



Development of a chlorine chemistry module for the Master Chemical Mechanism

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Abstract. The chlorine atom ($\text{Cl}\cdot$) has a high potential to perturb atmospheric photochemistry by oxidizing volatile organic compounds (VOCs), but the exact role it plays in the polluted troposphere remains unclear. The Master Chemical Mechanism (MCM) is a near-explicit mechanism that has been widely applied in the atmospheric chemistry research. While it addresses comprehensively the chemistry initiated by the OH, O_3 and NO_3 radicals, its representation of the $\text{Cl}\cdot$ chemistry is incomplete as it only considers the reactions for alkanes. In this paper, we develop a more comprehensive $\text{Cl}\cdot$ chemistry module that can be directly incorporated within the MCM framework. A suite of 205 chemical reactions describes the $\text{Cl}\cdot$ -initiated degradation of alkenes, aromatics, alkynes, aldehydes, ketones, alcohols, and some organic acids and nitrates, along with the inorganic chemistry involving $\text{Cl}\cdot$ and its precursors. To demonstrate the potential influence of the new chemistry module, it was incorporated into a MCM box model to evaluate the impacts of nitryl chloride (ClNO_2), a product of nocturnal halogen activation by nitrogen oxides (NO_x), on the following day's atmospheric photochemistry. With constraints of recent observations collected at a coastal site in Hong Kong, southern China, the modeling analyses suggest that the $\text{Cl}\cdot$ produced from ClNO_2 photolysis may substantially enhance the atmospheric oxidative capacity, VOC oxidation and O_3 formation, particularly in the early morning period. The results demonstrate the critical need for photochemical models to include more detailed chlorine chemistry in order to better understand the atmospheric photochemistry in polluted environments subject to intense emissions of NO_x , VOCs and chlorine-containing constituents.

1 Introduction

The chlorine atom ($\text{Cl}\cdot$) acts as a major oxidant that can “jump-start” the photochemistry of the atmosphere (Finlayson-Pitts, 1993). It oxidizes various volatile organic compounds (VOCs) in a similar fashion to the hydroxyl radical (OH) but with reaction rates up to 2 orders of magnitude faster, and hence facilitates faster removal of VOCs and formation of ozone (O_3) and other oxidants (Atkinson et al., 1999; Chang et al., 2002; Tanaka et al., 2003b). In the troposphere, $\text{Cl}\cdot$ originates from a number of potential sources and the most recognized ones include the reaction of hydrochloric acid (HCl) with OH and photolysis of molecular chlorine (Cl_2), hypochlorous acid (HOCl), nitryl chloride (ClNO_2) and ClONO_2 (Riedel et al., 2014). These so-called $\text{Cl}\cdot$ precursors are either emitted from anthropogenic activities or formed through chemical activation of stable Cl-containing compounds (Tanaka et al., 2000). An example of the latter that has been recently demonstrated is the hydrolysis of dinitrogen pentoxide (N_2O_5) on Cl-containing aerosols producing ClNO_2 (Thornton et al., 2010). Despite ultra-trace ambient abundance, $\text{Cl}\cdot$ may play important roles in atmospheric chemistry in a variety of environments (e.g., polar, coastal and inland regions) wherever anthropogenic or natural chlorine sources exist.

The role that $\text{Cl}\cdot$ plays in VOC oxidation and O_3 formation remains a large uncertainty of tropospheric chemistry. Chemical mechanisms form the core of atmospheric models that are usually used to simulate the formation of air pollution and formulate science-based control strategies (Luecken et al., 2008; Stockwell et al., 2012). The degree by which the $\text{Cl}\cdot$ chemistry is accounted for in current major chemical mecha-

nisms is inhomogeneous. To our knowledge, the organic and inorganic chemistry involving $\text{Cl}\cdot$ has not been represented in detail by most mechanisms. Tanaka et al. (2003a) developed a chlorine chemistry module containing 13 reactions for the carbon bond IV (or CB04) mechanism, and Sarwar et al. (2012) extended it for use in CB05 (including 25 reactions) to assess the impact of N_2O_5 hydrolysis on O_3 formation. Basic chemical modules describing the ClNO_2 formation and $\text{Cl}\cdot$ oxidation of VOCs have been incorporated in the SAPRC07 and its updates (Carter, 2010).

The Master Chemical Mechanism (MCM) is one of the most widely deployed chemical mechanisms, which near-explicitly describes the degradation of 143 primarily emitted VOCs (Jenkin et al., 2003, 2015; Saunders et al., 2003). In contrast to the comprehensive chemistry initiated by OH, O_3 and NO_3 , the representation of the $\text{Cl}\cdot$ chemistry in the MCM remains incomplete. It considers only the reactions of $\text{Cl}\cdot$ with alkanes for which the oxidation by $\text{Cl}\cdot$ may play a dominant role (see Table S1 in the Supplement), while the reactions between $\text{Cl}\cdot$ and other VOC species are not represented. Recently, Riedel et al. (2014) added to the MCM $\text{Cl}\cdot$ reactions for 13 major reactive VOCs (i.e., ethene, propene, benzene, toluene, *o*-xylene, styrene, formaldehyde, methanol, ethanol, isopropanol, ethanal, propanal, acetone) with the aim to evaluate the impacts of ClNO_2 on the atmospheric photochemistry in the Los Angeles Basin. Nonetheless, this update only considers a small set of VOCs. There is still a need to further develop a more comprehensive $\text{Cl}\cdot$ chemical mechanism that can be applied to a wider range of tropospheric conditions.

A major goal of the present work is to develop a $\text{Cl}\cdot$ chemical mechanism that can be directly adopted in the MCM framework. Following the construction approach of MCM (Jenkin et al., 2003; Saunders et al., 2003), the existing chemical kinetics literature data were surveyed (mostly from the IUPAC database; <http://iupac.pole-ether.fr/index.html>) for the reactions of $\text{Cl}\cdot$ with various VOCs and compiled into a chemical module. This module contains 205 reactions and describes the $\text{Cl}\cdot$ -initiated degradation of all the MCM primary alkenes, alkynes, aromatics, aldehydes, ketones, alcohols, selected organic acids and nitrates as well as the inorganic chemistry of $\text{Cl}\cdot$ and its precursors. This new chemistry module introduces 22 additional chlorinated products that can be simulated with negligible increased cost of running time for the MCM models. It was then incorporated into a MCM-based chemical box model, with constraints of observations from a coastal site in southern China, to evaluate the impacts of ClNO_2 on the atmospheric photochemistry. With the observed maximum nighttime ClNO_2 (i.e., 1997 pptv), the modeling results suggest that the $\text{Cl}\cdot$ produced by photolysis of ClNO_2 plays a significant role in the next day's VOCs oxidation, O_3 formation and atmospheric oxidative capacity, especially during the early morning period.

2 Mechanism development

For the developed $\text{Cl}\cdot$ mechanism module to be readily incorporated within the MCM, the same approach, protocols and stoichiometry of the MCM are strictly followed (Jenkin et al., 2003, 2015; Saunders et al., 2003). The chemical reactions that are compiled in the mechanism module are summarized in Table 1, Table S2 and Figs. 1–3. A detailed description of the construction procedures is given below.

2.1 Inorganic reactions

Five types of inorganic reactions that are of potential significance to the production and fate of $\text{Cl}\cdot$ are considered. They include photolysis reactions of $\text{Cl}\cdot$ precursors, reactions of $\text{Cl}\cdot$ with inorganic species, reactions of OH with Cl -containing species recycling $\text{Cl}\cdot$ or its precursors, reactions of ClO , and heterogeneous reactions that have been recently found to be involved in chlorine activation (e.g., Thornton et al., 2010; Sarwar et al., 2012; Riedel et al., 2014). A total of 24 inorganic reactions are compiled, as outlined in Table 1. The rate coefficients and product yields are mostly taken from the latest IUPAC database.

2.2 Organic reactions

2.2.1 Aldehydes

The $\text{Cl}\cdot$ reactions are considered for formaldehyde, acetaldehyde, propanal, butanal, isobutyl aldehyde, pentanal, benzaldehyde, glyoxal, methylglyoxal and methacrolein (MACR) (see Table S2). Based on the available literature, the reactions are assumed to proceed primarily via H atom abstraction by $\text{Cl}\cdot$ to form an HCl molecule and a RO_2 radical, both of which are already present in the MCM framework. For formaldehyde, acetaldehyde and propanal, the chemical kinetic data including rate coefficients and product yields are adopted from the latest IUPAC database. For glyoxal and methylglyoxal, the rate constants are assumed to be same to those for formaldehyde and acetaldehyde according to the SAPRC mechanism (<http://www.engr.ucr.edu/~carter/SAPRC/saprc07.pdf>). For the other aldehydes for which kinetic data are unavailable, the approach of the MCM protocol is followed, to adapt the known experimental data to give reasonable estimates for the unknown kinetics (Saunders et al., 2003). The basic assumption is that they react with $\text{Cl}\cdot$ similar to OH with a rate constant of $k_{X+\text{OH}}$ times a generic $k_{\text{Cl}}/k_{\text{OH}}$ ratio. The generic $k_{\text{Cl}}/k_{\text{OH}}$ ratio is estimated based on the known measured rate constants for acetaldehyde and propanal (note that formaldehyde is excluded here considering that the reaction rate of a C_1 species usually stands out from the remainder of a series). In this case, the generic $k_{\text{Cl}}/k_{\text{OH}}$ ratio of 6.08 (average) is adopted. Sensitivity tests were conducted by using the lower and upper limits of the $k_{\text{Cl}}/k_{\text{OH}}$ ratio, and suggested that the differences among the modeling results were negligible under typical polluted ur-

Table 1. Summary of inorganic reactions added to the MCM to represent Cl• chemistry.

Category	Reaction	k ($\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ or s^{-1}) or J (s^{-1})	Remarks
Photolysis reactions	$\text{Cl}_2 \rightarrow \text{Cl} + \text{Cl}$	J_{Cl_2}	–
	$\text{ClONO}_2 \rightarrow \text{NO}_2 + \text{Cl}$	J_{ClONO_2}	–
	$\text{ClONO}_2 \rightarrow \text{NO}_3 + \text{Cl}$	$0.83 \times J_{\text{ClONO}_2}$	a
	$\text{ClONO}_2 \rightarrow \text{NO}_2 + \text{ClO}$	$0.17 \times J_{\text{ClONO}_2}$	a
	$\text{HOCl} \rightarrow \text{OH} + \text{Cl}$	J_{HOCl}	–
Cl + X	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$2.8 \times 10^{-11} \times \exp(-250/T)$	b
	$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	3.5×10^{-11}	b
	$\text{Cl} + \text{HO}_2 \rightarrow \text{ClO} + \text{OH}$	$7.5 \times 10^{-11} \times \exp(-620/T)$	b
	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	$1.1 \times 10^{-11} \times \exp(-980/T)$	b
	$\text{Cl} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{ClO}$	2.4×10^{-11}	b
	$\text{Cl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{NO}_3$	$6.2 \times 10^{-12} \times \exp(145/T)$	b
OH + X	$\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}$	$1.7 \times 10^{-12} \times \exp(-230/T)$	b
	$\text{OH} + \text{Cl}_2 \rightarrow \text{HOCl} + \text{Cl}$	$3.6 \times 10^{-12} \times \exp(-1200/T)$	b
	$\text{OH} + \text{HOCl} \rightarrow \text{ClO} + \text{H}_2\text{O}$	5.0×10^{-13}	b
	$\text{OH} + \text{ClO} \rightarrow \text{HO}_2 + \text{Cl}$	1.8×10^{-11}	b
	$\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$	1.2×10^{-12}	b
ClO + X	$\text{ClO} + \text{NO}_2 \rightarrow \text{ClONO}_2$	7.0×10^{-11}	b
	$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	$2.2 \times 10^{-12} \times \exp(340/T)$	b
	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$6.2 \times 10^{-12} \times \exp(295/T)$	b
Hetero. reactions	$\text{N}_2\text{O}_5 \rightarrow \text{NA} + \text{NA}$	$0.25 \times C_{\text{N}_2\text{O}_5} \times \gamma_{\text{N}_2\text{O}_5} \times S_{\text{AERO}} \times (1 - \varphi_{\text{CLNO}_2})$	c
	$\text{N}_2\text{O}_5 \rightarrow \text{NA} + \text{ClONO}_2$	$0.25 \times C_{\text{N}_2\text{O}_5} \times \gamma_{\text{N}_2\text{O}_5} \times S_{\text{AERO}} \times \varphi_{\text{CLNO}_2}$	c
	$\text{NO}_3 \rightarrow \text{products}$	$0.25 \times C_{\text{NO}_3} \times \gamma_{\text{NO}_3} \times S_{\text{AERO}}$	c
	$\text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$	$0.25 \times C_{\text{ClONO}_2} \times \gamma_{\text{ClONO}_2} \times S_{\text{AERO}}$	c
	$\text{HOCl} \rightarrow \text{Cl}_2$	$0.25 \times C_{\text{HOCl}} \times \gamma_{\text{HOCl}} \times S_{\text{AERO}}$	c

^a The branching ratio is determined based on the Tropospheric Ultraviolet Visible (TUV) Radiation model calculations (http://cpm.acd.ucar.edu/Models/TUV/Interactive_TUV/). ^b The kinetic data are taken from the IUPAC database (<http://iupac.pole-ether.fr/index.html>). ^c C_X is the molecular speed of X; γ_X is the uptake coefficient of X on aerosols; S_{AERO} is the aerosol surface area concentration; φ_{CLNO_2} is the product yield of ClONO₂ from the heterogeneous reactions of N₂O₅. NA is nitrate aerosol.

ban conditions (see Sect. 2.3 and Table 2 for the details of sensitivity tests).

The reactions of Cl• with MACR are represented as follows in the new module. The mechanism is assumed to be the same to that for OH. According to the MCM v3.2, the OH oxidation of MACR proceeds via two routes: H abstraction from the aldehyde group (45 %) and OH addition to the C=C double bond (55 %). Hence, 45 % of MACR is oxidized by Cl• as a common aldehyde by using the aforementioned generic $k_{\text{Cl}}/k_{\text{OH}}$ ratio, whilst the remainder can be treated as an alkene compound (being summed into a lumped species “OLEFIN”; see Sect. 2.2.7).

2.2.2 Ketones

The reactions of Cl• with ten primary ketones in the MCM are compiled following the same approach to that for aldehydes (Table S2). The reactions proceed via H atom abstraction by Cl• to form HCl and RO₂, which already exist in the

MCM. Kinetics data including rate coefficient and product yield are adopted from the latest IUPAC database for acetone and methyl ethyl ketone (MEK). For other ketones, it is assumed that they react with Cl• similarly to OH with rate constants of $k_{\text{X}+\text{OH}}$ times a generic $k_{\text{Cl}}/k_{\text{OH}}$ ratio. The generic ratio of 23.9 was derived by averaging the $k_{\text{Cl}}/k_{\text{OH}}$ values for acetone and MEK, for which experimental data are available. Sensitivity tests by adopting lower and upper limits of $k_{\text{Cl}}/k_{\text{OH}}$ suggest that the difference in modeling results is minor under typical polluted urban conditions (see Sect. 2.3 and Table 2).

The OH oxidation of methyl vinyl ketone (MVK) takes place mainly by addition of OH to the C=C double bond. The same mechanism was adopted for the Cl• reaction. Specifically, MVK can be treated as an alkene and is lumped into the “OLEFIN” species (see Sect. 2.2.7).

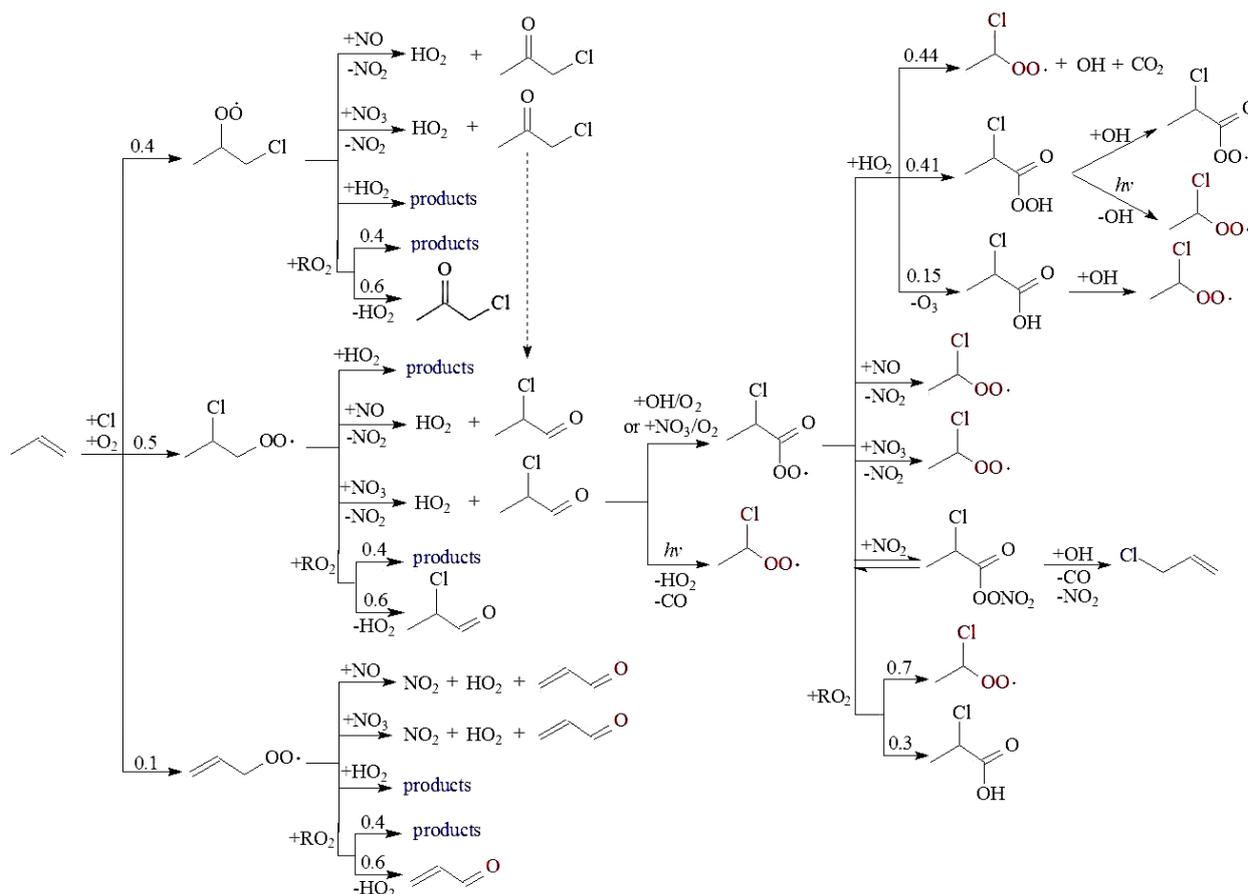


Figure 1. The oxidation mechanism of propene by $\text{Cl}\cdot$. Note that (1) the species in red already exist in the MCM; (2) degradation of the species in blue is not further considered for simplicity; (3) the preceding plus and minus indicate the reactants and products respectively; (4) for simplicity, the degradation of $\text{CH}_3\text{COCH}_2\text{Cl}$ was approximated to be the same as that of $\text{CH}_3\text{CH}(\text{Cl})\text{CHO}$.

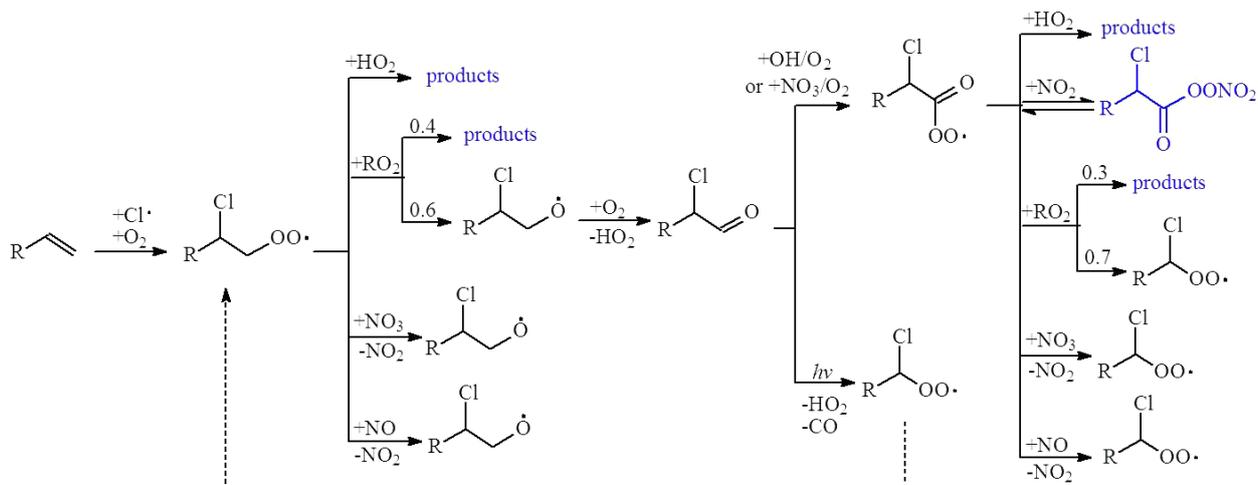


Figure 2. Simplified oxidation mechanism of the lumped “OLEFIN” by $\text{Cl}\cdot$. Note that (1) the degradation of species in blue is not further considered for simplicity; (2) the preceding plus and minus indicate the reactants and products respectively; (3) for simplicity, the degradation of $\text{RCH}(\text{Cl})\text{O}_2$ was approximated to be the same as that of $\text{RCH}(\text{Cl})\text{CH}_2\text{O}_2$.

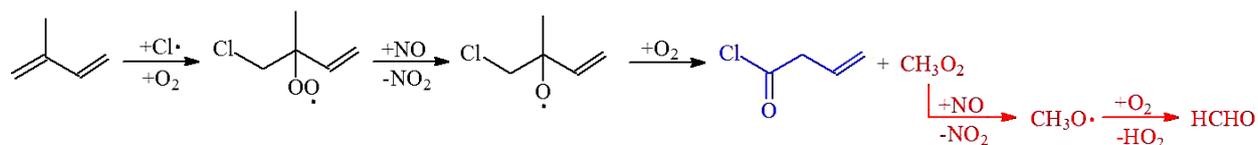


Figure 3. Simplified oxidation mechanism of isoprene by $\text{Cl}\cdot$. Note that (1) the species in red already exist in the MCM; (2) degradation of the species in blue is not further considered for simplicity; (3) the preceding plus and minus indicate the reactants and products respectively.

Table 2. Summary of sensitivity test results^a.

Scenario	Difference against the base model ^b	[Cl] = [OH] / 50		[Cl] = [OH] / 200	
		Difference in daytime $\text{P}(\text{O}_x)$	Difference in daytime OC_{Cl}	Difference in daytime $\text{P}(\text{O}_x)$	Difference in daytime OC_{Cl}
S1	With base MCM, without the developed $\text{Cl}\cdot$ chemistry module	12.8 %	186 %	4.5 %	166 %
S2	Turn off the “OLEFIN” chemistry (including $\text{Cl}\cdot$ reactions of C_2H_4 and C_3H_6)	5.5 %	7.7 %	1.7 %	7.4 %
S3	Generic $k_{\text{Cl}}/k_{\text{OH}} = 0$ for aromatics (turn off)	2.2 %	3.1 %	< 1 %	5.6 %
	Generic $k_{\text{Cl}}/k_{\text{OH}} = 220$ for aromatics (upper limit)	< 1 %	< 1 %	< 1 %	1.2 %
	Generic $k_{\text{Cl}}/k_{\text{OH}} = 150$ for aromatics (lower limit)	< 1 %	< 1 %	< 1 %	1.0 %
S4	Generic $k_{\text{Cl}}/k_{\text{OH}} = 0$ for aldehydes (turn off)	< 1 %	1.6 %	< 1 %	< 1 %
	Generic $k_{\text{Cl}}/k_{\text{OH}} = 8.5$ for aldehydes (upper limit)	< 1 %	< 1 %	< 1 %	< 1 %
	Generic $k_{\text{Cl}}/k_{\text{OH}} = 5.4$ for aldehydes (lower limit)	< 1 %	< 1 %	< 1 %	< 1 %
S5	Generic $k_{\text{Cl}}/k_{\text{OH}} = 0$ for ketones (turn off)	< 1 %	3.0 %	< 1 %	2.0 %
	Generic $k_{\text{Cl}}/k_{\text{OH}} = 36$ for ketones (upper limit)	< 1 %	< 1 %	< 1 %	< 1 %
	Generic $k_{\text{Cl}}/k_{\text{OH}} = 12$ for ketones (lower limit)	< 1 %	1.6 %	< 1 %	< 1 %
S6	Generic $k_{\text{Cl}}/k_{\text{OH}} = 0$ for alcohols (turn off)	< 1 %	< 1 %	< 1 %	< 1 %
S7	Turn off the chemistry of $\text{Cl}\cdot + \text{C}_5\text{H}_8$	< 1 %	< 1 %	< 1 %	< 1 %

^a The daytime $\text{P}(\text{O}_x)$ and OC_{Cl} are the daytime average (09:00–18:00 local time) net production rate of O_x and oxidative capacity of the $\text{Cl}\cdot$ atom. The differences are with respect to the base model results with the full chlorine mechanism. ^b The base model was with the newly developed chlorine mechanism in the present study. The sensitivity model runs were generally the same to the base version, but with difference as specified here.

2.2.3 Alcohols

Based on the above approach, presented in the chlorine mechanism are the reactions of $\text{Cl}\cdot$ with 18 primary alcohols in the MCM (Table S2). The reactions are assumed to occur via abstraction of H atom by $\text{Cl}\cdot$ to form HCl. Depending on the position of the abstracted H atom, these reactions also yield either a RO_2 or a HO_2 together with a carbonyl compound. The rate coefficients and product yields are taken from the latest IUPAC database for methanol, ethanol, *n*-propanol, *i*-propanol and *n*-butanol. For cresol, the mechanism used in the SAPRC is adopted here (<http://www.engr.ucr.edu/~carter/SAPRC/saprc07.pdf>). For the other alcohols where no kinetics data are available, we assume that they react with $\text{Cl}\cdot$ similarly to OH with rate constants of $k_{X+\text{OH}}$ times a generic $k_{\text{Cl}}/k_{\text{OH}}$ ratio. The generic ratio of 17.1 was estimated by averaging the $k_{\text{Cl}}/k_{\text{OH}}$ values for ethanol, *n*-propanol, *i*-propanol and *n*-butanol. Sensitivity studies show that the impact on modeling results of the treatment on other alcohols should be minor under typical polluted urban conditions (see also Sect. 2.3 and Table 2).

2.2.4 Organic acids and peroxides

Three major organic acids, i.e., formic acid, acetic acid and propanoic acid, are considered in the new chlorine mechanism. The reactions also proceed through H atom abstraction by $\text{Cl}\cdot$ to produce HCl and RO_2 (or HO_2), which already exist in the MCM. The kinetic data are taken from the latest IUPAC database for formic acid and acetic acid. For propanoic acid, we assume that it reacts with $\text{Cl}\cdot$ in the same way to OH but with a rate constant of $k_{X+\text{OH}}$ times the $k_{\text{Cl}}/k_{\text{OH}}$ ratio for acetic acid. In addition, the reaction of $\text{Cl}\cdot$ with methyl hydroperoxide (CH_3OOH) is also compiled according to the IUPAC data (see Table S2).

2.2.5 Organic nitrates

The $\text{Cl}\cdot$ reactions are only considered for five C_1 – C_4 alkyl nitrates (see Table S2). These species are selected because of their relatively higher atmospheric abundance and the availability of experimental kinetics data. The reactions of $\text{Cl}\cdot$ with alkyl nitrates are assumed to proceed by H atom abstraction to form HCl, NO_2 and carbonyl compounds, all of which are present in the MCM. The rate coefficients are adopted from the IUPAC database.

2.2.6 Aromatics

The reactions of OH with aromatic VOCs are very complex. They proceed primarily via addition of OH to the aromatic ring, with a minor route abstracting H atom from the non-ring alkyl substitute (Jenkin et al., 2003). On the contrary, the addition of Cl• to the aromatic ring is very slow, with the rate being approximately two orders of magnitude slower than addition of OH (Tanaka et al., 2003a). Hence, the reactions of Cl• with aromatic VOCs are assumed to proceed via H atom abstraction by Cl• from non-ring alkyl substitutes, forming HCl and a RO₂ radical that already exists in the MCM. The reaction of Cl• with benzene is rather slow and thus is not considered in this module (Riedel et al., 2014). Styrene is treated as an alkene compound and is lumped into the “OLEFIN” species (see Sect. 2.2.7). The Cl• reactions for the other primary aromatic VOCs are presented in the new mechanism module as follows. For toluene and *o*-xylene, the experimental data of Shi and Bernhard (1997) are adopted. For other species, it is assumed that they react with Cl• similarly to OH (the H abstraction pathway only) with rate constants of k_{X+OH} times a generic k_{Cl}/k_{OH} ratio. The generic ratio of 185 was derived by averaging the k_{Cl}/k_{OH} values for toluene and *o*-xylene (note that the k_{X+OH} only refer to the rate of the H atom abstraction route). Sensitivity studies by adopting lower and upper limits of k_{Cl}/k_{OH} indicate that the difference in modeling results is minor under typical polluted urban conditions (see Sect. 2.3 and Table 2).

2.2.7 Alkenes

The reactions of Cl• with alkenes proceed primarily by addition of Cl• to the double bond, forming a Cl-substituted RO₂ radical that is generally new to the MCM. Further degradation of the reaction intermediates need to be considered if applicable. Reaction of Cl• with ethene leads to formation of CH₂(Cl)CH₂O₂ that is already present in the MCM. The rate coefficient of this reaction is adopted from the latest IUPAC database (Table S2).

The mechanism of the Cl•-initiated oxidation of propene is depicted in Fig. 1, with a general and brief description on this complex scheme as follows. First, propene reacts with Cl• via three routes each of which produces a new RO₂ radical. These RO₂ radicals then react individually with NO, NO₃, HO₂ and other RO₂ radicals to form products including carbonyls, HO₂ and compounds already in the MCM (several less-reactive products are not considered for further reactions). The new carbonyls further react with OH and NO₃ to produce new acyl peroxy radicals. Finally, acyl peroxy radicals react individually with NO, NO₂, NO₃, HO₂ and RO₂ to yield products that already exist in the mechanism (a minor product is not considered for further reaction). The rate coefficients and product yields are taken from Riedel et al. (2014) for the initiation reaction of propene with Cl•. For reactions of the chlorine-substituted intermediates, experi-

mental kinetic data are unavailable and the data for the corresponding OH-substituted compounds are adopted as reasonable first approximations.

Given the complexity of the detailed reaction possibilities for the other individual alkene species, and for which no experimental data are available, a lumped method is applied, that is, a new model species “OLEFIN” is defined as the sum of all primary alkenes except for ethene and propene (note that styrene, MVK and 55 % of MACR are also included). The degradation of “OLEFIN” initiated by Cl• is assumed to be largely similar to that of propene, as illustrated in Fig. 2. Briefly, addition of Cl• to the double bond yields a Cl-substituted RO₂ radical, which then reacts with NO, NO₃, HO₂ and other RO₂ to form a Cl-substituted carbonyl and/or peroxide. The new carbonyl further reacts with OH and NO₃ to form an acyl peroxy radical, which finally reacts with NO, NO₂, NO₃, HO₂ and RO₂ to produce compounds already existing in the mechanism. Some less-reactive species (e.g., peroxides) are not considered for further reactions for simplicity. The reaction rates of Cl• + OLEFIN are assumed to be 11-fold faster than that of OH + OLEFIN, according to the k_{Cl}/k_{OH} ratios for ethene, propene and 1-butene (Tanaka et al., 2003a). The rate constant of OH + OLEFIN reaction ($k_{OH+OLEFIN}$) can be calculated by averaging the rate constants of individual species with consideration of their abundances. Sensitivity model test suggests that the impact of such a lumped approach on the modeling results should be of minor significance under typical urban conditions (see Sect. 2.3).

The degradation of isoprene is very complex and remains not fully elucidated (Jenkin et al., 2015). Given the inherent uncertainties in the mechanism, here a very simplified scheme from the CB04 mechanism is adopted, to represent the potential enhancement in ozone production by the Cl• oxidation. The reaction rate of Cl• with isoprene is assumed to be 4.75 times faster than that of OH (Tanaka et al., 2003a). The Cl•-initiated degradation mechanism of isoprene is illustrated in Fig. 3.

2.2.8 Alkyne

Only acetylene is considered for the Cl• reactions, with adoption of the mechanism used in the SAPRC07 (<http://www.engr.ucr.edu/~carter/SAPRC/saprc07.pdf>). Specifically, the reactions proceed through addition of Cl• to the triple bond, followed by further reactions of the intermediates with O₂ to form CO, HO₂ radical and a chlorinated aldehyde. The aldehyde is assumed to be relatively unreactive and is not further represented.

2.3 Sensitivity tests of the chlorine mechanism

A number of tests have been conducted with an observation-based MCM model to assess the sensitivity of model outputs to the reactions and estimated rate coefficients as de-

fined above, where experimental kinetics data were unavailable. A high-pollution episode observed on 7 May 2005 at a downwind site of Shanghai, the largest city of China, was analyzed. This case was selected because very high VOC concentrations with significant contributions of both alkenes and aromatics were observed, and hence representative of typical polluted urban conditions. This episode has been analyzed in our previous study where details of the data are given (Xue et al., 2014a), and the concentrations of individual non-methane hydrocarbons are documented in Fig. S1 in the Supplement. The model was based on the MCM version 3.2, with incorporation of the newly developed Cl• mechanism, and was constrained by the observed diurnal data of O₃, CO, NO, C₁-C₁₀ hydrocarbons and meteorological parameters (Xue et al., 2014a). The concentrations of Cl• were prescribed as a function of OH, which was simulated by the model. Two scenarios, i.e., a high Cl• case ([OH] / [Cl•] = 50) and a normal Cl• case ([OH] / [Cl•] = 200), were considered to represent a wide range of ambient conditions. The net O₃ production rate and oxidative capacity of Cl• (defined as the sum of the oxidation rates of VOCs by Cl•) were computed at a time resolution of 10 min within the model. Where experimental data are unavailable and generic rate coefficients were adopted, sensitivity tests were conducted by using both lower and upper limits of the generic ratio and/or switching off the target reactions. The differences in net O₃ production rate and oxidative capacity of Cl• between the sensitivity runs and base runs were examined.

All of the sensitivity test results are summarized in Table 2. Overall, the results indicate that the impacts of both generic rate estimation and the lumping approach for olefins on the modeling results are minor for the typical urban environments simulated (note that the difference may not be negligible for all polluted conditions, e.g., with high abundances of those heavy VOCs for which k_{Cl} was estimated using $k_{\text{Cl}}/k_{\text{OH}}$ ratios.). In addition, another set of sensitivity tests were conducted to evaluate the performance of the new Cl• mechanism. Including this full mechanism in the model resulted in significant enhancement in oxidative capacity of Cl• as well as moderate enhancement in ozone production rates, in comparison with the model run with the base MCM (including reactions of Cl• with alkanes alone; Table 2). It is clear that photochemical models need to represent more detailed chlorine chemistry when applied to polluted conditions with abundant reactive VOCs.

3 Mechanism application: the role of nitryl chloride in daytime photochemistry

Following the Cl• mechanism sensitivity tests, the module was incorporated into another MCM box model to specifically evaluate the impact of ClNO₂ on atmospheric oxidative capacity and O₃ formation, an area of major uncertainty in current tropospheric chemistry research. Recent studies have

confirmed the presence of high concentrations of ClNO₂, a product of nitrogen oxide induced halogen activation, in both coastal and inland regions, and have suggested its potential significance in enhancing O₃ formation (Osthoff et al., 2008; Phillips et al., 2012; Riedel et al., 2012; Thornton et al., 2010). Here we analyzed a high-pollution case observed at Hok Tsui, a coastal site of Hong Kong, in the summer of 2012, which provided the first ambient ClNO₂ observations in China. Elevated ClNO₂ concentrations of up to 1997 pptv (1 min data) were detected in a plume that originated from urban Hong Kong and the Pearl River Delta region during the night of 23–24 August. These measurement results have been reported in our previous work (Tham et al., 2014). In the present study, we focus on the consequence of ClNO₂ photolysis on the next day's photochemistry through a detailed modeling study. A full description of the observations and the target case is given in the Supplement.

The Observation-Based Model for investigating the Atmospheric Oxidative Capacity and Photochemistry (OBMAOCP), which has been applied in many previous studies (Xue et al., 2013, 2014a, b, c), was here updated to include the Cl• chemistry module and used for the analyses. In addition to the comprehensive chemistry addressed by the MCM v3.2, dry deposition and dilution with evolution of the planetary boundary layer were also considered (Xue et al., 2014a; wet deposition was not considered here). The model was initialized by the measured nighttime concentrations of a full list of chemical species and meteorological parameters when the maximum ClNO₂ value was observed (see Table S3 for the initial model conditions; note that the heterogeneous production of ClNO₂ was turned off here as the model is initialized by the measured ClNO₂ data), and was then run for a 24 h period to simulate the chemical evolution of the prescribed plume. The model was run 5 times consecutively to stabilize the unmeasured species (e.g., radicals and reaction intermediates), and the daytime output of the last run was subject to further analysis. Two scenarios with and without ClNO₂ were conducted to examine the impact of ClNO₂ chemistry.

With 1997 pptv of initial ClNO₂, the model predicted an early morning (~08:30 local time) peak of Cl• of 8.2×10^4 molecule cm⁻³ that then decreased with time of the day (see Fig. 4a). Such level of Cl• accounts for up to 2.0 % of the abundance of OH, the predominant daytime oxidant. Considering the much faster reaction rates of Cl• with VOCs than OH, Cl• should be an important oxidant in the early morning (see below for a detailed quantification). The addition of ClNO₂ enhanced significantly the in situ O₃ production within the plume, with increases of 33.7 and 10.3 % in the early morning and daytime average (08:00–18:00) net O₃ production rates respectively (Fig. 4b). Despite the weakened role of Cl• oxidation after the morning period, the model simulated peak O₃ increased by 5 ppbv (or 6.8 %) compared to the non-ClNO₂ case (Fig. 4c). Such enhancement is comparable to that derived from a chemical transport modeling

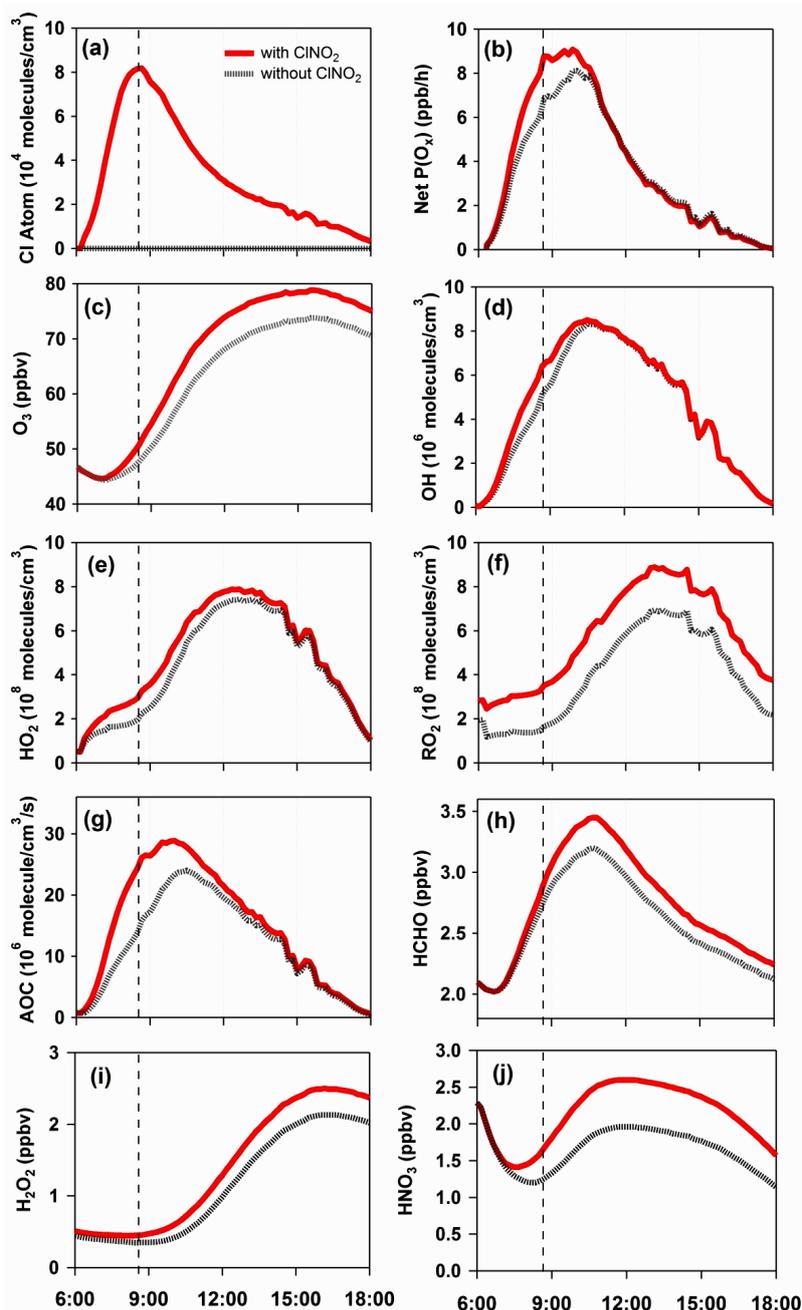


Figure 4. The model-simulated Cl atom (a), net O_x production rate (b), ozone (c), OH (d), HO₂ (e), RO₂ (f), atmospheric oxidative capacity (AOC; g), HCHO (h), H₂O₂ (i) and HNO₃ (j) with and without initial concentration of ClNO₂, for the polluted plume observed at Hok Tsui, Hong Kong, on 24 August 2012. The vertical dashed lines indicate the “early morning case” when the peak of Cl atom occurs and the ClNO₂ impacts are evaluated in parallel with the “daytime average case”.

study in North America (up to 6.6 ppbv or 10 % in summer; Sarwar et al., 2012). Evidently, the nighttime formation of ClNO₂ may pose a significant positive feedback to the next day’s ozone formation in southern China.

The reactions of Cl• with VOCs produce RO₂ radicals, which are then recycled to HO₂ and OH. Figure 4d–f show the significant impacts of the addition of ClNO₂ on the model

simulated OH, HO₂ and RO₂ radicals. In the early morning when the Cl• chemistry was the most active, the Cl• arising from ClNO₂ photolysis enhanced the concentrations of RO₂, HO₂ and OH by up to 120, 52.7 and 34.9 %, respectively. With photochemical processing, the Cl• became gradually exhausted while the other radical precursors (e.g., O₃ and OVOCs) accumulated, leading to decreasing contribu-

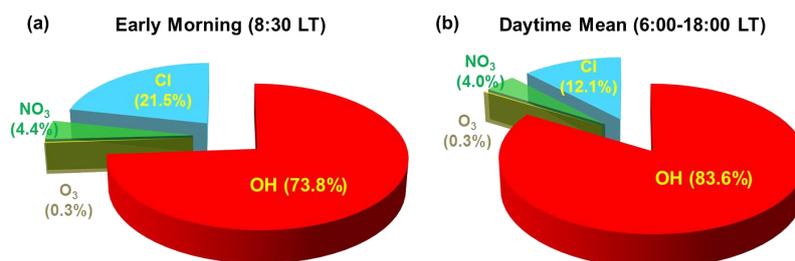


Figure 5. Breakdown of atmospheric oxidative capacity by individual oxidants in the early morning (a) and throughout the daytime (b) for the plume observed at Hok Tsui, Hong Kong, on 24 August 2012.

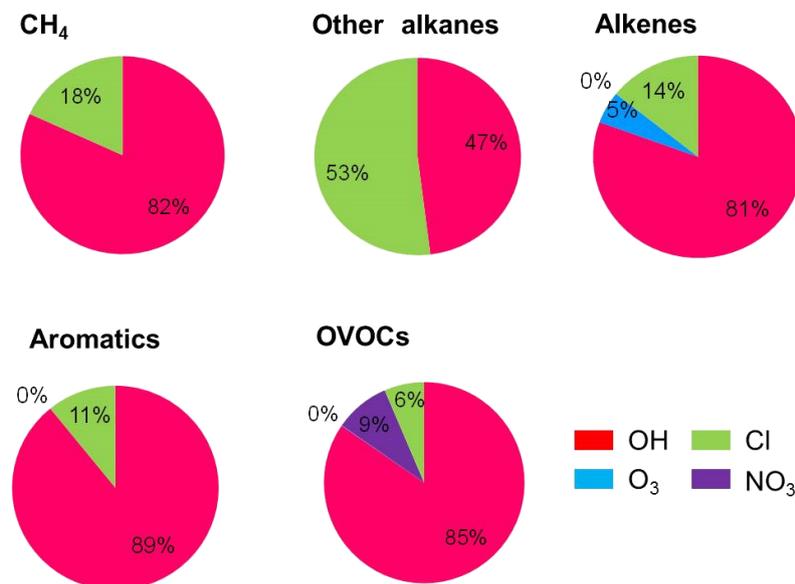


Figure 6. Oxidation of VOCs by individual oxidants in the early morning (08:30 local time) in the plume observed at Hok Tsui, Hong Kong, on 24 August 2012.

tions of Cl• to the radical production. In terms of the daytime average, nevertheless, the enhancements in the modeled RO₂ (45.1%), HO₂ (12.2%) and OH (6.6%) resulting from the VOC oxidation by Cl• are still significant or considerable. These results suggest the important impact of Cl• on the RO_x radicals and hence atmospheric oxidative capacity.

We further quantified the contributions of Cl• to the atmospheric oxidative capacity (AOC). AOC is defined in the present study as the sum of the oxidation rates of CO and individual VOCs by all major oxidants, i.e., OH, O₃, NO₃ and Cl•, commonly used as a proxy of the intensity of oxidation capability of the atmosphere (Elshorbany et al., 2009), and was computed by the model. With inclusion of ClNO₂ (thus Cl•) in the model, the AOC was substantially strengthened with increases of 90.3% in the early morning and of 25.4% for the daytime average (Fig. 4g). Such large enhancements are attributable to the direct oxidation capacity of Cl• as well as the indirect effect of increasing RO_x radicals. Figure 5 depicts the breakdown of AOC by the individual oxidants. The analysis shows Cl• to be the second most important oxidant

not only in the early morning (~21.5%) but also throughout the daytime (~12.1%). OH is clearly the predominant player in photochemical oxidation, while O₃ and NO₃ play a relatively minor role in this polluted plume observed in Hong Kong.

The role of Cl• in VOC oxidation was also assessed. The contributions of major oxidants to the degradation of individual VOC groups during the early morning period are summarized in Fig. 6. As expected, OH dominates the VOC oxidation contributing to 82, 47, 81, 89 and 85% of oxidation of methane, other alkanes, alkenes, aromatics and OVOCs. Cl• is another important oxidant and in particular the principal one for alkanes. It oxidizes 18% of methane and 53% of other alkanes, and also accounts for 14, 11 and 6% of the alkenes, aromatics and OVOCs oxidation. The significant role of Cl• in oxidizing alkanes agrees well with the previous studies (e.g., Young et al., 2014). Clearly, photolysis of ClNO₂ can facilitate the oxidation of VOCs (especially alkanes) in the early morning.

Figure 4h–j illustrate the impact of ClNO₂ photolysis on the formation of formaldehyde (HCHO), hydrogen peroxide (H₂O₂) and nitric acid (HNO₃), several major photochemical products in the atmosphere. The model-simulated maximum values of HCHO, H₂O₂ and HNO₃ increased by 8.0, 17.3 and 13.4% with inclusion of ClNO₂ compared to the non-ClNO₂ case, respectively. By enhancing radical production (i.e., RO_X and Cl) and hence oxidation of SO₂, NO_X and VOCs, photolysis of ClNO₂ also has a high potential to promote formation of secondary aerosols, such as sulfate, nitrate and secondary organic aerosol (SOA), but has not been quantified here.

In summary, the nocturnal ClNO₂ formation has a high potential to perturb the next day's atmospheric photochemistry by promoting VOC oxidation, radical production and cycling, and O₃ formation. Although the present analyses are only based on a high-pollution case at a coastal site (sensitivity tests with a lower level of initial ClNO₂ show lower impacts, see Fig. S2), our results should be representative of other polluted coastal environments of China, as indicated by our follow-on studies. Our recent observations have confirmed the ubiquitous presence of elevated ClNO₂ both at other sites in Hong Kong and over the region of the North China Plain. In particular, very high ClNO₂ concentrations (1 min value of 4.7 ppbv) were observed very recently at a mountain site (~957 m above sea level) in Hong Kong, which appears to be the highest reported value across the world (Wang et al., 2015). Intense emissions of nitrogen oxides, VOCs and particles (Zhang et al., 2009), which interact with the abundant chlorine-containing compounds released from both anthropogenic and natural sources (e.g., sea spray), are conducive to the heterogeneous formation of ClNO₂ and in turn Cl• photochemistry in the coastal environments of China. A recent chemical transport modeling study also suggests the importance of ClNO₂ chemistry to ozone formation and the atmospheric oxidative capacity in the Northern Hemisphere, especially over China and western Europe (Sarwar et al., 2014). Detailed mechanisms describing the Cl• chemistry are crucial for current models to more accurately represent and lead to better understanding of atmospheric photochemistry and formation of air quality problems.

4 Summary and conclusions

A chemical mechanism has been developed for use in the MCM to address the chemistry of chlorine atom, a potential important oxidant in the atmosphere. It includes 205 reactions and describes the Cl•-initiated degradation of alkenes, alkynes, aromatics, aldehydes, ketones, alcohols, organic acids and organic nitrates, in combination with the inorganic chemistry of Cl• and its precursors. Application of this mechanism in a MCM box model suggests the important role of the nocturnal formation of ClNO₂, a major Cl• precursor,

in the following day's atmospheric photochemistry. With 1997 pptv of ClNO₂ that was observed at a coastal site in Hong Kong, southern China, the Cl• produced from ClNO₂ photolysis strongly enhances the RO_X radical production and recycling, VOC oxidation, and ozone formation in the early morning period, and even has significant or moderate impacts throughout the daytime. It is therefore critical that photochemical models account for the detailed chemistry of chlorine to better understand the atmospheric oxidative capacity and ozone formation in polluted environments with abundant chlorine-containing compounds and VOCs.

Code availability

The code is written in the FACSIMILE language. A number of instructions are provided as comments in the code to make it easily adapted in the Master Chemical Mechanism framework. The code is freely available for the community and can be accessed by request from L. K. Xue (xuelikun@sdu.edu.cn) or S. M. Saunders (sandra.saunders@uwa.edu.au).

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Author contributions. L. K. Xue and S. M. Saunders developed the mechanism and wrote the paper. T. Wang designed and provided the field data for model test and demonstration. R. Gao and Q. Z. Zhang provided Figs. 1–3. X. F. Wang and X. Wang gave helpful suggestions and polished the writing.

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