INVESTIGATING DIFFERENCES IN OZONE PRODUCTION FROM CB05 AND CBMIV VERSIONS OF THE NAQFC

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1. INTRODUCTION

The NOAA National Air Quality Forecasting Capability (NAQFC) is based on the National Center for Environmental Prediction's North American Mesoscale model, the Non-hydrostatic Mesoscale Model (NMM), and the U. S. EPA's Community Multiscale Air Quality (CMAQ) modeling system. The operational NAQFC utilizes a modified version of the Carbon Bond Mechanism version IV (CBMIV, Gery et al., 1989) as the gas-phase chemical mechanism to provide ozone (O_3) forecasts for the conterminous U. S. (CONUS) domain. An experimental version of the NAQFC is run in parallel with the operational track which uses identical input emissions base inventories, meteorological datasets and initial and boundary conditions, but differs only in that the updated 2005 version of the Carbon Bond Mechanism (CB05, Yarwood et al., 2005) is used rather than CBMIV.

Parallel runs of the operational and experimental NAQFC have been observed to produce significantly different ozone distributions (Figure 1). The CB05 version of CMAQ consistently produces higher values of O_3 across most of the CONUS domain than occurs in the equivalent simulation using CBMIV and produces larger positive biases as compared to surface O_3 measurements. Sensitivity simulations of simple box model versions of each mechanism were performed to investigate the mechanistic reasons underlying the observed differences in O_3 distributions.

2. BOX MODEL DESCRIPTION

A box model of the convectively well-mixed boundary layer was constructed for each version of the gas-phase-only chemical mechanisms. The versions of CBMIV and CB05 that are used in the NAQFC have been altered significantly from the mechanisms as proposed in the original sources;

the NAQFC versions of the mechanisms were used to construct the box models used in this work. After Seinfeld and Pandis (1998), but neglecting surface removal by dry deposition and mixing with background air, the concentration of a gas-phase species in a well-mixed, constant depth boundary layer is given by

$$\frac{dC_i}{dt} = \frac{q_i}{H} + R_i \qquad (1)$$

where, C_i is the concentration of species i in the boundary layer, q_i is the emission rate of species i into the boundary layer, H is the boundary layer depth and R_i is the chemical production (or destruction) rate of species i. The box model for each mechanism consists of a set of equations of the form (1) for each mechanism species. The box models were constructed with a modified version of the Kinetic Pre-Processor (KPP) of Sandu and Sander (2006) and based on mechanism listings specific to the versions used in the NAQFC system.
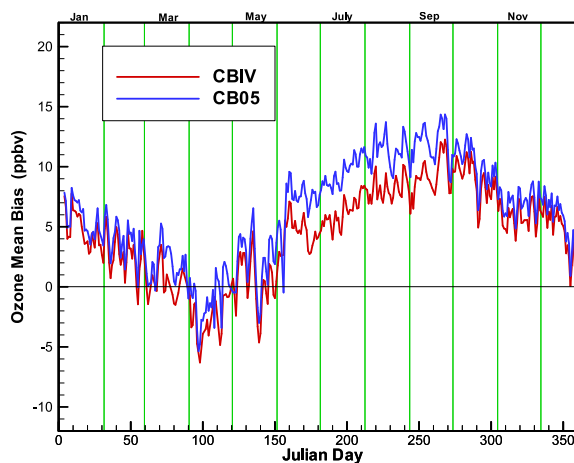
Figure 1. CONUS-averaged ozone mean bias (ppbv) in 2009 for the operational (CBIV) and experimental (CB05) versions of the NAQFC.

In a manner similar to Zaveri and Peters (1999), a suite of 18 box model simulations (of 10 days

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duration) was designed to exercise the box models across a broad range of urban and rural chemical ambient conditions, with varying NO_x, anthropogenic and biogenic hydrocarbon (HC) emission rates. Initial conditions of all scenarios were the same (T=298K; p =1 atm; 50% RH; O_3 = 10 ppbv; CO = 100 ppbv; CH_4 = 1600 ppbv; NO_x=HCs=0) so that the results of each scenario are driven by the specified emission rates. The emission rates and ratios of NO_x to HC emissions were chosen so that both NO_x-limited and HC-limited regimes would be represented. NO_x and HC emissions were constrained to vary diurnally in proportion to the cosine of the zenith angle (night = 0 and emission rate maximum at solar noon) for a mid-latitude location near ground level. Care was taken to ensure that emission rates of hydrocarbons were consistent for both CBMIV and CB05 versions of the box model in the cases where a single hydrocarbon species in CBMIV (e.g., OLE) is represented in CB05 as two separate species (e.g., OLE and IOLE). For each of the two base versions of the models (CBMIV and CB05), the full suite of 18 box model simulation scenarios was performed. Using these base runs as a starting point, several sensitivity tests were created by modifying reactions or rate constants of the CB05 mechanism and then re-running the full simulation suite with the modified CB05 version to determine the impact of the modifications on important ozone precursor species and overall ozone production.

3. SENSITIVITY TESTS

The CB05 mechanism was developed as a modification and extension of CBMIV to provide a basis for air quality modeling investigations of ozone, particulate matter, visibility, acid deposition and air toxics issues. Details of the updates included in CB05 are provided in Yarwood et al. (2005), but encompass changes made to better represent remote tropospheric chemistry, changes made to better simulate the formation of secondary organic aerosol, and changes made to better represent the latest understanding of hydrocarbon oxidation pathways.

Table 1 presents a list of the sensitivity tests performed with a brief description of how the base CB05 box model was altered for each test. Since there are substantial differences in PAN chemistry between the CBMIV and CB05 mechanisms (rate constants, separation of CBMIV PAN into PAN and PANX), many of the sensitivity tests were designed to investigate how these differences impacted ozone formation. However, the tests
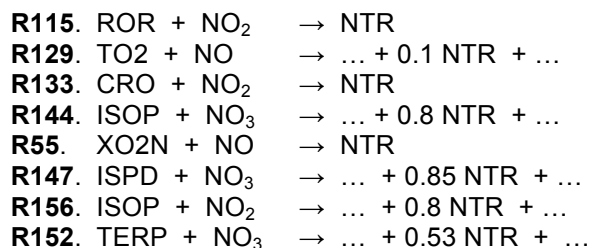
demonstrated that the differences in PAN chemistry between the mechanisms result in little impact on overall ozone production and therefore will not be discussed further here.

Table 1. Sensitivity tests as modifications of the base CB05 box model mechanism to investigate the impact of mechanistic changes between CBMIV and CB05 on ozone production.

Name	Description
xNTRrecycle	NTR recycling reactions removed
xiNOxrecycle	Inorganic NO_x recycling reactions removed
xallNOxrecycle	Both NTR and inorganic NO_x recycling reactions removed
xPANX	All PANX reactions removed (no ALDX emissions)
xPANXrecycle	PANX recycle reactions removed
xPANrecycle	PAN recycle reactions removed
PANcbm4	All PANX reactions removed and CBMIV PAN rate constants used
PANjpl06	PAN and PANX rate constants from NASA JPL 2006 used
xNTR-PANcbm4	xNTRrecycle + PANcbm4
xNTR-PANcbm4-xPANX	xNTRrecycle + PANcbm4 + xPANX
xPANX-xNTR	xPANX + xNTRrecycle
noALDXemis	No ALDX emissions (all as ALD2)

Another difference between the CBMIV and CB05 mechanisms is the addition of organic nitrate (NTR) recycling reactions. In CBMIV, NTR was produced via reactions of NO_x and/or NO_3 species with ROR, TO2, CRO, ISOP, XO2N, and ISPD. In CB05, an additional production reaction of NTR was included (TERP + NO_3) and two NTR recycling reactions (R61 and R62) were included which are absent from the CBMIV mechanism.
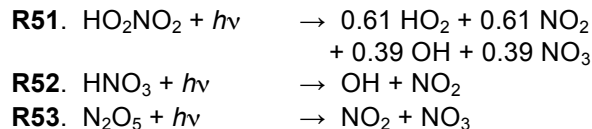
NTR Production Reactions in CB05

R115. ROR + NO_2 $\rightarrow$ NTR
R129. TO2 + NO $\rightarrow$ … + 0.1 NTR + …
R133. CRO + NO_2 $\rightarrow$ NTR
R144. ISOP + NO_3 $\rightarrow$ … + 0.8 NTR + …
R55. XO2N + NO $\rightarrow$ NTR
R147. ISPD + NO_3 $\rightarrow$ … + 0.85 NTR + …
R156. ISOP + NO_2 $\rightarrow$ … + 0.8 NTR + …
R152. TERP + NO_3 $\rightarrow$ … + 0.53 NTR + …

NTR Recycling Reactions in CB05

R61. NTR + OH $\rightarrow$ HNO$_3$ + …
R62. NTR + $h\nu$ $\rightarrow$ NO$_2$ + HO$_2$ + …

Additionally, a set of three inorganic nitrogen recycling reactions were added to the CB05 mechanism but are absent from CBMIV.

NO$_x$ Recycling Reactions in CB05

R51. HO$_2$NO$_2$ + $h\nu$ $\rightarrow$ 0.61 HO$_2$ + 0.61 NO$_2$
+ 0.39 OH + 0.39 NO$_3$
R52. HNO$_3$ + $h\nu$ $\rightarrow$ OH + NO$_2$
**R53**. N$_2$O$_5$ + $h\nu$ $\rightarrow$ NO$_2$ + NO$_3$

In both cases, the additional recycling reactions were added to CB05 in an attempt to better represent the fate of NO$_x$ over multiple days as a result of mid- to long-range transport from major NO$_x$ sources.

4. RESULTS AND DISCUSSION

Typical results of ozone production over the 10-day simulation period are shown in Figures 2 and 3 for two scenarios approximating urban conditions. In each case, the base CB05 run is shown in red and the base CBMIV run is shown as a black dashed line. The CB05 results show higher ozone concentrations as compared to the base CBMIV result, consistent with the historical results of the operational and experimental NAQFC tracks. Also shown in these figures are results from three sensitivity tests. For the sensi-tivity test *xNTRrecycle* (green), the NTR recycling reactions R61 and R62 were removed from the CB05 mechanism. For *xiNOxrecycle* (violet), the inorganic NO$_x$ recycling reactions R51, R52 and R53 were removed from CB05. And, for *xallNOxrecycle* (orange), both sets of recycling reactions (i.e., R61, R62 and R51, R52, R53) were removed from CB05. As the results in Figures 2 and 3 illustrate, removing the NTR recycling reactions from CB05 very nearly accounts for all of the difference between CB05 and CBMIV ozone. When only the inorganic NO$_x$ recycling reactions are removed from CB05, ozone production is decreased but not as much as when removing the NTR recycling reactions. When both sets of recycling reactions are removed, the amount of ozone produced is actually less than that produced by the CBMIV box model. Although only two scenarios are illustrated here, similar results

were obtained across most of the simulation suite scenarios.
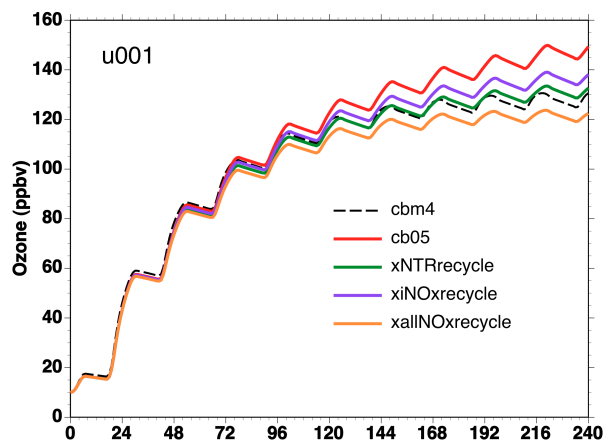
Figure 2. Ozone (ppbv) time series (hrs) results from box model simulation u001 for the two base models (CBM4 and CB05) and three sensitivity tests as described in the text.
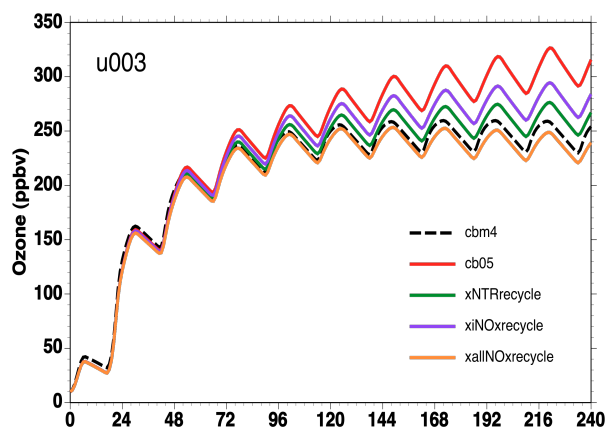
Figure 3. Ozone (ppbv) time series (hrs) results from box model simulation u003 for the two base models (CBM4 and CB05) and three sensitivity tests as described in the text.

In retrospect, the results obtained here are not surprising. By adding these recycling reactions into CB05, the effective level of NO$_x$ available for ozone production has been increased over that available with the CBMIV mechanism, given the same NO$_x$ emissions. In the CBMIV mechanism, the NTR species, in particular, is simply an irreversible sink for reactive nitrogen whereas in CB05, it serves a role similar to PAN and its homologues in that it is only a temporary reservoir and acts to redistribute NO$_x$ from major sources to

locations further downwind where additional ozone potentially may be produced. And likewise, the additional inorganic NO_x recycling reactions also act to increase the effective NO_x level in the model, although it should be expected that in a full model simulation the effect of these reactions may be lessened because some fraction of the HNO_3, HO_2NO_2 and N_2O_5 will be irreversibly removed via deposition processes that are not simulated in the simple box model. Full 3-D model sensitivity tests will be performed to confirm the box model results reported here.

5. CONCLUSIONS AND FUTURE WORK

Results of the sensitivity tests indicate that the NO_x recycling reactions that were included in CB05 but are absent from CBMIV are the primary cause of larger O_3 concentrations produced in the CB05 version of the NAQFC. These recycling reactions act to effectively increase the amount of NO_x available for O_3 production, even though NO_x emissions, initial and boundary conditions, and other parameters for the two simulations are identical. The presence of the recycling reactions has been shown to be important in regional- and global-scale simulations (Zaveri and Peters, 1999) and therefore should be included in a continental-scale air quality simulation. It seems likely that other compensating errors within the model framework account for better comparison of O_3 distributions with observations from the CBMIV version of the NAQFC system.

Future work will investigate individual chemical formation pathways of the organic nitrate species (NTR) and compare full model simulation results for NTR with available measurements. Other investigations have been performed to reduce the overall O_3 bias and additional studies are planned to evaluate other model processes that affect the effective NO_x budget.

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