

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

Review 1:

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 O₃) in China to changes in tropospheric chlorine chemistry, chlorine emissions, and the parameterization of heterogeneous N₂O₅/ClNO₂ chemistry. This study also provides an important evaluation of the inclusion of chlorine emissions and updated parameterizations for heterogeneous N₂O₅/ClNO₂ chemistry, showing that both updates better reproduce surface observations of N₂O₅, 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 'N₂O₅-ClNO₂ chemistry'. A more detailed discussion on the differences and similarities in the heterogeneous 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 N₂O₅ and ClNO₂ chemistry. It also shows that the model's sensitivity to emissions depends on these heterogeneous 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 N₂O₅ chemistry. I recommend that this study be accepted for publication after the specific comments below are addressed.

Thanks for the supportive and helpful comments. We have addressed all the concerns raised by the reviewer, including the term of "N₂O₅-ClNO₂ chemistry" and "the differences and similarities in the heterogeneous parameterizations" (e.g. the replies to the general comments #2 and #1,

respectively). Please see below for the point-by-point response to the reviewer's comments and concerns.

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 $ClNO_2$ 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.*

Thanks for the constructive comment. We agree with the reviewer that compared with the Yu parameterization, the underestimation of $\gamma_{N_2O_5}$ and ϕ_{ClNO_2} from the McDuffie parameterization in China is potentially due to (1) overpredicting the suppressive role of organic aerosol, (2) the lack of the uptake enhancement from particulate chloride, and (3) the scaling factor (i.e. 0.25 in Eq. 4) applied in the McDuffie parameterization. As suggested by the reviewer, we have added more discussion throughout the manuscript to make it much clearer about the difference and similarities in the Yu and McDuffie parameterizations.

Firstly, we added more detailed description about the Yu and McDuffie parameterizations, including adding Eq. 2 and 3 for the calculation of γ_{core} and γ_{coat} as well as the explanation of the forms of the two parameterizations. For example, in line 145 – 176 for the McDuffie parameterization: “McDuffie parameterization is the first field-based empirical parameterizations modified

from the framework proposed by previous laboratory studies including BT09 (Anttila et al., 2006; Bertram and Thornton, 2009; Riemer et al., 2009). It is adjusted to reproduce the mean values of $\gamma_{\text{N}_2\text{O}_5}$ and ϕ_{ClNO_2} observed from ambient wintertime aircraft measurements over the eastern U.S. The parameterization for $\gamma_{\text{N}_2\text{O}_5}$ accounts for both the inorganic and organic aerosol components ...”.

In line 177 – 186 for the Yu parameterization: “Recently, Yu et al. (2020) proposed new parameterizations of $\gamma_{\text{N}_2\text{O}_5}$ and ϕ_{ClNO_2} based on BT09 to account for the dependence on aerosol water, nitrate, and chloride concentrations but with coefficients derived from uptake coefficients directly measured on ambient aerosol in two rural sites in China. The parameterizations ...”.

The forms of the Eq. 2 and 5 and the forms of the Eq. 4 and 6 are adjusted to be consistent with each other so that the comparison between each other is more intuitive (see more details in the reply to the specific comment #4 below).

Secondly, we added detailed discussion providing a general picture of how the Yu and McDuffie parameterizations differ from each other in line 187 – 205: “Although both the two parameterizations are developed based on BT09, there exist significant differences of $\gamma_{\text{N}_2\text{O}_5}$ and ϕ_{ClNO_2} between McDuffie and Yu parameterizations. For $\gamma_{\text{N}_2\text{O}_5}$, McDuffie parameterization generally follows BT09 for the calculation of the uptake on inorganic aerosols (i.e. γ_{core}), but excludes the dependence on aerosol chloride so as to better reproduce observed wintertime reactive nitrogen in eastern U.S. Moreover, the parameterization accounts for the suppressive effects of the organics (i.e. γ_{coat}), which is not directly included in BT09 (Anttila et al., 2006; Riemer et al., 2009; Morgan et al., 2015). In contrast to McDuffie parameterization, Yu parameterization excludes the organic suppression but includes the chloride enhancement so as to better reproduce $\gamma_{\text{N}_2\text{O}_5}$ observed in China (Yu et al., 2020). It is worth mentioning that the coefficients applied in the parameterization of $\gamma_{\text{N}_2\text{O}_5}$ also differ between McDuffie and Yu parameterizations as both are fixed to reproduce the ambient observation representing different pollution conditions. For example, k_a is equal to 0.04 in Eq. 2 but 0.033 in Eq. 5. The $\gamma_{\text{N}_2\text{O}_5}$ in McDuffie parameterization is thus expected to be lower compared with the Yu parameterization due to the resistance from organic coating and the lack of the chloride enhancement. For ϕ_{ClNO_2} , both the McDuffie and Yu parameterizations are based on BT09, but with different coefficients (i.e. $k_c = 1/450$ in Eq. 4 and $1/150$ in Eq. 6). Although k_c in Eq. 4 is relatively smaller, the scaling factor of

0.25 applied in Eq. 4 ultimately results in a much smaller φ_{ClNO_2} in McDuffie parameterization compared with Yu parameterization under the same condition. Again, keep it in mind that McDuffie parameterization is derived from fits to observations over the eastern U.S. (McDuffie et al., 2018a) while Yu parameterization is fitted to observations at rural locations in China (Yu et al., 2020).”

Moreover, to help explain to the reader why Yu parameterization performs better, we also modified the corresponding discussion when comparing the results of N_2O_5 and ClNO_2 from different simulation cases:

For N_2O_5 in line 342 – 368: “The N_2O_5 results from the McDuffie case, which uses McDuffie parameterization (a default setting in GEOS-Chem, see Section 2.1.1 and 2.1.3) instead of Yu parameterization are also shown in Fig. 3a. The NMB for the McDuffie case are -53%, 154%, 143% and 37% at the Guangzhou, Wangdu, Taizhou and Mount Tai sites, respectively. The comparison between the McDuffie and Base cases indicates that Yu parameterization can reproduce observed N_2O_5 better in China in general, while McDuffie parameterization tends to overestimate N_2O_5 concentrations. The overestimate of N_2O_5 in McDuffie parameterization suggests the potential underestimate in the corresponding $\gamma_{\text{N}_2\text{O}_5}$. As shown Figure S3, the value of $\gamma_{\text{N}_2\text{O}_5}$ from the McDuffie case is much smaller than that from the Base case (0.0071 vs. 0.016 averaged over China).

The underestimate in $\gamma_{\text{N}_2\text{O}_5}$ from the McDuffie case could to large extent be explained by the suppressive effect of organic coatings (γ_{coat}) as discussed above in Section 2.1.1. The magnitude of the organic suppression is highly dependent on many factors (e.g. organic composition, particle phase state, etc.) and thus remains poorly quantified (Griffiths et al., 2009; Gross et al., 2009; Thornton et al., 2003). Although many studies have shown that organic aerosol can suppress the N_2O_5 uptake (Anttila et al., 2006; Riemer et al., 2009), the level of organic suppression may be overpredicted in currently implemented parameterization attributed to the poorly quantified and/or unknown factors (e.g. Morgan et al. (2015)). For example, some studies found that ignoring the difference between water-soluble and water-insoluble organics may lead to an upper limit for the suppressive effect of organic coatings and consequently an underestimate in the solubility and diffusivity of N_2O_5 in organic matter (Chang et al., 2016; Yu et al., 2020). Although the γ_{coat} in McDuffie parameterization is calculated as a

function of organic aerosol O:C ratio and RH (see Eq. 2), which could increase with higher RH and higher O:C ratio, it may still overpredict the suppressive role of organic coatings in China. On the other hand, the study by Yu et al. (2020) found that excluding the organic coating best reproduced uptake coefficients observed in China. In addition, the underestimate in $\gamma_{\text{N}_2\text{O}_5}$ in McDuffie parameterization in China could also be to some extent explained by the lack of the chloride enhancement (also discussed in Section 2.1.1). It is worth noting that the evaluation here is specific to China and the differences between Yu and McDuffie parameterizations have not been evaluated elsewhere.”.

For ClNO₂ in line 369 – 383: “For the comparison of ClNO₂ (Fig. 3b), we use the mean nighttime (excluding the data at local time of 10:00 – 16:00) maximum mixing ratio, as suggested by Wang et al. (2019). Observed ClNO₂ is high in Guangzhou (1121 pptv) and Wangdu (~ 990 pptv), followed by Changping (~ 500 pptv) and Beijing (~ 430 pptv). The lowest concentrations are obtained at Mount Tai and Mount TaiMoShan (~ 150 and 120 pptv, respectively) due to relatively clean condition at high altitude. The comparison between observed and simulated ClNO₂ at different sites also suggests a better model performance for the Base case with NMB in the range of -28% – 22%, compared with the NMB of -77% – -31% and -59% – -36% for the NoEm and McDuffie cases, respectively. The difference in ClNO₂ concentrations is mainly associated with distinct ϕ_{ClNO_2} values among different cases. As shown in Figure S4, the value of ϕ_{ClNO_2} is significantly higher in the Base case (0.36 averaged over China) than in the NoEm (0.14) and McDuffie (0.11) cases. The large difference between the NoEm and Base cases again emphasizes the important role of non-sea salt chlorine in the formation of ClNO₂. The overall underestimates in McDuffie parameterization on the other hand may suggest that the scaling factor of 0.25 applied to ϕ_{ClNO_2} in Eq. 4 is too much for the atmospheric condition in China. More field measurements and model evaluations are required to come up with a more precise parameterization better representing ϕ_{ClNO_2} in China.”.

2. *Throughout the text, the authors refer to the simulations with the Yu parameterization as simulations with ‘updated N₂O₅-ClNO₂ chemistry’. This is slightly confusing terminology for the reader as it is not actually the chemical*

reactions of N_2O_5 and $ClNO_2$ that are changing between the simulations. Rather, it is the parameterizations of gamma N_2O_5 and phi $ClNO_2$ that are changing. I would suggest editing the terminology throughout the paper to reflect this difference. E.g., Replace ‘ N_2O_5 - $ClNO_2$ chemistry’ with something along the lines of ‘updated parameterizations for heterogeneous N_2O_5 and $ClNO_2$ chemistry’.

Thanks for the comment. We have replaced the terminology “ N_2O_5 - $ClNO_2$ chemistry” by “heterogeneous N_2O_5 + Cl chemistry”. the term “updated N_2O_5 - $ClNO_2$ chemistry” was also replaced by “updated parameterizations for heterogeneous N_2O_5 + Cl chemistry” throughout the text.

- 3. The authors may also want to consider including maps or averages of model-calculated N_2O_5 uptake coefficients and $ClNO_2$ 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.*

Thanks for the comment. We have added the maps of $\gamma_{N_2O_5}$ and ϕ_{ClNO_2} for different simulation cases in the Supplementary Material (Fig. S3 and S4). The corresponding description was also added throughout the manuscript. A few examples are listed below:

line 335 – 338 for the comparison of $\gamma_{N_2O_5}$ between the Base and NoEm cases: “As shown in Figure S3, although the values of $\gamma_{N_2O_5}$ between the Base and NoEm cases are similar over the ocean, the Base case has relatively higher $\gamma_{N_2O_5}$ over China compared with the NoEm case (0.016 vs. 0.014 on annual mean basis).”.

Line 347 – 350 for the comparison of $\gamma_{N_2O_5}$ between the Base and McDuffie parameterization: “The overestimate of N_2O_5 in McDuffie parameterization suggests the potential underestimate in the corresponding $\gamma_{N_2O_5}$. As shown Figure S3, the value of $\gamma_{N_2O_5}$ from the McDuffie case is much smaller than that from the Base case (0.0071 vs. 0.016 averaged over China).”.

line 376 – 379 for the comparison of ϕ_{ClNO_2} : “The difference in $ClNO_2$ concentrations is mainly associated with distinct ϕ_{ClNO_2} values among different cases. As shown in Figure S4, the value of ϕ_{ClNO_2} is significantly higher in the Base case (0.36 averaged over China) than in the NoEm (0.14) and McDuffie (0.11) cases.”.

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.*

Thanks for the comment. We revised the sentences into: “The most widely used parameterization for $\gamma_{N_2O_5}$ and ϕ_{ClNO_2} was proposed by Bertram and Thornton (2009) (hereinafter referred to as BT09), which is based on the laboratory studies with considerations of aerosol water content, concentrations of nitrate and chloride, and specific surface area (i.e. the ratio of surface area concentrations to particle volume concentrations). However, recent field and model studies have shown that this parameterization would overestimate both $\gamma_{N_2O_5}$ and ϕ_{ClNO_2} , especially in regions with high Cl levels (Mcduffie et al., 2018b; Mcduffie et al., 2018a; Xia et al., 2019; Chang et al., 2016; Hong et al., 2020; Yu et al., 2020). The discrepancies could be partly attributed to the complexity of atmospheric aerosols (e.g. mixing state and complex coating materials) in contrast to the simple proxies used in laboratory studies (Yu et al., 2020). Specifically, the suppressive effect of organic coatings is not considered in BT09.”.

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.*

Thanks for the comment. We have modified the corresponding description into: “However, some of these previous field-based parameterizations were derived from observations under different ambient conditions which may not be applicable to the highly polluted regions in China. A full evaluation of the

representativeness of different parameterizations for the heterogeneous N₂O₅ + Cl chemistry and the associated impacts on ambient air quality in China is not available yet.”.

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.*

We agree with the reviewer that the study by Wang et al. (2019) has tested anthropogenic chlorine emissions in the simulation but found insignificant influence of anthropogenic Cl emission in the U.S. To avoid misleading, we have revised the corresponding description into: “In early modelling studies, global tropospheric chlorine is mainly from sea salt aerosols (SSA), and most of the chlorine over continental regions in North America and Europe is dominated by the long-range transport of SSA (Wang et al., 2019; Sherwen et al., 2017). The study by Wang et al. (2019) found an addition of anthropogenic chlorine emissions in the model would result in overestimates of HCl observations in the U.S and suggested insignificant influence of anthropogenic Cl in the U.S. However, there are also studies pointing out the importance of anthropogenic chlorine emissions in China (Le Breton et al., 2018; Yang et al., 2018; Hong et al., 2020). The study by Wang et al. (2020b) suggested that anthropogenic chlorine emissions in China are more than 8 times higher than those in the U.S., and could dominate reactive chlorine in China, resulting in an increase in PM_{2.5} and Ozone by up to 3.2 μg m⁻³ and 1.9 ppbv on annual mean basis, respectively.”.

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 γ_{coat} and γ_{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 γ_{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 γ_{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 , ClNO_2 , O_3 , and NO_x 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 k_2/k_3 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).

Thanks for the constructive comment. As replied to the general comment #1, we have modified the whole section (Section 2.1.1) to provide a more detailed description about the similarity and difference between these two parameterizations. Specifically, for (1 and 2), we have added Eq. 2 and 3 for the

calculation of γ_{core} and γ_{coat} , respectively. The forms of the Eq. 2 and 5 as well as the forms of the Eq. 4 and 6 are adjusted to be consistent with each other so that the comparison between each other is more intuitive. For example, we replaced k_2/k_3 with k_c in Eq. 4 and 6. We also used k_a in Eq. 2 and 5 as the rate constant ratio representing the competition between aerosol-phase H_2O and NO_3^- for the $\text{H}_2\text{ONO}_2^+(\text{aq})$ intermediate. For (3), as suggested by the reviewer, we have emphasized that “McDuffie parameterization is the first field-based empirical parameterization derived from the framework proposed in multiple laboratory studies including BT09 (Anttila et al., 2006; Bertram and Thornton, 2009; Riemer et al., 2009) to account for the uptake dependence on aerosol water and nitrate concentrations as well as the resistance from an organic coating. The coefficients for McDuffie parameterization were derived from applying a box model to observations of N_2O_5 , ClNO_2 , O_3 , and NO_x mixing ratios during the winter in the eastern U.S.” and that the Yu parameterization is “based on BT09 to account for the dependence on aerosol water, nitrate, and chloride concentrations but with coefficients derived from uptake coefficients directly measured on ambient aerosol in two rural sites in China.” Please see more detailed discussion in line 142-205 in Section 2.1.1.

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.*

Thanks for the comment. We have added Table S1 in the Supplementary Material to specify the contribution from different sectors to anthropogenic emissions of HCl, Cl₂, and Cl⁻.

6. *Line 221 – The authors should clarify that the NoHet case not only sets phi ClNO₂ to zero, but also removes the enhancement of N₂O₅ uptake from aerosol chloride. So this simulation actually tests the model sensitivities to a smaller gamma N₂O₅ and zero ClNO₂ production.*

Thanks for the comment. To avoid confusion, we have revised the corresponding description into: “In addition, while keeping others the same as the Base case, the NoHet case sets ϕ_{ClNO_2} to zero (Eq.6) and removes the enhancement of N_2O_5 uptake from aerosol chloride (i.e. $[\text{Cl}^-] = 0$ in Eq. 5). The comparison between the Base and NoHet cases could thus evaluate the

importance of the heterogeneous $\text{N}_2\text{O}_5 + \text{Cl}$ chemistry (i.e., the model sensitivities to a smaller gamma N_2O_5 and zero ClNO_2 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.*

To make it clear, we have revised the sentence into: “The improvement in the Base case is apparent at most sites, implying that additional chlorine emissions could effectively increase the uptake coefficient of N_2O_5 in Yu parameterization.”.

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 N_2O_5 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 N_2O_5 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.*

To avoid misleading, we have revised the corresponding discussion into: “The underestimate in $\gamma_{\text{N}_2\text{O}_5}$ from the McDuffie case could to large extent be explained by the suppressive effect of organic coatings (γ_{coat}) as discussed above in Section 2.1.1. The magnitude of the organic suppression is highly dependent on many factors (e.g. organic composition, particle phase state, etc.) and thus remains poorly quantified (Griffiths et al., 2009; Gross et al., 2009; Thornton et al., 2003). Although many studies have shown that organic aerosol can suppress the N_2O_5 uptake (Anttila et al., 2006; Riemer et al., 2009), the level of organic

suppression may be overpredicted in currently implemented parameterization attributed to the poorly quantified and/or unknown factors (e.g. Morgan et al. (2015)). For example, some studies found that ignoring the difference between water-soluble and water-insoluble organics may lead to an upper limit for the suppressive effect of organic coatings and consequently an underestimate in the solubility and diffusivity of N_2O_5 in organic matter (Chang et al., 2016; Yu et al., 2020). Although the γ_{coat} in McDuffie parameterization is calculated as a function of organic aerosol O:C ratio and RH (see Eq. 2), which could increase with higher RH and higher O:C ratio, it may still overpredict the suppressive role of organic coatings in China. On the other hand, the study by Yu et al. (2020) found that excluding the organic coating best reproduced uptake coefficients observed in China. In addition, the underestimate in $\gamma_{\text{N}_2\text{O}_5}$ in McDuffie parameterization in China could also be to some extent explained by the lack of the chloride enhancement (also discussed in Section 2.1.1). It is worth noting that the evaluation here is specific to China and the differences between Yu and McDuffie parameterizations have not been evaluated elsewhere.”.

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.

Thanks for the comment. As replied to the specific comment #8, we have modified the discussion about the underestimate of N_2O_5 uptake in China from McDuffie parametrization. Specifically, we have emphasized that the suppression effect in McDuffie parametrization is a function of RH and O:C ratio and added the discussion about the lack of chloride enhancement in

McDuffie parametrization in line 361 – 366: “Although the γ_{coat} in McDuffie parameterization is calculated as a function of organic aerosol O:C ratio and RH (see Eq. 2), which could increase with higher RH and higher O:C ratio, it may still overpredict the suppressive role of organic coatings in China. On the other hand, the study by Yu et al. (2020) found that excluding the organic coating best reproduced uptake coefficients observed in China. In addition, the underestimate in $\gamma_{\text{N}_2\text{O}_5}$ in McDuffie parameterization in China could also be to some extent explained by the lack of the chloride enhancement (also discussed in Section 2.1.1).”.

10. *Line 356 – It seems that this comparison (Base compared to NoHet) is not actually representing the full impact of $\text{N}_2\text{O}_5/\text{ClNO}_2$ 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 ($[\text{Cl}^-] = 0$) and the production of ClNO_2 . The authors should clarify that this comparison is mainly assessing the impact of ClNO_2 production, not the more general role of ‘ N_2O_5 - ClNO_2 chemistry’.*

As replied to the specific comment #6, we have revised the description of the NoHet case into: “The comparison between the Base and NoHet cases could thus evaluate the importance of the of heterogeneous $\text{N}_2\text{O}_5 + \text{Cl}$ chemistry (i.e., the model sensitivities to a smaller gamma N_2O_5 and zero ClNO_2 production”. To make it clear, we also modified the description in line 441 – 445 to clarify the comparison is mainly for the impact of ClNO_2 production instead of the more general role of the heterogenous chemistry of N_2O_5 : “Therefore, we further investigate the role that the heterogeneous $\text{N}_2\text{O}_5 + \text{Cl}$ chemistry plays in tropospheric chlorine chemistry through the comparison between the Base and NoHet (Fig. 6 and Fig. S8) cases. Keep it in mind that the comparison is mainly assessing the impact of ClNO_2 production, namely the uptake of N_2O_5 on chloride aerosol, not the general role of N_2O_5 heterogeneous 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 N₂O₅ observations in China.

Thanks for the comments. As replied to the general comment #1, we have added detailed discussion about the similarity and difference between these two parameterizations, including whether the effects of organic aerosol and chloride aerosol are included or excluded in the parameterizations. Also, as suggested by the reviewer, we added one sentence in line 558 – 560: “This is consistent with the dependence on chloride in Yu parameterization, which is included to better reproduce $\gamma_{\text{N}_2\text{O}_5}$ observations in China (Yu et al., 2020).” and also modified the text in line 565 – 567 into: “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.”.

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).*

Thanks for the comments. We have uploaded the revised code for each sensitivity simulation and also added the following sentence here: “The revised codes for different simulations could be downloaded via <https://zenodo.org/record/5957287#.YfyNMppBxPZ>”.

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).*

Thanks for the comments. We have added correlation maps of MAD8 O₃ and PM_{2.5} between the model and observations as Figure S6 in the Supplementary Material.

Technical Corrections – suggested changes are in *blue italics*

1. *Line 15 – Also note the impact of this chemistry on PM 2.5 in addition to O₃ (since this is one of the air pollutants you investigate in this study).*

Fixed!

2. *Line 19 – Change ‘...as well as their sensitivities to...’ to ‘...as well as the sensitivity of air pollution formation to...’*

Done!

3. *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, N₂O₅, and ClNO₂ when including anthropogenic chlorine emissions and updates to the parameterization of N₂O₅-ClNO₂ chemistry relative to the default model.”*

Done!

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

Fixed!

5. *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 O₃ ...”. Similarly, on line 28, update to say “With the additional chlorine emissions, simulations show that annual mean MDA8 O₃ in China would increase by up to...”*

Fixed!

6. *Line 27 – Change to “seen ozone underestimations relative to observations.”*

Done!

7. *Line 58 – Provide a reference for this statement.*

Done!

8. *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.*

Thanks for the comments! As suggested by the reviewer, the references are now cited in line 46 – 48: “In general, Cl atom can be produced from the photodissociation and the oxidation of chlorinated organic species (e.g. CH₃Cl, CH₂Cl₂ and CHCl₃) and inorganic chlorine species (i.e. HCl and Cl₂) (Saiz-Lopez and Von Glasow, 2012; Simpson et al., 2015).” and also in line 48 – 52: “Nitryl chloride (ClNO₂), formed through the heterogeneous reaction between dinitrogen pentoxide (N₂O₅) and chloride-containing aerosols (hereinafter referred to as the heterogeneous N₂O₅ + Cl chemistry), is found to be another important source of tropospheric Cl atoms in polluted regions (Liu et al., 2018; Haskins et al., 2019; Choi et al., 2020; Simpson et al., 2015).”.

9. *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’.*

As suggested by the reviewer, we modified the sentence into: “Previous global and hemispheric models found that the heterogeneous N₂O₅ + Cl chemistry could increase monthly mean values ...”

10. *Line 76 – Change to ‘There are two key parameters that determine the uptake efficiency of N₂O₅ and production ClNO₂, the aerosol uptake coefficient of N₂O₅ (gamma) and the ClNO₂ yield (phi).’*

Done!

11. *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>).*

Fixed.

12. 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.*

Done!

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

Fixed!

14. 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.*

Updated!

15. Line 143 -145– *This sentence is not quite correct as N_2O_5 uptake and $ClNO_2$ 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 , $ClNO_2$, O_3 , and NO_x 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.’*

Thanks for the suggestion. We have revised the corresponding discussion into: “For more detailed description of McDuffie parameterization, readers are referred to McDuffie et al. (2018b; 2018a). Keep it in mind that the coefficients for the parameterizations in Eq. 1 – 4 were derived to better reproduce wintertime observations 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.”

16. Line 198 – What do the authors mean by ‘...could be up to...’? Do the authors mean, ‘...are up to...’?

Yes. We now replaced “could be up to” with “are up to”.

17. 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 $ClNO_2$ production represented by the Yu parameterizations.”

Fixed!

18. 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 $\mu g m^{-3}$ (NMB -4.7%).

Done!

19. 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.

Done! As suggested by the reviewer, we also added the following sentence in line 366 – 368: “It is worth noting that the evaluation here is specific to China and the differences between Yu and McDuffie parameterizations have not been evaluated elsewhere.”

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

We modified the corresponding text into: “the effect of tropospheric chlorine chemistry without the heterogeneous N_2O_5 + Cl chemistry is much smaller (Fig. S10, the comparison between the NoHet and NoChem cases) ...” Similar modification has also been made in the captions of the figures.

21. *Line 442 – change ‘seas’ to ‘sea’*

Done!

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

Done!

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

Done!