Identifying the Causes of Differences In Ozone Production from the CB05 and CBMIV Mechanisms

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Goal: Identify Causes of Higher O_3 in CB05 as Compared to CBMIV

The NOAA National Air Quality Forecasting Capability (NAQFC) is a modeling system established by ARL and the National Weather Service (NWS) in 2004 to provide 48-hr ground-level ozone (O_3) forecasts for the conterminous U. S. (CONUS). Since its inception, the operational NAQFC has used a modified implementation of the Carbon Bond Mechanism version IV (CBMIV) as its gas-phase chemical mechanism. An experimental version of the NAQFC is run by the NWS in parallel with the operational track to provide a testbed for planned upgrades to the operational system. Since 2008, the experimental NAQFC has employed the updated 2005 version of the Carbon Bond Mechanism (CB05) as its gas-phase mechanism. The two parallel NAQFC tracks use identical base emissions inventories (with volatile organic compounds speciated appropriately for each mechanism), identical meteorological fields, and similar initial and boundary conditions. However, as seen in Figure 1, the CB05 version consistently produces higher O_3 concentrations than the CBMIV version, even though the emissions and input data for the systems are identical.

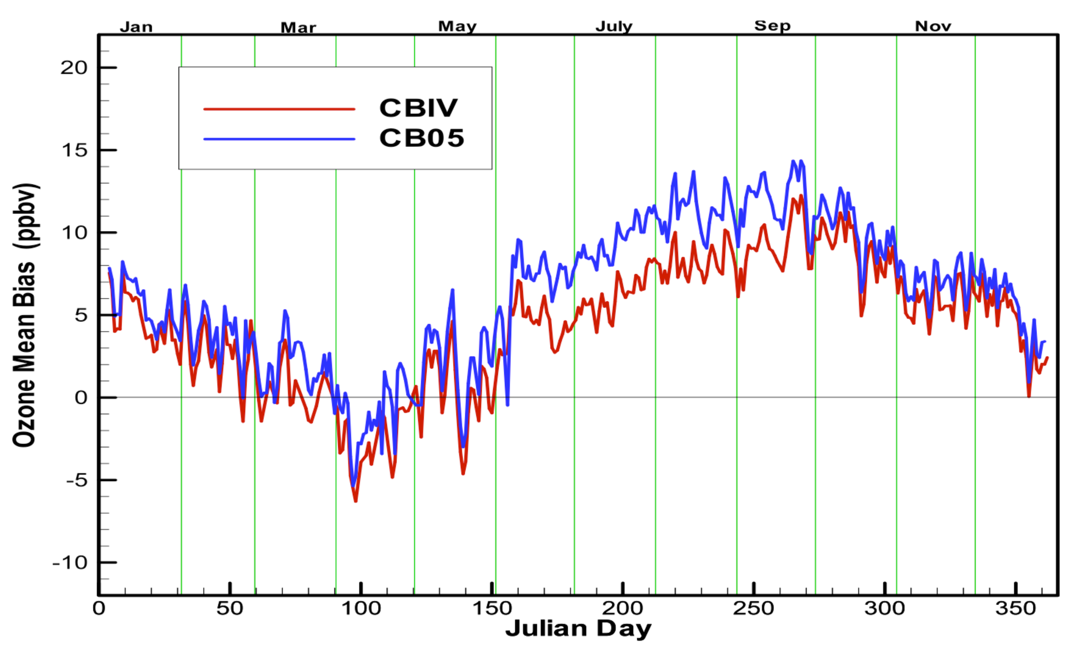

Figure 1. Ozone mean biases (CONUS-averaged) with respect to AIRNow measurements for the CBMIV and CB05 versions of the NAQFC for 2009

Approach

ARL initiated a research effort to identify the reasons for higher O_3 production from the CB05 version of NAQFC. Because air quality models include many processes (e.g., advection, turbulent diffusion, wet and dry deposition, etc.) that may obscure the underlying mechanistic reasons for the observed differences in O_3 concentrations, this work focused solely on differences between the CBMIV and CB05 mechanisms. Using this approach, and recognizing that CB05 is a "modified" version of CBMIV, a relatively simple comparison of the mechanisms was undertaken in ARL by performing sensitivity studies with box model versions of each of the mechanisms to identify which specific differences between CB05 and CBMIV account for the O_3 differences observed in full NAQFC simulations.

<u>Box Model Conditions</u>

- Fixed mixing layer height = 1000 m,
- No dry deposition,
- No mixing with background air,
- Fixed initial conditions for all scenarios.

T	= 298 K
p	= 1 atm
RH	= 50%
O_3	= 10 ppbv
CO	= 100 ppbv
CH_4	= 1600 ppbv
NO_x = all VOCs = 0	

Sensitivity Tests

Table 1 Description of the Box Model Sensitivity Tests as Modifications of Base CB05

Name	Description
xH2	molecular hydrogen reactions removed
xoddH&O	additional odd-H and odd-O reactions removed
xNO3night	additional NO_3 radical reactions removed
xNTRrecycle	organic nitrate recycling reactions removed
xiNOxrecycle	inorganic NO_x recycling reactions removed
xallNOxrecycle	both organic nitrate and inorganic NO_x recycling reactions removed
xexCH4	explicit methane chemistry removed
xETHA	explicit ethane chemistry removed (ETHA emissions as PAR)
xROOH	organic peroxide reactions removed
xIOLE	internal olefin chemistry removed; all emissions as OLE
xALDX	ALDX chemistry converted back to only ALD2 chemistry (no ALDX emissions)
xPANX	all PANX reactions removed (no ALDX emissions)
PANcbmiv	PAN chemistry as in CBMIV (xPANX + CBMIV PAN rate constants)
xTERP	explicit terpene chemistry removed; TERP emissions treated as in CBMIV -> 1 TERP = 1.5 ALD2 + 0.5 OLE + 6.0 PAR

Major Finding

Results of sensitivity tests performed by ARL (examples shown in Figures 2 and 3) indicate that the NO_x recycling reactions that are 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 systems are identical. The presence of the recycling reactions has been shown to be important in regional- and global-scale simulations 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. These results suggest that other studies must be performed to uncover and correct those compensating errors.

Inorganic NO_x recycling reactions included in CB05, but absent from CBMIV …

R51. $HO_2NO_2 + h\nu \rightarrow 0.61\ HO_2 + 0.61\ NO_2 + 0.39\ OH + 0.39\ NO_3$
R52. $HNO_3 + h\nu \rightarrow OH + NO_2$
R53. $N_2O_5 + h\nu \rightarrow NO_2 + NO_3$

Organic nitrate (NTR) recycling reactions included in CB05, but absent from CBMIV …

R61. $NTR + OH \rightarrow HNO_3 + HO_2 + 0.33\ HCHO + 0.33\ ALD2 + 0.33\ ALDX$
R62. $NTR + h\nu \rightarrow NO_2 + HO_2 + 0.33\ HCHO + 0.33\ ALD2 + 0.33\ ALDX$

Full model sensitivity simulations are being planned by ARL to confirm results from the box model study. A manuscript with a full description of the box model sensitivity studies and results is currently in preparation.

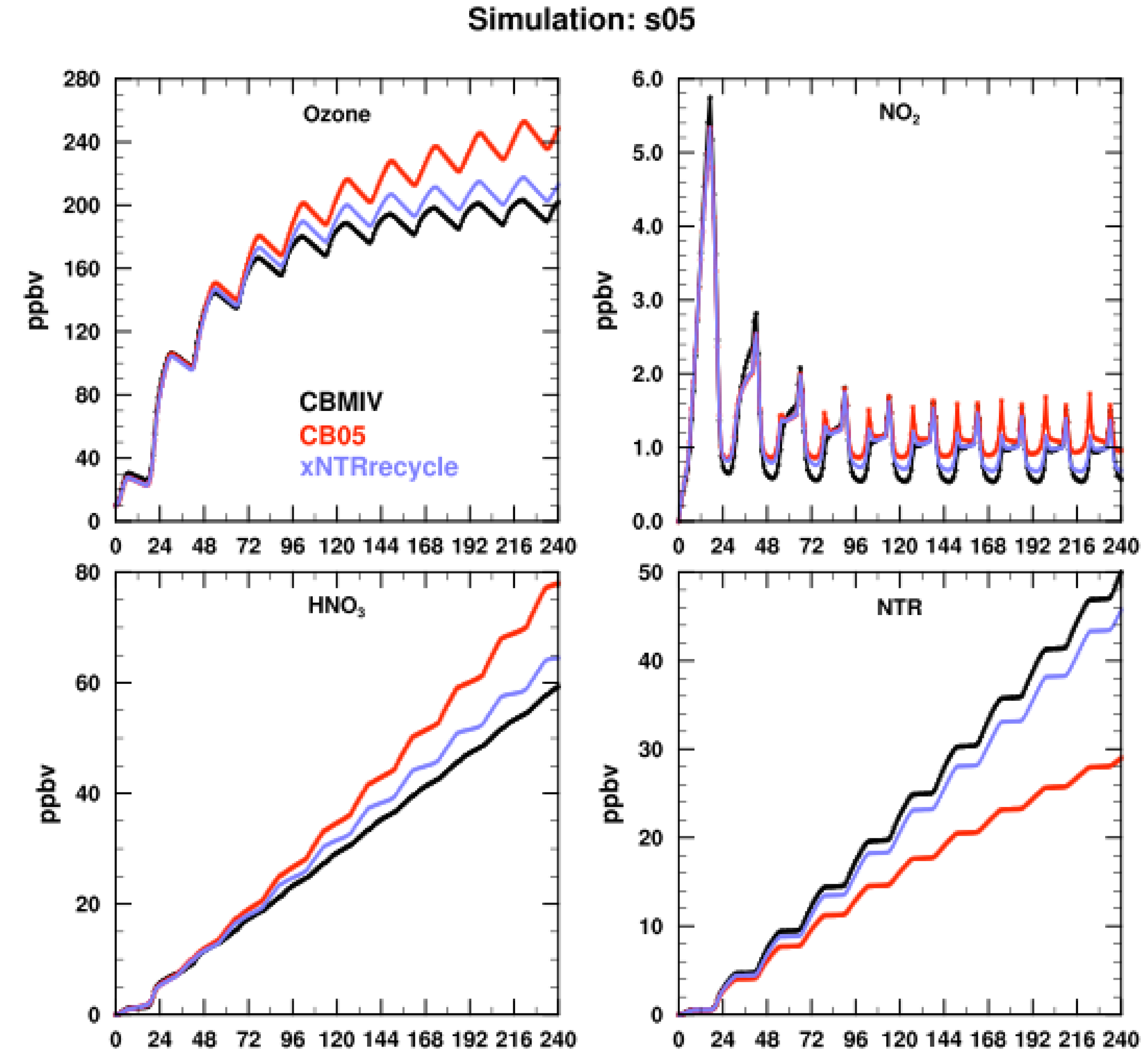

Figure 2. Box model results comparing base CB05, base CBMIV and sensitivity test xNTRrecycle for scenario simulation s05.

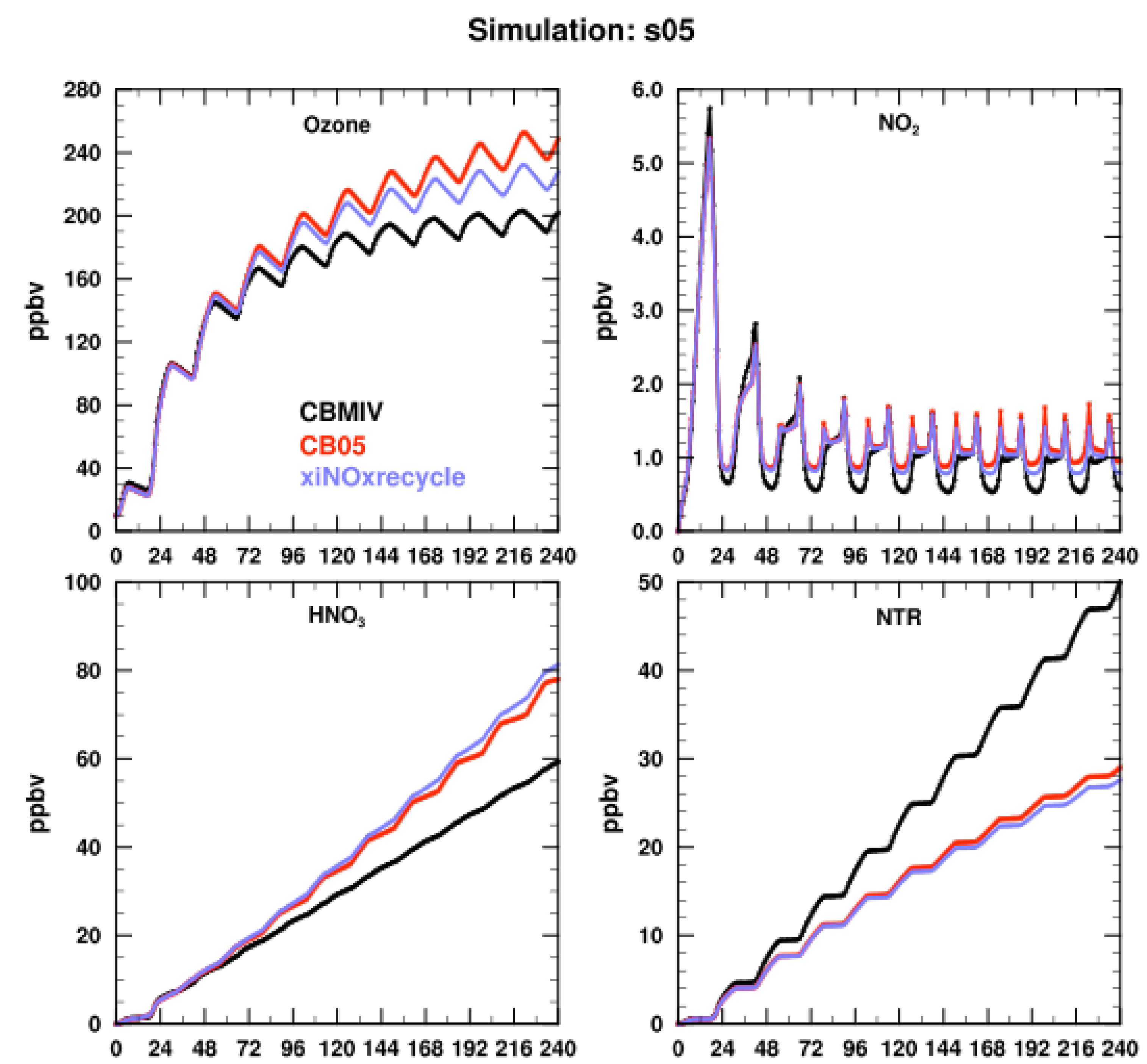

Figure 3. Box model results comparing base CB05, base CBMIV and sensitivity test xiNOxrecycle for scenario simulation s05.