

Supplement of Geosci. Model Dev., 8, 3151–3162, 2015
<http://www.geosci-model-dev.net/8/3151/2015/>
doi:10.5194/gmd-8-3151-2015-supplement
© Author(s) 2015. CC Attribution 3.0 License.



Supplement of

Development of a chlorine chemistry module for the Master Chemical Mechanism

L. K. Xue et al.

Correspondence to: L. K. Xue (xuelikun@sdu.edu.cn)

The copyright of individual parts of the supplement might differ from the CC-BY 3.0 licence.

Table S1. Summary of the organic reactions existing in the MCM to address Cl chemistry ^a

Reactions	<i>k</i> (cm ³ molecules ⁻¹ s ⁻¹)
Cl + CH ₄ = CH ₃ O ₂ + HCl	6.6×10 ⁻¹² ×exp (-1240/T)
Cl + C ₂ H ₆ = C ₂ H ₅ O ₂ + HCl	8.3×10 ⁻¹¹ ×exp (-100/T)
Cl + C ₃ H ₈ = IC ₃ H ₇ O ₂ + HCl	0.43×1.4×10 ⁻¹⁰ ×exp (75/T)
Cl + C ₃ H ₈ = NC ₃ H ₇ O ₂ + HCl	0.59×1.4×10 ⁻¹⁰ ×exp (-90/T)
Cl + NC ₄ H ₁₀ = NC ₄ H ₉ O ₂ + HCl	0.44×2.05×10 ⁻¹⁰ ×exp (-120/T)
Cl + NC ₄ H ₁₀ = SC ₄ H ₉ O ₂ + HCl	0.59×2.05×10 ⁻¹⁰ ×exp (55/T)
Cl + IC ₄ H ₁₀ = IC ₄ H ₉ O ₂ + HCl	0.564×1.43×10 ⁻¹⁰
Cl + IC ₄ H ₁₀ = TC ₄ H ₉ O ₂ + HCl	0.436×1.43×10 ⁻¹⁰
Cl + NC ₅ H ₁₂ = PEA ₂ O ₂ + HCl	0.222×2.80×10 ⁻¹⁰
Cl + NC ₅ H ₁₂ = PEBO ₂ + HCl	0.558×2.80×10 ⁻¹⁰
Cl + NC ₅ H ₁₂ = PECO ₂ + HCl	0.220×2.80×10 ⁻¹⁰
Cl + IC ₅ H ₁₂ = IPEA ₂ O ₂ + HCl	0.408×2.20×10 ⁻¹⁰
Cl + IC ₅ H ₁₂ = IPEBO ₂ + HCl	0.342×2.20×10 ⁻¹⁰
Cl + IC ₅ H ₁₂ = IPECO ₂ + HCl	0.250×2.20×10 ⁻¹⁰
Cl + NEOP = NEOPO ₂ + HCl	1.11×10 ⁻¹⁰
Cl + NC ₆ H ₁₄ = HEXA ₂ O ₂ + HCl	0.182×3.40×10 ⁻¹⁰
Cl + NC ₆ H ₁₄ = HEXBO ₂ + HCl	0.457×3.40×10 ⁻¹⁰
Cl + NC ₆ H ₁₄ = HEXCO ₂ + HCl	0.361×3.40×10 ⁻¹⁰
Cl + M ₂ PE = M ₂ PEA ₂ O ₂ + HCl	0.321×2.90×10 ⁻¹⁰
Cl + M ₂ PE = M ₂ PEBO ₂ + HCl	0.269×2.90×10 ⁻¹⁰
Cl + M ₂ PE = M ₂ PECO ₂ + HCl	0.213×2.90×10 ⁻¹⁰
Cl + M ₂ PE = M ₂ PEDO ₂ + HCl	0.197×2.90×10 ⁻¹⁰
Cl + M ₃ PE = M ₃ PEA ₂ O ₂ + HCl	0.317×2.80×10 ⁻¹⁰
Cl + M ₃ PE = M ₃ PEBO ₂ + HCl	0.530×2.80×10 ⁻¹⁰
Cl + M ₃ PE = M ₃ PECO ₂ + HCl	0.153×2.80×10 ⁻¹⁰
Cl + M ₂ 2C ₄ = M ₂ 2C ₄ 3O ₂ + HCl	0.461×1.71×10 ⁻¹⁰
Cl + M ₂ 2C ₄ = M ₃ 3C ₄ O ₂ + HCl	0.386×1.71×10 ⁻¹⁰
Cl + M ₂ 2C ₄ = M ₂ 2C ₄ O ₂ + HCl	0.154×1.71×10 ⁻¹⁰
Cl + M ₂ 3C ₄ = M ₂ 3C ₄ 3O ₂ + HCl	0.478×2.30×10 ⁻¹⁰
Cl + M ₂ 3C ₄ = M ₂ 3C ₄ O ₂ + HCl	0.522×2.30×10 ⁻¹⁰
Cl + NC ₇ H ₁₆ = HEPTO ₂ + HCl	3.90×10 ⁻¹⁰
Cl + M ₂ HEX = M ₂ HEXA ₂ O ₂ + HCl	0.779×3.50×10 ⁻¹⁰
Cl + M ₂ HEX = M ₂ HEXBO ₂ + HCl	0.221×3.50×10 ⁻¹⁰
Cl + M ₃ HEX = M ₃ HEXA ₂ O ₂ + HCl	0.793×3.11×10 ⁻¹⁰
Cl + M ₃ HEX = M ₃ HEXBO ₂ + HCl	0.207×3.11×10 ⁻¹⁰
Cl + NC ₈ H ₁₈ = OCTO ₂ + HCl	4.60×10 ⁻¹⁰
Cl + NC ₉ H ₂₀ = NONO ₂ + HCl	4.80×10 ⁻¹⁰

Cl + NC10H22 = DECO2 + HCl	5.55×10^{-10}
Cl + NC11H24 = UDECO2 + HCl	6.17×10^{-10}
Cl + NC12H26 = DDECO2 + HCl	6.74×10^{-10}
Cl + CHEX = CHEXO2 + HCl	3.50×10^{-10}

^a All species are variables existing in the MCM v3.2.

Table S2. Summary of organic reactions added to the MCM to represent the Cl chemistry ^a

Reactions	k ($cm^3 molecules^{-1} s^{-1}$)	Source
<i>Aldehydes + Cl</i>		
HCHO + Cl → HCl + HO2 + CO	$8.1 \times 10^{-11} \times \exp(-34/T)$	IUPAC
CH3CHO + Cl → CH3CO3 + HCl	7.92×10^{-11}	IUPAC
CH3CHO + Cl → HCOCH2O2 + HCl	8.0×10^{-13}	IUPAC
C2H5CHO + Cl → C2H5CO3 + HCl	1.3×10^{-10}	IUPAC
C3H7CHO + Cl → BUTALO2 + HCl	$5.5 \times 10^{-12} \times \exp(410/T)$	b
C3H7CHO + Cl → C3H7CO3 + HCl	$3.1 \times 10^{-11} \times \exp(410/T)$	b
IPRCHO + Cl → IBUTALBO2 + HCl	$2.2 \times 10^{-12} \times \exp(410/T)$	b
IPRCHO + Cl → IBUTALCO2 + HCl	$2.4 \times 10^{-12} \times \exp(410/T)$	b
IPRCHO + Cl → IPRCO3 + HCl	$3.7 \times 10^{-11} \times \exp(410/T)$	b
C4H9CHO + Cl → C4CHOBO2 + HCl	$7.3 \times 10^{-12} \times \exp(448/T)$	b
C4H9CHO + Cl → C4H9CO3 + HCl	$3.1 \times 10^{-11} \times \exp(448/T)$	b
BENZAL + Cl → C6H5CO3 + HCl	$3.6 \times 10^{-11} \times \exp(225/T)$	b
GLYOX + Cl → CO + CO + HO2 + HCl	$4.86 \times 10^{-11} \times \exp(-34/T)$	c
GLYOX + Cl → HCOCO3 + HCl	$3.24 \times 10^{-11} \times \exp(-34/T)$	c
MGLYOX + Cl → CH3CO3 + CO + HCl	8.0×10^{-11}	c
MACR + Cl → MACO3 + HCl	$4.86 \times 10^{-11} \times \exp(380/T) \times 0.45$	d
<i>Ketones + Cl</i>		
CH3COCH3 + Cl → CH3COCH2O2 + HCl	$1.5 \times 10^{-11} \times \exp(-590/T)$	IUPAC
MEK + Cl → MEKAO2 + HCl	$1.4 \times 10^{-11} \times \exp(80/T)$	IUPAC
MEK + Cl → MEKBO2 + HCl	$1.4 \times 10^{-11} \times \exp(80/T)$	IUPAC
MEK + Cl → MEKCO2 + HCl	$2.4 \times 10^{-12} \times \exp(80/T)$	IUPAC
MPRK + Cl → CO2C54O2 + HCl	9.6×10^{-11}	b
MPRK + Cl → MPRKAO2 + HCl	2.1×10^{-11}	b
DIEK + Cl → DIEKAO2 + HCl	2.4×10^{-11}	b
DIEK + Cl → DIEKBO2 + HCl	2.4×10^{-11}	b
MIPK + Cl → MIPKAO2 + HCl	3.5×10^{-11}	b

MIPK + Cl → MIPKBO2 + HCl	3.2×10^{-11}	b
HEX2ONE + Cl → HEX2ONAO2 + HCl	1.56×10^{-10}	b
HEX2ONE + Cl → HEX2ONBO2 + HCl	3.5×10^{-11}	b
HEX2ONE + Cl → HEX2ONCO2 + HCl	2.7×10^{-11}	b
HEX3ONE + Cl → HEX3ONAO2 + HCl	1.05×10^{-10}	b
HEX3ONE + Cl → HEX3ONBO2 + HCl	2.3×10^{-11}	b
HEX3ONE + Cl → HEX3ONCO2 + HCl	1.8×10^{-11}	b
HEX3ONE + Cl → HEX3ONDO2 + HCl	1.8×10^{-11}	b
MIBK + Cl → MIBKAO2 + HCl	3.1×10^{-10}	b
MIBK + Cl → MIBKBO2 + HCl	3.0×10^{-11}	b
MTBK + Cl → MTBKO2 + HCl	2.9×10^{-11}	b
CYHEXONE + Cl → CYHXONAO2 + HCl	1.3×10^{-10}	b

Alcohols + Cl

CH3OH + Cl → HO2 + HCHO + HCl	$7.1 \times 10^{-11} \times \exp(-75/T)$	IUPAC
C2H5OH + Cl → CH3CHO + HO2 + HCl	$5.5 \times 10^{-11} \times \exp(155/T)$	IUPAC
C2H5OH + Cl → HOCH2CH2O2 + HCl	$4.8 \times 10^{-12} \times \exp(155/T)$	IUPAC
NPROPOL + Cl → C2H5CHO + HO2 + HCl	$1.6 \times 10^{-11} \times \exp(525/T)$	IUPAC
NPROPOL + Cl → HO1C3O2 + HCl	$4.1 \times 10^{-12} \times \exp(525/T)$	IUPAC
NPROPOL + Cl → HYPROPO2 + HCl	$6.8 \times 10^{-12} \times \exp(525/T)$	IUPAC
IPROPOL + Cl → CH3COCH3 + HO2 + HCl	7.4×10^{-11}	IUPAC
IPROPOL + Cl → IPROPOLO2 + HCl	1.3×10^{-11}	IUPAC
NBUTOL + Cl → C3H7CHO + HO2 + HCl	$1.25 \times 10^{-11} \times \exp(550/T)$	IUPAC
NBUTOL + Cl → NBUTOLAO2 + HCl	$1.12 \times 10^{-11} \times \exp(550/T)$	IUPAC
NBUTOL + Cl → NBUTOLBO2 + HCl	$1.12 \times 10^{-11} \times \exp(550/T)$	IUPAC
BUT2OL + Cl → BUT2OLO2 + HCl	5.37×10^{-11}	b
BUT2OL + Cl → MEK + HO2 + HCl	9.51×10^{-11}	b
IBUTOL + Cl → IBUTOLBO2 + HCl	$2.6 \times 10^{-11} \times \exp(352/T)$	b
IBUTOL + Cl → IBUTOLCO2 + HCl	$4.2 \times 10^{-12} \times \exp(352/T)$	b
IBUTOL + Cl → IPRCHO + HO2 + HCl	$1.6 \times 10^{-11} \times \exp(352/T)$	b
TBUTOL + Cl → TBUTOLO2 + HCl	$2.4 \times 10^{-11} \times \exp(-121/T)$	b
TBUTOL + Cl → TC4H9O + HCl	$3.1 \times 10^{-12} \times \exp(-121/T)$	b
PECOH + Cl → DIEK + HO2 + HCl	9.1×10^{-11}	b
PECOH + Cl → HO3C5O2 + HCl	1.5×10^{-11}	b
PECOH + Cl → PE2ENEBO2 + HCl	1.0×10^{-10}	b
IPEAOH + Cl → BUT2CHO + HO2 + HCl	5.5×10^{-11}	b
IPEAOH + Cl → HM2C43O2 + HCl	4.9×10^{-11}	b
IPEAOH + Cl → M2BUOL2O2 + HCl	8.7×10^{-11}	b

ME3BUOL+Cl→C3ME3CHO+HO2 + HCl	6.45×10 ⁻¹¹	b
ME3BUOL + Cl → HM33C3O2 + HCl	1.02×10 ⁻¹⁰	b
ME3BUOL + Cl → ME3BUOLO2 + HCl	5.78×10 ⁻¹¹	b
IPECOH + Cl → HO2M2C4O2 + HCl	6.58×10 ⁻¹²	b
IPECOH + Cl → ME2BU2OLO2 + HCl	4.62×10 ⁻¹¹	b
IPECOH + Cl → PROL11MO2 + HCl	1.31×10 ⁻¹¹	b
IPEBOH + Cl → H2M3C4O2 + HCl	1.57×10 ⁻¹¹	b
IPEBOH + Cl → ME2BUOLO2 + HCl	9.82×10 ⁻¹¹	b
IPEBOH + Cl → MIPK + HO2 + HCl	9.82×10 ⁻¹¹	b
CYHEXOL+ Cl→ CYHEXOLAO2 + HCl	2.2×10 ⁻¹⁰	b
CYHEXOL + Cl→CYHEXONE+HO2+ HCl	7.9×10 ⁻¹¹	b
MIBKAOH+ Cl → MIBKAOHAO2+ HCl	3.4×10 ⁻¹¹	b
MIBKAOH+ Cl → MIBKAOHBO2+ HCl	1.3×10 ⁻¹¹	b
MIBKAOH + Cl → MIBKHO4O2 + HCl	1.8×10 ⁻¹²	b
ETHGLY+ Cl → HOCH2CHO+HO2+ HCl	2.5×10 ⁻¹⁰	b
PROPGLY+ Cl → ACETOL + HO2 + HCl	1.26×10 ⁻¹⁰	b
PROPGLY+ Cl → CH3CHOHCHO + HO2 + HCl	7.94×10 ⁻¹¹	b
CRESOL + Cl → OXYL1O2 + HCl	6.20×10 ⁻¹¹	e

Organic acids + Cl

CH3OOH + Cl → CH3O2 + HCl	3.54×10 ⁻¹¹	IUPAC
CH3OOH + Cl → HCHO + OH + HCl	2.36×10 ⁻¹¹	IUPAC
HCOOH + Cl → HO2 + HCl	1.9×10 ⁻¹³	IUPAC
CH3CO2H + Cl → CH3O2 + HCl	2.65×10 ⁻¹⁴	IUPAC
PROPACID + Cl → C2H5O2 + HCl	3.96×10 ⁻¹⁴	b

Organic nitrates + Cl

CH3NO3 + Cl → HCHO + NO2 + HCl	2.4×10 ⁻¹³	IUPAC
C2H5NO3 + Cl → CH3CHO + NO2 + HCl	4.7×10 ⁻¹²	IUPAC
NC3H7NO3 + Cl → C2H5CHO + NO2 + HCl	2.2×10 ⁻¹¹	IUPAC
IC3H7NO3 + Cl → CH3COCH3 + NO2 + HCl	3.8×10 ⁻¹²	IUPAC
NC4H9NO3 + Cl → C3H7CHO + NO2 + HCl	8.5×10 ⁻¹¹	IUPAC

Aromatics + Cl

TOLUENE + Cl → C6H5CH2O2 + HCl	5.9×10 ⁻¹¹	<i>Shi and Bernhard, 1997</i>
--------------------------------	-----------------------	-------------------------------

OXYL + Cl → OXYLO2 + HCl	1.5×10^{-10}	<i>Shi and Bernhard, 1997</i>
MXYL + Cl → MXYLO2 + HCl	1.7×10^{-10}	b
PXYL + Cl → PXYLO2 + HCl	2.6×10^{-10}	b
EBENZ + Cl → C6H5C2H4O2 + HCl	9.1×10^{-11}	b
PBENZ + Cl → PHC3O2 + HCl	7.5×10^{-11}	b
IPBENZ + Cl → PHIC3O2 + HCl	8.2×10^{-11}	b
TM123B + Cl → TM123BO2 + HCl	3.6×10^{-10}	b
TM124B + Cl → TM124BO2 + HCl	3.6×10^{-10}	b
TM135B + Cl → TMBO2 + HCl	3.1×10^{-10}	b
OETHTOL + Cl → ETOLO2 + HCl	1.1×10^{-10}	b
METHTOL + Cl → ETOLO2 + HCl	1.4×10^{-10}	b
PETHTOL + Cl → ETOLO2 + HCl	2.2×10^{-10}	b
Alkenes + Cl^f		
C2H4 + Cl → CH2CLCH2O2	1.0×10^{-10}	IUPAC
C3H6 + Cl → C3H5O2 + HCl	2.7×10^{-11}	<i>Riedel et al. 2014</i>
C3H6 + Cl → IPROCLO2	1.35×10^{-10}	<i>Riedel et al. 2014</i>
C3H6 + Cl → HYPROCLO2	1.08×10^{-10}	<i>Riedel et al. 2014</i>
OLEFIN + Cl → OLECLO2	5.86×10^{-10}	b,g
C5H8 + Cl → ISOCLO2	$1.28 \times 10^{-10} \times \exp(390/T)$	CB04
Alkyne + Cl		
C2H2 + Cl → CLCHO + CO + HO2	4.97×10^{-11}	h

^a All species are variables existing in the MCM, except for “OLEFIN” and some reaction products of Cl with C₃H₆, OLEFIN, C₅H₈ and ethyne.

^b Reaction with Cl is assumed to be similar to that with OH, and the Cl rate constant is calculated by multiplying the OH rate constant by the average k_{Cl}/k_{OH} for compounds with available kinetic data (note that the C₁ species was excluded from the k_{Cl}/k_{OH} calculation).

^c The mechanism is taken from the SAPRC07 (<http://www.engr.ucr.edu/~carter/SAPRC/saprc07.pdf>).

^d 45% of MACR is oxidized by Cl as a common aldehyde, whilst the remainder is treated as an alkene, being lumped into the ‘OLEFIN’.

^e The mechanism is taken from the SAPRC07 (<http://www.engr.ucr.edu/~carter/SAPRC/saprc07.pdf>). The reaction yields a new RO₂ radical, the degradation of which is approximated for simplicity to be the same as that of OXYL1O2.

^f Reactions of Cl with C₃H₆, OLEFIN and C₅H₈ introduce new model species and further reactions, which are represented in detail in Figures 1-3 in the main text.

^g OLEFIN is defined in the present study as the sum of *l*-butene, *i*-butene, *trans*-2-butene,

cis-2-butene, *1*-pentene, *trans*-2-pentene, *cis*-2-pentene, *1*-hexene, *2-methyl-1-butene*, *3-methyl-1-butene*, *2-methyl-2-butene*, *trans*-2-hexene, *cis*-2-hexene, *2,3-dimethyl-2-butene*, styrene, MVK and MACR (55%).

^h The mechanism is taken from the SAPRC07 (<http://www.engr.ucr.edu/~carter/SAPRC/saprc07.pdf>). CLCHO is a new species in the MCM, but is assumed to be less reactive and not considered for further reactions.

Table S3. Initial model conditions for simulations of the urban plum observed at Hok Tsui, Hong Kong during 24 August 2012.

Species	Concentration ^a	Species	Concentration ^a
Temperature ^b	301 K	C ₃ H ₆	280
Pressure	760 mm Hg	<i>l</i> -butene	80
H ₂ O ^b	2.8%	<i>cis</i> -2-butene	4
NO	20	<i>trans</i> -2-butene	40
NO ₂	15.6 ppb	<i>trans</i> -2-pentene	45
O ₃	64 ppb	<i>l</i> ,3-butadiene	40
PAN	2100	<i>l</i> -pentene	45
SO ₂	5.0 ppb	Isoprene	4
HONO	814	C ₂ H ₂	2150
CINO ₂	1997	Benzene	390
CO	297 ppb	Toluene	1130
CH ₄	2.01 ppm	<i>o</i> -xylene	110
C ₂ H ₆	1860	<i>m</i> , <i>p</i> -xylene	260
C ₃ H ₈	2840	Ethylbenzene	280
<i>n</i> -butane	2640	<i>l</i> ,2,3-trimethylbenzene	6
<i>i</i> -butane	1640	<i>l</i> ,2,4-trimethylbenzene	6
<i>n</i> -pentane	440	<i>l</i> ,3,5-trimethylbenzene	5
<i>i</i> -pentane	710	HCHO	2790
<i>n</i> -hexane	71	CH ₃ CHO	1180
2-methylpentane	18	C ₂ H ₅ CHO	114
<i>n</i> -heptane	61	Benzaldehyde	120
<i>n</i> -octane	470	acetone	1100
2,2,4-trimethylpentane	610	MEK	137
C ₂ H ₄	560		

^aThe unit is pptv unless otherwise specified.

^b For temperature, water content and J_{NO2}, the measured diurnal profiles at Hok Tsui were used to constrain the model.

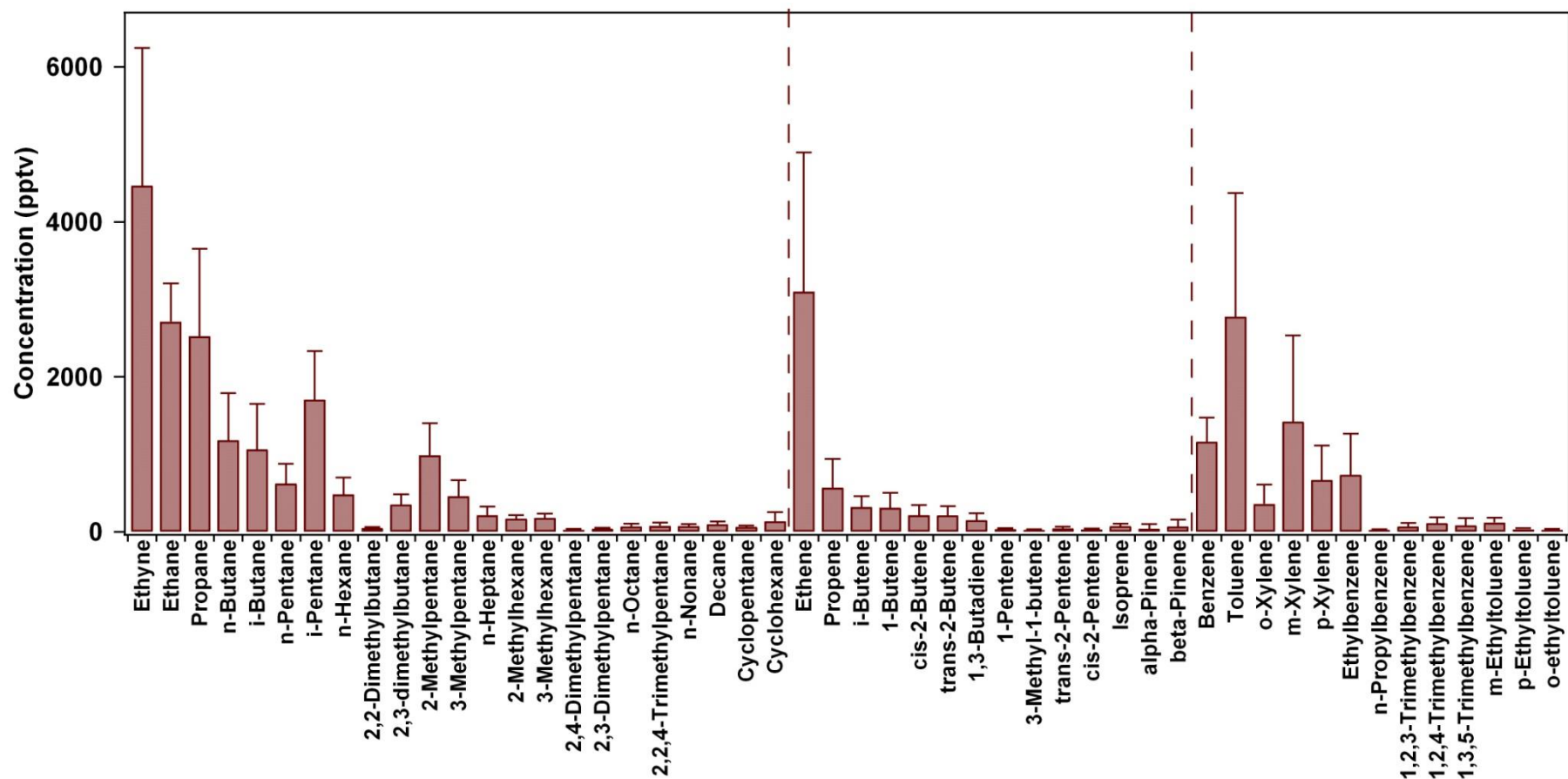


Figure S1. Average concentrations of individual hydrocarbon species observed at Shanghai on 7 May 2005 when the data were used for sensitivity tests of the new Cl \cdot mechanism. Error bars refer to standard deviations.

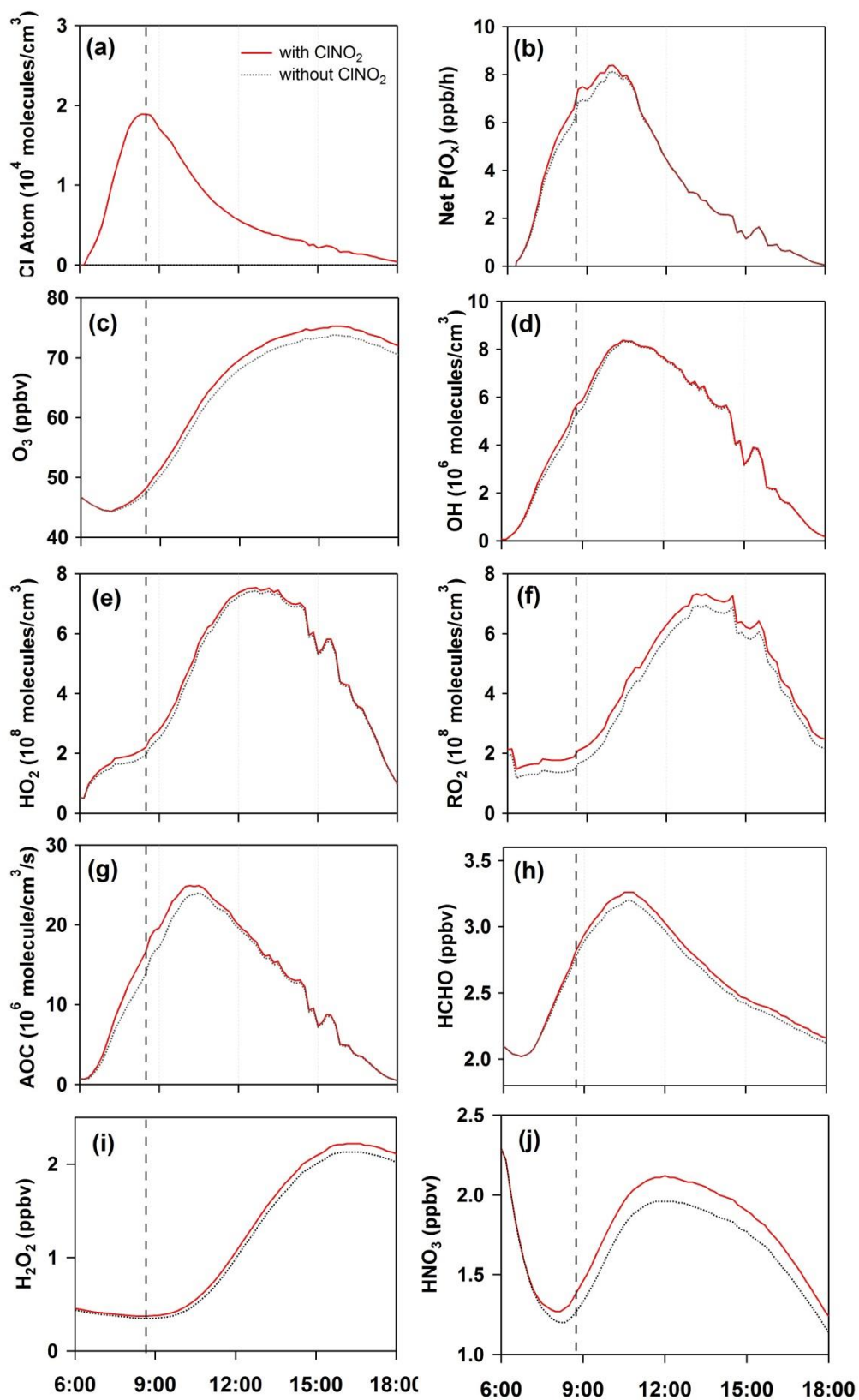


Figure S2. The same as Figure 4 in the main text but from a sensitivity model test with 500 pptv of initial ClNO₂.

1. Description of the high ClNO₂ plume and intensive observations at Hok Tsui

Field observations were conducted from 23 August to 1 September 2012 at Hok Tsui (22°13' N, 114°15' E, 60 m above sea level), a coastal site at the southeast tip of Hong Kong Island. This site receives either polluted plumes from urban Hong Kong and/or the Pearl River Delta region under northerly winds or clean marine air masses when southerly winds dominate. It has been deployed as the sampling platform in many previous studies (*e.g.*, Wang *et al.*, 2009; Zha *et al.*, 2014). A full list of chemicals and meteorological parameters were measured *in-situ* during this intensive study.

ClNO₂ and N₂O₅ were concurrently measured by an iodide-chemical ionization mass spectrometer (CIMS) (THS Instruments Inc., Atlanta), in which the target molecules are ionized to iodide clusters followed by detection by a quadrupole mass spectrometer. The detailed descriptions of the instrument principles and operation/calibration procedures have been provided elsewhere (Tham *et al.*, 2014; Wang *et al.*, 2015). Ozone was measured by a commercial UV photometric analyzer (TEI, Model 49i). Carbon monoxide was measured with a non-dispersive infrared analyzer (API, Model 300EU). Nitrogen oxides (NO and NO₂) were measured with a chemiluminescence instrument (TEI, Model 42i) equipped with a photolytic converter. NO_y was determined by another chemiluminescence analyzer (TEI, Model 42i) with an externally placed molybdenum oxide (MoO) catalytic converter. C₂-C₁₀ hydrocarbons were measured in real-time by a commercial analyzer that combines gas chromatography (GC) separation, photoionization detection (PID), and flame-ionization detection (FID) (Syntech Spectras, model GC955 Series 600/800 POC). In addition, whole air samples were also collected on selected days for detection of C₁-C₁₀ hydrocarbons, and analyzed at the University of California, Irvine (UCI) laboratory (Xue *et al.*, 2013). C₁-C₈ carbonyls were measured by collecting air samples in sorbent cartridges coated by 2,4-dinitrophenylhydrazine (DNPH) equipped with an O₃ scrubber, followed by analysis by a high pressure liquid chromatography (Xue *et al.*, 2014). HONO was measured in real-time using a long path absorption photometer (LOPAP). Temperature, relative humidity, wind speed and direction, and J_{NO₂} values were also measured by commercial probes/sensors (Zha *et al.*, 2014).

The time series of ClNO₂, O₃, NO₂ and J_{NO₂} is depicted in Figure S3. The plume with the highest ClNO₂ pollution was observed during the night of 23-24 August. The maximum value of ClNO₂ was recorded as 1997 pptv (1-min data) at around 3:00 AM local time on 24 August. Such a level is among the highest values ever reported over the world. Examination of surface winds and backward trajectories suggested that this polluted plume originated from urban Hong Kong and the Pearl River Delta region. This case has been analyzed in detail in our previous work (Tham *et al.*, 2014).

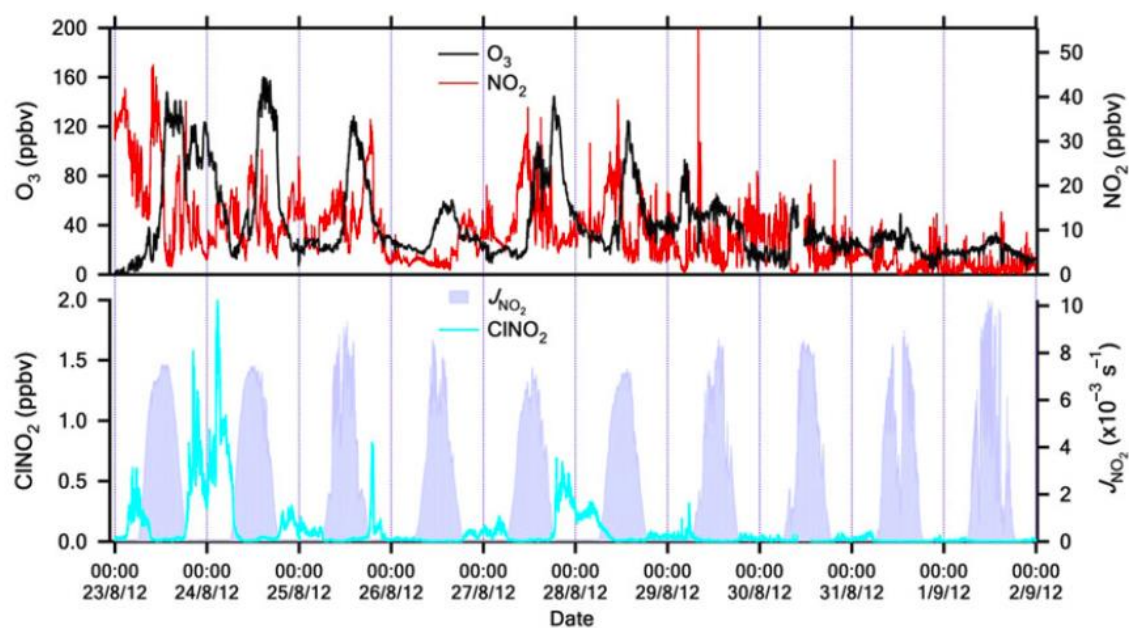


Figure S3. Time series of CINO₂, O₃, NO₂ and J_{NO₂} observed at Hok Tsui in summer 2012. (from Tham et al. 2014).

References

- Riedel, T. P., Wolfe, G. M., Danas, K. T., Gilman, J. B., Kuster, W. C., Bon, D. M., Vlasenko, A., Li, S. M., Williams, E. J., Lerner, B. M., Veres, P. R., Roberts, J. M., Holloway, J. S., Lefer, B., Brown, S. S., and Thornton, J. A.: An MCM modeling study of nitryl chloride (ClNO₂) impacts on oxidation, ozone production and nitrogen oxide partitioning in polluted continental outflow, *Atmos Chem Phys*, 14, 3789-3800, 2014.
- Shi, J. C. and Bernhard, M. J.: Kinetic studies of Cl-atom reactions with selected aromatic compounds using the photochemical reactor-FTIR spectroscopy technique, *Int J Chem Kinet*, 29, 349-358, 1997.
- Tham, Y. J., Yan, C., Xue, L. K., Zha, Q. Z., Wang, X. F., and Wang, T.: Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry, *Chinese Sci Bull*, 59, 356-359, 2014.
- Wang, T., Wei, X. L., Ding, A. J., Poon, C. N., Lam, K. S., Li, Y. S., Chan, L. Y., and Anson, M.: Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994–2007, *Atmos. Chem. Phys.*, 9, 6217–6227, 2009.
- Wang, T., Tham, Y. J., Xue, L. K., Li, Q. Y., Zha, Q. Z., Wang, Z., Poon, S. C. N., Dube, W. P., Brown, S. S., Louie, P. K. K., Luk, C. W. Y., Blake, D. R., Tsui, W.: High levels of nitryl chloride in the planetary boundary layer: A case study at a mountain site in Hong Kong, *Geophys. Res. Lett.*, submitted, 2015.

- Xue, L. K., Wang, T., Guo, H., Blake, D. R., Tang, J., Zhang, X. C., Saunders, S. M., and Wang, W. X.: Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: results from the Mt. Waliguan Observatory, *Atmos Chem Phys*, 13, 8551-8567, 2013.
- Xue, L. K., Wang, T., Wang, X. F., Blake, D. R., Gao, J., Nie, W., Gao, R., Gao, X. M., Xu, Z., Ding, A. J., Huang, Y., Lee, S. C., Chen, Y. Z., Wang, S. L., Chai, F. H., Zhang, Q. Z., and Wang, W. X. On the use of an explicit chemical mechanism to dissect peroxy acetyl nitrate formation, *Environmental Pollution*, 195, 39-47, 2014.
- Zha, Q. Z., Xue, L. K., Wang, T., et al., Large conversion rates of NO₂ to HNO₂ observed in air masses from the South China Sea: evidence of strong production at sea surface?, *Geophys. Res. Lett.*, 41, 7710- 7715, 2014.