Impact of CB6 and CB05TU chemical mechanisms on air quality

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1. Introduction

Atmospheric chemical mechanism plays an important role in air quality models. The Community Multiscale Air Quality (CMAQ) model uses the Carbon Bond 2005 chemical mechanism with updated toluene chemistry (CB05TU) (Whitten et al., 2010) for air quality model predictions. Yarwood et al. (2010) developed the Carbon Bond 6 (CB6) chemical mechanism. Here, we examine model (CMAQv5.0.1) predictions using the CB6 and CB05TU chemical mechanisms.

2. Model configuration

Feature	Description	Reference
Domain	Continental United States	
Horizontal grid size	12-km x 12-km	
Vertical layers	35 layers (1000-100 mb)	
Simulation period	July 1-31, 2006	
Meteorological model	WRFv3.3	Skamarock et al., 2008
Anthropogenic emissions	NEI 2005	
Biogenic emissions	BEISv3.14	Schwede et al., 2005
Boundary conditions	GEOS-CHEM v8-02-03	Bey et al., 2001
Initial conditions	Clean air	
Gas-phase chemistry		
CB05TU	74 species, 182 reactions	Whitten et al., 2010
CB6	90 species, 227 reactions	Yarwood et al., 2010

3. Results

The CB6 enhances monthly-mean surface-level O_3 by 3%, HO by 25%, TNO_3 by 16%, sulfate by 6%, and SOA by 3% while reducing H_2O_2 by 4%, organic nitrate by 22%, NO_z by 10%, MEPX (methyl hydroperoxide) by 36%, and PACD (peroxyacetic acid) by 69% (Table 1). MEPX and PACD decrease due to lower product yields and HO_2 levels in CB6. They play an important role in aqueous-phase oxidation of SO_2 into sulfate.

Table 1: Surface-level domain-wide mean prediction with each mechanism

Mechanism	CB05TU	CB6	CB6/ CB05TU
O_3 (ppbv)	38.9	40.1	1.03
H_2O_2 (ppbv)	1.32	1.27	0.96
HO (pptv)	0.073	0.091	1.25
Org. nitrate (pptv)	468	366	0.78
TNO_3 ($\mu g/m^3$)	0.965	1.12	1.16
NO_Z (ppbv)	1.36	1.22	0.90
MEPX (pptv)	760	489	0.64
PACD (pptv)	836	263	0.31
Sulfate ($\mu g/m^3$)	1.63	1.73	1.06
SOA ($\mu g/m^3$)	0.652	0.674	1.03

The CB6 reduces organic nitrate compared to the CB05TU values [Figure 1(a)]. The CB05TU contains one organic nitrate species while the CB6 contains two organic nitrate species. The CB6 contains isoprene nitrate which reacts much faster with HO than NTR. The inclusion of isoprene nitrate in CB6 leads to reduced organic nitrate predictions. The CB6 enhances inorganic nitrate [Figure 1(b)]. The CB6 produces much greater HO concentrations compared to those obtained with the CB05TU which consequently lead to greater daytime production of HNO_3 via NO_2 + HO reaction. Enhanced HNO_3 production in CB6 leads to greater levels of TNO_3.

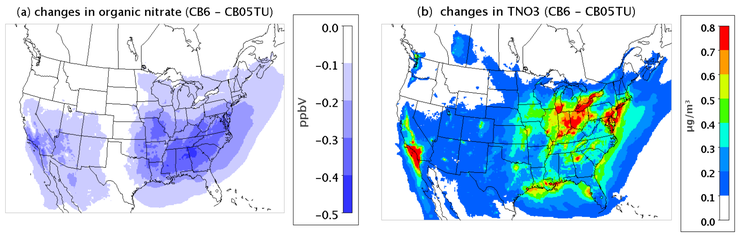

Figure 1: (a) Changes in organic nitrate concentrations between the CB6 and CB05TU (b) changes in TNO_3 concentrations between the CB6 and CB05TU.

Predicted changes in monthly mean surface-level ozone concentrations are presented in Figure 2(a). The CB6 enhances ozone by up to 3 ppbv in the eastern US and 4 ppbv in the western US. Predicted daily maximum 8-hr ozone concentrations are compared to observed data from the CASTNET sites in Figure 2(b). The CB05TU over-predicts ozone at the lower observed levels while under-predicting at the higher observed levels. The CB6 further deteriorates the agreement at the lower observed levels. However, it improves the agreement with the observed data at the higher end of observations.

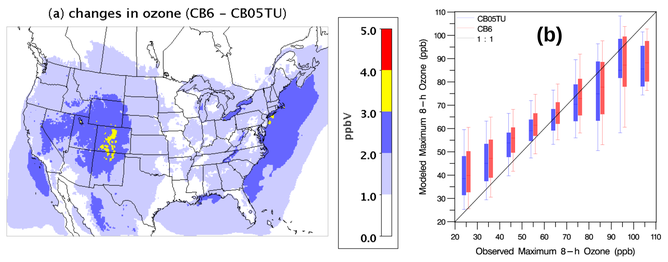

Figure 2: (a) Changes in ozone concentrations between the CB6 and CB05TU (b) a comparison of predicted daily maximum 8-hr ozone with observations from the CASTNET sites.

The CB6 enhances sulfate over a large area in eastern US [Figure 3(a)] due primarily to the increased SO_2 oxidation by enhanced HO. It enhances sulfate over a large area in Ohio River Valley by more than 1.0 $\mu g/m^3$. Its impact on sulfate in western US is small. Predicted sulfate concentrations are compared to observed data from the CASTNET sites in Figure 3(b). Both mechanisms under-predict sulfate compared to observed data. The CB05TU under-predicts by larger margins while the CB6 improves the agreement with the observed data. Additional sulfate production is needed for improving the agreement with observations.

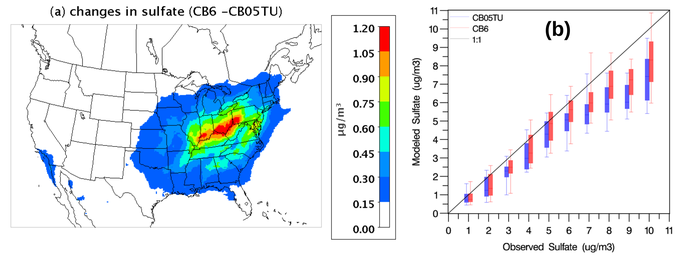

Figure 3: (a) Changes in sulfate concentrations between the CB6 and CB05TU (b) a comparison of sulfate predictions to observations from the CASTNET sites.

4. Summary

- CB6 reduces organic nitrate, NO_z, MEPX, and PACD compared to those obtained with the CB05TU.
- CB6 enhances hydroxyl radical, O_3, TNO_3, and sulfate compared to those obtained with the CB05TU.
- CB6 predicted sulfate agree better with observed data.
- CB6 predicted daily maximum 8-hr O_3 agree better with the observed data at the higher range of observed values.

5. References

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