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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 first anonymous reviewer for their significant contributions. These comments were thorough and much appreciated. Broad updates to portions of the text, as recommended by the reviewer, include reallocation of portions of the text that are more appropriate in other sections and a verification of spelling/grammar. The updated document will be available following the closing date of the discussion. Specific comments by Anonymous Referee #1 are addressed below.

Comment: 3220, 21: Instead of speaking of "trade off", simply state "In comparison to regional models, GCTM's have decreased sensitivity to boundary conditions and increased sensitivity to emissions, transport, and chemistry." A reference to some paper

showing this comparison would be useful.

Response: Agreed and a reference discussing this comparison has been added.

Comment: Section 2: In the methods section, the authors need to clarify how they compute an annual forcing, when they only seem to run the GEOS-chem model for the INTEX-A periods.

Response: The portion of the modeling/evaluation related to oxidized nitrogen partitioning was limited by the observation periods; the INTEX-NA Phase-A periods. As such, GEOS-Chem with the updated chemical mechanism was run for that period to develop simulated/observed vertically binned population datasets for analysis. When approaching the radiative effects portion of this study, there were no such limitations. Therefore, a full model year worth of GEOS-Chem output was utilized to determine the annual averaged instantaneous radiative forcing. This clarification will be added to the text.

Comment: 3225, 14: Is there a reference for P. Wennberg's data? If not, this is fine.

Response: An experiment description for P. Wennberg's data is not provided on the INTEX website. Also, the observation data was retrieved from the INTEX-NA data archive, not from a published paper.

Comment: 3227, 13: Could the authors be specific as to which techniques are precluded? In addition, is there a reason that a simple rËĘ2 regression test would not be valid?

Response: Due to the difference in variance between the two populations, a standard student t-test was precluded. An r^2 regression test can be used to compare observed/modeled pairs. However, the method of evaluation used in this study compared observed/modeled vertical bin populations. In addition, the method used in this analysis enabled the display of accepting/rejecting the simulated vs. observed population means as being similar, as shown in Figure 3 (filled/non-filled circles).

Comment: 3229, 5: "The affect of temper ... altitude." This sentence is misleading. There may be other ways to see the effects. Perhaps the authors choose to evaluate this sensitivity in this manner?

Response: This is the method of evaluation we decided to pursue. The referenced sentences have been updated to the following: “For each simulation, we evaluate the model in 1 km vertical bins. This method of evaluation was chosen since temperature, pressure and transport have large variability throughout the vertical troposphere, and these variables play a strong role in the rate of Reaction R1.”

Comment: Section 2.5: Surface radiative forcing is confounded discussion. The authors need to clarify if the forcing is "instantaneous radiative forcing" or "radiative forcing". "Radiative forcing" was defined as the change in flux (at the top of atmosphere or tropopause) including a stratospheric temperature adjustment under the assumption of fixed dynamical heating. If the authors have computed "instantaneous" forcing, then the surface forcing makes sense, otherwise they need to address the extent of atmospheric and surface process adjustments.

Response: The values used in this analysis were based on instantaneous radiative forcing.

Comment: 3230, 15: While previous papers by Henderson, et. al., have focused on the 8-10 km region, readers of this paper will be caught off guard by this sentence. Perhaps a note in the introduction, or something clarifying the reason for this focus at this point in the paper would be useful.

Response: An added sentence to provide additional clarification was added to the introduction.

Comment: In addition, the authors need to clarify whether the radiative forcing is computed as an instantaneous effect, or with the stratospherically adjusted temperature due to fixed dynamical heating. If Strat. Adjust. was not used, then the 4 month

equilibrium is a red herring.

Response: The radiative effects were calculated as an instantaneous radiative forcing and all values relating to the radiative effects analysis were reported as annual average instantaneous radiative forcing in mW/mˆ2. Updates to the manuscript have been made to make this clearer. As well, the 4-month equilibrium was eliminated and the calculations were re-run. The annual average instantaneous radiative forcing values changed by < 0.1 mW/mˆ2. The values have been updated.

Comment: One more clarification would be to state that the "change in flux" is a net increase in net downward solar and terrestrial flux due to the change in mechanism. (both "net"s are necessary as well as the "downward") You could, instead, simply refer to net trapped energy.

Response: “The radiative flux, which is how results in this analysis are presented, is defined as the net increase in net downward solar and terrestrial (combined) radiation.” This sentence has been added in the radiative effects methods section to provide clarification.

Comment: 3235, 3: "Due to the increase... " "The increased ozone leads to a net increase in trapped energy beneath the top of the atmosphere of ... and beneath the atmosphere of...” Please also clarify that for the sulfate aerosol, the increase the albedo of the earth system, reflecting additional solar radiation to space.

Response: These sentences were updated to the following: “The increase in ozone caused an increase in instantaneous radiative forcing at the surface and the top of the model of 10.4 mW/mˆ2 and 31.1 mW/mˆ2, respectively. Similar to ozone, there was a net increase in sulfate aerosols, which occurred mainly in the lower troposphere and over landmasses. These increases resulted in a net decrease in instantaneous radiative forcing, driven by the reflectance of incoming solar radiation. The decreases were -3.3 mW/mˆ2 and -3.0 mW/mˆ2 at the surface and top of the model, respectively.”

Comment: 3235, 10-20: I am uncertain what the authors are trying to say. This paragraph needs to be rewritten. Perhaps they are trying to say that while the methods and altitude at which radiative forcing are computed are different from those used in the IPCC, the relative magnitude of the correction indicated that the change to the kinetics could be important to understanding processes relevant to policy? If so, this paragraph may belong in the conclusion rather than results.

Response: This paragraph was re-written to provide clarification and moved to the discussion portion of the paper.

Comment: 3235, 26: "Also, a larger magnitude of forcing.... surface. The net atmos..... precipitation." Perhaps the authors mean "The net absorption of energy by the atmosphere ′ as seen in the third panel of figure 4 will affect convective and transport processes." While the reference to Shindell's analysis is nice, does the total of the ozone effect and the aerosol effect lead to a clear effect on precipitation that is explicitly confirmed by the results in this paper, or should this also be in the discussion?

Response: Those sentences were poorly constructed. The updated sentence in the results section defines net atmospheric forcing, as defined by Shindell. The portions related to the significance of atmospheric forcing have been relocated to the discussion.

Comment: 3236, 5: Do the authors mean "indirect effects" or "atmospheric responses and feedbacks"?

Response: First, this sentence was moved from the results to the discussion. Second, atmospheric responses and feedbacks is the better description.

Comment: 3236, 5: Do the authors mean "simulation" or "offline computation"?

Response: Offline computation.

Comment: 3236, 7: Are the "localized adjustments" an increase or decrease in oxidation of the SO2 -> SO4? And is there data to back up this assertion?

Response: The adjustments led to an increase in the oxidation of SO2. The sentence was updated to the following: “This increase in OHˆ-1 enables an increase in the oxidation of SO2 to SO4.” This was inferred based on the decrease in the reaction rate of R1, which increases OHˆ-1.

Comment: 3236, 23: both HNO3 and NOx have an inverse relationship with what? Perhaps with each other? Would a scatter plot make that inverse relationship clear?

Response: For the purposes of this assessment, where the only change in the GCTM was an update to R1, HNO3 and NOx are expected to have an inverse relationship with each other. I believe a reference to R1 within the text around this area should suffice and a scatter plot is not required.

3236, 25: Why are these counterintuitive? Is there a reason for these to be opposite our intuition? It would be useful to have a reason why these results are the opposite of the direct effect of the kinetics.

Response: The decrease in the reaction rate of R1 would lead one to believe that NOx would increase and HNO3 would decrease. However, the opposite was seen at the surface. When reviewing the vertical spatial profiles of these two species, it is seen that this only occurred at the surface and the rest of the troposphere produced changes in NOx and HNO3 concentrations in patterns that would be expected due to the decrease in R1’s reaction rate. The reasoning will be further explored in the coming weeks while the re-write is being completed.

Comment: 3237, 10: "The previous hypothesis"... I do not know to which hypothesis the authors refer. Perhaps the discussion of sulfate distribution belongs in another paragraph stating that the sulfate concentrations are more localized to the surface and to more polluted areas.

Response: This was a poorly constructed sentence. The sentence was updated to the following: “For sulfate, Fig. 8 indicates that the surficial changes occurred in the same

localized regions as the concentration changes to HNO3 and NOx."

Comment: 3237, 19: I do not know what is meant by "Literature updates". Perhaps "Updates to the NO2+HO reaction rate provided by () have been implemented in GEOS-Chem. The resulting changes in chemistry composition more closely match the INTEX observations. In particular we find..."

Response: Clarifications were made and the two sentences were updated to the following: "Updates to the NO2 + HOˆ-1 reaction rate, as suggested by Mollner (2010) and Henderson (2012), have been implemented in GEOS-Chem. The resulting model performance was evaluated using observations from the INTEX-A campaign."

Comment: 3238, 1 I don't know what is meant by "was decreases". Perhaps the authors mean to say, "Decreases in Nox lead to a near global increase in ozone. The resulting increase in oxidation potential leads to an increase in sulfate. Additional work needs to be done to understand the surface layer concentrations of HNO3 and NOx, as they are contrary to the direct implication of the decreased reaction rate coefficient."

Response: That more clearly states what was intended. As well, it was moved to a more appropriate place in the discussion. That particular sentence was simplified and rewritten.

Comment: 3238, 18: The authors need to clarify what they mean by "performance".

Response: This is acknowledged and further clarification will be included in the re-write.

Comment: 3238, 28: "change in ozone sensitivity". Sensitivity to what?

Response: Sensitivity was a poor choice of words. Rather "Similar to the changes in oxidized nitrogen concentrations, the change in simulated ozone concentrations is modest."

Comment: Paragraph starting at 3238, 28: This paragraph needs help. I don't know

what is meant by "modest", or how a "model uses NOx". Do the authors mean "sensitivity of predicted O3" or "change in O3 concentrations"? I am having a hard time understand the specific meaning of these sentences.

Response: This paragraph will be revised in the re-write.

Comment: Paragraph starting at 3239, 9: The first two lines of this paragraph could be rewritten to say, "The radiative effects of the change in ozone and sulfate distributions was evaluated with an offline radiative transfer code". Please refer to previous discussion of how to be precise about forcing numbers. (Yes, I know this is a bother. Thanks for being precise.) Do you mean variance or change?

Response: The forcing numbers were the results of annual average instantaneous radiative forcing. The sentence was changed to the following: "The radiative effects due to the changes in ozone and sulfate concentrations were evaluated using an offline radiative transfer model." Also, this is not a bother. Being precise is important.

Comment: 3239, 25: To which policy implications do the authors refer? I do not understand the second sentence of this paragraph. Do the authors mean "robust" or "very similar"? Why do the updates need lab confirmation? What additional evidence, in particular, would be helpful?

Response: References to policy implications relate to surficial pollutant concentrations and emissions. While the mechanism largely improved oxidized nitrogen partitioning, the changes in trace gas concentrations that we analyzed were not significant enough to alter either of these policy drivers. Overall, this final paragraph was mostly rewritten.

Comment: For all figures: Are these annual averages, or only average during the INTEX period.

Response: They actually vary and updates to specify which is used have been added to each necessary figure description.

Comment: 3232, 29: In addition, is there a reference for the fact that the baseline

model has a high bias?

Response: The high bias in the model that is being referenced is based on the results from the baseline model and the INTEX-A observations.

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