Impact of RACM2, halogen chemistry, and updated ozone deposition velocity on hemispheric ozone predictions

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Abstract We incorporate the Regional Atmospheric Chemistry Mechanism (RACM2) into the Community Multiscale Air Quality (CMAQ) hemispheric model and compare model predictions to those obtained using the existing Carbon Bond chemical mechanism with the updated toluene chemistry (CB05TU). The RACM2 enhances monthly mean ozone by 2-10 ppbv in polluted areas compared to the CB05TU while reducing mean ozone by 2-6 ppbv in remote areas. We develop an effective halogen reaction that can consume ozone over the gulfs and oceans. The current CMAQ model uses substantially lower ozone deposition velocity over water compared to observed data. We modify the CMAQ deposition velocity to account for the enhanced deposition due to chemical interactions between ozone and oceanic iodide. The effective halogen reaction and enhanced deposition velocity reduce monthly mean ozone by 2-8 ppbv over water. The majority of the reduction occurs via the halogen reaction. A comparison of model predictions with available observed profile reveals that the RACM2 over-predicts surface ozone in polluted areas while improving the comparison in remote areas. Model predictions with the halogen chemistry and enhanced deposition velocity compare better with the observed data.

1. Introduction

The Carbon Bond chemical mechanism uses a lumped structure approach and was originally developed for modeling polluted urban conditions though it has been revised in recent years for applications to cleaner and remote conditions. The Regional Atmospheric Chemistry Mechanism (RACM2) uses a lumped molecular approach and was specifically designed for regional applications ranging from the Earth's surface to the upper troposphere (Goliff et al., 2013). In this study, we examine the impacts of the Carbon Bond 2005 chemical mechanism with the updated toluene chemistry (CB05TU) (Whitten et al., 2010) and the RACM2 on air quality using the Community Multiscale Air Quality (CMAQ) model. A comparison of ozone (O_3) deposition velocities in CMAQ with observed data (Helmig et al., 2012) suggests that CMAQ uses substantially lower values than

observed data over water. Results of recent field studies also suggest that halogens can be emitted over gulfs and oceans and destroy O_3 (Read et al., 2008). However, the CMAQ model does not employ such reaction. We develop and employ an effective halogen reaction for O_3 destruction over oceans and gulfs. Additionally, we revise the treatment of model O_3 deposition velocities over water to account for the chemical enhancement of deposition due to the interaction of O_3 and oceanic iodide. We also examine impacts of these two additional processes on air quality in the northern hemisphere.

2. Method

The study uses the WRF-CMAQ coupled modeling system (Wong et al., 2012) to simulate air quality. Evaluations for the CMAQ model have previously been conducted by comparing model predictions to measured ambient pollutants (Foley et al., 2010). The CMAQ model has displayed considerable skill in simulating O_3 and other chemical species in the atmosphere. The modeling domain for this study covers the entire northern hemisphere using 108-km grid spacings and 44 vertical layers. Model simulations are performed for three summer months in 2006. Initial conditions are obtained from a different CMAQ simulation with one month spin-up period. The study uses Emissions Database for Global Atmospheric Research (http://edgar.jrc.ec.europa.eu/index.php) for generating model-ready emissions. The first simulation uses the CB05TU while the second simulation uses the RACM2. Differences in the results are attributed to the changes in the chemical mechanisms.

Helmig et al. (2012) reported measurements of O_3 deposition velocities over oceanic areas. Observed median values ranged from 0.009 to 0.27 cm s^{-1} while CMAQ currently uses values less than 0.001 cm s^{-1}. We follow the procedures of Chang et al. (2004) to revise model O_3 deposition velocities over water. The revised treatment produces deposition velocities similar to the observed O_3 deposition velocities over water.

Using long-term measurements in the Cape Verde archipelago in Atlantic Ocean, Read et al. (2008) suggested that halogens, emitted from oceans and gulfs, chemically destroy O_3. However, the details of these emissions and their atmospheric reactions are complex and emerging, and are not included in any air quality models. Here, we develop an effective halogen reaction that can destroy O_3 over gulfs and oceans only during the day and within the planetary boundary layer. We derive a first order rate constant of 2.0×10^{-6} s^{-1} for the reaction using observed data of Read et al. (2008). It is an effective surrogate reaction of the detailed halogen chemistry that can occur in the atmosphere and allows examining their impacts without knowing the detailed halogen emissions and associated chemical reactions. The third simulation was conducted using the RACM2 with the effective halogen reaction and the enhanced O_3 deposition velocities.

Differences in the results are attributed to the halogen chemistry and enhanced O_3 deposition velocities over water.

3. Results and Discussion

Predicted monthly-mean (August) surface O_3 with the CB05TU and differences in the model predictions due to the RACM2 are shown in Figure 1. The CB05TU predicts values of 20-60 ppbv in North America and 20-80 ppbv in Europe and Asia. The RACM2 enhances O_3 by 2-10 ppbv in polluted areas due primarily to greater recyling of nitrogen oxides and more active organic chemistry. It reduces O_3 by 2-6 ppbv in remote clean areas due primarily to differences in organic nitrate representation. The CB05TU predicts a maximum value of 103 ppbv in the modeling domain while the RACM2-predicted maximum value is reduced to 97 ppbv. Sarwar et al. (2013) examined the impacts of the two mechanisms and reported that RACM2 enhances O_3 in the continental United States. Results presented here over the continental United States are consistent with their findings. The effective halogen reaction and enhanced deposition velocity reduce O_3 by 2-8 ppbv over water bodies [Figure 1(c)]. The majority of the reduction occurs due to the halogen chemistry. Results obtained for other months are similar and not shown due to space limitation.

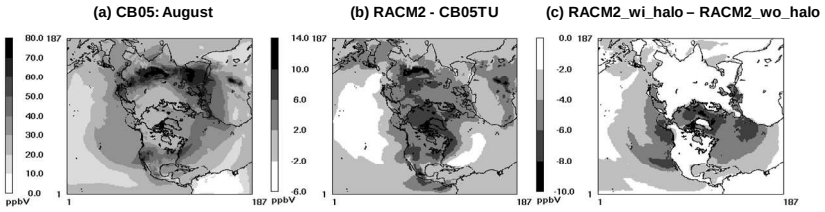

Figure 1: (a) Monthly-mean (August) O_3 obtained with the CB05TU (b) differences in monthly-mean O_3 obtained with the RACM2 and CB05TU (c) differences in monthly-mean O_3 obtained with the effective halogen reaction and enhanced O_3 deposition velocity and without any halogen reaction and the existing O_3 deposition velocity (using RACM2).

Model predictions are compared to observed ozonesonde profiles from four sites in Figure 2. The RACM2 over-predicts O_3 near the surface at Sable Island, Gulf of Mexico, and Trinidad Head. However, its predictions aloft tend to agree better with the observations from Sable Island and Trinidad Head. The RACM2 predictions also agree better with the observed data at Hilo than the CB05TU predictions. Model predictions with the halogen reaction and enhanced O_3 deposition velocity improve the comparison with observed data at all sites.

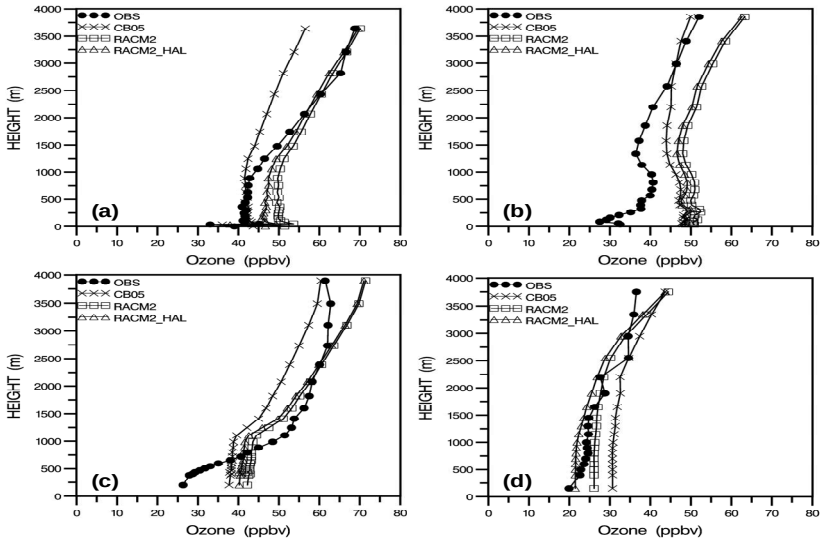

Figure 2: A comparison of model O_3 predictions to observed data (August) at (a) Sable Island, NS (b) Gulf of Mexico (c) Trinidad Head, CA (d) Hilo, HI.

4. Summary

We compare model predictions with RACM2 to those obtained with the CB05TU. The RACM2 enhances O_3 in polluted areas while reducing O_3 in remote clean areas. The RACM2 over-predicts surface ozone in polluted areas; however, it tends to improve the predictions aloft in these areas. The RACM2 improves the predictions in remote clean areas. We develop an effective halogen reaction for simulating O_3 loss due to the halogen chemistry and revise O_3 deposition treatment. Predictions obtained with these additional processes reduce O_3 over water and improve the comparison with the observed data, particularly at Hilo, HI.

Disclaimer: Although this paper has been reviewed by EPA and approved for publication, it does not necessarily reflect EPA's policies or views.

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Questions and Answers on NATO-ITM Paper No. 4.12

1. Questioner name: Douw Steyn

   Question: I noticed notable ozone reductions over east Greenland Sea which is frozen for much of the year. How did you model ozone deposition over frozen area?

   Answer: The current model treats all oceans same way. Thus, it currently does not differentiate between frozen and liquid water in the oceans.

2. Questioner name: Amir Hakami

   Question: Did you consider differences between CB05 and RACM2 separately for day and night?

   Answer: Indeed we evaluated the diurnal pattern of model predictions obtained with the two mechanisms. Model predictions with RACM2 are consistently higher than those obtained with the CB05 during the day as well as at night.