

Supporting information for

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

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Table S1. Summary of observed mixing ratios, bond dissociation energies, and atmospheric lifetimes for most chlorinated species expected to be present in appreciable amounts in the troposphere.

Chemical formula	Observed mixing ratio (pptv)		Atmospheric lifetime (years)	Cl-containing bond dissociation energy (kJ mol ⁻¹)	Expected TCl _g (pptv)*	
	Outdoor	Indoor			Outdoor	Indoor**
Chlorofluorocarbons (CFCs)						
CCl ₃ F (CFC-11)	228.9 ^a	-	52 ^a	305 ^b	686.8	686.8
CCl ₂ F ₂ (CFC-12)	514.6 ^a	-	102 ^a	344 ^c	1029.3	1029.3
CClF ₃ (CFC-13)	3.04 ^a	-	640 ^a	364 ^c	3.04	3.04
CCl ₂ FCCL ₂ F (CFC-112)	0.42 ^a	-	63.6 ^a	-	1.68	1.68
CCl ₃ CClF ₂ (CFC-112a)	0.067 ^a	-	52 ^a	351 ^c	0.27	0.27
CCl ₂ FCClF ₂ (CFC-113)	71.3 ^a	-	93 ^a	-	214	214
CCl ₃ CF ₃ (CFC-113a)	0.66 ^a	-	55 ^a	309 ^c	1.98	1.98
CClF ₂ CClF ₂ (CFC-114)	15.45 ^a	-	189 ^a	365 ^c	30.9	30.9
CCl ₂ FCF ₃ (CFC-114a)	1.04 ^a	-	105 ^a	-	2.08	2.08
CClF ₂ CF ₃ (CFC-115)	8.58 ^a	-	540 ^a	365 ^c	8.58	8.58

Hydrochlorofluorocarbons (HCFCs)						
CHClF ₂ (HCFC-22)	239.1 ^a	-	11.9 ^a	360 ^c	239.1	239.1
CH ₂ ClCF ₃ (HCFC-133a)	0.39 ^a	-	4.6 ^a	360 ^c	0.39	0.39
CH ₃ CCl ₂ F (HCFC-141b)	24.53 ^a	-	9.4 ^a	388 ^c	49.1	49.1
CH ₃ CClF ₂ (HCFC-142b)	22.6 ^a	-	18 ^a	410 ^c	22.6	22.6
Halons						
CBrClF ₂ (Halon-1211)	3.6 ^a	-	16 ^a	-	3.6	3.6
Chlorocarbons						
CH ₃ Cl (Methyl chloride)	555.9 ^a	-	0.9 ^a	339 ^b	555.9	555.9
CCl ₄ (Carbon tetrachloride)	81 ^a	-	26 ^a	293 ^b	324	324
CH ₃ CCl ₃ (Methyl chloroform)	2.7 ^a	-	5 ^a	368 ^c	8.26	8.26
CH ₂ Cl ₂ (Dichloromethane)	35.95 ^a	-	180 days ^a	310 ^b	71.9	71.9
CHCl ₃ (Chloroform)	8.9 ^a	-	183 days ^a	311 ^c	26.7	26.7
CH ₂ ClCH ₂ Cl (1,2-Dichloroethane)	12.8 ^a	-	82 days ^a	-	25.6	25.6
C ₂ Cl ₄ (Tetrachloroethylene)	1.1 ^a	-	110 days ^a	350 ^c	4.54	4.54
Inorganic chlorine						
HCl	0–8000 ^d	0–700 ⁿ	1–2 days [15 days] ^j	432 ^b	0–8000 ^d	0–700
Cl ₂	0–20 ^e	0–100 ppbv ⁱ	<1 min ^g	242 ^b	0–20 ^e	0–200 ppbv
HOCl	0–60 ^e	0–300 ppbv ⁱ	<1 min ^g	251 ^b	0–60 ^e	0–300 ppbv
ClO	0–10 ^f	-	-	272 ^b	0–10 ^f	-
ClNO	0–3 ^d	-	5–45 min ^k	159 ^b	0–3 ^d	-

ClNO ₂	0–8000 ^d	0–20 ppbv ⁱ	0.73–31 hrs ^l	142 ^b	0–8000 ^d	0–20 ppbv
ClONO ₂	0–10 ^g	-	-	109 ^h	0–10 ^g	-
Chloramines						
NH ₂ Cl	-	0–60 ⁱ	-	251 ^b	-	0–60 ppbv
NHCl ₂	-	0–20 ppbv ⁱ	9.1 min ^m	280 ^b	-	0–40 ppbv
NCl ₃	-	0–4 pbbv ⁱ	5.3 min ^m	381 ^b	-	0–12 ppbv
Expected TCl _g					3.3–19 (2.6) ppbv ^{**}	3.3–640 ppbv ^{***}

(a) Tropospheric mixing ratios from 2018 world meteorological organization scientific ozone depletion assessment (World Meteorological Organization et al., 2019). (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., (2017b). (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. Green shaded longer-lived compounds included in calculated background TCl_g.

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

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

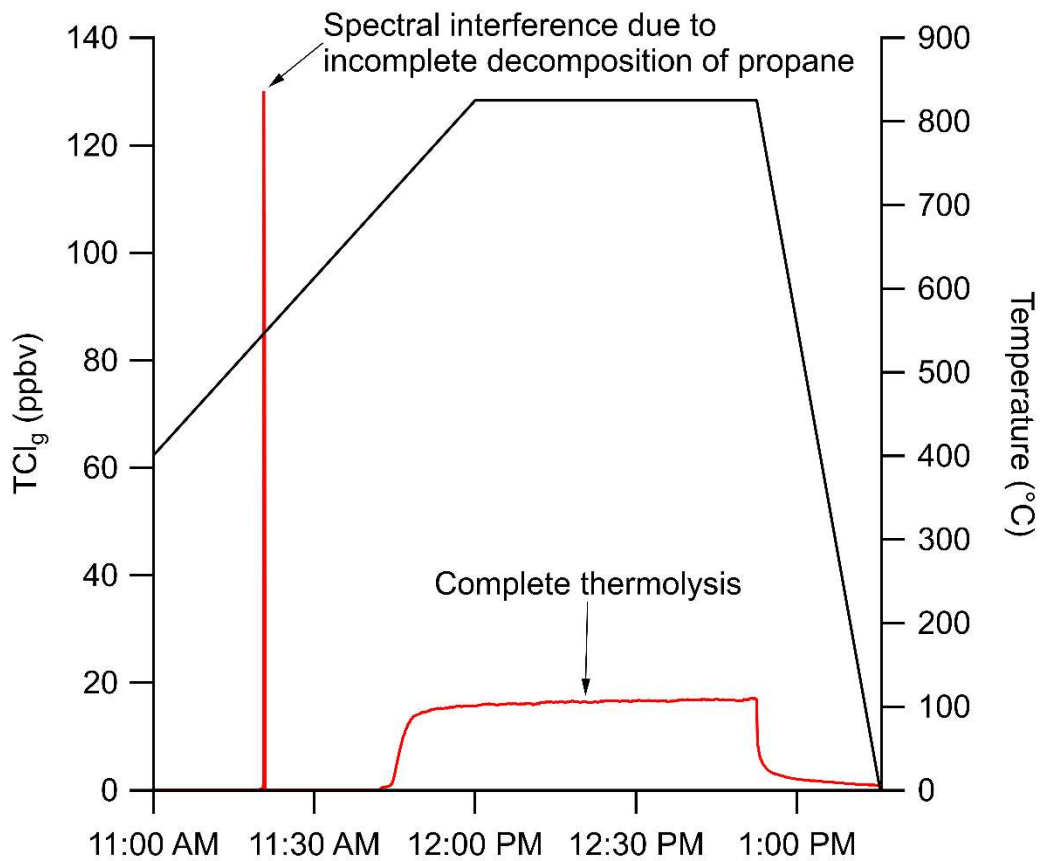


Figure S1. High spectral interference of added propane at low temperatures (<650 °C). TCl_g (red) and temperature (black) during a typical ramping program. Propane disconnected immediately after interference observed to preserve cavity health.

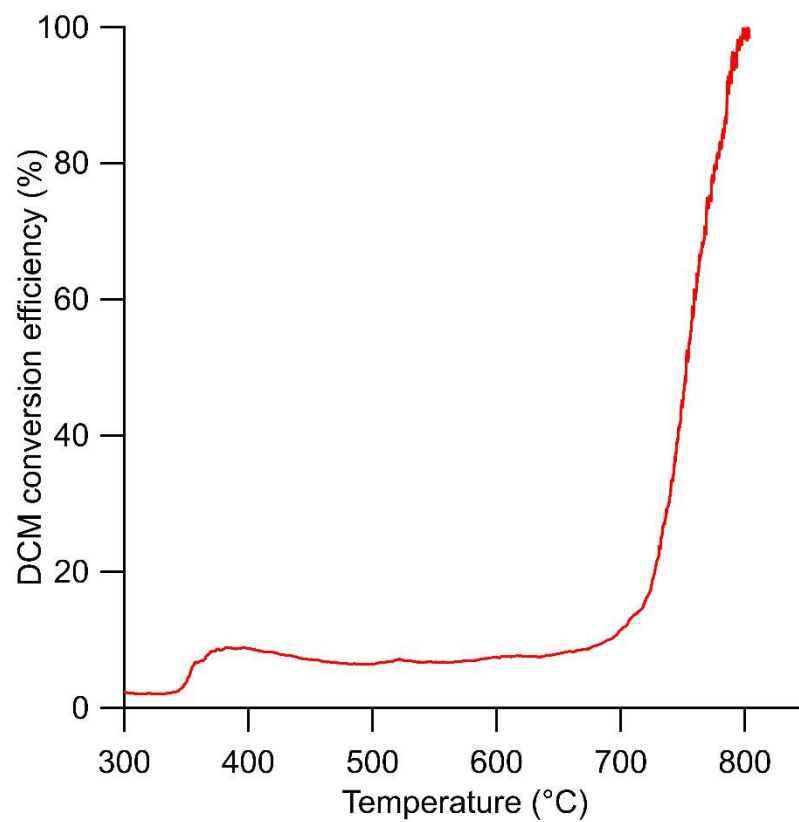


Figure S2. Monitoring DCM conversion from 300–800 °C.

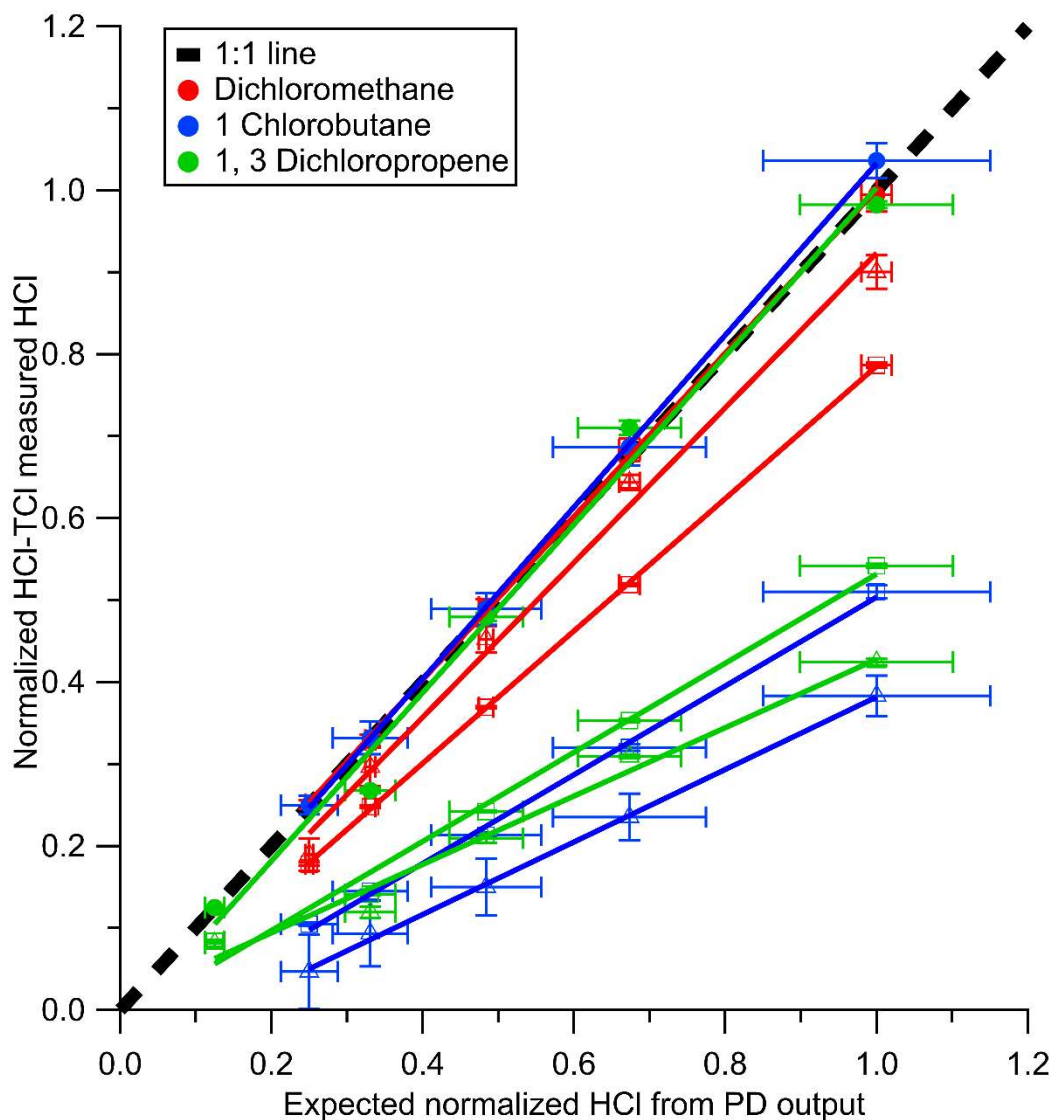


Figure S3. HCl measured by CRDS plotted against the expected HCl from HCl-TCl converted DCM (red), 1 Chlorobutane (blue), and 1, 3 Dichloropropene (green) under three conditions. All values are normalized to the highest expected HCl concentration to better illustrate deviations from unity (dashed black line). HCl-TCl conversion is shown for both Pt and propane added (condition (1), solid circles), with only Pt (condition (2), hollow squares), and only propane (condition (3), hollow triangles). 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 used to generate DCM.

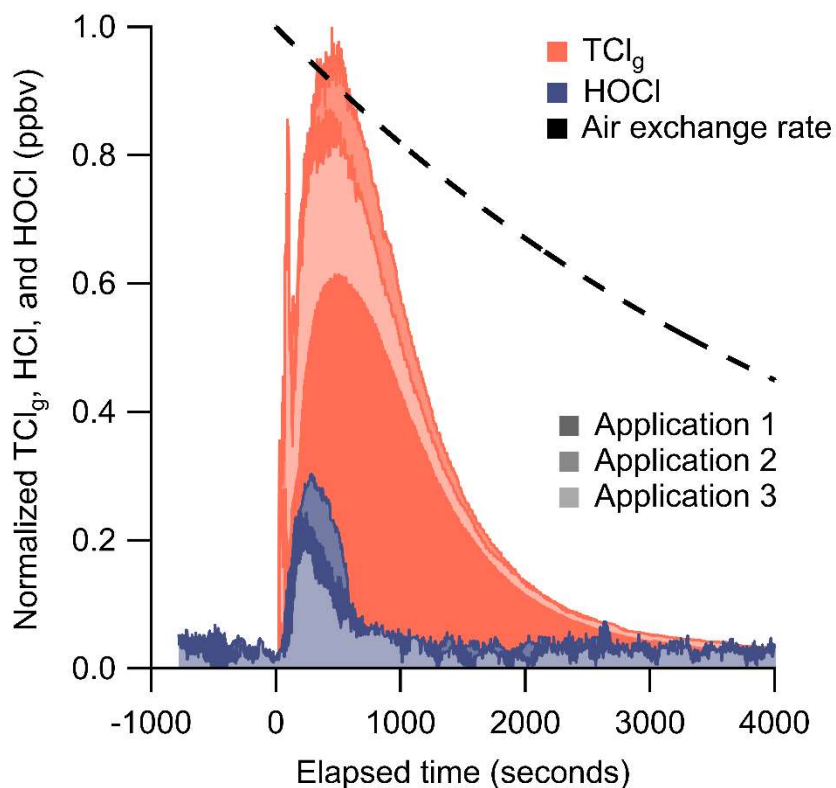


Figure S4. Air exchange rate (dashed black), HOCl (dark blue), and TCl_g (orange) observed during cleaning spray events. Mixing ratios were background corrected to levels prior to each cleaning event. Each subsequent application of cleaner is illustrated by a lighter shade for HOCl and TCl_g. Values all normalized to the highest value.

S.1 References

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