Impact of an updated toluene mechanism on air quality in the western US

Golam Sarwar, Wyat Appel, Annmarie Carlton, Rohit Mathur, Kenneth Schere
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mohammed A. Majeed
Delaware Dept. of Natural Resources & Environmental Control, New Castle, DE

ABSTRACT

Air quality model simulations were performed using the CB05 mechanism containing the base and an updated toluene mechanism for the western US. The updated toluene mechanism increased the monthly mean of daily maximum 8-hr ozone concentration by 1.0 ppbv or more in Los Angeles, Portland, and Seattle compared to those simulations using the base toluene chemistry. The updated chemistry reduced mean bias of ozone when compared to observed data. The updated toluene mechanism increased monthly mean secondary organic aerosol from toluene by a maximum of 7%, hydroxyl radical by a maximum of 11%, and hydroperoxy radical by a maximum of 18% compared to those with the base toluene chemistry.

INTRODUCTION

Toluene is an important aromatic compound that can affect ozone (O_3) and secondary organic aerosol (SOA) concentrations in the atmosphere. However, existing knowledge of toluene chemistry has large uncertainty (Calvert et al., 2002). Faraji el al. (2008) noted that toluene chemistry in CB-IV and SAPRC-99 mechanisms can cause a large difference in model predictions. Recently, an updated condensed mechanism for toluene has been proposed for use with the Carbon Bond 2005 (CB05) mechanism (Whitten et al., 2010). In this study, the impact of the updated toluene mechanism on air quality in the western US is examined.

METHOD

Model description

The study uses the Community Multiscale Air Quality (CMAQ) modeling system (version 4.7) (Byun and Schere, 2006; Foley et al., 2010) to simulate air quality. Evaluations for the CMAQ modeling system have been conducted by comparing model predictions to measured ambient pollutants (Eder and Yu, 2006; Appel et al., 2007). The modeling domain consisted of 213 x 188 horizontal grid-cells covering the western 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 a mass continuity scheme to describe vertical advection processes, the Asymmetric Convective Model Version 2 (ACM2) (Pleim, 2007) to describe vertical diffusion processes, a multiscale method to describe horizontal diffusion processes, and an adaptation of the ACM algorithm for convective cloud mixing. In addition to the gas-phase chemistry, 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 CMAQ modeling domain. Two model simulations were performed using the CB05 mechanism (Yarwood et al., 2005) for July 2002. 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). For a typical day, the use of CB05-TU increased computational time of the model by 6% compared to that of the CB05-Base.

Toluene chemistry

Yarwood et al. (2005) updated the CB-IV mechanism into the CB05 mechanism. The major changes in CB05 were updates in photolysis and kinetic rates, more detailed inorganic reactions, and improved representation of the chemistry of ethane, higher aldehydes, alkenes with internal double bonds, oxygenated products and intermediates, and terpenes. Toluene chemistry in CB05 was retained from the CB-IV mechanism. Toluene chemistry in CB05-Base contains 10 chemical reactions involving 5 chemical species. Reaction of toluene with hydroxyl radical (OH) can proceed via three different channels: 36% of the reaction produces cresol (CRES), 56% produces toluene-hydroxyl radical adduct (TO2), and 8% produces benzaldehyde. Contribution of benzaldehyde to O_3 is negligible and is not retained in CB05. TO2 can react with nitric oxide (NO) to produce organic nitrate (NTR) and a ring opening product (OPEN) or thermally beak down to produce CRES. During day time, CRES can react with OH to produce alkoxy radical (CRO) and OPEN both of which undergo further reactions.

Whitten et al. (2010) described the detailed chemistry of updated toluene mechanism. CB05-TU contains 26 chemical reactions involving 13 species for toluene oxidation. It contains several additional nitrogen-containing species and organic peroxy radicals. Reaction of toluene with OH can proceed via four different channels: 18% of the reaction produces CRES, 65% produces TO2, 10% produces benzaldehyde, and 7% produces OH. TO2 can react with NO to produce NTR, OPEN, and methyl glyoxal; all of these products can undergo further reactions. During day time, CRES can react with OH to produce CRO and methyl catechol both of which can undergo further reactions. Whitten et al. (2010) performed simulations using CB05-Base and CB05-TU for environmental chamber experiments involving toluene and oxides of nitrogen (NO_x); CB05-TU was found to better explain the results of these chamber experiments. CB05-TU can change O_3 in several ways including: (1) increases in existing organic peroxy radical (TO2) concentrations (2) formation of new organic peroxy radicals (3) increases in OH (4) increases in HO_2.

Emissions

Anthropogenic emissions were derived from the 2002 National Emissions Inventory and biogenic emissions were estimated using the Biogenic Emissions Inventory System (version 3.13) (*Schwede et al.*, 2005). Domain-wide total emissions used in the study for a representative day are shown in Table 1; toluene emissions were 23 tons. Mobile sources (on-road and off-road vehicles) contributed 43%, fire sources contributed 28%, area sources contributed 24%, and point sources contributed 5% of toluene emissions. Thus, mobile source sector was the largest contributor to toluene emissions.

Table 1: Domain-wide total daily emissions on July 1

Pollutants	Tons	Pollutants	Tons
NO_x	226	SO_2	96
CO	2138	NH_3	109
NMVOC	1997	$PM_{2.5}$	120
Toluene	23	$PM_{2.5-10.0}$	175

RESULTS AND DISCUSSION

The monthly mean of daily 8-hr maximum O_3 with CB05-Base and increases in mean 8-hr O_3 between CB05-TU and CB05-Base are shown in Figure 1. CB05-TU increased monthly mean 8-hr O_3 by a maximum of 2.8 ppbv in Los Angeles, CA; 1.5 ppbv in Portland, OR and Seattle, WA. 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 (weighted by OH-reaction rate constant) is also shown in Figure 1. CB05-TU enhanced O_3 in areas with higher toluene to total VOC concentration ratios. CB05-TU affected O_3 in more grid-cells in Los Angeles than either in Portland or Seattle.
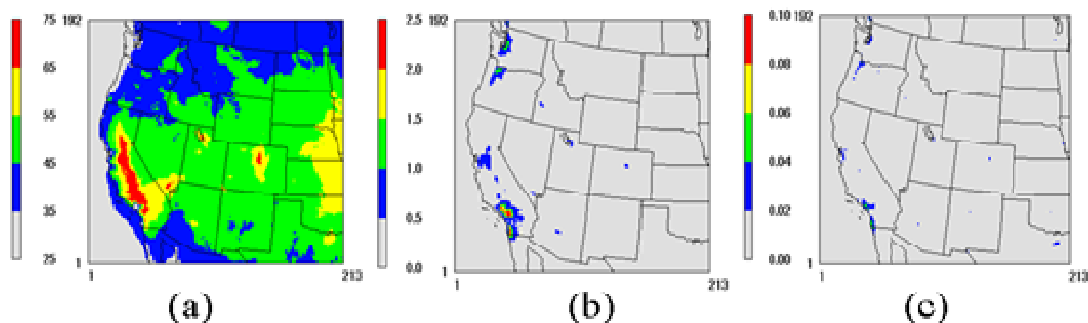

(a)   (b)   (c)

Figure 1: (a) monthly mean of daily 8-hr max O_3 (ppb) with CB05-Base (b) increases in monthly mean 8-hr O_3 (ppb) between CB05-TU & CB05-Base (c) mean toluene/VOC ratio with CB05-Base.

The day-to-day variation of the increases in daily 8-hr maximum O_3 is presented in Figure 2 for the three largest affected areas: Los Angeles, Portland, and Seattle. 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 Los Angeles occurred on most days while increases in Portland and Seattle occurred on fewer days. The largest increase in Los Angeles was 6.7 ppbv (July 7), Portland was 6.9 ppbv (July 22), and Seattle was 6.3 ppbv (July 10).
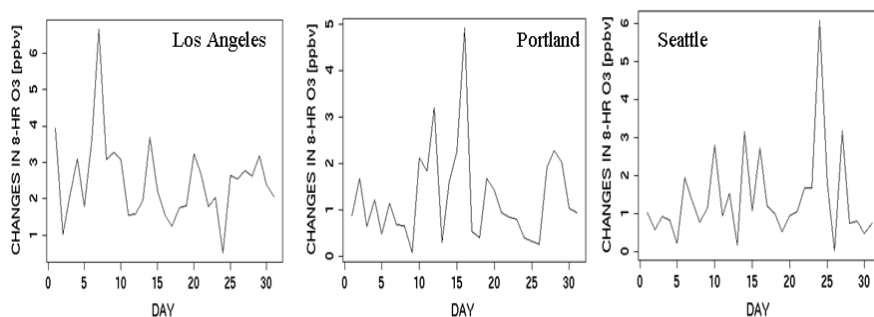

Figure 2: Variation of the increases in daily 8-hr max O_3 between CB05-TU & CB05-Base

Ozone production efficiency (OPE) is defined as the number of O_3 molecules formed from each NO_x molecule oxidized to NO_z (total oxidized nitrogen) and can be calculated from the slope of a plot of O_3 and NO_z. OPE was estimated using O_3 and NO_z values during daytime (10:00 – 5:00 pm) and when $O_3/NO_x > 46$ (aged air mass) (Arnold et al., 2003). OPE

3

obtained with CB05-TU was slightly lower than the value obtained with CB05-base. Monthly mean NO_z concentrations with CB05-Base and increases in mean NO_z between CB05-TU and CB05-Base are shown in Figure 3. Mean NO_z with CB05-TU were greater than those with CB05-Base. Increases in O_3 were associated with increased NO_z. The slope of the fitted curve decreased with CB05-TU; thus OPE decreased marginally with CB05-TU.
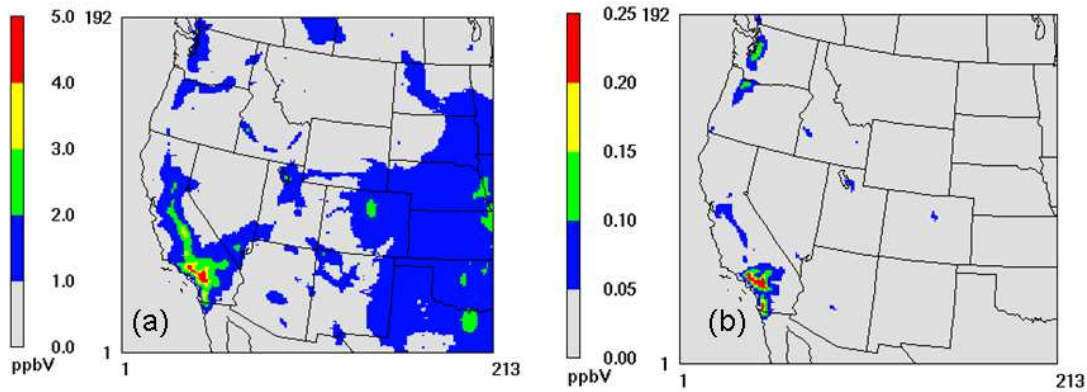

Figure 3: (a) Mean NO_z (ppbv) with CB05-Base (b) NO_z increases (ppbv) between CB05-TU & CB05-Base

Overall mean bias (MB) for O_3 improved from -10.6 to -9.6 ppbv in Los Angeles, from -2.1 to -1.1 ppbv in Portland, and from -0.3 to +0.3 ppbv in Seattle with CB05-base and CB05-TU, respectively. The median and inter-quartile range of MB for the daily maximum 8-hr O_3 with CB05-TU and CB05-Base is presented in Figure 4. Ambient monitoring data from the Environmental Protection Agency's Air Quality System are used for this model evaluation. Simulated daily maximum 8-hr O_3 concentrations with CB05-Base were lower than the observed data in Los Angeles and results with CB05-TU reduced MB. In Portland and Seattle, CB05-TU increased simulated O_3 for all observed O_3. It increased MB at lower observed O_3 and decreased MB at higher observed O_3. Overall, predictions with CB05-TU reduced MB when observed O_3 are generally high.
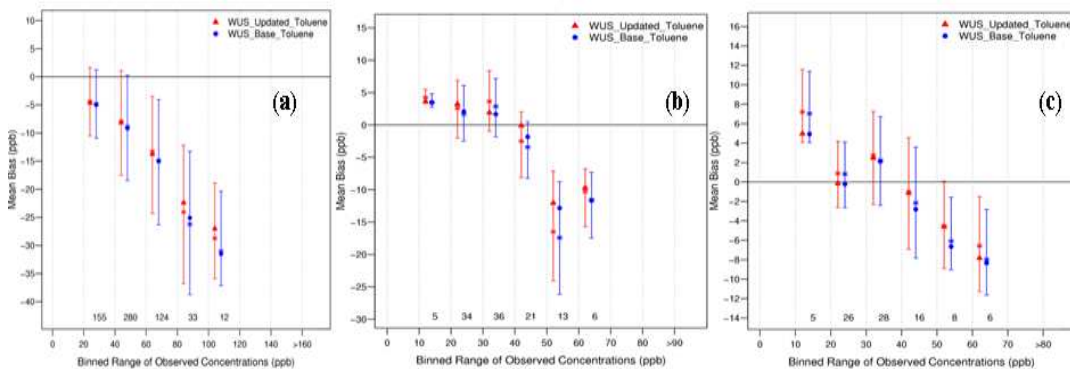

Figure 4: MB with CB05-TU and CB05-Base at (a) Los Angeles (b) Portland (c) Seattle

The ratio of monthly mean SOA from toluene with CB05-TU and CB05-Base is shown in Figure 5. The CB05-TU increased monthly mean SOA from toluene by up to 7%

4

compared to those with the CB05-Base. Locations of SOA increases generally coincided with the locations of O_3 increases; the largest percent increase occurred in Seattle. Carlton et al. (2010) have provided a detailed description of the SOA mechanism in the CMAQ model. CB05-TU increased mean OH concentrations by up to 11% compared to those obtained with CB05-Base; consequently the reaction rate of toluene and OH increased and produced more peroxy radical from toluene (first generation product that further reacts with hydroperoxy radical (HO_2) and NO to produce semi-volatile organic compounds). CB05-TU increased mean HO_2 by up to 18% and decreased NO by up to 9% compared to those obtained with CB05-Base. Thus, the reaction rate of the peroxy radical (from toluene) with HO_2 increased while the reaction rate of the peroxy radical with NO decreased. The reaction of peroxy radical (from toluene) with HO_2 is more important than the corresponding reaction with NO for SOA production. Thus CB05-TU enhanced semi-volatile organic compounds and subsequently SOA production from toluene. The impact of CB05-TU on $PM_{2.5}$ was even smaller.
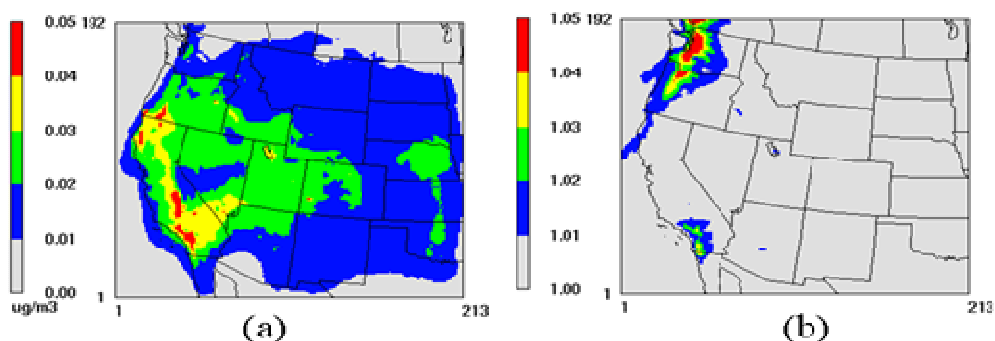

Figure 5: (a) monthly mean SOA from toluene with the CB05-Base (b) ratio of mean SOA obtained with CB05-TU and CB05-Base

To evaluate the sensitivity of O_3 production with CB05-Base and CB05-TU, two additional model runs were completed by reducing NO_x emissions by 25% for the first 10 days in July. Changes in mean 8-hr O_3 with CB05-Base and CB05-TU are shown in Table 3. Changes in O_3 with CB05-TU were slightly larger in Los Angeles when NO_x emissions were reduced. Ambient NO_x concentrations in Los Angeles are generally high; reduction in NO_x emissions increased O_3 with CB05-Base as well as CB05-TU. However, increases with CB05-TU were only slightly greater than those with CB05-Base. Thus, CB05-TU appears to be not highly sensitive with NO_x emissions.

Table 3: Change of 8-hr O_3 with NO_x emissions (CB05-TU - CB05-Base)

Location	Changes in mean 8-hr O_3 with base NO_x	Changes in mean 8-hr O_3 with reduced NO_x
Los Angeles	3.5	4.2
Portland	1.7	1.7
Seattle	1.4	1.5

While predicted O_3 concentrations are important for model evaluation, relative reduction factors (RRF) are important for developing emissions control strategies. RRF were calculated using results obtained with base and reduced NO_x emissions for each mechanism.

RRF in Portland and Seattle did not change and RRF in Los Angeles only changed by a small margin (<0.01). Thus, CB05-TU has only minor impact on RRF.

SUMMARY

CB05-TU enhanced monthly mean of daily 8-hr maximum O_3 in some urban areas in the western US by a maximum of 2.8 ppbv. Results obtained with CB05-TU improved MB when observed O_3 concentrations were greater than 85 ppbv. CB05-TU increased SOA from toluene by a maximum of 7%, OH by a maximum of 11%, and HO_2 by a maximum of 18% compared to those obtained with 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.

REFERENCES

Appel, K. W., Gilliland, A. B., Sarwar, G., and Gilliam, R. C., 2007. Evaluation of the Community Multiscale Air Quality (CMAQ) model version 4.5: Sensitivities impacting model performance Part I-Ozone. *Atmospheric Environment* 41, 9603–9615.

Arnold, J.R., Dennis, R.L., Tonnesen, G.S., 2003. Diagnostic Evaluation of Numerical Air Quality Models with Specialized Ambient Observations: Testing the Community Multiscale Air Quality Modeling System (CMAQ) at Selected SOS 95 Ground Sites; *Atmospheric Environment 37,* 1185-1198.

Byun, D., and Schere, K.L, 2006. Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system, *Applied Mechanics Reviews,* 59**,** 51–77.

Calvert, J.G., Atkinson, R., Becker, K.H., Kamens, R.M., Seinfeld, J.H., Wallington, T.J., Yarwood, G., 2002. The mechanisms of atmospheric oxidation of aromatic hydrocarbons. Oxford University Press, New York, 566 pp.

Carlton, A., et al., 2010. Improved treatment of secondary organic aerosol in CMAQ. *Environmental Science & Technology*, in press.

Eder, B., Yu, S. 2006. A performance evaluation of the 2004 release of Models-3 CMAQ. *Atmospheric Environment 40*, 4811-4824.

Faraji, M., Kimura, Y., McDonald-Buller, E, Allen, D., 2008. Comparison of the carbon bond and SAPRC photochemical mechanisms under conditions relevant to southeast Texas, Atmospheric Environment, 42, 5821-5836.

Foley, K. M., et al., 2010. Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7, Geosci. Model Dev., 3, 205–226, 2010.

Grell, G., Dudhia, J., and Stauffer, D., 1994. A description of the fifth-generation Penn State/NCAR Mesoscale model (MM5), NCAR Tech. Note NCAR/TN-398+STR.

Pleim, J. E.: A combined local and nonlocal closure model for the atmospheric boundary layer. Part I: Model description and testing, *J. Appl. Meteor. Climatol*., 46, 1383–1395, 2007.

Schwede, D., Pouliot, G., and Pierce, T., 2005. Changes to the biogenic emissions inventory system version 3 (BEIS3), 4th Annual CMAS Models-3 Users' Conference, September 26-28, 2005, UNC-Chapel Hill, NC. Available at http://www.cmascenter.org/html/2005_conference/abstracts/2_7.pdf

Yarwood, G., Rao, S., Yocke, M. and Whitten, G., 2005. Updates to the carbon bond chemical mechanism: CB05. Final report to the U.S. EPA, RT-0400675. Available at www.camx.com.

Whitten, G. Z., G. Heo, Y. Kimura, E. McDonald-Buller, D. Allen, W.P.L. Carter, G. Yarwood, 2010. A new condensed toluene mechanism for Carbon Bond: CB05-TU. *Atmospheric Environment,* in press.