Simulation of atmospheric oxidation capacity in Houston, Texas

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Abstract Air quality model simulations are performed and evaluated for Houston using the Community Multiscale Air Quality (CMAQ) model. The simulations use two different emissions estimates: the EPA 2005 National Emissions Inventory (NEI) and the Texas Commission on Environmental Quality (TCEQ) Emissions Inventory. A comparison of predictions with observed data from the 2006 TexAQS-II Radical and Aerosol Measurement Project (TRAMP) suggest that while the predicted oxides of nitrogen are greater than observations, predicted volatile organics (e.g., ethane, acetone) are substantially lower than the observations. Predicted hydroxyl radical predictions are in good agreement with the observations. Hydroperoxy radical predictions, however, are substantially lower than the observations.

1. Introduction

Hydroxyl radical (OH) reacts with numerous chemical species present in the atmosphere, thereby determining the atmospheric oxidation capacity. Atmospheric OH, however, is not routinely measured. Hydroxyl radical, hydroperoxy radical (HO_2), and a suite of other chemical species were measured during the 2006 TexAQS-II Radical and Aerosol Measurement Project (TRAMP) (Lefer and Rappenglueck, 2010, Mao et al., 2010) and represent an opportunity for model evaluation. Chen et al. (2010) used a constrained zero-dimensional box model and compared the predictions to observed OH and HO_2 levels from the TRAMP. In the constrained box-model, measured precursors are used to predict OH and HO_2 concentrations while in three-dimensional models emissions and meteorological fields drive the model predictions. Here, we compare OH and HO_2 predictions of a three-dimensional air quality model to observed data from the TRAMP.

2. Method

The study uses the CMAQ modeling system (version 5.0) (Byun and Schere, 2006; Foley et al., 2010) to simulate air quality. Evaluations for the CMAQ

modeling system have previously been conducted by comparing model predictions to measured ambient pollutants (Appel et al., 2007; Foley et al., 2010; Ngan et al., 2012). The CMAQ model has displayed considerable skill in simulating ozone and other chemical species in the atmosphere. The modeling domain covers most of Texas and Louisiana with 4-km grid spacings. It contains 35 vertical layers with the surface layer thickness of approximately 20-meters. Model simulations are performed for August 30-September 4, 2006. This simulation period covers an ozone episode in Houston during which measured ozone reached over 160 ppb. Initial and boundary conditions are obtained from a larger modeling domain using 12-km horizontal grid-spacings covering the continental US. Meteorological fields are obtained from the Weather Research and Forecasting (version 3.2) model. Two different emissions inventories are used: the EPA 2005 National Emissions Inventory (NEI) and the Texas Commission on Environmental Quality (TCEQ) Emissions Inventory (EI). The Biogenic Emissions Inventory System (version 3.14) is used to prepare biogenic emissions for the study (Schwede et al., 2005). The Statewide Air Pollution Research Center (SAPRC-99) chemical mechanism (Carter, 2000) is used.

3. Results and Discussion

Predicted oxides of nitrogen (NO_x) are compared to the observed data in Figure 1. Model predictions with the 2005 NEI are much greater than the observed data while predictions with the TCEQ EI agree better with the observed data. Thus, the modeling results using the TCEQ EI are presented.

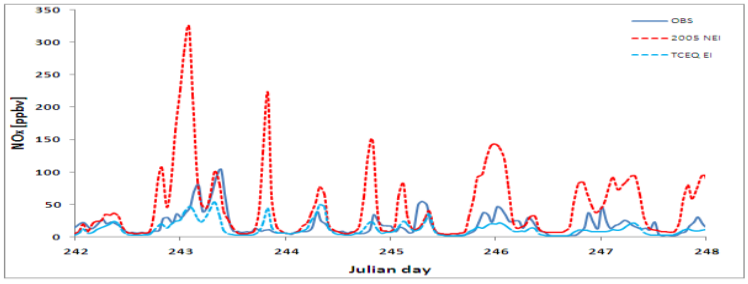

Figure 1: A comparison of CMAQ predicted NO_x with TRAMP data.

Predicted ethane levels are compared to observed values in Figure 2. Predicted ethane levels are substantially lower than observed data, with predicted mean value eleven times lower than mean observed data. While not shown here, predicted mean acetone level is ten times lower than observed data. Predicted levels of some other VOCs are lower than the observed values by factor of 2 or less. Thus, the model emissions are enhanced by multiplying emissions estimates in the TCEQ EI with appropriate factors and the CMAQ model was re-run with

the enhanced emissions. Kim et al. (2011), Brioude et el. (2011), and Byun et al., (2012) also report that model with 2005 NEI predicts greater NO_x and lower VOCs than observed values.

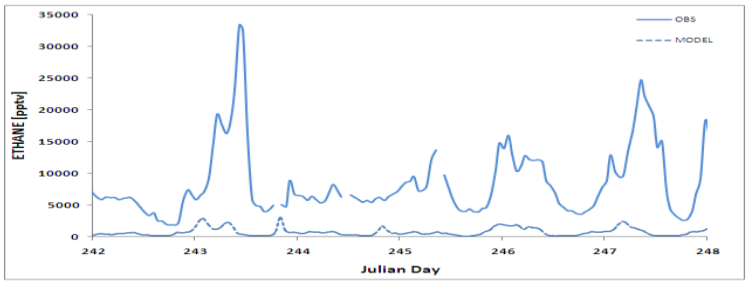

Figure 2: A comparison of CMAQ predicted ethane with TRAMP data.

Predicted OH levels are compared to observed values in Figure 3. Predicted OH closely levels follow the diurnal trend of the observed data. Predicted daytime values are in good agreement with observed data although predicted peak values are somewhat lower. Predicted daily peak values reach to within 20% of the observed data on all days except on September 2 (Julian day 245). Predicted nighttime OH values are lower than the observed data.

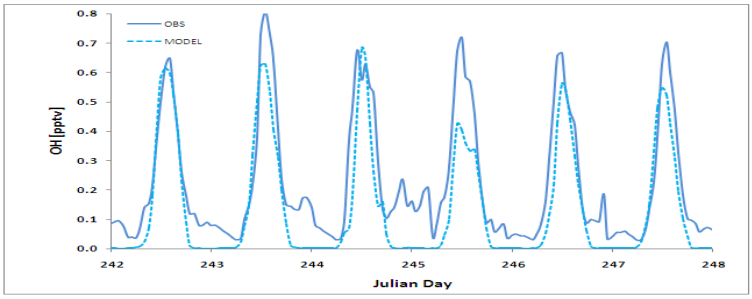

Figure 3: A comparison of CMAQ predicted OH with TRAMP data.

Predicted HO_2 levels are compared to the observed values in Figure 4. Predicted HO_2 generally follow the diurnal trend of the observed data. While the model captures the observed day-to-day variability in OH levels reasonably well, predicted daytime peak HO_2 levels are lower than the observed data by factor of up to 4. Predicted nighttime values are also lower than the observed data. Fuchs et al., 2011 suggested that several organic peroxy radicals can interfere with the measurements of HO_2; thus true HO_2 values are lower than the observed values. Unfortunately, peroxy radicals were not measured in Houston. However, we estimate the true HO_2 values are within 20% of the observed data.

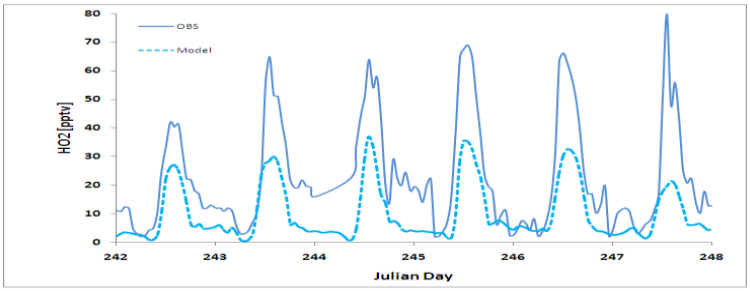

Figure 4: A comparison of CMAQ predicted HO_2 with TRAMP data.

4. Summary

The 2005 NEI contains more NO_x emissions than those in the TCEQ EI. Model predicted NO_x levels with 2005 NEI are much greater than the observed data. Predicted ethane levels with the TCEQ EI are substantially lower than the observed data. Predicted OH levels compare well with the observed data from TRAMP. However predicted daytime peak HO_2 levels are substantially lower than the observed data.

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.

Brioude, J., et al., 2011: Top-down estimate of anthropogenic emission inventories and their interannual variability in Houston using a mesoscale inverse modeling technique, *JGR*, *116*(D20305), 10.1029/2011JD016215.

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 modeling system, *App. Mechanics Reviews*, 59, 51–77.

Byun D., Lee D.-G., Ngan F., Kim S., Kim H.-C., Li X., Czader B., Rappenglueck B., Lefer B., Estes M., and Olaguer E., 2012: Retrospective Air Quality Simulations of the 2006 TexAQS II TRAMP episode, Atmos. Env., in prep.

Carter, W.P.L., 2000: Implementation of the SAPRC-99 chemical mechanism into the Models-3 Framework, report to the United States Environmental Protection Agency. Available at http://www.cert.ucr.edu/~carter/absts. htm#s99mod3.

Chen, et al., 2010: A comparison of chemical mechanisms based on TRAMP-2006 field data, *Atmos. Env.* 44, 4116-4125.

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.

Fuchs, H., Bohn, B., Hofzumahaus, A., Holland, F., Lu, K. D., Nehr, S., Rohrer, F., and Wahner, A.: Detection of HO_2 by laserinduced fluorescence: calibration and interferences from RO_2 radicals, Atmos. Meas. Tech., 4, 1209–1225, 2011.

Kim, et al., 2011: Evaluations of NO_x and highly reactive VOC emission inventories in Texas and their implications for ozone plume simulations during the Texas Air Quality Study 2006, Atmos. Chem. Phys., 11, 11361-11386.

Lefer and Rappenglueck, 2010: The TexAQS-II radical and aerosol measurement project, *Atmos. Env.* 44, 3997-4004.

Ngan F., Byun D., Kim H., Lee D., Rappenglueck B., Pour-Biazar A., 2012: Performance assessment of retrospective meteorological inputs for use in Air Quality Modeling during TexAQS 2006, Atmos. Environ., doi: 10.1016/j.atmosenv.2012.01.035, in press.

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.

Questions and Answers on NATO-ITM Paper No. 6.04

1. Questioner name: Sarav Arunachalam

Question: Previous studies suggested Houston emissions have large episodic releases which are not captured in emissions inventory. Does the new emissions inventory account for these episodic releases?

Answer: Indeed previous studies suggested Houston emissions have large episodic releases. The new inventory attempted to capture these episodic releases. However, incorporation of these episodic releases in the inventory is a huge challenge. While significant improvement has been made in improving the emissions inventory, the model with the new inventory suggests that it still lacks VOCs although to a much lower extent than suggested by previous studies.