Examining the impact of an updated toluene mechanism on air quality in the eastern US

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Abstract Model simulations were performed using the CB05 chemical mechanism containing the base and an updated toluene mechanisms for the eastern US. The updated toluene mechanism increased monthly mean 8-hr ozone by 1.0-2.0 ppbv in urban areas of Chicago, the northeast US, Detroit, Cleveland, and Cincinnati compared to those with the base toluene chemistry. The updated chemistry reduced mean bias and root mean square error in ozone predictions when compared with observations greater than 85 ppbv and increased mean secondary organic aerosol from toluene by a maximum of 4%.

1. Introduction

Toluene is an important aromatic compound that can affect ozone (O_3) and secondary organic aerosol (SOA) in the atmosphere. However, there is currently a great deal of uncertainty about toluene chemistry (Calvert et al., 2002). Whitten et al. (2010) recently proposed an updated condensed mechanism for toluene for use with the Carbon Bond 2005 (CB05) chemical mechanism. The updated toluene mechanism can better explain results of environmental chamber experiments involving toluene and oxides of nitrogen (NO_x). This study examines the impact of the updated toluene mechanism on air quality modeling results for the eastern US.

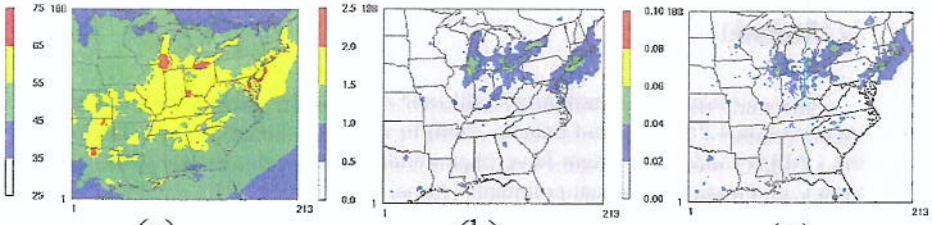
2. Method

The study uses the Community Multiscale Air Quality (CMAQ) modeling system (version 4.7) (Byun and Schere, 2006) to simulate air quality. Evaluations for the CMAQ modeling system have been conducted by comparing model predictions with measured ambient pollutants (Appel et al., 2007). The modeling domain consisted of 213 x 188 horizontal grid-cells covering the eastern US with 12-km grid spacings and 14 vertical layers; the surface layer thickness was approximately 36 meters. The CMAQ chemical transport model was configured to use the mass continuity scheme to describe 3-D advection, the Asymmetric Convective Model

Version 2 (ACM2) (Pleim, 2007) to describe vertical diffusion processes, the multiscale method to describe horizontal diffusion processes, and an adaptation of the ACM algorithm for convective cloud mixing. Aqueous chemistry, aerosol processes, and dry/wet deposition were included. The meteorological driver for the CMAQ modeling system was the PSU/NCAR MM5 system (version 3.5) (Grell et al., 1994). Initial and boundary conditions for this study were obtained from results of a larger modeling domain. Anthropogenic emissions were derived from the 2001 National Emissions Inventory and biogenic emissions were estimated using the Biogenic Emissions Inventory System (version 3.13) (*Schwede et al.*, 2005). Two model simulations were performed using the CB05 mechanism (Yarwood at el., 2005) for a summer month. One simulation used the base toluene mechanism in CB05 (CB05-Base) and the other simulation used the updated toluene mechanism in CB05 (CB05-TU) (Whitten et al., 2010). The CB05-TU contains 26 chemical reactions involving 13 species for toluene oxidation while the CB05-Base contains 10 chemical reactions involving 5 chemical species. The use of CB05-TU increased computational time of the model by approximately 3-5% compared to those with the CB05-Base.

3. Results and Discussion

Monthly mean of daily 8-hr maximum O_3 with CB05-Base and changes in mean 8-hr O_3 between CB05-TU and CB05-Base are displayed in Figure 1. CB05-TU increased monthly mean 8-hr O_3 by a maximum of 2.0 ppbv in Chicago, IL; 1.9 ppbv in Cleveland, OH; 1.7 ppbv northeastern US; 1.3 ppbv in Detroit, MI; and 1.0 ppbv in Cincinnati, OH and Louisville, KY compared to those obtained with the CB05-Base. CB05-TU also increased mean 8-hr O_3 by 0.5 ppbv or more in several other urban areas. Monthly mean toluene to total VOC concentration ratio is also shown in Figure 1. CB05-TU enhanced O_3 in areas with higher toluene to total VOC concentration ratios. Although not shown here, modeled VOC/NO_x ratios in these areas were less than 8.0; thus these areas were VOC-limited for O_3 production. The impact of CB05-TU on O_3 occurred only in VOC-limited areas.



(a) (b) (c)

Figure 1: (a) monthly mean of daily 8-hr maximum O_3 with CB05-Base (b) increases in monthly mean 8-hr O_3 between CB05-TU and CB05-Base (c) mean toluene to VOC concentrations ratio for CB05-Base (all units in ppbv)

Day-to-day variation of the changes in the daily maximum 8-hr O_3 is presented in Figure 2 for three representative areas: Chicago, northeastern US, and Detroit. For each area, changes in daily 8-hr maximum O_3 between CB05-TU and CB05-Base varied from day to day. While increases were relatively high on some days, it was modest on many other days. Increases in Chicago and northeastern US were comparable while increases in Detroit were lower than those in Chicago or northeastern US.

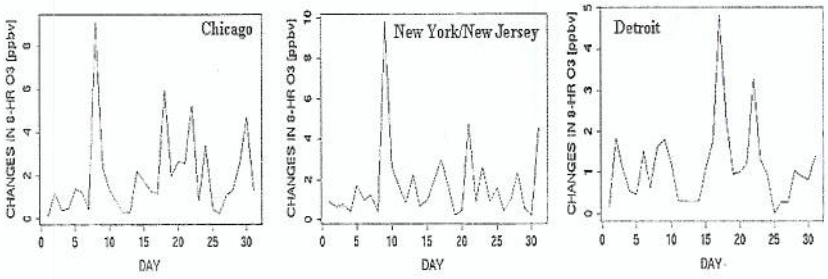


Figure 2: Variation of increases in daily 8-hr max O_3 with the two mechanisms

Ozone production efficiency (OPE) is defined as the number of O_3 molecules formed from each NO_x molecule oxidized to NO_z and can be calculated from a regression of the O_3-NO_z relationship. OPE values with CB05-TU in Chicago, the northeast US, Detroit, Cleveland, and Cincinnati were marginally lower (<0.1) compared to those with CB05-Base.

Mean bias (MB) for O_3 changed from 9.1 to 10.7 ppbv in Chicago, -0.53 to +0.52 ppbv in New York/New Jersey, and -4.1 to -3.1 ppbv in Detroit with CB05-Base and CB05-TU, respectively. Root mean square error (RMSE) for O_3 changed from 18.6 to 20.0 ppbv in Chicago, 12.7 to 12.5 ppbv in New York/New Jersey, and 12.9 to 12.5 ppbv in Detroit with CB05-Base and CB05-TU, respectively. Predictions with CB05-TU reduced both MB and RMSE at these locations when observed data were greater than 85 ppbv.

Monthly mean SOA from toluene with CB05-Base and the ratio of mean SOA obtained with CB05-TU to that from CB05-Base are shown in Figure 3. The CB05-TU increased monthly mean SOA from toluene by a maximum of 4% compared to that with the CB05-Base. Locations of SOA increases generally coincided with the locations of O_3 increases; the largest impact occurred in the northeastern US. CB05-TU increased monthly mean hydroxyl and hydroperoxy radicals by a maximum of 19% and 20%, respectively. Impact on $PM_{2.5}$ was smaller (largest increase 1%).

4. Summary

CB05-TU enhanced monthly mean of daily maximum 8-hr O_3 in some urban areas in the eastern US by up to 2.0 ppbv. Results obtained with CB05-TU did not substantially change the MB and RMSE for O_3. CB05-TU increased SOA from toluene by a maximum of 4% compared to those obtained with CB05-Base. Next we plan to evaluate the impact of CB05-TU on air quality in the western US.

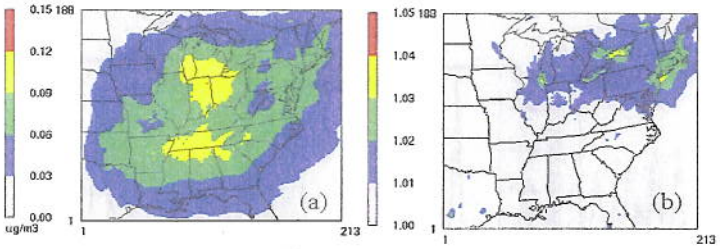


Figure 3: (a) monthly mean SOA from toluene with the CB05-Base (b) ratio of mean SOA obtained with CB05-TU and CB05-Base

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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