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Geoscientific
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Discussions

Interactive comment on “CESM/CAM5 improvement and application: comparison and evaluation of updated CB05_GE and MOZART-4 gas-phase mechanisms and associated impacts on global air quality and climate” *by* J. He et al.

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Reply to Comments by Reviewer #2

General comments:

The authors implemented two different gas-phase chemical mechanisms (CB05_GE and MOZART-4x) into the CESM/CAM5 model and performed model simulations for three years. Model predictions obtained with one mechanism are compared to those obtained with the other mechanism and also to measurements from a large number

of observational datasets. The article will be useful to air quality scientists and merits publication. However, several issues need to be addressed. Specific comments are provided below:

Reply:

We thank the reviewer for the positive review. We have addressed all the comments, please see below our point-by-point reply. The page and section numbers correspond to those in the manuscript with revision in track mode.

Specific comments:

Grid issue Large horizontal grids are employed in the simulation since a global model is used in the study. Surface measurements are generally done at fixed locations. Large spatial variations exist in pollutant concentrations (especially between urban, semi-urban and rural areas). A global model utilizing coarse horizontal grids is unable to capture such spatial variation. Presumably model comparisons with observed data from the Air Quality System (AQS) in the US are not performed for such reason. Comparison of model predictions employing large grids to observed data from fixed surface monitors contain inherent uncertainty. The readers will benefit from a general discussion on the ability of such models to capture spatial gradients of pollutants (especially near urban areas) and comparison with observed data.

Reply:

We agree with the reviewer that there may be large uncertainties associated with comparison of grid averaged model output with pointwise observations. The horizontal grid used in this work is 0.9 o×1.25o. For model evaluation, there may be multiple observational sites located in one grid cell, so all the observations within one grid cell are averaged and compared to the simulated results in that grid cell. While using grid averaged observations helps reduce the uncertainties to some extent, this approach cannot address the inherent uncertainties associated with the evaluation of the model results obtained at a coarse grid resolution.

To address the reviewer's comments, we have provided more information regarding the evaluation and also indicated the inherent uncertainties associated with the approach we used in Section 3.3.

NOx issue Column (Table 3) and zonal NOx (Figure 3) are over-predicted. In contrast, NOx from surface-based monitors (Table 3) and aircraft based monitors (Figure 4) are under-predicted. Despite under-prediction of NOx compared to observations from surface-based and aircraft based monitors, model over-predicts NOx compared to satellite data. Can the authors discuss some reasons for such behavior? A presentation on the comparison of model and satellite NO2 is available at: (https://www.cmascenter.org/conference/2012/slides/yarwood_evaluating_nox_2012.pdf)

Reply:

The underpredictions of NOx against surface-based observations can be attributed to the uncertainties in the anthropogenic NOx emissions as well as vertical transport. It is likely that more NOx are transported into upper layers, resulting in the underpredictions in surface NOx predictions. The underpredictions of NOx against aircraft based observations may be due in part to the uncertainties in the measurements. Some field campaigns (e.g., ARCPAC) focused on the polluted regions with a significant contribution from biomass burning and local sources (Tilmes et al., 2015). The underestimations of emissions from these sources and uncertainties in the vertical mixing scheme can result in the underpredictions of their profiles.

The comparison of tropospheric NO2 column against satellite data (e.g., SCIAMACHY) can be attributed to the uncertainties in NOx emissions and the satellite retrievals. As indicated in Yarwood et al. (2012), errors in satellite NO2 retrievals are dominated by atmospheric mass factor, which has a large uncertainty due to errors in specification of clouds, surface albedo, a priori NO2 profile shape, and aerosols. Boersma et al. (2004) found there is an error of 35-60% in the tropospheric NO2 retrievals, especially

over polluted areas.

To address the reviewer's comments, we have included the above points along with relevant references in the revised paper, Section 4.2.

Ozone issue The model over-predicts ozone for both mechanisms compared to the observed data (Table 3). The over-predictions has been liked to less titration resulting from the under-prediction of NOx, coarse resolution, as well as dilution of NOx. It is well-known that the addition of more NOx reduces ozone only in NOx rich areas. As the additional NOx is transported to outside the NOx rich areas, it increases ozone in those areas. Thus, the addition of NOx may not necessarily reduce overall ozone. I think the use of coarse resolution is diluting NOx; thus coarse resolution and dilution of NOx are not independent reasons. In addition, model under-predicts VOC. If the model is revised to add corrected amount of VOC emissions, then it will produce more ozone which will further deteriorate the model performance.

Reply:

We agree with the reviewer that O3 titration is more important over NOx rich areas and diluting NOx associated with coarse resolution can be one of the reasons for O3 overpredictions. VOCs are underpredicted in the current model, so it cannot explain the O3 overpredictions. Another possible reason for O3 overpredictions may be underestimation in dry deposition. For example, Martin et al. (2014) reported the uncertainties in O3 dry deposition associated with vegetation phenology in CAM-chem, which were responsible for the mean positive biases of 16 ppb in summertime surface O3 mixing ratios over eastern U.S. and 8 ppb over Europe, respectively. Therefore, uncertainties in O3 dry deposition can also partly explain the O3 overpredictions.

To address the reviewer's comments, we have included the above discussion in the revised paper.

While the model under-predicts NOx, its NOY predictions agree closer to observed data (Figure 4). If the model is revised to use corrected NOx, then it is likely to overpredict NOY. Predictions with the CB05-GE mechanism agree better with observed NOY. Column NOY obtained with MOZART-4x is 46% lower than that that with CB05-GE (section 4.2) which suggests that NOx is processed quite differently in the two mechanisms. Which specific chemical reactions are causing such a large difference in NOY predictions and how are they different in the two mechanisms? What are the largest 2 chemical species in NOY and how they differ between the two mechanisms?

Reply:

To address the reviewer's comments, we have performed additional analyses and added a new Table (Table S2) and two new figures, i.e., Figure S1, to show the dominant species in NOy for both MOZART-4x and CB05_GE, and Figure S2 to show the absolute and relative differences for major NOy species between MOZART-4x and CB05_GE. As shown in Figure S1, NOx, HNO3, and TPAN (PAN+PANX for CB05_GE and PAN+MPAN for MOZART-4x) are the major components for NOy concentrations, with ratios of 90.5% and 91.7%, respectively, for the sum of the mixing ratios of the top three species to that of NOy. NOx dominates over East Asia, eastern U.S., and western Europe, whereas TPAN dominates over most oceanic area. As shown in Figure S2, MOZART-4x predicts lower TPAN by 2.9×1019 molecules m-2 (or by 63.4%), which dominates the differences in NOy predictions between the two simulations. The differences in TPAN predictions can be attributed to the differences in the kinetic reactions. Table S2 lists the reactions involving TPAN. As shown in Table S2, besides the differences in the reaction rate calculation, MOZART-4x includes one additional reaction for PAN destruction by OH, which is not included in CB05_GE. In addition, OH levels are higher in MOZART-4x than CB05_GE, which could result in more TPAN loss through oxidation by OH. These differences can explain the lower TPAN in MOZART-4x than in CB05_GE. We have included the above information in the revised paper, see pages 35-36.

Some of the nitrogen species partition into aerosol nitrate. Does the difference in

NOY between two mechanisms decrease if aerosol nitrate is accounted in the NOY definition? How does the model predictions compare to observed data (Figure 4) if aerosol nitrate is accounted in the NOY definition?

Reply:

Table S3 lists the NOy species used in the calculation for Figure 4 and other NOy related comparisons. Note that Figure 8b includes the column comparison of aerosol nitrate. To address the reviewer's questions, we have included aerosol nitrate in the NOy calculation and replace the NOy plots in Figures 4 and 8a by those plots accounting for aerosol nitrate in NOy. Figure S3 shows the absolute differences in NOy (with and without inclusion of aerosol nitrate) between MOZART-4x and CB05_GE. If aerosol nitrate is accounted for in the NOy definition, the differences in NOy between two mechanisms decrease over East Asia, eastern U.S., Europe, and middle Africa as aerosol nitrate is higher in MOZART-4x over these regions (see Figure 6b). For the rest of areas, the differences in NOy between two mechanisms increase if aerosol nitrate is accounted for in the NOy definition.

To address the reviewer's comments, we added the above discussions in page 36.

NOY definition includes BrONO2 which suggests bromine chemistry is being used in the model. Which bromine emissions are used in the model?

Reply:

We have bromine chemistry included in both MOZART-4x and CB05_GE. For bromine/chlorine species (e.g., CF2CLBR, CF3BR, CFC11, CFC12, CH3BR, and CH3CL), their surface concentrations are specified using the historical reconstruction from Meinshausen et al. (2011). No bromine emissions were included.

The above point was added in Section 3.1.

Also, need to clarify that section 4.2 contains only model-to-model comparison.

Reply:

This has been clarified in Section 4.2.

HNO3 issue The model over-predicts HNO3 over CONUS while under-predicting it over Europe. Under-prediction of HNO3 over Europe is linked to under-prediction on NOx. Surface NO2 comparison for CONUS is not shown in Table 3. Does the over-prediction of HNO3 over CONUS occur due to over-prediction on NOx?

Reply:

To address the reviewer's comment, we have included NO2 evaluation against AQS sites over CONUS. The results show that both CB05_GE and MOZART-4x underpredict surface NO2 concentrations, with NMBs of -52.2% and -51.4%, respectively. The overpredictions of HNO3 over CONUS are mainly due to more total nitrate partitioned into HNO3 (which is reflected by the underpredictions of NO3- over CONUS) resulted from the overpredictions of SO42- over CONUS. Compared to NO3-, SO42- can more easily combine with NH4+ to stay in aerosol phase. There are not enough NH4+ to neutralize NO3-, driving NO3- to HNO3 in the gas-phase resulting in overpredictions of HNO3 over CONUS. We have included this explanation in the revised paper, Section 4.1.1.

Cl- issue The model under-predicts Cl- over CONUS while over-predicting it over Europe. Over-prediction of Cl- over Europe has been linked to gas/particle partitioning. Can the authors suggest any reasons for under-prediction of Cl- over CONUS? Reff et al. (2009) suggest many sources can emit Cl-; are emissions from these sources included in the study? Reff, et al.: Emissions inventory of PM2.5 trace elements across the United States, Environmental Science & Technology, 43, 5790–5796, 2009.

Reply:

We did not include any anthropogenic Cl- emissions in the model except from sea-salt emissions, which is calculated online in CESM/CAM5. The missing sources can

contribute to the underpredictions of Cl-. On the other hand, due to the overpredictions of SO42-, there are less NH4+ available to neutralize Cl-, driving Cl- to HCl in the gas-phase, resulting in underpredictions of Cl-. In addition, the performance of Cl- over CONUS is only for fine Cl- (Aitken, accumulation, fine sea-salt, and fine dust modes), whereas the performance of Cl- over Europe is for fine and coarse Cl- (all seven modes). As the thermodynamic equilibrium is not treated for coarse particles (the irreversible condensation of HCl is assumed to occur on the surface of coarse particles), it is likely that the model overpredicts coarse Cl-, but underpredicts fine Cl- due to the missing sources.

To address the reviewer's comments, we have clarified the above issues in page 23, Section 4.1.1.

SO2/SO42− issue The model over-predicts surface SO2/SO42−compared to the observed data (Table 3). The over-estimation of SO2 has been explained with SO2 emissions, injection height uncertainty, and vertical mixing issue while the over-prediction of SO2 has been suggested to be the reason for over-prediction of SO42−. Most models over-predict surface SO2 and tend to under-predict surface SO42−compared to observed data. Here, the model over-predicts both surface SO2/SO42−. Interestingly column SO2 is underpredicted which suggests possible problem with vertical mixing in the model that may have contributed to the over-prediction of surface SO2.

Reply:

As we explained, the overpredictions of surface SO2 concentrations may be due to the uncertainties in the SO2 emissions, injection height uncertainty, and vertical mixing. The underpredictions of column SO2 can also be attributed to the uncertainties in the vertical mixing as well as uncertainties in the satellite retrievals. For example, Lee et al. (2009) found that there is an overall error in the annual SO2 retrievals of 45-80% over polluted regions, especially over eastern China. Therefore, the uncertainties in the satellite SO2 retrievals can affect the model evaluation. The overpredictions of

SO42- can be due to the overpredictions of SO2 as well as uncertainties in the SO42- emissions. CESM/CAM5 also reads the default vertical SO42- emission profiles for the simulations. The uncertainties in the SO42- emissions can contribute to the inaccurate predictions of SO42- as well.

To address the reviewer's comments, we have included the above explanation in the revised paper in Section 6.

Other factors may also affect SO42−predictions. Aqueous-phase reaction with H2O2 and gas-phase reaction with OH tend to be the most important pathways for the conversion into SO42−. The article does contain any discussion of predicted oxidant levels (H2O2 and OH). If the predicted oxidant levels are too high, SO42−predictions will also be high. I am not suggesting to perform any detailed comparison of predicted H2O2 and OH with observed data but some discussion of predicted oxidants levels and typical observed values will be helpful to readers.

Reply:

We agree with the reviewer that aqueous phase reaction with H2O2 and gas-phase reaction with OH are important pathways for SO42- formation. We have added the comparisons of OH and H2O2 profiles with aircraft measurements in Figure 4 in the revised paper. As shown in Figure 4, both OH and H2O2 are underpredicted, but MOZART-4x predicts slightly higher H2O2 within 4-km above the surface compared to CB05_GE. However, the performance here only represents the local condition, instead of global condition.

To address the reviewer's comment, we also compared the global mean tropospheric OH concentrations with other studies. The simulated air-mass weighted tropospheric mean OH concentrations predicted by MOZART-4x and CB05_GE are both 13.1×105 molec cm-3, which is slightly higher than Naik et al. (2013) with present-day tropospheric mean OH levels of 11.1 ± 1.6 molec cm-3. So both CB05_GE and MOZART-4x tend to predict higher OH levels, which may partly explain the overpredictions of SO42-. We have included this explanation in the revised paper, Section 4.1.1.

The model under-predicts cloud liquid water path compared to MODIS data (Table 5). If the model is revised to include the correct amount of cloud liquid water, then it will produce more SðİŚĆ42−and the model performance for SðİŚĆ42−will further deteriorate and the model performance for SO2 will improve. It is also possible that the model produces more SðİŚĆ42− by placing clouds in incorrect vertical layers. Inadequate precipitation in the model may also lead to higher than observed SðİŚĆ42−in the model.

Reply:

Cloud liquid water path (LWP) is moderately underpredicted by both MOZART-4x and CB05_GE against MODIS data, but it is relatively well predicted against Bennartz (2007), which filtered out large uncertainties associated with MODIS retrievals. Therefore, the model predicts LWP relatively well against Bennartz (2007). But we agree with the reviewer that the model may inaccurately predict clouds vertically as the simulations with both MOZART-4x and CB05_GE show moderate biases for COT and CDNC.

We also agree with the reviewer that inadequate precipitation can contribute to the overpredictions of SO42-. Both simulations are driven by prescribed meteorology, so we did not compare meteorology from the two simulations. To address the reviewer's comment, we evaluated precipitation and the results show that precipitation is well predicted by both MOZART-4x and CB05_GE, with NMBs of 1.9% and 1.6%, respectively. Therefore, the overpredictions of SO42- are not due to the insufficient precipitation.

SOA issue The model is able to capture observed SOA (Table 3 and Figure 2). However, VOCs are under-predicted. If the model is revised to use corrected amount of VOC emissions, then SOA predictions will be higher. Does the model capture SOA for the correct reason? Again, discussion of predicted oxidant levels with typical observed values will also be helpful for discussing SOA predictions?

Reply:

We agree with the reviewer that using correct VOCs emissions can increase the SOA concentrations. As we discussed above, our model tends to predict higher OH levels on a global scale, which can partly explain the well predicted SOA despite the underpredictions of VOCs. Also, the SOA statistics are calculated using only four pairs of seasonal mean values at four sites in the U.S. where the observed SOA data are available during 2008-2010; they, therefore, are not be representative of the entire CONUS because of limited data used for calculation. We have indicated this limitation in the paper.

Minor editorial suggestions The objectives of the study are to examine the differences in the SOA predictions . . .., and study the sensitivity of air quality and climate predictions to different gas-phase chemical mechanisms (introduction section). However, the title does not reflect that SOA predictions are being examined. Perhaps the authors can reconcile the apparent difference.

Reply:

SOA is part of the global air quality, so the title does include examination of SOA predictions from both simulations.

Most chemical species in the article have been defined. However, some have not been defined. For example, CO, HOx, and NOx in line 24 (page 7191) are not defined. I suggest that the authors check the entire article and define the chemical species when it is used first time. In the description, two names for α-pinene (alpha-pinene and α-pinene) and β-pinene are used. One name should be used throughout the article (Chemical mechanism - 2.1)

Reply:

We have checked the paper thoroughly and defined all the species and we also use consistent names for the species in the revised paper.

Figure 1 also contains a comparison of SOA which is not mentioned in the caption

Reply:

SOA has been added in the Figure 1 caption in the revised paper.

Conclusion section is long and can be shortened

Reply:

Conclusion has been shortened in the revised paper.

References cited in this reply

Boersma, K. F., Eskes, H. J., and Brinksma E. J.: Error analysis for tropospheric NO2 retrieval from space, J. Geophys. Res., 109, D04311, doi:10.1029/2003JD003962, 2004.

Lee, C., Martin, R. V., Donkelaar, A. van, O'Byrne, G., Krotkov, N., Richter, A., Huey, L. G., and Holloway, J. S.: Retrieval of vertical columns of sulfur dioxide from SCIAMACHY and OMI: Air mass factor algorithm development, validation, and error analysis, J. Geophys. Res., 114, D22303, doi:10.1029/2009JD012123, 2009.

Martin, M. V., Heald, C. L., and Arnold, S. R.: Coupling dry deposition to vegetation phenology in the Community Earth System Model: Implications for the simulation of surface O3, Geophys. Res. Lett., 41, 2988-2996, doi:10.1002/2014GL059651, 2014.

Meinshausen, M., Smith, S. J., Calvin, K., Daniel, J. S., Kainuma, M. L. T., Lamarque, J.-F., Matsumoto, K., Montzka, S., Raper, S., Riahi, K., Thomson, A., Velders, G. J. M., and van Vuuren, D. P.: The RCP Greenhouse Gas Concentrations and their Extensions from 1765 to 2300, Climatic Change, 109, 213-241, 2011.

Naik, V., Voulgarakis, A., Fiore, A. M., Horowitz, L. W., Lamarque, J.-F., Lin, M., Prather, M. J., Young, P. J., Bergmann, D., Cameron-Smith, P. J., Cionni, I., Collins, W. J., Dalsøren, S. B., Doherty, R., Eyring, V., Faluvegi, G., Folberth, G. A., Josse, B., Lee, Y. H., MacKenzie, I. A., Nagashima, T., van Noije, T. P. C., Plummer, D. A., Righi, M., Rumbold, S. T., Skeie, R., Shindell, D. T., Stevenson, D. S., Strode, S., Sudo, K., Szopa, S., and Zeng, G.: Preindustrial to present-day changes in tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), Atmos. Chem. Phys., 13, 5277-5298, doi:10.5194/acp-13-5277-2013, 2013.

Tilmes, S., Lamarque, J.-F., Emmons, L. K., Kinnison, D. E., Ma, P.-L., Liu, X., Ghan, S., Bardeen, C., Arnold, S., Deeter, M., Vitt, F., Ryerson, T., Elkins, J. W., Moore, F., Spackman, R., and Martin, M. V.: Description and evaluation of tropospheric chemistry and aerosols in the Community Earth System Model (CESM1.2), Geosci. Model Dev., 8, 1395-1426, doi:10.5194/gmd-8-1395-2015, 2015. Yarwood, G., Kemball-Cook, S., Johnson, J, Wilson, G, Dornblaser, B, and Estes, M: Evaluating NOx Emission Inventories for Air Quality Modeling Using Satellite, Model and SEARCH NO2 Data, 11th Annual CMAS Conference, Chapel Hill, NC, October 16, 2012.

Interactive comment on Geosci. Model Dev. Discuss., 8, 7189, 2015.