Geosci. Model Dev. Discuss., 8, 4823–4849, 2015
www.geosci-model-dev-discuss.net/8/4823/2015/
doi:10.5194/gmdd-8-4823-2015

Geoscientific Model Development
Discussions
Open Access

Development of a chlorine chemistry module for the Master Chemical Mechanism

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Received: 27 May 2015 – Accepted: 03 June 2015 – Published: 23 June 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

The chlorine atom (Cl•) 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 Cl• chemistry is incomplete as it only considers the reactions for alkanes. In this paper, we develop a more comprehensive Cl• chemistry module that can be directly incorporated within the MCM framework. A suite of 199 chemical reactions describes the Cl• -initiated degradation of alkenes, aromatics, aldehydes, ketones, alcohols, and some organic acids and nitrates, along with the inorganic chemistry involving Cl• 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 Cl• 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 fully 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 (Cl•) 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, $Cl\cdot$ 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), hypochloric acid (HOCl), nitryl chloride ($ClNO_2$) and $ClONO_2$ (Riedel et al., 2014). These so-called $Cl\cdot$ 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, $Cl\cdot$ 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 $Cl\cdot$ 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 $Cl\cdot$ chemistry is accounted for in current major chemical mechanisms is inhomogeneous. To our knowledge, the organic and inorganic chemistry involving $Cl\cdot$ 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 (CB-IV) mechanism, and Sarwar et al. (2012) extended it for use in CB-V (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 $Cl\cdot$ oxidation of VOCs have been incorporated in the CB-VI, SAPRC-07 and its updates (Carter, 2010; Yarwood et al., 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 Cl• chemistry in the MCM remains incomplete. It considers only the reactions of Cl• with alkanes for which the oxidation by Cl• may play a dominant role, while the reactions between Cl• and other VOC species are not represented (Saunders et al., 2003). Recently, Riedel et al. (2014) added to the MCM Cl• 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 Cl• chemical mechanism that can be applied to a wider range of tropospheric conditions.

A major goal of the present work is to develop a Cl• 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 Cl• with various VOCs and compiled into a chemical module. This module contains 199 reactions and describes the Cl• -initiated degradation of all the MCM primary alkenes, aromatics, aldehydes, ketones, alcohols, selected organic acids and nitrates as well as the inorganic chemistry of Cl• and its precursors. This module 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 Cl• 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.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

2 Mechanism development

For the developed Cl• mechanism module to be readily incorporated with 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 S1 in the Supplement 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 Cl• are considered. They include photolysis reactions of Cl• precursors, reactions of Cl• with inorganic species, reactions of OH with Cl-containing species recycling Cl• 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 Cl• reactions are considered for formaldehyde, acetaldehyde, propanal, butanal, isobutyl aldehyde, pentanal, and benzaldehyde (see Table S1). Based on the available literature, the reactions are assumed to proceed via H atom abstraction by Cl• 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 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 Cl• similar to OH with a rate constant of k_{X+OH} times a generic k_{Cl}/k_{OH} ratio. The generic k_{Cl}/k_{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_{Cl}/k_{OH} ratio of 6.08 (average) is adopted. Sensitivity tests were conducted by using the lower and upper limits of the k_{Cl}/k_{OH} ratio, and suggested that the differences among the modeling results were negligible under typical polluted urban conditions (see Sect. 2.3 and Table 2 for the details of sensitivity tests).

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 S1). The reactions proceed via H atom abstraction by Cl• to form HCl and RO_2, 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_{X+OH} times a generic k_{Cl}/k_{OH} ratio. The generic ratio of 23.9 was derived by averaging the k_{Cl}/k_{OH}values for acetone and MEK, for which experimental data are available. Sensitivity tests by adopting lower and upper limits of k_{Cl}/k_{OH} suggest that the difference in modeling results is minor under typical polluted urban conditions (see Sect. 2.3 and Table 2).

2.2.3 Alcohols

Based on the above approach, presented in the chlorine mechanism are the reactions of Cl• with 17 primary alcohols in the MCM (Table S1). The reactions are assumed to occur via abstraction of H atom by Cl• 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 the other alcohols where no kinetics data are available, we assume that they react with Cl• similarly to OH with rate constants of k_{X+OH} times a generic k_{Cl}/k_{OH} ratio. The generic ratio of 17.1 was estimated by averaging the k_{Cl}/k_{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 Cl• 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 Cl• in the same way to OH but with a rate constant of k_{X+OH} times the k_{Cl}/k_{OH} ratio for acetic acid. In addition, the reaction of Cl• with methyl hydroperoxide (CH_3OOH) is also compiled according to the IUPAC data (see Table S1).

2.2.5 Organic nitrates

The Cl• reactions are only considered for five C_1–C_4 alkyl nitrates (see Table S1). These species are selected because of their relatively higher atmospheric abundance and the availability of experimental kinetics data. The reactions of Cl• 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 RO_2 radical that already exists in the MCM. The Cl• reactions for 13 primary aromatic VOCs are presented in the new mechanism module (see Table S1). 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 RO_2 radical that is generally new to the MCM. Further degradation of the reaction intermediates need be considered if applicable. Reaction of Cl• with ethene leads to formation of $CH_2(Cl)CH_2O_2$ that is already present in the MCM. The rate coefficient of this reaction is adopted from the latest IUPAC database (Table S1).

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 RO_2 radical. These RO_2

radicals then react individually with NO, NO_3, HO_2 and other RO_2 radicals to form products including carbonyls, HO_2 and compounds already in the MCM (several less-reactive products are not considered for further reactions). The new carbonyls further react with OH and NO_3 to produce new acyl peroxy radicals. Finally, acyl peroxy radicals react individually with NO, NO_2, NO_3, HO_2 and RO_2 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, experimental 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 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. 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 RO_2 radical, which then reacts with NO, NO_3, HO_2 and other RO_2 to form a Cl-substituted carbonyl and/or peroxide. The new carbonyl further reacts with OH and NO_3 to form an acyl peroxy radical, which finally reacts with NO, NO_2, NO_3, HO_2 and RO_2 to produce compounds already existing in the mechanism. Some less-reactive species (e.g., peroxides) are not considered for further reactions for simplicity. According to the CB-IV mechanism, the reaction rate of Cl• + OLEFIN is assumed to be 20 fold faster than that of OH + OLEFIN (Tanaka et al., 2003a). The rate constant of OH + OLEFIN reaction ($k_{\mathrm{OH+OLEFIN}}$) 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 CB-IV 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.

2.3 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 defined above, where experimental kinetics data were unavailable. A high pollution episode observed on 07 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 O_3, CO, NO, C_1–C_{10} 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 O_3 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 O_3 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. 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). The results show how important it is for photochemical models to represent more fully 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 $ClNO_2$ on atmospheric oxidative capacity and O_3 formation, an area of major uncertainty in current tropospheric chemistry research. Recent studies have confirmed the presence of high concentrations of $ClNO_2$, a product of nitrogen oxides induced halogen activation, in both coastal and inland regions, and have suggested its potential significance in enhancing O_3 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 $ClNO_2$ observations in China. Elevated $ClNO_2$ 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 $ClNO_2$ 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 Supplementary materials.

The Observation-Based Model for investigating the Atmospheric Oxidative Capacity and Photochemistry (OBM-AOCP), 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). The model was initialized by the measured nighttime concentrations of a full list of chemical species and meteorological parameters when the maximum $ClNO_2$ value was observed (see Table S2 for the initial model conditions), 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 $ClNO_2$ were conducted to examine the impact of $ClNO_2$ chemistry.

With 1997 pptv of initial $ClNO_2$, the model predicted an early morning (~ 08:30 local time) peak of Cl• of 8.65×10^4 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 $ClNO_2$ enhanced significantly the in-situ O_3 production within the plume, with increases of 34.6 and 9.2 % in the early morning and daytime average (08:00–18:00) net O_3 production rates respectively (Fig. 4b). Despite the weakened role of Cl• oxidation after the morning period, the model simulated peak O_3 increased by 7.8 ppbv (or 6.2 %) compared to the non-$ClNO_2$ case (Fig. 4c). Evidently, the nighttime formation of $ClNO_2$ may pose a significant positive feedback to the next-day's ozone formation in southern China.

The reactions of Cl• with VOCs produce RO_2 radicals, which are then recycled to HO_2 and OH. Figure 4d–f shows the significant impacts of the addition of $ClNO_2$ on the model simulated OH, HO_2 and RO_2 radicals. In the early morning when the Cl• chemistry was the most active, the Cl• arising from $ClNO_2$ photolysis enhanced the concentrations of RO_2, HO_2 and OH by up to 67.1, 53.4 and 34.3 %, respectively. With photochemical processing, the Cl• became gradually exhausted while the other radical precursors (e.g., O_3 and OVOCs) accumulated, leading to decreasing contributions of Cl• to the radical production. In terms of the daytime average, nevertheless, the enhancements in the modeled RO_2 (24.5 %), HO_2 (12.3 %) and OH (4.7 %) 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, O_3, NO_3 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 $ClNO_2$ (thus Cl•) in the model, the AOC was substantially strengthened with increases of 91.4 % in the early morning and of 25.6 % 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 (∼ 21.6 %) but also throughout the daytime (∼ 12.6 %). OH is clearly the predominant player in photochemical oxidation, while O_3 and NO_3 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 89, 47, 77, 92 and 89 % 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 11 % of methane and 53 % of other alkanes, and also accounts for 18, 8 and 4 % 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). The model simulated maximum formaldehyde, a major oxidation product of methane, increased by 8.2 % with inclusion of $ClNO_2$ compared to the non-$ClNO_2$ case (Fig. 4h). Clearly, photolysis of $ClNO_2$ can facilitate the oxidation of VOCs (especially alkanes) in the early morning.

In summary, the nocturnal $ClNO_2$ formation has a high potential to perturb the next-day's atmospheric photochemistry by promoting VOC oxidation, radical production and cycling, and O_3 formation. Although the present analyses are only based on one case at a coastal site, our results should be representative of other polluted coastal environments of China, as indicated by our follow-up studies. Our recent observations have confirmed the ubiquitous presence of elevated $ClNO_2$ both at other sites in Hong Kong and over the region of the North China Plain. In particular, very high $ClNO_2$ 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 conductive to the heterogeneous formation of $ClNO_2$ and in turn Cl• photochemistry in the coastal environments of China. 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 199 reactions and describes the Cl• -initiated degradation of alkenes, 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 $ClNO_2$, a major Cl• precursor, in the following-day's atmospheric photochemistry. With 1997 pptv of $ClNO_2$ that was observed at a coastal site in Hong Kong, southern China, the Cl• produced from $ClNO_2$ 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 the photochemical models account for the full 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).

The Supplement related to this article is available online at doi:10.5194/gmdd-8-4823-2015-supplement.

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 W. X. Wang gave helpful suggestions and polished the writing.

Acknowledgements. The authors would like to thank the University of Leeds for providing the Master Chemical Mechanism, the IUPAC for providing the chemical kinetics data, and the NCAR for providing the TUV model. We are also grateful to Yee Jun Tham, Qiaozhi Zha and Steven Poon for their efforts collecting the field data which are used for the present modeling study, and to Aijun Ding for the helpful discussions. This work was funded by the National Natural Science Foundation of China (project no. 41275123), Shandong University (11460075617010), and the Research Grant Council of Hong Kong (PolyU5125/12P).

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

Category	Reaction	k (cm^3 molecules^{-1} s^{-1} or s^{-1}) or J (s^{-1})	Remarks
Photolysis reactions	$Cl_2 \rightarrow Cl + Cl$	J_{Cl2}	–
	$ClNO_2 \rightarrow NO_2 + Cl$	J_{ClNO2}	–
	$ClONO_2 \rightarrow NO_3 + Cl$	$0.83 \times J_{ClONO2}$	a
	$ClONO_2 \rightarrow NO_2 + ClO$	$0.17 \times J_{ClONO2}$	a
	$HOCl \rightarrow OH + Cl$	J_{HOCl}	–
Cl + *X*	$Cl + O_3 \rightarrow ClO + O_2$	$2.8 \times 10^{-11} \exp(-250/T)$	b
	$Cl + HO_2 \rightarrow HCl + O_2$	3.5×10^{-11}	b
	$Cl + HO_2 \rightarrow ClO + OH$	$7.5 \times 10^{-11} \times \exp(-620/T)$	b
	$Cl + H_2O_2 \rightarrow HCl + HO_2$	$1.1 \times 10^{-11} \times \exp(-980/T)$	b
	$Cl + NO_3 \rightarrow NO_2 + ClO$	2.4×10^{-11}	b
	$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$	$6.2 \times 10^{-12} \times \exp(145/T)$	b
OH + *X*	$OH + HCl \rightarrow Cl + H_2O$	$1.7 \times 10^{-12} \times \exp(-230/T)$	b
	$OH + Cl_2 \rightarrow HOCl + Cl$	$3.6 \times 10^{-12} \times \exp(-1200/T)$	b
	$OH + HOCl \rightarrow ClO + H_2O$	5.0×10^{-13}	b
	$OH + ClO \rightarrow HO_2 + Cl$	1.8×10^{-11}	b
	$OH + ClO \rightarrow HCl + O_2$	1.2×10^{-12}	b
ClO + *X*	$ClO + NO_2 \rightarrow ClONO_2$	7.0×10^{-11}	b
	$ClO + HO_2 \rightarrow HOCl + O_2$	$2.2 \times 10^{-12} \times \exp(340/T)$	b
	$ClO + NO \rightarrow Cl + NO_2$	$6.2 \times 10^{-12} \times \exp(295/T)$	b
Hetero. reactions	$N_2O_5 \rightarrow NA + NA$	$0.25 \times C_{N2O5} \times \gamma_{N2O5} \times S_{AERO} \times (1 - \varphi_{CLNO2})$	c
	$N_2O_5 \rightarrow NA + ClNO_2$	$0.25 \times C_{N2O5} \times \gamma_{N2O5} \times S_{AERO} \times \varphi_{CLNO2}$	c
	$NO_3 \rightarrow$ products	$0.25 \times C_{NO3} \times \gamma_{NO3} \times S_{AERO}$	c
	$ClONO_2 \rightarrow Cl_2 + HNO_3$	$0.25 \times C_{ClONO2} \times \gamma_{ClONO2} \times S_{AERO}$	c
	$HOCl \rightarrow Cl_2$	$0.25 \times C_{HOCl} \times \gamma_{HOCl} \times S_{AERO}$	c

[a] The branching ratio is determined based on the Tropospheric Ultraviolet Visible (TUV) Radiation model calculations (http://cprm.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_{CLNO2} is the product yield of $ClNO_2$ from the heterogeneous reactions of N_2O_5. NA is nitrate aerosol.

Table 2. Summary of sensitivity test results[a].

Scenario	Description	[Cl] = [OH]/50		[Cl] = [OH]/200	
		Difference in daytime $P(O_x)$	Difference in daytime OC_{CL}	Difference in daytime $P(O_x)$	Difference in daytime OC_{CL}
S1	Base without expanded Cl chemistry	12.5 %	182 %	4.4 %	165 %
S2	Base without OLEFIN (only includes Cl oxidation of C_2H_4 and C_3H_6)	5.3 %	7.4 %	1.7 %	7.3 %
S3	Base with $k_{Cl}/k_{OH} = 0$ for aromatics	2.2 %	3.1 %	< 1 %	5.6 %
	Base with $k_{Cl}/k_{OH} =$ 220 for aromatics	< 1 %	< 1 %	< 1 %	1.2 %
	Base with $k_{Cl}/k_{OH} =$ 150 for aromatics	< 1 %	< 1 %	< 1 %	1.0 %
S4	Base with $k_{Cl}/k_{OH} = 0$ for aldehydes	< 1 %	1.5 %	< 1 %	< 1 %
	Base with $k_{Cl}/k_{OH} =$ 8.5 for aldehydes	< 1 %	< 1 %	< 1 %	< 1 %
	Base with $k_{Cl}/k_{OH} =$ 5.4 for aldehydes	< 1 %	< 1 %	< 1 %	< 1 %
S5	Base with $k_{Cl}/k_{OH} = 0$ for ketones	< 1 %	3.0 %	< 1 %	2.0 %
	Base with $k_{Cl}/k_{OH} =$ 36 for ketones	< 1 %	< 1 %	< 1 %	< 1 %
	Base with $k_{Cl}/k_{OH} =$ 12 for ketones	< 1 %	1.6 %	< 1 %	< 1 %
S6	Base with $k_{Cl}/k_{OH} = 0$ for alcohols	< 1 %	< 1 %	< 1 %	< 1 %
S7	Base without $Cl + C_5H_8$	< 1 %	< 1 %	< 1 %	< 1 %

[a] The daytime $P(O_x)$ and OC_{CL} are the daytime average (09:00–18:00 local time) net production rate of O_x and oxidative capacity of the Cl• atom. The differences are with respect to the base model results with the full chlorine mechanism.

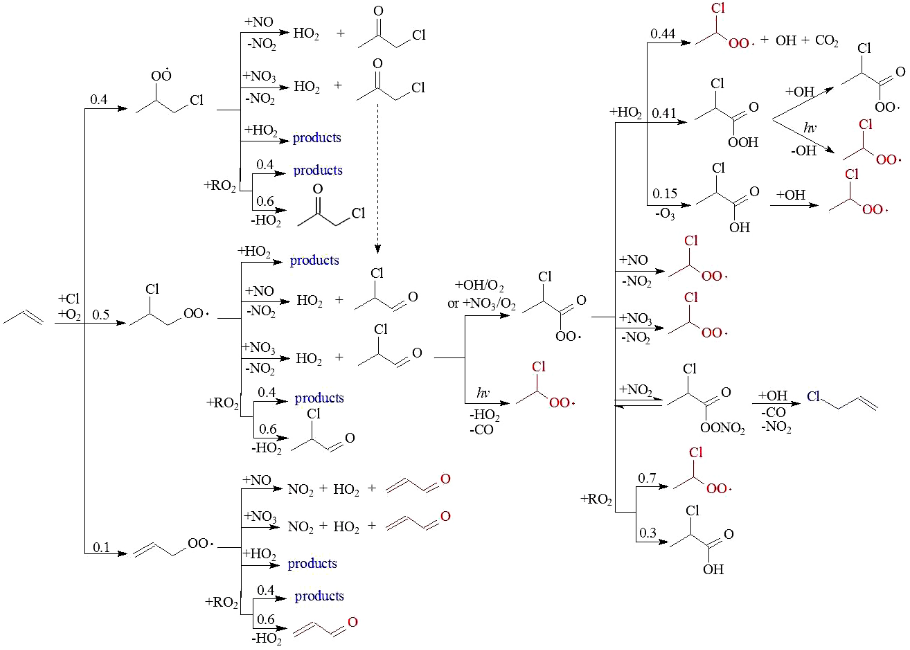

Figure 1. The oxidation mechanism of propene by Cl•. Note that (1) the species in red already exist in the MCM; (2) degradation of the species in blue is not further considered for simplicity; (3) the preceding plus and minus indicate the reactants and products respectively; (4) for simplicity, the degradation of CH_3COCH_2Cl was approximated to be the same as that of $CH_3CH(Cl)CHO$.

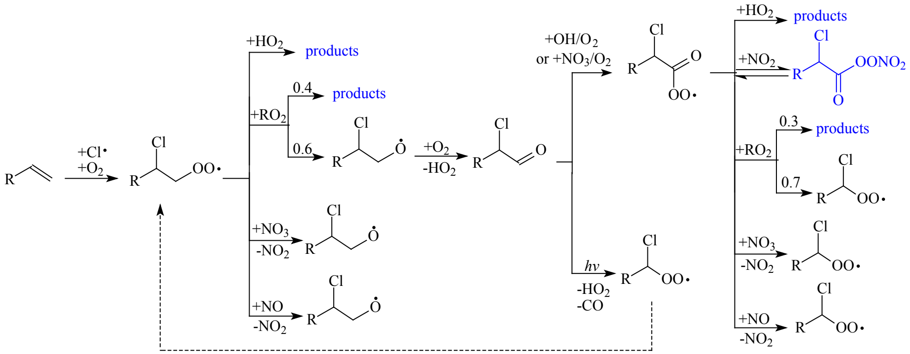

Figure 2. Simplified oxidation mechanism of the lumped "OLEFIN" by Cl•. Note that (1) the degradation of species in blue is not further considered for simplicity; (2) the preceding plus and minus indicate the reactants and products respectively; (3) for simplicity, the degradation of $RCH(Cl)O_2$ was approximated to be the same as that of $RCH(Cl)CH_2O_2$.

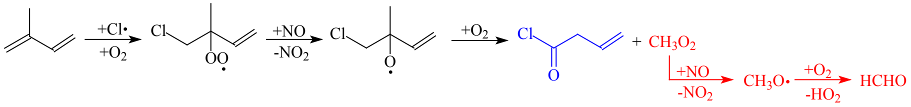

Figure 3. Simplified oxidation mechanism of isoprene by Cl•. Note that (1) the species in red already exist in the MCM; (2) degradation of the species in blue is not further considered for simplicity; (3) the preceding plus and minus indicate the reactants and products respectively.

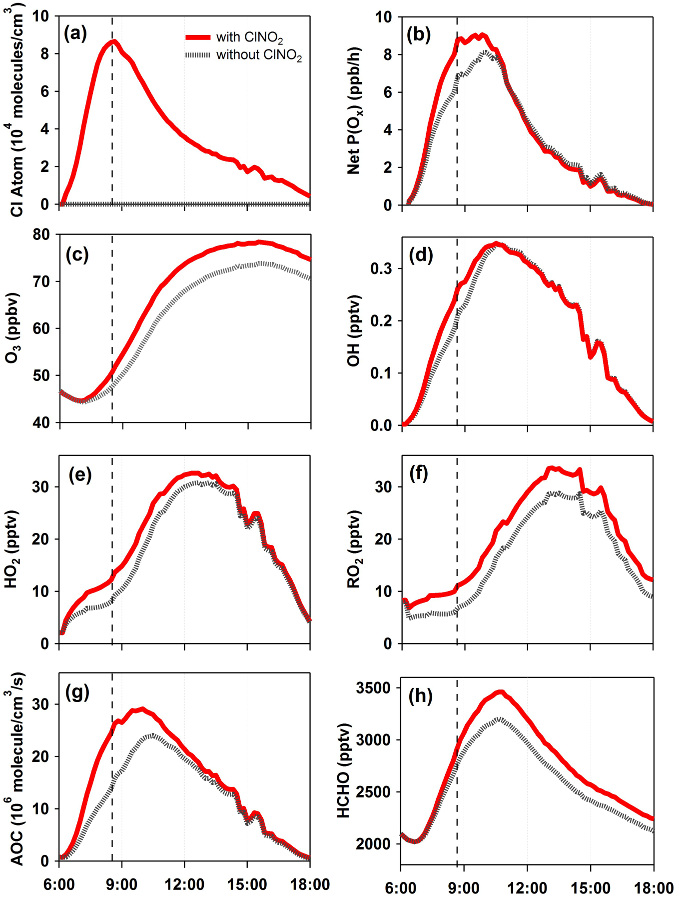

Figure 4. The model-simulated Cl atom **(a)**, net O_x production rate **(b)**, ozone **(c)**, OH **(d)**, HO_2 **(e)**, RO_2 **(f)**, atmospheric oxidative capacity (AOC; **g**) and HCHO **(h)**, with and without initial concentration of $ClNO_2$, for the polluted plume observed at Hok Tsui, Hong Kong on 24 August 2012.

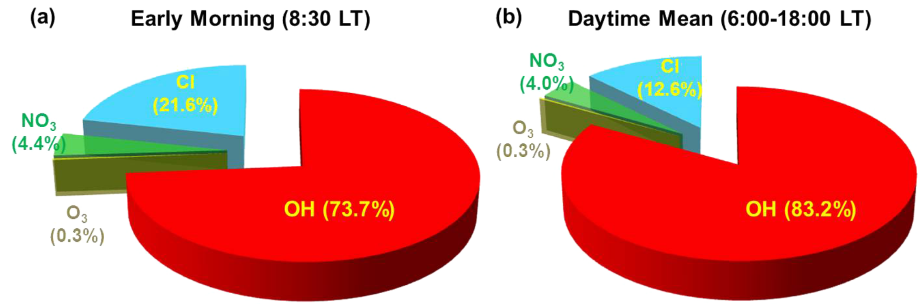

Figure 5. Breakdown of atmospheric oxidative capacity by individual oxidants in the early morning **(a)** and throughout the daytime **(b)** for the plume observed at Hok Tsui, Hong Kong on 24 August 2012.

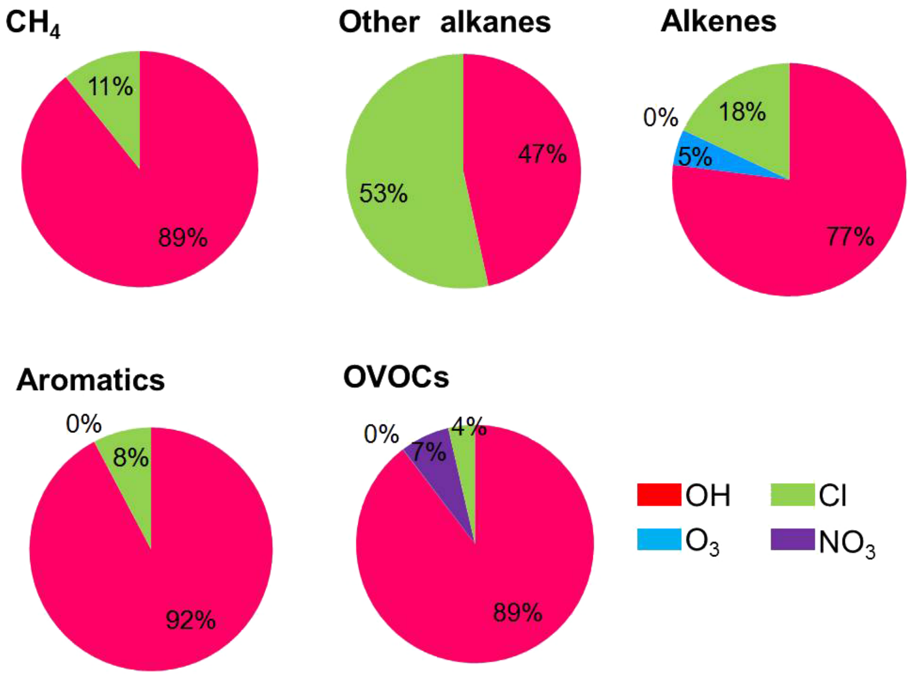

Figure 6. Oxidation of VOCs by individual oxidants in the early morning (08:30 local time) in the plume observed at Hok Tsui, Hong Kong on 24 August 2012.