

Anonymous 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 and 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 ClNO₂. Can the authors explain the likely impact on chemistry under low ClNO₂ conditions? High ClNO₂ conditions are unlikely to be prevalent in normal atmospheric conditions.*

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).

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

Response: this sentence has been modified as follows.

“It is obvious that the photochemical models need 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 ClNO₂? An explanation for the reader would be appreciated.*

Response: the dotted line indicates the ‘early morning case’ when the peak of Cl atom occurs and the ClNO₂ impacts are evaluated in parallel with the ‘daytime average case’. We have added a sentence in figure caption to clarify this.