We thank the Reviewer for their detailed and constructive comments. Please find our responses below in blue highlight, with changes to the manuscript indicated in **bold**.

General Comments:

Furlani et al. built a system to measure total gaseous chlorine (TClg) in ambient air. The system converts total chlorinated species to HCl using a heated platinum converter and measures the Cl content using an HCl analyzer. The conversion efficiency was validated using 3 organochlorine molecules. They examined the efficiency of the converter at different conditions, including conversion temperature and flow rates. They tested the system by applying it to measure both outdoor air and indoor air when cleaning with chlorine bleach. Overall, the paper is well written and presents a new method in measuring total chlorine in the atmosphere, which is valuable to the community. However, they should address the following major comments and a few specific comments.

Major comments:

The system was only evaluated for 3 organochlorine molecules, including dichloromethane, 1-chlorobutane, and 1,3-dichloropropene. These three molecules are relatively similar in structure, i.e., they are all chlorinated alkanes/alkenes. However, in the atmosphere, various chlorinated species (both organic and inorganic) are present, and they likely have different conversion efficiency to HCl in the system. They should conduct evaluation for more chlorinated species, e.g., chemicals with more diverse structures and properties. Furthermore, the authors should test the conversion efficiency for major inorganic chlorine species, such as Cl2, inorganic chloramines, HOCl, ClNO2, HCl, etc. These are major chlorinated species from indoor bleach cleaning (Mattila et al., 2020; Wong et al., 2017), and are important reactive chlorines in the ambient air.

We have added conversion efficiency tests to three aryl organochlorine compounds. Our conversion efficiency tests now encompass alkyl, allyl, and aryl organochlorines, with six separate compounds tested. The text and Table 1 have been updated to reflect these additional experiments. Unfortunately, calibration standards cannot be created for most inorganic Cl-containing compounds, which precludes our ability to test them in the HCl-TCl. This is an ongoing challenge in the community (e.g. Mattila et al., (2020)). However, we note that we did generate a mix of inorganic chlorinated species through the surface bleaching experiment. Thus, this set of measurements indicates that inorganic chlorinated species are being converted in the HCl-TCl.

> Section 2.4:
>
> **"We tested the HCl-TCl conversion efficiency for two different quantities of three chlorobenzenes (TrCB, TeCB, and PeCB). Due to their high boiling points, PDs of these compounds could not be prepared. Instead, small volumes of approximately 1 mM solutions of these compounds dissolved in toluene were directly introduced to the HCl-TCl while it was sampling room air. Room air measurements of HCl were consistently <100 pptv, therefore should not influence experimental measurements. With a short piece of tubing used as an inlet, 1 and 2 µL of each compound was injected onto the inner surface**

of the tubing, which was heated to ~100 °C with a heat gun to facilitate volatilization. The resulting signals were integrated over a time period of 2.5 hours to obtain the total quantity of HCl detected by the CRDS, which was used to calculate conversion efficiency. To account for uncertainties in peak integration, a high and low peak area boundary was determined, with the average peak area taken for each injection. Duplicates of each injected quantity were performed, except for 1 µL TrCB, which was performed in triplicate."

Section 3.2:

"To further validate the HCl-TCl, the conversion efficiency of three aryl chlorine compounds were tested under the final operating conditions (i.e., Condition 1, in the presence of both Pt and added propane). The TCl_g measured from the three aryl compounds was unity, within the uncertainty of the measurement (Table 1).

The results for all **six** compounds show that the HCl-TCl is capable of complete conversion of mono and polychlorinated species on sp^3 and sp^2 carbons using the determined temperature and flow conditions. The complete thermolysis of the strong**est** C-Cl bond on the primary alkyl chloride (CB) demonstrates the efficacy of the HCl-TCl. Breaking these relatively strong C-Cl bonds, **with consistent conversion efficiency across alkyl, allyl, and aryl C-Cl bonds**, is a good proof of concept for complete conversion of all bonds of similar or weaker bond energies that characterize all other TCl_g."

Table 1. Conversion efficiency for tested Cl-containing compounds under different conditions (both Pt and propane; Pt only; propane only).

Tested TCl_g species	Cl bond dissociation energy (kJ mol^{-1})	Conversion efficiency (%)		
		Pt and propane	**Pt only**	**Propane only**
Dichloromethane (DCM)[a]	310	99.6 ± 3.2	80.7 ± 2.4	94.4 ± 6.6
1-Chlorobutane (CB)[a]	410	104.8 ± 5.6	54.1 ± 6.6	44.2 ± 5.9
1, 3-Dichloropropene (DCP)[a]	350	102.7 ± 7.8	54.3 ± 5.2	41.7 ± 5.1
Trichlorobenzene (TrCB)[b]	**400**	**97.0 ± 19.9**		
Tetrachlorobenzene (TeCB)[b]	**400**	**90.6 ± 10.3**		
Pentachlorobenzene (PeCB)[b]	**400**	**90.2 ± 14.8**		

[a]Conversion efficiency was determined from the orthogonal distance regression slope and ± σ and propagated error from individual permeation devices.

[b]Conversion efficiency was determined directly by the quantity (mol) of HCl measured from liquid injections of 1 mM standards. The error represents ±σ of measurements for n = 5 (TrCB) or n = 4 (TeCB, PeCB) injections.

Another related question: How did the authors evaluate potential loss of reactive chlorine species on the inlet and instrument surfaces?

Inlet losses for most TCl_g compounds are relatively unimportant compared to potential inlet losses of the produced HCl. While inlet losses may reduce the slower response time, the heated surfaces minimise permanent losses to the inlet.

The introduction: In the current version, the authors focused on discussing the importance of chlorine in the atmosphere in the Introduction. They should focus more on the measurement techniques of chlorine, especially if there are any total chlorine measurement techniques in the literature, rather than the discussion on the importance of chlorine in the atmosphere. This helps to put the study in the right context, i.e., “development of measurement techniques for chlorine in ambient air”. Thus, I suggest the authors to rewrite the introduction of the paper.

We have provided a discussion of the existing techniques that have been used to understand total chlorine (see fourth paragraph of the introduction). These have primarily been focused on the condensed phase. We believe our discussion of chlorine chemistry and reactive chlorine in the atmosphere is necessary to motivate the development of our technique and, thus, should remain in the introduction.

Specific comments:

Can the instrument measure particle phase chlorine?

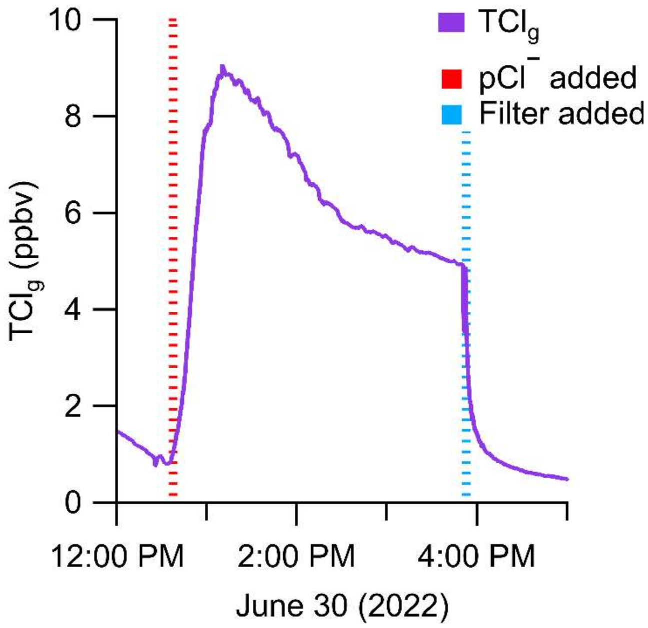
Yes, additional experiments were performed to access this and show that a filter before the HCl-TCl will reduce the affects. We have tested the impacts of particulate chloride and added relevant text to the manuscript, as well as a figure to the SI:

Text has been added to the methods (Section 2.4):

“To determine if there was any positive bias in the TClg, measurement from the conversion of particulate chloride (pCl^{-}), NaCl aerosols were generated by flowing 2 L min−1 of chlorine free zero air through a nebulizer containing a solution of 2% w/w NaCl in deionized water. The aerosol flow was then mixed with 1 L min−1 of chlorine free dry zero air to achieve a total flow of 3 L min−1, The HCl-TCl (2 L min-1) then sampled off this main mixing line. Chloride was added after monitoring background zero air levels. After ~3 hours of measuring the converted pCl^{-}, a PTFE filter (2 µm pore size, 47 mm diameter, TISCH scientific, North Bend, Ohio, USA) was added inline onto the inlet of the HCl-TCl.”

Text has been added to the results and discussion (Section 3.1):

“Conversion of particulate chloride (pCl^{-}) was observed to take place in the HCl-TCl (Figure S3), but once a filter was introduced the signal returned to background levels. Thus, to capture only gaseous TCl_g from samples that may contain particulate chloride, a particulate filter must be used.”



“Figure S3. Testing the impacts of added particulate chloride (pCl^-) to the HCl-TCl. TCl_g was monitored while pCl^- is added (red vertical dashed line) and then a Teflon filter is added (blue vertical dashed line) to the HCl-TCl inlet. Added filter showed complete reduction of the pCl^- signal.”

Line 143: what is the size of the platinum mesh? Would the amount of Pt catalyst and the size affect the conversion of Cl species? For example, does finer Pt provide more surface area for the conversion reaction?

We have provided the surface area within the text (134 cm^2). Had any conversion limitations be observed, one approach we would have taken would have been to increase the surface area.

Line 149: the authors mention that “all lines and fittings were made of perfluoroalkoxy (PFA)”. Were there any issues to use the PFA fittings and lines at high temperatures (~ 650 C-800 C)?

The Reviewer raises a good point. The insulation kept most heat within the furnace; most heat transfer occurred through the sample gas flow and left the transfer tubing and fittings warm to the touch, but never above manufacturer’s recommended working temperature.

Line 154: Please explain about “inlet effects”.

This has been revised.

> “The coupled CRDS can capture transient fast HCl formation processes on the timescale of a few minutes, **limited by the high adsorption activity of HCl on inlet surfaces (discussed further in Section 3.3).”**
>
> Additional information about inlet response time is now included in Section 3.3. and the SI:
>
> **“The response time of the instrument was assessed during experiments with DCM, CB, and CP. The time for the signal to decay after removal of the PDs was determined to 37**

% (1/e) and 90 % (t_{90}) of the maximum signal. The maximum time to achieve 1/e was 23 seconds, while the maximum time to achieve t_{90} was 189 seconds (Table S3). Given the high mixing ratios used to test the response times, we argue that under most conditions relevant to indoor and outdoor atmospheric chemistry, a sample integration time of one minute will minimize any time response effects. Data for outdoor and indoor sampling described in Sections 3.4 and 3.5 were therefore averaged to one minute."

Table S3. Response time of the HCl-TCl tested using for three chlorinated compounds.

Tested TCl_g species	Mixing ratio (ppbv)	Residence time (s)	$^1/_e$ (s)	t_{90} (s)
Dichloromethane (DCM)	164	1.5	23	189
1-Chlorobutane (CB)	14.5	1.5	14	162
1, 3-Dichloropropene (CP)	950	1.5	22	42

The method for quantifying response time is by calculating the e-folding response time (1/e) a 37% signal loss and t90 a 90% signal loss with respect to time in seconds.

Figure 1: Add flow rates in the diagram. Where is the inlet position? Please add the sampling inlet location.

The figure has been updated.

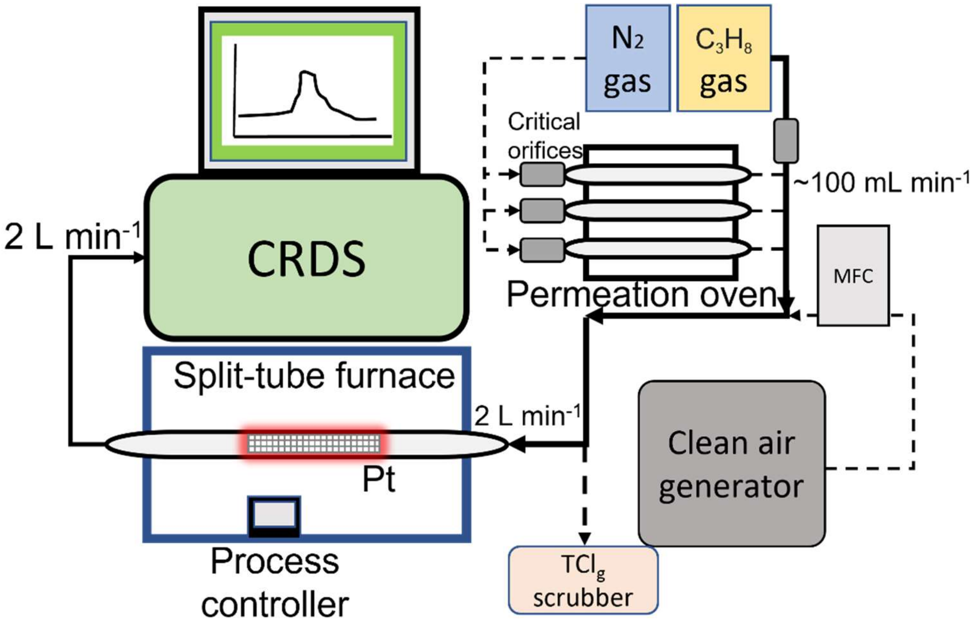


Figure 1. Sampling schematic showing the key components of the HCl-TCl coupled to the CRDS analyzer. Dashed lines indicate parts of the apparatus used only during validation. Not to scale.

Line 177: "DryCal Definer" should be "DryCal Defender"

This is an older model to the Defender and is called Definer.

Session 2.4: Was the HCl-TCl optimized for “inorganic chlorine species”?

Providing calibrated sources of inorganic chlorine species is an ongoing challenge for the measurement of these species (e.g. Mattila et al., (2020)). Our confidence in the conversion efficiency is further boosted by the lower bond dissociation energies of inorganic compared to organic chlorinated species. While we did not generate calibrated standards of inorganic chlorine to test in our system, we generated a mix of inorganic chlorinated species through the surface bleaching experiment. Studies have shown that the chlorinated species emitted from these processes are primarily inorganic. Thus, this set of measurements indicates that inorganic chlorinated species are being converted in the HCl-TCl.

Line 203: CRDs flowrate of 2 L/min. Is this flow a subflow of the inlet flow? It would be helpful to specify the flows in the diagram in Figure 1.

Updated

Line 214-215: If the inlet lines and fittings were maintained at 20-25 C, which is lower than outdoor temperatures (25-28 C), was there water condensation when the humid air from outdoors (at higher T) come indoors (at lower T) into the instrument?

There was no condensation observed in the lines during ambient sampling. We have removed the references to temperature during the ambient sampling period.

Other than conversion temperature and flow rate, did the authors test the effect of water/humidity on conversion efficiency? And how does RH influence the ambient measurement? This is important for ambient air measurement when RH varies.

Relative humidity would likely not play a factor in the conversion efficiency due to the fact that even 100% humidity at 25 °C will amount to negligible humidity at 825 °C, given the saturation temperature of water at 825 °C. Humidity effects have been studied previously in the group for the HCl measurement using CRDS, see Furlani et. al., (2021). In addition, a previously-described Pt-based total carbon method (Yang and Fleming, 2019), did not see any variation with RH in their Pt-based total carbon method.

Line 218: a URG Teflon coated aluminum cyclone was used to remove particles?

Changed to:

> “The outdoor air was pulled through a **2.5 µm particulate matter cut-off** URG Teflon Coated Aluminum Cyclone (URG Corporation, Chapel Hill, North Carolina, USA) **to remove larger particles.”**

Line 247: please define what is “strong Cl-containing bonds”. Is there a threshold for “strong” vs. “weak”?

The strong vs weak argument here is all just stronger or weaker relative to the HCl BDE the highest tested chlorine containing compound.

See changed text:

> "… of **relatively** weaker Cl-containing bonds (Tables S1 and S2)."

Line 254: what is "breakthrough temperature"?

Text added to clarify.

> "The temperature breakthrough was **observed when complete conversion of the expected HCl for tested compounds was stable after reaching the optimal temperature and was** found to be ~800 °C for the tested organochlorines (Figure S2)."

Line 256: how about the temperature for inorganic chlorine?

As described later on in the text, we did not test any inorganic chlorine directly in experiments. Unfortunately, generating pure standards for calibration of these compounds is difficult and/or impossible. From the relatively weaker Cl-containing bonds in inorganic species compared to the tested compounds, we infer these bonds will also break and yield good efficiency. We have indirect evidence that we had good conversion of inorganic Cl-containing chemicals through the measurement of the bleach application.

Line 283: these are very high levels. In the real ambient air, their mixing ratios are a lot lower.

Correct, but due to the difficulty of generating atmospherically relevant mixing ratios of these compounds using PDs we could not go any lower.

Line 289: why are some conversion efficiency >100%?

All measurements are within the uncertainty near 100%.

Line 290-292 are repeating the information on line 289

Text added for clarity:

> "… 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**), as the average conversion efficiency ± relative standard deviation**. From Figure 3 the comparison between expected and measured TClg is illustrated by near unity in the orthogonal distance regression slope (±1σ**, the error in the regression analysis**), and was 0.996 ± 0.012, 1.048 ± 0.0060, and 1.027 ± 0.061 for DCM, CB, and DCP, respectively."

Line 330: why not test the effect of particle chloride on TCl measurement? The authors could test with chloride containing salt particles.

See above explanation.

Line 331-332: "the conditions required to convert chloride to chlorine atoms ..." Do the authors mean organic or inorganic chloride?

This was deleted and replaced with the results to our particulate chloride measurements (see above).

Line 343: “in the during the”- delete “in the” or “during the”.

Changed.

Line 359: “productfour” should be “product four”

Changed.

Line 361 and 362: is it “pptv” or “ppbv”? Mattila and Wong et al. observed 100s ppb level, not ppt.

This was in pptv and was only in reference to work done by Dawe et. al. The following sentence that refers to Mattila and Wong is related to the fast increase and short-lived nature of the emitted chlorinated compounds.

Line 379: It is unclear what the authors meant - “there was on average 82% of integrated TCl for which we cannot account.”

This has been rephrased:

> “In our experiments, there was on average 82 ± 4 % of integrated TClg **that could not be accounted for by the HOCl measurement**.”

References

Furlani, T. C., Veres, P. R., Dawe, K. E., Neuman, J. A., Brown, S. S., VandenBoer, T. C., and Young, C. J.: Validation of a new cavity ring-down spectrometer for measuring tropospheric gaseous hydrogen chloride. Accepted, Atmos Meas Tech, 14, 5859–5871, https://doi.org/https://doi.org/10.5194/amt-2021-105, 2021.

Mattila, J. M., Lakey, P. S. J., Shiraiwa, M., Wang, C., Abbatt, J. P. D., Arata, C., Goldstein, A. H., Ampollini, L., Katz, E. F., Decarlo, P. F., Zhou, S., Kahan, T. F., Cardoso-saldan, F. J., Ruiz, L. H., Abeleira, A., Boedicker, E. K., Vance, M. E., and Farmer, D. K.: Multiphase chemistry controls inorganic chlorinated and nitrogenated compounds in indoor air during bleach cleaning, Environ Sci Technol, 54, 1730–1739, https://doi.org/10.1021/acs.est.9b05767, 2020.

Yang, M. and Fleming, Z. L.: Estimation of atmospheric total organic carbon (TOC) – paving the path towards carbon budget closure, Atmos Chem Phys, 19, 459–471, https://doi.org/10.5194/acp-19-459-2019, 2019.