Dear Editor,

We have revised our manuscript based on the review comments, and addressed all of the comments in the Response to Reviewers. For clarity, all the changes we have made based on the review comments are highlighted in red in the revised manuscript. Now we would like to submit it for further evaluation for potential publication at GMD. Thank you so much for handling our submission!

We look forward to hearing from you again about further evaluation of our work.

Best regards,

Likun Xue

Ph.D. Professor,

Environment Research Institute

Shandong University

Response to Reviewer 1

General comments:

Chlorine chemistry representation of the current MCM is incomplete. Here, the authors developed a comprehensive chlorine chemistry for the MCM. The authors then implement the MCM along with the comprehensive chlorine chemistry in a box model and perform sensitivity analyses. Then they used the detailed chlorine chemistry to examine the role of nitryl chloride chemistry on air quality. The article will improve the current understanding of chlorine chemistry, be useful to air quality scientists, and merits publication. However, it needs a revision to resolve some issues. Specific comments are provided below:

Response: we thank the reviewer for the helpful comments, which are much useful for improving our manuscript. We have revised the manuscript accordingly and address the specific comments below.

Specific comments:

Page 4824, lines 19-22: Perhaps "more detailed chlorine chemistry" or something similar may be better suited than "more fully chlorine chemistry".

Response: the original phrase has been modified as "more detailed chlorine chemistry".

Page 4825, lines 14-15: Please check the first sentence.

Response: this sentence has been modified as follows.

"The role that Cl · plays in VOC oxidation and O_3 formation remains a large uncertainty of tropospheric chemistry."

Page 4825, lines 22: Sarwar et al. (2012) identifies the mechanism as CB05 not CB-V.

Response: "CB-V" has been rephrased as "CB05".

Page 4825, lines 25: Yarwood et al. (2010) identifies the mechanism as CB6 not CB-VI. Yarwood et al. (2010) does not include any chlorine chemistry.

Response: we got the information that CB6 includes Cl · chemistry from the presentation of Dr. Yarwood for the TCEQ, but could not find a formal reference for it. So we have removed this information in the revised manuscript.

Page 4826, lines 1-11: Saunders et al. (2003) does not provide any chlorine chemistry. Can the authors provide a reference for the existing chlorine chemistry in MCM? If a reference is not available, can the authors add a table presenting the existing chlorine chemistry in MCM?

Response: a table presenting the existing chlorine chemistry in the MCM has been provided in the supplementary materials of the revised manuscript.

Page 4826, lines 17-19: The authors mention that the module contains 199 chemical reactions for chlorine. However, Table 1 and Table S1 do not contain 199 reactions.

Response: only the initial reactions of chlorine with alkenes are included in Table S1. The addition of Cl ·to the double bond of alkenes introduces new species and hence new reactions, which are not included in Table S1 but in Figures 1-3. So the reactions summarized in Table 1 and Table S1 are less than 199. The code containing all of the reactions will be shared freely with the community later.

Page 4827-4833: Sensitivity tests were conducted by using lower and upper limits of kCl/kOH ratios to demonstrate that the differences among the modeling results are negligible for polluted urban conditions. Figure S1 shows that concentrations for most organic compounds for which kCl were estimated using kCl/kOH ratios are either negligible or small. Thus, the sensitivity test results showed that the differences are negligible. If concentrations for these organic compounds are not negligible, then the differences may not be negligible. Some discussions are needed to address that the differences may not be negligible for all polluted conditions.

Response: we agree that the difference may not be negligible with higher concentrations of organic compounds with which k_{Cl} was estimated using k_{Cl}/k_{OH} ratios, although these heavy VOCs (containing more carbons) are generally in low levels in the ambient atmosphere. The following statement has been added in the revised paper to address this issue.

"Note that the differences may not be negligible for all polluted conditions, *i.e.*, with high abundances of those heavy VOCs with which the k_{Cl} was estimated using k_{Cl}/k_{OH} ratios."

Riedel et al. (2014) considered reactions of benzene and styrene with Cl which are not considered here. Carter considered the reactions of glyoxal, methylglyoxal, cresol, methacrolein, methyl vinyl ketone, acetylene with Cl, which are not considered here. Some discussions are needed for not including these reactions in this study. http://www.engr.ucr.edu/~carter/SAPRC/saprc07.pdf (Table A-5)

Response: the reactions of Cl with glyoxal, methylglyoxal, cresol, MACR, MVK, styrene and acetylene have been considered in the revised mechanism. The mechanism used in the SAPRC is adopted to represent the oxidation of glyoxal, methylglyoxal, cresol and acetylene by Cl. MVK is treated as an alkene species assuming that reactions only involve Cl addition to the C=C double bond, according to the OH-oxidation mechanism in the MCM, and is lumped into the 'OLEFIN'. The reactions of Cl with MACR are assumed to proceed via two routes: H abstraction from the CHO (45%) and Cl addition to the C=C (55%), based on the OH-oxidation scheme in the MCM. Hence, 45% of MACR is oxidized by Cl as a common aldehyde, while 55% is treated as an alkene species and is summed into the lumped 'OLEFIN' species.

Addition of Cl to the aromatic ring proceeds very slow, with the rate being approximately two orders of magnitude slower than addition of OH (*Tanaka et al., 2003*). Thus, the reaction of Cl with benzene is not considered here (with a slow rate constant of 1.5×10^{-15} cm^3 $molecule^{-1}$ s^{-1}; *Riedel et al., 2014*). The reactions of Cl with styrene are assumed to proceed primarily via addition of Cl to double bond, so styrene is summed into the 'OLEFIN' species in the revised mechanism.

A total of six reactions have been added to the original chlorine mechanism to represent the aforementioned chemistry. All of the models have been re-run with the updated mechanism, and the results remained and have been updated in the revised manuscript.

Page 4831: The rate constant for the OLEFIN + OH reaction at 298 K in CBIV is $2.8x10^{-11}$ which means the rate constant for the OLEFIN + Cl reaction is $5.6x10^{-10}$. The rate constant for the reactions of external and internal olefin with Cl reported by Sarwar et al. (2012) are $2.5x10^{-10}$ and $3.5x10^{-10}$, respectively. The rate constant for the OLEFIN + Cl reaction used in this study is $1.16x10^{-9}$, which is substantially greater than used in other studies.

Response: the rate constant for the OLEFIN + Cl reaction has been revised as follows.

We further checked the CBIV mechanism and found that the factor of 20 is largely affected by the big K_{Cl}/K_{OH} ratio (43) for *1,2*-propadiene, while the K_{Cl}/K_{OH} ratios for ethene, propene and *1*-butene are all around 11. Since the OLEFIN primarily comprises of monoalkenes, the factor of 11 is then adopted in the revised mechanism to approximate the rate constant for the OLEFIN + Cl reaction according to the OLEFIN + OH reaction.

The rate constant for the OLEFIN + OH reaction is calculated here as the average of the OH reaction rate constants for *1*-butene, *i*-butene, *trans-2*-butene, *cis-2*-butene, *1*-pentene, *trans-2*-pentene, *cis-2*-pentene, *2-methyl-1*-butene, *3-methyl-1*-butene, *2-methyl-2*-butene, *1*-hexene, *trans-2*-hexene, *cis-2*-hexene, *2,3-dimethyl-2*-butene, styrene, MVK and MACR. The value is calculated as 5.33×10^{-11}, so the updated rate constant for the OLEFIN + Cl reaction is 5.86×10^{-10}.

Page 4833-4836:

What is the impact on H_2O_2 and HNO_3?

Response: we have examined the impact of $ClNO_2$ photolysis and Cl chemistry on H_2O_2 and HNO_3. With inclusion of 1997 pptv of $ClNO_2$, the model-simulated daytime peaks of H_2O_2 and HNO_3 increased by 17.3% and 13.4% compared to the non-$ClNO_2$ case. We have added a discussion on this in the revised manuscript.

The chemistry is likely to affect the daytime production of aerosol sulfate, aerosol nitrate, and secondary organic aerosols. Can the authors discuss the possible impacts of the chemistry on *aerosol sulfate, nitrate, and secondary organic aerosols?*

Response: yes, the chlorine chemistry is likely to promote the daytime formation of sulfate, nitrate and secondary organic aerosols by enhancing the radical production (thus atmospheric oxidative capacity) and oxidation of SO_2, NO_X and VOCs. Nonetheless, such impacts are not quantified with our model in the present study, which mainly focuses on ozone production, VOC oxidation and radical chemistry. The following sentence has been added in the revised paper to address the potential impacts of Cl chemistry on secondary aerosol formation.

"By enhancing the radical production (i.e., RO_X and Cl) and hence oxidation of SO_2, NO_X and VOCs, photolysis of $ClNO_2$ also has a high potential to promote formation of secondary aerosols, such as sulfate, nitrate and organic aerosols, but has not been quantified here."

How these results compare to the findings of the Sarwar et al. (2012, 2014).
Sarwar et al., Examining the impact of heterogeneous nitryl chloride production on air quality across the United States, ACP, 12, 1-19, 2012.
Sarwar et al., Importance of tropospheric $ClNO_2$ chemistry across the Northern Hemisphere, GRL, 41, 4050–4058, 2014.

Response: overall, our findings are consistent with the modeling results of Sarwar et al. (2012 and 2014), which underscore the importance of $ClNO_2$ chemistry to ozone formation and the atmospheric oxidative capacity in North America, Europe, and China. The following statements have been added in the revised manuscript to compare our results against Sarwar et al., (2012 and 2014).

"Such enhancement is comparable to that derived from a chemical transport modeling study in North America (up to 6.6 ppbv or 10% in summer; Sarwar et al., 2012)."

"A recent chemical transport modeling study suggests the importance of $ClNO_2$ chemistry to O_3 formation and the atmospheric oxidative capacity in the Northern Hemisphere, especially over China and western Europe (Sarwar et al. 2014)."

Model simulations were performed using the highest value of measured $ClNO_2$ concentrations; consequently the impact of the chemistry is also high. Ambient $ClNO_2$ concentrations will not be high on all days. The impact of the chemistry is likely to be lower when lower $ClNO_2$ concentrations are used. Some discussions are needed on the possible impact of the chemistry when $ClNO_2$ concentrations are lower.

Response: we have performed a sensitivity model run with 500 pptv of initial $ClNO_2$, representing a lower $ClNO_2$ case. With the lower $ClNO_2$, the impact of Cl chemistry is as expected lower. For instance, the daytime-average (and early-morning) OH, HO_2, RO_2 and O_3 production rate increased with inclusion of $ClNO_2$ by 2.3% (9.8%), 3.2% (13.8%), 9.7% (29.8%) and 3.3% (9.6%), respectively, compared to the non-$ClNO_2$ case.

In recent follow-on studies we have found the presence of elevated $ClNO_2$ at a mountain site in Hong Kong (up to 4.7 ppbv) and several sites in North China (all up to ~2 ppbv). So the impacts estimated from the higher $ClNO_2$ case in the present study could also occur in other highly polluted regions of China, though it presents an upper case.

In the revised manuscript, we have clarified that our estimate presents an upper case, and also discussed the smaller impacts when adopting lower levels of $ClNO_2$ (having added a figure in SI).

Table 1: Heterogeneous reactions show that the production of $ClNO_2$ *depends on uptake coefficient, aerosol surface area, and product yields. Does the model account for the heterogeneous production of* $ClNO_2$*? What values were used in the model for these parameters? What are the predicted minimum and maximum* $ClNO_2$ *concentrations?*

Response: the heterogeneous production of $ClNO_2$ from N_2O_5 hydrolysis is included in our developed mechanism. When the measurement of $ClNO_2$ is not available, such mechanism facilitates prediction of $ClNO_2$ with realistic values of N_2O_5 uptake coefficient and $ClNO_2$ product yield. But for the model we used in the present study to assess the impact of $ClNO_2$ chemistry, the heterogeneous $ClNO_2$ production was turned off and the model was initialized by the measured $ClNO_2$ concentrations. Constraining the model with measured data would provide a more realistic estimation of the impact of $ClNO_2$ chemistry. We have clarified this in the revised manuscript.

Table 2: Here, the authors present differences of model results for multiple scenarios. Need better description so that readers can easily understand which two models are being used for the differences of results.

Response: in the revised manuscript, more explanations have been added in the subscript of Table 2 to better clarify the differences of sensitivity model runs against the base model run.

Figure 4: Please clarify the purpose of the dotted lines in the figure?

Response: the dotted lines indicate the ‘early morning case’, for which the impacts of $ClNO_2$ are evaluated in parallel with ‘daytime average case’. We have added a sentence to clarify this.

Units of Cl atom and OH are different. Is there any particular reason?

Response: we have used the same unit (*i.e.*, molecule cm^{-3}) for Cl atom, OH, HO_2 and RO_2 radicals in the revised manuscript.

Table S2: Unit for H_2O *is confusing and initial condition appears to be too low.*

Response: the concentration of H_2O is the volume ratio of water vapor in the air. Such initial condition (2.8%) is normal and corresponds to the ambient condition with temperature of ~28 ℃ and RH of ~74%. The unit here may be confusing, and has been deleted in the revised manuscript (actually no unit is required here).

Response to Referee #2

General Comments

A mechanism of chlorine chemistry has been added to the renown Master Chemical Mechanism (MCM) to address the MCM's lack of chlorine comprehensive chemistry. The authors have tested the new chemical scheme in a box model by looking at sensitivity studies in model runs with and without chlorine chemistry. They then discuss what impact the chlorine chemistry has on the role of nitryl chloride chemistry in the polluted environment. The paper adds new and much needed knowledge to the current understanding of chlorine chemistry and its impact on air quality and deserves publication subject to just a few minor revisions.

Response: we thank the reviewer for the helpful and positive comments. We have revised the manuscript accordingly and address the specific comments as follows.

Specific comments

1. *The addition of chlorine chemistry to the MCM is both timely and obviously of much benefit to air quality models. What is the status with respect to the other halogens? Is their chemistry not as significant?*

   Response: some studies have revealed the potential significant role of other halogens (e.g., bromine and iodine) in some circumstances such as polar region and marine boundary layer. To our knowledge, the current MCM doesn't include the chemistry of bromine and iodine. Hence, there is also necessity of developing chemistry schemes for bromine and/or iodine, but it is beyond the scope of the present study that focuses on chlorine.

2. *If I am right, the box model conditions under which these studies have been performed do not consider wet deposition. Would the authors comment on the impact of wet deposition on these newly added chlorine-substituted intermediates?*

   Response: the present study mainly focuses on the chemistry of atmospheric constituents. Our box model considers dry deposition of pollutants but not consider the wet deposition process. Wet deposition may play a role in the sinks of the newly added chlorinated intermediates, but was not evaluated in the present study. We have clarified in the revised manuscript that our box model doesn't consider the wet deposition process.

3. *Page 4826 line 17: Please indicate how many additional new chlorinated products in the new MCM scheme are involved in these 199 reactions. And also, with the additional 199 reactions, can the authors indicate the increased cost of running the model with the new reactions?*

Response: there are 22 additional new chlorinated products (including 17 organics and 5 inorganics) in the new chlorine chemistry scheme. These new chlorinated products are outlined in the code that is to be shared with the community later. The increased cost of running time should not be a problem here because the additional ~200 reactions only present a very minor fraction (~1.2%) of the ~17000 reactions already existing in the MCM.

The following sentence has been added in the revised manuscript.

"This new chemistry module introduces 22 additional chlorinated products that can be simulated with negligible increased cost of running time for the MCM models."

4. *Page 4826: The authors have used conditions with observed maximum of 1997 pptv for $ClNO_2$. Can the authors explain the likely impact on chemistry under low $ClNO_2$ conditions? High $ClNO_2$ conditions are unlikely to be prevalent in normal atmospheric conditions.*

   Response: we have performed a sensitivity model run with 500 pptv of initial $ClNO_2$, representing a lower $ClNO_2$ case. With the lower $ClNO_2$, the impact of Cl chemistry is as expected lower. For instance, the daytime-average (and early-morning) OH, HO_2, RO_2 and O_3 production rate increased with inclusion of $ClNO_2$ by 2.3% (9.8%), 3.2% (13.8%), 9.7% (29.8%) and 3.3% (9.6%), respectively, compared to the non-$ClNO_2$ case.

   In recent follow-on studies we have found the presence of elevated $ClNO_2$ at a mountain site in Hong Kong (up to 4.7 ppbv) and several sites in North China (all up to ~2 ppbv). So the impacts estimated from the higher $ClNO_2$ case in the present study could also occur in other highly polluted regions of China, though it presents an upper case.

   In the revised manuscript, we have clarified that our estimate presents an upper case, and also discussed the smaller impacts when adopting lower levels of $ClNO_2$ (having added a figure in SI).

5. *Page 4833 lines 8-10: Please revise the sentence.*

   Response: this sentence has been modified as follows.

   "It is clear that photochemical models need to represent more detailed chlorine chemistry when applied to polluted conditions with abundant reactive VOCs."

6. *Page 4847 Figure 4: What does the vertical dotted line stands for? Is it to mark maximum $ClNO_2$? An explanation for the reader would be appreciated.*

   Response: the dotted line indicates the 'early morning case' when the peak in Cl occurs and the $ClNO_2$ impacts are evaluated in parallel with the 'daytime average case'. We have added a sentence in the figure caption to clarify this.

Development of a chlorine chemistry module for the Master Chemical Mechanism

L. K. Xue[1*], S. M. Saunders[2], T. Wang[3, 1], R. Gao[1], X. F. Wang[1], Q. Z. Zhang[1], and W. X. Wang[1]

[1]Environment Research Institute, Shandong University, Ji'nan, Shandong, China

[2]School of Chemistry and Biochemistry, University of Western Australia, WA, Australia

[3]Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong, China

[*]*To whom correspondence should be addressed*

E-mail: xuelikun@sdu.edu.cn, *Tel: +86-531-8836 1185*

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 205 chemical reactions describes the Cl·-initiated degradation of alkenes, aromatics, alkynes, 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 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 (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 · 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 · 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 · 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 Cl · 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 · chemistry is accounted for in current major chemical mechanisms is inhomogeneous. To our knowledge, the organic and inorganic chemistry involving Cl · 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

Cl · 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 and 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 (see Table S1 in SI), while the reactions between Cl · and other VOC species are not represented. 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 205 reactions and describes the Cl ·-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 Cl · 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 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.

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 and 2015; Saunders et al., 2003). The chemical reactions that are compiled in the mechanism module are summarized in *Table 1*, *Table S2* and *Figures 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, 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 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 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 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 *Section 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_{Cl}/k_{OH} ratio, whilst the remainder can be treated as an alkene compound (being summed into a lumped species 'OLEFIN'; see Section 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 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 *Section 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 Section 2.2.7).

2.2.3. Alcohols

Based on the above approach, presented in the chlorine mechanism are the reactions of Cl ·with 18 primary alcohols in the MCM (*Table S2*). 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 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 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 *Section 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 S2*).

2.2.5. Organic nitrates

The Cl ·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 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 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 Section 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 *Section 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 S2*).

The mechanism of the Cl ·-initiated oxidation of propene is depicted in *Figure 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 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 *Figure 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. 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 *Section 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 *Figure 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 O_2 to form CO, HO_2 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 defined 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 *Figure S1*. 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-minutes 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 (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_{Cl}/k_{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 $ClNO_2$ 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-minute 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; 2014b and 2014c), 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 $ClNO_2$ value was observed (see *Table S3* for the initial model conditions; note that the heterogeneous production of $ClNO_2$ was turned off here as the model is initialized by the measured $ClNO_2$ data), and was then run for a 24-hour 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 (~8:30 local time) peak of Cl · of 8.2×10^{4} *molecule* cm^{-3} that then decreased with time of the day (see *Figure 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 33.7% and 10.3% in the early morning and daytime average (08:00–18:00) net O_3 production rates respectively (*Figure 4b*). Despite the weakened role of Cl · oxidation after the morning period, the model simulated peak O_3 increased by 5 ppbv (or 6.8%) compared to the non-$ClNO_2$ case (*Figure 4c*). Such enhancement is comparable to that derived from a chemical transport modeling study in North America (up to 6.6 ppbv or 10% in summer; Sarwar et al., 2012). 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. *Figures 4d-4f* show 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 120%, 52.7% and 34.9%, 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 (45.1%), HO_2 (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, 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 90.3% in the early morning and of 25.4% for the daytime average (*Figure 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 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 *Figure 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 $ClNO_2$ can facilitate the oxidation of VOCs (especially alkanes) in the early morning.

Figures 4h-4j illustrate the impact of $ClNO_2$ photolysis on the formation of formaldehyde (HCHO), hydrogen peroxide (H_2O_2), and nitric acid (HNO_3), several major photochemical products in the atmosphere. The model-simulated maximum values of HCHO, H_2O_2 and HNO_3 increased by 8.0%, 17.3% and 13.4% with inclusion of $ClNO_2$ compared to the non-$ClNO_2$ case, respectively. By enhancing radical production (*i.e.*, RO_X and Cl) and hence oxidation of SO_2, NO_X and VOCs, photolysis of $ClNO_2$ 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 $ClNO_2$ 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 a high pollution case at a coastal site (sensitivity tests with a lower level of initial $ClNO_2$ 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 $ClNO_2$ both at other sites in Hong Kong and over the region of the North China Plain. In particular, very high $ClNO_2$ concentrations (1-minute 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. A recent chemical transport modeling study also suggests the importance of $ClNO_2$ 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 $ClNO_2$, 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 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).

Author contribution

L. X. and S. S. developed the mechanism and wrote the paper. T. W. designed and provided the field data for model test and demonstration. R. G. and Q. Z. provided figures 1-3. X. W. and W. W. 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 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 Prof. Aijun Ding for the helpful discussions. We also thank the two anonymous referees for their helpful comments to improve the original manuscript. 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).

References

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Kerr, J. A., Rossi, M. J., Troe, J., and Evaluation, I. S. G. K. D.: Evaluated kinetic and photochemical data for atmospheric chemistry, organic species: Supplement VII, *J Phys Chem Ref Data*, 28, 191-393, 1999.

Carter, W. P. L.: Development of the SAPRC-07 chemical mechanism, *Atmos Environ*, 44, 5324-5335, 2010.

Chang, S. Y., McDonald-Buller, E., Kimura, Y., Yarwood, G., Neece, J., Russell, M., Tanaka, P., and Allen, D.: Sensitivity of urban ozone formation to chlorine emission estimates, *Atmos Environ*, 36, 4991-5003, 2002.

Elshorbany, Y. F., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M., Villena, G., Gramsch, E., Rickard, A. R., Pilling, M. J., and Kleffmann, J.: Oxidation capacity of the city air of Santiago, Chile, *Atmos Chem Phys*, 9, 2257-2273, 2009.

Finlaysonpitts, B. J.: Chlorine Atoms as a Potential Tropospheric Oxidant in the Marine Boundary-Layer, *Res Chem Intermediat*, 19, 235-249, 1993.

Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, *Atmos Chem Phys*, 3, 181-193, 2003.

Jenkin, M. E., Young, J. C., Richard, A. R.,: The MCM v3.3 degradation scheme for isoprene, *Atmos. Chem. Phys. Discuss.*, 15, 9709-9766, 2015.

Luecken, D. J., Phillips, S., Sarwar, G., and Jang, C.: Effects of using the CB05 vs. SAPRC99 vs. CB4 chemical mechanism on model predictions: Ozone and gas-phase photochemical precursor concentrations, *Atmos Environ*, 42, 5805-5820, 2008.

Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., Bates, T. S., Coffman, D., Quinn, P. K., Dibb, J. E., Stark, H., Burkholder, J. B., Talukdar, R. K., Meagher, J., Fehsenfeld, F. C., and Brown, S. S.: High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nat Geosci*, 1, 324-328, 2008.

Phillips, G. J., Tang, M. J., Thieser, J., Brickwedde, B., Schuster, G., Bohn, B., Lelieveld, J., and Crowley, J. N.: Significant concentrations of nitryl chloride observed in rural continental Europe associated with the influence of sea salt chloride and anthropogenic emissions, *Geophys Res Lett*, 39, 2012.

Riedel, T. P., Bertram, T. H., Crisp, T. A., Williams, E. J., Lerner, B. M., Vlasenko, A., Li, S. M., Gilman, J., de Gouw, J., Bon, D. M., Wagner, N. L., Brown, S. S., and Thornton, J. A.: Nitryl Chloride and Molecular Chlorine in the Coastal Marine Boundary Layer, *Environ Sci Technol*, 46, 10463-10470, 2012.

Riedel, T. P., Wolfe, G. M., Danas, K. T., Gilman, J. B., Kuster, W. C., Bon, D. M., Vlasenko, A., Li, S. M., Williams, E. J., Lerner, B. M., Veres, P. R., Roberts, J. M., Holloway, J. S., Lefer, B., Brown, S. S., and Thornton, J. A.: An MCM modeling study of nitryl chloride (ClNO2) impacts on oxidation, ozone production and nitrogen oxide partitioning in polluted continental outflow, *Atmos Chem Phys*, 14, 3789-3800, 2014.

Sarwar, G., Simon, H., Bhave, P., and Yarwood, G.: Examining the impact of heterogeneous nitryl chloride production on air quality across the United States, *Atmos Chem Phys*, 12, 6455-6473, 2012.

Sarwar, G., Simon, H., Xing, J., and Mathur, R.: Importance of tropospheric $ClNO_2$ chemistry across the Northern Hemisphere, *Geophys., Res. Lett.*, 41, 4050-4058, doi:10.1002/2014GL059962, 2014.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos Chem Phys*, 3, 161-180, 2003.

Shi, J. C. and Bernhard, M. J.: Kinetic studies of Cl-atom reactions with selected aromatic compounds using the photochemical reactor-FTIR spectroscopy technique, *Int J Chem Kinet*, 29, 349-358, 1997.

Stockwell, W. R., Lawson, C. V., Saunders, E., and Goliff, W. S.: A Review of Tropospheric Atmospheric Chemistry and Gas-Phase Chemical Mechanisms for Air Quality Modeling, *Atmosphere,* 3, 1-32, 2012.

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

Tanaka, P. L., Oldfield, S., Neece, J. D., Mullins, C. B., and Allen, D. T.: Anthropogenic sources of chlorine and ozone formation in urban atmospheres, *Environ Sci Technol*, 34, 4470-4473, 2000.

Tanaka, P. L., Riemer, D. D., Chang, S. H., Yarwood, G., McDonald-Buller, E. C., Apel, E. C., Orlando, J. J., Silva, P. J., Jimenez, J. L., Canagaratna, M. R., Neece, J. D., Mullins, C. B., and Allen, D. T.: Direct evidence for chlorine-enhanced urban ozone formation in Houston, Texas, *Atmos Environ*, 37, 1393-1400, 2003b.

Tham, Y. J., Yan, C., Xue, L. K., Zha, Q. Z., Wang, X. F., and Wang, T.: Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry, *Chinese Sci Bull*, 59, 356-359, 2014.

Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dube, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S.: A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry, *Nature*, 464, 271-274, 2010.

Wang, T., Tham, Y. J., Xue, L. K., Li, Q. Y., Zha, Q. Z., Wang, Z., Poon, S. C. N., Dube, W. P., Brown, S. S., Louie, P. K. K., Luk, C. W. Y., Blake, D. R., Tsui, W.: High levels of nitryl chloride in the planetary boundary layer: A case study at a mountain site in Hong Kong, *Geophys. Res. Lett.*, submitted, 2015.

Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S. M., Fan, S. J., Zuo, H. C., Zhang, Q. Z., and Wang, W. X.: Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes, *Atmos Chem Phys*, 14, 13175-13188, 2014a.

Xue, L. K., Wang, T., Guo, H., Blake, D. R., Tang, J., Zhang, X. C., Saunders, S. M., and Wang, W. X.: Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: results from the Mt. Waliguan Observatory, *Atmos Chem Phys*, 13, 8551-8567, 2013.

Xue, L. K., Wang, T., Louie, P. K. K., Luk, C. W. Y., Blake, D. R., and Xu, Z.: Increasing External Effects Negate Local Efforts to Control Ozone Air Pollution: A Case Study of Hong Kong and Implications for Other Chinese Cities, *Environ Sci Technol*, 48, 10769-10775, 2014b.

Xue, L. K., Wang, T., Wang, X. F., Blake, D. R., Gao, J., Nie, W., Gao, R., Gao, X. M., Xu, Z., Ding, A. J., Huang, Y., Lee, S. C., Chen, Y. Z., Wang, S. L., Chai, F. H., Zhang, Q. Z., and Wang, W. X.: On the use of an explicit chemical mechanism to dissect peroxy acetyl nitrate formation, *Environ Pollut*, 195, 39-47, 2014c.

Young, C. J., Washenfelder, R. A., Edwards, P. M., Parrish, D. D., Gilman, J. B., Kuster, W. C., Mielke, L. H., Osthoff, H. D., Tsai, C., Pikelnaya, O., Stutz, J., Veres, P. R., Roberts, J. M., Griffith, S., Dusanter, S., Stevens, P. S., Flynn, J., Grossberg, N., Lefer, B., Holloway, J. S., Peischl, J., Ryerson, T. B., Atlas, E. L., Blake, D. R., and Brown, S. S.: Chlorine as a primary radical: evaluation of methods to understand its role in initiation of oxidative cycles, *Atmos Chem Phys*, 14, 3427-3440, 2014.

Zhang, Q., Streets, D. G., Carmichael, G. R., He, K. B., Huo, H., Kannari, A., Klimont, Z., Park, I. S., Reddy, S., Fu, J. S., Chen, D., Duan, L., Lei, Y., Wang, L. T., and Yao, Z. L.: Asian emissions in 2006 for the NASA INTEX-B mission, *Atmos Chem Phys*, 9, 5131-5153, 2009.

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

Category	**Reaction**	$\boldsymbol{k}$ (cm^3 molecules^{-1} s^{-1} or s^{-1}) **or** $\boldsymbol{J}$ (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*	$Cl + O_3 \rightarrow ClO + O_2$	$2.8 \times 10^{-11} \times \exp(-250/T)$	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	$N_2O_5 \rightarrow NA + NA$	$0.25 \times C_{N2O5} \times \gamma_{N2O5} \times S_{AERO} \times (1-\phi_{CLNO2})$	c
	$N_2O_5 \rightarrow NA + ClNO_2$	$0.25 \times C_{N2O5} \times \gamma_{N2O5} \times S_{AERO} \times \phi_{CLNO2}$	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	**Difference against the base model** [b]	**[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	With base MCM, without the developed Cl ·chemistry module	12.8%	186%	4.5%	166%
S2	Turn off the 'OLEFIN' chemistry (including Cl ·reactions of C_2H_4 and C_3H_6)	5.5%	7.7%	1.7%	7.4%
S3	Generic k_{Cl}/k_{OH} = 0 for aromatics (turn off)	2.2%	3.1%	<1%	5.6%
	Generic k_{Cl}/k_{OH} = 220 for aromatics (upper limit)	<1%	<1%	<1%	1.2%
	Generic k_{Cl}/k_{OH} = 150 for aromatics (lower limit)	<1%	<1%	<1%	1.0%
S4	Generic k_{Cl}/k_{OH} = 0 for aldehydes (turn off)	<1%	1.6%	<1%	<1%
	Generic k_{Cl}/k_{OH} = 8.5 for aldehydes (upper limit)	<1%	<1%	<1%	<1%
	Generic k_{Cl}/k_{OH} = 5.4 for aldehydes (lower limit)	<1%	<1%	<1%	<1%
S5	Generic k_{Cl}/k_{OH} = 0 for ketones (turn off)	<1%	3.0%	<1%	2.0%
	Generic k_{Cl}/k_{OH} = 36 for ketones (upper limit)	<1%	<1%	<1%	<1%
	Generic k_{Cl}/k_{OH} = 12 for ketones (lower limit)	<1%	1.6%	<1%	<1%
S6	Generic k_{Cl}/k_{OH} = 0 for alcohols (turn off)	<1%	<1%	<1%	<1%
S7	Turn off the chemistry of Cl ·+ C_5H_8	<1%	<1%	<1%	<1%

[a] The daytime $P(O_x)$ and OC_{CL} are the daytime average (9:00 – 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.

[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.

Figure Captions:

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), HCHO (h), H_2O_2 (i) and HNO_3 (j) with and without initial concentration of $ClNO_2$, for the polluted plume observed at Hok Tsui, Hong Kong on 24 August, 2012. The dashed lines indicate the 'early morning case' when the peak of Cl atom occurs and the $ClNO_2$ impacts are evaluated in parallel with the 'daytime average case'.

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 (8:30 local time) in the plume observed at Hok Tsui, Hong Kong on 24 August, 2012.

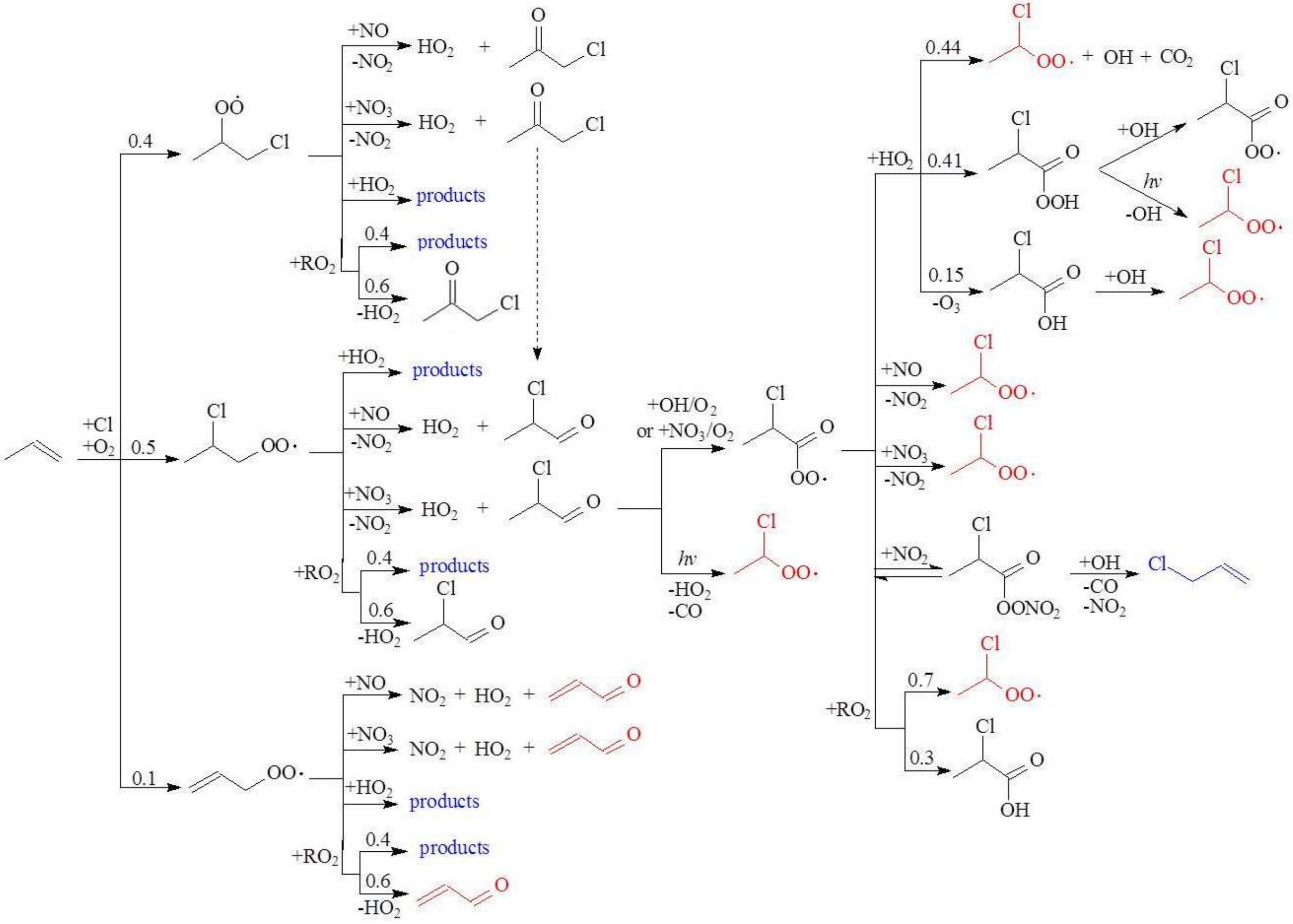
+Cl
+O2
0.4
0.5
0.1
OO·
Cl
+NO
-NO2
+NO3
+HO2
+RO2
HO2
O
0.6
-HO2
products
NO2
+OH/O2
or +NO3/O2
hv
-CO
0.44
0.41
0.15
-O3
OH
CO2
OOH
+OH
-OH
OONO2
0.7
0.3

Figure 1

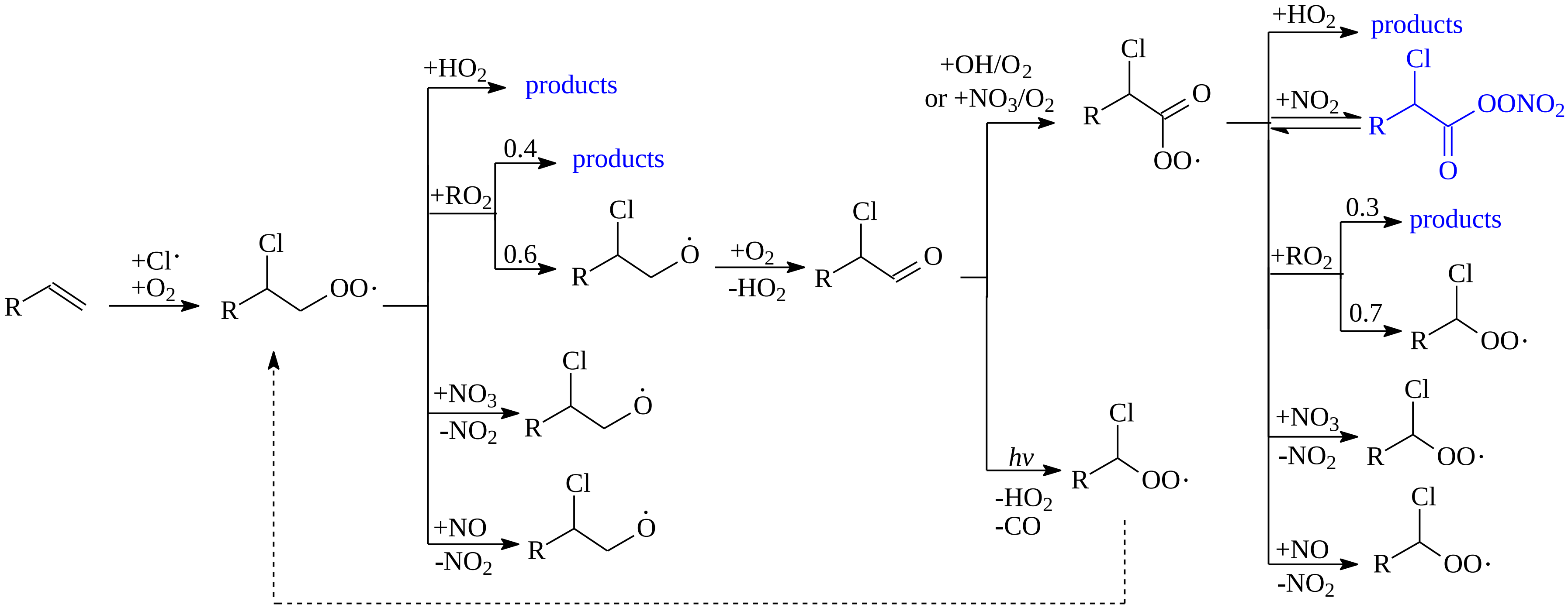

Figure 2

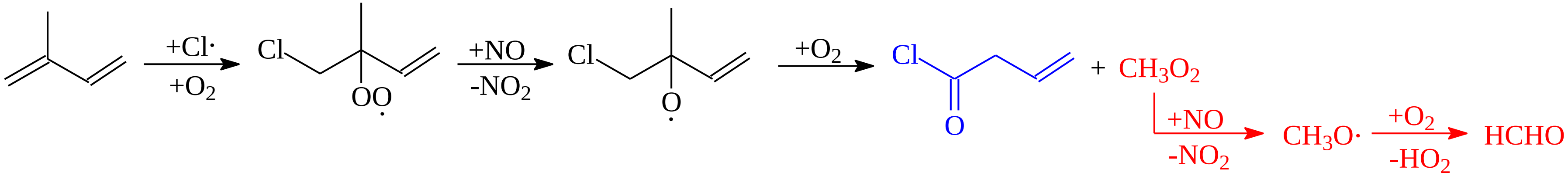

Figure 3

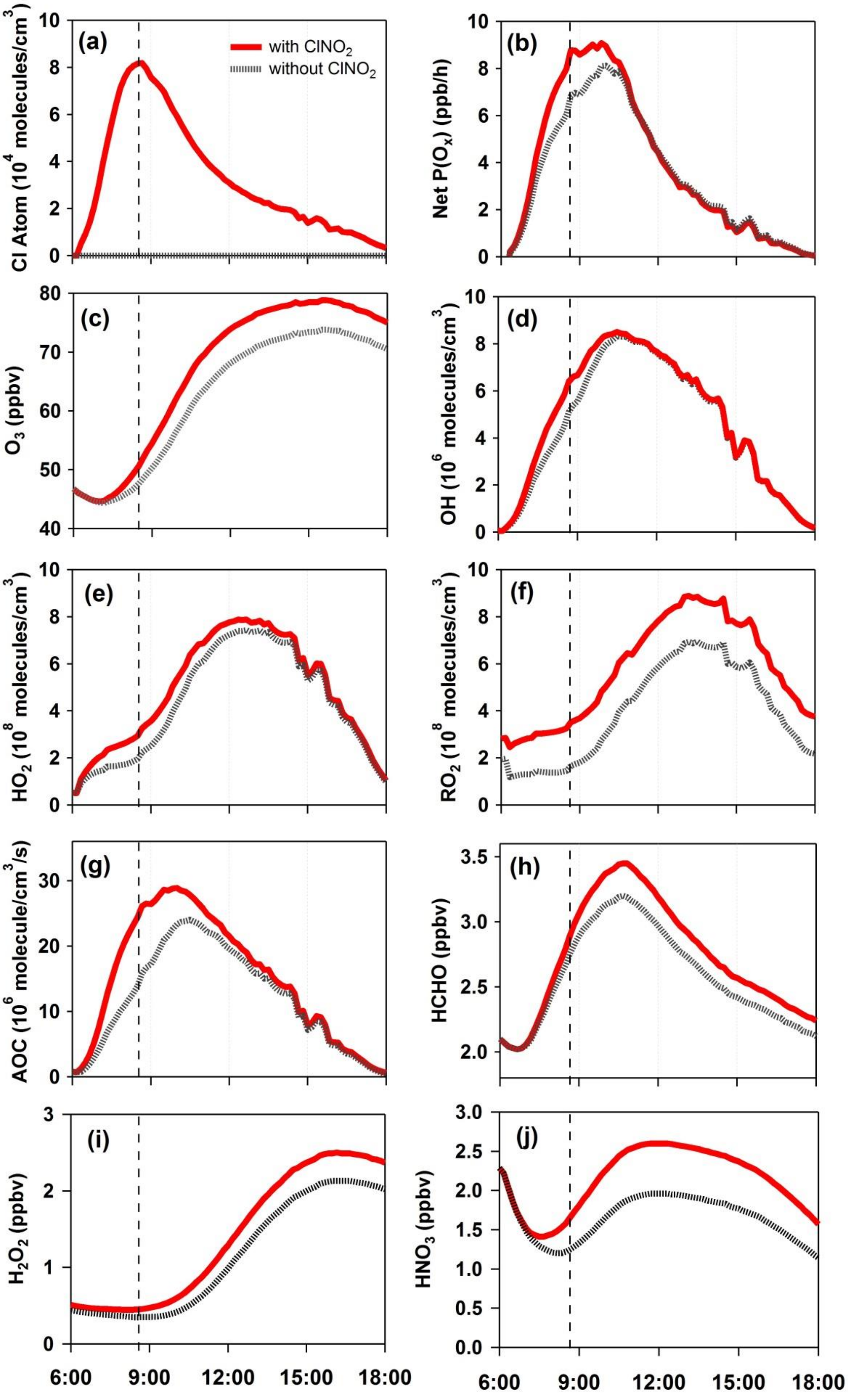
(a)
with ClNO$_2$
without ClNO$_2$
Cl Atom (10^4 molecules/cm^3)
0
2
4
6
8
10
(b)
Net P(O$_x$) (ppb/h)
0
2
4
6
8
10
(c)
O$_3$ (ppbv)
40
50
60
70
80
(d)
OH (10^6 molecules/cm^3)
0
2
4
6
8
10
(e)
HO$_2$ (10^8 molecules/cm^3)
0
2
4
6
8
10
(f)
RO$_2$ (10^8 molecules/cm^3)
0
2
4
6
8
10
(g)
AOC (10^6 molecule/cm^3/s)
0
10
20
30
(h)
HCHO (ppbv)
2.0
2.5
3.0
3.5
(i)
H$_2$O$_2$ (ppbv)
0
1
2
3
(j)
HNO$_3$ (ppbv)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
6:00
9:00
12:00
15:00
18:00
6:00
9:00
12:00
15:00
18:00

Figure 4

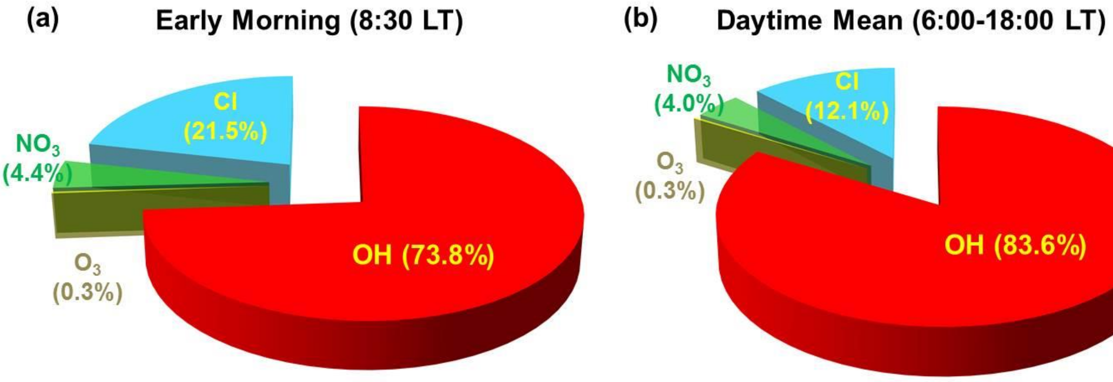

Figure 5

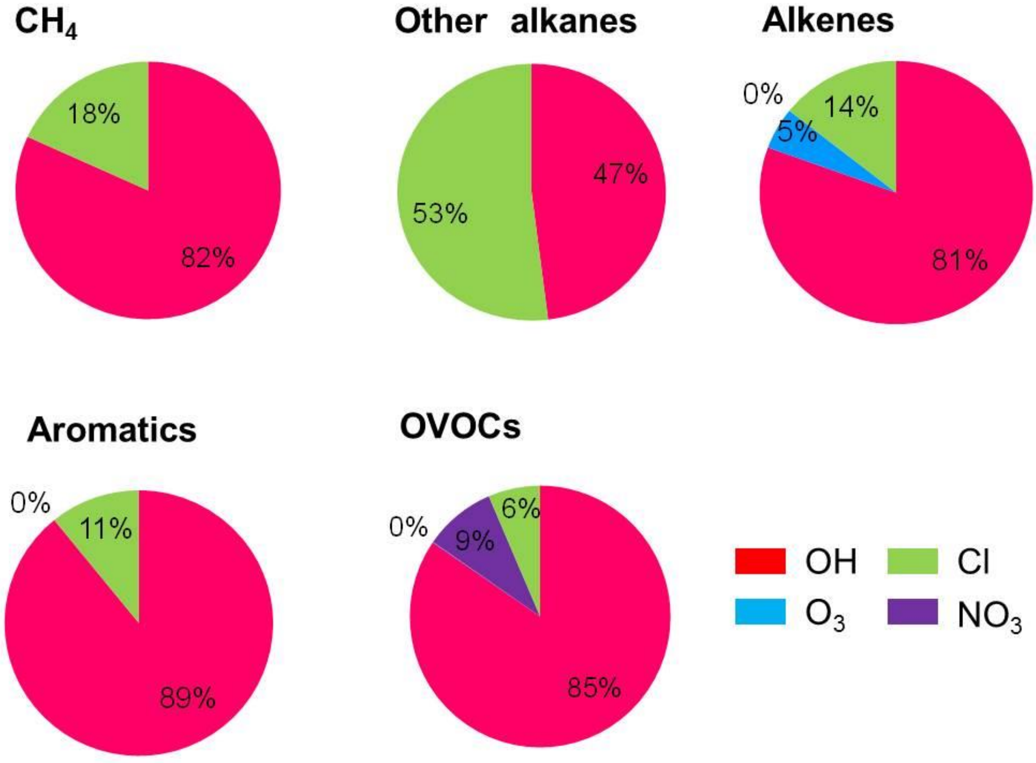

Figure 6

Supplementary Materials *of*

Development of a chlorine chemistry module for the Master Chemical Mechanism

L. K. Xue[1*], S. M. Saunders[2], T. Wang[3, 1], R. Gao[1], X. F. Wang[1], Q. Z. Zhang[1], and W. X. Wang[1]

[1]Environment Research Institute, Shandong University, Ji'nan, Shandong, China

[2]School of Chemistry and Biochemistry, University of Western Australia, WA, Australia

[3]Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong, China

[*]*To whom correspondence should be addressed*

E-mail: xuelikun@sdu.edu.cn, Tel: +86-531-8836 1185

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

Reactions	***k* ($cm^3 molecules^{-1} s^{-1}$)**
Cl + CH4 = CH3O2 + HCl	$6.6\times10^{-12}\times\exp(-1240/T)$
Cl + C2H6 = C2H5O2 + HCl	$8.3\times10^{-11}\times\exp(-100/T)$
Cl + C3H8 = IC3H7O2 + HCl	$0.43\times1.4\times10^{-10}\times\exp(75/T)$
Cl + C3H8 = NC3H7O2 + HCl	$0.59\times1.4\times10^{-10}\times\exp(-90/T)$
Cl + NC4H10 = NC4H9O2 + HCl	$0.44\times2.05\times10^{-10}\times\exp(-120/T)$
Cl + NC4H10 = SC4H9O2 + HCl	$0.59\times2.05\times10^{-10}\times\exp(55/T)$
Cl + IC4H10 = IC4H9O2 + HCl	$0.564\times1.43\times10^{-10}$
Cl + IC4H10 = TC4H9O2 + HCl	$0.436\times1.43\times10^{-10}$
Cl + NC5H12 = PEAO2 + HCl	$0.222\times2.80\times10^{-10}$
Cl + NC5H12 = PEBO2 + HCl	$0.558\times2.80\times10^{-10}$
Cl + NC5H12 = PECO2 + HCl	$0.220\times2.80\times10^{-10}$
Cl + IC5H12 = IPEAO2 + HCl	$0.408\times2.20\times10^{-10}$
Cl + IC5H12 = IPEBO2 + HCl	$0.342\times2.20\times10^{-10}$
Cl + IC5H12 = IPECO2 + HCl	$0.250\times2.20\times10^{-10}$
Cl + NEOP = NEOPO2 + HCl	1.11×10^{-10}
Cl + NC6H14 = HEXAO2 + HCl	$0.182\times3.40\times10^{-10}$
Cl + NC6H14 = HEXBO2 + HCl	$0.457\times3.40\times10^{-10}$
Cl + NC6H14 = HEXCO2 + HCl	$0.361\times3.40\times10^{-10}$
Cl + M2PE = M2PEAO2 + HCl	$0.321\times2.90\times10^{-10}$
Cl + M2PE = M2PEBO2 + HCl	$0.269\times2.90\times10^{-10}$
Cl + M2PE = M2PECO2 + HCl	$0.213\times2.90\times10^{-10}$
Cl + M2PE = M2PEDO2 + HCl	$0.197\times2.90\times10^{-10}$
Cl + M3PE = M3PEAO2 + HCl	$0.317\times2.80\times10^{-10}$
Cl + M3PE = M3PEBO2 + HCl	$0.530\times2.80\times10^{-10}$
Cl + M3PE = M3PECO2 + HCl	$0.153\times2.80\times10^{-10}$
Cl + M22C4 = M22C43O2 + HCl	$0.461\times1.71\times10^{-10}$
Cl + M22C4 = M33C4O2 + HCl	$0.386\times1.71\times10^{-10}$
Cl + M22C4 = M22C4O2 + HCl	$0.154\times1.71\times10^{-10}$
Cl + M23C4 = M23C43O2 + HCl	$0.478\times2.30\times10^{-10}$
Cl + M23C4 = M23C4O2 + HCl	$0.522\times2.30\times10^{-10}$
Cl + NC7H16 = HEPTO2 + HCl	3.90×10^{-10}
Cl + M2HEX = M2HEXAO2 + HCl	$0.779\times3.50\times10^{-10}$
Cl + M2HEX = M2HEXBO2 + HCl	$0.221\times3.50\times10^{-10}$
Cl + M3HEX = M3HEXAO2 + HCl	$0.793\times3.11\times10^{-10}$
Cl + M3HEX = M3HEXBO2 + HCl	$0.207\times3.11\times10^{-10}$
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}

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

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

Reactions	***k* (cm^{3}molecules^{-1}s^{-1})**	**Source**
Aldehydes + Cl		
HCHO + Cl → HCl + HO2 + CO	$8.1\times10^{-11}\times\exp(-34/T)$	IUPAC
CH3CHO + Cl → CH3CO3 + HCl	7.92×10^{-11}	IUPAC
CH3CHO + Cl → HCOCH2O2 + HCl	8.0×10^{-13}	IUPAC
C2H5CHO + Cl → C2H5CO3 + HCl	1.3×10^{-10}	IUPAC
C3H7CHO + Cl → BUTALO2 + HCl	$5.5\times10^{-12}\times\exp(410/T)$	b
C3H7CHO + Cl → C3H7CO3 + HCl	$3.1\times10^{-11}\times\exp(410/T)$	b
IPRCHO + Cl → IBUTALBO2 + HCl	$2.2\times10^{-12}\times\exp(410/T)$	b
IPRCHO + Cl → IBUTALCO2 + HCl	$2.4\times10^{-12}\times\exp(410/T)$	b
IPRCHO + Cl → IPRCO3 + HCl	$3.7\times10^{-11}\times\exp(410/T)$	b
C4H9CHO + Cl → C4CHOBO2 + HCl	$7.3\times10^{-12}\times\exp(448/T)$	b
C4H9CHO + Cl → C4H9CO3 + HCl	$3.1\times10^{-11}\times\exp(448/T)$	b
BENZAL + Cl → C6H5CO3 + HCl	$3.6\times10^{-11}\times\exp(225/T)$	b
GLYOX + Cl → CO + CO + HO2 + HCl	$4.86\times10^{-11}\times\exp(-34/T)$	c
GLYOX + Cl → HCOCO3 + HCl	$3.24\times10^{-11}\times\exp(-34/T)$	c
MGLYOX + Cl → CH3CO3 + CO + HCl	8.0×10^{-11}	c
MACR + Cl → MACO3 + HCl	$4.86\times10^{-11}\times\exp(380/T)\times0.45$	d
Ketones + Cl		
CH3COCH3 + Cl → CH3COCH2O2 + HCl	$1.5\times10^{-11}\times\exp(-590/T)$	IUPAC
MEK + Cl → MEKAO2 + HCl	$1.4\times10^{-11}\times\exp(80/T)$	IUPAC
MEK + Cl → MEKBO2 + HCl	$1.4\times10^{-11}\times\exp(80/T)$	IUPAC
MEK + Cl → MEKCO2 + HCl	$2.4\times10^{-12}\times\exp(80/T)$	IUPAC
MPRK + Cl → CO2C54O2 + HCl	9.6×10^{-11}	b
MPRK + Cl → MPRKAO2 + HCl	2.1×10^{-11}	b
DIEK + Cl → DIEKAO2 + HCl	2.4×10^{-11}	b
DIEK + Cl → DIEKBO2 + HCl	2.4×10^{-11}	b
MIPK + Cl → MIPKAO2 + HCl	3.5×10^{-11}	b

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

Alcohols + Cl

CH3OH + Cl → HO2 + HCHO + HCl	$7.1\times10^{-11}\times\exp(-75/T)$	IUPAC
C2H5OH + Cl → CH3CHO + HO2 + HCl	$5.5\times10^{-11}\times\exp(155/T)$	IUPAC
C2H5OH + Cl → HOCH2CH2O2 + HCl	$4.8\times10^{-12}\times\exp(155/T)$	IUPAC
NPROPOL+ Cl → C2H5CHO + HO2 + HCl	$1.6\times10^{-11}\times\exp(525/T)$	IUPAC
NPROPOL + Cl → HO1C3O2 + HCl	$4.1\times10^{-12}\times\exp(525/T)$	IUPAC
NPROPOL + Cl → HYPROPO2 + HCl	$6.8\times10^{-12}\times\exp(525/T)$	IUPAC
IPROPOL + Cl → CH3COCH3 + HO2 + HCl	7.4×10^{-11}	IUPAC
IPROPOL + Cl → IPROPOLO2 + HCl	1.3×10^{-11}	IUPAC
NBUTOL+ Cl → C3H7CHO + HO2 + HCl	$1.25\times10^{-11}\times\exp(550/T)$	IUPAC
NBUTOL + Cl → NBUTOLAO2 + HCl	$1.12\times10^{-11}\times\exp(550/T)$	IUPAC
NBUTOL + Cl → NBUTOLBO2 + HCl	$1.12\times10^{-11}\times\exp(550/T)$	IUPAC
BUT2OL + Cl → BUT2OLO2 + HCl	5.37×10^{-11}	b
BUT2OL + Cl → MEK + HO2 + HCl	9.51×10^{-11}	b
IBUTOL + Cl → IBUTOLBO2 + HCl	$2.6\times10^{-11}\times\exp(352/T)$	b
IBUTOL + Cl → IBUTOLCO2 + HCl	$4.2\times10^{-12}\times\exp(352/T)$	b
IBUTOL + Cl → IPRCHO + HO2 + HCl	$1.6\times10^{-11}\times\exp(352/T)$	b
TBUTOL+ Cl → TBUTOLO2 + HCl	$2.4\times10^{-11}\times\exp(-121/T)$	b
TBUTOL+ Cl → TC4H9O + HCl	$3.1\times10^{-12}\times\exp(-121/T)$	b
PECOH + Cl → DIEK + HO2 + HCl	9.1×10^{-11}	b
PECOH + Cl → HO3C5O2 + HCl	1.5×10^{-11}	b
PECOH + Cl → PE2ENEBO2 + HCl	1.0×10^{-10}	b
IPEAOH+ Cl → BUT2CHO + HO2 + HCl	5.5×10^{-11}	b
IPEAOH + Cl → HM2C43O2 + HCl	4.9×10^{-11}	b
IPEAOH + Cl → M2BUOL2O2 + HCl	8.7×10^{-11}	b

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

Organic acids + Cl

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

Organic nitrates + Cl

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

Aromatics + Cl

TOLUENE + Cl → C6H5CH2O2 + HCl	5.9×10^{-11}	*Shi and Bernhard*, 1997

OXYL + Cl → OXYLO2 + HCl	1.5×10^{-10}	*Shi and Bernhard*, 1997
MXYL + Cl → MXYLO2 + HCl	1.7×10^{-10}	b
PXYL + Cl → PXYLO2 + HCl	2.6×10^{-10}	b
EBENZ + Cl → C6H5C2H4O2 + HCl	9.1×10^{-11}	b
PBENZ + Cl → PHC3O2 + HCl	7.5×10^{-11}	b
IPBENZ + Cl → PHIC3O2 + HCl	8.2×10^{-11}	b
TM123B + Cl → TM123BO2 + HCl	3.6×10^{-10}	b
TM124B + Cl → TM124BO2 + HCl	3.6×10^{-10}	b
TM135B + Cl → TMBO2 + HCl	3.1×10^{-10}	b
OETHTOL + Cl → ETOLO2 + HCl	1.1×10^{-10}	b
METHTOL + Cl → ETOLO2 + HCl	1.4×10^{-10}	b
PETHTOL + Cl → ETOLO2 + HCl	2.2×10^{-10}	b
	Alkenes + Cl [f]	
C2H4 + Cl → CH2CLCH2O2	1.0×10^{-10}	IUPAC
C3H6 + Cl → C3H5O2 + HCl	2.7×10^{-11}	*Riedel et al.* 2014
C3H6 + Cl → IPROCLO2	1.35×10^{-10}	*Riedel et al.* 2014
C3H6 + Cl → HYPROCLO2	1.08×10^{-10}	*Riedel et al.* 2014
OLEFIN + Cl → OLECLO2	5.86×10^{-10}	b,g
C5H8 + Cl → ISOCLO2	$1.28\times10^{-10}\times\exp(390/T)$	CB04
	Alkyne + Cl	
C2H2 + Cl → CLCHO + CO + HO2	4.97×10^{-11}	h

[a] All species are variables existing in the MCM, except for "OLEFIN" and some reaction products of Cl with C_3H_6, OLEFIN, C_5H_8 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 C_1 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 RO_2 radical, the degradation of which is approximated for simplicity to be the same as that of OXYL1O2.

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

[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.

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

Species	**Concentration** [a]	**Species**	**Concentration** [a]
Temperature [b]	301 K	C_3H_6	280
Pressure	760 mm Hg	*1*-butene	80
H_2O [b]	2.8%	*cis*-*2*-butene	4
NO	20	*trans*-*2*-butene	40
NO_2	15.6 ppb	*trans*-*2*-pentene	45
O_3	64 ppb	*1,3*-butadiene	40
PAN	2100	*1*-pentene	45
SO_2	5.0 ppb	Isoprene	4
HONO	814	C_2H_2	2150
$ClNO_2$	1997	Benzene	390
CO	297 ppb	Toluene	1130
CH_4	2.01 ppm	*o*-xylene	110
C_2H_6	1860	*m,p*-xylene	260
C_3H_8	2840	Ethylbenzene	280
n-butane	2640	*1,2,3*-trimethylbenzene	6
i-butane	1640	*1,2,4*-trimethylbenzene	6
n-pentane	440	*1,3,5*-trimethylbenzene	5
i-pentane	710	HCHO	2790
n-hexane	71	CH_3CHO	1180
2-methylpentane	18	C_2H_5CHO	114
n-heptane	61	Benzaldehyde	120
n-octane	470	acetone	1100
2,2,4-trimethylpentane	610	MEK	137
C_2H_4	560		

[a] The unit is pptv unless otherwise specified.

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

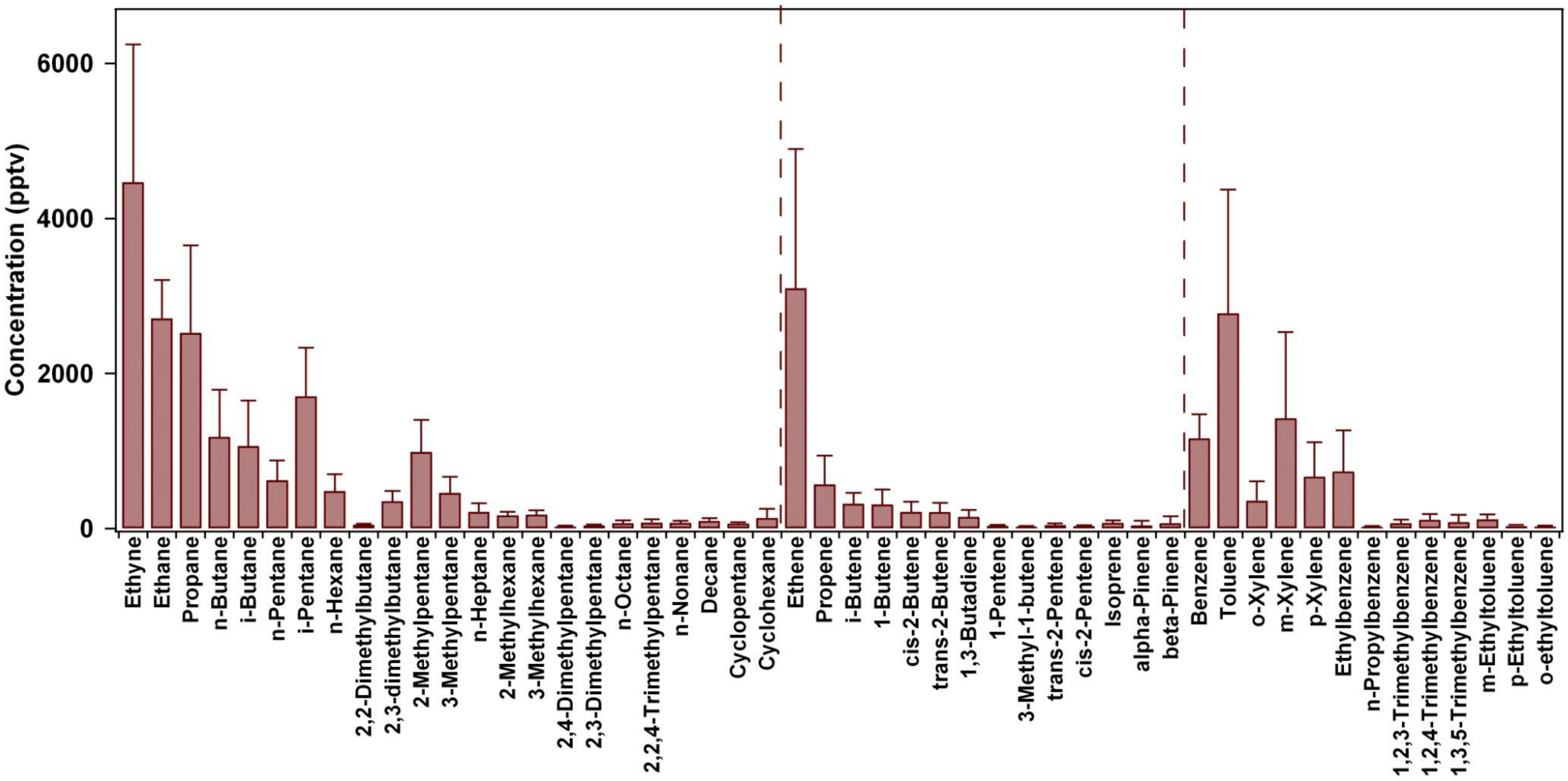

Figure S1. Average concentrations of individual hydrocarbon species observed at Shanghai on 7 May 2005 when the data were used for sensitivity tests of the new Cl ·mechanism. Error bars refer to standard deviations.

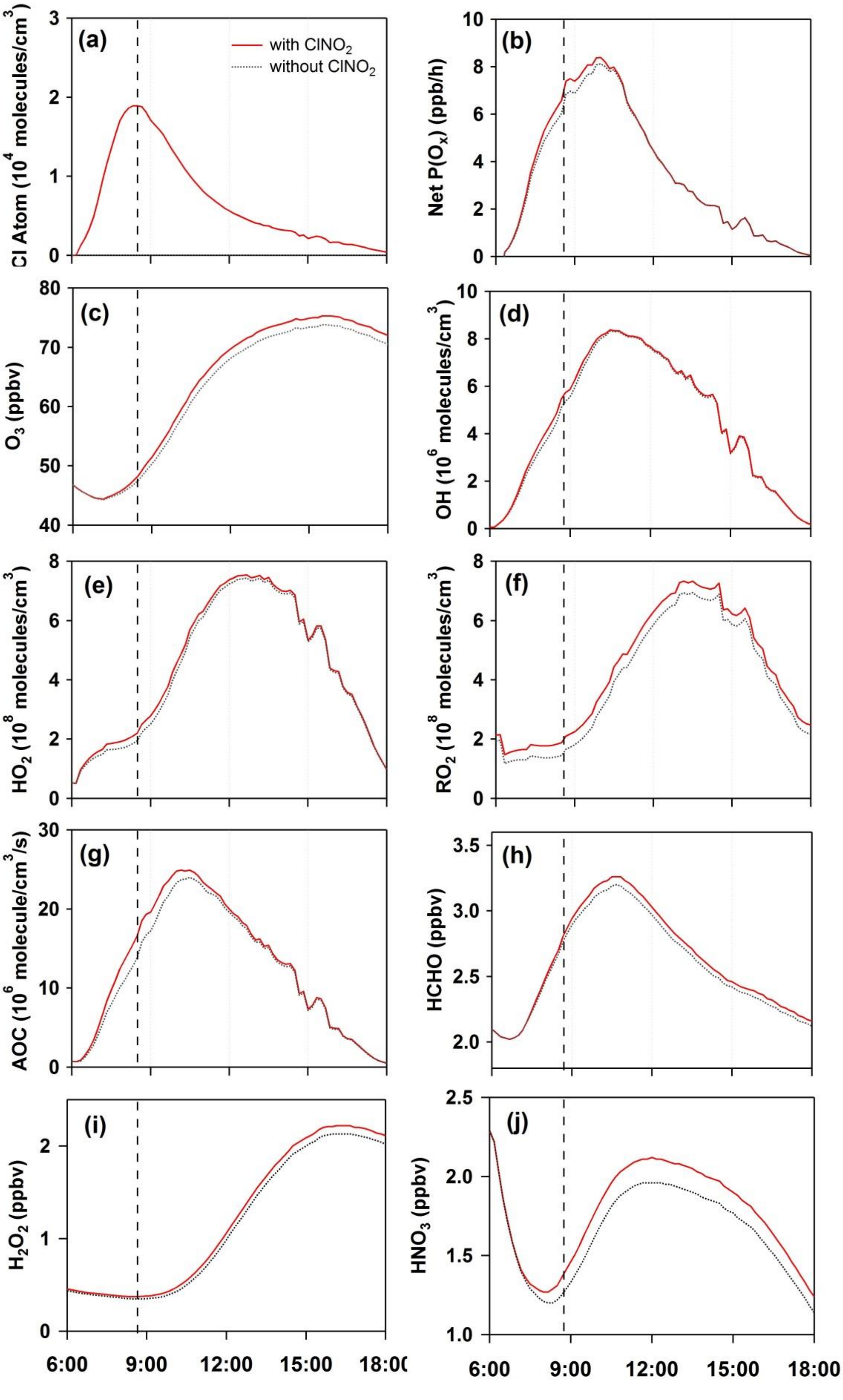

Figure S2. The same as Figure 4 in the main text but from a sensitivity model test with 500 pptv of initial $ClNO_2$.

1. Description of the high $ClNO_2$ plume and intensive observations at Hok Tsui

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

$ClNO_2$ and N_2O_5 were concurrently measured by an iodide-chemical ionization mass spectrometer (CIMS) (*THS Instruments Inc., Atlanta*), in which the target molecules are ionized to iodide clusters followed by detection by a quadruple mass spectrometer. The detailed descriptions of the instrument principles and operation/calibration procedures have been provided elsewhere (*Tham et al.*, 2014; *Wang et al.*, 2015). Ozone was measured by a commercial UV photometric analyzer (*TEI, Model 49i*). Carbon monoxide was measured with a non-dispersive infrared analyzer (*API, Model 300EU*). Nitrogen oxides (NO and NO_2) were measured with a chemiluminescence instrument (*TEI, Model 42i*) equipped with a photolytic converter. NOy was determined by another chemiluminescence analyzer (*TEI, Model 42i*) with an externally placed molybdenum oxide (MoO) catalytic converter. C_2-C_{10} hydrocarbons were measured in real-time by a commercial analyzer that combines gas chromatography (GC) separation, photoionization detection (PID), and flame-ionization detection (FID) (*Syntech Spectras, model GC955 Series 600/800 POCP*). In addition, whole air samples were also collected on selected days for detection of C_1-C_{10} hydrocarbons, and analyzed at the University of California, Irvine (UCI) laboratory (*Xue et al.,* 2013). C_1-C_8 carbonyls were measured by collecting air samples in sorbent cartridges coated by 2,4-dinitrophenylhydrazine (DNPH) equipped with an O_3 scrubber, followed by analysis by a high pressure liquid chromatography (*Xue et al.,* 2014). HONO was measured in real-time using a long path absorption photometer (LOPAP). Temperature, relative humidity, wind speed and direction, and J_{NO2} values were also measured by commercial probes/sensors (*Zha et al.,* 2014).

The time series of $ClNO_2$, O_3, NO_2 and J_{NO2} is depicted in *Figure S3*. The plume with the highest $ClNO_2$ pollution was observed during the night of 23-24 August. The maximum value of $ClNO_2$ was recorded as 1997 pptv (1-min data) at around 3:00 AM local time on 24 August. Such a level is among the highest values ever reported over the world. Examination of surface winds and backward trajectories suggested that this polluted plume originated from urban Hong Kong and the Pearl River Delta region. This case has been analyzed in detail in our previous work (*Tham et al.*, 2014).

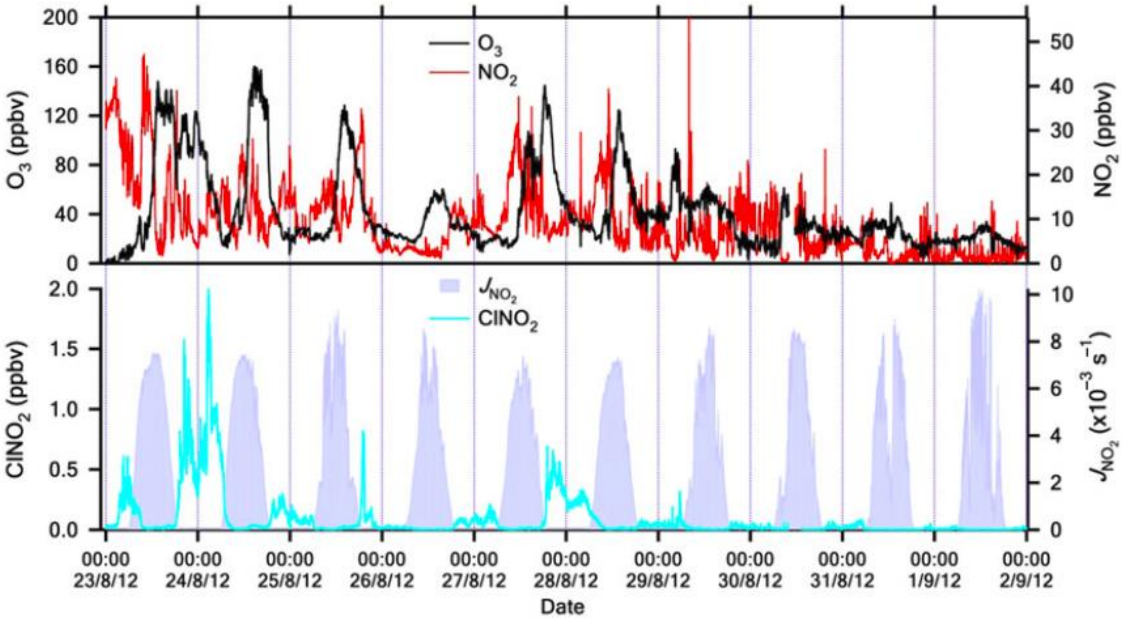

Figure S3. Time series of $ClNO_2$, O_3, NO_2 and J_{NO2} observed at Hok Tsui in summer 2012. (from Tham et al. 2014).

References

Riedel, T. P., Wolfe, G. M., Danas, K. T., Gilman, J. B., Kuster, W. C., Bon, D. M., Vlasenko, A., Li, S. M., Williams, E. J., Lerner, B. M., Veres, P. R., Roberts, J. M., Holloway, J. S., Lefer, B., Brown, S. S., and Thornton, J. A.: An MCM modeling study of nitryl chloride ($ClNO_2$) impacts on oxidation, ozone production and nitrogen oxide partitioning in polluted continental outflow, *Atmos Chem Phys*, 14, 3789-3800, 2014.

Shi, J. C. and Bernhard, M. J.: Kinetic studies of Cl-atom reactions with selected aromatic compounds using the photochemical reactor-FTIR spectroscopy technique, *Int J Chem Kinet*, 29, 349-358, 1997.

Tham, Y. J., Yan, C., Xue, L. K., Zha, Q. Z., Wang, X. F., and Wang, T.: Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry, *Chinese Sci Bull*, 59, 356-359, 2014.

Wang, T., Wei, X. L., Ding, A. J., Poon, C. N., Lam, K. S., Li, Y. S., Chan, L. Y., and Anson, M.: Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994–2007, Atmos. Chem. Phys., 9, 6217–6227, 2009.

Wang, T., Tham, Y. J., Xue, L. K., Li, Q. Y., Zha, Q. Z., Wang, Z., Poon, S. C. N., Dube, W. P., Brown, S. S., Louie, P. K. K., Luk, C. W. Y., Blake, D. R., Tsui, W.: High levels of nitryl chloride in the planetary boundary layer: A case study at a mountain site in Hong Kong, *Geophys. Res. Lett.*, submitted, 2015.

Xue, L. K., Wang, T., Guo, H., Blake, D. R., Tang, J., Zhang, X. C., Saunders, S. M., and Wang, W. X.: Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: results from the Mt. Waliguan Observatory, *Atmos Chem Phys*, 13, 8551-8567, 2013.

Xue, L. K., Wang, T., Wang, X. F., Blake, D. R., Gao, J., Nie, W., Gao, R., Gao, X. M., Xu, Z., Ding, A. J., Huang, Y., Lee, S. C., Chen, Y. Z., Wang, S. L., Chai, F. H., Zhang, Q. Z., and Wang, W. X. On the use of an explicit chemical mechanism to dissect peroxy acetyl nitrate formation, *Environmental Pollution*, 195, 39-47, 2014.

Zha, Q. Z., Xue, L. K., Wang, T., et al., Large conversion rates of NO_2 to HNO_2 observed in air masses from the South China Sea: evidence of strong production at sea surface?, Geophys. Res. Lett., 41, 7710- 7715, 2014.