

1. Introduction

Sulfate is an important constituent of fine particulate matter that affects human health (Pope et al., 2002) and alters the Earth's energy balance (Murphy et al., 2009). We examine sulfate predictions in the Northern Hemisphere using the Carbon Bond chemical mechanism with updated toluene chemistry (Whitten et al., 2010), the Regional Atmospheric Chemistry Mechanism (RACM2) (Goliff et al., 2013), and RACM2 coupled with Stabilized Criegee Intermediate (SCI) chemistry (Welz et al., 2012). We use the Community Multiscale Air Quality model (CMAQv5.0.2) with the sulfur tracking option (www.cmascenter.org).

2. Model configuration

Feature	Description	Reference
Domain	Northern Hemisphere	
Horizontal grid size	108km x 108km	
Vertical layers	44 layers (1000-50 mb)	
Simulation period	June, 2006	
Meteorological model	WRF v3.3	Skamarock et al., 2008
Anthropogenic emissions	EDGAR	edgar.jrc.ec.europa.eu/index.php
Boundary conditions	Clean air	
Initial conditions	Results of another model run	
Gas-phase chemistry		
CB05TU	85 species, 206 reactions	Whitten et al., 2010
RACM2	133 species, 373 reactions	Goliff et al., 2013
RACM2+SCI	136 species, 409 reactions	Welz et al., 2012

3. Stabilized Criegee Intermediate (SCI) Chemistry

We modify RACM2 to represent three explicit SCIs and their subsequent reactions with SO₂, NO₂, CO, aldehydes, ketones, water monomer, and water dimer. We also account for uni-molecular decomposition of SCIs. Welz et al. (2012) reported a directly measured rate constant of 3.9x10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for the reaction of SO₂ and the simplest SCI. We use it for SCI and SO₂ reactions. Welz et al. (2012) also measured a rate constant of 7.0x10⁻¹² cm³ molecule⁻¹ s⁻¹ for the reaction of NO₂ and SCI and this is used in this study. We use 1.2x10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ for the rate constant of the SCI/CO reaction following Master Chemical Mechanism (Jenkin et al., 1997). Taatjes et al. (2012) directly measured a rate constant of 9.5x10⁻¹³ cm³ molecule⁻¹ s⁻¹ for the reaction of SCI with acetaldehyde and a rate constant of 2.3x10⁻¹³ cm³ molecule⁻¹ s⁻¹ for the reaction of SCI and acetone which we use in this study. Rate constants for the reactions of SCIs and water monomer can vary substantially and direct measurements are not currently available. We use conformer dependent estimates of Anglada et al. (2012) for these reactions (2.9x10⁻¹⁹ - 2.4x10⁻¹⁵ cm³ molecule⁻¹ s⁻¹). Vereecken et al. (2012) estimated rate constants for the reactions of SCIs and water dimer (1.2x10⁻¹⁶ - 1.0x10⁻¹⁰ cm³ molecule⁻¹ s⁻¹) which we use in this study. We use first order rate constants reported by Vereecken et al. (2012) for uni-molecular decomposition of SCIs (0.21 - 0.388 s⁻¹).

4. Results

CB05TU produces the lowest sulfate prediction, RACM2 enhances sulfate production, and RACM2 with SCI chemistry even further enhances the sulfate production (Table 1). In addition to the gas-phase SO₂ oxidation by HO, CMAQ contains five aqueous-phase SO₂ oxidation pathways: H₂O₂, O₃, CH₃COOOH, CH₃OOH, and O₂ (metal catalysis). The domain-wide monthly-mean surface sulfate prediction by each pathway was calculated using the sulfur tracking model. In CB05TU, the H₂O₂ oxidation pathway produces the highest contribution of sulfate and the HO oxidation pathway produces the second highest contribution. In RACM2, the HO oxidation pathway produces the highest contribution and the H₂O₂ oxidation pathway produces the second highest contribution. The production of sulfate by the gas-phase pathway exceeds the collective production of sulfate by all aqueous-phase pathways. The inclusion of the SCI oxidation pathway in RACM2 further enhances sulfate production and the gas-phase pathways produce substantially more sulfate than the aqueous-phase pathways. The overall production of sulfate via the SCI initiated pathway exceeds the production via the O₃ oxidation pathway. The production of sulfate via CH₃COOOH pathway is substantially lower in RACM2 than that in CB05TU.

Table 1: Monthly-mean contribution of predicted sulfate in the surface layer (µg/m³)

Pathway	CB05TU	RACM2	RACM2 + SCI
Initial/boundary condition	0.149	0.149	0.149
Emissions	0.053	0.053	0.053
SO ₂ + gas (HO/SCI)	0.372	0.573	0.652
SO ₂ + H ₂ O ₂	0.564	0.526	0.511
SO ₂ + O ₃	0.040	0.038	0.034
SO ₂ + CH ₃ COOOH	0.045	0.001	0.001
SO ₂ + CH ₃ OOH	0.002	0.002	0.002
SO ₂ + O ₂ (metal catalysis)	0.002	0.002	0.002
Total	1.23	1.35	1.41

CB05TU produces sulfate concentrations by up to 5 µg/m³ in North America, 23 µg/m³ in Asia, 11 µg/m³ in Africa, and 6 µg/m³ in Europe [Figure 1(a)]. It predicts high sulfate concentrations over a large portion of China, India, and Middle East. RACM2 enhances sulfate by >0.4 µg/m³ in many areas of North America, >0.8 µg/m³ in large areas in Asia, Africa, and Europe [Figure 1(b)]. The oxidation by SCI enhances sulfate by >0.8 µg/m³ in large areas of North America and Asia [Figure 1(c)]. It also enhances sulfate in other areas by smaller margins. The production of sulfate by the SCI initiated oxidation pathway occurs in biogenically active areas.

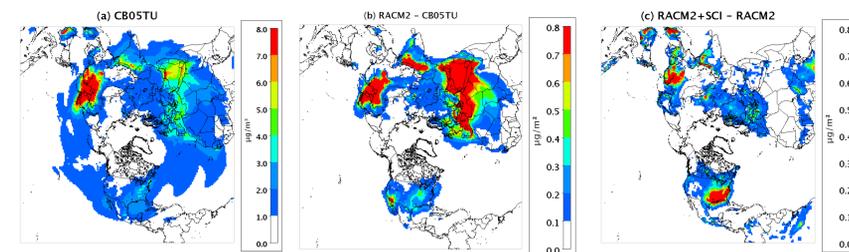


Figure 1: (a) Monthly mean sulfate concentration obtained with the CB05TU (b) difference of sulfate concentration obtained with the RACM2 and CB05TU (c) difference of sulfate concentration obtained with the RACM2+SCI and RACM2.

Mean observed sulfate concentration at the 87 CASTNET sites is 3.5 µg/m³. The CB05TU predicted value is 1.9 µg/m³ (r=0.82), RACM2 predicted value is 2.2 µg/m³ (r=0.83), and the RACM2+SCI predicted value is 2.6 µg/m³ (r=0.87). The model underestimates observed data primarily due to the large grid-size used in the study. Predicted sulfate concentrations are compared to observed data from the CASTNET sites in Figure 2. CB05TU under-predicts observed data. RACM2 improves the agreement with the observed data but its predictions are also lower than the observed data. RACM2 +SCI further improves the agreement with the observed data; however, its predictions are also lower than the observed data. Additional sulfate production is needed in the model for improving the agreement of model predictions with observed data.

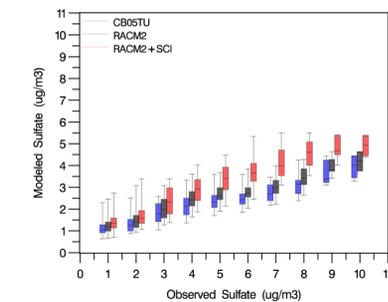


Figure 2: A comparison of predicted sulfate concentrations to the observed data from the CASTNET sites in the US.

5. Summary

- CB05TU predicts the lowest sulfate concentrations among the three mechanisms examined in this study.
- RACM2 enhances sulfate compared to those obtained with CB05TU due primarily to enhanced SO₂ oxidation by increased hydroxyl radical.
- SO₂ oxidation by SCI further enhances sulfate.
- Gas-phase oxidation produces the highest contribution and H₂O₂ oxidation produces the second highest contribution to predicted sulfate in RACM2.
- RACM2 + SCI predictions are the highest among the three mechanisms and compare best with the observed data.

6. References

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