

CESM/CAM5 improvement and application: comparison and evaluation of updated CB05\_GE and MOZART-4 gas-phase mechanism and associated impacts on global air quality and climate

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:

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.

NO<sub>x</sub> issue

Column (Table 3) and zonal NO<sub>x</sub> (Figure 3) are over-predicted. In contrast, NO<sub>x</sub> from surface-based monitors (Table 3) and aircraft based monitors (Figure 4) are under-predicted. Despite under-prediction of NO<sub>x</sub> compared to observations from surface-based and aircraft based monitors, model over-predicts NO<sub>x</sub> compared to satellite data. Can the authors discuss some reasons for such behavior?

A presentation on the comparison of model and satellite NO<sub>2</sub> is available at:

[https://www.cmascenter.org/conference/2012/slides/yarwood\\_evaluating\\_nox\\_2012.pdf](https://www.cmascenter.org/conference/2012/slides/yarwood_evaluating_nox_2012.pdf)

Ozone issue

The model over-predicts ozone for both mechanisms compared to the observed data (Table 3). The over-predictions has been linked to less titration resulting from the under-prediction of NO<sub>x</sub>, coarse resolution, as well as dilution of NO<sub>x</sub>. It is well-known that the addition of more NO<sub>x</sub> reduces ozone only in NO<sub>x</sub> rich areas. As the additional NO<sub>x</sub> is transported to outside the NO<sub>x</sub> rich areas, it increases ozone in those areas. Thus, the addition of NO<sub>x</sub> may not necessarily reduce overall ozone. I think the use of coarse resolution is diluting NO<sub>x</sub>; thus coarse resolution and dilution of NO<sub>x</sub> 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.

#### NO<sub>Y</sub> issue

While the model under-predicts NO<sub>x</sub>, its NO<sub>Y</sub> predictions agree closer to observed data (Figure 4). If the model is revised to use corrected NO<sub>x</sub>, then it is likely to over-predict NO<sub>Y</sub>.

Predictions with the CB05-GE mechanism agree better with observed NO<sub>Y</sub>. Column NO<sub>Y</sub> obtained with MOZART-4x is 46% lower than that that with CB05-GE (section 4.2) which suggests that NO<sub>x</sub> is processed quite differently in the two mechanisms. Which specific chemical reactions are causing such a large difference in NO<sub>Y</sub> predictions and how are they different in the two mechanisms? What are the largest 2 chemical species in NO<sub>Y</sub> and how they differ between the two mechanisms?

Some of the nitrogen species partition into aerosol nitrate. Does the difference in NO<sub>Y</sub> between two mechanisms decrease if aerosol nitrate is accounted in the NO<sub>Y</sub> definition? How does the model predictions compare to observed data (Figure 4) if aerosol nitrate is accounted in the NO<sub>Y</sub> definition?

NO<sub>Y</sub> definition includes BrONO<sub>2</sub> which suggests bromine chemistry is being used in the model. Which bromine emissions are used in the model?

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

#### HNO<sub>3</sub> issue

The model over-predicts HNO<sub>3</sub> over CONUS while under-predicting it over Europe. Under-prediction of HNO<sub>3</sub> over Europe is linked to under-prediction on NO<sub>x</sub>. Surface NO<sub>2</sub> comparison for CONUS is not shown in Table 3. Does the over-prediction of HNO<sub>3</sub> over CONUS occur due to over-prediction on NO<sub>x</sub>?

#### Cl<sup>-</sup> issue

The model under-predicts Cl<sup>-</sup> over CONUS while over-predicting it over Europe. Over-prediction of Cl<sup>-</sup> over Europe has been linked to gas/particle partitioning. Can the authors suggest any reasons for under-prediction of Cl<sup>-</sup> over CONUS? Reff et al. (2009) suggest many sources can emit Cl<sup>-</sup>; 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.

#### SO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> issue

The model over-predicts surface SO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> compared to the observed data (Table 3). The over-estimation of SO<sub>2</sub> has been explained with SO<sub>2</sub> emissions, injection height uncertainty, and vertical mixing issue while the over-prediction of SO<sub>2</sub> has been suggested to be the reason for over-prediction of SO<sub>4</sub><sup>2-</sup>. Most models over-predict surface SO<sub>2</sub> and tend to under-predict surface SO<sub>4</sub><sup>2-</sup> compared to observed data. Here, the model over-predicts both surface SO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>. Interestingly column SO<sub>2</sub> is underpredicted which suggests possible problem with vertical mixing in the model that may have contributed to the over-prediction of surface SO<sub>2</sub>.

Other factors may also affect  $SO_4^{2-}$  predictions. Aqueous-phase reaction with  $H_2O_2$  and gas-phase reaction with OH tend to be the most important pathways for the conversion into  $SO_4^{2-}$ . The article does contain any discussion of predicted oxidant levels ( $H_2O_2$  and OH). If the predicted oxidant levels are too high,  $SO_4^{2-}$  predictions will also be high. I am not suggesting to perform any detailed comparison of predicted  $H_2O_2$  and OH with observed data but some discussion of predicted oxidants levels and typical observed values will be helpful to readers. 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  $SO_4^{2-}$  and the model performance for  $SO_4^{2-}$  will further deteriorate and the model performance for  $SO_2$  will improve. It is also possible that the model produces more  $SO_4^{2-}$  by placing clouds in incorrect vertical layers. Inadequate precipitation in the model may also lead to higher than observed  $SO_4^{2-}$  in the model.

#### 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?

#### 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.

Most chemical species in the article have been defined. However, some have not been defined. For example, CO,  $HO_x$ , and  $NO_x$  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  $\alpha$ -pinene (alpha-pinene and  $\alpha$ -pinene) and  $\beta$ -pinene are used. One name should be used throughout the article (Chemical mechanism - 2.1)

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

Conclusion section is long and can be shortened