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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaluation of updated nitric acid chemistry on ozone precursors and radiative effects" *by* K. M. Seltzer et al.

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The authors would like to thank the second anonymous reviewer for their contributions and comments. Each of the specific comments outlined by the reviewer are addressed below.

Comment: 1. The chemical reaction examined here critically influences NOy and HOx chemistry and compounds oxidized by HO. Thus, it should be noted that changing this reaction rate may affect other aspects of model performance not examined here, and the potential shortcomings of adjusting one reaction rate in isolation.

Response: This was considered in Henderson et al. (2012; doi: 10.5194/acp-12-653-2012), where the magnitude of the updated mechanism used in this study was

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developed. A detailed explanation of these other considerations was detailed in that publication. However, this is a very important point and should certainly be reiterated in this paper. I will make sure a discussion regarding this topic is included at some point in the introduction.

Comment: 2. It would be helpful to compare the new reaction rate with the rate assumed in the base case as a function of temperature, and to more clearly note which study is used in the base case (p. 3224).

Response: The base case used in this study is the "out-of-the-box" version of the GEOS-Chem model. And I agree it is useful to visualize the different reaction rates. This can be seen in Figure 5 of Henderson et al. (2012; doi: 10.5194/acp-12-653-2012).

Comment: 3. What is the basis for determining that CH3O2NO2 was estimated within a factor of two (p. 3225, lines 27-29)? Also, it is unclear what is referred to by the GEOS-Chem levels of 15 ppt are 34 ppt (p. 3226, line 2) – are these medians in each layer?

Response: Clarifications can and will be made to this paragraph. The factor of two for MPN is the difference between the estimated concentrations of MPN from the discussed chemical box-model and GEOS-Chem results from an updated version that includes MPN. The results from each model are the median values and this has been added to the text for clarity.

Comment: 4. How were duplicates removed (p. 3229, line 15)? Was an average of the observations kept for the corresponding model prediction?

Response: 'Removed' is probably the wrong way to view this model/observation population formation and a re-phrasing would help. Rather, the model results weren't double counted. If the observations produced X number of values that would all correspond to a particular grid cell in a particular temporal period (one 4-D modeled point), the

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modeled population pool would not be diluted with X number of repeated values.

Comment: 5. What is the basis for concluding that lightning NOx is the reason for the high bias in NOy?

Response: The certainty with which that was stated on p. 3231, line 25 should be more along the lines of a hypothesis; and probably moved to the discussion. This study did not focus on lightning produced NOx and as such, should probably not reach such sweeping conclusions. Nonetheless, this is hypothesized for the following reasons:

Sources of NOx in the upper troposphere include convectively lofted anthropogenic NOx, lightning, transport from the stratosphere and aircraft emissions (Jaegle et al. (1998; doi:10.1029/97GL03591), Hudman et al. (2007; doi:10.1029/2006JD007912)). The observations are filtered to exclude stratospheric intrusion and Allen et al. (2012; doi:10.5194/acp-12-1737-2012) found that the impact of aircraft NO emissions on upper tropospheric NOx on a flight path from the INTEX-A campaign were generally small. Though, it was stated that the impacts related to aircraft NO emissions are more evident in periods of low lightning NO emissions. This leaves either lightning NOx or convectively lofted anthropogenic NOx as the main culprits. Hudman et al. (2007; doi:10.1029/2006JD007912) studied upper tropospheric NOx during the INTEX-A campaign using GEOS-Chem and found that lightning was the dominant factor in upper tropospheric NOx bias. Though, their main bias was in regions of the upper troposphere above the domain of interest for this study and was low biased. As well, their version of GEOS-Chem utilized an older vertical release profile of lightning NOx. Newer GEOS-Chem versions, such as the one used in this study, utilize the vertical release profiles developed by Ott et al., (2010; doi:10.1029/2009JD011880). In these updated profiles, large portions of upper and lower tropospheric lightning NOx fractions were moved to the middle troposphere. These areas happen to be the areas where the high bias of NOx/NOy partitioning and NOx concentrations mainly occur. Therefore, it was hypothesized that these biases were a result of the vertical lightning NOx release profiles.

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This will be added to the discussion, as well.

Comment: 6. It is unclear whether “significant improvements” have in fact been demonstrated by the evaluations against aircraft data. Both cases had substantial biases for concentrations, leading to the use of the fractional approach. In most cases, the changes in the modeled fractions were small relative to the gaps between model and observations. It was also difficult to view these differences in Figure 3, as the white lines in the grey bars are barely visible, and the meaning of the large circles is not explained. The justification for focusing on results above 8 km was also unclear. In sum, more caution is warranted in the conclusions, especially given the shortcomings of the emissions inventory and the possibility of other errors in the chemical mechanism.

Response: The large circles are the mean values for the observation population in each vertical bin. This description will be added to the Figure description. The reason why this evaluation focused mainly on the upper troposphere is because Henderson et al. (2012; doi: 10.5194/acp-12-653-2012) targeted the upper troposphere when updating the chemical mechanism. Also, the changes between the base case and the HNO3 case are strongest in the upper troposphere, where temperatures are lowest. Nonetheless, the evaluation in this analysis spanned most of the troposphere.

Regarding “significant improvements,” I agree with your assessment on the use of such words, though approached from a different viewpoint. In model evaluations, the use of statistics is paramount and in statistics, the word “significant” generally has a specific definition. In this evaluation, partitioned oxidized nitrogen species and oxidized nitrogen species concentrations did improve in statistically significant manners for a few vertical profile bins through the use of the updated mechanism; but, it is certainly limited. However, there are still some instances of significant model bias, as you pointed out. On an overall basis, the updated chemical mechanism did provide, at least, incremental improvements in the model; and that has value.

Comment: 7. Given the fractional approach, PAN does not provide unique information.

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Also, NOx and HNO3 are more clearly affected by this reaction rate than PAN. A more direct evaluation might be obtained by considering the ratio (NOx/HNO3), rather than the three fractional components.

Response: I agree that NOx and HNO3 are more clearly affected by this reaction rate than PAN. However, PAN is a significant portion of NOy and is affected by the update (as mentioned in the discussion). Regarding the NOx/HNO3 ratio, that value was utilized in the development of the HNO3 chemistry used in this analysis.

Comment: 8. I encourage the authors to find a different name for their sensitivity case than "HNO3 case," which is unclear and becomes cumbersome given the numerous comparisons of HNO3 levels.

Response: This point is noted and will be considered.

Comment: 9. Why weren't the radiation comparisons evaluated at the tropopause?

Response: The version of PORT that was used in the assessment only computed the radiative flux at the surface and the top of the model. Since the ACPD publication, I've compiled a newer version with tropopause data included. Therefore, that can be added, if recommended.

Comment: 10. Though it's noted that the increase in HNO3 and decrease in NOx are "counter intuitive" and limited to the surface (Figure 6), this surprising result warrants further investigation and explanation.

Response: Upon revisitation of the text, I do agree that this result warrants further investigation and discussion. The reasoning will be further explored in the coming weeks while the re-write is being completed.

Comment: 11. A high-bias is noted for HO (p. 3238); does reducing the reaction rate exacerbate that change?

Response: Yes, and this loops back to the thoughts in comment #1 above. Decreasing

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the formation of nitric acid certainly increases the availability of NOx and OH. However, this radical will then adjust other atmospheric chemistry process (ex. sulfate), rather than creating a 1:1 ratio increase in OH concentrations.

Comment: Figure 2: The VHF and SADS profiles are not explained in the text

Response: That omission will be corrected in the write-up.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 3219, 2015.