We thank the reviewers for their supportive and thoughtful comments. Our responses to the comments are provided below, with the reviewers' comments italicized.

Review 2:

This paper analyses the ability of the GEOS-Chem model, run in a regional configuration, to simulate the concentration of Cl-, N2O5, ClNO2, O3 and PM under different assumptions about the anthropogenic emissions of HCl and Cl2, and for the parameterization of the heterogenous N2O5->HNO3, ClNO2 processes over China. In general the paper provides a good assessment of model performance against a good set of observations and explores the limitations of the current generation of parameterizations.

I have some comments about some aspects of the paper (described below) but in general I am supportive of publications if these aspects can be addressed.

Thanks for the supportive and helpful comments. We have addressed all the concerns raised by the reviewer, including the impacts on NO_y and OH. Please see below for the point-by-point response to the reviewer's comments and concerns.

My major comment is on how the model is being analysed. Much is made of the impacts on NOx of the production of ClNO2. I think more could be made on the impacts on NOy. The reactions involved conserve NOy on some levels (if NO3- is included in the definition) but they should change the partitioning of NOy from HNO3 into more reactive forms (ClNO2, NOx etc). This is one key way in that this chemistry influences the composition - the other in the production of Cl atoms. It would be informative to look at how the fraction of NOy as NOx (if we include ClNO2 in our NOx definition) increases with the inclusion of the new chemistry. It would be useful to explore the ratio of NOx to NOy, NO3- to NOy etc with and without the chlorine chemistry switched on.

Thanks for the constructive comment. We agree with the reviewer that the formation of $ClNO_2$ also affect the portioning of NO_y from HNO_3 into more reactive forms. Therefore, we have added the analysis on the impacts of the heterogeneous N_2O_5 + Cl chemistry on the partitioning of NO_y. The maps of the changes in the ratios of NO_x to NO_y and NO_3^- to NO_y are now provided as Fig. S9 in the supplement. The corresponding discussions are added in line 452

– 462: “In addition to the production of Cl atoms, the $ClNO_2$ formation also affects the partitioning of NO_y from HNO_3 into more reactive forms (e.g., NO_x and $ClNO_2$) through the recycling of NO_x, and therefore of great importance in atmospheric chemistry (Bertram et al., 2013; Li et al., 2016; Wang et al., 2020a). To analyze the impact of the heterogeneous N_2O_5 + Cl chemistry on NO_y partitioning, Figure S9 shows the change in the ratios of NO_x to NO_y and NO_3^- to NO_y as the difference between the Base and NoHet cases. Since $ClNO_2$ could be treated as a reservoir for reactive nitrogen at night, we include $ClNO_2$ as part of NO_x in the calculation ($NO_x = NO + NO_2 + ClNO_2$ and $NO_y = NO + NO_2 + ClNO_2 + HNO_3 + 2 \times N_2O_5 + NO_3 + HONO + HNO_4 + NO_3^- +$ various organic nitrates). The results show that due to the $ClNO_2$ production, the ratios of NO_x to NO_y increase by 1.8% averaged in China and up to 5.4% in the Sichuan Basin, Northeast Plain and North China Plain on annual mean basis. Meanwhile, the ratios of NO_3^- to NO_y decrease by 1.1% averaged in China and up to 5.1% in the Sichuan Basin on annual mean basis.”.

Similarily the authors sugges that the increased Cl leads to increased VOC oxidation. Perhaps some figures to explore this might also be useful and provide some evidence for their inferences on the impact on OH?

Thanks for the suggestion. We have added the map of the changes in HO_2 from different simulation cases as Fig. S7 (a) in the supplement accordingly. The map of the changes in OH is already provided in Fig. S7 (b). We have also added more discussion about the impact on OH and HO_2 in line 425 – 435: “The increased Cl atoms could react with VOCs (especially alkanes) producing more peroxy radicals, including organic peroxy radicals (RO_2) and hydroperoxyl radicals (HO_2). As shown in Figure S7 (a), the chlorine chemistry could increase annual mean HO_2 concentrations by 1.6×10^6 molec cm^{-3} averaged in China (up to 8.6×10^6 molec cm^{-3} in the coastal regions). In the presence of NO, the peroxy radicals recycle OH while oxidize NO to NO_2. The subsequent photolysis of NO_2 could further lead to more O_3 production and consequently also more OH (Osthoff et al., 2008; Riedel et al., 2014; Simpson et al., 2015). On the other hand, the recycling of NO_x back into the atmosphere associated with the photolysis of $ClNO_2$ could also lead to more O_3 production. The results here show a significant increase in surface annual mean OH (Fig. S7 (b)) and MDA8 O_3 (Fig. 5c) by 3.8×10^4 molec cm^{-3} and 1.1 ppbv

respectively averaged in China (up to 1.2 $\times$ 10^5 molec cm^{-3} and 4.5 ppbv respectively in the Sichuan Basin).”

Minor Comments:

1. *I don't find the phase "N2O5-ClNO2 Chemistry" sitting well with my ear. It is basically one reaction (or two if you include the photolysis) in the scheme (reaction R3) and so describing it as "N2O5-ClNO2 chemistry" makes it sound like something more different. I would suggest something like the "parameterization of gN2O5" might better reflect what is happening.*

   Thanks for the comment. We have replaced "N_2O_5-$ClNO_2$ chemistry" with "heterogeneous N_2O_5 + Cl chemistry" to specifically refer to the reaction between N_2O_5 and chloride-containing aerosols. Besides, "updated N_2O_5-$ClNO_2$ chemistry" is also replaced with "updated parameterizations for the heterogeneous N_2O_5 + Cl chemistry" throughout the manuscript.

2. *Line 45. I'm not sure that "Recently" describes the literature of ClNO2. The original experimental paper Finlayson-Pitts et al., 1989 probably doesn't classify are recent and there have been a number of papers from the late 2000s which describe much of this matierla.*

   Sorry for the misleading. We now delete the word "Recently".

3. *Line 56. Can the products of the reaction been moved to the right to make it clear that this is a single reaction? It would probably be normal to include some of the products on the same line as the reactants to make this clear.*

   Fixed.

4. *Line 76. I think the word including should be replaced by a comma.*

   Thanks for the comment. We revised the sentence into: "There are two key parameters that determine the uptake efficiency of N_2O_5 and production of $ClNO_2$, the aerosol uptake coefficient of N_2O_5 (γ_{N2O5}) and the ClNO2 yield (φ_{ClNO2})."

5. *Line 80. What is the "specific surface area"?*

It refers to the ratio of surface area concentrations to particle volume concentrations. To make it clear, we added a specific explanation in the corresponding text: "… and specific surface area (i.e. the ratio of surface area concentrations to particle volume concentrations)."

6. *Line 103. I found the phrase "and its chemical species" difficult to understand. Does this mean the chemical composition of the PM2.5?*

Yes, it means the chemical composition of the $PM_{2.5}$. To avoid confusion, we replaced "chemical species" with "chemical compositions" throughout the manuscript.

7. *Line 143. The ratio given in the equation is k2/k3 but its value is given as k3/k2. I think these should probably be given the same way up to avoid confusion.*

We have modified the equation by using the coefficient "k_c" instead of "k_2/k_3", and added the following description in line 170 – 171: "Where k_c is the rate constant ratio representing the competition between aerosol-phase H_2O and Cl^- for the $H_2ONO_2^+$(aq) intermediate and is fixed at 1/450 here, …".

8. *Line 152. The units of H2O, CL- and NO3 should be specified for completeness.*

Thanks for the comment. The units of [H_2O], [Cl^-] and [NO_3^-] are mol L^{-1}. We have added the units of all variables throughout the text.

9. *Line 181. When the authors use the word estimate this is slightly confusing. If they have calculated the flux from these reactions its not an estimate it's a calculation. If they have found this from previous papers they should give the reference.*

Thanks for the comment. We have replaced "estimate" with "calculate" in the corresponding text as the results are calculated in the model.

10. *Line 197. The authors have defined acronyms for 4 areas in China. They don't use the acronyms that extensively. I would suggest they remove these acronyms*

from the paper as it just confuses the reader who has to look back to the definition to find out what the areas are.

We removed the acronyms and used full names for the 4 areas in China throughout the text.

11. *Line 310. The authors argue that more field measurements and model evaluations are needed for a more precise scaling factor. I would argue that they are needed not to come up with an improved scaling factor but to come up with an appropriate parameterisations which doesn't need a scaling factor at all.*

Thanks for the comment. We revised the corresponding text into "More field measurements and model evaluations are required to come up with a more precise parameterization better representing φ_{ClNO2} in China."

12. *Line 318. The acronym CNEMC probably needs to be explained and more details provided of the data source.*

The full name and description of CNEMC are provided in line 302 – 305: "we also use observed hourly data of O_3 and $PM_{2.5}$ published by the China National Environmental Monitoring Center (CNEMC, http://www.cnemc.cn/sssj/, last access on June 20, 2021) to evaluate the model's overall performance in China. The network was launched in 2013 as part of the Clean Air Action Plan, and includes ~1500 stations located in 370 cities by 2018 (Fig. S2)."

To make it clear, we also modified the text here into: "Figure 4 shows observed annual mean MDA8 O_3 and $PM_{2.5}$ in 2018 in China from CNEMC (China National Environmental Monitoring Center, introduced in Section 2.2) ..."

13. *Line 349. The authors argue that the increase in OH concentration is due to increased VOC oxidation. They have not provided any evidence for this. You might also expect the increased NOx concentration to lead to more OH through enhanced HO2+NO reactions, and the increased O3 concentration to lead to more primary OH production. Without a budget for the OH terms its no possible to attribute mechanism to the increased OH concentrations. Similarily its not*

possible to attribute mechanism to the increased O3 concentration. Increases in NOx could lead to more O3 just as increased in VOC oxidation could.

Thanks for the comment. We agreed with the reviewer that an increase in either NO_x or VOCs could lead to more O_3. Therefore, as replied to the general comment #2, in addition to the map of changes in OH, we also added the map of changes in HO_2 between different simulation cases (Fig S7 (a)). We also revised the discussion here into: "The increased Cl atoms could react with VOCs (especially alkanes) producing more peroxy radicals, including organic peroxy radicals (RO_2) and hydroperoxyl radicals (HO_2). As shown in Figure S7 (a), the chlorine chemistry could increase annual mean HO_2 concentrations by 1.6×10^6 molec cm^{-3} averaged in China (up to 8.6×10^6 molec cm^{-3} in the coastal regions). In the presence of NO, the peroxy radicals recycle OH while oxidize NO to NO_2. The subsequent photolysis of NO_2 could further lead to more O_3 production and consequently also more OH (Osthoff et al., 2008; Riedel et al., 2014; Simpson et al., 2015). On the other hand, the recycling of NO_x back into the atmosphere associated with the photolysis of $ClNO_2$ could also lead to more O_3 production. The results here show a significant increase in surface annual mean OH (Fig. S7 (b)) and MDA8 O_3 (Fig. 5c) by 3.8×10^4 molec cm^{-3} and 1.1 ppbv respectively averaged in China (up to 1.2×10^5 molec cm^{-3} and 4.5 ppbv respectively in the Sichuan Basin).".

14. *Line 353. The studies described here (Schmidt, Wang), suggest that Cl chemistry leads to reduced O3 concentration on global scale. The regional studies, notably in polluted regions highlight its importance in producing O3. This isn't clear in this paragraph and it is suggesting a disagreement in the literature that I don't think exists.*

    Sorry for the confusion. We now revised the sentence into: "Both global and regional studies suggested that the heterogeneous N_2O_5 + Cl chemistry can enhance O_3 production through the production of Cl atoms and the recycling of NO_x (Li et al., 2016; Sarwar et al., 2014; Wang et al., 2019).".

15. *Line 406. As mentioned earlier the attribution to the increased OH being due to increased VOC oxidation isn't supported by any evidence from the simulations. I would either perform a budget analysis on the ROx and OH production or soften*

the language here to indicate that it may be due to these processes (Increased VOC oxidation, increased NOx leading to recuyling of HO2 into OH, or increased primary production from O3+hv).

Thanks for the comment. As replied to the minor comment #13, we have added analysis on HO_2 in addition to OH. Accordingly, we also revised the text here into: "As discussed earlier in Section 3.2, increased Cl atoms could lead to more HO_2 and OH via VOCs oxidation. Combined with increased NO_x associated with the release of NO_2 upon the photolysis of $ClNO_2$, further increases in both O_3 and OH could also be expected. The increase in OH is around $2 - 9 \times 10^4$ molec cm^{-3} in central and eastern China on annual mean basis.".

16. *Line 460. I found the argument for the insensitivity of N2O5 to Chlorine emissions difficult to understand. Do the authors mean equation 1 or do they mean equation 2? Equation 1 doesn't really describe the gamma being used as presumabley the two terms have equations for describing the individual rates. I found the overall argument here difficult.*

Sorry for the confusion. We have added Eq. 2 and 3 for the calculation of γ_{core} and γ_{coat}, respectively in the revised manuscript. More discussion is also provided to show the similarity and difference between different parameterizations. To make it clear, we also revised the text here into: "Unlike Yu parameterization, N_2O_5 concentrations have little dependence on chlorine emissions in McDuffie parameterization (Fig. 3a). This insensitivity to chlorine emissions could be expected from Eq. 2 where the dependence on aerosol chloride is not included so as to better reproduce wintertime reactive nitrogen observations in the eastern U.S.".

17. *Would it be useful to provide maps of the surface values for gamma N2O5 and the ratio of ClNO2 to HNO3 production for the different simulations run? How do these important values change spatially and between parameterizations?*

Thanks for the comment. We have added the maps of γ_{N2O5}, φ_{ClNO2} and the ratios of $ClNO_2$ to HNO_3 for different simulation cases as Fig. S3 – S5 in the Supplementary Material. More discussion about the changes of γ_{N2O5}, φ_{ClNO2}, and $ClNO_2/HNO_3$ among different simulation cases are added in Section 3.1.

For example, in line 347 – 350 for the discussion of γ_{N2O5} between the Base and McDuffie cases: “The overestimate of N_2O_5 in McDuffie parameterization suggests the potential underestimate in the corresponding γ_{N2O5}. As shown Figure S3, the value of γ_{N2O5} from the McDuffie case is much smaller than that from the Base case (0.0071 vs. 0.016 averaged over China).”

For more detailed results, please see the discussion in Section 3.1 in the revised manuscript.