Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
https://doi.org/10.5194/acp-2021-850-RC2, 2021

Comment on acp-2021-850

Anonymous Referee #2

Referee comment on "The impact of chlorine chemistry combined with heterogeneous N_2O_5 reactions on air quality in China" by Xiajie Yang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-850-RC2, 2021

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.

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.

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?

Minor Comments

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.

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.

Line 56. Can the products of the reaction been moved to the right to make t 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.

Line 76. I thin the work including should be replaced by a comma

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

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

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.

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

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.

Line 197. The authors have defined acronyms for 4 areas in China. They don't uses 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.

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.

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

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.

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.

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).

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.

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?