Review of Yang, X., et al., The impact of chlorine chemistry combined with heterogeneous N_2O_5 reactions on air quality in China.

General Comments

In this manuscript, the authors present an analysis that uses simulations with the GEOS-Chem model to assess the sensitivity of air quality (e.g., $PM_{2.5}$ and O_3) in China to changes in tropospheric chlorine chemistry, chlorine emissions, and the parameterization of heterogeneous N_2O_5/ClNO2 chemistry. This study also provides an important evaluation of the inclusion of chlorine emissions and updated parameterizations for heterogenous N_2O_5/ClNO2 chemistry, showing that both updates better reproduce surface observations of N_2O_5, ClNO2, and particulate chloride as compared to the default GEOS-Chem model performance. This is a well-designed study and well-written manuscript, though I have specific comments and suggestions below to help deepen the discussion and improve the clarity of the text. For example, there are a few cases where it would help if the authors could be more specific about the processes they are referring to when they say 'N_2O_5-ClNO2 chemistry'. A more detailed discussion on the differences and similarities in the heterogenous parameterizations would also help the reader better interpret the simulation results (see more comments below).

Overall, this study is an important contribution to the field as it highlights that simulations of absolute air pollutant concentrations are sensitive to both chloride emissions and the parameterization of heterogeneous N_2O_5 and ClNO2 chemistry. It also shows that the model's sensitivity to emissions depends on these heterogenous parameterizations. Not only do these results help improve our understanding of the importance of these processes, but they also show that air quality impacts from anthropogenic chlorine sources should be considered in air quality improvement strategies, and that our ability to accurately predict the magnitude of the reduction benefits will depend on the modeled representation of heterogeneous N_2O_5 chemistry. I recommend that this study be accepted for publication after the specific comments below are addressed.

General Comments:

1. This comment applies to all sections of the manuscript. In cases where the authors simply state that one parameterization performs better than another, it would be helpful if the authors could provide additional discussions on *why* one might be outperforming the other in terms of the processes controlling N_2O_5 uptake and ClNO2 yield. For example, the Yu and McDuffie parameterizations for N_2O_5 uptake are actually based on the same general parameterization (see specific comment 4), but the differences are that the Yu parameterization does not consider added suppression from organic aerosol (included in McDuffie), includes an uptake enhancement from particulate chloride (not included in McDuffie), and uses different rate coefficient ratios than McDuffie. Therefore, since this study shows that the Yu parameterization is able to better reproduce available surface observations, the results here suggest that in China, it may be important to consider particulate chloride in the uptake of N_2O_5 and that organics may not play as important of a suppressive role as shown in previous studies. Including these details helps explain to the reader why one parameterization may be outperforming another and provides insight into specific modeled processes that could be improved. Many of my specific comments below are related to this general comment.

2. Throughout the text, the authors refer to the simulations with the Yu parameterization as simulations with 'updated N_2O_5-ClNO2 chemistry'. This is slightly confusing terminology for the reader as it is not actually the chemical reactions of N_2O_5 and ClNO2 that are changing between the simulations. Rather, it is the parameterizations of gamma N_2O_5 and phi ClNO2 that are changing. I would suggest editing the terminology throughout the paper to reflect this difference. E.g., Replace 'N_2O_5-ClNO2 chemistry' with something along the lines of 'updated parameterizations for heterogeneous N_2O_5 and ClNO2 chemistry'.

3. The authors may also want to consider including maps or averages of model-calculated N_2O_5 uptake coefficients and ClNO2 yields. Reporting these values could help future studies compare the results from each parameterization with available field-derived values. The model diagnostics should be able to provide these values. This could be included in the supplement.

Specific Comments

1. Line 80-83 – These two sentences are technically correct, but the authors should adjust them to specifically note the possible role of organics (not considered in the (Bertram and Thornton, 2009) study). It is the presence of organic aerosol species that is thought to reduce the uptake of N_2O_5 relative to that predicted by the Bertram and Thornton parameterization. It is not just the mixing state that is a possible difference, but the presence of hydrophobic organic aerosol that lead to a potentially complex aerosol mixing state.

2. Line 87-89 – To strengthen this last point, the authors could mention that some of these previous field-based parameterizations were derived from observations in locations with conditions may not be applicable to the highly polluted regions in China. This makes it important to evaluate these parameterizations under different conditions. The authors should also clarify that in this study, a full evaluation of this chemistry is being conducted for China specifically. As written, 'full evaluation' makes it sound as if this study will be conducting a global analysis.

3. Line 93 – My comment is on the statement 'The importance of anthropogenic chlorine emissions, which were ignored in most studies…". While these emissions are not commonly included in modeling studies, there is a clear example in (Wang et al., 2019) where they did not 'ignore' chlorine emissions but rather found that the addition of anthropogenic chlorine emissions in GEOS-Chem resulted in overestimates of HCl observations in the U.S. This is an important study to cite in this section. The authors could still note that anthropogenic emissions in China may be relatively more important in China than in the U.S., which is why it is important to study their impacts here.

4. Lines 131 - 154 – Per my general comment above, it would be helpful in this section for the authors to provide a more detailed narrative on 1) the differences between the various parameterizations, 2) the processes that they are trying to represent, and 3) a brief summary of how each parameterization was derived.

   For example, for (1 and 2), the authors should include in Eq. 1 the detailed equations for both gamma_coat and gamma_core (found in (McDuffie et al., 2018b)). These details are important to include here because the functional form of the Yu parameterization is actually the same as that of gamma_core from the McDuffie parameterization. By showing the full equations, the readers can better understand that the only differences between the Yu and McDuffie uptake parameterizations are that Yu parameterization includes an enhancement from aerosol chloride (not included in McDuffie), does not consider the added resistance from an organic coating (included in McDuffie) and uses different coefficients (reaction rate constant ratios) than McDuffie in the gamma_core equation.

   For (3), to better understand why the parameterizations are different, it would be useful to briefly explain that the form of the McDuffie parameterization is derived from parameterizations proposed in multiple laboratory studies ((Bertram and Thornton, 2009), Riemer et al., 2009, and (Anttila et al., 2006)) to account for the uptake dependence on aerosol water and nitrate concentrations and added resistance from an organic aerosol coating. The coefficients in this parameterization were then derived by fitting a chemical box model to aircraft observations of N_2O_5, ClNO2, O_3, and NOx during the winter over the eastern U.S. In contrast, for the Yu parameterization, it would be important to note that the form of this parameterization is from Bertram and Thornton to account for the dependence on aerosol water, nitrate, and chloride concentrations, with coefficients derived from uptake coefficients directly measured on ambient aerosol in two rural sites in China. It would also be important to note that while previous studies have found that organics can suppress N_2O_5 uptake, (Yu et al., 2020) found that including the chloride enhancement and excluding the organic coating best reproduced the observed N_2O_5 uptake coefficients in their study.

Similarly for Eq 2., replace k2/k3 with 1/450 to make this form consistent with Eq. 4. Also add a note that both forms are from Bertram and Thornton, again with coefficients and scaling factors (in the case of McDuffie) derived from fits to observations over the eastern U.S. (McDuffie) and rural locations in China (Yu).

5. Line 183 – It would be helpful context for the reader to specify which sectors contribute to emissions of HCl, Cl2, and particulate chloride in the inventories.

6. Line 221 – The authors should clarify that the NoHet case not only sets phi ClNO2 to zero, but also removes the enhancement of N_2O_5 uptake from aerosol chloride. So this simulation actually tests the model sensitivities to a smaller gamma N_2O_5 and zero ClNO2 production.

7. Line 278 – The comparison here is between the Base and NoEm cases. Therefore, it seems that the results imply that additional chlorine emissions could increase the uptake coefficient due to increased aerosol chloride. This comparison does not directly evaluate the Yu parameterization as implied, since the Yu parameterization is included in both Base and NoEm simulations. This sentence should be updated accordingly.

8. Line 290 – There are many other studies (see section 4.2.6 in (McDuffie et al., 2018b)) that have shown that organics can suppress uptake, which should also be referenced here (the authors can still note that Yu found that excluding the organic coating best reproduced uptake coefficients observed in China). In addition, (Morgan et al., 2015) actually state that "An additional suppression of the parameterised (N_2O_5) uptake is likely required to fully capture the variation in N2O5 uptake, which could be achieved via the known suppression by organic aerosol. However, existing parameterisations representing the suppression by organic aerosol were unable to fully represent the variation in N2O5 uptake." Therefore, the sentence should be amended to clarify that organic suppression may be important to consider in the estimate of N_2O_5 uptake, but that the currently implemented parameterization may overpredict the level of suppression.

9. Line 293 – 297 – The McDuffie parameterization is slightly more sophisticated than indicated in this sentence. For example, in the McDuffie parameterization, the gamma_coat value is actually calculated as a function of organic aerosol O:C ratio and RH. These factors

are meant to account for conditions where higher relative humidity and higher O:C ratio may represent less likely liquid-liquid aerosol phase separation, a partially coated aerosol, or thinner organic coating, each of which could increase N_2O_5 uptake.

It is also important here to note that the lack of chloride enhancement in McDuffie may also contribute to the lower uptake coefficients from McDuffie compared to Yu and that Yu et al. included the chloride dependence in their parameterization specifically because they found that it better reproduced observed uptake coefficients in China.

10. Line 356 – It seems that this comparison (Base compared to NoHet) is not actually representing the full impact of N_2O_5/ClNO2 chemistry as indicated here. For that, the N_2O_5 uptake would also need to be set to zero. Instead, this comparison is showing the sensitivity of the model to the aerosol chloride enhancement of N_2O_5 uptake ([Cl-] = 0) and the production of ClNO2. The authors should clarify that this comparison is mainly assessing the impact of ClNO2 production, not the more general role of 'N_2O_5-ClNO2 chemistry'.

11. Lines 459-462 – clarify that the McDuffie parameterization purposefully does not include any dependence on aerosol chloride since the exclusion of this enhancement (original proposed by Bertram and Thornton) was found to better reproduce wintertime reactive nitrogen observations in the eastern U.S. And conversely, in the previous paragraph, clarify that the Yu parameterization includes a dependence on chloride because the study authors found that this form better reproduced gamma N_2O_5 observations in China.

12. Line 517 – To increase study reproducibility and transparency, the authors may want to consider including a link to their model simulation code (or at least copies of the files that were changed in each sensitivity simulation).

13. Figure 4 – In addition to the maps, it would be helpful to show the correlation plots between the model and observations (perhaps as a supplemental figure).

Technical Corrections – suggested changes are in *blue italics*

Line 15 – Also note the impact of this chemistry on $PM_{2.5}$ in addition to O_3 (since this is one of the air pollutants you investigate in this study).

Line 19 – Change '…as well as their sensitivities to…' to '…as well as *the sensitivity of air pollution formation* to…'

Line 20-22 – Suggest changing this sentence to improve clarity, for example: "*Model simulations are evaluated against multiple observational datasets across China and show significant improvement in reproducing observations of particulate chloride, N_2O_5, and ClNO2 when including anthropogenic chlorine emissions and updates to the parameterization of N_2O_5-ClNO2 chemistry relative to the default model*."

Line 23 – define MDA8 here, not on line 29.

Lines 22-33. Make sure to specify that the model 'simulations' show changes in pollutants concentrations. For example, the sentence on line 22 could say, "*Model simulations show that* total tropospheric chlorine chemistry could increase annual mean MDA8 O_3…". Similarly, on line 28, update to say "With the additional chlorine emissions, *simulations show that* annual mean MDA8 O_3 in China would increase by up to…"

Line 27 – Change to "seen ozone underestimations *relative to observations*."

Line 58 – Provide a reference for this statement.

In the introduction – The authors could also cite (Simpson et al., 2015) or (Saiz-Lopez and von Glasow, 2012) as reviews of chlorine chemistry in the troposphere.

Line 67 – Change this sentence to more explicitly state that previous global and hemispheric models found that ClNO2 formation could impact ozone. Not just that it was 'suggested'.

Line 76 – Change to '*There are two key parameters that determine the uptake efficiency of N_2O_5 and production ClNO2*, the aerosol uptake coefficient of N_2O_5 (gamma) and the ClNO2 yield (phi)."

Line 112 – The doi of the 12.9.3 version should also be included here, as per GEOS-Chem recommendations (https://geos-chem.seas.harvard.edu/narrative).

Line 119 – It is also appropriate to cite (Wang et al., 2019) here since the recent updates to the model halogen chemistry are described in that paper.

Line 124 – The reference to (Wang et al., 2019) that is listed here does not appear in the reference list at the end.

Line 139 – The 75% scaling factor as implemented in GEOS-Chem is actually from (McDuffie et al., 2018a), not Lee et al., 2018. This reference should be updated.

Line 143 -145– This sentence is not quite correct as N_2O_5 uptake and ClNO2 yield were not directly observed in this study. It is more accurate to say here that '*The coefficients for the parameterizations in Eq. 1 and E. 2 were derived from applying a box model to observations of N_2O_5, ClNO2, O_3, and NOx mixing ratios during the winter in the eastern U.S. However, there are large uncertainties in both the values of the coefficients and functional form of the parameterizations, specifically related to their applicability to other regions*.'

Line 198 – What do the authors mean by '…could be up to…'? Do the authors mean, '…are up to…'?

Line 214 – Remove 'improved' here since the chemistry is the same in both parameterizations and at this point in the text, the Yu vs. McDuffie parameterizations have not been evaluated. Suggest changing to "… *as well as N_2O_5 uptake and ClNO2 production represented by the Yu parameterizations*."

Line 262 – The authors could consider moving the NMB results to this sentence to more easily compare with the NoEm case. E.g., *0.77 +/- 0.54 (NMB 39%), 0.71 +/- 0.52 (NMB -36%), and 4.5 +/- 2.4 ug m-3 (NMB -4.7%)*.

Line 287 – Replace 'The comparison indicates…' with '*The comparison between the McDuffie and Base simulations indicate*...". It is also important to clarify that this evaluation is specific to China and that differences between the Yu and McDuffie parameterizations have not been evaluated elsewhere.

Line 386 – Specify which simulations are being compared in this paragraph (and Figure 5) (e.g., the Base and NoAll simulations?)

Line 442 – change 'seas' to '*sea'*

Figure 1 – in the figure caption, define the 5 regions highlighted in panel A.

Figure 3. In the figure caption, note that the simulation definitions are provided in Table 2.

References

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