SIMULATION OF PRIMARY AND SECONDARY (BIOGENIC AND ANTHROPOGENIC) ORGANIC AEROSOLS OVER THE UNITED STATES BY US EPA MODELS-3/CMAQ: EVALUATION AND REGIONAL ANALYSIS

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1. INTRODUCTION

Determination of the relative contributions of primary, secondary, biogenic and anthropogenic organic aerosols (OC) is important both for the design of air pollution control strategies and for understanding how different sources become mixed during long-range transport over the different regions of the US. In this paper, we present simulation results of primary and secondary (biogenic and anthropogenic) OC over the US with US EPA Models-3/CMAQ. We evaluate model performance in detail by comparing the simulated biogenic fractions, spatial and temporal variations of OC, elemental carbon (EC), total carbon (TC), primary OC, and secondary OC, with in-situ observations over the US for the periods from June 15 to July 15, 1999. Finally, we present regional analyses of distributions of primary, and secondary (biogenic, and anthropogenic) OC over the US.

2.0 MODE DESCRIPTION

The EPA Models-3/CMAQ (2003 release) modeling system is used in this study. The 32-km model domain covers the continental United States with a horizontal mesh of 178x124 32-km grid cells (See Figure 1). The vertical resolution is 22 layers, which are set on a sigma coordinate, from the surface to ~1600 hPa. The model is driven by meteorological fields from the MM5 meteorological model. Emissions inputs from version 1 of the 1999 EPA National Emissions Inventory (NEI99) are used. A condensed version of SAPRC-99 gas-phase chemical mechanism is used. The anthropogenic secondary OC consists of oxidation products from aromatics, alkanes, and cresol. Biogenic secondary OC is produced from the oxidation of monoterpenes. Gas/particle partitioning of these organic products is parameterized as an absorption process by assuming the formation of a quasi-ideal solution on the basis of their saturation concentrations.

3.0 SIMULATION AND MODEL EVALUATION OVER THE US

3.1 Measurements used for model evaluations

In the IMPROVE network, two 24-hour samples were collected at 63 sites over the US on quartz filters each week, on Wednesday and Saturday, beginning midnight local time. Daily $PM_{2.5}$ OC and EC concentrations were obtained at 8 SEARCH sites. Both IMPROVE and SEARCH networks use the thermal optical reflectance method (TOR). In the Southern Oxidants Study (SOS)/Nashville '99 Experiment (June 15-July 15, 1999), hourly $PM_{2.5}$ EC and OC concentrations were measured by the Magee scientific Aethalemeter, and flash vaporization carbon analyzer of ADI (Aerosol Dynamics, Inc.), respectively. The 11.5-hour (11.5 hours, beginning

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at 7 am and 7 pm) mean ratios of $^{14}C/^{13}C$ measured by radiocarbon analysis were used to determine the fractions of contemporary and fossil fuel carbon within an aerosol sample at the Nashville site. Daily $PM_{2.5}$ OC and EC concentrations were determined by thermal optical transmittance (TOT) at 3 ASACA sites. Observed primary and secondary OC concentrations were estimated on the basis of observed OC and EC, and air quality modeled primary OC/EC ratios by the emission/transport of primary OC/EC ratio method (Yu et al., 2003a).

3.2 Evaluation of model and discussions

In comparison with IMPROVE and SEARCH measurements, the model calculations match most of the observed EC and primary OC concentrations within a factor of 2 (r>0.4, NMB:-8% to 14%, see Table 1 and Figure 1). The model systematically underpredicts the OC, TC and secondary OC concentrations over the eastern US but not over the western US (NMB= -1%% to –45% for the US continent) (see Figure 2 and Table 1). The model results are in much better agreement with the EC, OC, secondary and primary OC concentrations determined by the TOR method (IMPROVE and SEARCH) than by the TOT method (ASACA) although TC concentrations of both methods were close (Figure 3). This is consistent with the fact that the OC/EC split factors used in the CMAQ emissions inputs are based on the TOR method. This points out that the consistent measurement methods for EC and OC is a necessary prerequisite to evaluate model performance. The reflectance method (such as IMPROVE and SEARCH) has been reported to have OC concentrations 10-15% lower and EC concentrations roughly a factor of two higher than the transmittance method (such as ASACA). The results in Figure 3 are consistent with these reports. The time-series comparisons of observed and modeled fractions of biogenic TC (BTC), and concentrations of OC, BTC, EC, and TC at the Nashville site show that there is general agreement between model results and observations.

4.0 REGIONAL DISTRIBUTIONS OF OC (PRIMARY, BIOGENIC AND ANTHROPOGENIC) OVER THE US

As shown in Figure 1, biogenic secondary OC was the highest over the West Pacific (~60%), followed by Southeast (~20%). Anthropogenic secondary OC over the eastern part (Midwest, Northeast and Southeast) was much higher than most of the west part, except in southern California (Los Angeles area). Primary EC was highest over the West Pacific, followed by Northeast and Southeast. There were similar patterns for the distributions of primary anthropogenic OC and TC with the highest concentrations over the southeast and west Pacific. The biogenic secondary OC of TC over the west and West Pacific regions were higher than 50% whereas these values were lower over the Central and Midwest.

4.4 References

Shaocai Yu, Robin Dennis, Prakash Bhave and Brian Eder, 2003a: Primary and secondary organic aerosols over the United States: estimates on the basis of observed organic carbon (OC) and elemental carbon (EC), and air quality modeled primary OC/EC ratios. *Atmos. Environ.,* (in review).

Shaocai Yu, et al., 2003b:. New unbiased symmetric metrics for evaluation of the air quality model. *Atmos. Environ.,* (in submission).

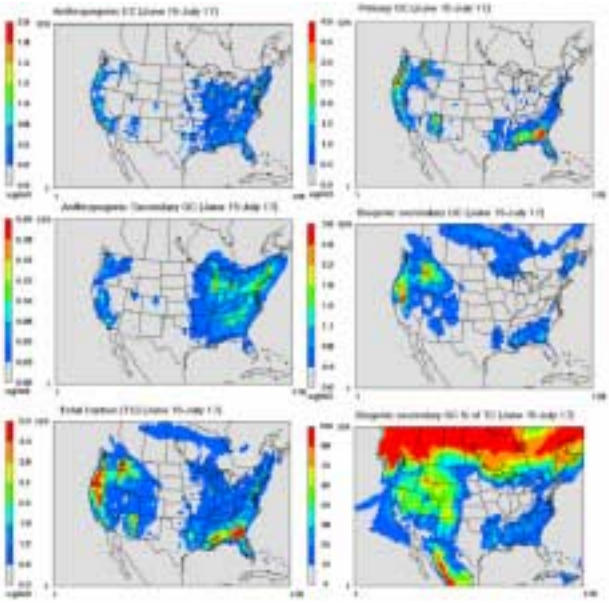

Figure 1. Spatial distribution of averages of primary EC and OC, secondary biogenic and anthropogenic OC, TC (μg C m^{-3}), and secondary biogenic OC % of total carbon (TC) over the US during June 15 and July 17, 1999.

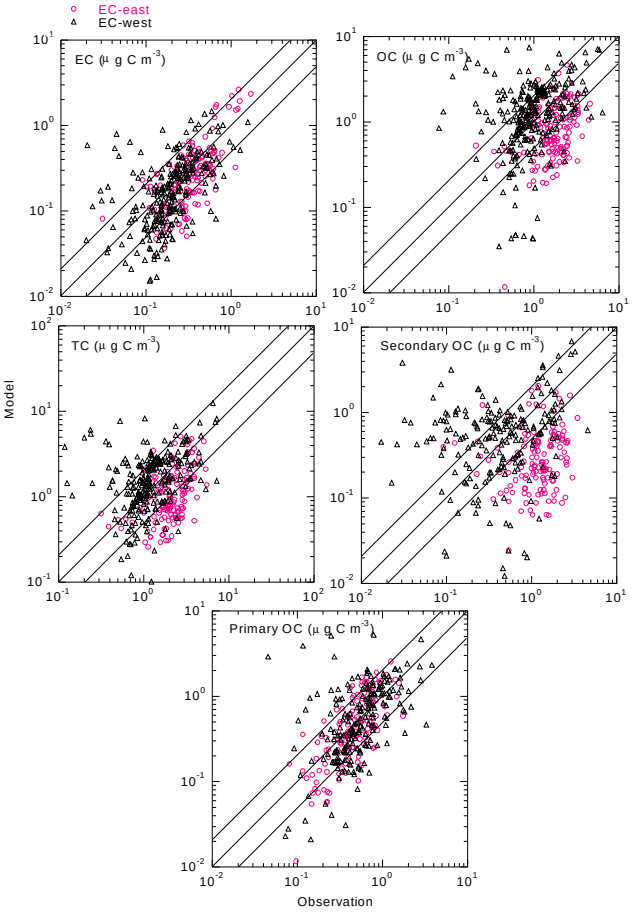

Figure 2. Comparison of model and IMPROVE observations for EC, OC, TC, primary OC and secondary OC over the US during June 15 and July 17, 1999.

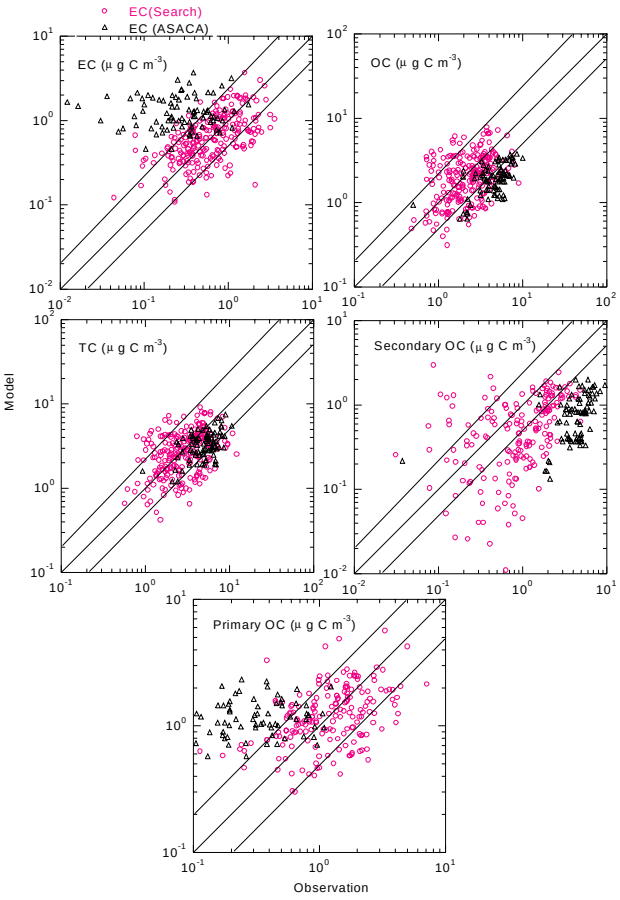

Figure 3. Same as Figure 2 but for SEARCH and ASACA.

Table 1.Statistical analysis.

	EC	OC	TC	OC_{sec}	OC_{pr}
IMPROVE					
Observation, mean	0.29	1.44	1.75	0.94	0.61
Model, mean	0.29	1.42	1.73	0.63	0.70
N	389	396	389	338	338
R	0.69	0.32	0.38	0.22	0.45
MB	0.00	-0.02	-0.02	-0.31	0.09
RMSE	0.24	1.35	1.48	1.01	0.66
NMB	-0.01	-0.01	-0.01	-0.33	0.14
NME	0.53	0.67	0.60	0.80	0.61
NMBF	-0.01	-0.02	-0.01	-0.50	0.14
NMEF	0.53	0.68	0.61	1.20	0.61
SEARCH					
Observation, mean	0.81	2.56	3.37	1.24	1.49
Model, mean	0.74	2.36	3.10	0.68	1.38
N	237	237	237	185	185
R	0.51	0.34	0.36	0.48	0.38
MB	-0.06	-0.20	-0.27	-0.55	-0.11
RMSE	0.59	1.69	2.10	1.02	1.04
NMB	-0.08	-0.08	-0.08	-0.45	-0.07
NME	0.50	0.48	0.45	0.62	0.50
NMBF	-0.09	-0.09	-0.09	-0.81	-0.08
NMEF	0.54	0.53	0.49	1.12	0.53
ASACA					
Observation, mean	0.36	4.84	5.28	4.56	0.35
Model, mean	1.37	2.05	3.45	0.86	1.22
N	82	84	82	82	82
R	0.07	0.58	0.52	0.52	0.04
MB	1.01	-2.80	-1.82	-3.71	0.87
RMSE	1.22	3.15	2.44	3.99	1.00
NMB	2.76	-0.58	-0.35	-0.81	2.52
NME	2.80	0.58	0.38	0.81	2.55
NMBF	2.76	-1.37	-0.53	-4.32	2.52
NMEF	2.80	1.38	0.58	4.33	2.55

MB, NME, NMB, RMSE, NMBF, and NMEF are mean bias, normalized mean error, normalized mean bias, root mean of square error, normalized mean bias factor, and normalized mean error factor, respectively (Yu et al., 2003b).