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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

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Abstract

The temporal and spatial distributions of primary and secondary organic carbon aerosols (OC) over the continental US from 15 June–31 August 1999, were estimated by using observational OC and elemental carbon (EC) data from Interagency Monitoring of Protected Visual Environments (IMPROVE) and Southeastern Aerosol Research and Characterization project (SEARCH) networks, coupled with the primary OC/EC ratios, $(OC/EC)_{pri}$, obtained from an emission/transport-model (i.e., US EPA Models-3/Community Multiscale Air Quality (CMAQ) model). It was found that the mean primary OC concentrations over the Northeast, Southeast, Central, West and West Pacific regions were 0.39 ± 0.09 (mean $\pm$ standard deviation), 1.02 ± 0.55, 0.47 ± 0.34, 0.51 ± 0.24, and $0.96\pm0.68\,\mu g\,C\,m^{-3}$, respectively, while the mean secondary OC concentrations were 1.27 ± 0.15, 1.52 ± 0.59, 0.90 ± 0.51, 0.51 ± 0.29, and $0.94\pm0.52\,\mu g\,C\,m^{-3}$, respectively. The contribution of secondary OC to the measured OC ranged from $48\pm16\%$ over the West to $77\pm3\%$ over the Northeast. The mean values of modeled $(OC/EC)_{pri}$ ratios ranged from 1.16 ± 0.13 over the Northeast to 3.49 ± 1.22 over the West Pacific. The results at the SEARCH sites indicate that the daily mean values of modeled $(OC/EC)_{pri}$ ratios ranged from 0.84 to 2.99 at Yorkville and the contributions of secondary OC to OC ranged from 0% to 66% at North Birmingham. Our results indicate significant temporal and geographic variability in the relative contributions of primary and secondary OC and that the use of a constant value to represent the $(OC/EC)_{pri}$ ratio at a location is not appropriate over the time scales studied here.
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Keywords: Primary and secondary organic aerosols; Air quality model; Primary OC/EC ratio; Observation; USA

1. Introduction

Fine particulate matter (PM) is a major concern in the US. Regulations call for the designation of areas that do not meet national standards and subsequent development of control strategies to attain the standards (EPA, 1998). Generally, over the continental US, the largest

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chemical component of the fine aerosol is sulfate in the East, carbonaceous aerosol in the Pacific Northwest, and nitrate in southern California (Malm et al., 1994; Yu et al., 2003). In most speciated measurements carbonaceous aerosol is one of the top three components of fine PM. Therefore, air pollution control strategies across the US will likely need to consider reducing ambient concentrations of carbonaceous aerosol.

Carbonaceous aerosol consists of particulate organic carbon (OC) and elemental carbon (EC). EC is directly emitted whereas particulate OC exists in two forms: primary OC (OC_{pri}), which is directly emitted to the atmosphere, and secondary OC (OC_{sec}), which is formed through atmospheric oxidation of reactive organic gases and subsequent gas-to-particle conversion processes. It is important to determine the relative contributions of OC_{pri} and OC_{sec} to the ambient aerosol burden, so that policymakers may determine which portion of the organic aerosol complex to target in their control strategy selection process. Up to now, much of the research work on determining the relative contributions of OC_{pri} and OC_{sec} over the US has focused on southern California (Gray et al., 1986; Pandis et al., 1992; Turpin and Huntzicker, 1995; Strader et al., 1999; Schauer et al., 1996). However, OC is a complex mixture of hundreds of different compounds whose individual concentrations, composition, distributions, and formation mechanisms are not quantitatively understood (Turpin et al., 2000). In fact, definitive measurement standards for OC and EC are lacking. Hence, the split between OC and EC must be operationally defined by the analysis methods or analysis protocol. Although the determination of total carbon ($TC = OC + EC$) is comparable between the two main analysis protocols, the thermo-optical transmittance method (TOT) and the thermo-optical reflectance method (TOR), the EC determinations differ by a factor of 2 (Chow et al., 2001). It is important to recognize this difference and account for it.

Due to the lack of an analytical technique for directly quantifying the atmospheric concentrations of OC_{pri} and OC_{sec}, four indirect methods have been developed to estimate their concentrations to date. One approach involves the application of an organic tracer-based receptor model to quantitatively apportion the source contributions to OC_{pri}, and then subtract the total apportioned OC_{pri} from the measured OC to obtain an estimate of OC_{sec} (Schauer et al., 1996; Zheng et al., 2002). This method, though quite robust, requires a speciated characterization of all major emission sources of organic aerosol in the study region as well as speciated measurements of the ambient organic aerosol. Obtaining such information is costly and labor-intensive, and may require sampling periods as long as 1 month to collect sufficient ambient aerosol mass such that the individual organic tracers can be quantified (Zheng et al., 2002). A second approach is to develop reactive chemical transport models for predicting the concentrations of OC_{pri} and OC_{sec} (Pandis et al., 1992; Strader et al., 1999). The input requirements of these models include inventories of gas and particle-phase emissions, chemical mechanisms for the oxidation of reactive organic gases, and partitioning characteristics of a variety of semi-volatile organic compounds. At present, these inputs are either unavailable or highly uncertain. A third approach is to use a non-reactive transport model to estimate OC_{pri}, and then calculate OC_{sec} at ambient monitoring sites by subtracting the modeled OC_{pri} from the measured OC (Hildemann et al., 1996). A disadvantage of this approach is that it is particularly sensitive to the emission inventory and transport algorithms used. A common result is that the modeled OC_{pri} exceeds the observed OC concentration (Hildemann et al., 1996) yielding unphysical, negative estimates of the OC_{sec} concentrations. A fourth approach that has received widespread application is to use EC as a tracer for OC_{pri} (Turpin et al., 1995; Castro et al., 1999). The advantage of this method is it relies mainly on ambient measurements of OC and EC, which are readily available. A major difficulty in applying this method is that the ratio of primary OC to EC, $(OC/EC)_{pri}$, is a function of the various emission sources contributing to a given atmospheric sample, and therefore, is influenced by meteorological conditions and emissions fluctuations (Turpin et al., 1995). Consequently, it is rather difficult to estimate the $(OC/EC)_{pri}$ ratio from ambient measurements alone (Strader et al., 1999).

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 concentrations of OC_{sec} and OC_{pri}. Our approach is termed the emission/transport of primary OC/EC ratio method. The advantages of this method are that it can provide $(OC/EC)_{pri}$ ratios at any time and any place, and therefore, OC_{pri} and OC_{sec} concentrations can be determined quantitatively at any time and location where EC and OC measurements are available. The shortcomings of this method are that the modeled $(OC/EC)_{pri}$ ratios depend on the accuracy of the emission source profiles, the emission rates and activity data in the emission inventory, and the meteorological fields by which the model is driven. In this application we use an air quality model to calculate hourly $(OC/EC)_{pri}$ ratios across the continental US. The transport model used is the US EPA Models-3/Community Multiscale Air Quality (CMAQ) model (Byun and Ching, 1999) and the emissions are from the 1999 EPA National Emissions Inventory (NEI99 version 1) (http://www.epa.gov/ttn/chief/). The methodology is developed below and the CMAQ predictions of OC_{pri} and EC are evaluated against observational data or the best available surrogates. The approach is applied to estimate OC_{pri} and OC_{sec} across two monitoring networks,

Interagency Monitoring of Protected Visual Environments (IMPROVE) and Southeastern Aerosol Research and Characterization project (SEARCH) that consistently use the same TOR method to define the split between OC and EC. To the authors' knowledge, this is the first attempt to estimate the spatial distributions of OC_{pri} and OC_{sec} over the continental US. Comparisons are made to the empirical primary OC/EC ratio method and to the source-apportionment of OC_{pri} method.

2. Description of methodology and observational databases

2.1. 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 (Turpin and Huntzicker, 1995; Strader et al., 1999). In this method, the OC_{pri} and OC_{sec} can be estimated as follows:

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

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

where OC_{tot} is the measured OC. Note that OC_{pri} and OC_{sec} may include both biogenic and anthropogenic contributions. The difficulty in applying these equations to atmospheric observations is that $(OC/EC)_{pri}$ ratios are unknown. In this study, the $(OC/EC)_{pri}$ ratios are calculated by using the procedure described below.

The 2003 release version of EPA Models-3/CMAQ modeling system is used to obtain $(OC/EC)_{pri}$ ratios. The EPA Models-3/CMAQ is documented by Byun and Ching (1999). A brief summary relevant to the present study is presented here. The model domain covers the continental US with a horizontal grid of 178×124 32-km grid cells (See Fig. 1a). The vertical resolution is

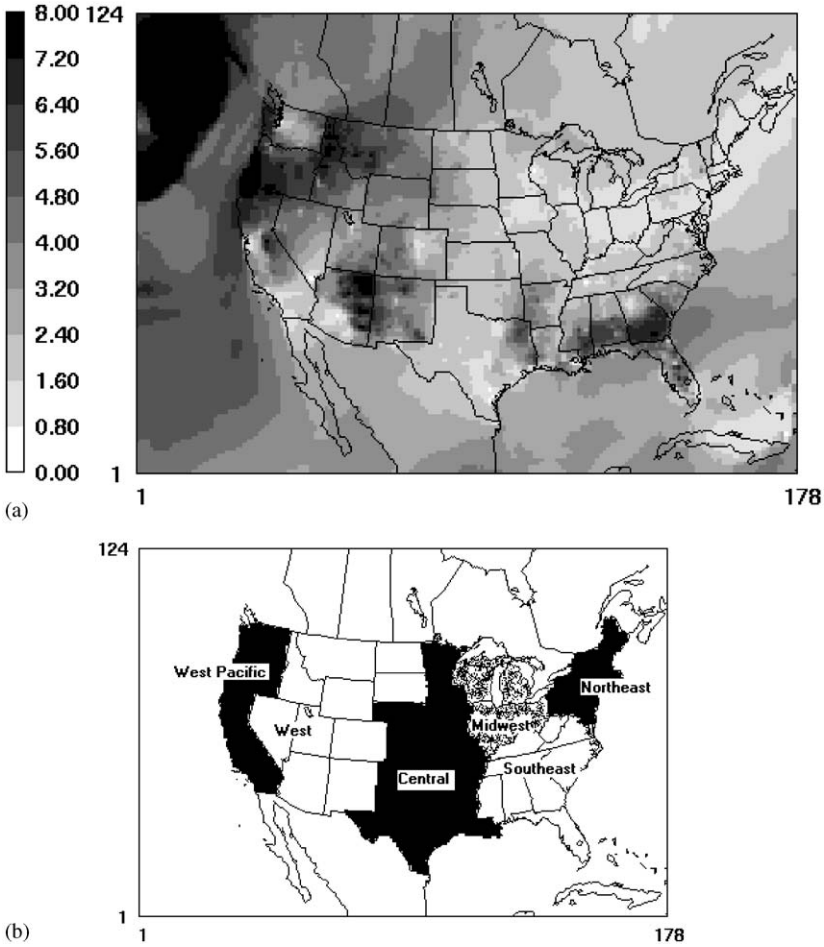

Fig. 1. (a) Spatial distribution of modeled mean $(OC/EC)_{pri}$ ratios over the US from 15 June to 31 August; (b) regional analysis map used in this study.

21 layers, which are set on a sigma coordinate, from the surface to ~100 mb. The model is driven by meteorological fields from the fifth Generation Pennsylvania State/National Center for Atmospheric Research Mesoscale Meteorological Model (MM5) (Grell et al., 1994). The aerosol processes performed in the CMAQ model include primary emissions, nucleation–condensation, coagulation, dry and wet depositions, and cloud processing. Emissions of gas-phase SO_2, CO, NO, NO_2, NH_3, VOC and primary $PM_{2.5}$ are based on the ozone season inventory in version 1 of the NEI99. The primary $PM_{2.5}$ emissions inventory is chemically speciated into SO_4^{2-}, NO_3^-, OC, EC and other material. Information on the speciation profiles and conversion factors used in NEI99 can be found on the Emissions Modeling Clearinghouse (EMCH) website (http://www.epa.gov/ttn/chief/emch/speciation/). For most source profiles in the NEI99, the TOR method was used to define the split between OC and EC (T. Pace, personal communication, 2003). Over the continental US, the most important sources of OC_{pri} are agricultural burning, soil dust, paved road dust and non-road diesel. The most important sources of primary EC are non-road diesel, on-road heavy-duty diesel vehicle, agricultural burning and jet fuel combustion (http://www.epa.gov/ttn/chief). In the CMAQ model, OC_{pri} and EC are tracked individually and treated as inert species, while participating in all aerosol processes.

As shown in Fig. 1a, boundaries of the model domain are located over the ocean or remote areas. The concentrations of all species were set to be those of clear tropospheric air conditions for initial and boundary conditions. A model spin-up period of 3 days was used to mitigate the effects of initial conditions on the model results. The hourly OC_{pri} and EC concentrations in the lowest vertical layer of the CMAQ model results from 15 June to 31 August 1999, are used in this study.

2.2. Observational databases

Over the continental US, observed OC and EC concentrations are available from two networks

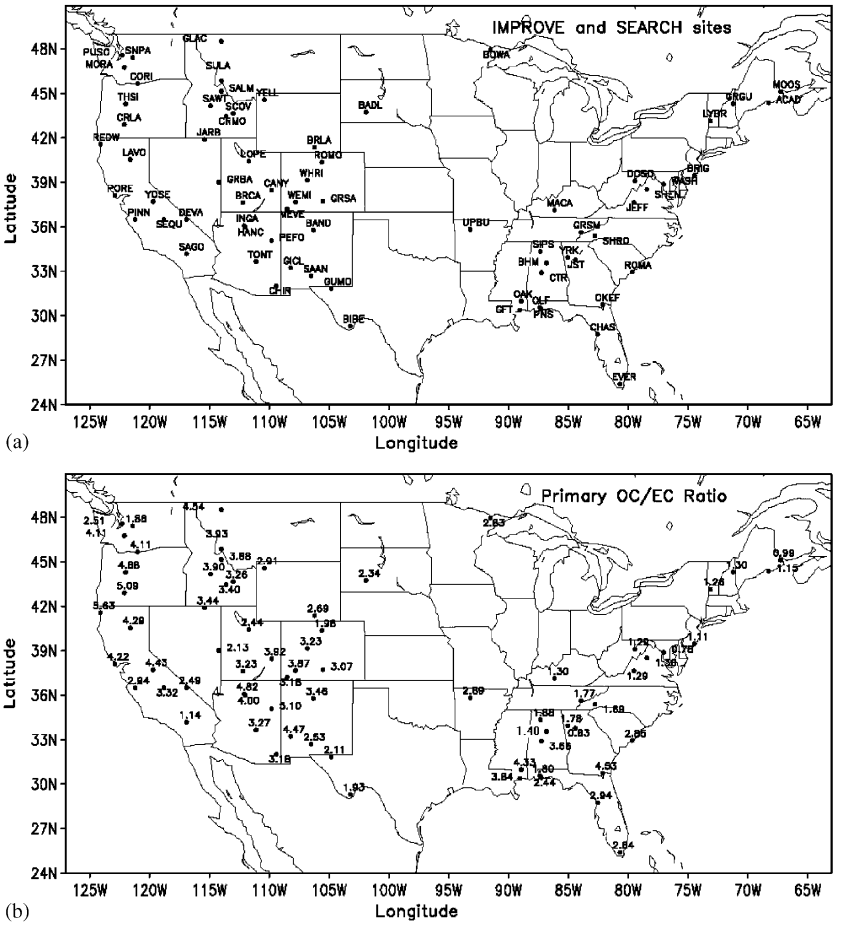

Fig. 2. (a) IMPROVE and SEARCH sites over the US; (b) mean values of modeled $(OC/EC)_{pri}$ ratios at each site.

IMPROVE and SEARCH. The observational data between 15 June and 31 August 1999 are used. Both networks used the TOR protocol to determine $PM_{2.5}$ OC and EC concentrations (Malm et al., 1994; Hansen et al., 2003). In the IMPROVE network, two 24-h samples are collected on quartz filters each week, on Wednesday and Saturday, beginning at midnight local time (Malm et al., 1994). The IMPROVE network data are available at 62 rural sites over the US. In the SEARCH network, daily (24-h sample, beginning midnight local time) $PM_{2.5}$ OC and EC concentrations are available at eight sites, i.e., three rural sites (Yorkville (YRK), GA; Oak Grove (OAK), MS; Centreville (CTR), AL) and four urban sites (Jefferson Street (JST), Atlanta; North Birmingham (BHM), AL; Gulfport (GFT), MS; Downtown Pensacola (PNS), FL) and Suburban Pensacola (OLF), FL (Hansen et al., 2003). Fig. 2a shows the locations of the IMPROVE and SEARCH stations whose observations are used in this study.

3. Comparison of the modeled OC_{pri} and EC with observations over the US

As EC concentrations are available from the IMPROVE and SEARCH networks, they can serve as a good test to evaluate the performance of the model on EC. Fig. 3 shows that the model captures most of the observations within a factor of 2, especially for the mean concentrations at each location (see Fig. 3b), over the continental US from 15 June to 31 August 1999. The domain mean of modeled EC is $0.60 \pm 0.64\,\mu g\,m^{-3}$ (mean $\pm$ standard deviation), close to that of the observations ($0.60 \pm 0.72\,\mu g\,m^{-3}$). The statistical *t*-test shows that there is not a significant difference in the domain means of the model predictions and observations for EC at the 95% confidence level. Fig. 4 shows comparisons between the model predictions and observations for daily EC concentrations at the 8 SEARCH sites. The model captures the daily variations of EC very well at all SEARCH sites with the exception of the BHM site.

Although there are no observations of OC_{pri} to evaluate the model results, monthly averaged OC_{pri} concentrations were calculated at eight SEARCH sites using the source-apportionment of OC_{pri} method (Zheng et al., 2002). Those results provide an indirect way to evaluate model performance for OC_{pri}. Table 1 lists the comparison of modeled OC_{pri} with those reported by Zheng et al. (2002) at the 8 SEARCH sites for July 1999. August results at the JST site are also compared. There is general agreement between the model and observation-based results for OC_{pri} and $(OC/EC)_{pri}$ ratios, especially at the rural sites. For example, the mean modeled OC_{pri} and $(OC/EC)_{pri}$ ratio at the

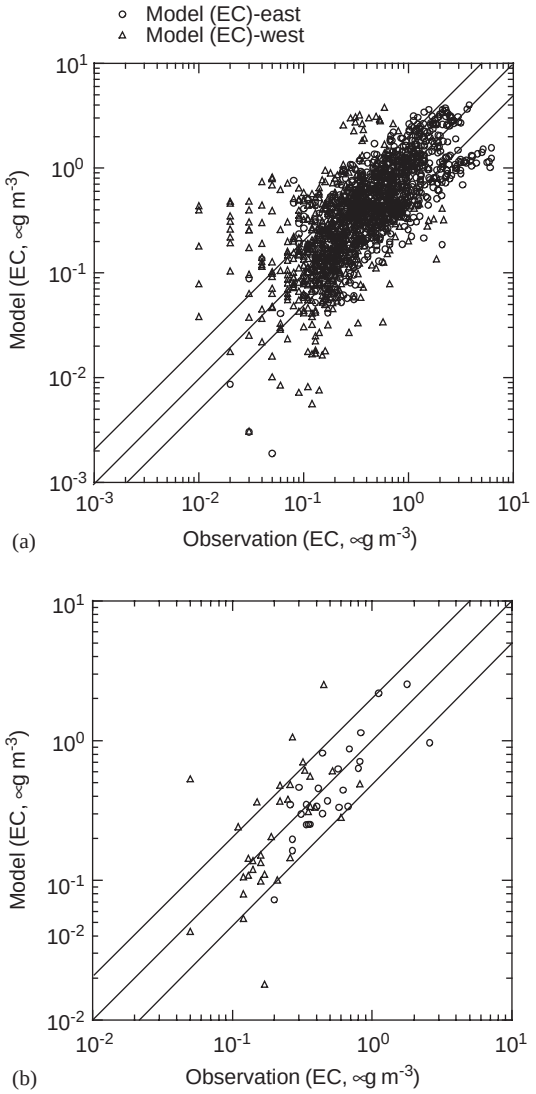

Fig. 3. Comparison of modeled and observed EC concentrations over the US (a) individual and (b) mean values during the simulation period. The 1:1, 2:1 and 1:2 lines are shown for reference. The "east" and "west" here represent the eastern and western parts with the divide being 100° West longitude.

OAK site are $2.20 \pm 1.13\,\mu g\,C\,m^{-3}$ and 4.39 ± 0.43, respectively, very close to the observations (OC_{pri}: $2.22 \pm 0.36\,\mu g\,C\,m^{-3}$; $(OC/EC)_{pri}$ ratio: 4.63). It is of interest to note that the model captures the observed OC_{pri} and $(OC/EC)_{pri}$ ratio very well at the JST site in July but underpredicts OC_{pri} 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.

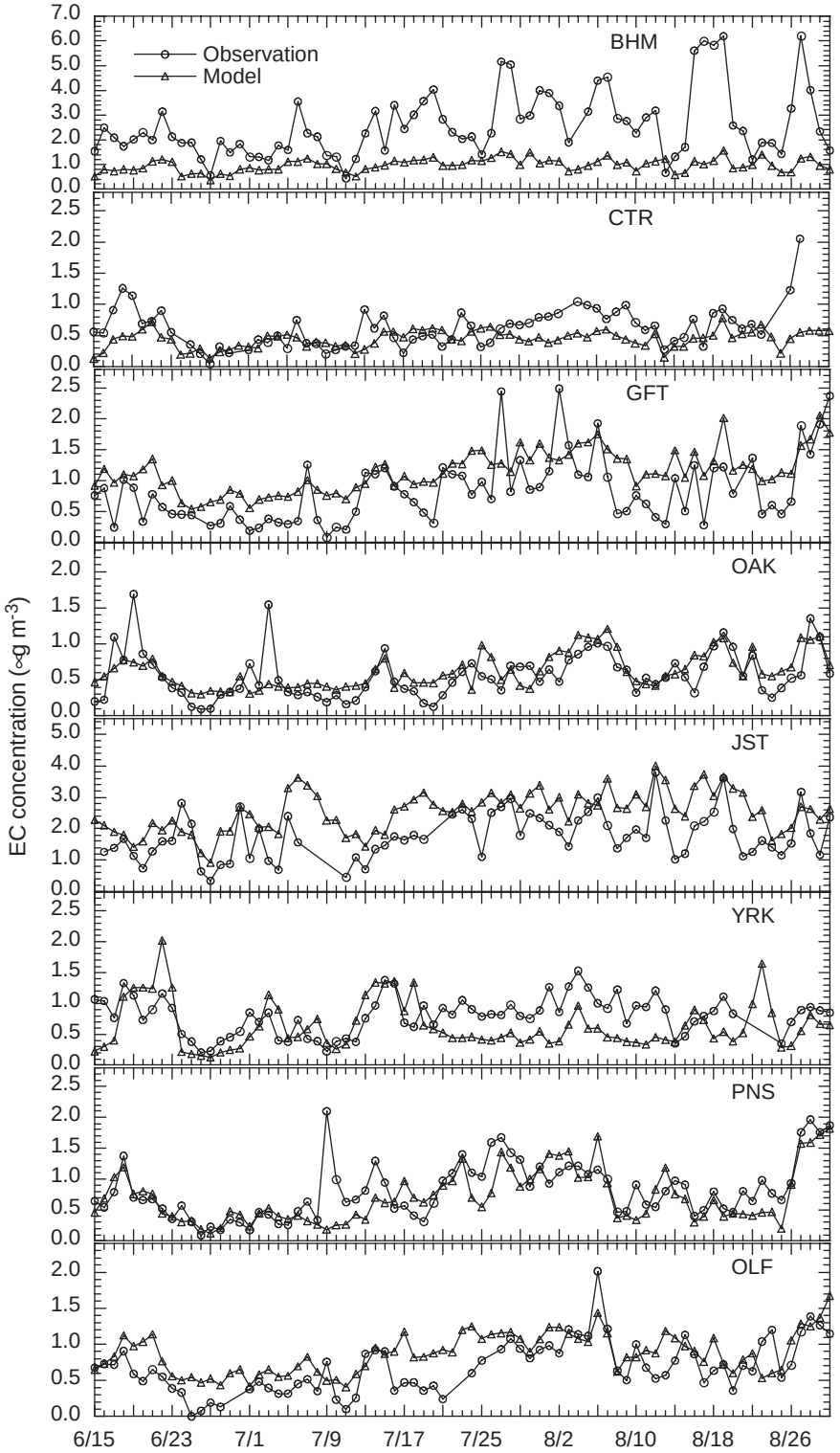

Fig. 4. The time-series of daily modeled and observed EC concentrations at the 8 SEARCH sites.

Table 1
Comparison of the modeled primary OC and EC concentrations ($\mu g\,C\,m^{-3}$), and mean primary OC/EC ratios ($(OC/EC)_{pri}$) with the observations (the value is mean ± standard deviation)

Site	Month (1999)	Type	Model			Observation		
			OC_{pri}	EC	$(OC/EC)_{pri}$	OC_{pri}[a]	EC	$(OC/EC)_{pri}$[b]
BHM	July	Urban	1.64±0.45	1.05±0.23	1.59±0.36	3.15±0.35	2.48±1.14	1.27
CTR	July	Rural	1.92±0.64	0.46±0.12	4.18±0.57	0.67±0.08	0.50±0.20	1.34
GFT	July	Urban	4.08±1.25	1.05±0.29	3.93±0.31	1.17±0.13	0.75±0.49	1.56
OAK	July	Rural	2.20±1.13	0.51±0.16	4.39±0.43	2.22±0.36	0.48±0.28	4.63
JST	July	Urban	2.25±0.36	2.60±0.56	0.88±0.14	1.87±0.23	1.75±0.70	1.07
YRK	July	Rural	1.18±0.27	0.67±0.34	1.94±0.58	1.03±0.11	0.74±0.27	1.39
PNS	July	Urban	1.56±1.20	0.65±0.34	2.35±0.35	1.53±0.15	0.86±0.48	1.78
OLF	July	Suburban	1.48±0.74	0.84±0.25	1.70±0.40	0.67±0.06	0.55±0.28	1.22
JST	August	Urban	2.17±0.43	2.82±0.57	0.77±0.06	3.78±0.31	1.98±0.72	1.91

[a]Based on the estimations of Zheng et al. (2002).
[b]Mean $(OC/EC)_{pri}$ values are calculated on the basis of mean OC^{a}_{pri} and observed EC concentrations.

The reasonably good agreement between model predictions and observations of the spatial and temporal variations of EC, OC_{pri}, and $(OC/EC)_{pri}$ ratios, especially at the rural sites, provides a basis to apply the modeled $(OC/EC)_{pri}$ ratios to IMPROVE and SEARCH observations for the purpose of estimating OC_{pri} and OC_{sec} concentrations in this work.

4. Applications of the emission/transport of primary OC/EC ratio method

4.1. Regional analysis of modeled $(OC/EC)_{pri}$ ratios over the US

Using the CMAQ model and the NEI99, the emission/transport-model procedure was carried out for the period from 15 June to 31 August 1999, to calculate $(OC/EC)_{pri}$ ratios across the US. In the regional analysis, Northeast, Southeast, Midwest, and Central geographic regions were defined to match those used in the EPA regional haze regulations (http://www.epa.gov/air/visibility/index.html) as shown in Fig. 1b. The regional haze western region was further divided into West and West Pacific sub-regions in this work because the aerosol concentrations over the West Pacific were much higher than those over the West region as shown below. As aerosols are major contributors to regional haze, these regional groupings in Fig. 1b are considered to be reasonable. Fig. 1a shows the spatial distribution of the modeled mean $(OC/EC)_{pri}$ ratios over the US. As shown in Figs. 1a and 2b, and Table 2, the $(OC/EC)_{pri}$ ratios are the highest over the West (3.49±0.89) and West Pacific (3.49±1.22) regions with the lowest value over the Northeast (1.16±0.13). The mean $(OC/EC)_{pri}$ ratios can vary substantially from 0.78 at Washington DC (WASH) in the Southeast, to 5.63 at Redwood National Park (REDW) in CA (see Fig. 2b). Note that the mean values over the Northeast and Central regions in Table 2 may not be regionally representative because the observational sites over these two regions are sparse (see Figs. 1 and 2).

4.2. Spatial distributions and regional analyses of OC_{pri} and OC_{sec} over the US

The modeled $(OC/EC)_{pri}$ 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 15 June to 31 August 1999. As shown in Fig. 5 and Table 2, the OC_{pri} concentrations can vary greatly from $0.19\,\mu g\,C\,m^{-3}$ at Point Reyes National Seashore (PORE), CA, to $3.30\,\mu g\,C\,m^{-3}$ at BHM, AL, and OC_{sec} concentrations from $0.09\,\mu g\,C\,m^{-3}$ at REDW to $3.01\,\mu g\,C\,m^{-3}$ at JST. Both OC_{pri} and OC_{sec} concentrations are the highest over the southeast area (OC_{pri}: $1.52\pm0.59\,\mu g\,C\,m^{-3}$ and OC_{sec}: $1.02\pm0.55\,\mu g\,C\,m^{-3}$). It is of interest to note that OC_{sec} accounts for a large fraction of OC over the Northeast and Southeast (>60%), whereas, OC_{pri} and OC_{sec} concentrations make an approximately equal contribution to OC over the West and West Pacific regions (Fig. 5 and Table 2).

4.3. Time-series of OC_{pri} and OC_{sec} at 8 SEARCH sites

The daily averaged OC_{pri} and OC_{sec} concentrations were calculated at 8 SEARCH sites. The significant daily variations of the $(OC/EC)_{pri}$ ratios and percentages of secondary OC contributing to OC at each site are shown in Fig. 6. Generally speaking, the daily means of $(OC/EC)_{pri}$ ratios can vary more significantly at the rural sites (CTR, OAK, and YRK) than at 4 urban sites.

Table 2
Mean values of measured OC, EC, TC (OC + EC), calculated primary and secondary OC, percentages of primary and secondary OC (OC_{sec}/OC, OC_{pri}/OC) and modeled primary OC/EC ratios ($(OC/EC)_{pri}$) for each region over the US on the basis of results of IMPROVE and three rural SEARCH sites (CTR, OAK and YRK) (see Fig. 1) during 15 June to 31 August, 1999. The value is "mean ± standard deviation"

$\mu g\,C\,m^{-3}$	No. of sites	Observation			Calculated				Modeled
		OC	EC	TC	OC_{sec}	OC_{pri}	$OC_{sec}/OC(\%)$	$OC_{pri}/OC(\%)$	$(OC/EC)_{pri}$
Northeast	5	1.66 ± 0.23	0.34 ± 0.07	2.00 ± 0.29	1.27 ± 0.15	0.39 ± 0.09	77 ± 3	23 ± 3	1.16 ± 0.13
Southeast	15	2.54 ± 0.65	0.52 ± 0.23	3.06 ± 0.84	1.52 ± 0.59	1.02 ± 0.55	60 ± 18	40 ± 18	2.28 ± 1.17
Central	4	1.37 ± 0.84	0.21 ± 0.10	1.59 ± 0.94	0.90 ± 0.51	0.47 ± 0.34	66 ± 6	34 ± 6	2.44 ± 0.50
West	28	1.02 ± 0.44	0.18 ± 0.08	1.20 ± 0.51	0.51 ± 0.29	0.51 ± 0.24	48 ± 16	52 ± 16	3.49 ± 0.89
West Pacific	13	1.91 ± 1.11	0.37 ± 0.20	2.28 ± 1.25	0.94 ± 0.52	0.96 ± 0.68	53 ± 19	47 ± 19	3.49 ± 1.22
Average	65	1.68 ± 0.91	0.33 ± 0.21	2.01 ± 1.09	0.96 ± 0.59	0.72 ± 0.51	56 ± 18	44 ± 18	2.97 ± 1.22

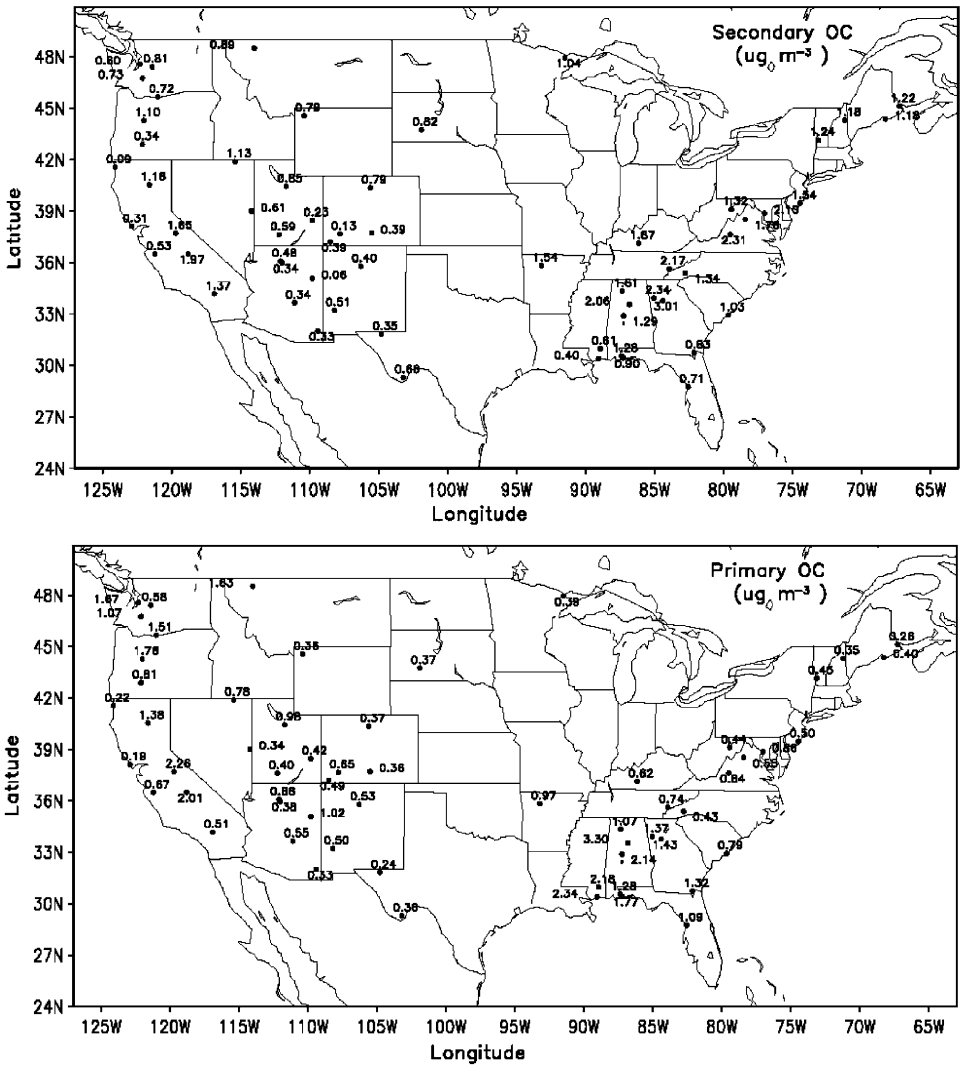

Fig. 5. Spatial distribution of mean values of estimated primary and secondary OC concentrations over the US.

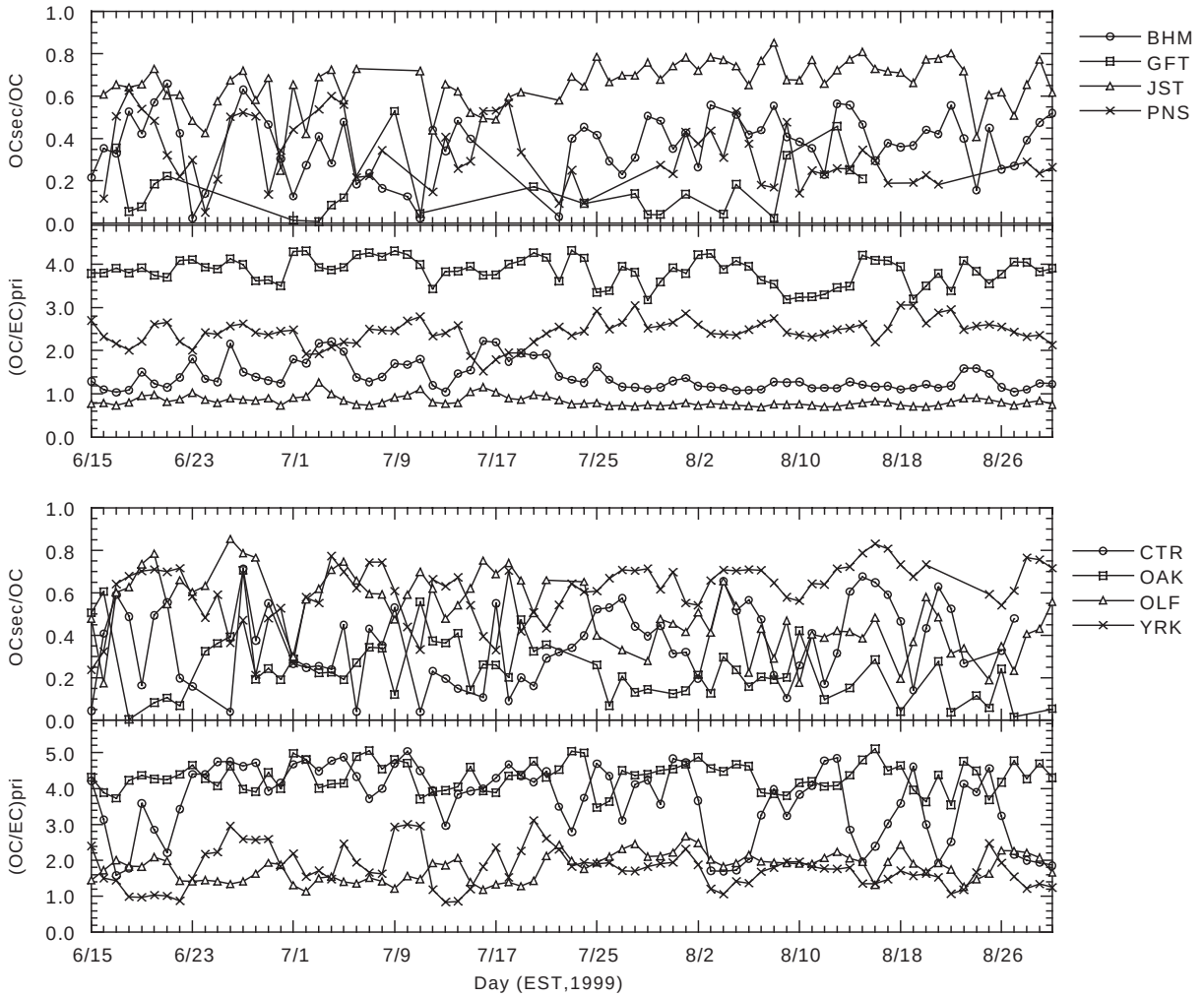

Fig. 6. Daily variations of percentages of secondary OC to OC and $(OC/EC)_{pri}$ ratios at eight SEARCH sites.

For example, the $(OC/EC)_{pri}$ ratios varied from 1.59 to 5.11 (mean: 3.66 ± 1.01) at CTR whereas these values varied from only 0.73 to 1.27 (mean: 0.83 ± 0.11) at JFT (see Table 3). This differing variability is likely due to the fact that the background air conditions at the rural sites are more easily affected by the long-range transport of pollutants. It is of interest to compare the results at the nearest paired urban/rural sites (i.e., JST/YRK, BHM/CTR, GFT/OAK, and PNS/OLF, see Table 3). The EC, TC and OC_{pri} concentrations at the urban sites were consistently higher than those in the corresponding paired rural sites (Table 3). However, the OC_{sec} concentrations at rural sites may exceed those at the nearby urban sites (e.g., compare the OAK site with the GFT site).

The daily concentrations of OC_{sec} varied from $0.26\,\mu g\,C\,m^{-3}$ at GFT to $1.75\,\mu g\,C\,m^{-3}$ at JST while the OC_{pri} daily concentrations varied from $0.78\,\mu g\,C\,m^{-3}$ at OLF to $2.68\,\mu g\,C\,m^{-3}$ at BHM. The OC_{sec} can make a significant contribution to OC as large as $66 \pm 11\%$ at JST. This provides supportive evidence that secondary OC formation might explain the high percentage of unapportioned PM OC concentrations observed in July as noted by Zheng et al. (2002). Table 3 also shows that OC_{pri} made more contributions to OC than OC_{sec} at most of the SEARCH sites.

With the availability of the hourly air quality model predictions of OC and EC as pseudo- data, it is instructive to compare the ratio derived by the empirical $(OC/EC)_{pri}$ ratio approach using the measurement data, first, with the $(OC/EC)_{pri}$ ratio that would be derived from the model concentrations following the empirical $(OC/EC)_{pri}$ ratio approach and, second, with the ratio derived directly by the emission/transport of $(OC/EC)_{pri}$ ratio method. This is possible for the Atlanta data. At the Atlanta site, the hourly $PM_{2.5}$ OC and EC

Table 3
Mean values ($\mu g\,C\,m^{-3}$) of measured OC, EC, TC, calculated primary and secondary OC, percentages of primary and secondary OC and modeled primary OC/EC ratios at eight paired urban/rural sites of SEARCH from 15 June to 31 August, 1999. The value is "mean ± standard deviation"

$\mu g\,C\,m^{-3}$	Type	Observation			Calculated				Modeled
		OC	EC	TC	OC_{sec}	OC_{pri}	OC_{sec}/OC (%)	OC_{pri}/OC (%)	$(OC/EC)_{pri}$
BHM1	Urban	5.15 ± 2.31	2.60 ± 1.34	7.77 ± 3.54	2.09 ± 1.19	3.32 ± 1.51	37 ± 15	63 ± 15	1.40 ± 0.32
CTR1	Rural	3.35 ± 1.37	0.62 ± 0.32	3.98 ± 1.66	1.29 ± 0.87	2.14 ± 0.92	36 ± 18	64 ± 18	3.66 ± 1.01
GFT1	Urban	2.60 ± 1.59	0.83 ± 0.54	3.49 ± 2.09	0.40 ± 0.34	2.34 ± 1.34	16 ± 14	84 ± 14	3.84 ± 0.31
OAK1	Rural	2.82 ± 1.43	0.57 ± 0.33	3.39 ± 1.73	0.61 ± 0.42	2.18 ± 1.24	24 ± 15	76 ± 15	4.33 ± 0.39
JST1	Urban	4.44 ± 1.74	1.78 ± 0.74	6.22 ± 2.35	3.01 ± 1.45	1.43 ± 0.52	66 ± 11	34 ± 11	0.83 ± 0.11
YRK1	Rural	3.70 ± 1.42	0.80 ± 0.30	4.51 ± 1.65	2.34 ± 1.17	1.37 ± 0.52	61 ± 14	39 ± 14	1.78 ± 0.55
PNS1	Urban	2.51 ± 1.47	0.82 ± 0.45	3.33 ± 1.84	0.90 ± 0.79	1.77 ± 1.03	33 ± 15	67 ± 15	2.44 ± 0.29
OLF1	Suburban	2.51 ± 1.32	0.69 ± 0.36	3.21 ± 1.61	1.28 ± 0.78	1.28 ± 0.81	51 ± 17	49 ± 17	1.80 ± 0.36

concentrations were determined by the Rutgers in situ thermal–optical carbon analyzer (RU/ORI method) for the month of August, 1999 (Lim and Turpin, 2002). Following Castro et al. (1999) and Strader et al. (1999), a linear least-squares regression was performed on the Atlanta hourly pseudo-data from the CMAQ model and the Atlanta semi-continuous measurement data that comprised the lowest 10% of the set of OC/EC ratios, respectively. The regression yielded $OC = 1.47 \times EC + 2.05$ ($r^2 = 0.79$, $n = 24$) and $OC = 1.67 \times EC + 1.37$ ($r^2 = 0.84$, $n = 24$) for the Atlanta semi-continuous measurement data and model pseudo-data, respectively. These $(OC/EC)_{pri}$ ratios of 1.47 and 1.67 are somewhat less than those of Zheng et al. (2002) (see Table 1) and are within the estimations of Lim and Turpin (2002), who found that $(OC/EC)_{pri}$ ratios ranged from 1.37 to 2.14 for the Atlanta data, on basis of the same Atlanta semi-continuous measurement data using a Demming regression approach. The assumption is that data in the lowest 5–10% of the OC/EC ratio distribution most likely are dominated by primary carbonaceous aerosols. However, the $(OC/EC)_{pri}$ ratios calculated directly by the emission/transport of $(OC/EC)_{pri}$ ratio method are smaller than 1.0 most of the time at the Atlanta site with a mean value of 0.80 ± 0.11 (ranging from 0.66 to 1.53). These results suggest that the empirical $(OC/EC)_{pri}$ ratio approach might yield OC_{pri} concentrations that are biased high. Strader et al. (1999) suggested that there is a possibility of secondary OC produced during the previous day being carried over and transported to the receptor site. Examination of CMAQ model time series animations clearly show that secondary OC produced during the previous day and transported from other locations influenced the receptor site, even in the very early morning and during nighttime. These discrepancies should be further explored and air quality model concentration predictions can help to probe for explanations.

4.4. Discussion of uncertainties

A large uncertainty affecting the results of the present study comes from the emission inventory. As pointed out by Battye et al. (2002), the largest uncertainties in the EC source categories are from the non-road diesel, residential incineration, non-road gasoline, on-road diesel vehicles and prescribed forest burning. In addition, a comparison of the ozone season and annual emission inventories indicates that there are large uncertainties in the estimates of OC_{pri} from prescribed burning and other area sources over the US. Although the ozone season emission inventory was used for the current work, a sensitivity test shows that the high modeled mean $(OC/EC)_{pri}$ ratios over the Northwest and Southeast in Fig. 1a will decrease if the annual emission inventory is chosen. Future modeling efforts will focus on relating the $(OC/EC)_{pri}$ ratios to the main contributing source signatures and resolving the differences between the ozone season and annual emission inventories. The results of the present study can be influenced by the meteorological fields by which the model is driven as well.

It is important to note that the OC/EC ratio method described in this work can provide meaningful insight into OC_{pri} and OC_{sec} concentrations only if the OC/EC split is obtained by the same analytical technique in the observations and in the emission measurements that are used as input to the model. As discussed above, OC and EC measurements are operationally defined by the analysis method or protocol applied. Chow et al. (2001)

found that the EC concentrations measured with the TOT method of National Institute of Occupation Safety and Health (NIOSH) were typically less than half of those determined by the TOR method of IMPROVE when they were applied to the same samples. They also suggested that the primary difference was the allocation of carbon evolving at the NIOSH with 850 °C temperature in a helium atmosphere to the OC rather than EC fraction. When the same analytic method is used, the measurement accuracy (ability to measure a standard) and precision (variation of identical collocated samplers) for EC are 10% and 20%, respectively (Fehsenfeld et al., 2002; Solomon et al., 2003). These values are applicable to the current analysis, in which the TOR method was used in both the observations and the emission inventory.

5. Summary and conclusions

To the authors' knowledge, this is the first attempt to estimate the spatial distributions of OC_{pri} and OC_{sec} over the continental US. Since the emission and transport assisted approach used in this study can provide $(OC/EC)_{pri}$ ratios at any time and any place, OC_{pri} and OC_{sec} concentrations can now be determined quantitatively at any time and location where EC and OC measurements are available. Our results reveal significant temporal and geographic variability in the relative contribution of OC_{pri} and OC_{sec}. Furthermore, results indicate that the use of a constant value to represent the ratio of $(OC/EC)_{pri}$ at a location is not appropriate for the time scales studied here. On the basis of results from 15 June to 31 August 1999, the daily OC_{pri} concentrations can vary from 0.19 to $3.30\,\mu g\,C\,m^{-3}$ ($0.72\pm0.51\,\mu g\,C\,m^{-3}$) while daily OC_{sec} concentrations vary from 0.09 to $3.01\,\mu g\,C\,m^{-3}$ ($0.96\pm0.59\,\mu g\,C\,m^{-3}$) over the US. Regional analysis shows that OC_{pri} and OC_{sec} make an equal contribution to OC over the West and West Pacific areas whereas OC_{sec} makes a dominant contribution to OC over Northeast ($77\pm3\%$). On the basis of daily observations from SEARCH sites, this study provides supportive evidence that OC_{sec} formation might explain the high-percentage of unexplained PM OC concentrations observed in July as suggested by Zheng et al. (2002).

The uncertainty in the determination of the relative contributions of OC_{pri} and OC_{sec} to the overall organic concentrations continues to be large. While air quality models are known to contain errors, bringing air quality modeling results together with measurements in a hybrid approach can provide a valuable method for quantification of OC_{pri} and OC_{sec} and for further investigation into the uncertainties. As demonstrated in this paper, the modeled $(OC/EC)_{pri}$ ratio approach can provide quantitative information and create additional insight on regional differences over a continental scale, and be used to contrast and compare urban and rural areas. The approach described in this paper utilizes the strengths of the air quality models and measurements to provide spatially and temporally resolved estimates of OC_{pri} and OC_{sec} across the US at sites that have only aggregate data from routine monitoring networks. As such, it provides an important addition to current methods.

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