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

Shaocai Yu[+], Robin Dennis[+], Prakash Bhave[+] and Brian Eder[+]
Atmospheric Modeling Division
National Exposure Research Laboratory
U.S. EPA, NC 27711
e-mail: **yu.shaocai@epa.gov**
Voice (919) 541-0362 Fax (919) 541-137

1. INTRODUCTION

It is very difficult to quantify the relative contributions of primary OC (OC_{pri}) and secondary OC (OC_{sec}) in the atmosphere due to the lack of a direct chemical analysis technique. In this paper a hybrid approach is developed that combines the empirical primary OC/EC ratio method with a transport/emission model of OC_{pri} and EC, to estimate the relative contributions of OC_{sec} and OC_{pri}. Our approach is termed the emission/transport of primary OC/EC ratio method.

2. DESCRIPTION OF THE OBSERVATIONAL DATABASES AND METHODOLOGY

2.1. Observational Databases

Over the continental US, observed OC and EC concentrations are available from two networks, i.e., IMPROVE and SEARCH. The observational data between June 15 and August 31, 1999 are used. Both networks used the thermal optical reflectance method (TOR) to determine $PM_{2.5}$ OC and EC concentrations. In the IMPROVE network, two 24-hour samples are collected on quartz filters each week, on Wednesday and Saturday, beginning at midnight local time. The observed OC and EC data are available at 62 rural sites over the US. In the SEARCH network, daily (24-hour sample, beginning midnight local time) $PM_{2.5}$ OC and EC concentrations are available at 8 sites. In addition, hourly $PM_{2.5}$ OC and EC concentrations are available from two field campaigns in 1999 summer (i.e., SOS/Nashville '99 Experiment from June 15 to July 15, 1999, and SOS/Atlanta '99 Supersite Experiment from August 3 to September 1, 1999).

2.2 Methodology

Measurements of EC have been used to derive OC_{pri} based on the assumption that EC can serve as a tracer for OC_{pri} in the empirical primary OC/EC ratio approach . In this method, the OC_{pri} and OC_{sec} can be estimated as follows:

$$(OC_{pri}) = (OC/EC)_{pri}*(EC) \quad (1)$$

$$(OC_{sec}) = (OC_{tot}) - (OC_{pri}) \quad (2)$$

where $(OC/EC)_{pri}$ is the ratio of primary OC/EC, and OC_{tot} is measured total OC. In this study, the 2003 release version of EPA Models-3/CMAQ modeling system is used to obtain primary OC/EC ratios. The model domain covers the continental United States with a horizontal grid of 178x124 32-km grid cells. The vertical resolution is 21 layers. The model is driven by meteorological fields from the fifth Generation Pennsylvania State/National Center for Atmospheric Research Mesoscale Meteorological Model (MM5).

3. COMPARISON OF THE MODELED PRIMARY OC AND EC WITH OBSERVATIONS OVER THE US

Figure 1 shows that the model captures most of the observations within a factor of 2, especially for the mean results at each location . The domain mean of modeled EC is 0.60±0.64 $\mu g\ m^{-3}$, close to that (0.60±0.72 $\mu g\ m^{-3}$) of the observations. Table 1 lists the comparison of the modeled primary OC with those obtained by Zheng et al. [2002] at the 8 SEARCH sites for July 1999. There is general agreement between the model and observation-based results for both

[+] On assignment from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce

primary OC and primary OC/EC ratios, especially at the rural sites. For example, the mean modeled primary OC and primary OC/EC ratio at the OAK site are 2.20 and 4.31 μg C m^{-3}, respectively, very close to the observations (primary OC: 2.22 μg C m^{-3}; primary OC/EC ratio: 4.63). It is of interest to note that the model captures the observed primary OC and primary OC/EC ratio very well at the JST site in July but underpredicts the primary OC in August. A close inspection of results of Zheng et al. (2002) shows that there are significant OC_{pri} contributions from meat cooking in August, but none in July. This and other large, unexplained differences between the July and August results suggest that the JST comparisons in Table 1 be viewed with caution.

4. APPLICATIONS OF THE MODELED PRIMARY OC/EC RATIO APPROACH

4.1. Regional analysis of primary and secondary OC over the US

The modeled primary OC/EC ratios were applied to measurements of OC and EC from IMPROVE and SEARCH sites to calculate OC_{pri} and OC_{sec} for the period of June 15 to August 31, 1999. In the regional analysis, Northeast, Southeast, Midwest, and Central geographic regions were defined to match those used in the EPA regional haze regulations. As shown in Figure 2 and Table 2, the OC_{pri} concentrations can vary greatly from 0.19 μg C m^{-3} at PORE (Point Reyes National Seashore), CA, to 3.30 μg C m^{-3} at BHM (North Birmingham), AL, and OC_{sec} concentrations from 0.09 μg C m^{-3} at REDW to 2.06 μg C m^{-3} at BHM. Both OC_{pri} and OC_{sec} concentrations are the highest over the southeast area (OC_{pri}: 1.45 μg C m^{-3} and OC_{sec}: 1.40 μg C m^{-3}). It is of interest to note that OC_{sec} accounts for a large fraction of OC over the Northeast and Southeast.

4.2. Time-series of primary and secondary OC at Nashville and Atlanta sites

The hourly time-resolved OC and EC measurement data at Nashville and Atlanta can provide useful insights into the atmospheric processes of secondary OC formation. Figures 3 and 4 clearly show substantial diurnal variations of the measured EC and the calculated OC_{pri} and OC_{sec}. As expected, OC_{sec} makes the largest contribution to OC during the afternoon daylight hours (13:00 to 18:00 EST (or CST)) at both sites (54.9% for Nashville and 82.4% for Atlanta) because secondary OC formation is highly dependent on temperature and relative humidity. On average, OC_{sec} makes a greater contribution to OC at Atlanta (79.1%) than at Nashville (44.7%).

During the nighttime (19:00 to 6:00), OC_{pri} dominated at Nashville (61.0% to 62.2%), whereas OC_{sec} still dominated at the Atlanta site (78.9% to 80.5%). The mean primary (OC/EC) ratios at the Nashville urban site were modestly (less than 20%) higher than 1.0 whereas their mean values at the Atlanta urban site were modestly (20%) lower than 1.0.

5. REFERENCES

Zheng, M., Cass, G.R., Schauer, J.J., Edgerton, E.S., 2002. Source Apportionment of PM2.5 in the Southeastern United States using solvent-extractable organic compounds as tracers. *Environ.Sci. & Technology* **36**, 2361-2371.

Table 1 Comparison of the modeled primary OC concentrations (μg C m^{-3}) with those obtained by a chemical mass balance receptor model (Zheng et al. 2002) at 8 SEARCH sites. The modeled EC and primary OC/EC ratios ($(\frac{OC}{EC})_{pri}$) are also compared with the observations. The value is "mean ± standard deviation"

Site	Month (1999)	Type	Model			Observation		
			OCpri	EC	(OC/EC)pri	OCpri*	EC	(OC/EC)pri
BHM	7	Urban	1.64±0.45	1.05±0.23	1.56	3.15±0.35	2.48±1.14	1.27
CTR	7	Rural	1.92±0.64	0.46±0.12	4.17	0.67±0.08	0.50±0.20	1.34
GFT	7	Urban	4.08±1.25	1.05±0.29	3.89	1.17±0.13	0.75±0.49	1.56
OAK	7	Rural	2.20±1.13	0.51±0.16	4.31	2.22±0.36	0.48±0.28	4.63
JST	7	Urban	2.25±0.36	2.60±0.56	0.87	1.87±0.23	1.75±0.70	1.07
YRK	7	Rural	1.18±0.27	0.67±0.34	1.76	1.03±0.11	0.74±0.27	1.39
PNS	7	Urban	1.56±1.20	0.65±0.34	2.40	1.53±0.15	0.86±0.48	1.78
OLF	7	Suburban	1.48±0.74	0.84±0.25	1.76	0.67±0.06	0.55±0.28	1.22
JST	8	Urban	2.17±0.43	2.82±0.57	0.77	3.78±0.31	1.98±0.72	1.91

* Based on the estimations of Zheng et al. (2002).

Table 2 Mean values of estimated primary and secondary OC, percentages of primary and secondary OC ($\frac{OC_{sec}}{OC}$, $\frac{OC_{pri}}{OC}$) for each region over the US on the basis of results of IMPROVE and 3 rural SEARCH sites (CTR, OAK and YRK) (see Fig.1) during June 15 to August 31, 1999.

µg C m^{-3}	No. of sites	OC_{sec}	OC_{pri}	$\frac{OC_{sec}}{OC}$	$\frac{OC_{pri}}{OC}$
Northeast	5	1.27	0.39	0.76	0.24
Southeast	15	1.52	1.02	0.60	0.40
Central	4	0.98	0.53	0.65	0.35
West	28	0.51	0.51	0.50	0.50
West Pacific	13	0.94	0.96	0.49	0.51
Average	65	0.96	0.73	0.57	0.43

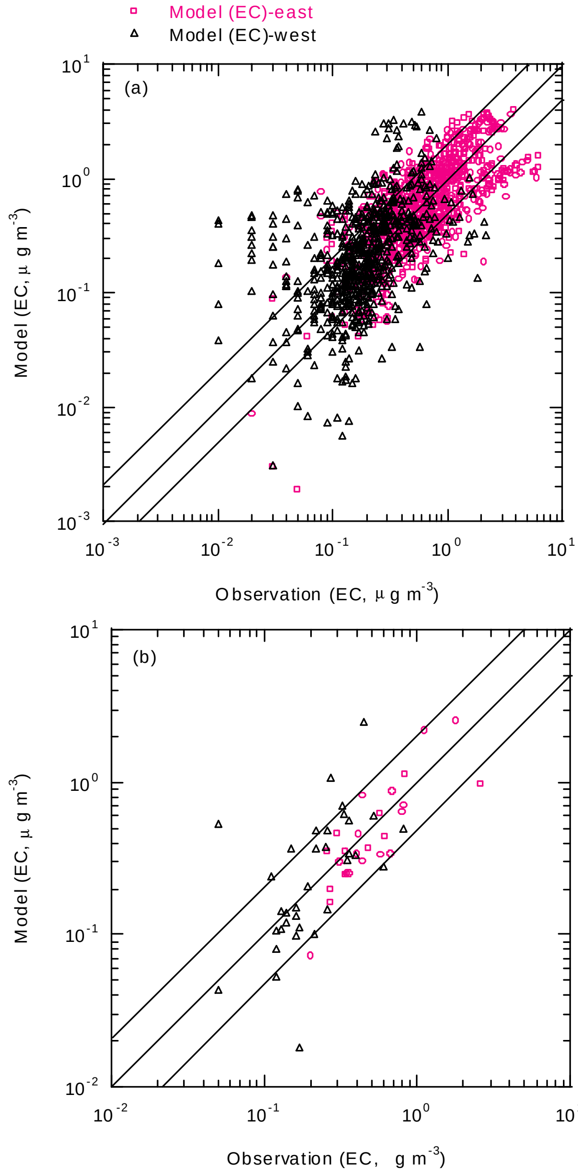

Figure 1. Comparison of modeled and observed EC concentrations over the US (a) individual and (b) mean values during the simulation period. The 1:1, 2:1 and 1:2 lines are shown for reference.

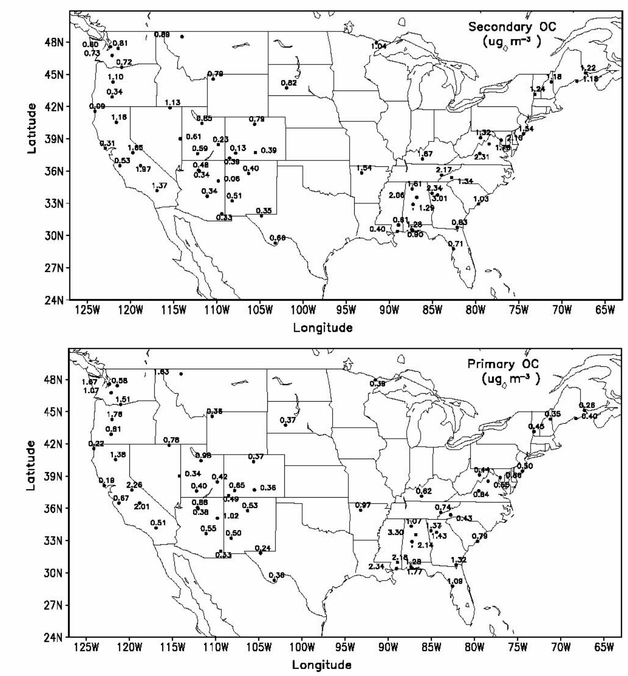

Figure 2. Distributions of mean values of estimated primary and secondary OC over the US

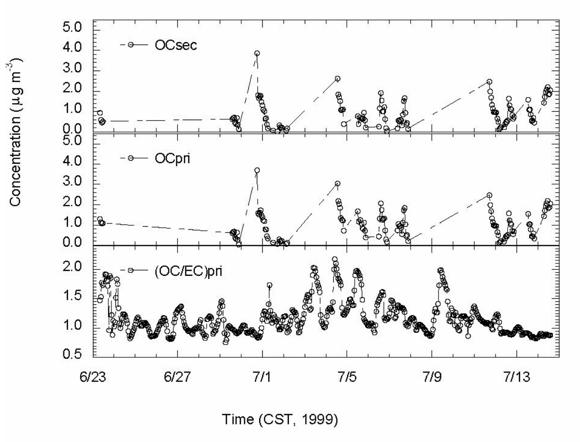

Figure 3. Hourly variations of estimated primary and secondary OC concentrations, and modeled primary OC/EC ratios at the Nashville site.

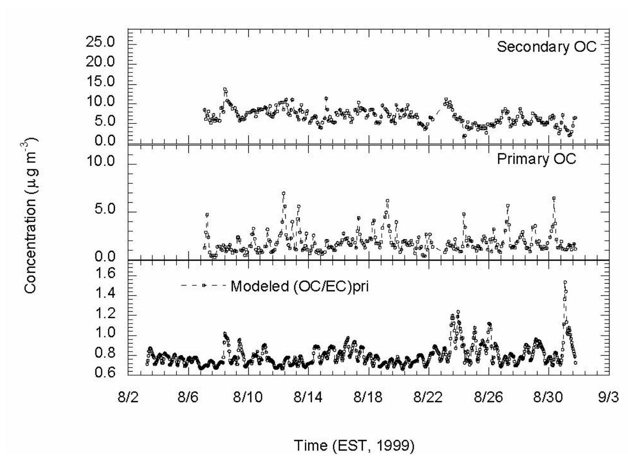

Figure 4. Same as Figure 3 but for the Atlanta site.