

Development of a chlorine chemistry module for the Master Chemical Mechanism

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 O₃ 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 Cl₂ 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 k_{Cl}/k_{OH} 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 k_{Cl} were estimated using k_{Cl}/k_{OH} 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 $1.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; 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 2.8×10^{-11} which means the rate constant for the OLEFIN + Cl reaction is 5.6×10^{-10} . The rate constant for the reactions of external and internal olefin with Cl reported by Sarwar *et al.* (2012) are 2.5×10^{-10} and 3.5×10^{-10} , respectively. The rate constant for the OLEFIN + Cl reaction used in this study is 1.16×10^{-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 $K_{\text{Cl}}/K_{\text{OH}}$ ratio (43) for *1,2*-propadiene, while the $K_{\text{Cl}}/K_{\text{OH}}$ 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 SO₂, 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 SO₂, NO_x and VOCs, photolysis of ClNO₂ has also 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 ClNO₂ 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 ClNO₂ chemistry to ozone formation and 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 percentage in summer; Sarwar et al., 2012).”

“A recent chemical transport modeling study suggests the importance of ClNO₂ chemistry to O₃ formation and 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 ClNO₂ concentrations; consequently the impact of the chemistry is also high. Ambient ClNO₂ concentrations will not be high on all days. The impact of the chemistry is likely to be lower when lower ClNO₂ concentrations are used. Some discussions are needed on the possible impact of the chemistry when ClNO₂ concentrations are lower.

Response: we have performed a sensitivity model run with 500 pptv of initial ClNO₂, representing a lower ClNO₂ case. With such lower ClNO₂, the impact of Cl chemistry is as expected lower. For instance, the daytime-average (and early-morning) OH, HO₂, RO₂ and O₃ production rate increased with inclusion of ClNO₂ by 2.3% (9.8), 3.2% (13.8), 9.7% (29.8) and 3.3% (9.6%), respectively, compared to the non-ClNO₂ case.

In recent, our follow-up studies have found presence of elevated ClNO₂ 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 ClNO₂ 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 present an upper case, and also discussed the smaller impacts when adopting lower levels of ClNO₂ (having added a figure in SI).

Table 1: Heterogeneous reactions show that the production of ClNO₂ depends on uptake coefficient, aerosol surface area, and product yields. Does the model account for the heterogeneous production of ClNO₂? What values were used in the model for these parameters? What are the predicted minimum and maximum ClNO₂ concentrations?

Response: the heterogeneous production of ClNO₂ from N₂O₅ hydrolysis is included in our developed mechanism. When the measurement of ClNO₂ is not available, such mechanism facilitates prediction of ClNO₂ with realistic values of N₂O₅ uptake coefficient and ClNO₂ product yield. But for the model we used in the present study to assess the impact of ClNO₂ chemistry, the heterogeneous ClNO₂ production was turned off and the model was initialized by the measured ClNO₂ concentrations. Constraining the model with measured data would provide a more realistic estimation of the impact of ClNO₂ 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 ClNO₂ 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, HO₂ and RO₂ radicals in the revised manuscript.

Table S2: Unit for H₂O is confusing and initial condition appears to be too low.

Response: the concentration of H₂O 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 °C and RH of ~74%. The unit here may be confusing, and has been deleted in the revised manuscript (actually no unit is required here).