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Supplement of

Oxidative capacity and radical chemistry in the polluted atmosphere of Hong Kong and Pearl River Delta region: analysis of a severe photochemical smog episode

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Table S1. Summary of field measurements at Tung Chung in summer 2011

Species	Instrument or techniques	Time resolution
O ₃	<i>TEI 49i</i>	1 min
CO	<i>API 300EU</i>	1 min
SO ₂	<i>TEI 43i</i>	1 min
NO & NO ₂	<i>TEI 42i + blue light converter</i>	1 min
NO & NO _y	<i>TEI 42cy + MoO converter</i>	1 min
HONO	<i>LOPAP</i>	1 min
CINO ₂	<i>CIMS</i>	6 sec
PANs	<i>CIMS</i>	6 sec
H ₂ O ₂ & organic peroxides	<i>Aerolaser AL-2021</i>	1 min
C ₁ -C ₁₀ hydrocarbons	<i>Canister + GC/FID/ECD/MS</i>	24-hour
C ₂ -C ₁₀ hydrocarbons	<i>Syntech Spectras, model GC955 Series 600/800 POC</i>	30 min
C ₁ -C ₈ carbonyls	<i>DNPH-coated sorbent cartridge sampling + HPLC</i>	24-hour in general; 3-hour on episode
PM _{2.5} & PM ₁₀ mass	<i>SHARP</i>	1 min
SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , Cl ⁻ , Na ⁺ , Ca ²⁺ , K ⁺ in PM _{2.5}	<i>MARGA</i>	1 hour
OC & EC in PM _{2.5}	<i>Sunset OCEC analyzer</i>	1 hour
BC in PM _{2.5}	<i>Magee</i>	5 min
Aerosol scattering coefficient	<i>Ecotech Nephelometer</i>	1 min
Particle number concentration (5 nm-10 μm)	<i>MSP/WPS Model 1000XP</i>	8 min
<i>J_{NO2}</i>	<i>Metcon Filter Radiometer</i>	5 sec
Temperature & RH	<i>Young RH/T probe</i>	5 sec
Wind speed and direction	<i>Gill WindSonic</i>	5 sec
Solar Radiation	<i>LI-200 Pyranometer Sensor</i>	5 sec

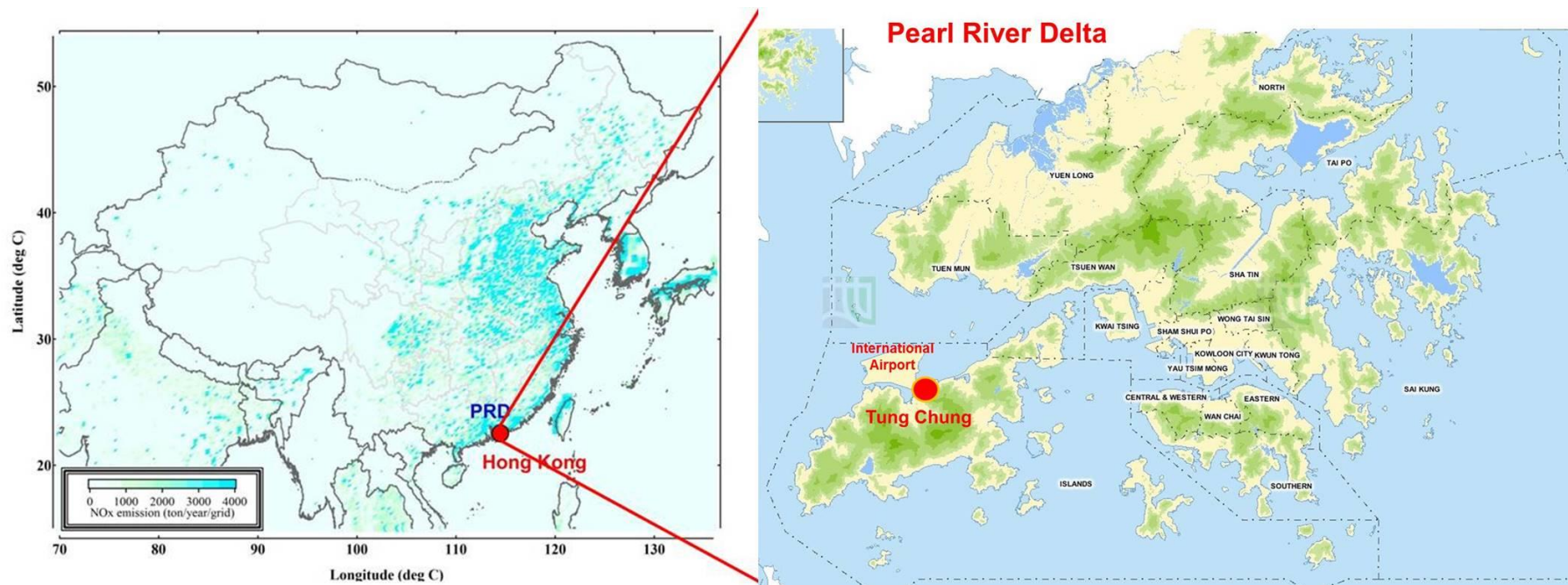


Figure S1. Map showing the locations of Hong Kong, the Pearl River Delta region and the study site at Tung Chung (TC).

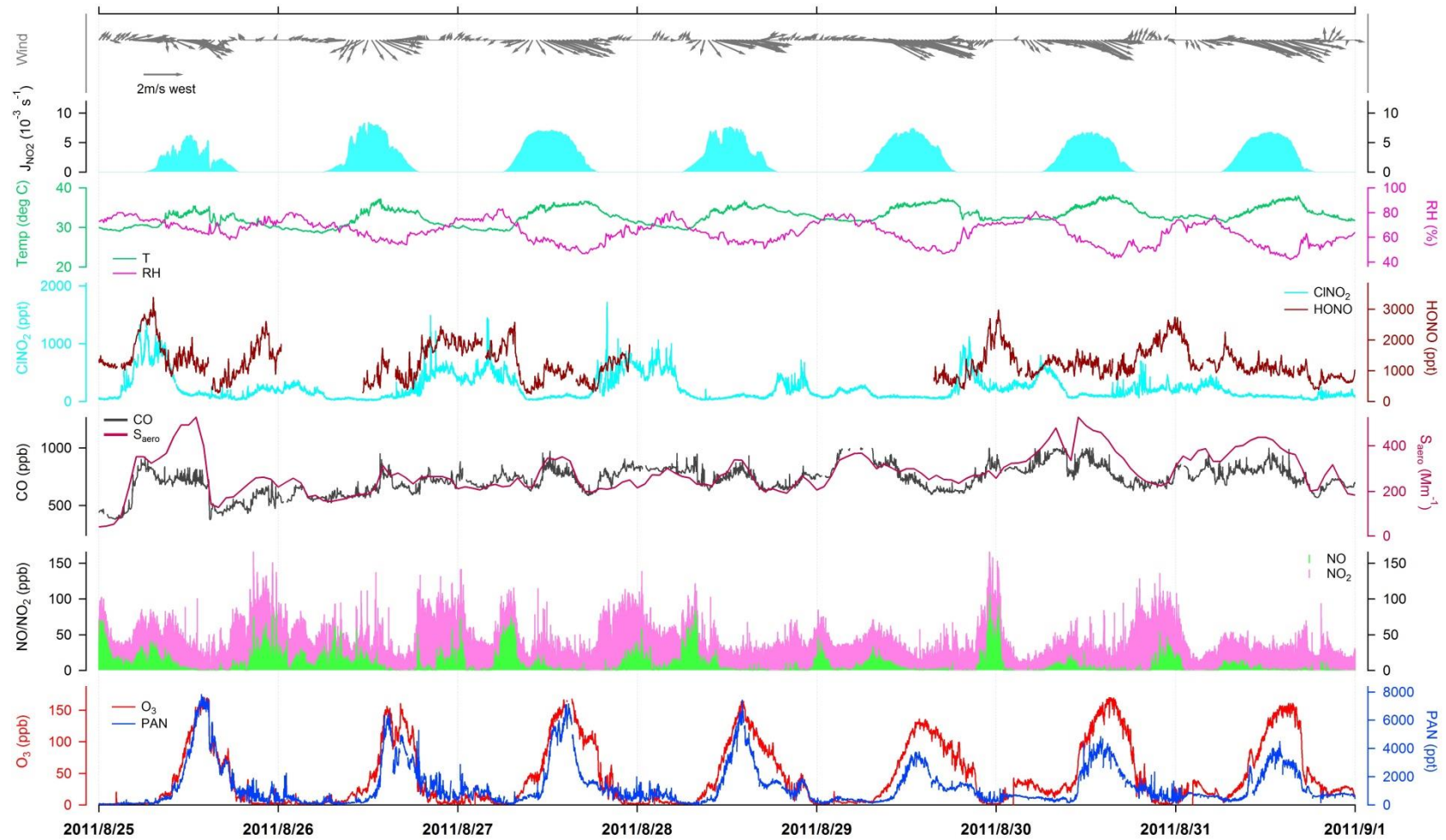


Figure S2. Time series of air pollutants and meteorological parameters observed at Tung Chung from 25-31 August 2011. S_{aero} stands for the scattering coefficient of $PM_{2.5}$. The data gap for HONO was mainly due to the calibration and maintenance of the instrument.

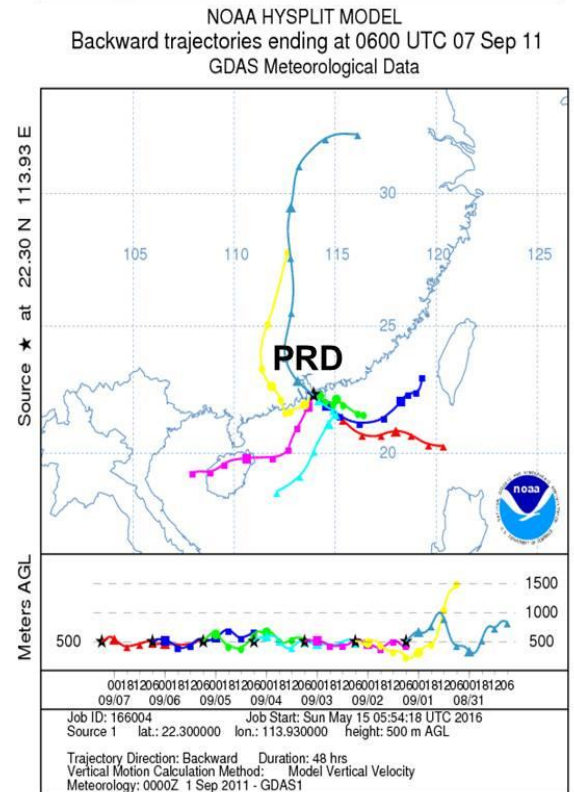
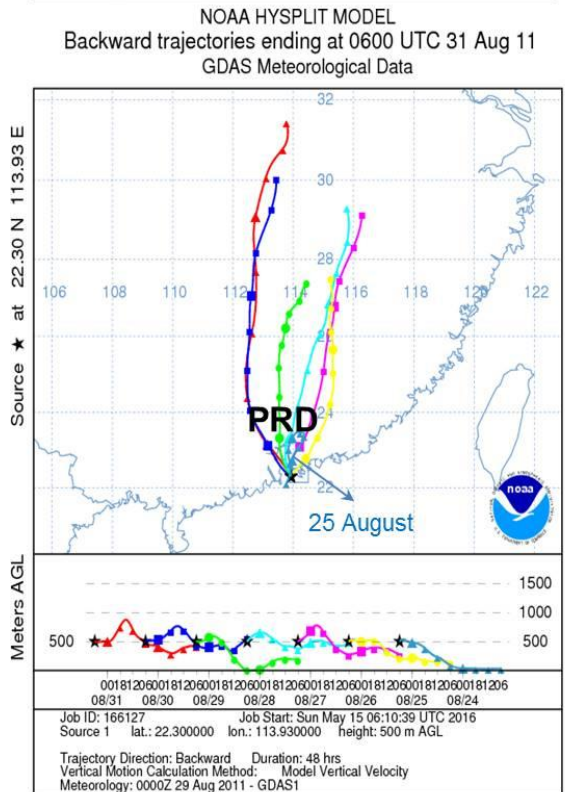
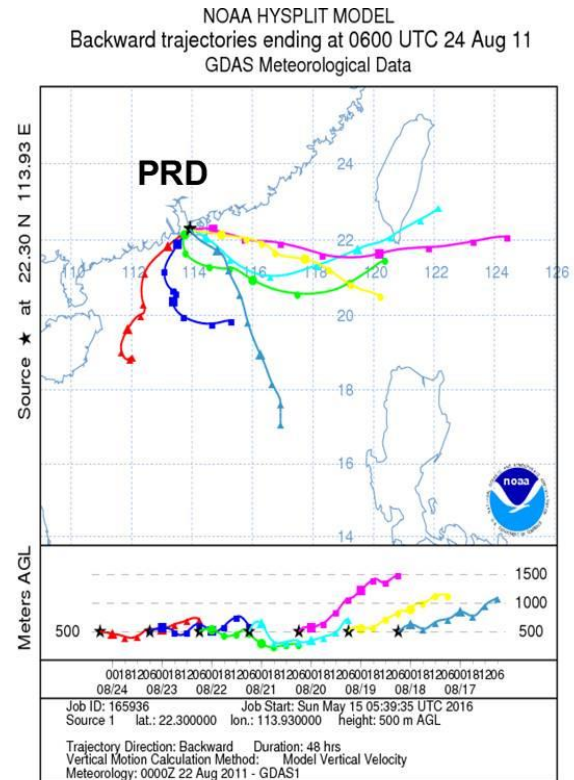
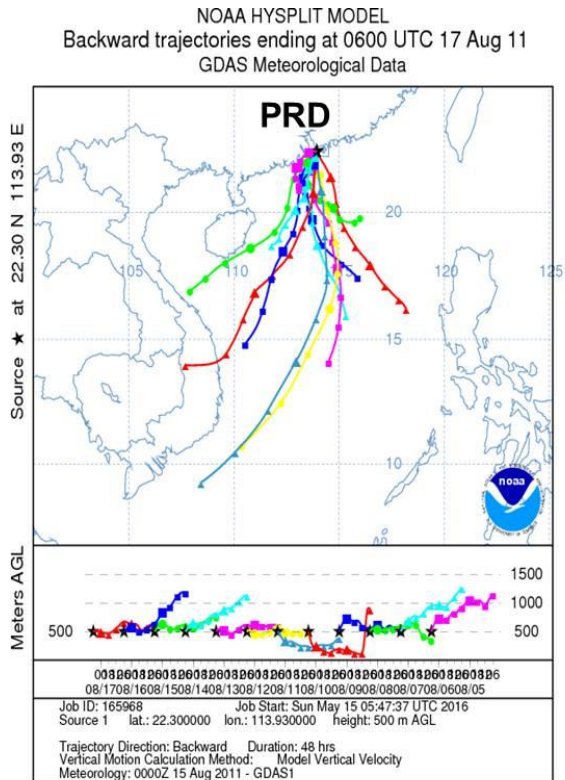


Figure S3. 48-hour backward trajectories calculated by the HYSPLIT model for air masses at TC at 12:00 LT each day from 6th August to 7th September. The height of the starting point was set as 500 m a.g.l. See the lower panels for the legend of trajectories each day.

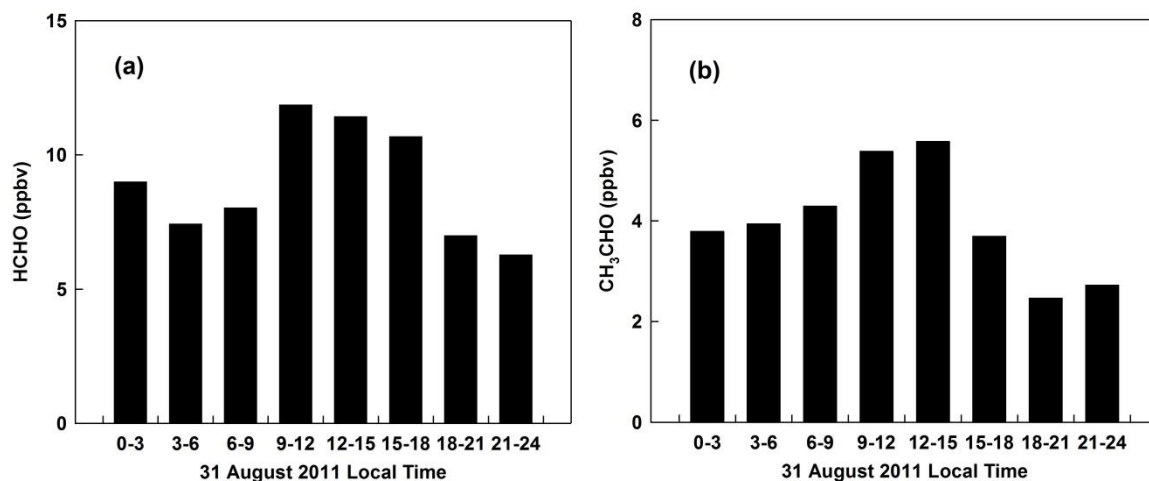


Figure S4. Diurnal variations of (a) formaldehyde and (b) acetaldehyde measured at Tung Chung on 31 August 2011.

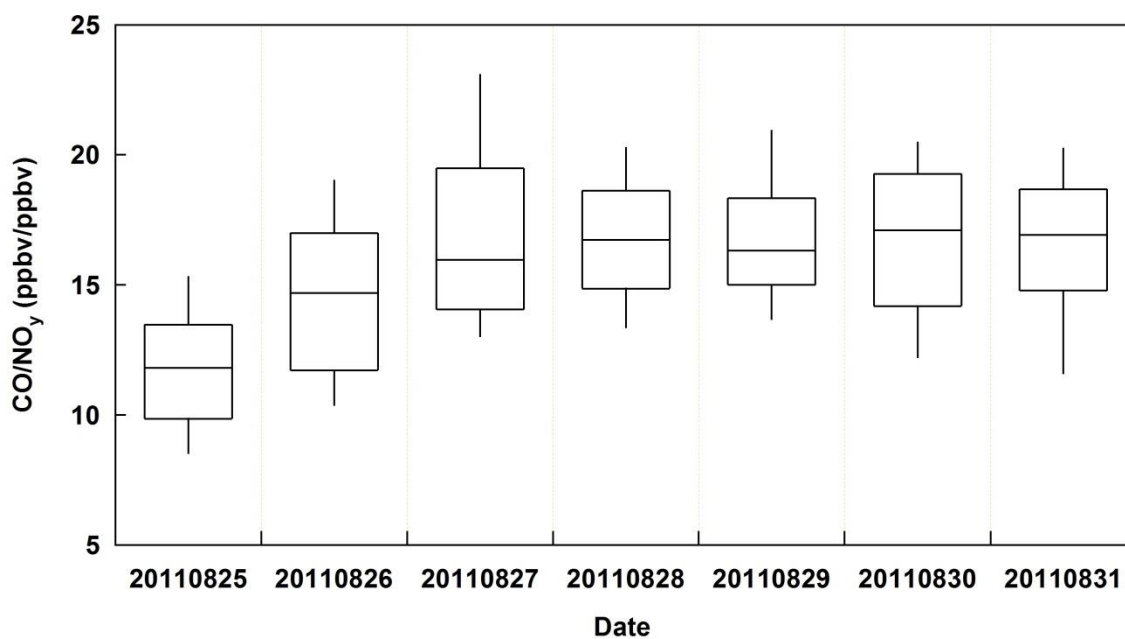


Figure S5. Distributions of the daytime (08:00–18:00 local time) CO/NO_y ratios measured at Tung Chung from 25–31 August 2011. The whisker plot provides the 90th, 75th, 50th, 25th and 10th percentiles of the measurement data.

1. Details of the OBM-AOCP model

The OBM-AOCP (Observation-Based Model for investigating the Atmospheric Oxidative Capacity and Photochemistry) is a zero-dimensional chemical box model that is capable of predicting the concentrations of reactive species (e.g., radicals) and quantifying the rates of various atmospheric photochemical processes. It has been used for evaluation of O₃ and PAN formation, radical budget, and heterogeneous photochemistry in many previous studies (e.g., Xue et al., 2013; 2014a; 2014b; 2014c; 2015). The configuration of this model is detailed as follows.

1.1. Chemical mechanisms

1.1.1. Basic mechanism

The OBM-AOCP is built on the Master Chemical Mechanism (MCM, v3.2). MCM is a nearly explicit mechanism describing the gas phase degradation of 143 primarily emitted VOC species together with the latest inorganic chemistry. It involves about 6700 chemical species (including intermediates and products) and includes approximately 17000 reactions. The detailed description of the MCM has been provided by Jenkin et al. (2003) and Saunders et al. (2003).

1.1.2. Heterogeneous chemistry module

In addition, the OBM-AOCP also incorporated a chemistry module describing several key heterogeneous processes in the atmosphere, namely, heterogeneous loss of N₂O₅ on particle surface and subsequent formation of ClNO₂, reactions of NO₂ on aerosol and ground surfaces producing HONO, uptake of HO₂ and NO₃ on aerosol surfaces, and heterogeneous reactions of HOCl and ClONO₂ on aerosol surface. The chemical reactions and related parameters, which are relevant to the present study, have been summarized in *Table S2*.

Table S2. Summary of the heterogeneous reactions incorporated into the OBM-AOCP

Heterogeneous Reaction	k (cm ³ molecules ⁻¹ s ⁻¹)	Remarks
N ₂ O ₅ → NA + ClNO ₂	$0.25 \times v_{\text{N}_2\text{O}_5} \times \gamma_{\text{N}_2\text{O}_5} \times S_{\text{AERO}} \times \varphi_{\text{ClNO}_2}$	a
N ₂ O ₅ → NA + NA	$0.25 \times v_{\text{N}_2\text{O}_5} \times \gamma_{\text{N}_2\text{O}_5} \times S_{\text{AERO}} \times (1 - \varphi_{\text{ClNO}_2})$	a
HO ₂ → products	$-\left(\frac{r}{Dg} + \frac{4}{\gamma_{\text{HO}_2}} \times v_{\text{HO}_2}\right)^{-1} \times S_{\text{AERO}}$	b

$\text{NO}_3 \rightarrow \text{products}$	$0.25 \times v_{\text{NO}_3} \times \gamma_{\text{NO}_3} \times S_{\text{AERO}}$	c
$\text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$	$0.25 \times v_{\text{ClONO}_2} \times \gamma_{\text{ClONO}_2} \times S_{\text{AERO}}$	d
$\text{HOCl} \rightarrow \text{Cl}_2$	$0.25 \times v_{\text{HOCl}} \times \gamma_{\text{HOCl}} \times S_{\text{AERO}}$	e
$\text{NO}_2 \rightarrow \text{HONO}$	aerosol: $\frac{1}{4} \times v_{\text{NO}_2} \times \gamma_{\text{NO}_2_{\text{a}}} \times S_{\text{AERO}}$	f
	ground: $\frac{1}{8} \times v_{\text{NO}_2} \times \gamma_{\text{NO}_2_{\text{g}}} \times \frac{S}{V}$	f

v_x : mean molecular speed of x; γ_x : uptake coefficient of x on surfaces; S_{AERO} : aerosol surface area concentration.

^a φ_{ClONO_2} : product yield of ClONO_2 from heterogeneous reaction of N_2O_5 . In the present study, we turned off the formation of ClONO_2 and constrained the model with the measured ClONO_2 profiles. We adopted a moderate $\gamma_{\text{N}_2\text{O}_5}$ of 0.014 in the present study, which was the observationally-derived average value from our recent field study in Hong Kong (Wang et al., 2016). NA: nitrate aerosol.

^b r : surface-weighted particle radius; D_g : gas phase diffusion coefficient. In the present study, we adopted a moderate γ_{HO_2} value of 0.02.

^c $\gamma_{\text{NO}_3} = 0.004$.

^d $\gamma_{\text{ClONO}_2} = 0.01$.

^e $\gamma_{\text{HOCl}} = 0.01$.

^f $\gamma_{\text{NO}_2_{\text{g/a}}}$: uptake coefficient of NO_2 on ground/aerosol surfaces. Considering the photo-enhanced production of HONO from surface reactions, higher values of $\gamma_{\text{NO}_2_{\text{g/a}}}$ were used during daytime than at night. For $\gamma_{\text{NO}_2_{\text{a}}}$, we used a value of 1×10^{-6} at nighttime and increased it to 5×10^{-6} during daytime. For $\gamma_{\text{NO}_2_{\text{g}}}$, when solar radiation was smaller than 400 W m^{-2} , we used the values of 1×10^{-6} and 2×10^{-5} during night and daytime respectively; with more intense solar radiation, $\gamma_{\text{NO}_2_{\text{g}}} = 2 \times 10^{-5} \times (\text{solar radiation}/400)$ was used. S/V refers to the effective surface density of the ground. An effective surface area of 1.7 m^2 per geometric ground surface was used to calculate the S/V . Please refer to Xue et al. (2014a) for the details.

1.1.3. Chlorine chemistry module

The MCM (v3.2) only considers the reactions of chlorine atom ($\text{Cl}\cdot$) with alkane species (Saunders et al., 2003). To comprehensively represent the $\text{Cl}\cdot$ chemistry, we have developed a detailed chlorine chemistry module and incorporated it into the OBM-AOCP. The protocol for compiling this new chemistry scheme has been published in recent (Xue et al., 2015), and the code in the format of FACSIMILE language is freely available per request. The chemical reactions and kinetic data are summarized below in *Tables S3-S5*.

Table S3. Summary of inorganic reactions added in the MCM to represent chlorine chemistry

Category	Reactions	k ($\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) or J (s^{-1})	Remarks
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Photolysis reactions	$\text{Cl}_2 \rightarrow \text{Cl} + \text{Cl}$	J_{Cl_2}	-
	$\text{ClNO}_2 \rightarrow \text{NO}_2 + \text{Cl}$	J_{ClNO_2}	a
	$\text{ClONO}_2 \rightarrow \text{NO}_3 + \text{Cl}$	$0.83 \times J_{\text{ClONO}_2}$	b
	$\text{ClONO}_2 \rightarrow \text{NO}_2 + \text{ClO}$	$0.17 \times J_{\text{ClONO}_2}$	b
	$\text{HOCl} \rightarrow \text{OH} + \text{Cl}$	J_{HOCl}	-
Cl + X	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$2.8 \times 10^{-11} \times \exp(-250/T)$	c
	$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	3.5×10^{-11}	c
	$\text{Cl} + \text{HO}_2 \rightarrow \text{ClO} + \text{OH}$	$7.5 \times 10^{-11} \times \exp(-620/T)$	c
	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	$1.1 \times 10^{-11} \times \exp(-980/T)$	c
	$\text{Cl} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{ClO}$	2.4×10^{-11}	c
	$\text{Cl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{NO}_3$	$6.2 \times 10^{-12} \times \exp(145/T)$	c
OH + X	$\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}$	$1.7 \times 10^{-12} \times \exp(-230/T)$	c
	$\text{OH} + \text{Cl}_2 \rightarrow \text{HOCl} + \text{Cl}$	$3.6 \times 10^{-12} \times \exp(-1200/T)$	c
	$\text{OH} + \text{HOCl} \rightarrow \text{ClO} + \text{H}_2\text{O}$	5.0×10^{-13}	c
	$\text{OH} + \text{ClO} \rightarrow \text{HO}_2 + \text{Cl}$	1.8×10^{-11}	c
	$\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$	1.2×10^{-12}	c
ClO + X	$\text{ClO} + \text{NO}_2 \rightarrow \text{ClONO}_2$	7.0×10^{-11}	c
	$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	$2.2 \times 10^{-12} \times \exp(340/T)$	c
	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$6.2 \times 10^{-12} \times \exp(295/T)$	c
Heterogeneous reactions	$\text{N}_2\text{O}_5 \rightarrow \text{NA} + \text{NA}$	$0.25 \times v_{\text{N}_2\text{O}_5} \times \gamma_{\text{N}_2\text{O}_5} \times S_{\text{AERO}} \times (1 - \phi_{\text{ClNO}_2})$	d
	$\text{N}_2\text{O}_5 \rightarrow \text{NA} + \text{ClNO}_2$	$0.25 \times v_{\text{N}_2\text{O}_5} \times \gamma_{\text{N}_2\text{O}_5} \times S_{\text{AERO}} \times \phi_{\text{ClNO}_2}$	d
	$\text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$	$0.25 \times v_{\text{ClONO}_2} \times \gamma_{\text{ClONO}_2} \times S_{\text{AERO}}$	d
	$\text{HOCl} \rightarrow \text{Cl}_2$	$0.25 \times v_{\text{HOCl}} \times \gamma_{\text{HOCl}} \times S_{\text{AERO}}$	d

^a In the present study, J_{ClNO_2} was scaled as a function of the measured J_{NO_2} , i.e., $J_{\text{ClNO}_2} = 0.040 \times J_{\text{NO}_2}$.

^b The branching ratio is determined based on the Tropospheric Ultraviolet Visible (TUV) Radiation model calculations (http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/).

^c The kinetic data are taken from the IUPAC database (<http://iupac.pole-ether.fr/index.html>).

^d The same as those described in Table S2.

Table S4. Summary of organic reactions existing in the MCM to represent chlorine chemistry

Reactions	k ($\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$)
$\text{Cl} + \text{CH}_4 = \text{CH}_3\text{O}_2 + \text{HCl}$	$6.6 \times 10^{-12} \times \exp(-1240/T)$
$\text{Cl} + \text{C}_2\text{H}_6 = \text{C}_2\text{H}_5\text{O}_2 + \text{HCl}$	$8.3 \times 10^{-11} \times \exp(-100/T)$
$\text{Cl} + \text{C}_3\text{H}_8 = \text{IC}_3\text{H}_7\text{O}_2 + \text{HCl}$	$0.43 \times 1.4 \times 10^{-10} \times \exp(75/T)$
$\text{Cl} + \text{C}_3\text{H}_8 = \text{NC}_3\text{H}_7\text{O}_2 + \text{HCl}$	$0.59 \times 1.4 \times 10^{-10} \times \exp(-90/T)$
$\text{Cl} + \text{NC}_4\text{H}_{10} = \text{NC}_4\text{H}_9\text{O}_2 + \text{HCl}$	$0.44 \times 2.05 \times 10^{-10} \times \exp(-120/T)$
$\text{Cl} + \text{NC}_4\text{H}_{10} = \text{SC}_4\text{H}_9\text{O}_2 + \text{HCl}$	$0.59 \times 2.05 \times 10^{-10} \times \exp(55/T)$
$\text{Cl} + \text{IC}_4\text{H}_{10} = \text{IC}_4\text{H}_9\text{O}_2 + \text{HCl}$	$0.564 \times 1.43 \times 10^{-10}$

Cl + IC4H10 = TC4H9O2 + HCl	0.436×1.43×10 ⁻¹⁰
Cl + NC5H12 = PEA02 + HCl	0.222×2.80×10 ⁻¹⁰
Cl + NC5H12 = PEBO2 + HCl	0.558×2.80×10 ⁻¹⁰
Cl + NC5H12 = PECO2 + HCl	0.220×2.80×10 ⁻¹⁰
Cl + IC5H12 = IPEAO2 + HCl	0.408×2.20×10 ⁻¹⁰
Cl + IC5H12 = IPEBO2 + HCl	0.342×2.20×10 ⁻¹⁰
Cl + IC5H12 = IPECO2 + HCl	0.250×2.20×10 ⁻¹⁰
Cl + NEOP = NEOPO2 + HCl	1.11×10 ⁻¹⁰
Cl + NC6H14 = HEXAO2 + HCl	0.182×3.40×10 ⁻¹⁰
Cl + NC6H14 = HEXBO2 + HCl	0.457×3.40×10 ⁻¹⁰
Cl + NC6H14 = HEXCO2 + HCl	0.361×3.40×10 ⁻¹⁰
Cl + M2PE = M2PEAO2 + HCl	0.321×2.90×10 ⁻¹⁰
Cl + M2PE = M2PEBO2 + HCl	0.269×2.90×10 ⁻¹⁰
Cl + M2PE = M2PECO2 + HCl	0.213×2.90×10 ⁻¹⁰
Cl + M2PE = M2PEDO2 + HCl	0.197×2.90×10 ⁻¹⁰
Cl + M3PE = M3PEAO2 + HCl	0.317×2.80×10 ⁻¹⁰
Cl + M3PE = M3PEBO2 + HCl	0.530×2.80×10 ⁻¹⁰
Cl + M3PE = M3PECO2 + HCl	0.153×2.80×10 ⁻¹⁰
Cl + M22C4 = M22C43O2 + HCl	0.461×1.71×10 ⁻¹⁰
Cl + M22C4 = M33C4O2 + HCl	0.386×1.71×10 ⁻¹⁰
Cl + M22C4 = M22C4O2 + HCl	0.154×1.71×10 ⁻¹⁰
Cl + M23C4 = M23C43O2 + HCl	0.478×2.30×10 ⁻¹⁰
Cl + M23C4 = M23C4O2 + HCl	0.522×2.30×10 ⁻¹⁰
Cl + NC7H16 = HEPTO2 + HCl	3.90×10 ⁻¹⁰
Cl + M2HEX = M2HEXAO2 + HCl	0.779×3.50×10 ⁻¹⁰
Cl + M2HEX = M2HEXBO2 + HCl	0.221×3.50×10 ⁻¹⁰
Cl + M3HEX = M3HEXAO2 + HCl	0.793×3.11×10 ⁻¹⁰
Cl + M3HEX = M3HEXBO2 + HCl	0.207×3.11×10 ⁻¹⁰
Cl + NC8H18 = OCTO2 + HCl	4.60×10 ⁻¹⁰
Cl + NC9H20 = NONO2 + 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

Table S5. Summary of organic reactions added to the MCM to represent the chlorine chemistry

Reactions ^a	<i>k</i> (cm ³ molecules ⁻¹ s ⁻¹)	Source
<i>Aldehydes + Cl</i>		
HCHO + Cl → HCl + HO2 + CO	8.1×10 ⁻¹¹ ×exp(-34/T)	IUPAC

CH ₃ CHO + Cl → CH ₃ CO ₃ + HCl	7.92×10 ⁻¹¹	IUPAC
CH ₃ CHO + Cl → HCOCH ₂ O ₂ + HCl	8.0×10 ⁻¹³	IUPAC
C ₂ H ₅ CHO + Cl → C ₂ H ₅ CO ₃ + HCl	1.3×10 ⁻¹⁰	IUPAC
C ₃ H ₇ CHO + Cl → BUTALO ₂ + HCl	5.5×10 ⁻¹² ×exp(410/T)	b
C ₃ H ₇ CHO + Cl → C ₃ H ₇ CO ₃ + HCl	3.1×10 ⁻¹¹ ×exp(410/T)	b
IPRCHO + Cl → IBUTALBO ₂ + HCl	2.2×10 ⁻¹² ×exp(410/T)	b
IPRCHO + Cl → IBUTALCO ₂ + HCl	2.4×10 ⁻¹² ×exp(410/T)	b
IPRCHO + Cl → IPRCO ₃ + HCl	3.7×10 ⁻¹¹ ×exp(410/T)	b
C ₄ H ₉ CHO + Cl → C ₄ CHOB ₂ O ₂ + HCl	7.3×10 ⁻¹² ×exp(448/T)	b
C ₄ H ₉ CHO + Cl → C ₄ H ₉ CO ₃ + HCl	3.1×10 ⁻¹¹ ×exp(448/T)	b
BENZAL + Cl → C ₆ H ₅ CO ₃ + HCl	3.6×10 ⁻¹¹ ×exp(225/T)	b
GLYOX + Cl → CO + CO + HO ₂ + HCl	4.86×10 ⁻¹¹ ×exp(-34/T)	c
GLYOX + Cl → HCOCO ₃ + HCl	3.24×10 ⁻¹¹ ×exp(-34/T)	c
MGLYOX + Cl → CH ₃ CO ₃ + CO + HCl	8.0×10 ⁻¹¹	c
MACR + Cl → MACO ₃ + HCl	4.86×10 ⁻¹¹ ×exp(380/T) ×0.45	d

Ketones + Cl

CH ₃ COCH ₃ + Cl → CH ₃ COCH ₂ O ₂ + HCl	1.5×10 ⁻¹¹ ×exp(-590/T)	IUPAC
MEK + Cl → MEKAO ₂ + HCl	1.4×10 ⁻¹¹ ×exp(80/T)	IUPAC
MEK + Cl → MEKBO ₂ + HCl	1.4×10 ⁻¹¹ ×exp(80/T)	IUPAC
MEK + Cl → MEKCO ₂ + HCl	2.4×10 ⁻¹² ×exp(80/T)	IUPAC
MPRK + Cl → CO ₂ C ₅ H ₄ O ₂ + HCl	9.6×10 ⁻¹¹	b
MPRK + Cl → MPRKAO ₂ + HCl	2.1×10 ⁻¹¹	b
DIEK + Cl → DIEKAO ₂ + HCl	2.4×10 ⁻¹¹	b
DIEK + Cl → DIEKBO ₂ + HCl	2.4×10 ⁻¹¹	b
MIPK + Cl → MIPKAO ₂ + HCl	3.5×10 ⁻¹¹	b
MIPK + Cl → MIPKBO ₂ + HCl	3.2×10 ⁻¹¹	b
HEX ₂ ONE + Cl → HEX ₂ ONAO ₂ + HCl	1.56×10 ⁻¹⁰	b
HEX ₂ ONE + Cl → HEX ₂ ONBO ₂ + HCl	3.5×10 ⁻¹¹	b
HEX ₂ ONE + Cl → HEX ₂ ONCO ₂ + HCl	2.7×10 ⁻¹¹	b
HEX ₃ ONE + Cl → HEX ₃ ONAO ₂ + HCl	1.05×10 ⁻¹⁰	b
HEX ₃ ONE + Cl → HEX ₃ ONBO ₂ + HCl	2.3×10 ⁻¹¹	b
HEX ₃ ONE + Cl → HEX ₃ ONCO ₂ + HCl	1.8×10 ⁻¹¹	b
HEX ₃ ONE + Cl → HEX ₃ ONDO ₂ + HCl	1.8×10 ⁻¹¹	b
MIBK + Cl → MIBKAO ₂ + HCl	3.1×10 ⁻¹⁰	b
MIBK + Cl → MIBKBO ₂ + HCl	3.0×10 ⁻¹¹	b
MTBK + Cl → MTBKO ₂ + HCl	2.9×10 ⁻¹¹	b
CYHEXONE + Cl → CYHXONAO ₂ + HCl	1.3×10 ⁻¹⁰	b

Alcohols + Cl

CH ₃ OH + Cl → HO ₂ + HCHO + HCl	7.1×10 ⁻¹¹ ×exp(-75/T)	IUPAC
C ₂ H ₅ OH + Cl → CH ₃ CHO + HO ₂ + HCl	5.5×10 ⁻¹¹ ×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		
CH ₃ OOH + Cl → CH ₃ O ₂ + HCl	3.54×10 ⁻¹¹	IUPAC
CH ₃ OOH + Cl → HCHO + OH + HCl	2.36×10 ⁻¹¹	IUPAC
HCOOH + Cl → HO ₂ + HCl	1.9×10 ⁻¹³	IUPAC
CH ₃ CO ₂ H + Cl → CH ₃ O ₂ + HCl	2.65×10 ⁻¹⁴	IUPAC
PROPACID + Cl → C ₂ H ₅ O ₂ + HCl	3.96×10 ⁻¹⁴	b
Organic nitrates + Cl		
CH ₃ NO ₃ + Cl → HCHO + NO ₂ + HCl	2.4×10 ⁻¹³	IUPAC
C ₂ H ₅ NO ₃ + Cl → CH ₃ CHO + NO ₂ + HCl	4.7×10 ⁻¹²	IUPAC
NC ₃ H ₇ NO ₃ + Cl → C ₂ H ₅ CHO + NO ₂ + HCl	2.2×10 ⁻¹¹	IUPAC
IC ₃ H ₇ NO ₃ + Cl → CH ₃ COCH ₃ + NO ₂ + HCl	3.8×10 ⁻¹²	IUPAC
NC ₄ H ₉ NO ₃ + Cl → C ₃ H ₇ CHO + NO ₂ + HCl	8.5×10 ⁻¹¹	IUPAC
Aromatics + Cl		
TOLUENE + Cl → C ₆ H ₅ CH ₂ O ₂ + HCl	5.9×10 ⁻¹¹	Shi and Bernhard, 1997
OXYL + Cl → OXYLO ₂ + HCl	1.5×10 ⁻¹⁰	Shi and Bernhard, 1997
MXYL + Cl → MXYLO ₂ + HCl	1.7×10 ⁻¹⁰	b
PXYL + Cl → PXYLO ₂ + HCl	2.6×10 ⁻¹⁰	b
EBENZ + Cl → C ₆ H ₅ C ₂ H ₄ O ₂ + HCl	9.1×10 ⁻¹¹	b
PBENZ + Cl → PHC ₃ O ₂ + HCl	7.5×10 ⁻¹¹	b
IPBENZ + Cl → PHIC ₃ O ₂ + HCl	8.2×10 ⁻¹¹	b
TM123B + Cl → TM123BO ₂ + HCl	3.6×10 ⁻¹⁰	b
TM124B + Cl → TM124BO ₂ + HCl	3.6×10 ⁻¹⁰	b
TM135B + Cl → TMBO ₂ + HCl	3.1×10 ⁻¹⁰	b
OETHTOL + Cl → ETOLO ₂ + HCl	1.1×10 ⁻¹⁰	b
METHTOL + Cl → ETOLO ₂ + HCl	1.4×10 ⁻¹⁰	b
PETHTOL + Cl → ETOLO ₂ + HCl	2.2×10 ⁻¹⁰	b
Alkenes + Cl		
C ₂ H ₄ + Cl → CH ₂ CLCH ₂ O ₂	1.0×10 ⁻¹⁰	IUPAC
C ₃ H ₆ + Cl → C ₃ H ₅ O ₂ + HCl	2.7×10 ⁻¹¹	Riedel et al. 2014
C ₃ H ₆ + Cl → IPROCLO ₂	1.35×10 ⁻¹⁰	Riedel et al. 2014
C ₃ H ₆ + Cl → HYPROCLO ₂	1.08×10 ⁻¹⁰	Riedel et al. 2014
OLEFIN + Cl → OLECLO ₂	5.86×10 ⁻¹⁰	b, g
C ₅ H ₈ + Cl → ISOCLO ₂	1.28×10 ⁻¹⁰ × exp(390/T)	CB04
Alkyne + Cl		
C ₂ H ₂ + Cl → CLCHO + CO + HO ₂	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 Cl 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 (see Xue *et al.* 2015 for the further reactions).

^g OLEFIN is defined in the present study as the sum of 1-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.

1.2. Physical processes

1.2.1. Photolysis frequencies

In the OBM-AOCP, photolysis frequencies (J values) are computed as a function of solar zenith angle (SZA), as defined by Saunders *et al.* (2003). To account for the potential impacts of cloud cover and particles, the model-calculated J values were further scaled in the present study with the measured J_{NO_2} data, which were read in the model at a time interval of 10 minutes.

1.2.2. Dilution mixing with evolution of the planetary boundary layer

The dilution mixing was considered for all model species by introducing a dilution factor, which is defined as a function of the change in the height of planetary boundary layer (PBL). In the present study, the PBL height was assumed to vary linearly from 300 m at night to 1500 m at 14:00 local time in the afternoon. Sensitivity model runs with other maximum PBL heights (e.g., 1000 m and 2000 m) indicated that its impacts on the modeling results are negligible (i.e., <3% for modeled radical concentrations and primary source strengths of OH).

1.2.3. Dry Deposition

Dry deposition was considered for various inorganic gases and organic species including PANs, carbonyls, organic peroxides and acids in our model. The dry deposition velocities are taken from the literature of Zhang *et al.* (2003).

1.3. Observational Constraint

The model was constrained in real-time with a full suite of measurement data to simulate the in-situ atmospheric chemistry. In the present study, it was constrained by the observed diurnal data of CO, NO, NO₂, SO₂, O₃, H₂O₂, HONO, ClNO₂, PAN, CH₄, C₂-C₁₀ NMHCs, C₁-C₈ carbonyls, aerosol surface area and radius, RH, temperature, pressure and J_{NO₂}. The observational data were averaged or interpolated with a time resolution of 10 minutes as the model constraints. The model was made with 00:00 LT as the initial time and ran for a 24-hour period. Before each simulation, the model was pre-run for five days with constraints of the campaign-average data so as to reach a steady state for the unconstrained species (e.g., radicals). Finally, the model outputs were extracted and applied for further analyses.

2. Model-simulated RO_x levels

Figure S6 shows the model-predicted daytime concentrations of OH, HO₂ and RO₂ at TC during the two episodes. The maximum concentrations of OH, HO₂ and RO₂ were 6.4×10^6 , 7.7×10^8 and 9.2×10^8 molecules cm⁻³ (equivalent as 0.27, 32 and 39 pptv) on 25 August, and were 7.0×10^6 , 5.3×10^8 and 4.8×10^8 molecules cm⁻³ (0.30, 23 and 20 pptv) on 31 August. To put our simulated results in a global perspective, the RO_x radical levels at TC are well within the measured or modeled ranges in the polluted urban environments (Stone et al., 2012; and references therein). For instance, the peak concentrations of OH and HO₂ in Hong Kong are higher than those measured in Los Angeles U.S. (George et al., 1999), Birmingham U.K. (Emmerson et al., 2005) and Tokyo Japan (Kanaya et al., 2007), similar to those in New York U.S. (Ren et al., 2003) and Mexico City Mexico (Dusanter et al., 2009; Shirley et al., 2006), and lower than those in Nashville U.S. (Martinez et al., 2003) and Houston U.S. (Mao et al., 2010). In comparison with the limited results available in China, the RO_x levels at TC are comparable to those simulated in Beijing (Liu et al., 2012) and Mt. Tai (Kanaya et al., 2009).

It is noteworthy that our simulated concentrations of OH/HO₂ are much lower than the measured levels at a rural site (Back Garden) in the northern PRD (Hofzumahaus et al., 2009). The discrepancy may be due to the difference in the environments (e.g., high-NO_x condition at TC and low-NO_x condition at Back Garden) and/or the deficiency of current models to represent radical chemistry. Without direct observations of HO_x, it is impossible to address the potential ‘discrepancy’ between measured and modeled radical levels, which is usually

found in the low-NO_x environments. Here, the rationale of this study is to identify the major species and reaction pathways affecting the radical chemistry in the high-NO_x environment of Hong Kong and the PRD region, based on the ‘known chemistry’ and comprehensive measurements of related parameters. Obviously, direct measurements of HO_x radicals are quite needed to pin down this issue in the high-NO_x environment of Hong Kong and the PRD region.

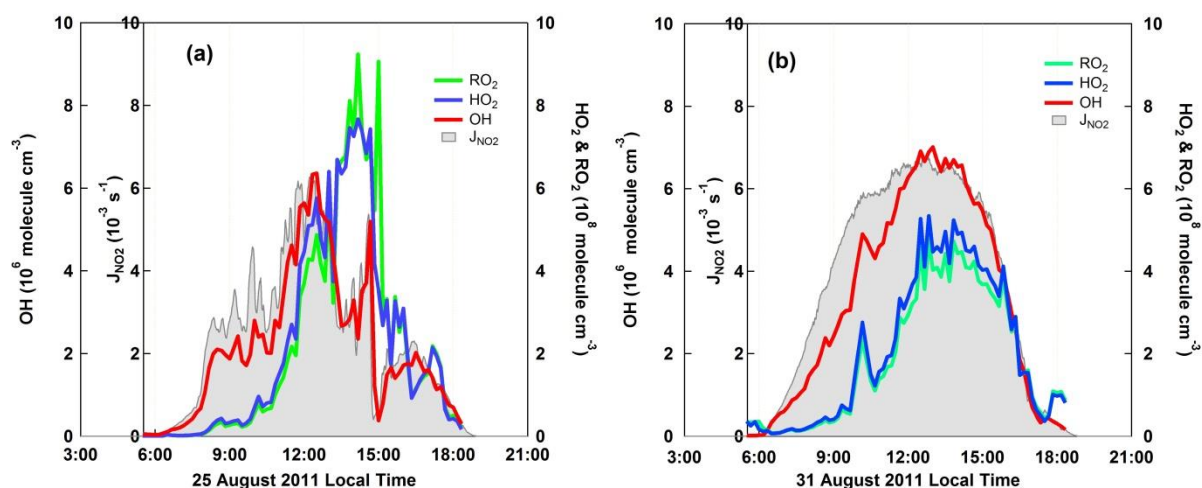


Figure S6. Model-simulated daytime concentrations of OH, HO₂ and RO₂ radicals at Tung Chung on (a) 25 August 2011 and (b) 31 August 2011.

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