The CRDS collects data at 0.5 Hz, which was averaged to 30 sec for the purposes of this work. LODs were calculated as three times the Allan–Werle deviation in raw signal intensity when overflowing the inlet with zero air directed into the CRDS for ~ 10 h. The 30-sec limit of detection (LOD) is 18 pptv and well below expected HCl from TCl_g conversion (Furlani et al., 2021).

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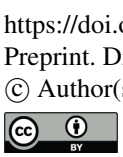

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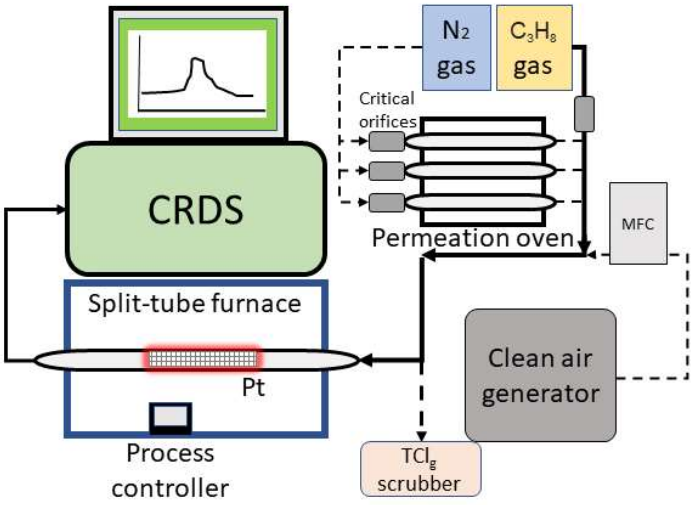

Figure 1. Sampling schematic showing the key components of the HCl-TCl coupled to the CRDS analyzer. Dashed lines indicate parts of the apparatus used only during validation. Not to scale.

2.3. Preparation of permeation devices (PDs)

Permeation devices (PDs) were prepared as follows: approximately 200 µL of DCM, CB, or DCP was pipetted into a 50 mm PFA tube (3 mm i.d. with 1 mm thickness), thermally sealed at one end and plugged at the other end with porous polytetrafluoroethylene (PTFE) (13 mm length by 3.17 mm o.d.). The polymers allow a consistent mass of standard gas to permeate at a given temperature and pressure. The method for temperature and flow control of the PDs is described in detail in Lao et al. (2020). Briefly, an aluminum block that was temperature-controlled (Omega™; CN 7823, Saint-Eustache, QC, Canada) using a cartridge heater (Omega™; CIR-2081/120V, Saint-Eustache, QC, Canada) housed the PD and was regulated to 30.0 ± 0.1 °C. Dry N_2 gas flowed through a PFA housing tube (1.27 cm o.d.) in the block that contained the PD. Stable flows of carrier gases passed through the housing tube in the oven were achieved using a 50 µm diameter critical orifice (Lenox laser, Glen Arm, Maryland, USA, 30 psi; SS-4-VCR-2-50) and were 120 ± 12, 99 ± 9.9 and 120 ± 12 sccm for DCM, CB, and DCP,

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177 respectively. Flows were measured using a DryCal Definer 220 (Mesa Labs, Lakewood,
178 Colorado, USA). The mass emission rate of each organochlorine from the PDs was quantified
179 gravimetrically over a period of approximately 4 weeks (mass accuracy ± 0.001 g). Mass
180 emission rates for each PD were determined as 640 ± 10, 240 ± 40, and $1.20\times10^4 \pm 0.02\times10^4$ ng
181 min^{-1} (n=3, ± 1σ) at 30 °C for DCM, CB, and DCP, respectively.

182 **2.4. HCl-TCl optimization**

183 Gas phase standards of DCM, CB, and DCP were used to test the conversion efficiency of
184 chlorinated compounds to form HCl. Bond dissociation energies for carbon-Cl bonds typically
185 range between 310 and 410 kJ mol^{-1} (Tables S1, S2). The split-tube furnace has a process
186 controller capable of increasing or decreasing temperature at a set °C min^{-1}, which allowed us to
187 identify the temperature at which enough energy was provided to break the bonds. By
188 introducing a consistent amount of each of the organochlorines, separately, to the HCl-TCl set
189 over a simple temperature ramping program we could monitor in real-time the conditions
190 necessary to break the bonds by measuring the formation of the resulting HCl. The conversion
191 temperature was determined when the measured HCl plateaued at 100% conversion.

192 To determine the optimal residence time in the quartz tube with the Pt catalyst, flows of
193 0.6–5.5 L min^{-1} containing DCM sample gas in clean air were tested yielding a range of
194 residence times between 0.5 and 4.5 sec in the furnace. Temperature remained constant at 825 °C
195 throughout the experiment, and a dilution flow of 4.0 L min^{-1} of clean air was added to the
196 sample flow exiting the furnace before introduction to the CRDS.

197 We tested the HCl-TCl conversion efficiency for 5 different mixing ratios of three
198 organochlorine PD standards (DCM, CB, and DCP) under three conditions: (1) both Pt catalyst
199 and added propane, (2) only Pt catalyst, and (3) only added propane. Each gas was tested

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200 individually under the same conditions; sample gas from PDs was mixed with propane and
201 immediately diluted into clean air using a 10 L min^{-1} MFC (GM50A, MKS instruments,
202 Andover, Massachusetts, USA). The dilution flows ranged from 2.2–9.0 L min^{-1}. The sampling
203 lines were the same lengths as stated previously. In this experiment, the CRDS flowrate of 2 L
204 min^{-1} was sufficient to give an optimal residence time of 1.5 sec through the HCl-TCl (see
205 Section 3.1). In all experiments the CRDS subsampled through the furnace from the main
206 transfer line and the excess gas was directed outdoors through a waste line containing a carbon
207 trap (Purakol, Purafil, Inc, Doraville, Georgia, USA).

208 **2.5. Outdoor air HCl-TCl measurements**

209 Outdoor air sampling was performed on August 6 and November 17–19, 2021 (Eastern
210 daylight time, EDT). The sampling site was the air quality research station located on the roof of
211 the Petrie Science and Engineering building at York University in Toronto, Ontario, Canada
212 (43.7738° N, 79.5071° W, 220 m above sea level). The HCl-TCl was co-located with a Campbell
213 scientific weather station paired with a cr300 datalogger. All inlet lines and fittings were made of
214 PFA unless stated otherwise. All indoor inlet lines and fittings were kept at room temperature (20
215 to 25 °C) while outdoor temperatures ranged from 25 to 28 °C on August 6, and 0 to 17 °C in
216 November. A mass flow controller (GM50A, MKS instruments, Andover, Massachusetts, USA)
217 regulated a sampling flow of 14.7 L min^{-1} using a diaphragm pump through a 2.4 m sampling
218 inlet (I.D. of 0.375") from outdoors. The outdoor air was pulled through a URG Teflon Coated
219 Aluminum Cyclone (URG Corporation, Chapel Hill, North Carolina, USA) with a 2.5 µm
220 particulate matter cut-off. The CRDS subsampled 2 L min^{-1} through the furnace off the main
221 inlet line, yielding a total inlet flow of 16.7 L min^{-1}. The apparatus had zero air overflow the inlet
222 1 hour prior to and after outdoor sampling. The CRDS sample flow passed first through a PTFE

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filter (2 µm pore size, 47 mm diameter, TISCH scientific, North Bend, Ohio, USA) and then two high efficiency particulate air (HEPA) filters contained within the CRDS outer cavity metal compartment heat-regulated to 45 °C. Instances of flagged instrument errors in the CRDS data during ambient observations were removed as standard practice in quality control procedures (Furlani et al., 2021).

2.6. Indoor air HCl-TCl and HOCl analyzer measurements

To test indoor applications of the HCl-TCl, a 1 m^2 area of laboratory floor was cleaned with a commercial spray bottle cleaner (1.84 % sodium hypochlorite w/w) and emissions were compared with an HOCl analyzer. The HOCl analyzer is a commercial instrument designed to quantify gaseous hydrogen peroxide (H_2O_2) using CRDS (Picarro PI2114 Hydrogen Peroxide Analyzer; Picarro Inc.). The instrument is also sensitive to HOCl due to similar absorbance wavelengths of their first overtone stretches in the near IR. The wavelengths monitored have been altered to selectively detect HOCl. Details on instrument calibration and validation are provided in [Stubbs et al., in prep].

The distance from the suspended 2 m inlet lines of both instruments to the floor was ~1 m. The flowrate through the furnace and inlet was the 2 L min^{-1} CRDS flowrate. The flowrate for the HOCl analyzer was 1 L min^{-1}. The sectioned off area was cleaned four times, spraying 32 times for each application using the commercial cleaner. Three of these events were measured using the HCl-TCl and HOCl analyzer, while one event was measured using the HCl CRDS only.

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3. Results and Discussion

3.1. HCl-TCl temperature and residence time optimization

We validated this method by testing conversion efficiency of organochlorines under different operating parameters and conditions. Testing all TCl_g species is not feasible, but by testing compounds that contain strong Cl-containing bonds, we infer at least equal efficacy of the system in the breakage of weaker Cl-containing bonds (Tables S1 and S2). We selected very strong Cl-containing bonds (i.e., alkyl chlorides) and used them as a proxy for compounds containing weaker Cl bonds; therefore, by demonstrating their complete conversion we set precedent for conversion of all TCl_g. The temperature of the furnace is a key factor in accomplishing complete thermolysis, and the minimum temperature of the furnace containing the Pt catalyst to break the C-Cl bonds in DCM was determined. A simple temperature ramping program was used to determine the breakthrough temperature. The temperature was increased at a rate of 2.7 °C min^{-1} starting at 300 °C and ending at 800 °C. The temperature breakthrough was found to be ~800 °C for the tested organochlorines (Figure S2).

Determining the optimal residence time of sample gas in the HCl-TCl is also essential for an optimized TCl_g conversion method. Using a temperature slightly above the observed breakthrough temperature of 800 °C determined above (825 °C), six residence times were tested with DCM, ranging from 0.5 to 4.5 seconds in the HCl-TCl (Figure 2). At each residence time the conversion efficiency was determined, where conversion efficiency was calculated as follows:

$$\text{Conversion efficiency} = \frac{\text{Measured } TCl_g}{\text{Expected } TCl_g} \times 100\ \% \qquad \text{E1}$$

The optimal residence time was ~1.5 seconds, corresponding to a conversion efficiency of 100.1 ± 0.1 %. The uncertainty in conversion efficiency measurements is the variability in the

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measured HCl signal for 30 minutes after a signal plateau was observed. The reported uncertainty does not include uncertainties in mixing, or turbulence induced surface effects, which we cannot quantify. When residence times were lower (i.e., sample gas traveled more quickly through the system) than 1.5 seconds, the conversion efficiencies were lower by 2 – 10 %, the measured HCl signal was more erratic, and it took longer to stabilize. When residence times were higher (i.e., sample gas traveled more slowly through the system) than 1.5 seconds, the conversion efficiencies were comparable (± 2 %), but the measured HCl suffered from longer equilibration times and therefore a slower response time due to increased surface effects of HCl after exiting the furnace. A residence time of 1.5 seconds was selected for all HCl-TCl experiments.

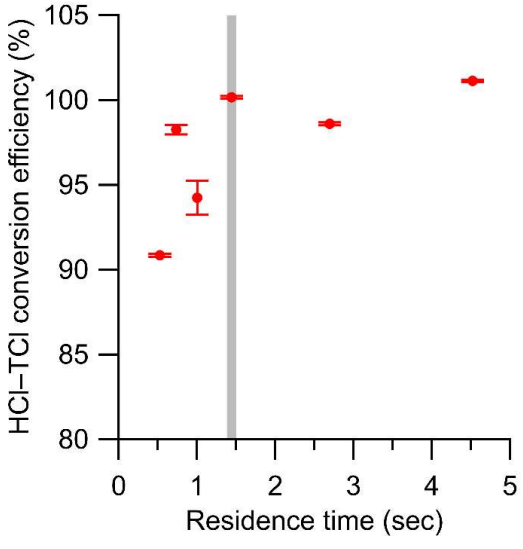

Figure 2. Conversion efficiency of DCM plotted against residence time in the HCl-TCl. Error bars represent the percent relative standard deviation of the measured HCl by the CRDS over ~30 minutes, after signal has plateaued. Grey vertical line denotes the selected residence time.

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3.2. HCl-TCl conversion efficiency

The conversion efficiency of each of the three chosen organochlorines using the HCl-TCl was tested at 5 different mixing ratios. The mixing ratios tested for DCM were 41, 54, 80, 111, and 165 ppbv. The mixing ratios tested for CB were 3.5, 4.6, 6.8, 9.5, and 14 ppbv. The mixing ratios tested for DCP were 121, 259, 468, 651, and 967 ppbv. All three showed good linearity and near 1:1 correlation with the HCl expected to be formed from the PD under standard operating conditions (Figure 3). Due to differences in PD emission rates, the values in Figure 3 are normalized to the highest mixing ratio to visualize comparisons more easily. Under condition (1) with both Pt and propane the HCl-TCl conversion was 99.6 ± 3.2, 104.8 ± 5.6, and 102.7 ± 7.8% for DCM, CB, and DCP, respectively (Table 1). From Figure 3 the comparison between expected and measured TCl_g is illustrated by near unity in the orthogonal distance regression slope (±σ), and was 0.996 ± 0.012, 1.048 ± 0.006, and 1.027 ± 0.061 for DCM, CB, and DCP, respectively. With only the Pt catalyst (condition (2)), the HCl-TCl conversion was 80.7 ± 0.4, 54.1 ± 1.6, and 54.3 ± 3.5% for DCM, CB, and DCP, respectively (Figure S3, Table 1). This result indicates the added hydrogen source (propane) is needed to promote R1. Although necessary in this laboratory scenario, some ambient conditions may be rich enough hydrogen-containing molecules that excess propane is not needed. However, providing propane in excess ensures the presence of an abundance of hydrogen atoms that can be readily abstracted by Cl atoms via R1. When the Pt catalyst was removed (condition (3)) the HCl-TCl conversion was 94.4 ± 4.6, 44.2 ± 0.9, and 41.7 ± 3.4% for DCM, CB, and DCP, respectively (Figure S3, Table 1). The observed dependence of the Pt catalyst indicates that a reactive surface is important to achieve complete thermolysis at 825 °C. The relatively higher conversion for DCM in the absence of the Pt catalyst or hydrogen source may be attributed to its lower bond dissociation energy (310 kJ mol^{-1}) compared to estimated bond dissociation energies for CB and DCP (CB

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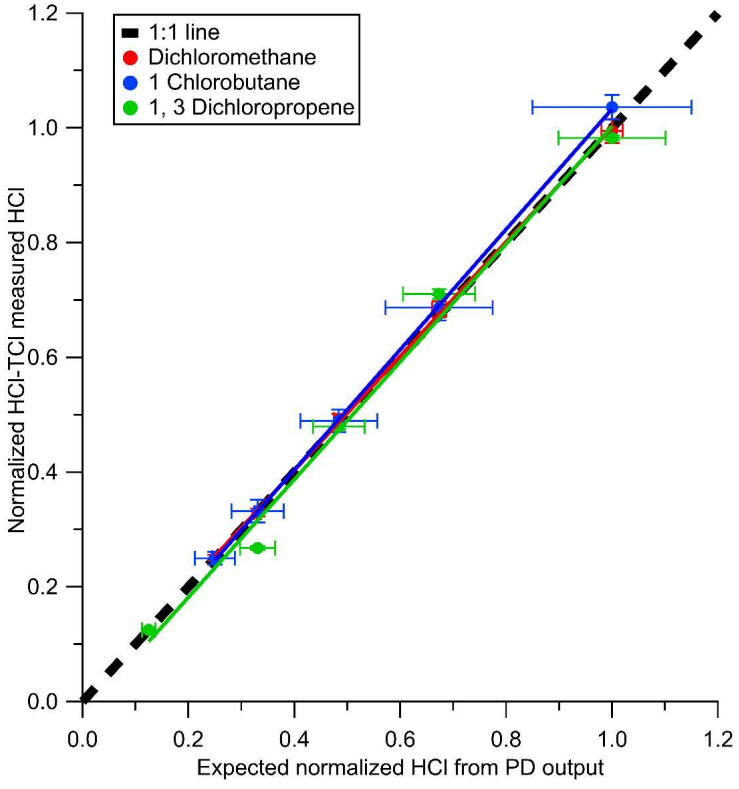

Figure 3. HCl measured by CRDS plotted against the expected HCl from HCl-TCl converted DCM (red), 1-chlorobutane (blue), and 1,3-dichloropropene (green) under condition (1). All values are normalized to the highest expected HCl concentration to better illustrate deviations from unity (dashed black line). Error bars on the y-axis represent 1σ in the HCl signal over 10 minutes. Error bars on the x-axis represent the uncertainty in the PD used to generate DCM.

Table 1. Conversion efficiency for tested organochlorine compounds under the three conditions (condition 1: both Pt and propane; condition 2: Pt only; condition 3: propane only). Conversion efficiency was determined from the orthogonal distance regression slope and ± σ and propagated error from individual PDs.

Tested TCl_g species	**Bond dissociation energy (kJ mol^{-1})**	**Conversion efficiency (%)**		
		Condition 1	Condition 2	Condition 3
Dichloromethane	310	99.6 ± 3.2	80.7 ± 2.4	94.4 ± 6.6
1-Chlorobutane	410	104.8 ± 5.6	54.1 ± 6.6	44.2 ± 5.9
1, 3-Dichloropropene	350	102.7 ± 7.8	54.3 ± 5.2	41.7 ± 5.1

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315 inferred from Table S2 (~410 kJ mol^{-1}), and DCP from tetrachloroethylene (350 kJ mol^{-1} in
316 Table S1)). It is possible that a higher temperature could lead to full conversion of TCl_g in the
317 absence of Pt catalyst; however, that was not explored in this study. The results for all three
318 compounds show that the HCl-TCl is capable of complete conversion of mono and
319 polychlorinated species on sp^3 and sp^2 carbons using the determined temperature and flow
320 conditions. The complete thermolysis of the strong C-Cl bond on the primary alkyl chloride (CB)
321 demonstrates the efficacy of the HCl-TCl. Breaking these relatively strong C-Cl bonds is a good
322 proof of concept for complete conversion of all bonds of similar or weaker bond energies that
323 characterize all other TCl_g. To practically validate the HCl-TCl under real-world conditions with
324 atmospherically relevant TCl_g mixtures and mixing ratios we deployed and configured the
325 system to measure outdoor and indoor air.

326 **3.3. HCl-TCl applications to outdoor air**

327 We deployed the system to measure ambient outdoor air, which we compare to the
328 expected TCl_g range from complete thermolysis of total Cl, expected to be between 3.3 and 19
329 ppbv (Table S1). A global background of approximately 2.6 ppbv is expected if only considering
330 the controlled very long-lived species (WMO, 2018, Table S1). The effects of particulate
331 chloride on TCl_g conversion were not explored here. The conditions required to convert chloride
332 to chlorine atoms is typically achieved using high energy photons or by electron beams, which
333 deliver energy much greater than possible in our system (Delahay, 1982; Kurepa and Belic,
334 1978). Thus, chloride, if it enters the system, is assumed to not be converted and measured. The
335 apparatus subsampled off a main inlet pulling ambient air (Figure 4) in summer (August 6) and
336 winter (November 17–19). The maximum, minimum, and mean of observed TCl_g on August 6
337 was 6.0, 3.4, and 4.2 ppbv, respectively, and was 3.5, 2.0, and 2.5 ppbv respectively from

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November 17–19. Measurements of HCl alone were not made during these periods but reported ranges of HCl mixing ratios for this sampling location from Furlani et al. (2021) and Angelucci et al. (2021) are typically below 110 pptv, with intermittent events up to 600 pptv. Mixing ratios of TCl_g were higher in the summer season when compared to the winter, suggesting a seasonal variance on the levels of TCl_g. The mean August TCl_g was 60% higher than the expected baseline of known long lived species. In contrast, levels of TCl_g in the during the winter were near the expected global baseline. We generally observed higher TCl_g during periods of lower relative humidity (RH), illustrated by the lower levels of TCl_g and high RH observed during November. There was no observed impact on observed TCl_g due to changes in wind direction or wind speed and likely indicates TCl_g is relatively well mixed. Our observed seasonal differences in TCl_g could have been caused, in part, by differences in meteorology (i.e., higher temperature in summer, higher relative humidity in winter) through changes in mixing and/or deposition. However, it seems likely that higher summer emissions, which have been observed for individual chlorinated species (Bin et al., 2014; Melymuk et al., 2012; Zhang et al., 2014) played an important role in the higher summertime TCl_g. Rapid temporal changes in TCl_g indicate the utility of an in-situ technique, which could be used to constrain sources and sinks of TCl_g.

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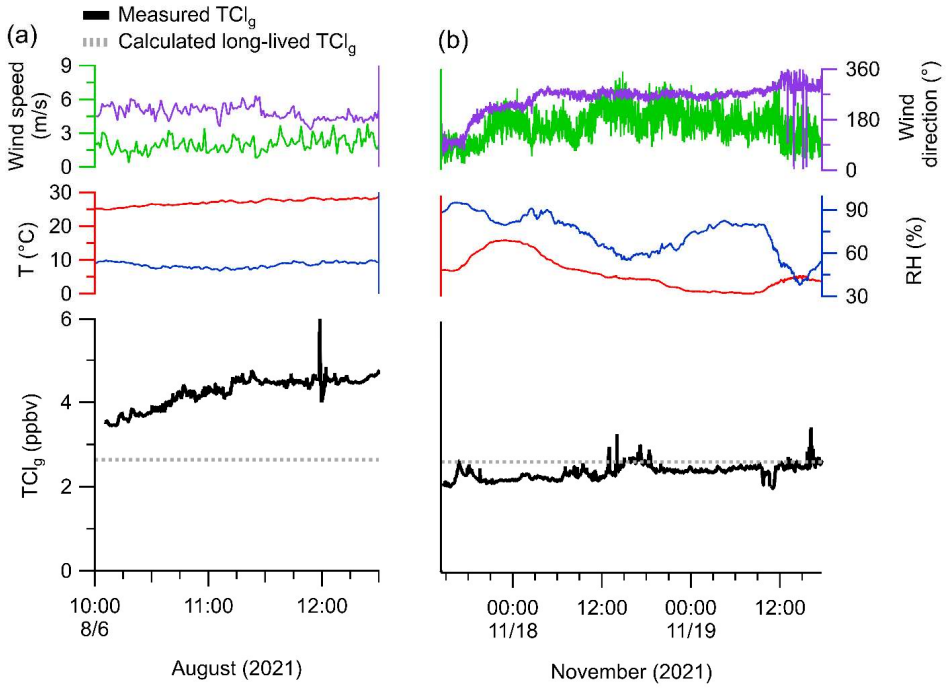

Figure 4. Monitoring meteorological conditions and TCl_g in outdoor air through HCl-TCl; (a) from 10 AM to 1 PM August 6, and (b) from 12 PM November 17 to 6 PM November 19. Grey dashed line represents the background mixing ratio for long-lived TCl_g species from Table S1.

3.4. HCl-TCl application to indoor cleaning

We applied a chlorine-based cleaning productfour times in a well-lit indoor room and measured TCl_g using the HCl-TCl and HOCl analyzer during three of the cleaning events (Figure 5). One cleaning experiment was done without the HCl-TCl and had a maximum of 370 pptv HCl. These levels are comparable to peak HCl levels of ~500 pptv observed from surface application of bleach (Dawe et al., 2019). Consistent with previous speciated measurements (Mattila et al., 2020; Wong et al., 2017), HCl, HOCl, and TCl_g levels increased rapidly over ~5 minutes after the application of the cleaning product. The maximum levels of TCl_g from HCl-TCl during application 1, 2, and 3, were 49.2, 80.0, and 69.7 ppbv, respectively. The maximum levels of HOCl from applications 1, 2, and 3, were 19.6, 24.2, and 16.8 ppbv, respectively,

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368 corresponding to 24 to 40 % of peak TCl_g and 14 to 22 % of integrated TCl_g. These TCl_g levels
369 were several times higher than observed in outdoor air (Section 3.3) and were within the range
370 expected from previous experiments (Table S1). The levels of chlorinated species observed
371 during bleaching events is variable, between 15 to 100s of ppbv (Mattila et al., 2020; Odabasi,
372 2008; Wang et al., 2019; Wong et al., 2017). By comparison, our highest observed mixing ratio
373 was 80 ppbv. Because the multiphase chemical processes involved in bleach application are
374 complex and poorly understood, it is difficult to compare levels between similar studies, given
375 that the underlying ambient conditions can be very different. In addition, physical parameters,
376 such as volume of cleaning solution applied, room size, and ventilation, can all affect observed
377 mixing ratios. For example, studies have observed that gaseous NH_3 partitioning into aqueous
378 bleach can produce large and variable amounts of chloramines, NH_2Cl, $NHCl_2$, and NCl_3
379 (Mattila et al., 2020; Wong et al., 2017). In our experiments, there was on average 82 ± 4 % of
380 integrated TCl_g for which we cannot account. Additional chlorinated species have previously
381 been observed to be emitted from surface bleaching include $ClNO_2$, NH_2Cl, $NHCl_2$, NCl_3, and
382 several chlorinated organics (Mattila et al., 2020; Odabasi, 2008; Wong et al., 2017) which likely
383 also contributed to our measured TCl_g. We observed that TCl_g decayed ~15% faster than the air
384 exchange rate (0.72 h^{-1}), indicating additional chemical loss pathways or surface interactions
385 (Figure S4). We observed a shorter lifetime of HOCl relative to TCl_g, which is consistent with
386 faster decay rates observed for HOCl and similar TCl_g species by Wong et. al., (2017). The
387 HOCl started decreasing after ~300 s had elapsed while the TCl_g levels were still increasing. This
388 suggests that reactions involving HOCl may have led to additional TCl_g species, which has been
389 observed in laboratory studies (Wang et al., 2019).

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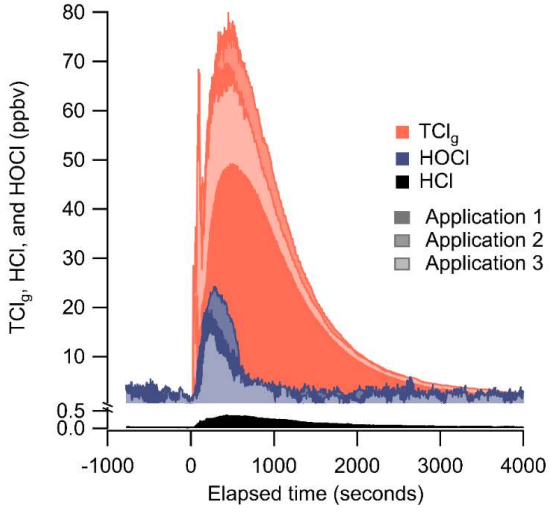
390 In-situ measurements of TCl_g could provide additional insight into sources of chlorinated
391 species to indoor environments by creating a total inventory from which the contributions of
392 individual measured species can be compared and used to elucidate unknown TCl_g levels and
393 mechanisms in real-time. Furthermore, several chlorinated species that have previously been
394 observed to be emitted from surface bleaching, including Cl_2, HOCl, $ClNO_2$, NH_2Cl, $NHCl_2$, and
395 NCl_3 (Mattila et al., 2020; Wong et al., 2017), have been measured by chemical ionization mass
396 spectrometry (CIMS). Quantifying chlorinated species using CIMS remains challenging due to
397 the required calibrations and difficulty in generating pure gas phase standards. It is therefore
398 desirable to have a technique such as the one proposed in this study that does not require
399 calibrations or knowledge of potential unknown TCl_g species. A combination of the two methods
400 would help constrain the total levels while still observing speciation for key TCl_g species.



401

402 **Figure 5.** HCl (black), HOCl (dark blue), and TCl_g (orange) observed during cleaning spray
403 events. Mixing ratios were background corrected prior to each cleaning event. Each subsequent
404 application of cleaner is illustrated by a lighter shade for HOCl and TCl_g.

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4. Conclusions

In this work we developed, optimized, validated, and applied a method capable of converting TCl_g into gaseous HCl amenable for CRDS detection. Our TCl_g measurement technique, the HCl-TCl, is composed of a platinum catalyst mesh inside a quartz glass flow tube all contained within a split-tube furnace. The temperature and flow rate were optimized at 825 °C and 1.5 seconds, respectively using DCM. These conditions were validated by the complete conversion of organochlorine compounds with strong C-Cl bonds. The HCl-TCl was used to measure TCl_g outdoors, observing a range of 2.0–6.0 ppbv. Levels were comparable to (winter) or exceeded (summer) the calculated background mixing ratio of long-lived TCl_g. We also applied the HCl-TCl to an indoor environment during commercial bleach spray cleaning events and observed varying increases in TCl_g (50–80 ppbv), which was in reasonable agreement with levels observed in previous speciated measurements. The agreement of HCl-TCl outdoor and indoor measurements with available bottom-up estimates indicates its efficacy under real-world scenarios. Rapid changes in TCl_g were observed in both outdoor and indoor environments indicating the utility of an in-situ technique to constrain the sources and chemistry of TCl_g, as well as its impact on air quality, climate, and health. We anticipate this approach could be used in several applications, including comparisons to speciated measurements and to further explore Cl reactivity and cycling with respect for indoor and outdoor TCl_g.

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Author contributions

TCF collected and analyzed the data. TCF and CJY conceived of and designed the experiments with input from PME and TFK. Funding was obtained by TFK and CJY. The manuscript was written by TCF with input from all authors.

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