



Supplement of

Development and validation of a new in situ technique to measure total gaseous chlorine in air

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Table S1. Summary of tropospheric mixing ratios, bond dissociation energies, and atmospheric lifetimes for Cl-containing species that are frequently measured and/or expected to be present in appreciable amounts in the troposphere. Calculated Cl_g values are also shown (determined as the observed mixing ratio multiplied by the number of Cl atoms in the molecule).

	Name	Chemical	Mixing ratio (pptv)		Atmospheric	Cl bond dissociati	Expected Clg (pptv)*	
		formula	Outdoor	Indoor	lifetime (years)	on energy (kJ mol ⁻¹)	Outdoor	Indoor**
	CFC-11	CCl ₃ F	228.9 ^a	-	52 ^a	305 ^b	686.8	686.8
	CFC-12	CCl_2F_2	514.6 ^a	-	102 ^a	344°	1029.3	1029.3
	CFC-13	CClF ₃	3.04 ^a	-	640 ^a	364°	3.04	3.04
	CFC-112	CCl ₂ FCCl ₂ F	0.42 ^a	-	63.6 ^a	-	1.68	1.68
C	CFC-112a	CCl ₃ CClF ₂	0.067^{a}	-	52 ^a	351°	0.27	0.27
CF	CFC-113	CCl ₂ FCClF ₂	71.3 ^a	-	93ª	-	214	214
	CFC-113a	CCl ₃ CF ₃	0.66 ^a	-	55 ^a	309°	1.98	1.98
	CFC-114	CClF ₂ CClF ₂	15.45 ^a	-	189 ^a	365°	30.9	30.9
	CFC-114a	CCl ₂ FCF ₃	1.04 ^a	-	105 ^a	-	2.08	2.08
	CFC-115	CC1F2CF3	8.58 ^a	-	540 ^a	365°	8.58	8.58
S	HCFC-22	CHClF ₂	239.1ª	-	11.9 ^a	360°	239.1	239.1
FC	HCFC-133a	CH ₂ ClCF ₃	0.39 ^a	-	4.6 ^a	360°	0.39	0.39
IC	HCFC-141b	CH ₃ CCl ₂ F	24.53 ^a	-	9.4 ^a	388°	49.1	49.1
	HCFC-142b	CH ₃ CClF ₂	22.6 ^a	-	18 ^a	410 ^c	22.6	22.6
Halon	Halon-1211	CBrClF ₂	3.6 ^a	-	16ª	-	3.6	3.6
Suo	Methyl chloride	CH ₃ Cl	555.9ª	-	0.9 ^a	339 ^b	555.9	555.9
	Carbon tetrachloride	CCl ₄	81 ^a	-	26 ^a	293 ^b	324	324
Irp	Methyl chloroform	CH ₃ CCl ₃	$2.7^{\rm a}$	-	5 ^a	368°	8.26	8.26
003	Dichloromethane	CH_2Cl_2	35.95 ^a	-	180 days ^a	310 ^b	71.9	71.9
lor	Chloroform	CHCl ₃	8.9 ^a	-	183 days ^a	311°	26.7	26.7
Ch	1,2-Dichloroethane	CH ₂ ClCH ₂ Cl	12.8 ^a	_	82 days ^a	-	25.6	25.6
	Tetrachloroethylene	C_2Cl_4	1.1 ^a	_	110 days ^a	350°	4.54	4.54

ganics	Hydrogen chloride	HC1	0-8000 ^d	0-700 ⁿ	1–2 days [15 days] ^j	432 ^b	0-8000 ^d	0–700
	Molecular chlorine	Cl ₂	0–20°	0–100 ppbv ⁱ	<1 min ^g	242 ^b	0–20 ^e	0–200 ppbv
	Hypochlorous acid	HOC1	0-60°	0–300 ppbv ⁱ	<1 min ^g	251 ^b	0–60 ^e	0–300 ppbv
nor	Chlorine monoxide	ClO	0–10 ^f	-	-	272 ^b	0–10 ^f	-
F	Nitrosyl chloride	ClNO	0-3 ^d	-	5–45 min ^k	159 ^b	0-3 ^d	_
	Nitryl chloride	ClNO ₂	0-8000 ^d	0–20 ppbv ⁱ	0.73–31 hrs ¹	142 ^b	0-8000 ^d	0–20 ppbv
	Chlorine nitrate	ClONO ₂	0–10 ^g	-	-	109 ^h	0–10 ^g	-
ramines	Monochloramine	NH ₂ Cl	-	0-60 ⁱ	-	251 ^b	-	0–60 ppbv
	Dichloramine	NHCl ₂	-	0–20 ppbv ⁱ	9.1 min ^m	280 ^b	-	0–40 ppbv
Chlc	Trichloramine	NCl ₃	-	0–4 pbbv ⁱ	5.3 min ^m	381 ^b	-	0–12 ppbv
			Expected TClg			3.3–19 ppbv**	3.3–640 ppbv***	

(a) Tropospheric mixing ratios from 2018 world meteorological organization scientific ozone depletion assessment (WMO (World Meteorological Organization), 2018). (b) Bond dissociation energies, data from (Huheey and Cottrell, 1958)). (c) Bond dissociation energies, data from (Shi et al., 2011). Tropospheric mixing ratios for inorganic chlorines are highly variable given local conditions, a conservative range is given. (d) Data from (Raff et al., 2009). (e) Data from (Lawler et al., 2011). (f) Data from (Platt and Janssen, 1995). (g) Data estimated from (Wang et al., 2019). (h) Data taken from (Casper et al., 1993). (i) Data taken from (Mattila et al., 2020), during an indoor air study; emissions after bleaching events represent a worst case scenario. (j) Lifetime with respect to deposition and lifetime with respect to OH in brackets, Data taken from (Crisp et al., 2014). (k) Data taken from (Keene et al., 1990). (l) lifetime ranges with solar zenith angle, data taken from (Ganske et al., 1992). (m) Lifetimes calculated from first order photolysis decay rates in a well lit room, data taken from (Wong et al., 2017). (n) This study during bleaching event (see Section 5.3.4.).(*) Expected TCl_g mixing ratio represents the total number of Cl atom yielded from complete conversion. (**) Indoor levels of CFCs, HCFCs, and chlorocarbons are assumed to be the same as outdoor (***) Upper estimates are highly depended on local conditions and direct emissions.

Carbon Type	Dissociation Energy (kJ/mol)
Primary	~410
Secondary	~400
Tertiary	~380

Table S2. Typical bond dissociation energies for sp³ alkyl chlorides (Wade, 1999).

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)	t90 (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.

DCM mixing ratio	CB mixing ratio	DCP mixing ratio	
(ppbv)	(ppbv)	(ppbv)	
41± 0.6	3.5 ± 0.6	121 ± 2	
54 ± 0.8	4.6 ± 0.8	259 ± 4	
80 ± 1	6.8 ± 1	468 ± 8	
111 ± 2	9.5 ± 2	651 ± 11	
165 ± 3	14 ± 2	967 ± 16	

Table S4. Summary of mixing ratios used for HC1-TC1 conversion efficiency experiments.



Figure S1. TCl_g signal derived at different temperatures from thermolysis of DCM. High signal related to spectral interference of added propane at low temperatures (<650 °C). TCl_g (red) and temperature (black) during a typical ramping program. Propane disconnected immediately after interference observed to preserve instrument integrity.



Figure S2. Monitoring DCM conversion from 300–800 °C. Flow rate was ~2 L min⁻¹, DCM mixing ratio was 165 ± 3 ppbv in chlorine free zero air. Propane and Pt catalyst were added as described in Section 2.2.



Figure S3. Testing the impacts of added particulate chloride (pCl^{-}) on HCl-TCl measurements. TCl_g was monitored under a flow of Cl-free air, while pCl^{-} was added to the air stream (red vertical dashed line), and after a Teflon filter was placed in front of the HCl-TCl inlet (blue vertical dashed line). Adding the filter showed complete reduction of the pCl^{-} signal.



Figure S4. HCl-TCl measured HCl plotted against the expected HCl from converted DCM (A), 1,3-dichloropropene (B), and Chlorobutane (C) under three conditions. HCl-TCl conversion is shown for both Pt and propane added (black), with only Pt (dark grey), and only propane (light grey). Error bars on the y-axis represents 1σ in the HCl signal for 10 minutes. Error bars on the x-axis represent the error in the PD.



Figure S5. (A) Conditional Probability Function (CPF) analyses of measured TCl_g, presented in as a polar plot, which displays the number of events when the concentration was greater than the 95th percentile as a function of both wind speed and direction. As a result, CPF polar plots present the probability that high concentrations of a pollutant came from a particular wind direction and speed and can give information on the contributions of local and regional sources (Uria-Tellaetxe and Carslaw, 2014). Polar plots were plotted in R using the openair function (Carslaw and Ropkins, 2012). (B) Map of sampling site (red star) and three facilities (purple dots) within 20 km of the site in the S-SW direction that reported release of 75 - 2700 kg of Cl-containing species to air in 2021 to the Canadian National Pollutant Release Inventory (National Pollutant Release Inventory, 2022).



Figure S6. Air exchange rate (dashed black), HOCl (dark blue), and TCl_g (orange) observed during cleaning spray events. Mixing ratios were background corrected to levels prior to each cleaning event. Each subsequent application of cleaner is illustrated by a lighter shade for HOCl and TCl_g . Values all normalized to the highest value.

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