

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:

Specific comments:

Page 4824, lines 19-22:

Perhaps “more detailed chlorine chemistry” or something similar may be better suited than “more fully chlorine chemistry”.

Page 4825, lines 14-15:

Please check the first sentence.

Page 4825, lines 22:

Sarwar et al. (2012) identifies the mechanism as CB05 not CB-V.

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.

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?

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.

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.

Reidel 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)

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.

Page 4833-4836:

What is the impact on H_2O_2 and HNO_3 ?

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?

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.

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.

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?

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.

Figure 4:

Please clarify the purpose of the dotted lines in the figure?

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

Table S2:

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