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Geoscientific Model Development Discussions

Supplement of

Development of a chlorine chemistry module for the Master Chemical Mechanism

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Table S1. Summary of organic reactions added to the MCM to represent the Cl chemistry [a]

Reactions	*k* ($cm^3 molecules^{-1} s^{-1}$)	Source
	Aldehydes + Cl	
HCHO + Cl → HCl + HO2 + CO	$8.1\times10^{-11}\times\exp(-34/T)$	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	$5.5\times10^{-12}\times\exp(410/T)$	b
C3H7CHO + Cl → C3H7CO3 + HCl	$3.1\times10^{-11}\times\exp(410/T)$	b
IPRCHO + Cl → IBUTALBO2 + HCl	$2.2\times10^{-12}\times\exp(410/T)$	b
IPRCHO + Cl → IBUTALCO2 + HCl	$2.4\times10^{-12}\times\exp(410/T)$	b
IPRCHO + Cl → IPRCO3 + HCl	$3.7\times10^{-11}\times\exp(410/T)$	b
C4H9CHO + Cl → C4CHOBO2 + HCl	$7.3\times10^{-12}\times\exp(448/T)$	b
C4H9CHO + Cl → C4H9CO3 + HCl	$3.1\times10^{-11}\times\exp(448/T)$	b
BENZAL + Cl → C6H5CO3 + HCl	$3.6\times10^{-11}\times\exp(225/T)$	b
	Ketones + Cl	
CH_3COCH_3 + Cl → $CH_3COCH_2O_2$ + HCl	$1.5\times10^{-11}\times\exp(-590/T)$	IUPAC
MEK + Cl → $MEKAO_2$ + HCl	$1.4\times10^{-11}\times\exp(80/T)$	IUPAC
MEK + Cl → $MEKBO_2$ + HCl	$1.4\times10^{-11}\times\exp(80/T)$	IUPAC
MEK + Cl → MEKCO2 + HCl	$2.4\times10^{-12}\times\exp(80/T)$	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	$7.1\times10^{-11}\times\exp(-75/T)$	IUPAC
C2H5OH + Cl → CH3CHO + HO2 + HCl	$5.5\times10^{-11}\times\exp(155/T)$	IUPAC
C2H5OH + Cl → HOCH2CH2O2 + HCl	$4.8\times10^{-12}\times\exp(155/T)$	IUPAC
NPROPOL+ Cl → C2H5CHO + HO2 + HCl	$1.6\times10^{-11}\times\exp(525/T)$	IUPAC
NPROPOL + Cl → HO1C3O2 + HCl	$4.1\times10^{-12}\times\exp(525/T)$	IUPAC
NPROPOL + Cl → HYPROPO2 + HCl	$6.8\times10^{-12}\times\exp(525/T)$	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	$1.25\times10^{-11}\times\exp(550/T)$	IUPAC
NBUTOL + Cl → NBUTOLAO2 + HCl	$1.12\times10^{-11}\times\exp(550/T)$	IUPAC
NBUTOL + Cl → NBUTOLBO2 + HCl	$1.12\times10^{-11}\times\exp(550/T)$	IUPAC
BUT2OL + Cl → BUT2OLO2 + HCl	5.37×10^{-11}	b
BUT2OL + Cl → MEK + HO2 + HCl	9.51×10^{-11}	b
IBUTOL + Cl → IBUTOLBO2 + HCl	$2.6\times10^{-11}\times\exp(352/T)$	b
IBUTOL + Cl → IBUTOLCO2 + HCl	$4.2\times10^{-12}\times\exp(352/T)$	b
IBUTOL + Cl → IPRCHO + HO2 + HCl	$1.6\times10^{-11}\times\exp(352/T)$	b
TBUTOL+ Cl → TBUTOLO2 + HCl	$2.4\times10^{-11}\times\exp(-121/T)$	b
TBUTOL+ Cl → TC4H9O + HCl	$3.1\times10^{-12}\times\exp(-121/T)$	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
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}	*Shi and Bernhard*, 1997
OXYL + Cl → OXYLO2 + HCl	1.5×10^{-10}	*Shi and Bernhard*, 1997
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 [C]		
C2H4 + Cl → CH2CLCH2O2	1.0×10^{-10}	IUPAC
C3H6 + Cl → C3H5O2 + HCl	2.7×10^{-11}	*Riedel et al.* 2014
C3H6 + Cl → IPROCLO2	1.35×10^{-10}	*Riedel et al.* 2014
C3H6 + Cl → HYPROCLO2	1.08×10^{-10}	*Riedel et al.* 2014
OLEFIN + Cl → OLECLO2	1.16×10^{-9}	CB-IV
C5H8 + Cl → ISOCLO2	$1.28\times10^{-10}\times\exp(390/T)$	CB-IV

[a] All species are variables existing in the MCM, except for "OLEFIN" and the reaction products of Cl with C_3H_6, OLEFIN and C_5H_8.

[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 C_1 species was excluded from the k_{Cl}/k_{OH} calculation).

[C] Reactions of Cl with C_3H_6, OLEFIN and C_5H_8 introduce new model species and further reactions, which are represented in detail in Figures 1-3 in the main text.

IUPAC: International Union of Pure and Applied Chemistry (http://iupac.pole-ether.fr/index.html);
CB-IV: Carbon Bond Mechanism IV (Tanaka et al., 2003).

Table S2. 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_3H_6	280
Pressure	760 mm Hg	*1*-butene	80
H_2O [b]	0.028 %/%	*cis-2*-butene	4
NO	20	*trans-2*-butene	40
NO_2	15.6 ppb	*trans-2*-pentene	45
O_3	64 ppb	*1,3*-butadiene	40
PAN	2100	*1*-pentene	45
SO_2	5.0 ppb	Isoprene	4
HONO	814	C_2H_2	2150
$ClNO_2$	1997	Benzene	390
CO	297 ppb	Toluene	1130
CH_4	2.01 ppm	*o*-xylene	110
C_2H_6	1860	*m,p*-xylene	260
C_3H_8	2840	Ethylbenzene	280
n-butane	2640	*1,2,3*-trimethylbenzene	6
i-butane	1640	*1,2,4*-trimethylbenzene	6
n-pentane	440	*1,3,5*-trimethylbenzene	5
i-pentane	710	HCHO	2790
n-hexane	71	CH_3CHO	1180
2-methylpentane	18	C_2H_5CHO	114
n-heptane	61	Benzaldehyde	120
n-octane	470	acetone	1100
2,2,4-trimethylpentane	610	MEK	137
C_2H_4	560		

[a] The 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.

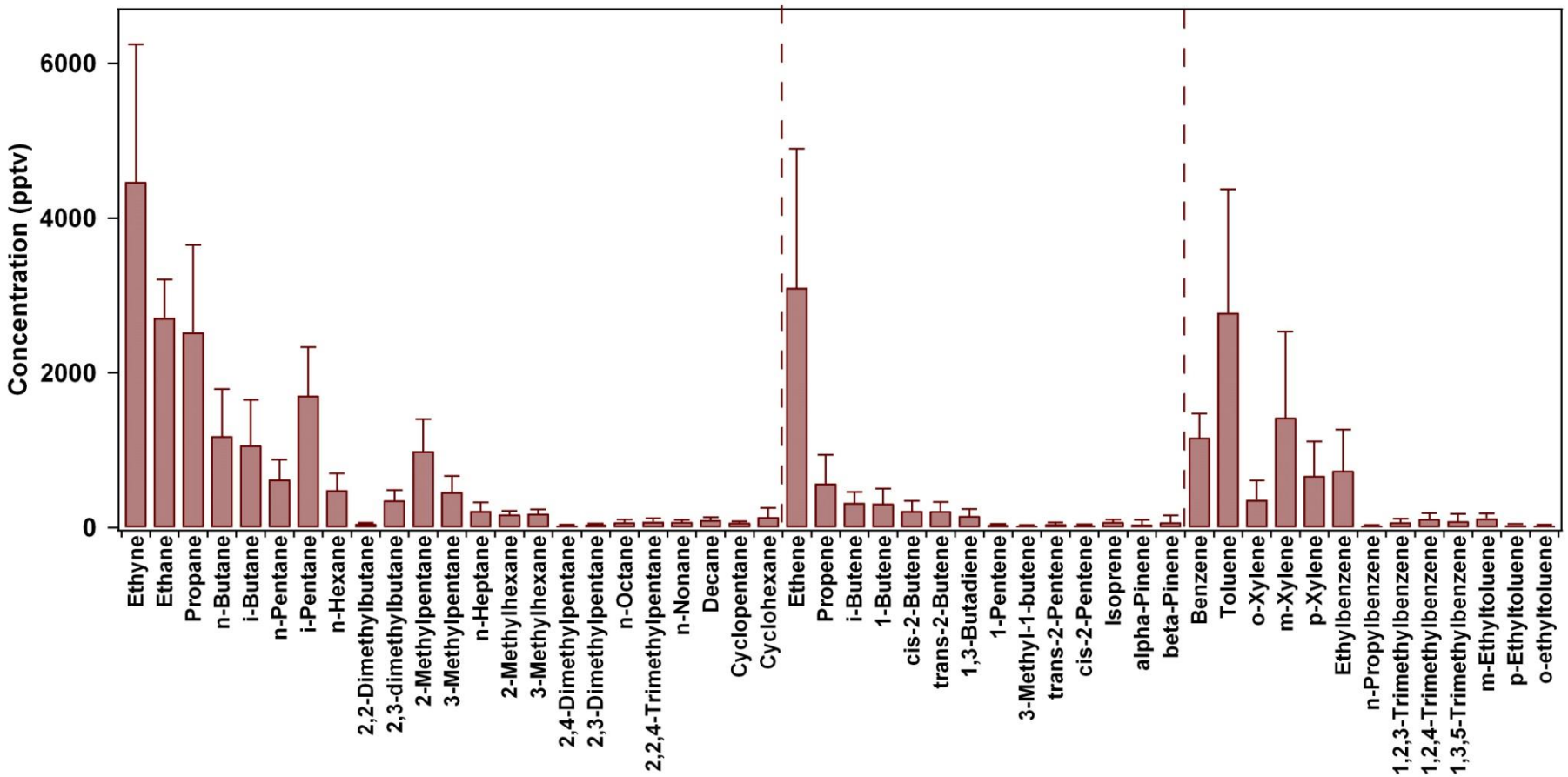

Figure S1. Average concentrations of individual hydrocarbon species observed at Shanghai on 7 May 2005 when the data were used for sensitivity tests of the new Cl ·mechanism. Error bars refer to standard deviations.

1. Description of the high $ClNO_2$ 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.

$ClNO_2$ and N_2O_5 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 quadruple 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 NO_2) were measured with a chemiluminescence instrument (*TEI, Model 42i*) equipped with a photolytic converter. NOy was determined by another chemiluminescence analyzer (*TEI, Model 42i*) with an externally placed molybdenum oxide (MoO) catalytic converter. C_2-C_{10} 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 POCP*). In addition, whole air samples were also collected on selected days for detection of C_1-C_{10} hydrocarbons, and analyzed at the University of California, Irvine (UCI) laboratory (*Xue et al.*, 2013). C_1-C_8 carbonyls were measured by collecting air samples in sorbent cartridges coated by 2,4-dinitrophenylhydrazine (DNPH) equipped with an O_3 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 $ClNO_2$, O_3, NO_2 and J_{NO2} is depicted in *Figure S2*. The plume with the highest $ClNO_2$ pollution was observed during the night of 23-24 August. The maximum value of $ClNO_2$ 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).

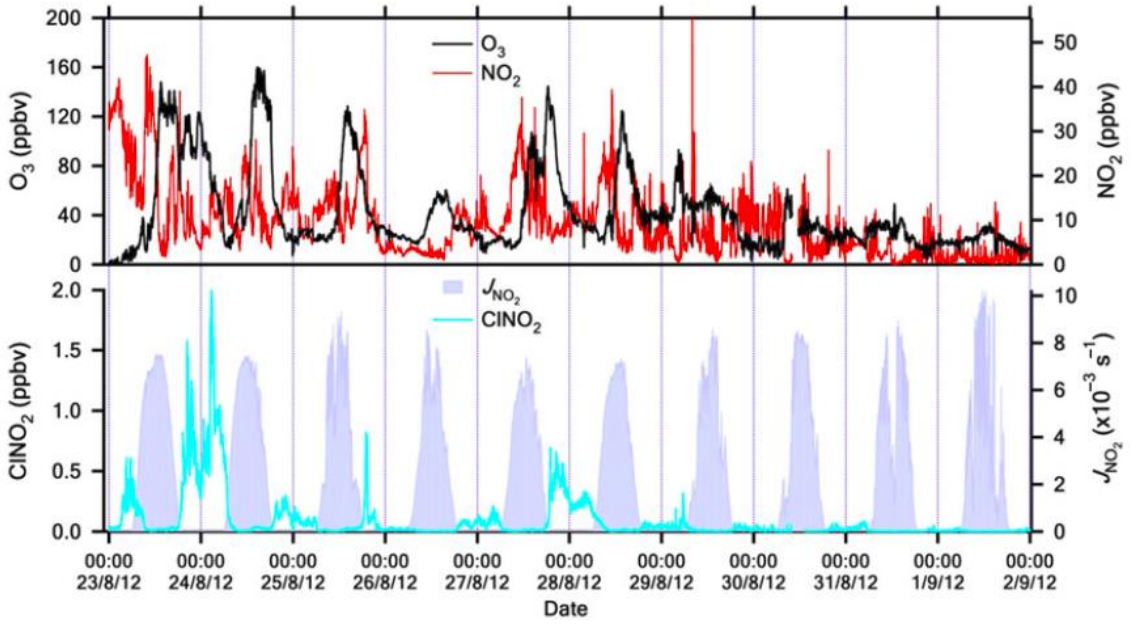

Figure S2. Time series of $ClNO_2$, O_3, NO_2 and J_{NO2} observed at Hok Tsui in summer 2012. (from Tham et al. 2014).

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 ($ClNO_2$) 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.

Tanaka, P. L., Allen, D. T., McDonald-Buller, E. C., Chang, S. H., Kimura, Y., Mullins, C. B., Yarwood, G., and Neece, J. D.: Development of a chlorine mechanism for use in the carbon bond IV chemistry model, *J Geophys Res-Atmos*, 108, 2003.

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 NO_2 to HNO_2 observed in air masses from the South China Sea: evidence of strong production at sea surface?, Geophys. Res. Lett., 41, 7710- 7715, 2014.