EFFECTS OF USING THE CB05 VERSUS THE CB4 CHEMICAL MECHANISMS ON MODEL PREDICTIONS

Deborah Luecken*, Golam Sarwar
Atmospheric Modeling Division
U.S. Environmental Protection Agency, Research Triangle Park, NC, USA

1. INTRODUCTION

The Carbon Bond 4 (CB4) chemical mechanism (Gery et al, 1989) has been widely used for many years in box and air quality models to predict the effect of atmospheric chemistry on pollutant concentrations. This mechanism has been used in numerous research studies and in the development of environmental regulations and control studies. Because of the importance of this mechanism and the length of time since its original development, the CB05 chemical mechanism was developed in 2005 (Yarwood et al., 2005) to provide a major update to CB4. A version of the CB05 mechanism was implemented in CMAQ release v4.5, and a final version is available in the 2006 CMAQ release (v4.6).

During 2006, concentration predictions by CMAQ using the CB05 chemical mechanism are being extensively compared with predictions using the older CB4 chemical mechanism, as well as with observational data. While some of the differences between the CB4 and the CB05 mechanisms are small, there are some significant differences in a few of the oxidant and particulate matter (PM) species, and the magnitude of these differences vary both temporally and spatially.

In this study, we examine where and when the largest differences between the two mechanisms tend to occur. We focus on 12 km model simulations where the only difference is the choice of chemical mechanism.

2. MAJOR CHEMICAL DIFFERENCES BETWEEN THE MECHANISMS

Updates to the CB4 mechanism have been performed in order to make it consistent with the most recent experimental measurements of the chemical reactions of both individual compounds and mixtures of compounds. Because the mechanisms are used for a large variety of conditions, the updates were also focused on representing our best understanding of how complex mixtures of chemicals react in the troposphere over a wide range of urban, suburban, rural and remote areas. Some of the updates have also been added to improve the appropriateness of CB05 under a variety of meteorological conditions, including temperature, sunlight, and humidity ranges. The most important changes from the original CB4 include: 1) updated rate constants and 2) additional lumped and explicit model species.

All rate expressions in CB4 have been examined, updated and modified to be consistent with the most recently reported values as reviewed by Atkinson et al. (2005) and Sander et al.(2003). Photolysis rates have been updated and specified explicitly where information is available, rather than by reference to nitrogen dioxide (NO_2) photolysis.

Additional model species have been added in the CB05 to better represent the atmospheric chemistry of species that are critical to ozone and PM formation. Methyl peroxy radicals, for example, are represented explicitly in CB05, because they are the most abundant peroxy radical, while CB4 lumped them in with other peroxy radicals. This improvement allows a more realistic representation of radical-radical reactions, which can be important in low-NO_x areas. Both acetaldehyde (represented in CB05 by ALD2) and higher aldehydes (ALDX) are modeled separately in CB05 because of the importance of accurately representing this class of reactive compounds. Another key improvement is differentiation of internal alkene reactions from those of terminal alkenes. In CB4, the reactivity of internal alkenes was represented by higher (C2+) aldehydes. Internal alkenes comprise a significant portion of the ambient VOC composition in urban air and they react differently than carbonyls, so CB05 can represent these reactions more appropriately.

3. DESCRIPTION OF MODEL SIMULATIONS

Model simulations have been performed using the CMAQ v.4.5 (Byun and Schere, 2006) for one

---

*Corresponding author: Deborah Luecken, MD E243-03, U.S. Environmental Protection Agency, Research Triangle Park, NC 27709; e-mail: luecken.deborah@epa.gov

month periods representing January and July 2001. We used emissions from the 2001 National Emissions Inventory (NEI) and meteorology from a 2001 MM5 simulation. Model simulations were run with a 36 km grid resolution over the continental U.S. and with a 12 km resolution over the eastern half of the U.S. Boundary and initial conditions for the 12 km simulations were derived from the initial 36 km simulations.

Both CB4 and CB05 were run with identical meteorology and model options. Overall emissions were identical; where additional species were represented explicitly in CB05, we have subtracted them from lumped model species in CB4, with speciation as described in Yarwood et al. (2005).

4. RESULTS: DIFFERENCES IN OZONE

4.1 Spatial Differences

Predicted ozone differences between the two mechanisms are shown in Figure 1, presented as the difference in the monthly average of the daily maximum 1-hr average ozone, for the 12 km simulation. Analyses done using the average 8-hour maximums show the same spatial patterns. While the differences shift slightly from day to day, depending on meteorology, a distinct pattern is apparent with the largest differences occurring around central Missouri/Kansas/Oklahoma. This area, identified as region A in Figure 1, also roughly corresponds to ozone Principal Component four identified by Lehman et. al. (2004), where isoprene and other biogenic alkene emissions are high and ozone is moderate-to-low. In the northeastern U.S. (Region D) and Illinois-Ohio Valley region (Region C), differences are smaller although this area has high predicted ozone. In the January simulations (Figure 2), the differences are smaller overall, and the area of largest difference is further south and west, centered around Texas.

In all areas, CB05 predicts higher ozone concentrations than CB4 on average. There are grids at some times during the simulation where CB05 predicts slightly less ozone than CB4, but these differences are small (generally less than 1 ppb, with a few 5-6 ppb differences). These occur in the late morning, and more often in the northern parts of the domain and the Mid-Atlantic coast.

In general, ozone differences between the two mechanisms are not a predictable function of the ozone concentrations. Absolute differences do vary as a function of region (Figure 3). While CB05 predicts average July ozone concentrations

about 9% larger than CB4, ozone levels in grids in region A are about 12% higher, region B is about
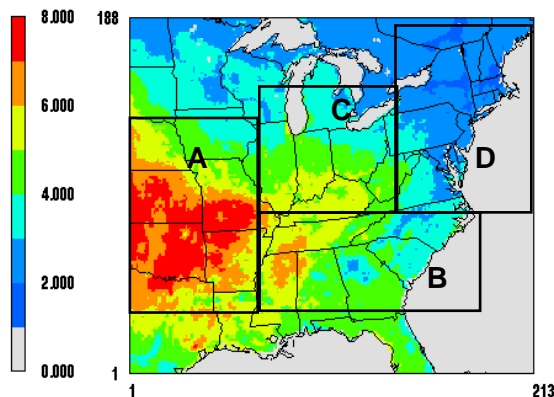

Figure 1. Ozone differences (CB05-CB4) for the average daily 1-hr maximum ozone concentrations during the July simulation (ppb).
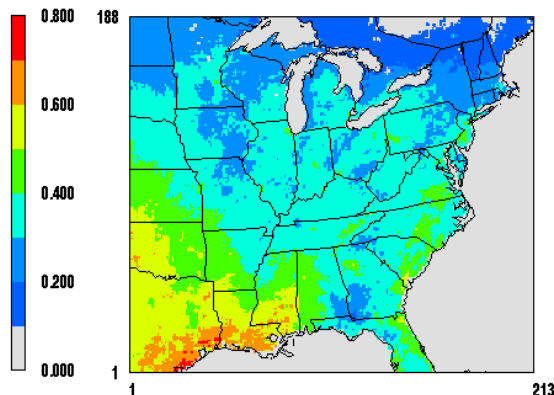

Figure 2. Ozone differences (CB05-CB4) for the monthly average daily 1-hr maximum ozone concentrations during the January simulation (ppb).

9% higher, region C is 7 % higher, while Region D is 6% higher on average.

The differences in ozone predictions among the regions are somewhat dependant on the concentration of aldehydes with 3 or more carbons (represented by ALDX) predicted by CB05. While ALDX is emitted, it is primarily produced in CB05 by reactions of isoprene and olefins. CB05 replaces part of the ALD2 in CB4 with ALDX, which can result in twice as many nitrogen oxide

2

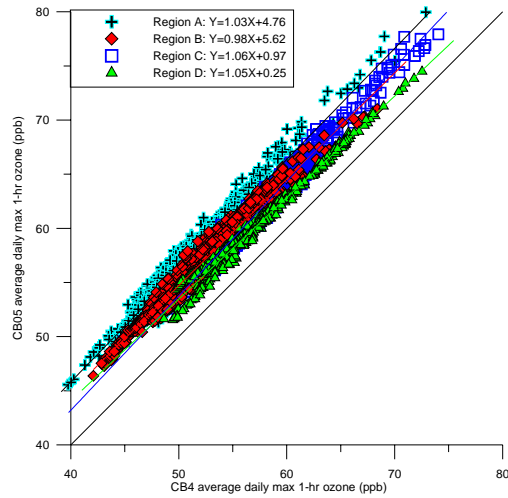(NO) oxidations for each ALD2 replaced, and can have a large effect on ozone production.

Figure 3. CB05 ozone predictions as a function of CB4 predictions for the July simulation, shown as the average of the daily 1 hour maximum ozone (ppb).

4.2 Temporal Differences in Ozone

Differences in ozone predictions between the two mechanisms are largest in summer, when photochemistry is most active and smallest in winter. Ozone differences also have a diurnal dependance. Figure 4 shows mean, centered 3-hr ozone concentrations in July, averaged over each region, to illustrate the general diurnal trend. The diurnal difference is largest in region A and smallest in Region D. The largest difference occurs about 2 hours after the ozone peak, and the smallest occurs in mid-morning.

5. DIFFERENCES IN PM$_{2.5}$

5.1 Overall PM$_{2.5}$

Monthly-averaged PM$_{2.5}$ concentrations predicted by CB05 are slightly higher than those predicted by CB4 in the January simulation, with the differences shown in Figure 6. However, the overall differences are small (generally less than 1%). There is an area in southern Georgia and Florida where CB05 predicts lower PM$_{2.5}$ than CB4, but these differences are still small.

By contrast, in July, CB05 predicts lower PM$_{2.5}$ concentrations than CB4 (Figure 7) over the whole domain, with differences in many areas approaching 6-10%, especially in the Ohio Valley and northern Georgia/Alabama. The largest differences occurred in northwestern Georgia,

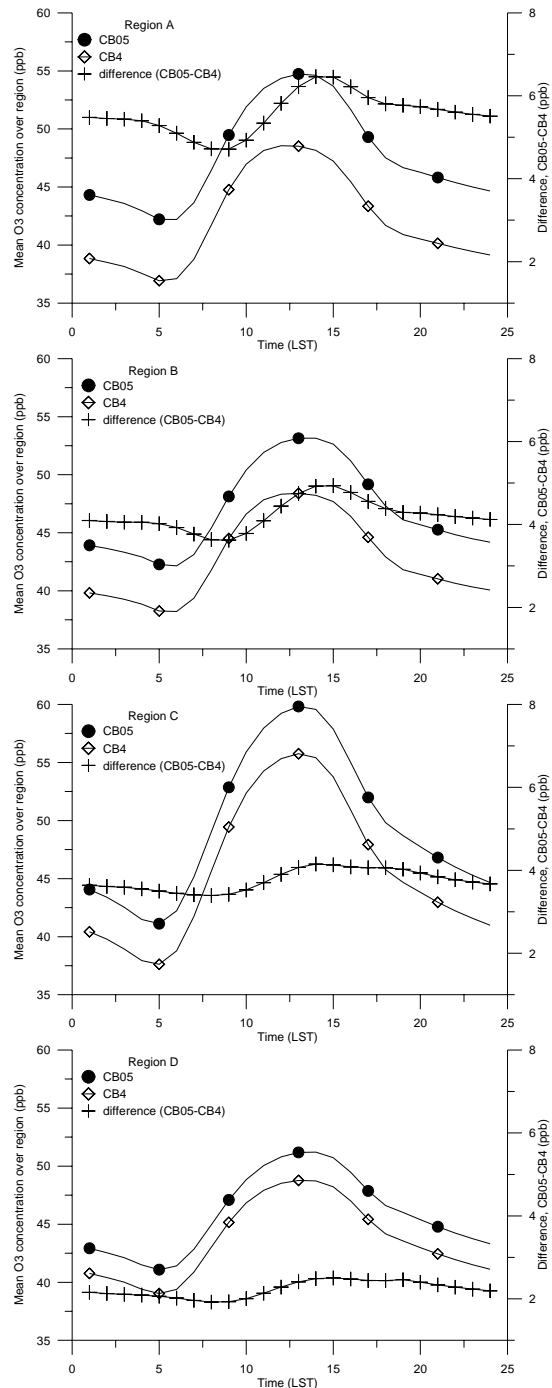where CB05 predicted PM$_{2.5}$ concentrations that were lower by as much as 1.6 $\mu g/m^3$.

Figure 4. Diurnal profiles of CB05 and CB4 ozone predictions (left axis) and the differences (right axis) over 3-h centered time blocks averaged for each of the four domains, July.
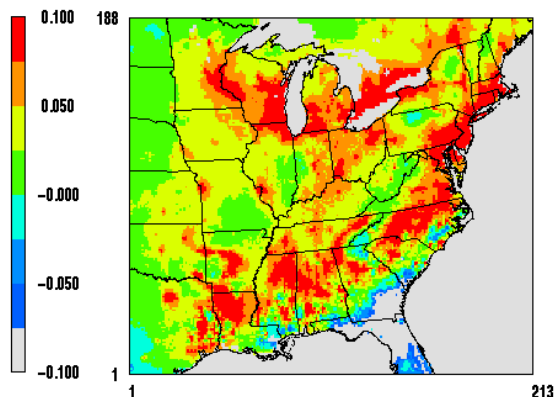
Figure 6. Differences in $PM_{2.5}$ (CB05 minus CB4) for the January simulations ($\mu g/m^3$). Concentrations over water bodies are not plotted.
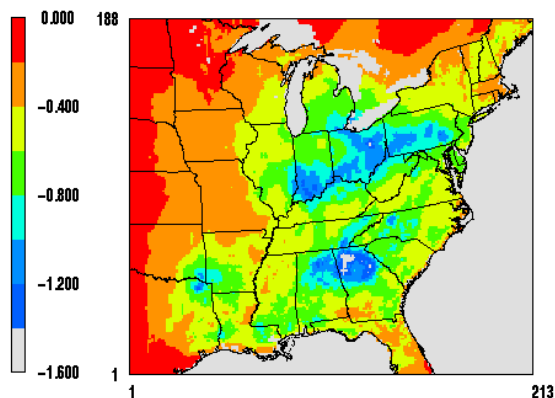

Figure 7. Differences in $PM_{2.5}$ (CB05 minus CB4) for the July simulations ($\mu g/m^3$). Concentrations over water bodies are not plotted.

5.2 $PM_{2.5}$ components: sulfate and secondary organic aerosol

Most of the differences in $PM_{2.5}$ between the two chemical mechanisms are due to differences in model predictions of production and partitioning of aerosol sulfate, nitrate and secondary organic compounds. All three components are affected to some extent by differences in the atmospheric chemistry described in the chemical mechanism, and the effects are larger in the summer, when photochemical activity is larger.

The lower $PM_{2.5}$ predictions by CB05 in the July simulation are primarily caused by lower aerosol sulfate predictions from CB05, which accounts for between 50% to greater than 90% of the total difference between the two mechanisms (Figure 8). The production of sulfate in CB05 is smaller largely due to lower OH concentrations (about 15% lower) during daylight hours, which results in less SO_2 oxidation and less sulfate production. Lower hydrogen peroxide, methyl hydroperoxide, and peroxycarboxylic acid concentrations also can contribute to a lesser extent to the lowered sulfate production in CB05.
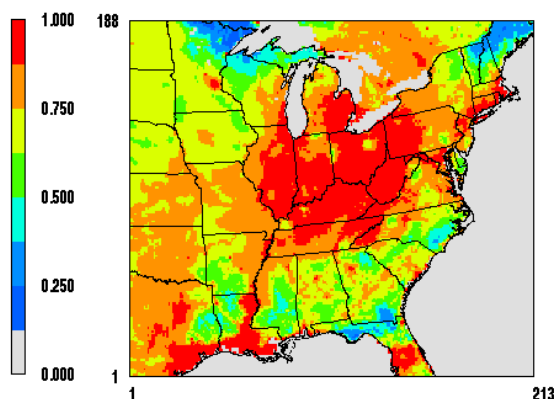

Figure 8. Fraction of the $PM_{2.5}$ differences between CB05 and CB4 due to differences in aerosol sulfate for the July simulations.

6. SUMMARY

Differences between predictions of ozone and PM using the CB4 and the updated CB05 mechanism in CMAQ show substantial spatial and temporal variability.

The largest differences in ozone occur in the summer, when high ozone concentrations are of the most concern. With very few exceptions, CB05 always has higher predictions of ozone than CB4, and the difference is generally independent of the ozone concentration. On average, CB05 predicts about 4 ppb more ozone than CB4, but exact amount depends on the season, region and metric used. The largest differences usually occur in the South-Central area of the domain, and are influenced by the changes made in CB05 to treat reactive aldehydes more realistically, as well as to better represent the peroxy radicals.

The largest differences in $PM_{2.5}$ also occur in the summer, when $PM_{2.5}$ concentrations can be high in some parts of the country. The major differences between CB05 and CB4 are in the treatment of photochemistry and therefore have the most effect when and where atmospheric chemistry, relative to emissions, has a greater influence on aerosol concentrations. Aerosol sulfate predictions in July are particularly sensitive to reductions in the daytime OH radical concentrations resulting from the large number of changes made to the CB05.

7. DISCLAIMER

The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. This work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

8. REFERENCES

Atkinson, R., D.L. Baulch, R.A. Cox, J.N. Crowley, R.F. Hampson, R.G. Hynes, M.E. Jenkin, J.A. Kerr, M.J. Rossi, and J. Troe, 2005: Evaluated kinetic and photochemical data for atmospheric chemistry - IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry. Available at http://www.iupac-kinetic.ch.cam.ac.uk/ index.html

Byun, D., and K.L. Schere, 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.

Gery, M.W., G.Z. Whitten, J.P. Killus, and M.C. Dodge, 1989: A photochemical kinetics mechanism for urban and regional scale computer modeling. *J. Geophys. Res.*, **94(D10)**, 12925-12956.

Lehman, J. K. Swinton, S. Bortnick, C. Hamilton, E. Baldridge, B. Eder, and B.Cox, 2004: Spatio-temporal characterization of tropospheric ozone across the eastern United States. *Atmos. Env.,* **38(2004)**: 4357-4369.

Sander, S.P., Friedl, R.R., Golden, D.M., Kurylo, M.J., Huie, R.E., Orkin, V.L., G. K. Moortgat, G.K., Ravishankara, A.R., Kolb, C.E., Molina, M.J., and B. J Finlayson-Pitts, 2003: Chemical kinetics and photochemical data for use in atmospheric studies, evaluation number 14. NASA Jet Propulsion Laboratory. Available at http://jpldataeval.jpl.nasa.gov/download.html.

Yarwood, G., S. Rao, M. Yocke, and G. Whitten, 2005: Updates to the Carbon Bond Chemical Mechanism: CB05. Final Report to the US EPA, RT-0400675. Available at www.camx.com.